

THERMODYNAMICS & CHEMICAL ENERGETICS

- ❖ System is a part of universe selected for our study
- ❖ surrounding means the rest of universe

System + Surrounding = Universe

Systems are of 2 types :-

- 1) **Homogenous system** → Pure NaCl :- System with uniform property ⇒ contain one phase.
- 2) **Heterogenous system** → Ice + Water :- System with non uniform property ⇒ contain more than one phase

Based on exchange of matter or energy with surrounding, systems are classified in to :-

- 1) **Open system** :- System with can exchange matter and energy with surrounding
ex: Hot water in an open steel cup
- 2) **Closed system** :- Can exchange only energy but not matter with surrounding
ex: Hot water in a sealed steel cup
- 3) **Isolated system**:- A system which can exchange neither energy nor matter with surrounding.
ex: Hot water in a well insulated thermoflask.

Thermodynamic Properties

- 1) **Extensive property** :- Depend on amount of substance
ex: Mass, volume, heat capacity, internal energy [U], enthalpy [H], entropy [S], gibbs energy [G].
- 2) **Intensive property**:- Independent of amount of substance. Depend only on nature of subs.
ex: Density, temp., conc. [Normality, Molarity], p^H , specific heat capacity, molar heat capacity, molar volume, surface tension, viscosity, refractive index etc.

Ratio b/w two extensive properties will be an intensive prpty.

$$\text{ex: } \frac{\text{mass}}{\text{vol.}} = \text{density}, \frac{\text{heat capac.}}{\text{no. of mole}} = \text{Molar heat capacity}$$

Thermodynamic functions

A function whose change in value depend only on initial & final state of system & not on path followed - state function

ex: Pressure, vol, temp, U, H, S, G,

$$\frac{F}{A} \rightarrow \text{Exothermic}$$

Path function:- A function which depend only on the path & not on the state of system.

ex: Heat [q], work [w]

Thermodynamic processes

- 1) Isothermal Process:- Process in which temp is const., $T = \text{const.}$, $\Delta T = 0$
- 2) Isobaric Process:- Pressure is const. $\Delta P = 0$
- 3) Isochoric Process:- Vol. is constant $\Delta V = 0$
- 4) Adiabatic Process:- No exchange of heat occur b/w system and surrounding $q = 0$
- 5) Cyclic Process:- Process which return to initial state after several changes.

For a cyclic process, $\Delta U = 0$, $\Delta H = 0$

- 6) Reversible Process :-

- Can be reversed by a small change in pressure, temp, conc. etc.
- Driving force & opposing force differ by an infinite decimal amount.
- It occurs through infinite num. of steps & each step is very slow.
 \therefore it take infinite time for completion.
- It is only an ideal process

- 7) Irreversible Process

- Cannot be reversed by a small change
- Occur in a single step and is very fast
 \therefore it is completed in a definite time.
- It is a real process
- All naturally occurring process are irreversible and spontaneous

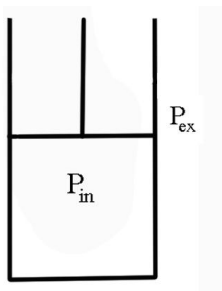
Mode of Energy Transfer

- 1) Heat [q]:- Occur due to diff. in temp. between system and surrounding.

If heat is absorbed by the system it is positive.

If heat is released by system, it is -ve

- 2) Work [w] : - Occur due to diff. in pressure b/w system & surrounding



$P_{\text{ext}} > P_{\text{in}}$, work done is on the system & is positive \rightarrow energy transfer from surrounding to system

$P_{\text{ext}} < P_{\text{in}}$, work done is by the system & is -ve.

This work is called Mechanical work or PV work./work of Expansion*

$$\boxed{W = -P\Delta V}$$

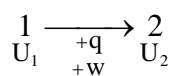
$P \Rightarrow$ const. ext. pressure

This work is irreversible work when a gas expand against const. ext. pressure

First Law of Thermodynamics OR Law of conservation of Energy

The total energy of an isolated system remains const. OR The total energy of universe remain const.

Consider the reaction,



According to Ist law $\rightarrow U_2 = U_1 + q + w$

$$U_2 - U_1 = q + w$$

$$\boxed{\Delta U = q + w} \quad w = -P\Delta V$$

$$\therefore \boxed{\Delta U = q - P\Delta V}$$

Application of First Law to A Chemical Reaⁿ

1) Reaction in a closed vessel (At const. vol.)

$$\Delta U = q + w \Rightarrow \Delta U = q - P\Delta V$$

$$\text{at const.vol.} \Rightarrow \boxed{\Delta U = q_v}$$

$$[\Delta V = 0]$$

The change in internal energy of a system is equal to amount of heat absorbed or evolved in a chemical reaⁿ at const. vol.

