Thermodynamics & Thermochemistry

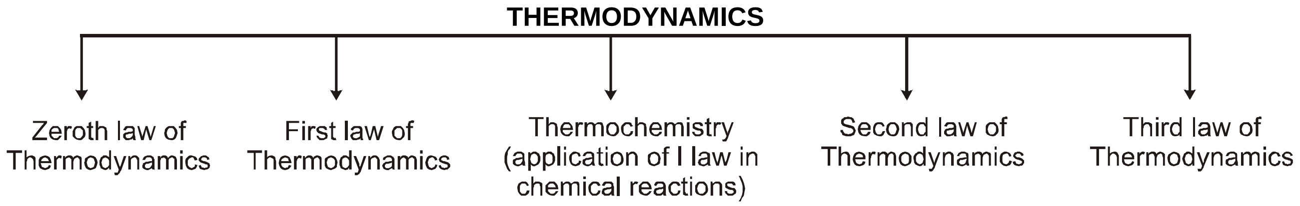
1. THERMODYNAMICS

Thermodynamics Ist Law

Section (A) : Basic definitions

Introduction:

Thermodynamics: The branch of science which deals with different forms of energy & their interconversion.



Application of thermodynamics:
In chemistry using thermodynamics

- We can predict feasibility of the reaction that is if two substances are mixed then the reaction between them will takes place or not.
- If reaction does take place then what are the energy changes involved during the reaction.
- If in a chemical reaction, equilibrium is going to get attained then what will be the equilibrium concentrations of different reactants & products, can be calculated with thermodynamics.

Limitations of thermodynamics:

- Laws of thermodynamics are applicable to matter in bulk or on system as a whole, these can not be applied on individual particles (temperature, pressure, enthalpy etc have meanings only for system as a whole).
- Using thermodynamics we cannot calculate the time taken for completion of a reaction or for attainment of chemical equilibrium.

Solved Examples

Ex-1 $A + B \rightleftharpoons C + D$ $K_{1,\,eq} = 10^3$

$E + F \rightleftharpoons G + H$ $K_{2,\,eq} = 10^{-3}$

Which of these reaction will attain equilibrium earlier ?

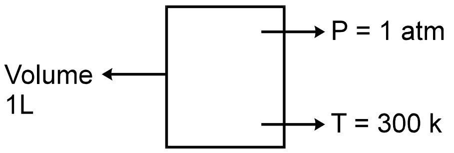
Sol. We cannot predict, because value of equilibrium constant has no relation with time taken to attain equilibrium.

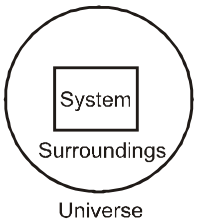
❖ More the equilibrium constant K, more will be the concentration of products at equilibrium state.

❖ Smaller the equilibrium constant K, lesser will be the concentration of products at equilibrium state.

Terms to be used in thermodynamics:

- **System :** Part of the universe which is under study for energy changes.





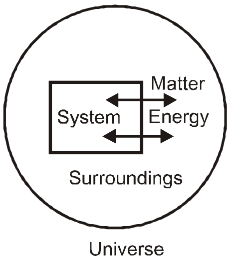
Ex. Air in a room, water in a bottle, any living body.

- **Surrounding :** Rest of the universe.
- **Universe :** Universe = System + Surroundings

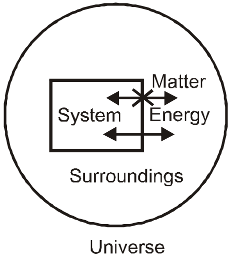
- **Boundary :** Anything which separates system & surroundings is called boundary.
  - Boundary can be real or imaginary.
  - Boundary can be flexible or rigid
    e.g. air in a flexible balloon (flexible boundary) while air in a room (fixed boundary).
  - Boundary can be adiabatic (non-conducting; $\Delta q = 0$) or diathermic (conducting; $\Delta q \neq 0$; $\Delta T = 0$).

