

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

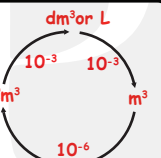
Properties which are independent of matter (size & mass) present in system
e.g. Pressure, temperature, Melting point, density, Specific heat, Surface tension etc.

WORK

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

$$\Delta W = \text{Joule} \begin{cases} P \rightarrow \text{Pascal} \\ V \rightarrow \text{m}^3 \end{cases}$$

1 atm = 1.01×10^5 Pa
1 L atm = 101 J

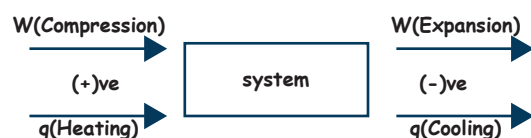


FIRST LAW OF THERMODYNAMICS

(Based on Law of conservation of energy)

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

SIGN CONVENTION

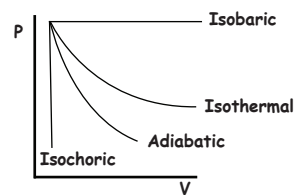


Adiabatic process $\rightarrow \Delta Q = 0, \Delta U = \Delta W$
Insulated, Rapid process
Isothermal process $\rightarrow \Delta T = 0, \Delta U = 0, \Delta Q + \Delta W = 0, \Delta Q = -\Delta W$
Isochoric process $\rightarrow \Delta V = 0, \Delta W = 0, \Delta U = \Delta Q = nC_V \Delta T$
Isobaric process $\rightarrow \Delta W = P \Delta V, \Delta U = \Delta Q + \Delta W$

FLOT

FREE EXPANSION $P_{\text{ext}} = 0, W = 0, \Delta U = 0, q = 0$
ISOTHERMAL $dT = 0; \Delta U = 0; q = -W$

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



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



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
 $\Delta S = nC_P \ln \frac{T_2}{T_1} = nC_P \ln \frac{V_2}{V_1}$

$\Delta S_{\text{total}} > 0$, Spontaneous
 $\Delta S_{\text{total}} = 0$, Equilibrium
 $\Delta S_{\text{total}} < 0$, Non-spontaneous

GIBBS'S 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

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

THERMODYNAMICS

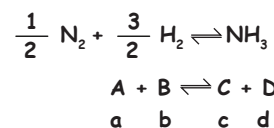
THERMOCHEMISTRY

1) Heat of Reaction (ΔH_{rxn})

$$\Delta H_{\text{rxn}} = H_{\text{products}} - H_{\text{reactants}}$$

2) Heat of Formation

Heat Change in formation of 1 mole of substance at 298 K and 1 atm Pressure (standard enthalpy of formation)



$$\Delta H_{\text{reaction}} = \text{Heat of formation of products} - \text{Heat of formation of reactants}$$

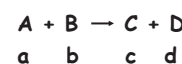
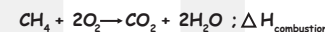
$$= (c + d) - (a + b)$$

Standard enthalpy of formation (298 K, 1 atm) of element at its standard state is zero e.g.,



3) Enthalpy of Combustion (1 mole, 298 K)

(standard enthalpy of combustion)

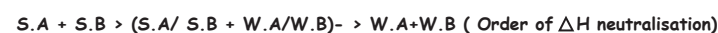
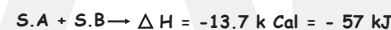


Enthalpy of combustion:

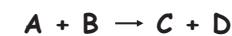
$$\Delta H_{\text{reaction}} = \text{Heat of combustion of reactants} - \text{Heat of combustion of products}$$

$$= (a + b) - (c + d)$$

4) Heat of Neutralisation ($\Delta H = (-)\text{ve}$)



BOND ENERGY



Bond energy: $\begin{matrix} a & b & c & d \end{matrix}$

$$\Delta H_{\text{reaction}} = \text{Bond energy of reactants} - \text{Bond energy of products}$$

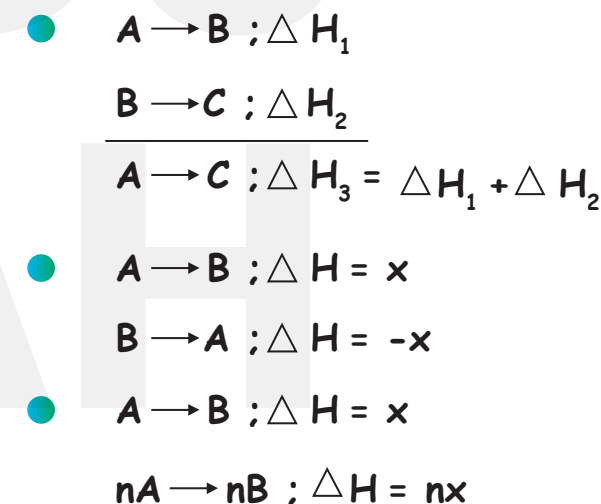
$$= (a + b) - (c + d)$$

$$\text{NH}_3 \Rightarrow \text{B.E} = x$$

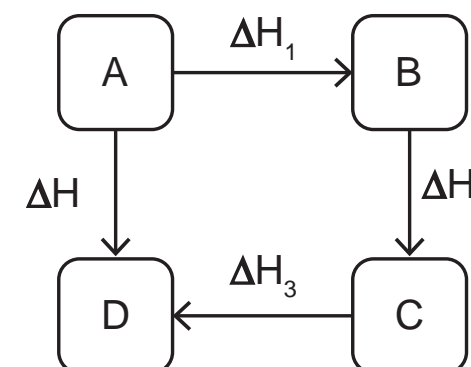
$$\text{B.E of N-H} = \frac{x}{3}$$

$$\text{CH}_4 \Rightarrow \text{B.E} = x$$

$$\text{B.E of C-H} = \frac{x}{4}$$



HESS' LAW OF CONSTANT HEAT SUMMATION



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

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.	Spontaneous at $T > T_e$
(-)	(-)	-ve @ low temp. +ve @ high temp.	Spontaneous at low temperature, $T < T_e$