2) Reaction in an open vessel [At const. pressure]

❖ **Enthalpy [Heat content] [H]**

It is used to study about a rean at const. pressure.

Enthalpy is defined as the sum of int. energy & pressure vol.energy of system

$$H = U + PV$$

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

at const. pressure, $\Delta H = \Delta U + P\Delta V$

$$\Delta U = q + w = q - P\Delta V$$

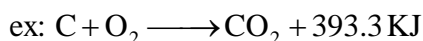
$$\Delta U + P\Delta V = q$$

At const.pressure $\boxed{\Delta H = q_p}$

Enthalpy change = amount of heat absorbed evolved in a chemical rean at const. pressure so is also called heat at const. pressure

Exothermic Reaction

Reaction combined with evolution of heat.

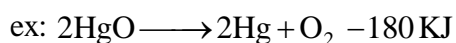


$$H_p < H_R \text{ or } \Delta H = H_p - H_R = -ve$$

In the above ex., $\Delta H = -393.3 \text{ KJ}$

Endothermic Reaction

Reactions accompanied by absorption of heat

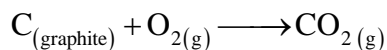


$$H_p > H_R \quad \Delta H = H_p - H_R = +ve$$

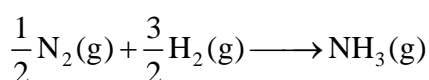
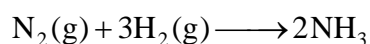
In the ex., $\Delta H = +180 \text{ KJ}$

Enthalpy of formation

It is the change in enthalpy [Heat absorbed or evolved] when 1 mole of a compound is formed from corresponding stable elements.



$$\Delta H_f(CO_2) = -393.5 \text{ KJ mol}^{-1}$$



$$\Delta H_f(NH_3) = -46 \text{ KJ mol}^{-1}$$

Standard Enthalpy of formation $[\Delta H_f^0]$ values are used to explain stability of compound.

- 1) If ΔH_f^0 of the compound is –ve, it is more stable. If it is +ve, less stable

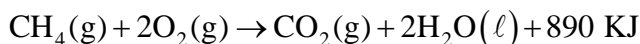
In exothermic reaction, more heat evolved – more stable element

$$2) \quad \Delta H_{\text{Reaction}}^0 = \sum \Delta H_{f(\text{Products})}^0 - \sum \Delta H_{f(\text{Reactants})}^0$$

$$\Delta H_f^0(\text{all elements}) = 0$$

Enthalpy of Combustion $[\Delta H_c]$

It is the change in enthalpy [heat evolved] when 1 mole of a substance is burned in excess oxygen.



$$\Delta H_c(\text{CH}_4) = -890 \text{ KJ}$$

Work Done in Reversible Isothermal Expansion of Ideal Gas

$$W = -p \cdot \Delta V$$

Integral form is,

$$dW = -p \cdot dV$$

$$W = \int dw = \int_{V_1}^{V_2} -p \cdot dV = \int_{V_1}^{V_2} \frac{-nRT}{V} dV = -nRT \int_{V_1}^{V_2} \frac{dv}{V}$$

$$W = -nRT (\ln V_2 - \ln V_1) = -nRT \ln \frac{V_2}{V_1}$$

$$W = -2.303 nRT \log \frac{V_2}{V_1}$$

$$W = -2.303 nRT \log \frac{P_1}{P_2}$$

$$W_{\text{rev.}} = W_{\text{irrev.}}$$

$$W_{\text{rex}} = W_{\text{max.}}$$

Heat capacity

Amount of heat required to raise the temp. of the substance through 1°C

$$C = \frac{q}{\Delta T}$$

Specific Heat Capacity

Amount of heat to raise the temp. of 1g substance through 1°C.

$$S = \frac{q}{m\Delta T}$$

q – amount of heat

m– mass of subst.

ΔT – rise in temp.

$$q = ms\Delta T$$

Molar capacity

Amount of heat to raise the temp. of 1 mole subst. through 1°C.

