THERMODYNAMICS

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

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

ΔW = Joule: P ⟶ Pascal; V ⟶ m^3

1 atm = 1.01×10^5 Pa

1 L atm = 101 J

dm^3 or L: 10^{-3} Cm^3, 10^{-2} m^3, 10^{-6}

FIRST LAW OF THERMODYNAMICS

(Based on Law of conservation of energy)

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

SIGN CONVENTION

W(Compression) (+)ve q(Heating) → system ← W(Expansion) (-)ve q(Cooling)

FLOT

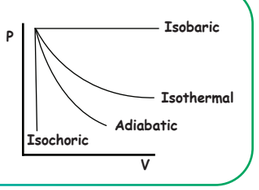
Adiabatic process (Insulated, Rapid process)	→	$\Delta Q = 0$, $\Delta U = \Delta W$
Isothermal process	→	$\Delta T = 0, \Delta U = 0$, $\Delta Q + \Delta W = 0$, $\Delta Q = -\Delta W$
Isochoric process	→	$\Delta V = 0$, $\Delta W = 0$, $\Delta U = \Delta Q = nC_v\Delta T$
Isobaric process	→	$\Delta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

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

ISOTHERMAL

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

Reversible Isothermal	Irreversible Isothermal
$W_{rev} = nRT\ln\left(\frac{V_2}{V_1}\right)$	$W_{irr} = -P_{ext}\left[\frac{nRT}{P_2} - \frac{nRT}{P_1}\right]$



Spontaneity

ENTHALPY

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

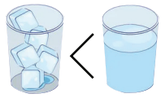
$\Delta n_g = 0, \Delta H = \Delta U$

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

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

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

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

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)

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

$$A + B \rightleftharpoons C + D$$

a b c d

$\Delta H_{reaction}$ = 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)

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

	A	+ B	⟶ C	+ D
Enthalpy of combustion:	a	b	c	d

$\Delta H_{reaction}$ = 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 ⟶ ΔH = -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)

BOND ENERGY

$$A + B \longrightarrow C + D$$

Bond energy: a b c d

$\Delta H_{reaction}$ = 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

  $A \longrightarrow C$; $\Delta H_3 = \Delta H_1 + \Delta H_2$

- $A \longrightarrow B$; $\Delta H = x$

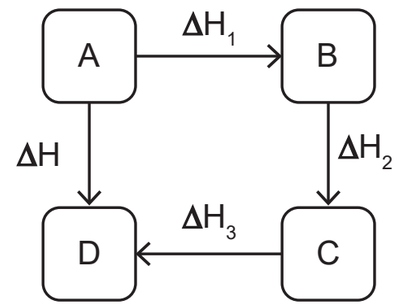
  $B \longrightarrow A$; $\Delta H = -x$

- $A \longrightarrow B$; $\Delta H = x$

  $nA \longrightarrow nB$; $\Delta H = nx$

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



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

PHYSICS WALLAH