Types of system :

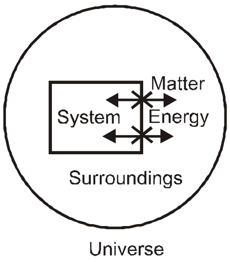
- **Open system:** System which can exchange energy & matter both with the surroundings.
  e.g. : Living systems(any living organism) are open systems, air in an open room; water flow in pipe.
- **Closed system:** System which can exchange only energy but cannot exchange matter with the surroundings is called closed system.
  e.g. : any matter in a closed container ; Heating of water in closed container.
- **Isolated system:** System which cannot exchange energy and matter both with the surroundings.
  e.g. : Water in thermos flask.(Though not a perfectly isolated system but can be taken as, for small interval of time as the energy exchanges are negligible) ; Hot tea in thermos (few time).
  - Whole of universe is a perfect isolated system.



Open System



Close System



Isolated system

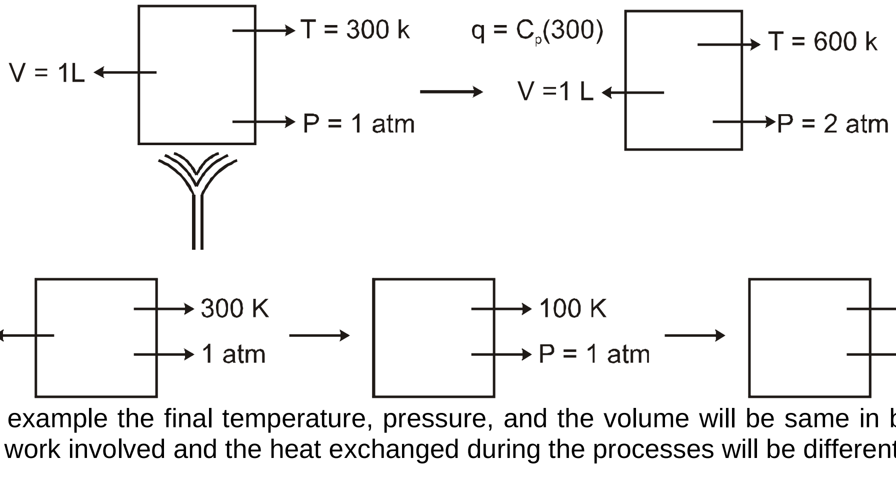
State of a system:

- It means the condition in which the system is present.
- It can be specified/defined by measuring/ specifying some observable/measurable properties of the system like pressure, volume, temperature, amount of substance, elasticity, heat capacity etc.
  e.g. For an ideal gaseous system state of the system can be defined by specifying volume, temperature and pressure.
- We may have to specify more properties of the system depending on the complexity of the system.

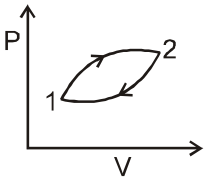
State function (State variables) :

- Property of a system which is dependent only on the state of the system i.e. it is a point function
- It is independent of the path adopted to attain a particular state.
  e.g. In Mechanics, Displacement of any object will a state function but distance travelled by the object will be a path function.
  For any thermodynamic system,
  Temperature, Pressure, Volume, Total internal energy (E or U), Enthapy(H), Gibbs free energy (G), Entropy (S) are all state functions.

e.g.



In the above example the final temperature, pressure, and the volume will be same in both the above ways but the work involved and the heat exchanged during the processes will be different.



- For a cyclic process the change in state functions must be zero.

  $$\oint dx = 0$$

- State variables can be extensive or intensive.
- Change in state function are not state function.

  Eq. ΔT, ΔV, ΔP, ΔH, ΔG, ΔV, etc are not state function.

Path function :

- Quantities which are dependent on the path/way the system has achieved a particular state.
  e.g. Heat, work, Heat capacities (Molar heat capacities, specific heat capacities etc.).
- These quantities are define when there is a process going on.
- These can not have any definite (particular) value in any particular state of the system.

