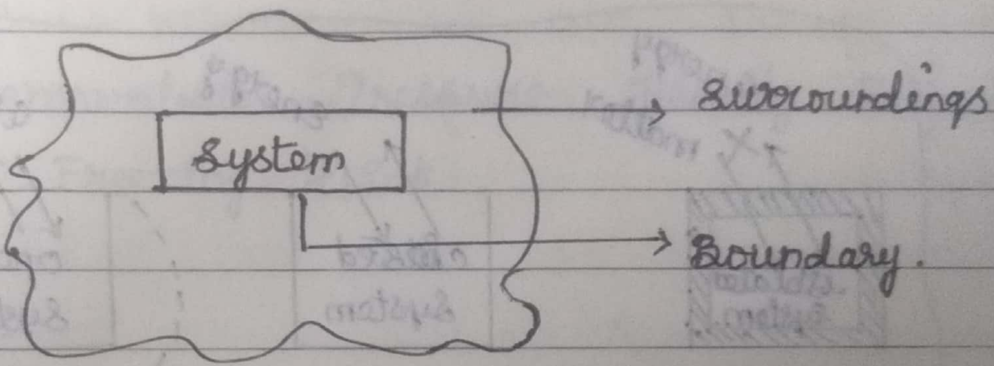
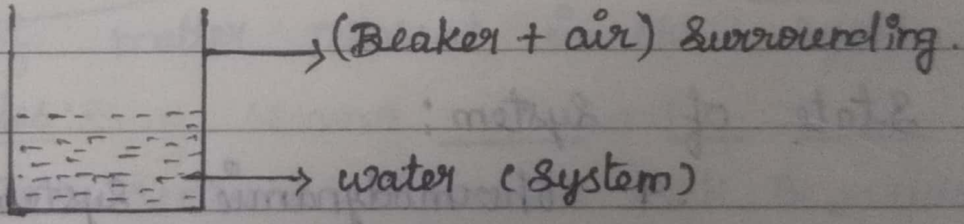
Thermodynamics - I

System and surrounding

A <u>system</u> is that part of the universe which is under thermodynamics study. the rest of the universe is <u>surroundings</u>.

The real or imaginary surface separating the system from the surroundings is called the <u>boundary</u>.





<u>Types of Thermodynamics systems</u>

According to boundary ① ② ③ systems

<u>isolated System</u>

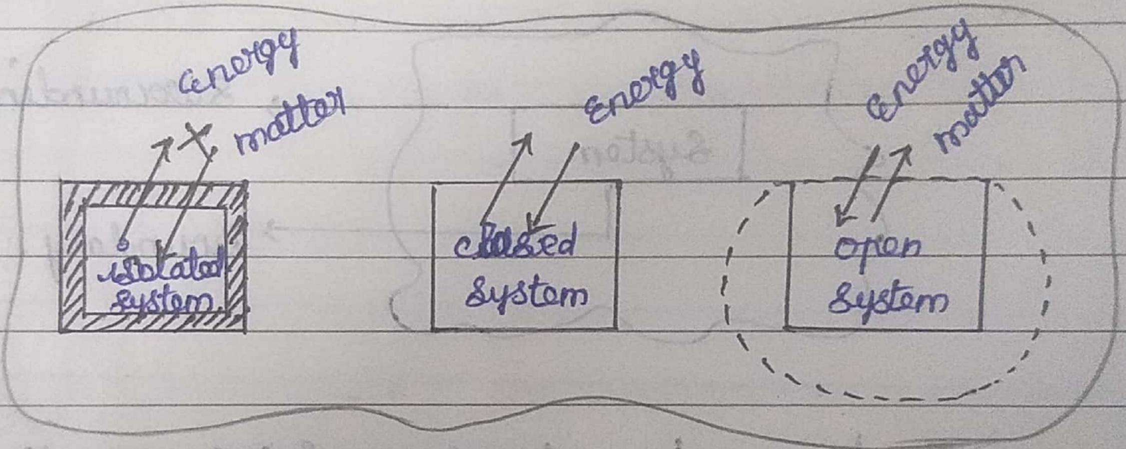
isolated system is one that can transfer neither matter nor energy to and from its surrounding closed system.
(boundary sealed & insulated)

Closed system:

Cannot transfer matter but transfer Energy in the form of heat. boundary (sealed)
not
(insulated)

Open system: (boundary open & uninsulated)

Can transfer both energy and matter to and from its surroundings.