For a gas, we have 2 molar heat capacities

$$1) \quad C_V = \left(\frac{dU}{dT} \right)_V \Rightarrow \text{change in int.energy} \rightarrow \text{with temp. at const. volume.}$$

$$dU = C_V dT \text{ [for 1mole gas]}$$

$$dU = nC_V dT \text{ [for n mole gas]}$$

$$\Delta U = nC_V \Delta T$$

$$2) \quad C_P = \left(\frac{dH}{dT} \right)_P \Rightarrow \text{change in enthalpy with temp. at const. pressure}$$

$$dH = C_P dT \text{ [1 mole gas]}$$

$$dH = nC_P dT \text{ [n mole gas]}$$

$$\Delta H = nC_P \Delta T$$

$$\begin{array}{l} C_P - C_V = R \\ \frac{C_P}{C_V} = \gamma \end{array}$$

For 'n' mole

$$C_p - C_v = nR$$

$$n = \text{no. of moles} = \frac{\text{Given mass}}{\text{Mol. mass}}$$

Gas	C_v	C_p	$\gamma = \frac{C_p}{C_v}$
Monoatomic gas	$\frac{3}{2}R$	$\frac{5}{2}R$	1.66
Diatomic gas	$\frac{5}{2}R$	$\frac{7}{2}R$	1.40
Triatomic gas	$3R$	$4R$	1.33

Work Done in Reversible Adiabatic Expansion of Ideal Gas

$$q = 0$$

$$\Delta U = q + W \Rightarrow 0 + W = W$$

$$\text{or } W = \Delta U$$

That is in adiabatic expansion work is done at the expense of int. energy of the system.

\therefore int. energy decre & temp. also decreases.

Hence, cooling effect is produced in adiabatic expansion.

In adiabatic compression, W.D is on the system, \therefore U increases \Rightarrow T also \uparrow

\therefore Heating effect is produced in adiabatic compression

Integral form is,

$$dW = dU$$

$$dW = nC_v dT$$

$$W = \int dW = \int_{T_1}^{T_2} nC_v dT = nC_v \int_{T_1}^{T_2} dT$$

$$W = nC_v (T_1 - T_2)$$

$$C_p - C_v = R \Rightarrow \frac{C_p}{C_v} - \frac{C_v}{C_v} = \frac{R}{C_v}$$

$$\Rightarrow r-1 = \frac{R}{C_v} \Rightarrow \boxed{C_v = \frac{R}{r-1}}$$

$$\Rightarrow \boxed{W = \frac{nR}{r-1} [T_2 - T_1]}$$

Heat of combustion At const. vol.

A known mass of the substance is burned in a bomb calorimeter & heat liberated raises the temp. of the calorimeter system [including water]. The rise in temp. is measured

Mass of subs.taken = M g

Rise in temp = ΔT

Let heat produced = q

Heat capacity, $C = \frac{q}{\Delta T}$ or $q = C\Delta T$

q from 1 mole subst. = $\frac{C\Delta T}{m} \times M$
[M—Molar mass]

$$\therefore \boxed{\Delta U = \frac{-C\Delta T}{m} \times M} \quad [\Delta U = q_v]$$

$$\boxed{\text{Specific heat of water} = 1 \text{ cal g}^{-1}}$$

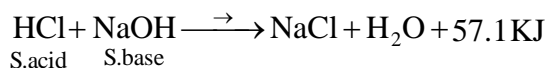
$\therefore 0.5 \text{ gc} \longrightarrow 4 \text{ kcal. heat}$

Calorific value is the amount of heat produced by the combustion of 1g substance

$$\text{Calorific value} = \frac{\text{Enthalpy of combustion}}{\text{G.M.M}}$$

Heat of Neutralisation [ΔH_n]

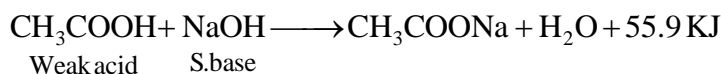
It is the change in enthalpy [Heat evolved] when 1g eqlvnt of an acid react with 1g eqlvnt of a base in dilute aq. solution.



$$\Rightarrow \Delta H_n = -57.1 / -13.7 \quad [13.7 \text{ kcal}]$$

The final reaction is always the same

\therefore the value remains a constant



Heat liberated is less than 57.1 KJ

[1.2 KJ less]

1.2 KJ is the heat absorbed by weak acid for its ionisation \Rightarrow 1.2 KJ = enthalpy of ionisation = ΔH_{ions} .

[$\Delta H \rightarrow +ve$ bcoz endothermic]

Weak acid – HF gives 68 KJ heat.