Types of properties

Extensive properties :

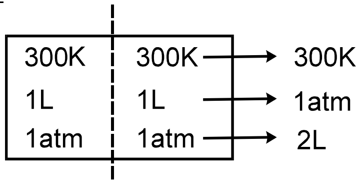
- Functions or properties of the system which are dependent on mass or on size of the system are called Extensive Properties.
- Extensive functions are additive in nature (The addition of the volumes of the two parts equals the volume of the whole of the room.)
  e.g. Volume, Mass, Total heat capacity, Total internal energy (E), Enthalpy(H), Gibbs Free Energy(G), Entropy(S) ; moles etc.

Intensive properties :

- Functions or properties which are not mass dependent or size dependent are called intensive function.
- Intensive properties are not additive in nature.
  eg. Temperature, pressure, molar heat capacity, specific heat capacity, density,concentration, vapour pressure; B.P. ; F.P. ; Viscosity ; pH etc.

How to identify extensive or intensive properties

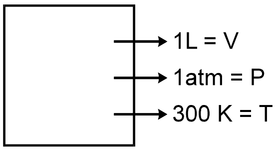
If a system in a particular state is divided into two equal or unequal parts, the properties which have value equal to the original value of that property for the whole of the system is called an ***Intensive property.*** *While the properties which have values different from the values for whole of the system are called* ***Extensive Properties.***



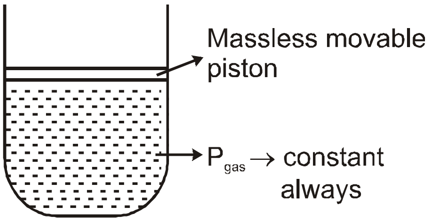
Room is divided into two equal halves

- For example consider air in a room at temp of 300K, 1 atm pressure. Now, if the room is divided by some boundary (imaginary or real) into two parts (equal or unequal) then in these two parts:
  - ❍ The temperature, pressure, density of the gas, concentration of gaseous molecules etc. will have the same value as that of for whole of the system. (intensive)
  - ❍ While the volume of two parts, mass of gas in two parts, total energy of the gaseous molecules in the two parts, entropy the two parts etc. will be different from the values of these properties as for the whole of the system initially. (extensive)

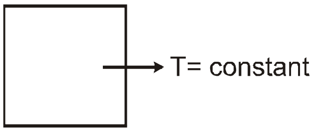
Thermodynamic equilibrium:



- When there is no change in any observable or measurable property of a system with time then the system is said to be in thermodynamic equilibrium.
- Thermodynamic equilibrium consist of three types of equilibrium.
  (a) Mechanical equilibrium
  (b) Thermal equilibrium
  (c) Chemical equilirbrium



- **Mechanical equilibrium:**
  There should not be any pressure gradient with time or with space (for any ideal gaseous system, for a liquid system there can be pressure gradient with space as pressure at the bottom of the container in which a liquid is filled will be greater than the pressure at the surface of the liquid.) in the system.

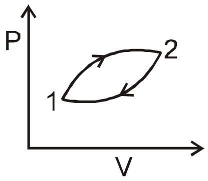


- **Thermal equilibrium:** There should not be any temperature gradient (difference).
  Temperature may have different values at different places/locations in a system but it should remain constant with time.
- **Chemical equilibrium:** There should not be any concentration gradient of any of the species in the system.

Section (B) : Thermodynamics processes & graph

- **Types of thermodynamic process on basis of state/conditions**
  Thermodynamic process : Any method/process by which system can change its state from one state of thermodynamic equilibrium to another state of thermodynamic equilibrium.
  There can be infinite type of thermodynamic processes, out of these the following are important ones:

