Path function: This is the property of the system that depends on the specific transition (Path) between two equilibrium states.

Ex. mechanical work, heat

Intrinsic Property: It is the essential (or) inherent property of a system/material. They depen mainly on chemical composition (or) structure of the material.

Extrinsic Property: A property that is not essential (or) inherent

Extensive Property: It is the property that changes when the size of the sample changes.

Ex. Enthalpy, Energy, mass, volum

Intensive Property: It is the property that does not change with respect to size of the sample

Ex. Temp, density, viscosity, mP, BP

State function: It is the property of the system that depends only on the current state of the system not on the way in which the system acquired the state.

Ex. Internal Energy, enthalpy, entropy.

Standard State ($^\ominus$) of a Substance is the pure substance at exactly 1 bar [10^5 Pascal] phase. Specific state of matter that is uniform throughout in composition and physical state.

Phase transition; Conversion of one phase of the substance to another phase.

Standard enthalpy of Vapourization $\Delta_{vap}H^\ominus$ The energy that must be supplied as heat at constant pre. Per mole of molecules that are vapourized under standard conditions.

FUSion: Phase transition from Solid to liquid.

Standard Enthalpy of fusion $\Delta H^{\ominus}_{fus}$ The change in molar enthalpy that accompanies fusion under Standard conditions.

condensation : Reverse (or) opposite of Vapourization

freezing : Reverse (or) opposite of fusion

$$\Delta_{forward} H^{\ominus} = - \Delta_{reverse} H^{\ominus}$$

Sublimation: Phase transition from Solid to Vapour

Standard Enthalpy of Sublimation $\Delta_{sub} H^{\ominus}$ The standard molar enthalpy change accompanying Sublimation.

$$\text{Solid} \xrightarrow{A} \text{Liquid} \xrightarrow{B} \text{Vapour} \uparrow$$

with C connecting Solid to Vapour
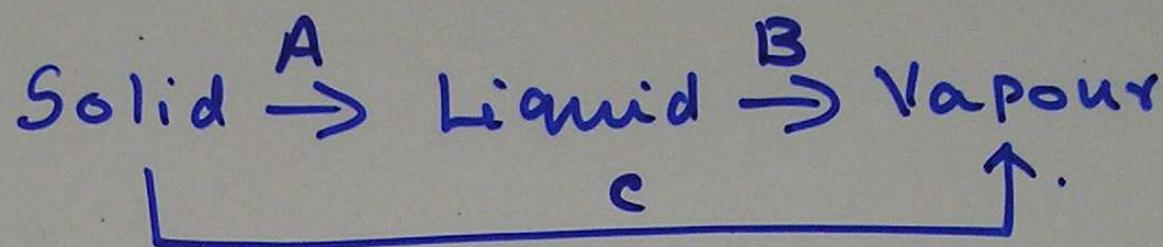
$$A + B = C$$

$$\Delta_{sub} H^{\ominus} = \Delta_{fus} H^{\ominus} + \Delta_{vap} H^{\ominus}$$

Hess Law:

The standard enthalpy of a reaction is the sum of the standard enthalpies of the reactions into which the overall reaction may be divided.

Standard enthalpy of ionization

$\Delta_{ion} H^{\ominus}$ The standard molar enthalpy change accompanying the removal of an electron from a gas phase atom (or) ion.

