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

ΔU, ΔH, ΔG

Properties of the system which only depend on the nature of matter

EXTENSIVE PROPERTIES

V, U, H

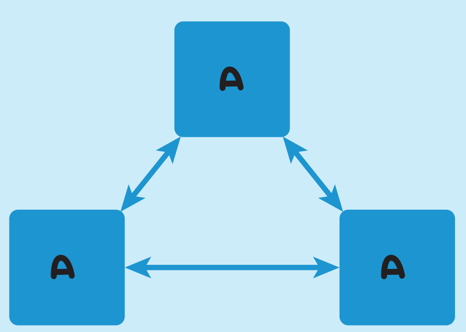
Properties of the system which depend on the path of the system

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.

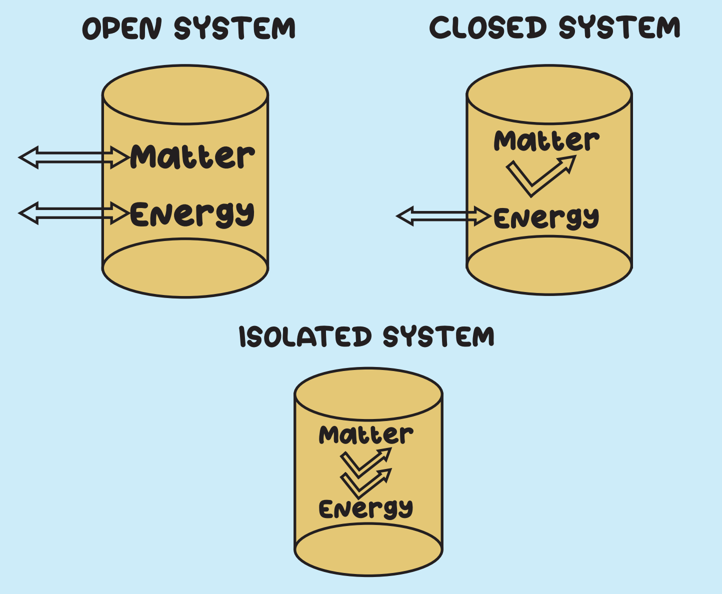
GIBB'S FREE ENERGY

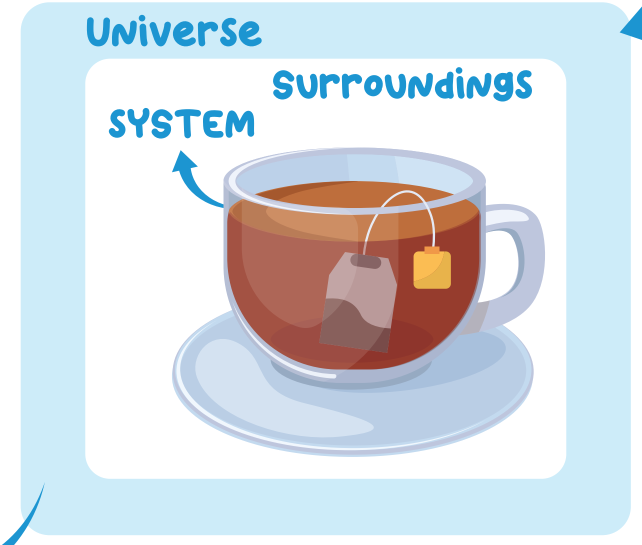
The net energy available to do useful work and is a measure of 'free energy'.

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

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

TYPES OF SYSTEM





GIBB'S ENERGY CHANGE & EQUILIBRIUM

$\Delta rG^\circ = -2.303RT \log K$

$\Delta G^\circ = 0$	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

DG < 0, rocess is spontaneous

DG > 0, rocess is non-spontaneous

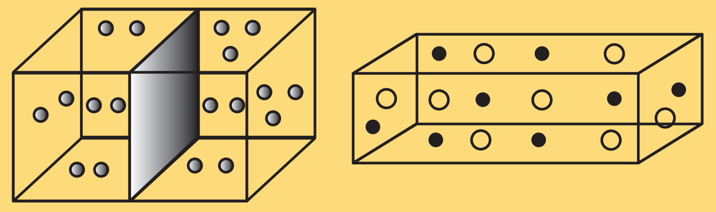
DG < 0, rocess is equilibrium

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. -ve @ low temp.	Non-spontaneous at all temperature Spontaneous at high temperature
Negative	Negative	-ve @ low temp. +ve @ low temp.	Spontaneous at low temperature Spontaneous at low temperature