State of system:

A thermodynamic system is said to be in a certain state. when all its properties are fixed.

P, V, T, mass, composition alters the state of the system. These are state variables (or) state functions (or) thermodynamic parameters.

Three variables P, V, T

P, T specified V is fixed automatically calculated from the equation of state.

($PV = RT$) P, T (Independent state variables)

V (Dependent state variables

Intensive & Extensive variables.

Macroscopic (or) bulk properties of a system (v, P, mass etc) divided in to two.

i) Intensive

ii) Extensive.

* **Intensive :**

A property which does not depend on the quantity of matter present in the system.

Examples:-

Temperature, Pressure, Density, B.P, ST, RI, Viscosity, Freezing Point.

* **Extensive :-**

A property that does depend on the quantity of matter present in the system.

Examples:-

Mass, volume, E (or) U, S, H, G, number of moles (n).

Thermodynamic Process :-

System changes from one state to another the operation is called a Process.

i) **Isothermal Processes :-**

The temperature remains fixed are termed isothermal Processes.

$$dT = 0$$

Jmc
confer

Adiabatic Processes :-

Those Process in which no heat can flow in to or out of the system, are called adiabatic process.

$$dq = 0$$

Reversible :-

This is the process that takes place infinitesimally slowly and its direction at any point can be reversed by an infinitesimal change in the state of the system.

Example :-

$$A \longrightarrow B$$
$$\longleftarrow$$

Irreversible :-

When a process goes from the initial to the final state in a single step and cannot be carried in the reverse order.

Example :-

$$A \longrightarrow B$$

* State function and Path function :

S, G, H, E are functions of state variables it is called state functions.

It is independent of path but dependent only the initial and final state of the system.

The functions are depend on the path of the system is called path functions.

Example :-

volume, mass, w, q.

Exact and inexact differentials

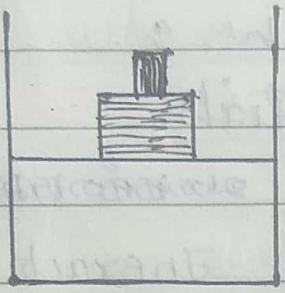
(துல்லியமான மற்றும் துல்லியமற்ற வகைக்கெழுக்கள்)

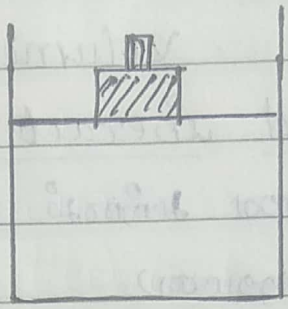
Exact (சரியான)	Inexact
* They integrate to finite difference $\int_1^2 \Delta E = E_2 - E_1$	Integrate to a total quantity.
* Independant of path of integration	Depends on path of integration $\int_1^2 \delta w = w$.
* The cyclic integral of an exact $\oint dE = 0$	The cyclic integral of an exact differential is generally not equal to zero $\oint \delta w \neq 0$

Work of expansion at constant pressure.

Work done during the expanssion of a gas is called work of expanssion.