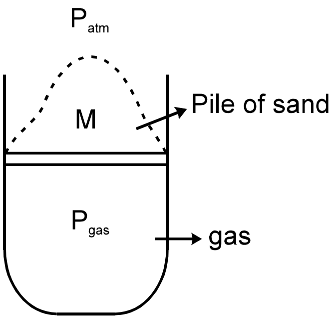
1. **Isothermal process :** T = constant
   $T_i = T_f$
   $\Delta T = 0$
2. **Isochoric process :** V = constant
   $V_i = V_f$
   $\Delta V = 0$
3. **Isobaric process :** P = constant
   $P_i = P_f$
   $\Delta P = 0$
4. **Adiabatic process :** q = constant
   or heat exchange with the surrounding = 0 (zero)
5. **Cyclic Process :** A system undergoes a series of changes and comes back to the initial state.
   $\Delta V = 0$
   $\Delta H = 0$



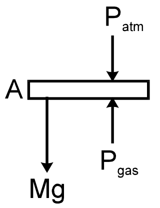
- **Types of thermodynamics processes on basis of the way the processes are carried out :**
- **Reversible process :**
  The process that can be reversed by a very small change is known as reversible process.
  - If a process is carried out in such a manner so that the system is always in thermodynamic equilibrium at every stage of the process.
  - If the process is carried out such that the difference in driving force and opposing force is infinitesimally small so that process takes place at infinitesimally slow rate.

$$F_{driving} - F_{opposing} = \Delta F \text{ and } \Delta F \rightarrow 0$$

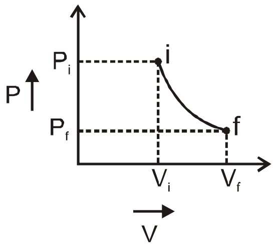
  - An ideal reversible process will take infinite time to get completed.
  - It is carried out infinitesimally slowly.
  - Strictly speaking there is no ideal reversible process in universe.
    To get an idea of a reversible process we can consider the following system an ideal gas is enclosed in a container and a massless piston is put on the gas on which a pile of sand is placed having particles of negligible mass. To carry out a reversible expansion we will slowing decrease the mass of the sand lets say by removing the particles one by one, so the expansion of the gas will take place at infinitesimally small rate and we can always assume the system to in thermodynamic equilibrium. So, the expansion will be of reversible type.



FBD of piston



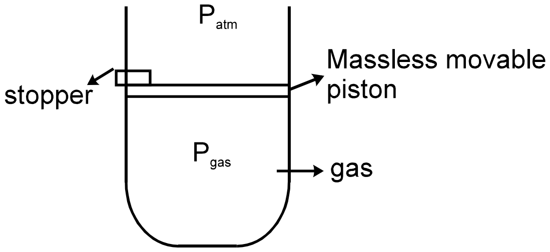
For piston to be in equilibrium : $P_{gas} = P_{atm} + Mg/A$

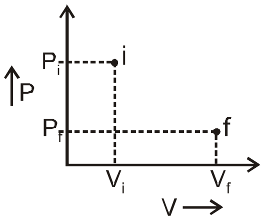


Sign : i – f : expainsion
f – i : compression

- **Irreversible process:** The process can not be reversed by a small change is known as irreversible.
  - ❍ If a process is carried out in such a manner so that the system is in thermodynamic equilibrium.
    (I) Only at initial & final state of the process but not at the intermediate stages.
    (II) System may be in thermodynamic equilibrium state at some finite number of intermediate stages only - for example - n step irreversible expansion of a gas.
  - ❍ If during the process there is a finite difference in driving force and opposing force so that process takes place with a finite rate; $F_{driving} – F_{opposing} = \Delta F$.
  - ❍ Irreversible processes will get completed in finite time.
  - ❍ At intermediate stages of the irreversible process, different state function such as pressure, temperature etc. are not defined.
  - ❍ All real process are irreversible.

Consider the above system. If the stopper placed over the piston is removed, then the piston will move with almost infinite acceleration and will keep moving to a position where the pressure of the gas becomes equal to the external pressure. Since the process will get completed in finite time and there was a finite difference between the driving force and the opposing force so, process is irreversible.During the process, the pressure of the gas can not be defined as it will be having different values at different locations.





