

THERMODYNAMICS

THERMODYNAMICS PROCESSES

- **Isothermal Process**
 $dt = \infty, \Delta U = 0$
- **Isochoric Process**
 $\Delta V = 0$
- **Adiabatic Process**
 $\Delta q = 0$
- **Cyclic Process**
 $\Delta U_{\text{cyclic}} = 0$

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

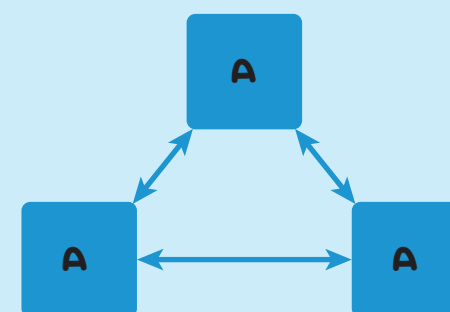
Properties of the system which depend on the path of the system

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: $\Delta_r G^\circ = \sum \Delta_f G^\circ_{\text{products}} - \sum \Delta_f G^\circ_{\text{reactants}}$

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

GIBB'S ENERGY CHANGE & EQUILIBRIUM

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

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

$\Delta G < 0$, process is spontaneous

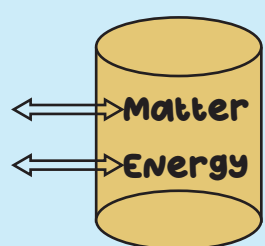
$\Delta G > 0$, process is non-spontaneous

$\Delta G = 0$, process is equilibrium

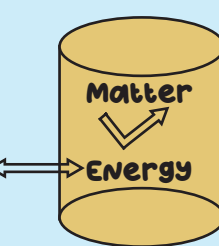
Sign of ΔH	Sign of ΔS	$\Delta G = \Delta H - T\Delta S$	Equilibrium reached
Negative	Positive	Always Negative	Spontaneous at all temp
Positive	Negative	Always Negative	Non-spontaneous at all temperature
Positive	Positive	+ve @ low temp. -ve @ high temp.	Non-spontaneous at all temperature Spontaneous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

TYPES OF SYSTEM

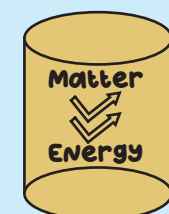
OPEN SYSTEM



CLOSED SYSTEM



ISOLATED SYSTEM



ENTHALPY

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

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

Enthalpy of reaction ($\Delta_r H$)

Reactants \rightarrow Products

$$\Delta_r H = \sum_i \nu_i H_{\text{products}} - \sum_j \nu_j H_{\text{reactants}}$$

STANDARD ENTHALPY OF REACTIONS ($\Delta_r H^\circ$)

Standard enthalpy of fusion $= \Delta_{\text{fus}} H^\circ$

Standard enthalpy of phase change

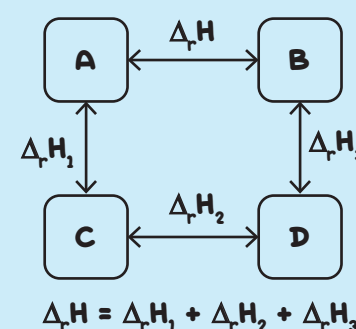
$\Delta_{\text{fus}} H^\circ, \Delta_{\text{vap}} H^\circ, \Delta_{\text{sub}} H^\circ$

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

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

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

HESS' LAW CONSTANT HEAT SUMMATION



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

HEAT CAPACITY

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

$$\text{Molar heat capacity} \Rightarrow C_p = nC_{\text{molar}}$$

$$\text{Specific heat capacity} \Rightarrow c_p = mC_{\text{molar}}$$

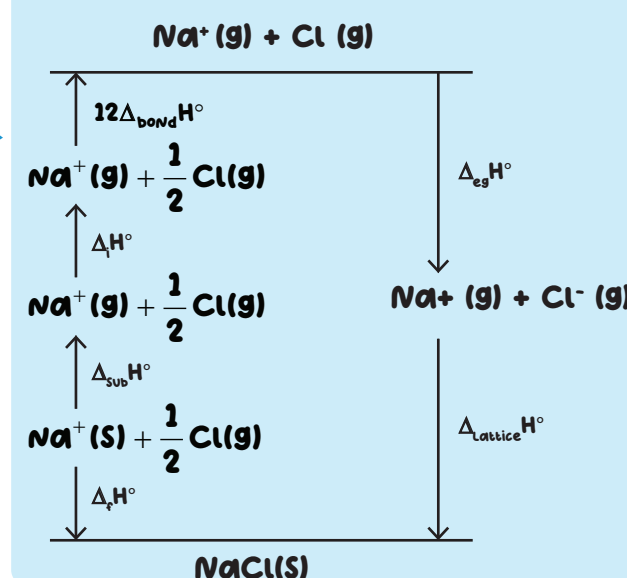
MEYER'S FORMULA

$$C_p - C_v = R$$

POISSON'S RATIO

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

EORN HABER CYCLE



HEAT (Q)

Exchange of energy due to temperature difference.

INTERNAL ENERGY

Total energy within the substance

WORK (W)

When there is difference between pressure of the system and surroundings, the work done is known as w_p, v

FIRST LAW OF THERMODYNAMICS

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

Mathematically, $\Delta U = q + w$

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

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

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

Expansion: $V_i > V_f$
Compression: $V_f < V_i$

$$w_{pv} = -P_{\text{ext}} \Delta V$$

ISOTHERMAL IRREVERSIBLE WORK

$$w_{\text{rev}} = \frac{nR}{\gamma - 1} (T_2 - T_1)$$

ADIABATIC REVERSIBLE

$$w_{\text{rev}} = -P_{\text{ext}} R \left(\frac{P_1 T_1 - P_2 T_2}{P_1 P_2} \right)$$

ISOTHERMAL REVERSIBLE

$$w_{\text{rev}} = -2.303nRT \log \left(\frac{V_2}{V_1} \right)$$

ADIABATIC IRREVERSIBLE

$$w_{\text{rev}} = -P_{\text{ext}} R \left(\frac{P_1 T_1 - P_2 T_2}{P_1 P_2} \right)$$

FREE EXPANSION

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

$$\therefore w = 0$$

SECOND LAW OF THERMODYNAMICS

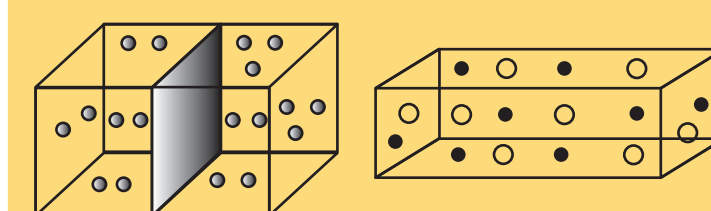
The entropy of the universe is always increasing in the course of every spontaneous or natural change.

THIRD LAW OF THERMODYNAMICS

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

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

SPONTANEITY



ENTROPY

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

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

$$\Delta S_{\text{Total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

Entropy changes during phase transformation

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

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

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