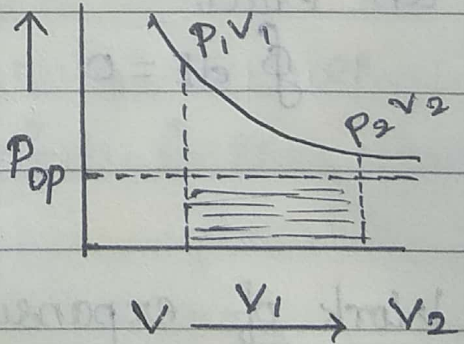
Consider a gas enclosed in a cylinder with the help of a weightless and frictionless piston. When this gas expands, it lifts the body placed on the piston. The initial state of the gas is discribed by T, P_1 & V_1 After the expansion the final state is described by T, P_2, V_2





During the expansion, the gas opposes the pressure on the piston. If A is the cross sectional area of the piston, the pressure on the piston is $P_{op} = mg/A$. M is the mass of the body on the piston. If the piston moves through a height 'h' the amount of work done is given as

$$W = mgh$$
$$W = P_{op}\ Ah$$
$$W = P_{op}\ \Delta V = P_{op}\ (V_2 - V_1)$$



ΔV is the $\uparrow$se in volume of the gas. In this particular expansion the opposing pressure is constant. The work of expansion can also be known from the following graph.

First law of thermodynamics.

Statements:

i) The total energy of an isalated system remains constant though it may change from one form to another.

$$\Delta E = q - W$$

W = Work done by the system.

q = amount of heat supplied to the system.

ii) The net energy change of a closed system is equal to the heat transferred to the system minus the work done by the system.

$$\Delta E = q - P\Delta V \qquad (q - W)$$

iii) Whenever energy of a particular type disappears equivalent amount of another type must be produced.

iv) Total energy of a system and surroundings remains constant.

v) $\Delta E = q - W$

Iso baric	cyclic	iso choric	adiabatic
(P constant)	Process	(V constant)	$q = 0$
$\Delta E = q - P\Delta V$	$\Delta E = 0$	$W = 0$	$\Delta E = -W$
	$q = W$	$\Delta E = q_v$	

Internal Energy :- (E (or) U)

The total of all the possible kinds of energy of a system is called Internal energy.

- state function
- Extensive property.

$$\Delta E = E_2 - E_1$$

SI unit → joule

calorie 1 cal = 4.184 J

Enthalpy of a system (H)

The tatal heat content of a system at constant pressure is equivalent to the internal energy E plus the PV energy. this is called enthalpy.

$$H = E + PV$$

- **state function**

$$\Delta H = H_2 - H_1$$

$$\Delta H = (E_2 + P_2V_2) - (E_1 + P_1V_1)$$

$$= (E_2 - E_1) + (P_2V_2 - P_1V_1)$$

$$\Delta E + \Delta PV$$

P constant, gas expand.

$$\Delta H = \Delta E + P\Delta V \quad \text{(or)}$$

$$\Delta H = \Delta E + W \qquad q - \cancel{W} + \cancel{W}$$

$$\downarrow$$

$$q - W \qquad \Delta H = q_p \text{ (at constant P)}$$

$$\boxed{\Delta H = q_p} \qquad \Delta H = q_p$$

Units

Kilocalories Kcal (or) KJ

ΔH +ve $H_2 > H_1$

ΔH −ve $H_1 > H_2$

Heat capacity :-

The amount of heat required to raise the temperature of one ~~of~~ mole of the substance by 1k.

$$c = \frac{dq}{dT}$$

(Or) the ratio of the amount of heat absorbed to the rise in temperature.

Units :-

cal k^{-1} mole^{-1} (or) JK^{-1} mol^{-1}

Molar heat capacity at constant volume.

The rate of change of internal energy with temperature at constant volume.

According to 1^{st} law

$$dq = dE + PdV \longrightarrow ①$$

dividing both side by dT

$$\frac{dq}{dT} = \frac{dE + PdV}{dT} \longrightarrow ②$$

at constant volume

$$\boxed{C_V = \left(\frac{dE}{dT}\right)_V} \quad dV = 0 \longrightarrow ③$$

Molar heat capacity at constant Pressure :-

The rate of change of enthalpy with temperature at constant Pressure.

$$C = \frac{dE}{dT} + \frac{PdV}{dT} \longrightarrow ①$$

$H = E + PV$

differentiating w.r. to T at constant Pressure.