Aluminium

$$\Delta_{sub} H^{\theta} = 326 \text{ KJ mol}^{-1}$$

$$\Delta H^{\theta}/KJ$$

$$Al(s) \longrightarrow Al(g) \quad +326$$

$$Al(g) \longrightarrow Al^{+}(g) + e^{(-)}(g) \quad +577$$

$$Al^{+}(g) \longrightarrow Al^{+2}(g) + e^{(-)}(g) \quad +1820$$

$$Al^{+2}(g) \longrightarrow Al^{+3}(g) + e^{(-)}(g) \quad +2740$$

$$\dotsc\dotsc$$
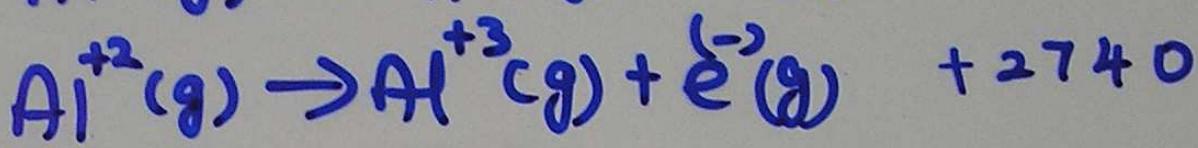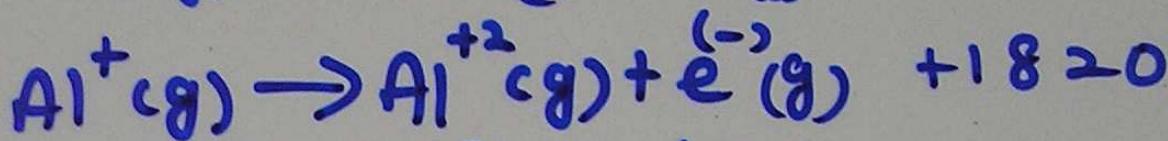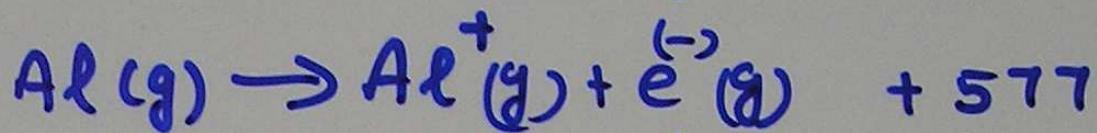
$$n_{Al} = \frac{1.0}{\underline{\qquad}} \qquad 5463$$

$$q = \left[\frac{1.0 \text{ mol}}{\underline{\qquad}} \right] (5463 \text{ KJ mol}^{-1}).$$

$$= 203 \text{ KJ}$$
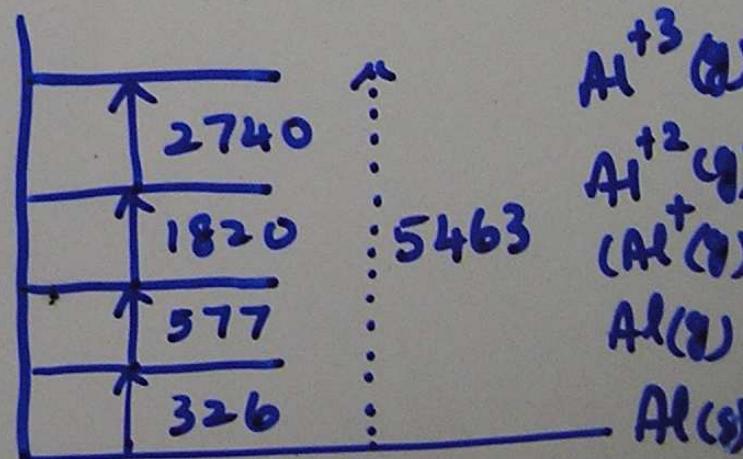
Electron gain: Reverse (or) opposite of ionization

$$atom + e^- \longrightarrow ion$$
(ion)
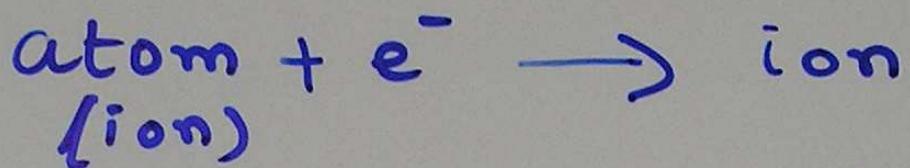
exothermic $\Delta H^\ominus = -Ve$

endothermic $\Delta H^\ominus = +Ve$

Bond enthalpy: The standard molar enthalpy change accompanying molecular dissociation (or) breaking o a chemical bond. (always +V

mean bond enthalpy: ΔH_B
Average of bond enthalpies over a related series of compounds.

