UNIT-6
CHEMICAL THERMODYNAMICS

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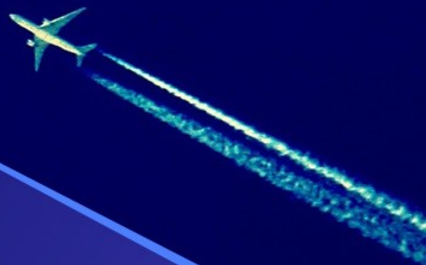
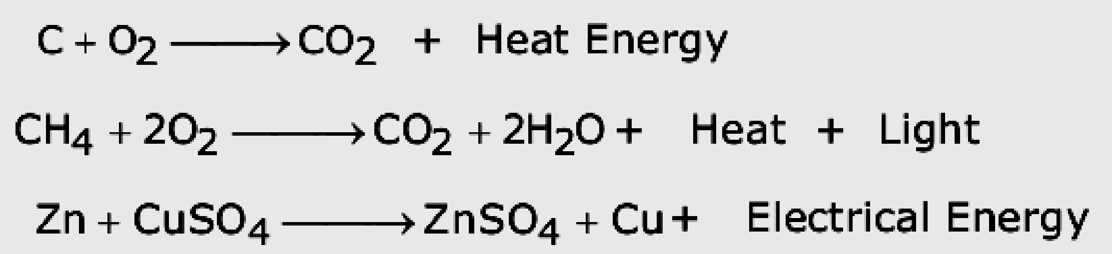


CHEMICAL ENERGETICS

The branch of chemistry which deals with energy changes associated with chemical reactions is called chemical energetics.



$$C + O_2 \longrightarrow CO_2 + \text{Heat Energy}$$

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O + \text{Heat} + \text{Light}$$

$$Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu + \text{Electrical Energy}$$

CHEMICAL THERMODYNAMICS

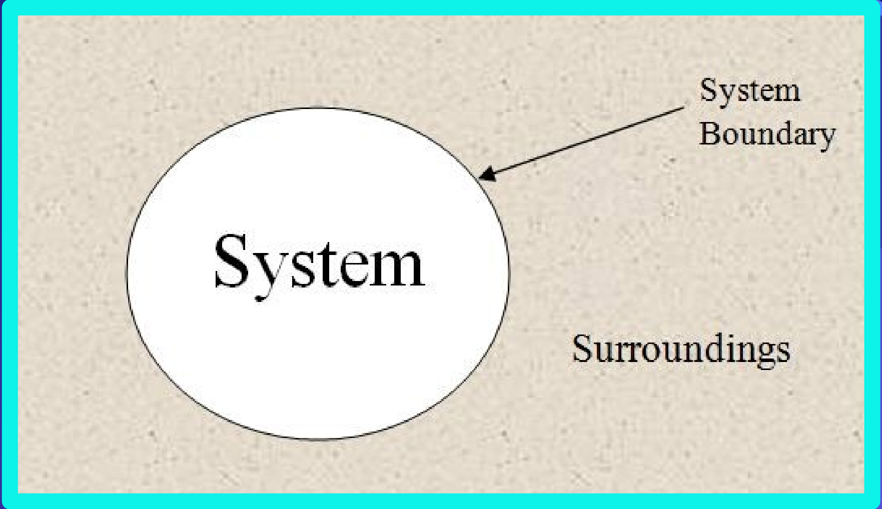
- The word ‘Thermo’ means heat and ‘dynamics’ means work.
- The term thermodynamics literally means flow of heat.
- It deals with the relation between heat and work.

CHEMICAL THERMODYNAMICS

The branch of science which deals with the study of energy changes associated with chemical reactions is called Chemical Thermodynamics.

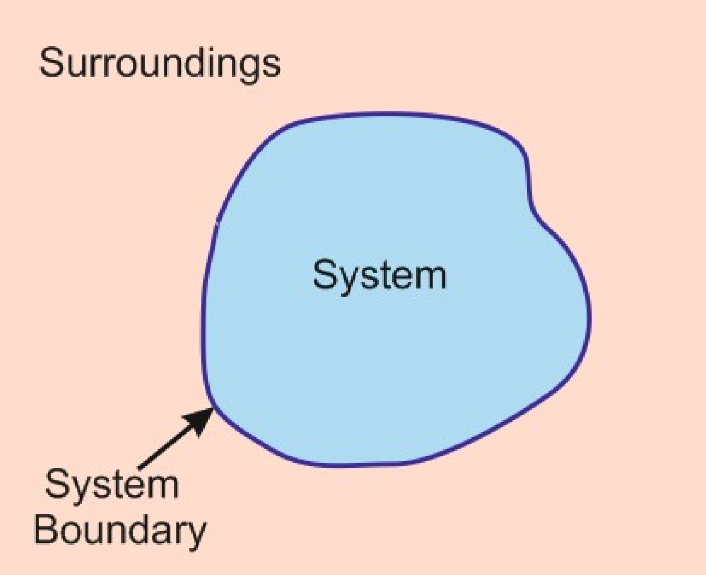
SYSTEM

A specified part of the universe which is under observation is called a system.



SURROUNDINGS

The rest of the universe which is not a part of the system is called surroundings.



TYPES OF SYSTEMS

OPEN SYSTEM

A system which can exchange matter as well as energy with the surroundings is called an open system.

Eg: Hot tea placed in an open cup.

CLOSED SYSTEM

A system which can exchange energy but not mass with the surroundings is called a closed system.

Eg: Hot tea placed in a closed cup.

ISOLATED SYSTEM

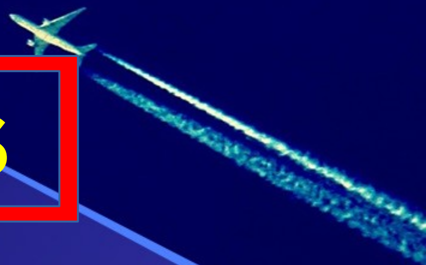
A system which can neither exchange mass nor energy with the surroundings is called an isolated system.

Eg: Hot water placed in a thermoflask.

HOMOGENEOUS AND HETEROGENEOUS SYSTEM

- In a homogeneous system, the physical properties and chemical composition are Identical throughout the system.
- In a heterogeneous system, the physical properties and chemical compositions are different.

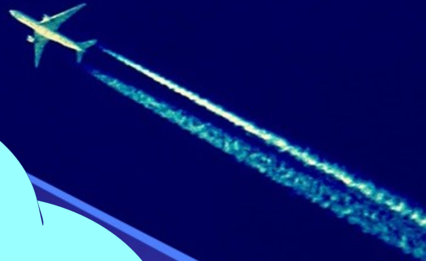
MACROSCOPIC PROPERTIES



- The properties which depend on the bulk of the system are called macroscopic properties.
- Eg: Pressure, Temperature, Volume, Composition, Surface Tension, Viscosity, Density.

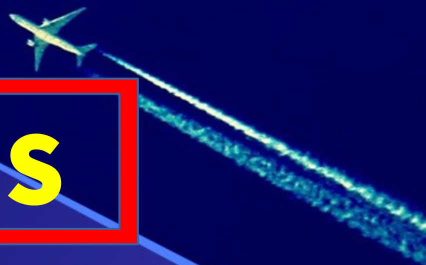
EXAMPLE

In order to measure the temperature of water we do not deal with individual molecules but we consider the molecules in the bulk.



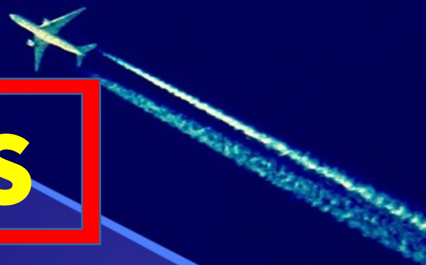
TYPES OF MACROSCOPIC PROPERTIES

EXTENSIVE PROPERTIES



- The properties of the system which depend on the amount of matter contained in it.
- Eg: Mass, Volume, Energy, Heat Capacity etc.

INTENSIVE PROPERTIES



- The properties of the system which are independent of the amount of matter present in it are called intensive properties.
- Eg: Pressure, Temperature, Density, Viscosity, Specific heat capacity etc.

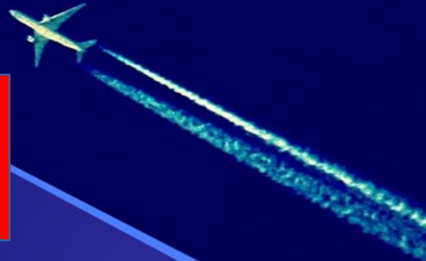
STATE OF A SYSTEM

A system is said to be in a certain state when the macroscopic properties such as pressure, temperature, volume, composition etc have definite values.

STATE VARIABLES

- **The measurable properties which are required to determine the thermodynamic state of a system are called state variables.**
- **Eg: Pressure, Volume, Temperature, Composition etc.**

STATE FUNCTION



- A state function is the property of the system whose value depends only on the state of the system and independent of the path or manner by which the state is reached.
- Eg: Pressure, Volume, Internal Energy, Enthalpy etc.