$$\left(\frac{dH}{dT}\right)_P = \underbrace{\left(\frac{dE}{dT}\right)_P + P\left(\frac{dV}{dT}\right)_P}_{C} \longrightarrow ②$$

Comparing eq ①

$$\boxed{C_p = \left(\frac{dH}{dT}\right)_P} \longrightarrow ③$$

<u>Relationship b/t Cp and Cv</u>

$$C_p = \frac{dH}{dT} \longrightarrow ①$$

$$C_v = \frac{dE}{dT} \longrightarrow ②$$

$H = E + PV$ for one mole of anideal gas

$\therefore PV = RT$ (ideal gas equation)

$$H = E + RT \longrightarrow ③$$

differentiating w.r.t temperature T

$$\frac{dH}{dT} = \frac{dE}{dT} + R$$

$$C_p = C_v + R$$

$$\boxed{C_p - C_v = R}$$

Calculation of w, q, dE and dH for Expansion of ideal and real gases under isothermal and adiabatic conditions of reversible and

processes.

'W' for ideal gas under isothermal condition

I^{st} law

$$\Delta E = Q - W$$

for isothermal process $\Delta E = 0$

$$\therefore \boxed{Q = W}$$

reversible

Work of Expansion of an ideal gas under isothermal condition.

$$W = 2.303\ RT \log \frac{V_2}{V_1} \quad (or)$$

$$W = 2.303\ RT \log \frac{P_1}{P_2}$$

Derivation :-

$$W = P_{op} \cdot dv$$

reverrisible expansion

$$P_{op} = P$$

$$\therefore \boxed{W = Pdv} \longrightarrow ①$$

for n moles of ideal gas

$$P = \frac{nRT}{V}$$

substitution ①

$$W = \frac{nRT}{V} \cdot dv \longrightarrow ②$$

integration eq ②

$$W = nRT \int_{V_1}^{V_2} \frac{dv}{V} = nRT \ln \frac{V_2}{V_1}$$

$$W = 2.303\ nRT \log \frac{V_2}{V_1}$$

$$\boxed{V \alpha 1/P}$$

$$\boxed{W = 2.303\ nRT \log \frac{P_1}{P_2}}$$

reverssible work of expansion of an ideal gas under adiabatic condition :-

for adiabatic $Q = 0$

1st law

$$\Delta E = Q - W$$

$$Q = 0$$

$$\Delta E = -W$$

$$\boxed{W = -\Delta E} \longrightarrow ①$$

$c_v = \frac{\partial E}{\partial T}$

$$\Delta E = C_v \Delta T$$

$$\boxed{\therefore W = -C_v dT} \longrightarrow ②$$

derivation

$$\boxed{W = C_v (T_1 - T_2)}$$

$$dE = q - W \longrightarrow ①$$

$$q = dE + W$$

$$E = f(T, V)$$

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dv \longrightarrow ②$$

$$W = Pdv \longrightarrow ③$$

$$\left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dv = q - Pdv$$

$$q = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV + PdV \longrightarrow ③$$

