THERMODYNAMICS

THERMODYNAMICS PROCESSES

- Isothermal Process
$dt = -. \Delta U = 0$

- Isochoric Process
$\Delta V = 0$

- Adiabatic Process
$\Delta q = 0$

- Cyclic Process
$\Delta U_{cyclic} = 0$

THERMODYNAMICS PROPERTIES

INTENSIVE PROPERTIES
P. T. N
Properties of the System which only depend on the nature of matter

STATE FUNCTION
$\Delta U, \Delta H, \Delta G$
Properties of the System which only depend on the nature of matter
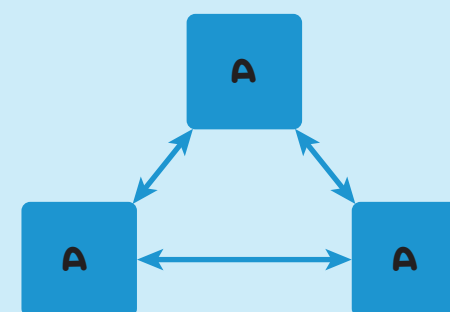
EXTENSIVE PROPERTIES
V. U. H
Properties of the System which only depend on the Path of the System

PATH FUNCTION
HEAT WORK
Properties of the System which depend on the Path of the System

ZEROTH LAW OF THERMODYNAMICS

If two thermodynamics States are in thermal equilibrium with a third one, then they are in thermal equilibrium with each other.

GIBB'S FREE ENERGY

The Net energy available to do useful work and is a measure of 'free energy'.

Standard free energy of a reaction: $\Delta_r G^\circ = \Sigma \Delta_f G^\circ_{products} - \Sigma \Delta_f G^\circ_{reactants}$

Gibb's – Helmholtz equation $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \Delta G^\circ = NFE^\circ_{cell}$

DG < 0. rocess is spontaneous

DG > 0. rocess is non-spontaneous

DG < 0. rocess is equilibrium

GIBB'S ENERGY CHANGE & EQUILIBRIUM

$\Delta_r G^\circ = -2.303RT \log K$

$\Delta G^\circ = 0$	$\log K = 0$	Equilibrium reached
$\Delta G^\circ < 0$	$\log K > 0$ $\log K < 0$	Mixture contains products
$\Delta G^\circ > 0$		Mixture contains reactants

Sign of ΔH	Sign of ΔS	$\Delta G = \Delta H - T\Delta S$	Equilibrium reached
Negative	Positive	Always Negative	Spontaneous at all temp
Positive	Negative	Always Negative	Non-Spontaneous at all temperature
Postive	Postive	+ve @ low temp.	Non-Spontaneous at all temperature
		-ve @ low temp.	Spontaneous at high temperature
Negative	Negative	-ve @ low temp.	Spontaneous at low temperature
		+ve @ low temp.	Spontaneous at low temperature

TYPES OF SYSTEM

OPEN SYSTEM — Matter, Energy

CLOSED SYSTEM — Matter, Energy

ISOLATED SYSTEM — Matter, Energy

Universe
SYSTEM — Surroundings

EXPANSION: $V_i > V_f$
COMPRESSION: $V_f < V_i$

$w_{PV} = -P_{ext}\Delta V$

ISOTHERMAL IRREVERSIBLE WORK

ISOTHERMAL REVERSIBLE
$w_{rev} = -2.303nRT \log\left(\dfrac{V_2}{V_1}\right)$

ADIABATIC REVERSIBLE
$w_{rev} = \dfrac{nR}{r-1}(T_2 - T_1)$

ADIABATIC IRREVERSIBLE
$w_{irrev} = -P_{ext}R\left(\dfrac{P_1 T_1 - P_2 T_2}{P_1 P_2}\right)$

SPONTANEITY
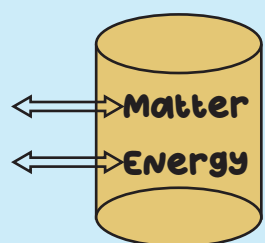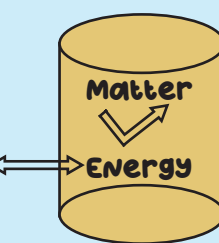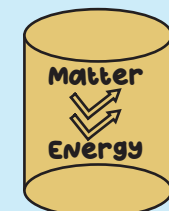
ENTHALPY

$\Delta H = \Delta U + \Delta(PV)$
$\Delta H = \Delta U + \Delta n_g RT$

Enthalpy of reaction $(\Delta_r H)$
Reactants $\rightarrow$ Products

$\Delta_r H = e\sum_i a_i H \text{ products} - \sum_i b_i H \text{ reactants}$

HEAT CAPACITY

Amount of heat required to raise the temperature of a System by 1°C. Molar heat capacity 1°C.