$$\Delta_r H^\ominus = \sum \gamma \, \Delta_f H^\ominus \text{(products)}$$
$$- \sum \gamma \, \Delta_f H^\ominus \text{(reactants)}$$

Std enthalpy for $\Delta_f H^\ominus = "0"$
reference state

Enthalpy H

+ve

Endothermic products

Element

−ve

Exothermic compound
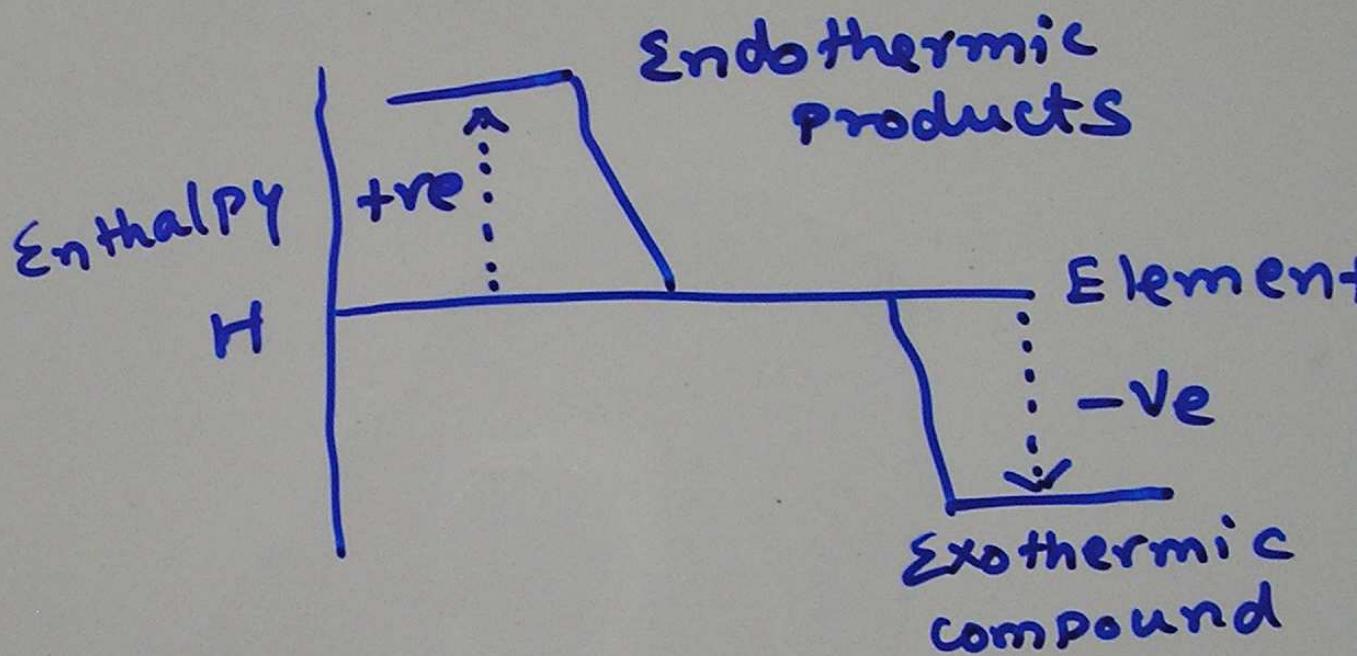
$\Delta_f H^\ominus$ and molecular modelling
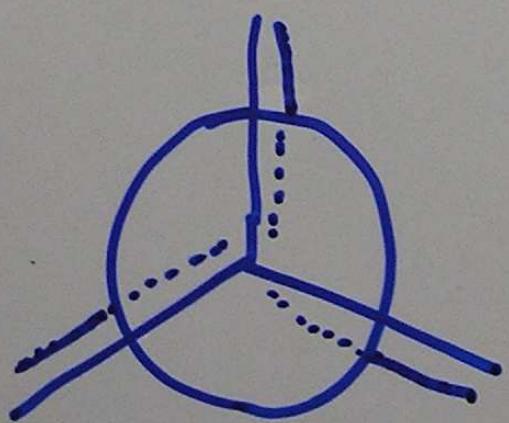
eclipsed conformation
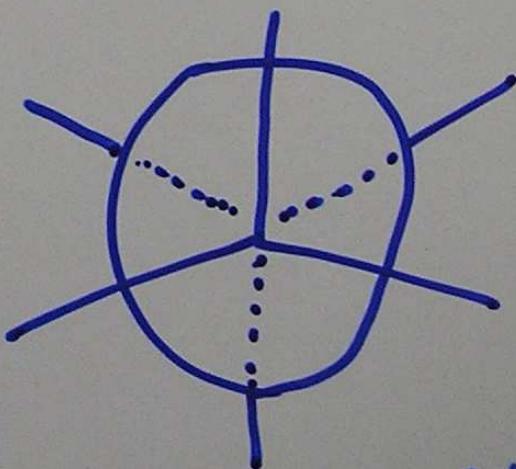
gauche staggered conformation

