STATE FUNCTION

Properties which depend only on initial and final state of system & do not depend on process or path

e.g. U, H , S etc.

PATH FUNCTION

Depends on path or process. as well as initial and final state of the system

e.g. work, heat

THERMODYNAMIC PROPERTIES

EXTENSIVE

Properties which are dependent of matter (size & mass)present in system
e.g. Mass, volume, Internal energy heat capacity, Entropy, Enthalpy etc.

INTENSIVE

Properties which are independent of matter(size & mass) present in system
e.g. Pressure, temperature, Melting point, density,Specific heat Surface tension etc

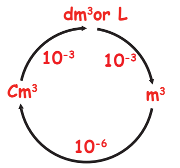
WORK

$\Delta W = P\Delta V = \Delta nRT$

$\Delta W = \text{Joule} \begin{cases} P \longrightarrow \text{Pascal} \\ V \longrightarrow m^3 \end{cases}$

1 atm = 1.01×10^5 Pa

1 L atm = 101 J

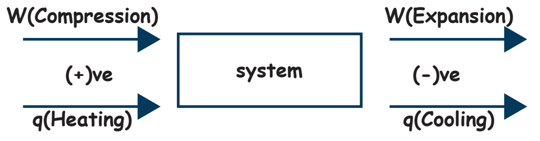


FIRST LAW OF THERMODYNAMICS

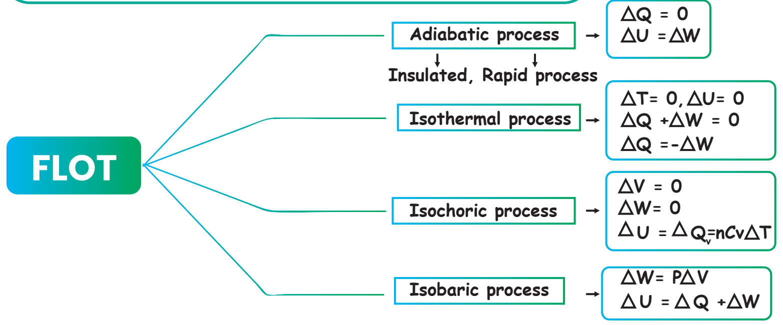
(Based on Law of conservation of energy)

$$\Delta U = \Delta q + \Delta W$$

SIGN CONVENTION



FLOT

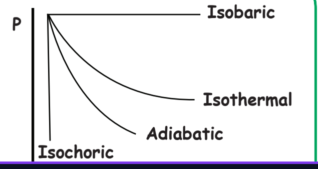


- Adiabatic process → $\Delta Q = 0$, $\Delta U = \Delta W$
  - Insulated, Rapid process
- Isothermal process → $\Delta T = 0, \Delta U = 0$; $\Delta Q + \Delta W = 0$; $\Delta Q = -\Delta W$
- Isochoric process → $\Delta V = 0$; $\Delta W = 0$; $\Delta U = \Delta Q_v = nC_v\Delta T$
- Isobaric process → $\Delta W = P\Delta V$; $\Delta U = \Delta Q + \Delta W$

FREE EXPANSION $P_{ext} = 0, W = 0, \Delta U = 0, q = 0$

ISOTHERMAL
$dT = 0; \Delta U = 0; q = -W$

Reversible Isothermal	Irreversible Isothermal
$W_{rev} = nRT\ln\left(\frac{V_2}{\ldots}\right)$	$W_{irr} = -P_{ext}\left[\frac{nRT}{P\ldots} - \frac{nRT}{P\ldots}\right]$



Spontaneity

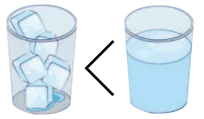
ENTHALPY

$\Delta H = \Delta U + \Delta n_g RT$

$\Delta n_g = 0, \Delta H = \Delta U$
$\Delta n_g > 0, \Delta H > \Delta U$
$\Delta n_g < 0, \Delta H < \Delta U$

All exothermic process are spontaneous

ENTROPY



$S_{gas} > S_{liquid} > S_{solid}$

ENTROPY CHANGE

1) Isothermal

$\Delta S = nR\ln\frac{V_2}{V_1} = nR\ln\frac{P_1}{P_2}$

2) Isochoric ($P \propto T$)