It is due to the hydration energy of fluoride ion

❖ Find the heat liberated when 50cm³ of 0.2 N H₂SO₄ is mixed with 50cm³ of

1 N KOH [Vol(ml) \times N]

millieqlvnt of H₂SO₄ = 50 \times 0.2 = 10 millieqlvnt

Milleqlvnt of KOH = 50 \times 1 = 50 milleqlvnt

[N – gr.eqlvnt / ℓ] \Rightarrow 1000 meq.

1000 meq \rightarrow 57.1 KJ

$$\therefore 10 \text{ meq} \rightarrow \frac{57.1}{1000} \times 10 = 0.571 \text{ KJ}$$

$$= 571 \text{ J}$$

Laws of thermo chemistry

1) Lavoisier Laplace Law

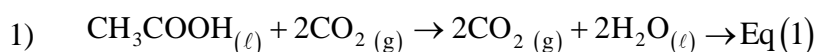
When a chemical reaction is reversed the magnitude of ΔH is the same but the sign is opposite.

2) Hess's Law of constant heat summation

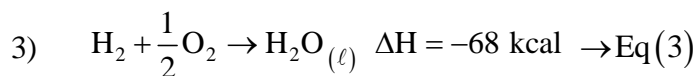
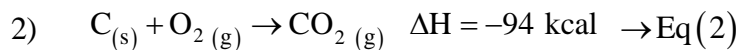
The total enthalpy change of a chemical reaⁿ is always the same; whether the reaⁿ occurs in a single step or in several steps. [Thermodynamic qty is additive. ΔH of many reaⁿ can be added]

Hess's law can be applied for calculating the ΔH values of certain reactions by an indirect method.

❖ Calculate the heat of formation of acetic acid from the following

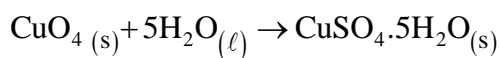


$$\Delta H = -200 \text{ cal}$$



Enthalpy of Hydration $[\Delta H_{\text{hyd}}]$

Change in enthalpy when 1 mole of anhydrous salt combine with required num. of moles of water to form hydrated salt.



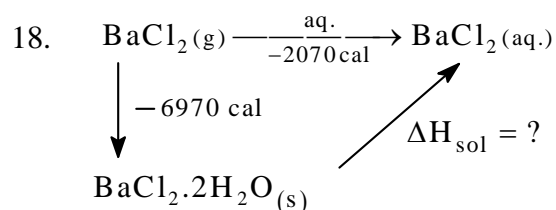
$$\Delta H = -78.2 \text{ KJ}$$

Enthalpy of solution (ΔH_s)

Change in enthalpy when 1 mole of the substance dissolve in excess solvent to form the solution.

For hydrated salts & for salt which do not form hydrates ΔH is +ve.

For anhydrous salts, ΔH is -ve



Applying Hess's law,

$$-2070 = -6970 + \Delta H_{\text{sol}}$$

$$\Delta H_s = -2070 + 6970 = +4900 \text{ cal}$$

Thermal equilibrium :- no flow of heat $\Rightarrow T = \text{const.}$

Mechanical equilibrium :- no flow of matter $\Rightarrow P = \text{const.}$

Chemical equilibrium :- no change in composition

Internal energy :- Heat absorbed / evolved at const. vol.

Enthalpy change :- Heat absorbed/evolved at const. pressure.

$$1 \text{ cal} = 4.184 \text{ J or } 1 \text{ J} = 0.239 \text{ cal}$$

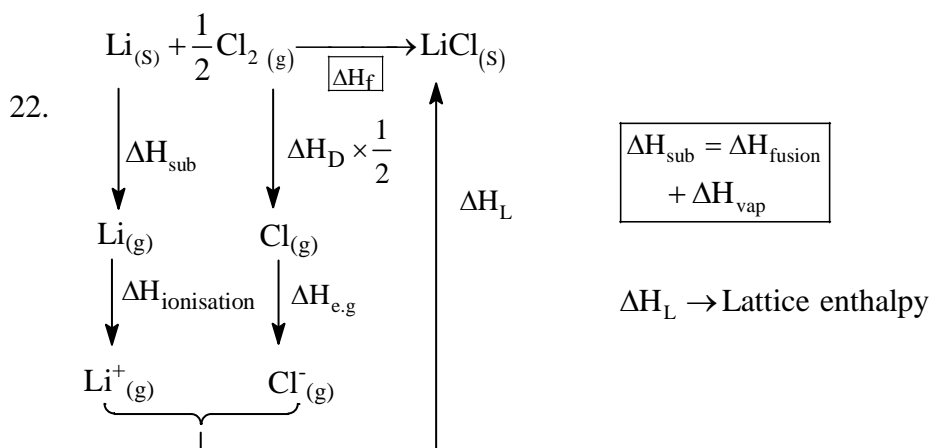
$$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$$