Molar heat capacity $\Rightarrow q = nc\Delta T$

Specific heat capacity $\Rightarrow q = mc\Delta T$

MEYERS'S FORMULA
$C_p - C_v = R$

POISSON'S RATIO
$\dfrac{C_p}{C_v} = r$

HEAT (Q)
Exchange of energy due to temperature differnece.

INTERNAL ENERGY
Total energy within the Substance

WORK (W)
When there is difference between Presence of the System and Surroundings, the work done is known as $w_p V$

FREE EXPANSION
When an ideal gas expands in vacuum then, $P_{ext} = 0$.
$\therefore w=0$

STANDARD ENTHALPY OF REACTIONS (ΔH°)

Standard enthalpy of fusion $= \Delta_{fus} H^\circ$
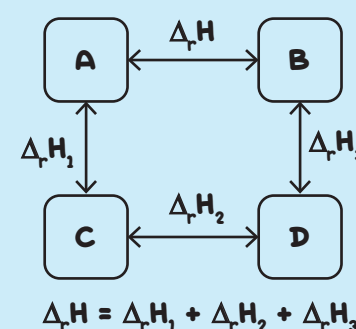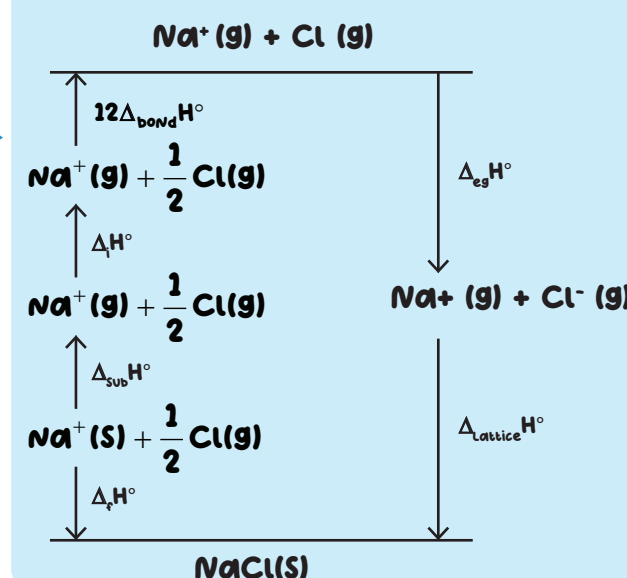
Standard enthalpy of phase change $\Delta_{fus} H^\circ. \Delta_{vap} H^\circ. \Delta_{sub} H^\circ$

Standard enthalpy of combustion $\Delta_c H^\circ$

Standard enthalpy $= \Delta_{bond} H^\circ$

Lattice enthalpy $= \Delta_{lattice} H^\circ$

FIRST LAW OF THERMODYNAMICS

Law of conservation of energy total energy of an isolated System is constant.

Mathematically. $\Delta U = q + w$

SECOND LAW OF THERMODYNAMICS

The entropy of the universe is always increasing in the course of every s pontaneous or Natural change.

ENTROPY

This is the measure of the degree of randomness or disorder of the system.

$\Delta S = \dfrac{q_{rev}}{T(\text{Reversible Process})}$

$\Delta S_{Total} = \Delta S_{system} + \Delta S_{Surroundings}$

Entropy changes during phase transformation

$\Delta_{fusion} S = \dfrac{\Delta_{fusion} H}{T_m}. \quad \Delta_{vap} S = \Delta_{vap} S = \dfrac{\Delta_{vap} H}{T_m}$

$\Delta_{sub} S = \dfrac{\Delta_{subs} H}{T_m}$

$\Delta_r S^\circ = \Sigma S^\circ_{products} - \Sigma S^\circ_{reactants}$

HESS' LAW CONSTANT HEAT SUMMATION

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

BORN HABER CYCLE

$Na^+ (g) + Cl (g)$

$12\Delta_{bond} H^\circ$

$Na^+ (g) + \frac{1}{2} Cl(g)$

ΔH°

$Na^+ (g) + \frac{1}{2} Cl(g)$

$\Delta_{sub} H^\circ$

$Na^+ (S) + \frac{1}{2} Cl(g)$

$\Delta_f H^\circ$

$\Delta_{eg} H^\circ$

$Na+ (g) + Cl^- (g)$

$\Delta_{lattice} H^\circ$

$NaCl(S)$

SIGN CONVENTION

Heat absorbed by the System = +ve

Heat evolved by the System = -ve

Work done by the System = -ve

Work done on the System = +ve

At constant volume $\Delta U = q_v$

At constant pressure $\Delta H = q_p$

CALORIMETRY

$(\Delta U) = CV \times \Delta T \times m$

$(\Delta U) = CV \times \Delta T \times m$

THIRD LAW OF THERMODYNAMICS

The Entropy of a Perfectly crystalline Substance at 0K or absolute zero is taken to be zero.

$\Delta S = \int_0^T C_p d \ln T$