$q = 0$ for an ideal gas

ΔE for adiabatic

$$\left(\frac{\partial E}{\partial V}\right)_T = 0$$

$$C_v = \left(\frac{\partial E}{\partial T}\right)_V$$

$$\left(\frac{\partial E}{\partial T}\right)_V = C_v$$

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Substitution in ③

$$\boxed{dE = C_v dT}$$

$\Delta E = C_v dT$

ΔH for adiabatic

$H = E + PV$

$\Delta H = \Delta E + P\Delta V$

$\Delta E = C_v dT$

$$0 = C_v dT + 0 + PdV$$

$$\boxed{PdV = -C_v dT}$$

$$W = PdV = -\int_{T_1}^{T_2} C_v dT$$

$$W = -C_v(T_2 - T_1) = C_v(T_1 - T_2)$$

$$\boxed{W = C_v(T_1 - T_2)}$$

Internal Energy change for isothermal

$$\left(\frac{\partial E}{\partial V}\right)_T = 0$$

constant V

$$(\Delta E)_{T,V} = 0$$

ΔH

$H = E + PV$

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

$PV = nRT$

$\Delta H = \Delta E + nR\Delta T$

$\Delta E = 0$

$\Delta T = 0$

$\Delta H = 0$

adiabatic

$Q = 0$

$\Delta E = Q - W$

$Q = 0$

$\boxed{\Delta E = -W}$

$$\left(\frac{\partial H}{\partial P}\right)_T = 0$$

$H = E + PV$

$PV = RT$

$H = E + RT$ difference c̄ respect

$$T\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial E}{\partial P}\right)_T + 0$$

$L = 0 \quad L = 0.$

Thermochemistry

$\Delta H = \Delta E + \Delta n RT$ (or)

$Q_P = Q_V + \Delta n RT$

$\Delta H = \Delta E + P\Delta V$

$PV = nRT$

$\frac{PV}{n} = RT \longrightarrow ①$ $\quad n_2 - n_1 = \Delta n$

$P\Delta V = \frac{PV}{n} = \Delta n \longrightarrow ②$ $\quad \Delta V = \left(\frac{V}{n}\right)\Delta n$

eq ① & ②.

$P\Delta V = RT\Delta n$ $\quad Q_p = Q_v + RT\Delta n$

$\Delta H = \Delta E + RT\Delta n$ $\quad dH = dE + RTdn$

$Q_v = \Delta E$ $\quad q_p = q_v + RTdn$

$Q_p = \Delta H$

$H = E + PV$

$H_1 =$

$H_2 =$

$\Delta H =$

$\Delta H = \Delta E + P\Delta V$

$Q_p = \Delta H$

$q_p = dH$

Application of kirchoff equation

* determine the heat of rean.

$$\Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta C_p \, dT$$

heat of rean

$$\Delta H_2 - \Delta H_1 = \Delta C_p (T_2 - T_1)$$

$Q_v = \Delta E_v$

$Q_p = \Delta H$

$H = E + PV$ $\quad \Delta H = \Delta E + P\Delta V$

$Q_p = \Delta E + P\Delta V \longrightarrow ①$

$= Q_V + P\Delta V \longrightarrow$ ②

$\Delta n = n_2 - n_1$

$\Delta V = V\Delta n$

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

Ideal gas $PV = RT$

$P\Delta V = PV\Delta n = RT\Delta n \longrightarrow$ ③

Substitute eq ①

$\boxed{Q_P = Q_V + RT\Delta n}$

Kirchoff's equation

The heat of reaction changes with change in temperature of a gas due to variation in its specific heat. The equation representing the variation of heat change of rxn with temperature are known as Kirchoff's equation.

At constant volume

$\Delta E = E_2 - E_1 \longrightarrow$ ①

Differentiating w.r. to temperature at constant volume

$$\left(\frac{d(\Delta E)}{dT}\right)_V = \left(\frac{dE_2}{dT}\right)_V - \left(\frac{dE_1}{dT}\right)_V$$

$$\left(\frac{dE}{dT}\right)_V = C_V$$

$$\frac{d(\Delta E)}{dT} = (C_V)_2 - (C_V)_1 = \Delta C_V \longrightarrow ②$$

$(C_V)_2, (C_V)_1$ heat capacities of Pdt and reactant.

integrating eq ②

$$\Delta E_2 - \Delta E_1 = \int_{T_1}^{T_2} \Delta C_v \, dT$$

$$\underset{|}{\Delta E_2} - \underset{|}{\Delta E_1} = \Delta C_v (T_2 - T_1) \longrightarrow ③$$

heats of reaction.

My at constant Pressure.