$CH_3 \longleftrightarrow H.$

H

$H-$

CH_3

axial   equitorial.
(repulsion)

$H_2N CH_2 COOH$ $^+H_3N CH_2 COO^-$
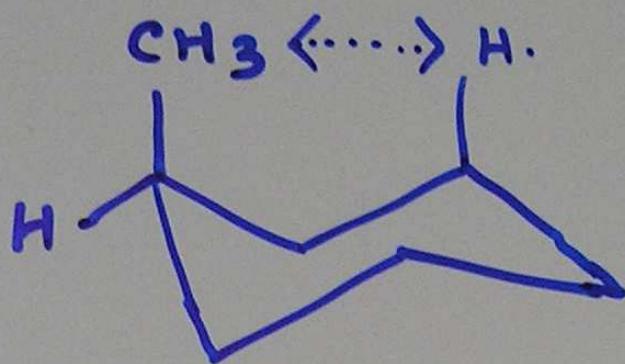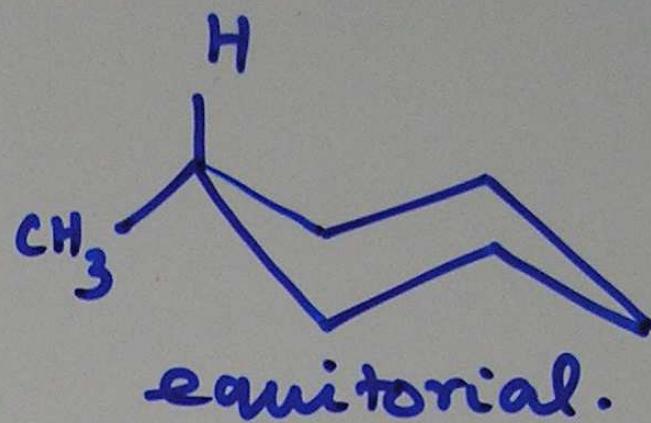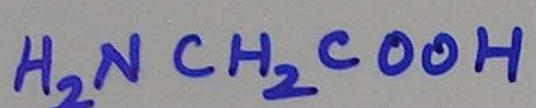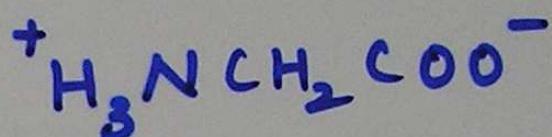
gas phase   in aqueous phase

lower $\Delta_f H^{\ominus}$ lower $\Delta_f H^{\ominus}$

Relationship between $\Delta_f H^{\ominus}$ & T

$$\Delta_r H^{\ominus} = \sum \Delta_f H^{\ominus} (products)$$
$$- \sum \Delta_f H^{\ominus} (reactants)$$

Thermochemical Equation

A conversion describing stochiometric coefficient and standard enthalpy change.