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

$w_{pv} = -P_{ext}\Delta V$ ISOTHERMAL IRREVERSIBLE WORK	ISOTHERMAL REVERSIBLE $w_{rev} = -2.303nRT \log\left(\frac{V_2}{V_1}\right)$
$w_{rev} = \frac{nR}{r-1}(T_2 - T_1)$ ADIABATIC REVERSIBLE	ADIABATIC IRREVERSIBLE $w_{irrev} = -P_{ext}R\left(\frac{P_1T_1 - P_2T_2}{P_1P_2}\right)$

SPONTANEITY



ENTHALPY

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

Enthalpy of reaction ($\Delta n_r H$)

Reactants → 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 ⇒ $q = nC\Delta T$

Specific heat capacity ⇒ $q = mC\Delta T$

MEYERS'S FORMULA

$C_p - C_v = R$

POISSON'S RATIO

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

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_pV

FREE EXPANSION

when an ideal gas expands in vacuum then, $P_{ext} = 0$.

∴ 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 $= \Delta_{bond}H^\circ$

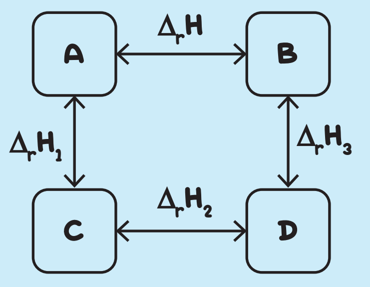
Lattice enthalpy $= \Delta_{lattice}H^\circ$

FIRST LAW OF THERMODYNAMICS

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

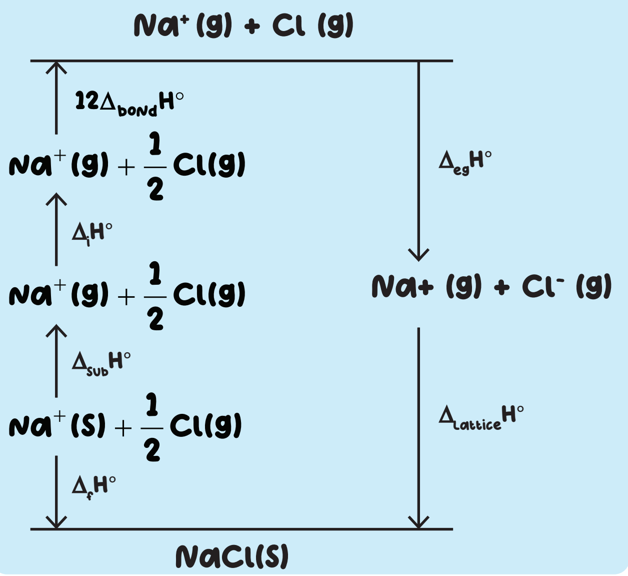
Mathematically, $\Delta U = q + w$

HESS' LAW CONSTANT HEAT SUMMATION



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

EORN HABER CYCLE



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

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

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

SECOND LAW OF THERMODYNAMICS

The entropy of the universe is always increasing in the course of every spontaneous or natural change.

THIRD LAW OF THERMODYNAMICS

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

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

ENTROPY

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

$\Delta S = \frac{q_{rev}}{T(\text{Reversible process})}$

$\Delta S_{Total} = \Delta S_{syestem} + \Delta S_{surroundings}$

Entropy changes during phase transformation

$\Delta_{fusion}S = \frac{\Delta_{fusion}H}{T_m}, \Delta_{vap}S = \Delta_{vap}S = \frac{\Delta_{vap}H}{T_m}$

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

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