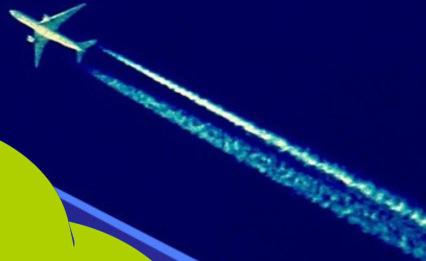
PATH FUNCTION

A path function is a property of a system whose value depends on the path followed to reach the system.

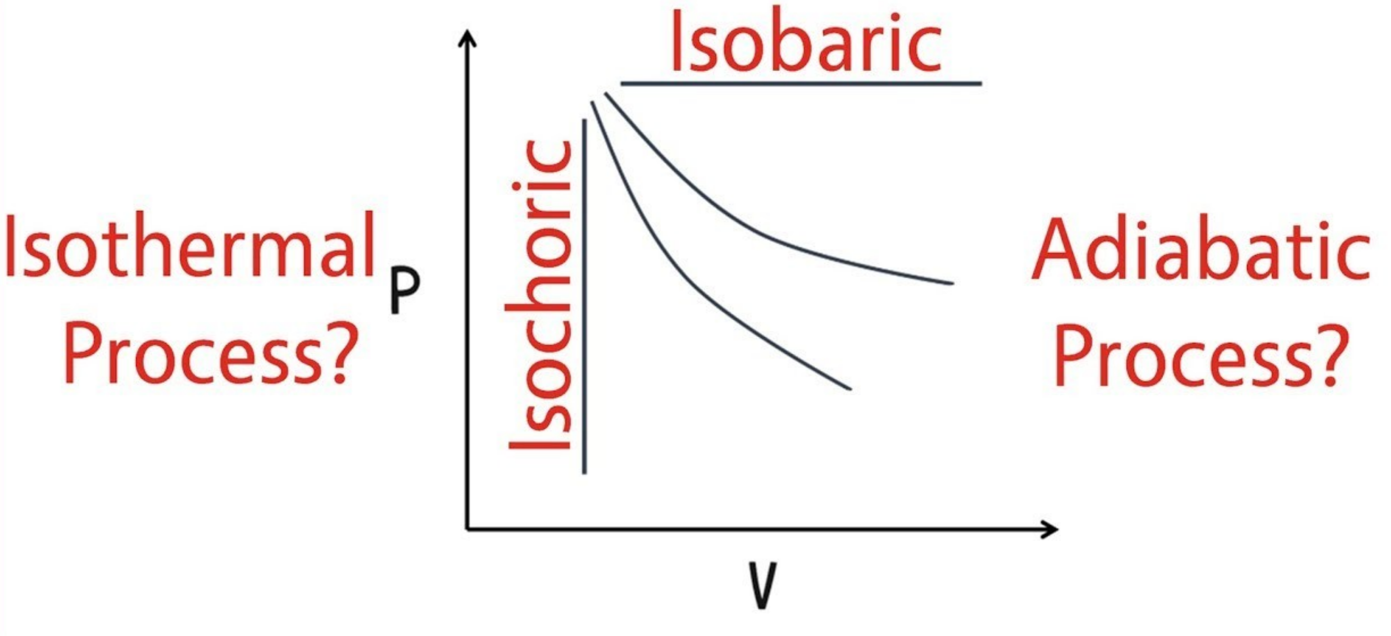
PROCESS

A process is a method or operation by which a system changes from one state to another.

TYPES OF PROCESS

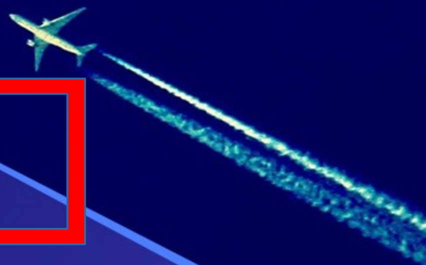


THERMODYNAMIC PROCESS



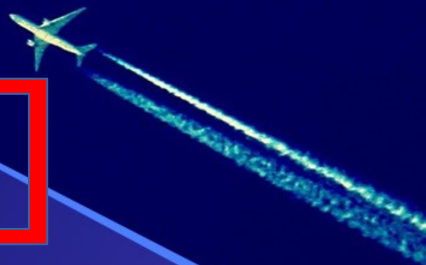
- A process in which temperature remains constant is called **Isothermal Process.**
- A process in which no heat enters or leaves the system is called an **Adiabatic Process.**
- A process in which pressure remains constant is called an **Isobaric Process.**
- A process in which volume of the system remains constant is called and **Isochoric Process.**

REVERSIBLE PROCESS



A process in which the change is carried out so slowly that the system and surroundings are always in equilibrium is called a reversible process.

IRREVERSIBLE PROCESS



A process which occurs suddenly or spontaneously such that it does not remain in equilibrium during the transformation is called irreversible process.

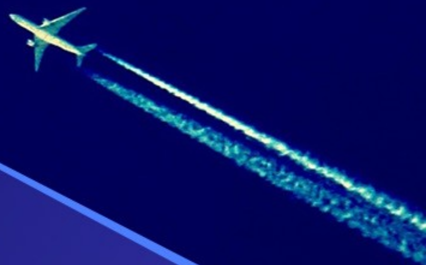
WORK

- Whenever a system changes from one state to another, the energy of the system also changes.
- Energy changes can occur either as heat or as work.
- Work is a form of energy that flows across the boundary of a system as a result of difference in pressure.

HEAT

- **Heat is a form of energy that flows across the boundary of a system as a result of a difference in temperature.**
- **It passes from a hot body to a cold body.**

SIGN CONVENTION

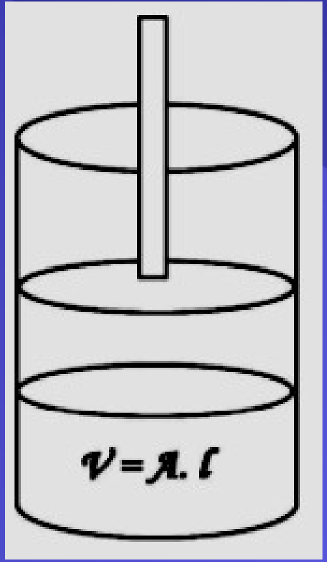


- If Heat is absorbed by the system, q is positive
- If Heat is evolved by the system, q is negative
- If Work is done on the system, w is positive
- If Work is done by the system, w is negative

PRESSURE-VOLUME WORK

- It is the work done when the system expands or contracts against the external pressure.
- Consider a cylinder provided with a piston having an area of cross section ‘A’.
- Let a gas of volume ‘V’ is enclosed in the cylinder.
- The pressure acting on the piston is ‘P’.

- When the internal pressure is slightly more than the external pressure, the gas expands.
- As a result the piston moves a very small distance dl.
- Then, the change in volume, dv = A. dl.
- We know that $\boxed{\text{pressure} = \frac{\text{force}}{\text{area}}}$
- i.e., Force acting on the piston, F = P x A



If a work, dw is done by the small movement of the piston, then

$$dw = \text{Force} \times \text{Distance}$$

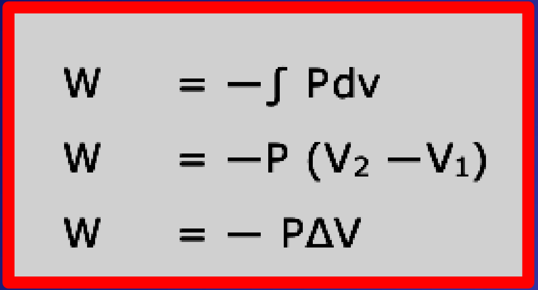
$$dw = -P \times A \times d\,l$$

(—ve sign indicates work is done by the system)

But $A \times dl = dv$

$$dw = -Pdv$$

If the volume of the system changes from V_1 to V_2, then the total work done is given by

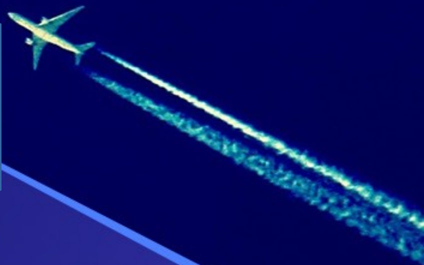


$$W = -\int P\,dv$$

$$W = -P\,(V_2 - V_1)$$

$$W = -\,P\Delta V$$

INTERNAL ENERGY



- Every substance is associated with a definite amount of energy by virtue of its constitution.
- This energy possessed by the system is called the Internal Energy or Intrinsic Energy.
- It is denoted by E or U.