$$1 \text{ J} = 10^7 \text{ erg.}$$

$$1 \text{ cal} > 1 \text{ J} > 1 \text{ erg}$$

Lattice Enthalpy

It is the energy liberated when 1 mole of a solid ionic compound is formed from the corresponding gaseous ions. Lattice energies of solid ionic compounds cannot be determined experimentally. They are usually calculated using Born-Haber cycle



Applying Hess's law,

$$\Delta H_f = \Delta H_{\text{sub}} + \Delta H_{\text{ionis.}} + \frac{1}{2} \Delta H_D + \Delta H_{\text{e.g}} + \Delta H_L$$

$$-401.66 = 160.67 + 520.07 + \frac{244.34}{2} + -365.26 + \Delta H_L$$

$$= -839.3 \text{ KJ mol}^{-1}$$

$$\Delta H_{\text{sol.}} = \Delta H_{\text{hyd.}} + \Delta H_L$$

Bond Dissociation Energy

[For diatomic molecules]

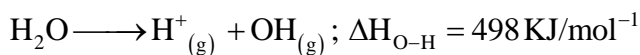


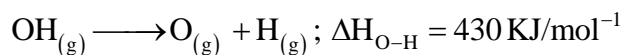
It is the energy required to break 1 mole of bonds in gaseous diatomic molecule in to free atoms in the gaseous state.

A compound is soluble in water if hydration enthalpy > lattice enthalpy

Bond Energy

[For polyatomic molecules like NH_3 , H_2O , CH_4]



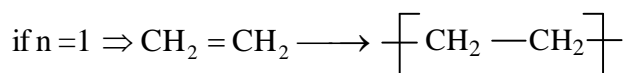
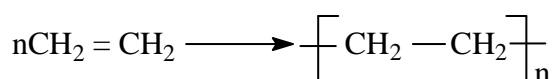


$$\Delta H_{\text{O-H}} = \frac{498 + 430}{2} = 464 \text{ KJ/mol}^{-1}$$

It is the avg. energy required to break one mole of bonds in a gaseous polyatomic molecule in to free atoms in the gaseous state.

$$\Delta H_{\text{Reaction}} = \sum \text{B.E of reactant} - \text{B.E. of products}$$

- ❖ Bond enthalpy of C=C bond & C-C bond at 298 K are 590 & 331 KJ/mol. Find the enthalpy of polymerisation per mole of ethylene



$$\begin{aligned} \Delta H_{R_n} &= [\Delta H_{\text{C=C}} - 2 \times \Delta H_{\text{C-C}}] \\ &= 590 - 2 \times 331 = -72 \text{ KJ/mol} \end{aligned}$$

Spontaneous Process

A process which occur by itself or a process having a natural tendency to occur.

- ex:
- 1) Dissolution of sugar in water
 - 2) Melting of ice at room temp.
 - 3) Water flow from higher level to a lower level.
 - 4) Mixing of gases

A process is spontaneous in one dirⁿ & non spontaneous in the opp.dirⁿ.

Dirⁿ of spontaneous process

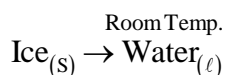
- 1) Compare the energy of initial & final state.

[or enthalpy]

The process is spontaneous in the dirⁿ in which energy or enthalpy decreases.

i.e. $\Delta H = -ve$ [exothermic]

- 2) Compare the Disorder or Randomness in the system.



This is spontaneous but ΔH is +ve. The disorder of water is greater than disorder of ice.

The process is spontaneous in the dirⁿ in which the disorder of system increases.

Entropy [S]

It is a thermodynamic quantity which measure the degree of disorder in a system.

Entropy = Disorder

$$S_{\text{water}} > S_{\text{ice}}$$

$$\Delta S = \Delta S_{\text{water}} - \Delta S_{\text{ice}} = +ve$$

Process is spontaneous in the dirⁿ in which entropy increases.