$\Delta S = nC_v\ln\frac{T_2}{T_1} = nC_v\ln\frac{P_2}{P_1}$

3) Isobaric

$\Delta S = nC_p\ln\frac{T_2}{T_1} = nC_p\ln\frac{V_2}{V_1}$

$\Delta S_{total} > 0$, Spontaneous
$\Delta S_{total} = 0$, Equilibrium
$\Delta S_{total} < 0$, Non-spontaneous

GIBBS FREE ENERGY

$\Delta G = \Delta H - T\Delta S$
$\Delta G < 0$ Or (-)ve, Spontaneous
$\Delta G > 0$ Or (+)ve, Non-spontaneous
$\Delta G = 0$, Equilibrium

Equilibrium Temperature

$$T_e = \frac{\Delta H}{\Delta S}$$

THERMODYNAMICS

THERMOCHEMISTRY

1) Heat of Reaction ($\Delta H_{rxn.}$)

$\Delta H_{rxn.} = \Delta H_{products} - \Delta H_{reactants}$

2) Heat of Formation

Heat Change in formation of 1 mole of substance at 298 K and 1 atm Pressure (standard enthalpy of formation)

$\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftharpoons NH_3$

$$\begin{array}{cccc} A + & B \rightleftharpoons & C + & D \\ a & b & c & d \end{array}$$

$\Delta H_{reaction}$ = Heat of formation of products- Heat of formation of reactants
= (c + d) - (a + b)

Standard enthalpy of formation (298 K, 1 atm) of element at it's standard state is zero e.g.,
$O_2(g) = 0$ $Cl_2(g) = 0$ $Br(g) \neq 0$ $Br_2(l) = 0$

3) Enthalpy of Combustion (1 mole, 298 K)

(standard enthalpy of combustion)

$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$; $\Delta H_{combustion}$

$$\begin{array}{lcccc} & A + & B \longrightarrow & C + & D \\ \text{Enthalpy of combustion:} & a & b & c & d \end{array}$$

ΔH_{react} = Heat of combustion of reactants - Heat of combustion of products
= (a + b) - (c + d)

4) Heat of Neutralisation (ΔH = (-)ve)

$HCl + NaOH \longrightarrow NaCl + H_2O$; $\Delta H_{neutalisation}$

S.A + S.B ⟶ $\Delta H = -13.7$ k Cal = - 57 kJ

S.A + S.B > (S.A/ S.B + W.A/W.B)- > W.A+W.B (Order of ΔH neutralisation)

PHYSICS WALLAH

BOND ENERGY

$$\begin{array}{lcccc} & A + & B \longrightarrow & C + & D \\ \text{Bond energy:} & a & b & c & d \end{array}$$

$\Delta H_{reaction}$ = Bond energy of reactants - Bond energy of products
= (a + b) - (c + d)

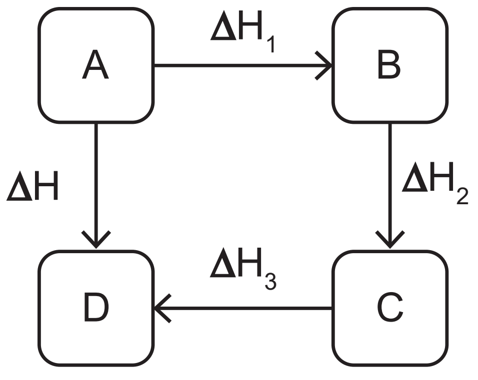
$NH_3 \Rightarrow$ B.E = x
B.E of N-H = $\frac{x}{3}$

$CH_4 \Rightarrow$ B.E = x
B.E of C-H = $\frac{x}{4}$

- $A \longrightarrow B$; ΔH_1
  $B \longrightarrow C$; ΔH_2
  $A \longrightarrow C$; $\Delta H_3 = \Delta H_1 + \Delta H_2$
- $A \longrightarrow B$; $\Delta H = x$
  $B \longrightarrow A$; $\Delta H = -x$
- $A \longrightarrow B$; $\Delta H = x$
  $nA \longrightarrow nB$; $\Delta H = nx$

ΔH	ΔS	ΔG = ΔH - TΔS	Spontaneity.
(-)	(+)	Always Negative	Spontaneous at all temp
(+)	(-)	Always Positive	Non-spontaneous at all temperature.
(+)	(+)	+ve @ low temp. -ve @ high temp.	Non spontaneous at low temperature Spontaneous at high temperature
(-)	(-)	-ve @ low temp. +ve @ high temp.	Spontaneous at low temperature, $T < T_e$ Non spontaneous at high temperature

HESS' LAW OF CONSTANT HEAT SUMMATION



$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$