It is the sum of translational kinetic energy (E_t), rotational kinetic energy (E_r), vibrational kinetic energy (E_v), electronic energy (E_e), nuclear energy (E_n) and the interaction energy (E_i) of the molecules.

$$\text{i.e., } E = E_t + E_r + E_v + E_e + E_n + E_i$$

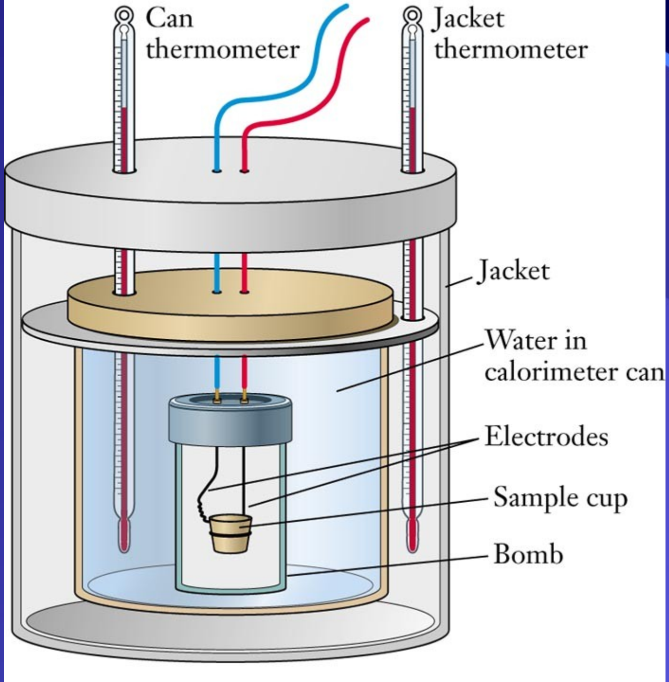
CHANGE IN INTERNAL ENERGY

- The change in internal energy of a reaction is equal to the heat evolved or absorbed in the reaction occurring at constant temperature and constant volume.
- If E_1 and E_2 are the internal energies of the system in the initial and the final states, then

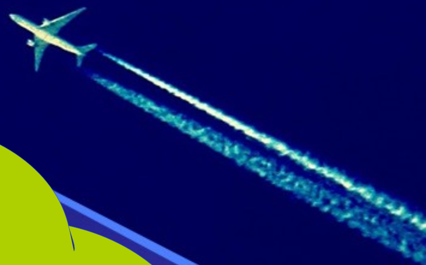
$$\Delta E = E_2 - E_1$$

BOMB CALORIMETER

The internal energy change of a reaction is determined with the help of Bomb Calorimeter.



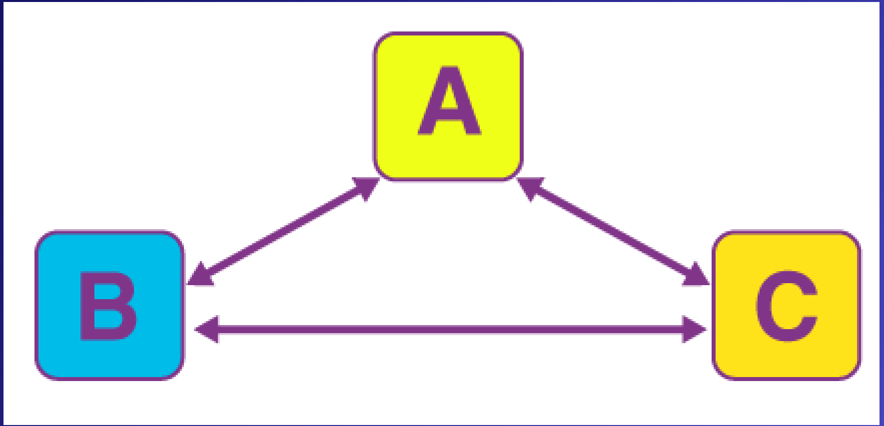
LAWS OF THERMODYNAMICS



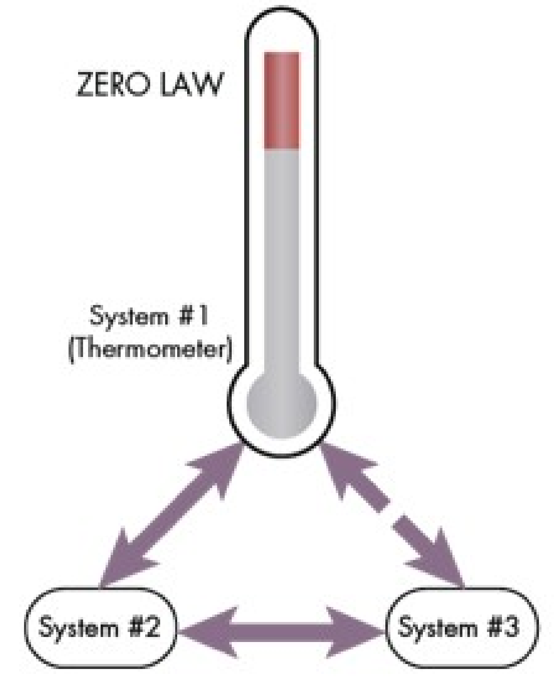
ZEROTH LAW

Zeroth law states that “when two bodies have equality of temperature with a third body, they in turn have equalities with each other”.

If two bodies A and B are in thermal equilibrium with another body C, then the bodies A and B will also be in thermal equilibrium with each other.



The basic principle of thermometer is Zeroth Law.



FIRST LAW

The law states that energy can neither be created nor be destroyed.

or

The total energy of the universe is a constant.

FIRST LAW OF THERMODYNAMICS AND INTERNAL ENERGY

- Consider a system whose internal energy is E_1 .
- If ‘q’ amount of heat is supplied, the internal energy of the system will increase to $E_1 + q$.
- If work is done on the system, the internal energy further increases and becomes E_2 .

Thus

$$E_2 = E_1 + q + w$$

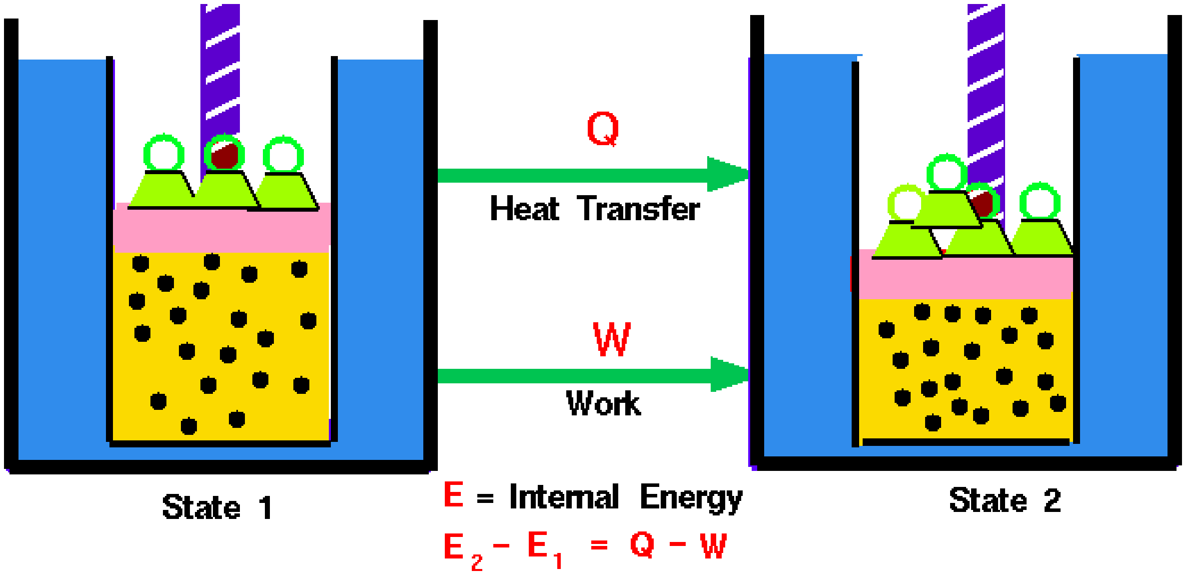
$$E_2 - E_1 = q + w$$

$$\Delta E = q + w \longrightarrow \quad (1)$$

Equation (1) is the mathematical statement of first law of thermodynamics.

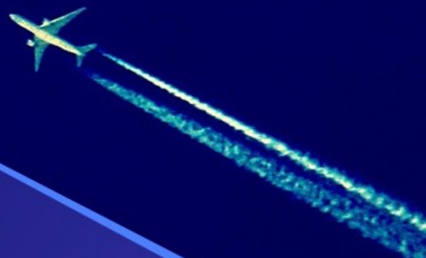
If work is done by the system, the w is —ve.

$$\Delta E = q - w \longrightarrow \quad (2)$$



$$E_2 - E_1 = Q - W$$

First Law of Thermodynamics



Consider a gas enclosed in a cylinder with a frictionless piston at a pressure ‘P’ and volume ‘V_1 ’.

Let its internal energy be ‘E_1 ’.

If ‘q’ amount of heat is supplied, the gas expands the volume from V_1 to V_2 at constant pressure ‘P’.

Then work done by the system is given as

$$W = -P(V_2 - V_1)$$

$$W = -P\Delta V$$

Substituting the value of W in equation (1), we get

$$\Delta E = q - P\Delta V \longrightarrow (3)$$

For a process occurring at constant volume,

$$\Delta V = 0$$

$$P\Delta V = 0$$

$$\Delta E = q \longrightarrow (4)$$

If ΔE = 0,
equation (1) becomes

$$0 = q + w$$

$$q = -W$$

i.e., heat involved in a process is completely converted into work or vice versa.