For a spontaneous process, $\Delta S = +ve$ or $\Delta S > 0$

For a spontaneous process in isolated system ΔS of system > 0

For a spontaneous process in non-isolated system, $\Delta S_{\text{Total}} > 0$

$$\text{i.e. } (\Delta S_{\text{system}} + \Delta S_{\text{surrounding}}) > 0$$

$$\Delta S_{\text{universe}} > 0$$

This is called **2nd Law of Thermodynamics**

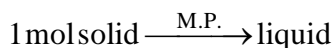
The 2nd law states that during s spontaneous process the entropy of universe is going on increasing.

$$\boxed{\Delta S = \frac{q_{\text{rev}}}{T}} = \text{The heat absorbed in a reversible process } \div \text{Temp. of absorption}$$

$$\Delta S = \frac{J}{K} = JK^{-1}[\text{s.i.unit}]$$

Types of Entropy changes

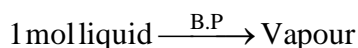
1) Entropy of fusion [ΔS_f]



It is the change in entropy when 1 mole of a solid changes to the liquid stage at the M.P.

$$\boxed{\Delta S_f = \frac{\Delta H_f}{T_f}}$$

2) Entropy of Vaporisation [ΔS_v]



It is the change in entropy when 1 mole liquid changes to vapour state at B.P.

$$\Delta S_v = \frac{\Delta H_v}{T_v}$$

3) Entropy change during Expansion of Ideal gas

$$1. \Delta S = nC_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} [T_1 V \rightarrow \text{variables}]$$

$$2. \Delta S = nC_p \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2} [T_1 P \rightarrow \text{variable}]$$

$$\text{I. } 1) \Delta S_{\text{isothermal}} = nR \ln \frac{V_1}{V_2}$$

$$2) \Delta S_{\text{isothermal}} = nR \ln \frac{P_1}{P_2}$$

$$\text{II. } 1) \Delta S_{\text{isobaric}} = nC_p \ln \frac{T_2}{T_1}$$

$$\text{III. } 1) \Delta S_{\text{isochoric}} = nC_p \ln \frac{T_2}{T_1}$$

4) Entropy change in A Chemical Reaction

Sign of ΔS = num. of moles of gaseous product – num. of mole of gaseous reactant.

Third Law of Thermodynamics

It deals with the entropy of solids. It states that the entropy of a perfectly crystalline solid become = to zero at absolute zero or zero kelvin.

From 3rd law, it can be concluded that all substances possess definite entropy values at various temp.

3rd law can be applied for calculating the **absolute entropy** for all substance at various temp. & hence the entropy change of a chemical reaⁿ can also be calculated.

$$\Delta S_{\text{Rea}^n} = \sum S_{(\text{products})} - \sum S_{(\text{Reactants})}$$

Gibbs Energy/Free Energy [G]

It is a part of T.E. of a system which can be converted in to useful work. The decrease in gibb's energy is equal to max. useful work done by the system. Gibbs energy is also defined as

$$\boxed{G = H - TS} \quad \text{or} \quad \boxed{\Delta G = \Delta H - T\Delta S}_{T,P}$$

Gibbs Helmholtz equation

criterion of Spontaneity

For a spontaneous process, ΔH is -ve & ΔS is +ve

$$\Delta G = \Delta H - T\Delta S$$

In such a case, ΔG will be always -ve

- 1) If ΔG is -ve, the process is spontaneous [is feasible]
- 2) If ΔG is +ve, the process is non-spontaneous or not feasible
- 3) If $\Delta G = 0$, the process is at eqm state

ΔH	ΔS	$\Delta G = \Delta H - T\Delta S$	Nature of Process
-	+	always -	Spontaneous at all temp.
+	-	always +	non spontaneous at all temp.
+	+	- ve at high temp.	spontaneous at high temp.
		+ ve at low temp.	non spontaneous at low temp.
-	-	- at low temp.	spontaneous at low temp.
		+ at high temp.	non spontaneous at high temp.

Std. Gibb's Energy of formation [ΔG_f^0]

It is the change in Gibbs energy when 1 mole of a compound is formed from the constituent stable elements under std. condition.

$$\Delta G_f^0 \text{ of all elements} = 0$$

$$\boxed{\Delta G_{\text{Reaction}}^0 = \sum \Delta G_f^0 (\text{Prod}) - \sum \Delta G_f^0 (\text{Reac})}$$

Krichoffs Equation

$$\boxed{\Delta H_2 - \Delta H_1 = \Delta C_P(T_2 - T_1)}$$

$$\left[\Delta C_P = \sum \Delta C_{P_{(P)}} - \sum \Delta C_{P_{(R)}} \right]$$

$$\Delta U_2 - \Delta U_1 = \Delta C_V(T_2 - T_1)$$