Sign : i – f : expainsion
f – i : compression

- ## Modes of energy exchange:

These are two ways by which a system can interact or can exchange energy with its surroundings.
(i) Heat & (ii) Work
Heat & Work both are forms of energy.

Heat: When the energy transfer across a boundary as a result of temperature difference between system & surroundings is known as heat.

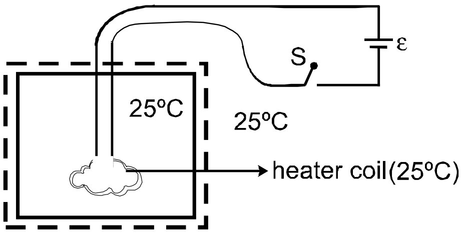
- **Modes of heat transfer:** Conduction (solids); Convection (fluids); Radiation (vacuum)

Work: Energy transfer which is not heat or which is not because of temperature difference is called work.

Work can be of many types: Mechanical work, Electrical work, Magnetic work, Gravitational work etc.

❍ **The same energy transfer can be called work or can also be called heat depending on choice of the system.**

To understand this, consider a system shown below in which water is taken in a closed container at 25ºC, the surroundings is also at temperature of 25ºC and there is a heater coil in the dipped in the water which is connected to a battery through a switch S.Heater coil is also at 25ºC initially. Now, there are two ways in which system can be chosen.



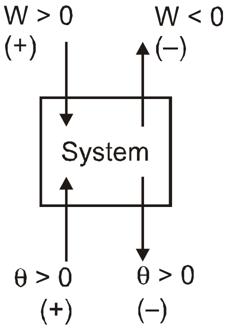
I–System: All contents of the container (water + Heater coil).

When switch is turned on there will be increment in the temperature of the system. Since the temperature of the surroundings was equal to temperature of the system so, heat can not flow but still there is increment in the energy of the system and hence, there is temperature increment. This must be because of electrical work done by the battery on the system not because of the heat transfer as initially temperatures were equal.

II–System: Water only is our system. Heater coil will be part of the surroundings.

In this case when switch is turned on the temperature of the heater coil will increase first so there will be a temperature difference between system & surroundings. Hence, this energy transfer will be called heat.

- ## IUPAC Sign convention about Heat and Work



Any energy given to system is taken positive so heat given to system = positive

heat taken out from system = Negative

Work done on the system = Positive

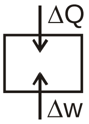
Work done by the system = Negative

The sign convention is different from physics, but the meaning always comes out to be same only in equation we have to use a different sign convention for work.

So if in any problem, w = – 10 J

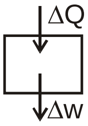
It means system has done work of 10 Joule on surroundings.

According to Chemistry :



$\Delta U = \Delta Q + \Delta W$

According to Physics :



$\Delta U = \Delta Q - \Delta W$

IUPAC convention of Heat

1. Heat given to the system = +ve
2. Heat coming out of the system = –ve
3. Work done on the system = +ve
4. Work done by the system = –ve

Section (C) : Work calculation

WORK DONE (w) :

Energy that is transmitted from one system to another in such a way that difference of temperature is not directly involved is known as work. It is a **path function**.

This definition is consistent with our understanding of work as dw = Fdx. The force F can arise from electrical, magnetic, gravitational & other sources.

Units : Heat & work both are forms of energy. Hence, their units are units of energy. i.e.SI system: Joules (J). Much data is available in the old units of calories (cal) as well.

P × V = (litre. atmosphere) term which has unit of energy. It is useful to remember the conversion

1 litre. atm = 101.3 Joules = 24.206 cal

- For irreversible processes, state parameters such as P, T etc cannot be defined. Hence, work cannot be estimated using P_{gas}. But by the work energy theorem

$W_{gas} = - W_{ext} + \Delta K_{pisston}$

When the piston comes to rest again $\Delta K_{piston} = 0$

$\therefore \quad W_{gas} = -W_{ext} = -\int P_{ext} dv$

as the external pressure is always defined hence, for all processes work can be calculated using

$$W_{gas} = -W_{ext} = -\int P_{ext}.dv = -P_{ext}\Delta V$$

Calculation of work for different type of process on an ideal gas.