ENTHALPY OR HEAT CONTENT

Enthalpy is defined as the sum of internal energy and the product of the pressure and volume.

This is given by the relation, $H = E + PV$

Where H is the enthalpy,
E is the internal energy,
P is the pressure and
V is the volume.

ENTHALPY CHANGE

- If H_1 is the enthalpy of a system in the initial state and H_2 that of the final state, the change in enthalpy ΔH is given by $\Delta H = H_2 - H_1$
- The enthalpy change of a reaction is equal to the heat absorbed or evolved during a reaction at constant temperature and pressure.

REACTION ENTHALPY

- **The enthalpy change accompanying a reaction is called the reaction enthalpy.**
- **The enthalpy change of a chemical reaction is given by the symbol $\Delta_r H$.**

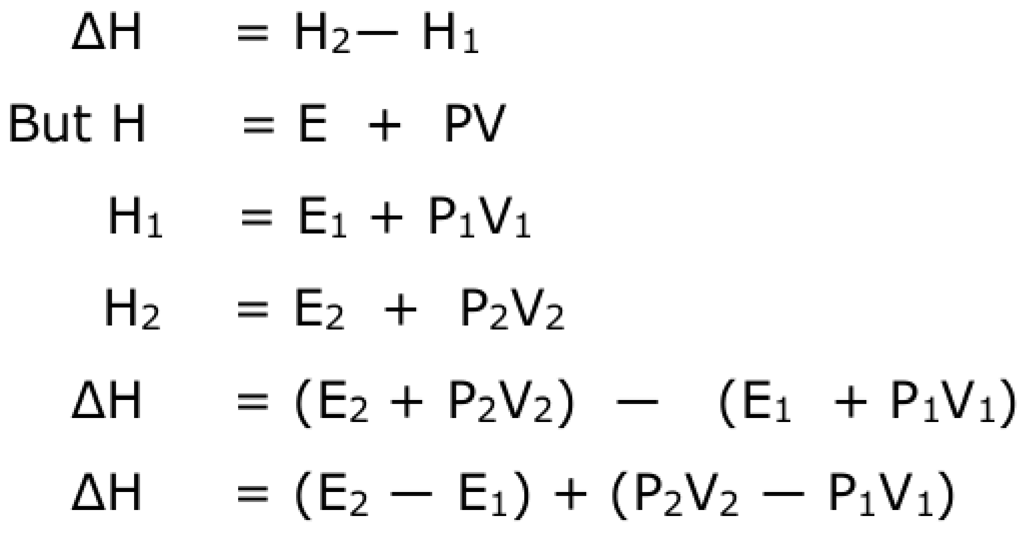
$$\Delta_r H = \text{Sum of enthalpies of products} - \text{Sum of enthalpies of reactants}$$

$$\Delta_r H = \sum a_i H_{pdts} - \sum b_i H_{reactants}$$

- **Where a_i and b_i are the stoichiometric coefficients of the products and reactants respectively.**

RELATION BETWEEN ΔH and ΔE

- Let H_1 be the enthalpy of the reactants and H_2 that of the products.
- Then change in enthalpy is given by the equation



$$\Delta H = H_2 - H_1$$

$$\text{But } H = E + PV$$

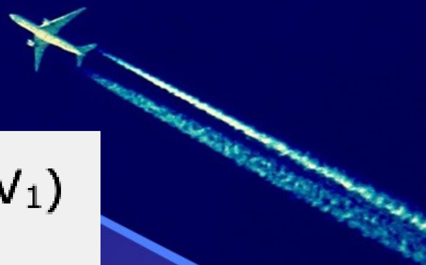
$$H_1 = E_1 + P_1V_1$$

$$H_2 = E_2 + P_2V_2$$

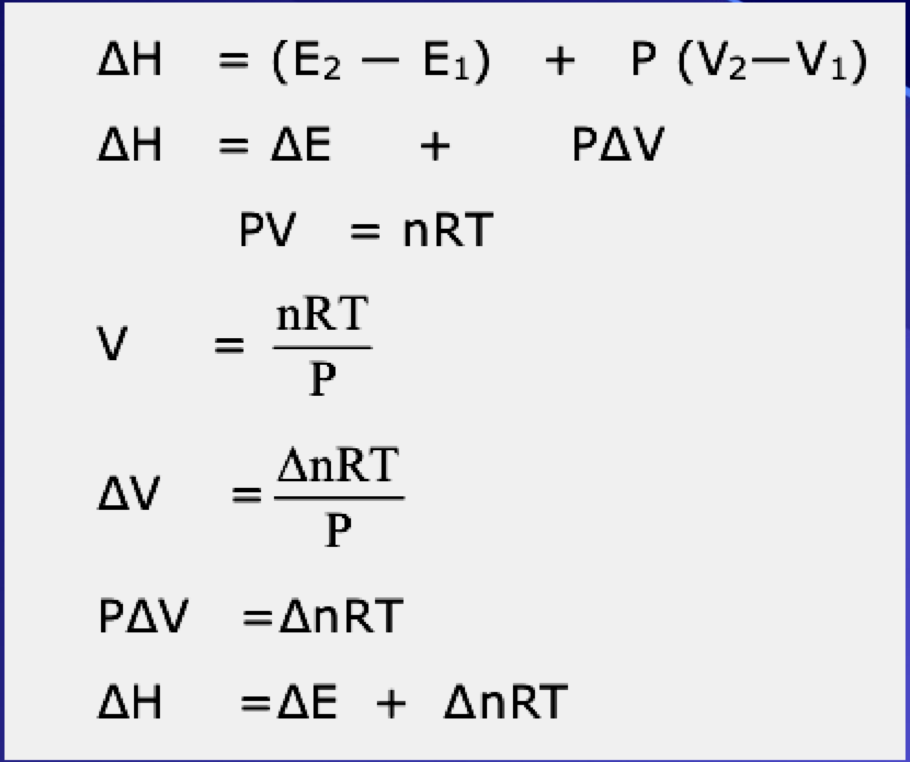
$$\Delta H = (E_2 + P_2V_2) - (E_1 + P_1V_1)$$

$$\Delta H = (E_2 - E_1) + (P_2V_2 - P_1V_1)$$

When the pressure is constant, $P_1 = P_2 = P$



In the case of gases



$$\Delta H = (E_2 - E_1) + P(V_2 - V_1)$$

$$\Delta H = \Delta E + P\Delta V$$

$$PV = nRT$$

$$V = \frac{nRT}{P}$$

$$\Delta V = \frac{\Delta nRT}{P}$$

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

$$\Delta H = \Delta E + \Delta nRT$$

STANDARD ENTHALPY OF REACTIONS (ΔH^0)

- **The standard enthalpy of a reaction is the enthalpy change when all the participating substances are in their standard states.**

ENTHALPY OF PHASE TRANSITIONS

STANDARD ENTHALPY OF FUSION(ΔH^0_{fusion})

The enthalpy change that accompanies the melting of one mole of a solid substance in standard state is called standard enthalpy of fusion or molar enthalpy of fusion, ΔH^0_{fusion}.

$$H_2O_{(s)} \rightarrow H_2O_{(l)} \qquad \Delta H^0_{fusion} = 6 \text{ kJ/mol}$$

STANDARD ENTHALPY OF VAPOURISATION (ΔH^0_{vap})

Amount of heat required to vaporize one mole of a liquid at constant temperature and under standard pressure (1 bar) is called its standard enthalpy of vaporization or molar enthalpy of vaporization, ΔH^0_{vap}.

$$H_2O_{(l)} \rightarrow H_2O_{(g)} \qquad \Delta H^0_{vap} = +40.79 \text{ kJ/mol}$$

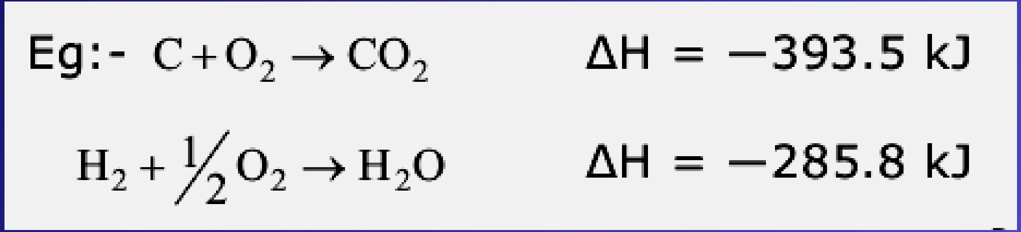
STANDARD ENTHALPY OF SUBLIMATION (ΔH^0_{sub})

Standard enthalpy of sublimation is the change in enthalpy when one mole of a solid substance sublimes at a constant temperature and at a standard pressure (1bar).

$$CO_{2(s)} \rightarrow CO_{2(g)} \qquad \Delta H^0_{sub} = 25.2\ \text{kJ/mol}$$

STANDARD ENTHALPY OF FORMATION (ΔH^0_f)

The enthalpy change accompanying the formation of one mole of a compound from its elements, all the substances being in their standard states is called standard enthalpy of formation.