$$2 H_2O(l) + \longrightarrow 2 H_2O(g)$$
$$\Delta H^\ominus = 88 \text{ KJ}$$
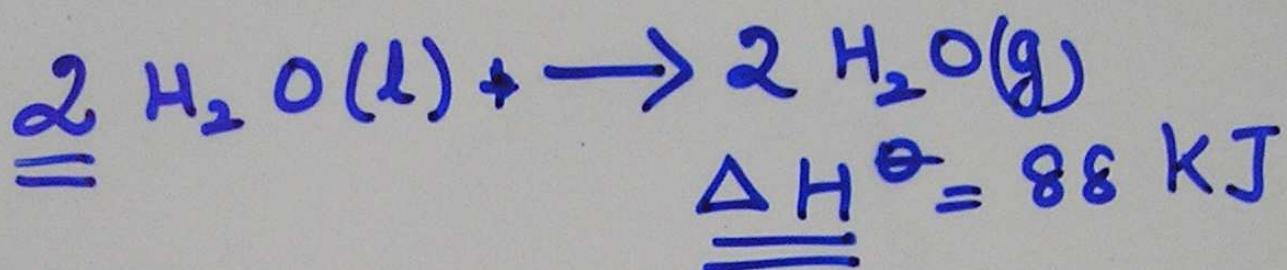
# Standard reaction enthalpy

$$\Delta_r H^\ominus = \sum \gamma H_m^\ominus (Products) - \sum \gamma H_m^\ominus \text{ (reactants)}$$

It is the difference between Std. molar enthalpies of the reactants and products multplied by stoichiometric coefficient "γ".

Standard Enthalpy of formation

$\Delta_f H^\ominus$ is the standard enthalpy for its formation from its elements in their reference state.

reference state $\neq$ standard state

$\Downarrow$
most stable form

$\Downarrow$
pure substance

combustion: complete reaction o
an organic compound
with oxygen.

Standard enthalpy of combustion.
$\Delta_c H^{\theta}$ The change in standard
enthalpy Per mole of combustible
substance.

Kirchoff's Equation

At Constant Volume heat of reaction $\Delta E = E_2 - E_1$

E_1 - internal energy of reactan

E_2 - ..   .. Product

differentiate w.r.t. T at constant

$$\left[\frac{d\,\Delta E}{dT}\right]_V = \left[\frac{dE_2}{dT}\right]_V - \left[\frac{dE_1}{dT}\right]_V$$

$$\therefore \left[\frac{dE}{dT}\right]_V = C_V$$

$$\frac{d\,\Delta E}{dT} = (C_V)_2 - (C_V)_1$$

$$\boxed{\frac{d\,\Delta E}{dT} = \Delta C_V}$$

$(C_v)_2$ - heat capacity of Product

$(C_v)_1$ - heat capacity of reactant

$\therefore$ change in heat of the reaction (ΔE) at constant volume per degree change in temperature (dT) is equal to ΔC_v

Integrate the above equation between T_1 and T_2

$$\int_{T_1}^{T_2} \frac{d\Delta E}{dT} = \int_{T_1}^{T_2} \Delta C_v$$

$$\Delta E_2 - \Delta E_1 = \Delta C_v (T_2 - T_1)$$

ΔE_2 heat of reaction at T_2

ΔE_1 heat of reaction at T_1

At constant Pressure heat of reaction $\Delta H = H_2 - H_1$

H_2 - enthalpy of product

H_1 - " " reactant

differentiate w.r.t "T" at constant "pre

$$\left(\frac{d\,\Delta H}{dP}\right)_P = \left(\frac{dH_2}{dT}\right)_P - \left(\frac{dH_1}{dT}\right)_P$$

$$\left(\frac{dH}{dT}\right)_P = C_P$$

$$\left(\frac{d\,\Delta H}{dT}\right)_P = (C_P)_2 - (C_P)_1 = \Delta C_P$$

$$d\Delta H = \Delta C_P \times dT$$

Change in heat of reaction at constant Pre. Per degree change of temp = difference in heat capaciti of products and reactants at constant "Pre".

Integrating the above eqn between T_1 & T_2

$$\int_{T_1}^{T_2} d\Delta H = \int_{T_1}^{T_2} \Delta C_p \, dT$$

$$\Delta H_2 - \Delta H_1 = \Delta C_p [T_2 - T_1]$$