$\Delta H = H_2 - H_1$ diffe w.r.T at constant 'P'

$$\left(\frac{d(\Delta H)}{dT}\right)_P = \left(\frac{dH_2}{dT}\right)_P - \left(\frac{dH_1}{dT}\right)_P \longrightarrow ①$$

$$\left(\frac{dH}{dT}\right) = C_p$$

$$\left(\frac{d(\Delta H)}{dT}\right)_P = (C_p)_2 - (C_p)_1 = \Delta C_p \longrightarrow ②$$

$$d(\Delta H) = \Delta C_p \times dT$$

$$\Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta C_p \, dT \longrightarrow ③$$

$$\boxed{\Delta H_2 - \Delta H_1 = \Delta C_p (T_2 - T_1)}$$

⑨ Eq ③ K-e

Bond Energy

The bond energy is defined as the average amount of energy required to break all bonds of a particular type in one mole of the substance.

k cal / mole (or) kJ / mol.

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H - H $\longrightarrow$ 433 kJ / mol (or) 103.58 kcal / m.

	kJ / mole
Cl - Cl $\longrightarrow$	243
O = O $\longrightarrow$	499
C - H $\longrightarrow$	414
O - H $\longrightarrow$	460

Bond energy is a measure of strength of the bond.

bond energy is measured by using some Thermochemical data.

E.g Bond Energy of methane.

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

The above equation obtained by combining the heat of formation of methane from $C_3 + H_{(g)}$ with the heat of sublimation of carbon. $C_3 \longrightarrow C_{(g)}$ and the heat of dissociation of hydrogen into atoms.

$$H_2 \longrightarrow 2H$$

four C-H $\longrightarrow$ 398 k cal / mole.

all are idendical so 398/4 = 99.5 kcal /

bond is broken the bond energy is ~~the~~ +ve heat is absorbed. -ve bond energy bond is formed. heat is evolved.

Eg:

$$H_2 + \frac{1}{2} O_2 \longrightarrow H_2O$$

H - H 104

O = O 118 k cal/mol

59.0

O - H 111

two O-H bonds are formed and one H-H bond is broken.

$\Delta H = -2\,\Delta H\,(OH) + \Delta H\,(H-H) + \frac{1}{2}\,\Delta H\,(O=O)$

② calculate the bond energy of HCl.

$H-H \longrightarrow 433$ kJ/mole

$Cl-Cl \longrightarrow 242$ kJ/mole

ΔH_f of HCl $\longrightarrow -91$ kJ/mole

$\frac{1}{2}H_2 + Cl \longrightarrow HCl \quad \Delta H = -91 \longrightarrow$ ①

$H_2 \longrightarrow 2H \quad \Delta H = 433 \longrightarrow$ ②

$Cl_2 \longrightarrow 2Cl \quad \Delta H = 242 \longrightarrow$ ③

multiply eq ① by ②

$H_2 + 2Cl \longrightarrow 2HCl \quad \Delta H = -182 \longrightarrow$ ④

Add eq ② & ③

$H_2 + Cl_2 \longrightarrow 2HCl \quad \Delta H = 675 \longrightarrow$ ⑤

Substracting eq (iv) & (v)

$HCl_{(g)} + 400\,H_2O\,(l) = HCl\,(400\,H_2O)$

$\Delta H = -17.70$

$HCl_{(g)} + 50\,H_2O\,(l) = HCl\,(50\,H_2O)$

$\Delta H = -17.40.$

Substract.

$HCl\,(50\,H_2O) + 350\,H_2O\,(l) = HCl\,(400\,H_2O)$

$\Delta H = -0.30$ k cal

Integral & differential heats of solution

Integral Heat :-

The heat change permole of solute disolved, referred to as the heat of solution. in other words, the heat of solution at a given temperature varies with concentration of the solution.

Solid disolved in a particular solvent the composition of the solution changes from pure solvent to the final solution. the heat of solution per mole at any instant thus varies during the course of the solution process this quantity known as the "differential heat of solution".

The total heat change per mole of solute when solution is complete, this is the integral heat of solution.

eg. 1,000 gms of solvent

integral heat of solution = $\Delta H / m$

molality	0.139	0.278	0.555	1.11
moles of HCl /	400	200	100	50
moles of H_2O	−17.70	−17.63	−17.54	−17.40.
$\Delta H / m$			k cals	