Eg:- $C + O_2 \rightarrow CO_2 \qquad \Delta H = -393.5 \text{ kJ}$

$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \qquad \Delta H = -285.8 \text{ kJ}$

EXOTHERMIC REACTIONS

A chemical reaction which is accompanied by the evolution of heat enthalpy is called an exothermic reaction. i.e., the total energy of the products is less than the enthalpy of the reactants.

$$\Delta H = H_{products} - H_{reactants} = -ve$$

Eg:- $C + O_2 \rightarrow CO_2$ $\Delta H = -393.5$ kJ

$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ $\Delta H = -285.8$ kJ

ENDOTHERMIC REACTIONS

A chemical reaction which is accompanied by the absorption of heat energy is called an endothermic reaction. i.e., total enthalpy of the products is greater than the total enthalpy of the reactants.

$$\Delta H = H_{products} - H_{reactants} = +ve$$

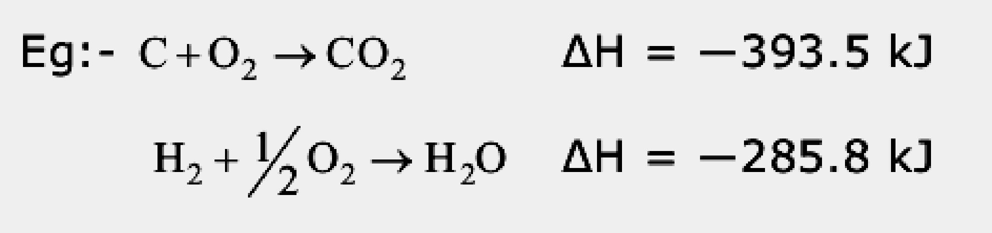
$H_2 + I_2 \rightarrow 2HI$ ΔH = 52.5 kJ

$N_2 + O_2 \rightarrow 2NO$ ΔH = +180.5 kJ

$C + 2S \rightarrow CS_2$ ΔH = +87.5 kJ

THERMOCHEMICAL EQUATIONS

A chemical equation which indicates the heat change during the reaction is called a thermochemical equation.



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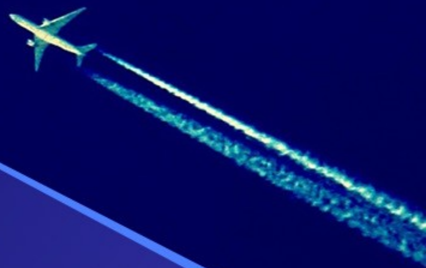
HEAT CAPACITY

- Heat capacity of a system is defined as the quantity of heat required to raise the temperature of the system through 1^0 C.
- If q is the quantity of heat required to raise the temperature of the system from T_1 to T_2 , then C is given as

$$C = \frac{q}{T_2 - T_1} = \frac{q}{\Delta T}$$

$$C = q\Delta T$$



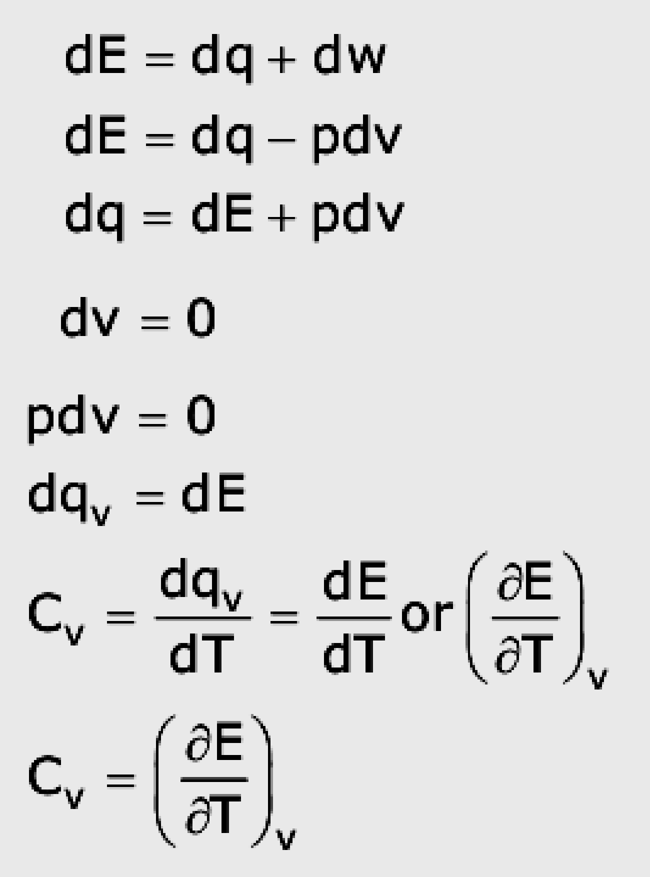
If dq is the quantity of heat required to raise the temperature of the system by dT, then C is given as

$$C = \frac{dq}{dT}$$

HEAT CAPACITY AT CONSTANT VOLUME (C_V)

- C_V is defined as the rate of change of internal energy with temperature at constant volume.
- For infinitesimally small changes, the first law of thermodynamics can be written as

At constant volume



$$dE = dq + dw$$

$$dE = dq - pdv$$

$$dq = dE + pdv$$

$$dv = 0$$

$$pdv = 0$$

$$dq_v = dE$$

$$C_v = \frac{dq_v}{dT} = \frac{dE}{dT} \text{ or } \left(\frac{\partial E}{\partial T}\right)_v$$

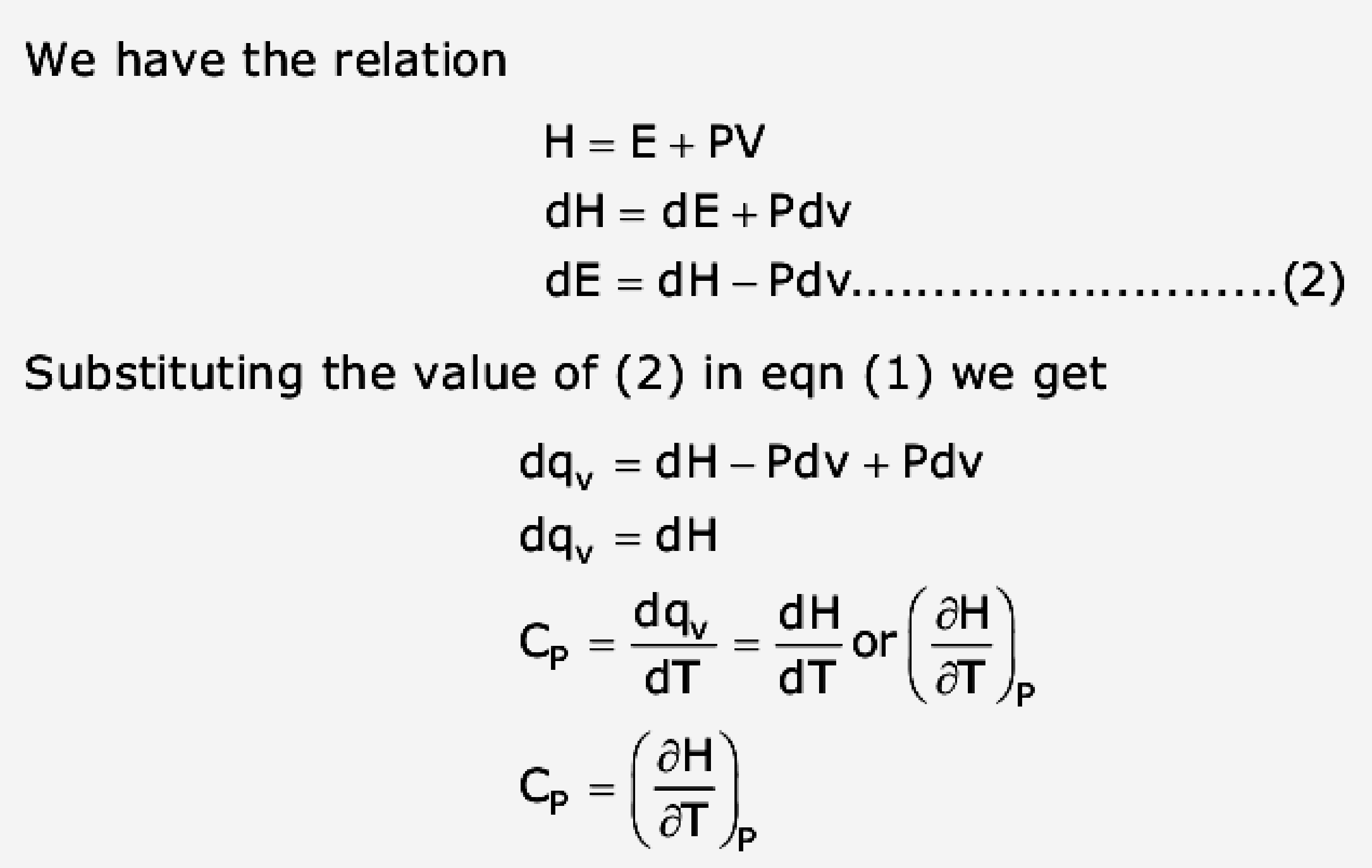
$$C_v = \left(\frac{\partial E}{\partial T}\right)_v$$

HEAT CAPACITY AT CONSTANT PRESSURE (C_P)

C_P is defined as the rate of change of enthalpy with temperature at constant pressure.

At constant Pressure $dv \neq 0$

$$dq_v = dE + pdv \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$



We have the relation

$$H = E + PV$$

$$dH = dE + Pdv$$

$$dE = dH - Pdv \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

Substituting the value of (2) in eqn (1) we get

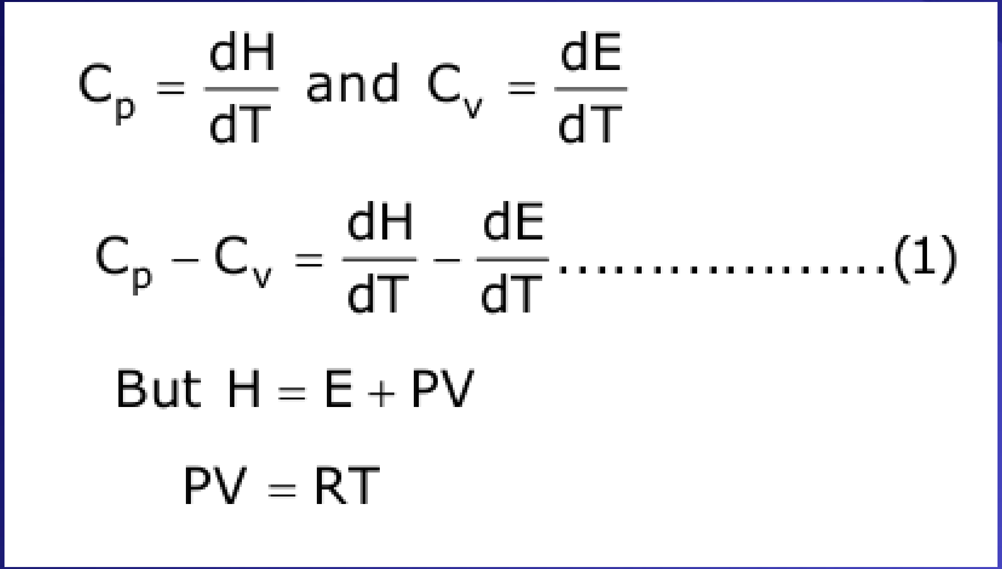
$$dq_v = dH - Pdv + Pdv$$

$$dq_v = dH$$

$$C_P = \frac{dq_v}{dT} = \frac{dH}{dT} \text{ or } \left(\frac{\partial H}{\partial T}\right)_P$$

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P$$

RELATION BETWEEN C_P AND C_V



$$C_p = \frac{dH}{dT} \text{ and } C_v = \frac{dE}{dT}$$

$$C_p - C_v = \frac{dH}{dT} - \frac{dE}{dT} \ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

But $H = E + PV$

$PV = RT$

$$H = E + RT$$

$$\frac{dH}{dT} = \frac{dE}{dT} + R.\frac{dT}{dT}$$

$$\frac{dH}{dT} = \frac{dE}{dT} + R \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Substituting the value of (2) in eqn (1)

$$C_p - C_v = \frac{dE}{dT} + R - \frac{dE}{dT}$$

$$C_p - C_v = R$$

SPECIFIC HEAT CAPACITY

- Specific heat capacity is defined as the quantity of heat required to raise the temperature of unit mass of a substance by one degree.
- If q is the quantity of heat required to raise the temperature of the system by ΔT, then

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

MOLAR HEAT CAPACITY

Molar heat capacity is the quantity of heat required to raise the temperature of one mole of a substance by one degree.

MEASUREMENT OF ΔE and ΔH

We can measure the energy changes associated with chemical or physical processes by an experimental technique called calorimetry.

MEASUREMENT OF ΔE

- For chemical reactions, heat absorbed at constant volume, is measured in a bomb calorimeter.
- Here, a steel vessel is immersed in water bath to ensure that no heat is lost to the surroundings.
- The whole device is called a calorimeter.

- A combustible substance is burnt in pure dioxygen supplied in the steel bomb.
- Heat evolved during the reaction is transferred to the water around the bomb and its temperature is monitored.
- Since the bomb calorimeter is sealed, its volume does not change.

- **Under these conditions, no work is done as the reaction is carried out at constant volume in the bomb calorimeter.**
- **The temperature of the bath is recorded at the beginning and at the end of the reaction.**
- **The change in temperature is noted and is then converted to q_v by the equation,**

$$q_v = C\Delta T$$

MEASUREMENT OF ΔH

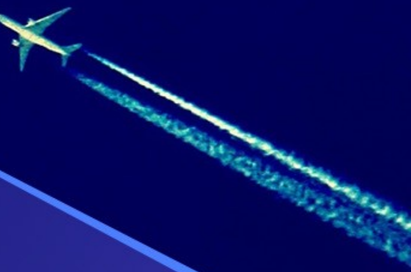
- The enthalpy change may be measured by using a calorimeter.
- The calorimeter is immersed in an insulated water bath fitted with a stirrer and the thermometer.
- The temperature of the bath is recorded at the beginning and after the end of the reaction.

- The change in temperature may be noted.
- By knowing the heat capacity of the calorimeter system and the change in temperature, the heat absorbed or evolved may be calculated.
- This will give the enthalpy change, ΔH of the reaction.

- In an exothermic reaction, heat is evolved and system loses heat to the surroundings.
- Therefore, q_p will be negative and ΔH will also be negative.
- Similarly in an endothermic reaction, heat is absorbed, q_p is +ve and ΔH will be positive.

HESS’S LAW OF CONSTANT HEAT SUMMATION

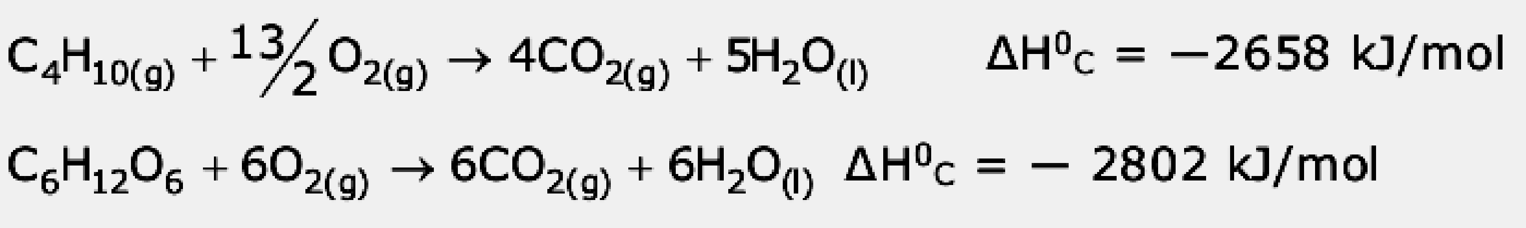
Hess’s law states that the enthalpy change of a chemical reaction is the same, whether the change takes place in one step or several steps.



$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$	$\Delta H = -393.5 \text{ kJ}$
	OR
$C + \frac{1}{2}O_2 \rightarrow CO$	$\Delta H_1 = -110.5 \text{ kJ}$
$CO + \frac{1}{2}O_2 \rightarrow CO_2$	$\Delta H_2 = -283 \text{ kJ}$
$C + O_2 \rightarrow CO_2$	$\Delta H = \Delta H_1 + \Delta H_2$
	$\Delta H = -393.5 \text{ kJ}$

STANDARD ENTHALPY OF COMBUSTION (ΔH^0_c)

It is the enthalpy change accompanied by the complete combustion of one mole of a substance, all the reactants and products being in their standard states at the specified temperature.

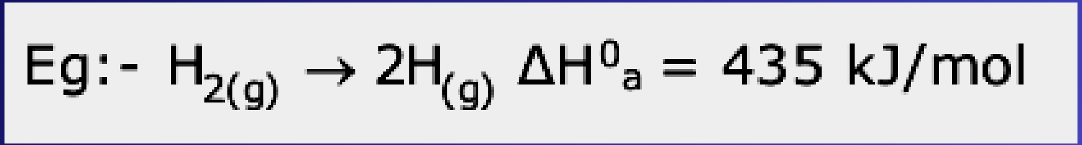


$$C_4H_{10(g)} + {}^{13}\!/\!_2\,O_{2(g)} \rightarrow 4CO_{2(g)} + 5H_2O_{(l)} \qquad \Delta H^0{}_C = -2658\ \text{kJ/mol}$$

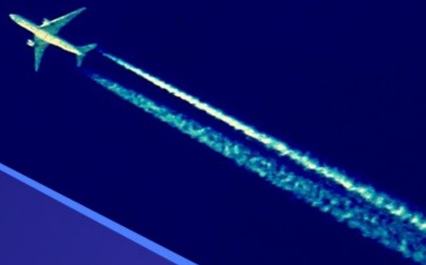
$$C_6H_{12}O_6 + 6O_{2(g)} \rightarrow 6CO_{2(g)} + 6H_2O_{(l)} \quad \Delta H^0{}_C = -\ 2802\ \text{kJ/mol}$$

ENTHALPY OF ATOMISATION (ΔH^0_a)

It is the enthalpy change on breaking one mole of bonds completely to obtain atoms in the gaseous phase.

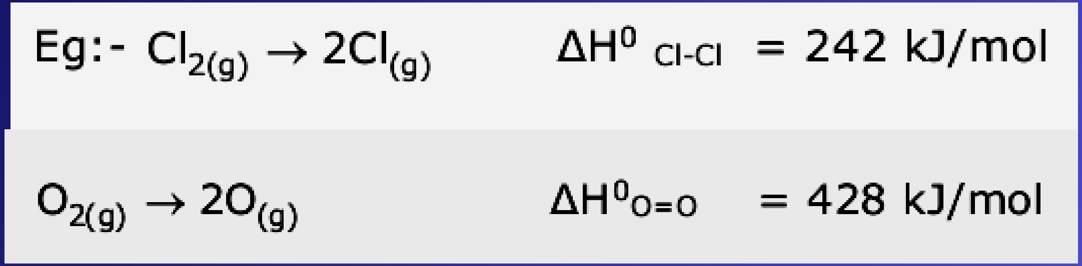


Eg:- $H_{2(g)} \rightarrow 2H_{(g)}$ $\Delta H^0_a = 435$ kJ/mol



BOND ENTHALPY

It is the change in enthalpy when one mole of covalent bonds of a gaseous covalent compound is broken to form products in the gaseous phase.



Eg:- $Cl_{2(g)} \rightarrow 2Cl_{(g)}$ $\Delta H^0{}_{Cl\text{-}Cl} = 242$ kJ/mol

$O_{2(g)} \rightarrow 2O_{(g)}$ $\Delta H^0{}_{O=O} = 428$ kJ/mol

ENTHALPY OF SOLUTION

Enthalpy of solution of a substance is the enthalpy change when 1 mole of a substance is dissolved in a specified amount of solvent at a temperature

Eg:- $NH_4NO_{3(S)} + H_2O_{(liq)} \rightarrow NH_4NO_{3(liq)}$ $\Delta H^0{}_{\text{solution}} = +26\,kJ/mol$

LATTICE ENTHALPY

It is the enthalpy change when 1 mole of an ionic compound dissociates into its ions in gaseous state.

DETERMINATION OF LATTICE ENTHALPY

BORN HABER CYCLE

To illustrate Born Haber Cycle, let us consider the determination of lattice enthalpy of NaCl.

The formation of NaCl involves the following steps.

- **Conversion of metallic sodium to gaseous sodium atoms.**
- **The amount of energy required to convert one mole of metallic sodium to gaseous atoms is called sublimation energy, ΔH_{sub}**

$$Na_{(S)} + \Delta H_{Sub} \rightarrow Na_{(g)}$$

- **Conversion of gaseous chlorine molecule to gaseous chlorine atoms.**

$$\tfrac{1}{2} Cl_{2(g)} + \tfrac{1}{2} \Delta H_D \rightarrow Cl_{(g)}$$

- **The amount of energy required to dissociate one mole of gaseous chlorine molecule to gaseous chlorine atoms is called dissociation energy, ΔH_D.**

- **Conversion of gaseous sodium atoms to sodium ions.**

$$Na_{(g)} + IE \rightarrow Na^{+}{}_{(g)} + 1e^{-}$$

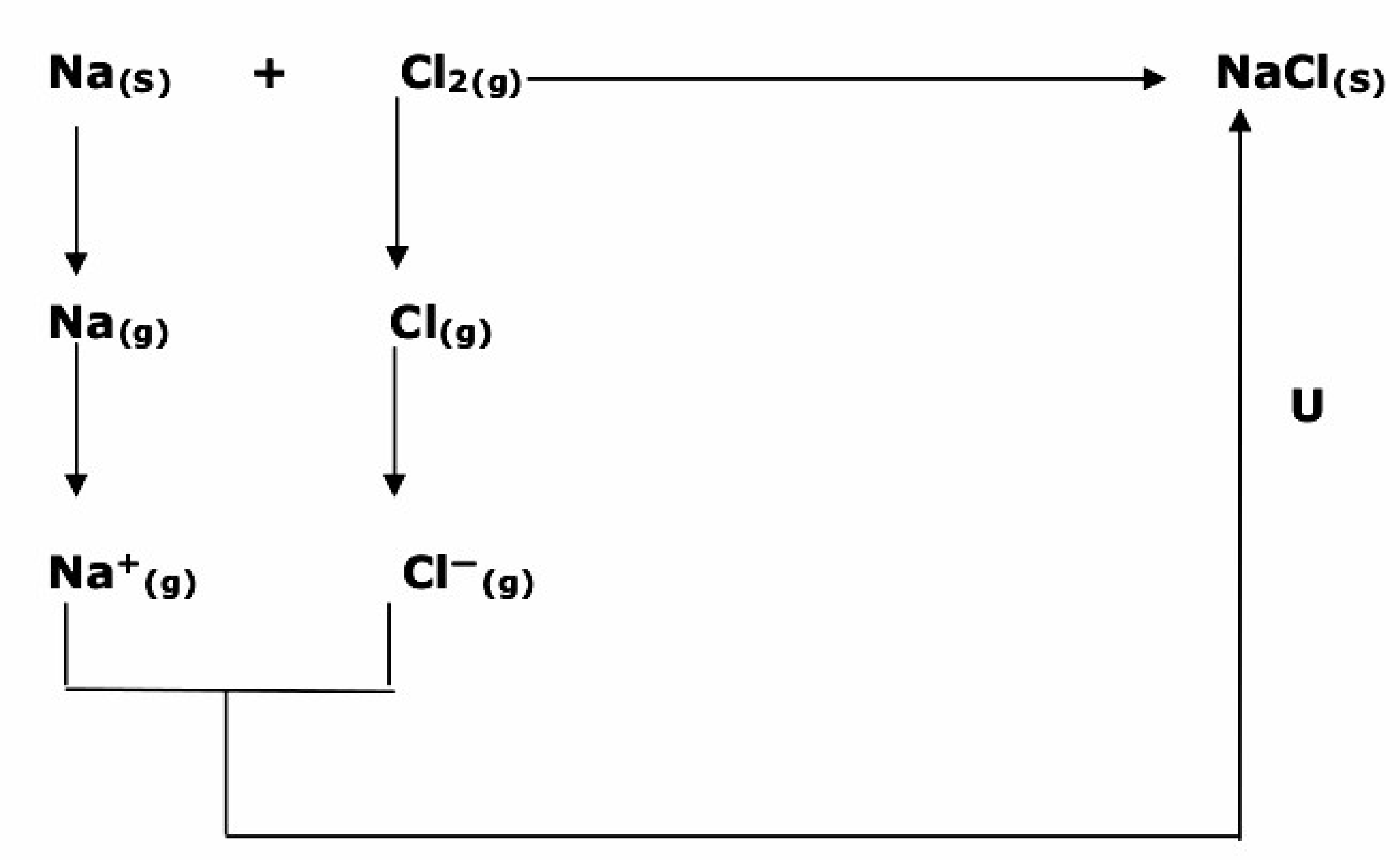
- **The amount of energy required to convert one mole of gaseous sodium atoms to sodium ions is called Ionisation energy.**

- **Conversion of gaseous chlorine atom to chloride ions.**

$$Cl_{(g)} + 1e^{-} \rightarrow Cl^{-}{}_{(g)} + \text{Energy}$$

- **The amount of energy released when one mole of gaseous chlorine atom is converted to chloride ions is called electron affinity.**

- **Combination of gaseous sodium ions and chloride ions to form NaCl.**
- **The amount of energy released when one mole of solid crystalline compound is formed from gaseous Na^+ and Cl^- ions is called lattice energy, U.**
- **The overall change is** $Na_{(S)} + \frac{1}{2}Cl_{2(g)} \rightarrow NaCl_{(S)}$



$Na_{(s)}$ + $Cl_{2(g)}$ → $NaCl_{(s)}$

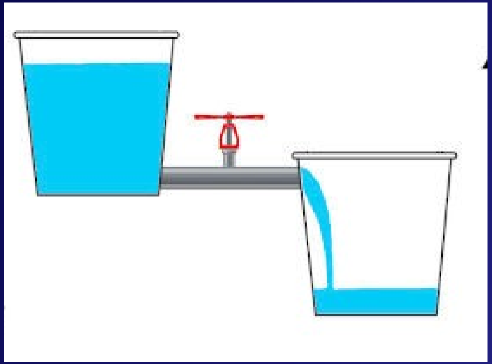
$Na_{(g)}$ $Cl_{(g)}$

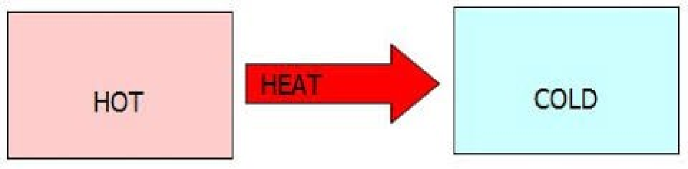
$Na^{+}_{(g)}$ $Cl^{-}_{(g)}$

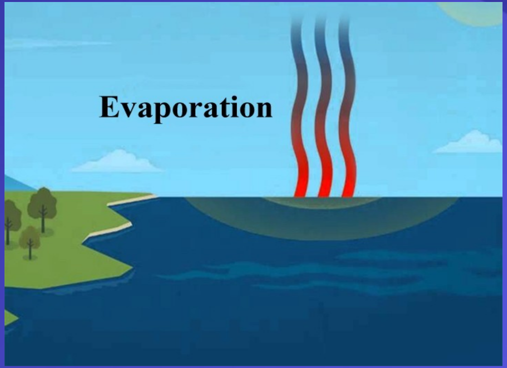
U

SPONTAENITY

The potential to proceed without the help of any external agency.







SPONTANEOUS PROCESS

- A process that occurs without the help of any external agency is called a spontaneous process.
- Eg: Flow of water from a high level to a low level.
- Flow of heat from a hot body to a cold body.
- Flow of gases from a high pressure region to a low pressure region.

PROCESS WHICH REQUIRE NO INITIATION

Evaporation of water from ponds, rivers, sea etc.

$$H_2O_{(liquid)} \rightarrow H_2O_{(gas)}$$

Combination of NO and O_2 .

$$2NO + O_2 \rightarrow 2NO_2$$

PROCESS WHICH REQUIRE SOME INITIATION

Combination of H_2 and O_2 should be initiated by an electric spark.

$$2H_2 + O_2 \rightarrow 2H_2O$$

Burning of carbon

$$C + O_2 \longrightarrow CO_2$$

ENTROPY

- The degree of randomness or disorder of a system is determined by a property called Entropy.
- Entropy is the measure of disorder of the system.
- Change in entropy is represented by ΔS. ΔS is related with q and T for a reversible reaction as

$$\Delta S = \frac{q_{rev}}{T}$$

- The greater the disorder in an isolated system, the higher is the entropy.
- The unit of entropy is $JK^{-1}mol^{-1}$.

SECOND LAW OF THERMODYNAMICS

The second law of thermodynamics gives the relationship between entropy and spontaneity.

For a spontaneous process in an isolated system, the change in entropy is +ve. i.e., $\Delta S > 0$.

- **If the system is not isolated, the total energy change will be equal to the sum of change in entropy of the system and surroundings.**
- **$\Delta\text{Stotal} = \Delta\text{Ssys} + \Delta\text{S surroundings}$**
- **$\Delta\text{Suniverse} > 0$**
- **The second law of thermodynamics states that the entropy of the universe always increases in the course of every spontaneous change.**

ENTROPY AND SPONTANEITY

The total entropy change for the system and surroundings of a spontaneous process is given by

$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surroundings} > 0$

i.e., when $\Delta S_{total} > 0$, the process is spontaneous.

When a system is in equilibrium, the entropy is maximum and the change in entropy, $\Delta S = 0$.

i.e., when $\Delta S_{total} = 0$, the process is at equilibrium.

When $\Delta S_{total} < 0$, the process is non spontaneous.

FREE ENERGY

Free energy is the maximum energy available from a system that can be converted into work during a process.

It is denoted by Gibbs energy or Gibbs function, G.

$$G = H - TS$$

Gibbs function, G is an extensive property and a state function.

FREE ENERGY CHANGE

The change in Gibbs energy for the system ΔG_{system} can be written as

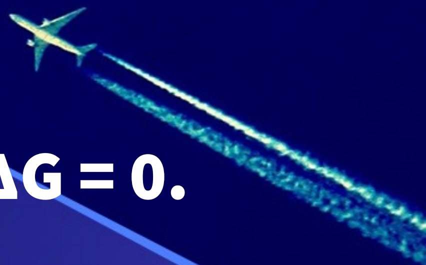
$$\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys}$$

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

The equation is called Gibbs Helmholtz equation.

PREDICTION OF SPONTANEITY IN TERMS OFΔG

- The equation ΔG system = $-T\Delta S$ total may be used to predict the spontaneity of a process.
- For a spontaneous process, ΔS is +ve so that ΔG is —ve.
- Therefore when ΔG is —ve, the process will be spontaneous.



- For a process at equilibrium, $\Delta S = 0$, so that $\Delta G = 0$.
- Therefore when ΔG is zero, the process will be at equilibrium.
- For a non spontaneous process, ΔS is —ve
- so that ΔG is +ve.
- Therefore when ΔG is +ve, the process will be non spontaneous.

CONDITIONS FOR ΔG TO BE NEGATIVE

- When ΔH is —ve and ΔS is +ve, ΔG will be —ve and the process will be spontaneous.
- when ΔH is +ve and ΔS is —ve, ΔG will be +ve and the process will be non spontaneous.

- **When ΔH is +ve and ΔS is +ve, ΔG will be —ve only when $\Delta H < T\Delta S$.**

- **Hence the reaction will be spontaneous only at high temperatures.**

- **When ΔH is —ve and ΔS is —ve, ΔG will be —ve only when $\Delta H > T\Delta S$.**

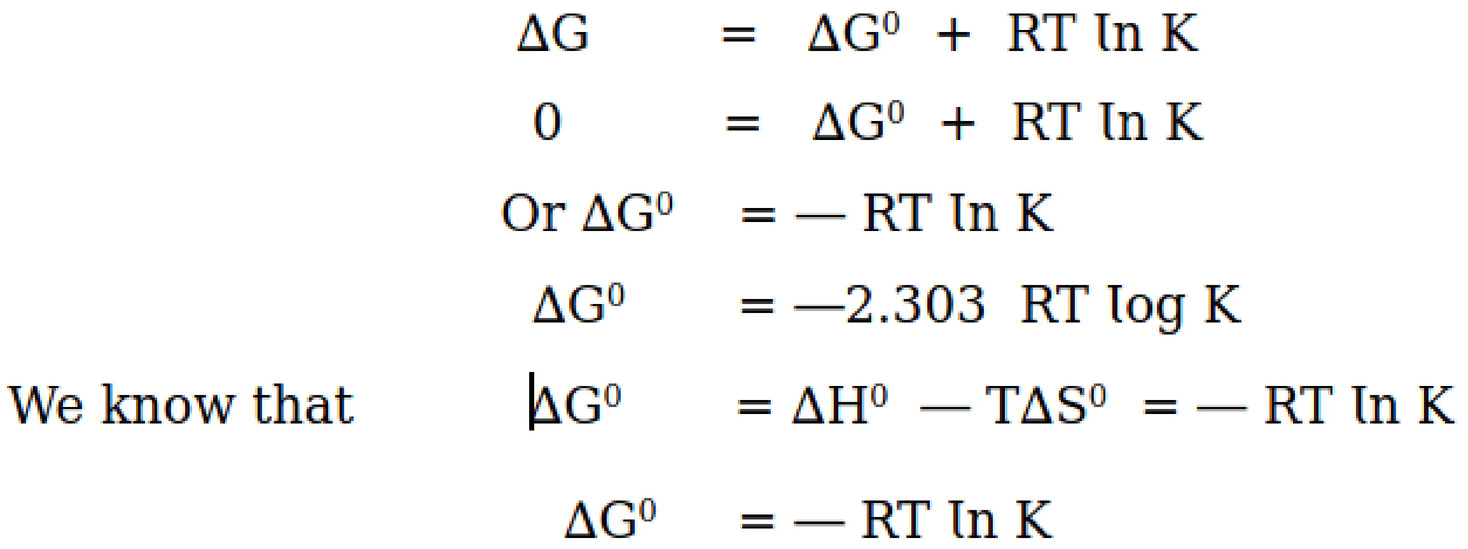
- **Hence the reaction will be spontaneous only at low temperatures.**

GIBBS FREE ENERGY CHANGE AND EQUILIBRIUM

Consider the reversible reaction, $A + B \rightleftharpoons C + D.$

The criterion for equilibrium is $\Delta G = 0$

Gibbs energy for a reaction in which, all the reactants and products are in the standard state, (ΔG^0) is related to the equilibrium constant of the reaction as



$$\Delta G = \Delta G^0 + RT \ln K$$

$$0 = \Delta G^0 + RT \ln K$$

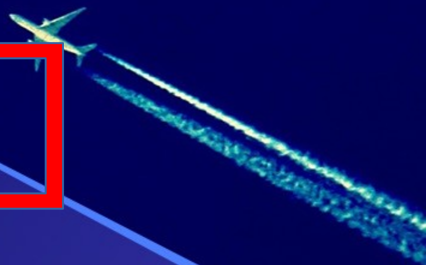
$$\text{Or } \Delta G^0 = -RT \ln K$$

$$\Delta G^0 = -2.303\ RT \log K$$

We know that $\Delta G^0 = \Delta H^0 - T\Delta S^0 = -RT \ln K$

$$\Delta G^0 = -RT \ln K$$

THIRD LAW OF THERMODYNAMICS



- **The law states that “the Entropy of a perfectly crystalline substance is zero at absolute zero temperature”.**

- **Third law helps to calculate the absolute entropies of pure substances at different temperatures.**


Thank
You