1. ISOTHERMAL PROCESS :

(A) Isothermal expansion: There are many ways in which a gas can be expanded isothermally.

(a) Isothermal reversible expansion :

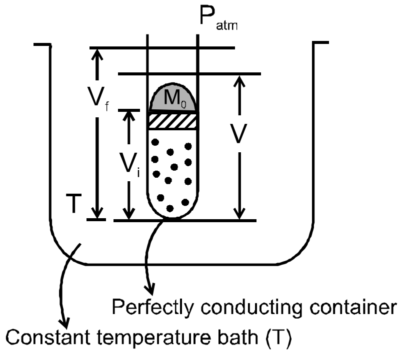
$$P_{ext} = P_0 + \frac{mg}{A} = P_{gas} = P \text{ (always)}$$

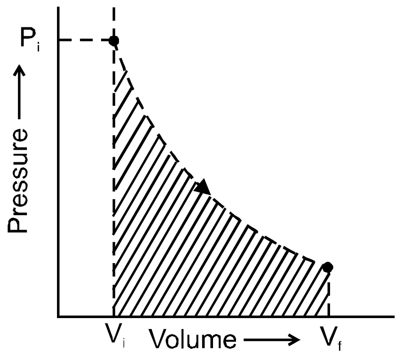
In reversible process, $P_{ext} = P_{gas}$ (thermodynamic equilibrium always)

Since process is isothermal ; $P = \frac{nRT}{V}$

$$W = -\int_{V_i}^{V_f} P_{ext}\,dV = -\int_{V_i}^{V_f} P\,dV \Rightarrow W = -\int_{V_i}^{V_f} \frac{nRT}{V}\,dV$$

$$W = -nRT \ln\left(\frac{V_f}{V_i}\right)$$





PV diagram Representation

Work = Area under the P–V diagram

In expansion work is done by system on the surroundings and $V_f > V_i$

$W = -ve$

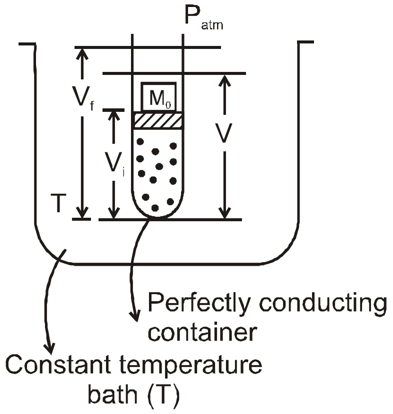
(b) Irreversible isothermal expansion :

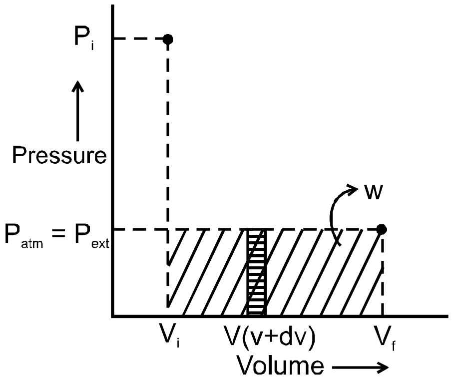
(i) Single step isothermal expansion

We are assuming expansion against atmospheric pressure which need not be the case in a given problem.

A mass equal to m_0 is placed on piston initially to maintain equilibrium.

Initially, $P_i = P_{gas} = P_{atm} + m_0 g/A$





PV diagram Representation

For expansion to take place, m_0 mass is suddenly removed so gas expands against constant external pressure of P_{atm}

In this case, the pressure of the gas will not be defined as the sudden expansion has taken place so all the molecules of sample will not get the information of expansion simultaneously, there will be a time gap and hence, there will be a **state of turbulence**.

From some intermediate state of volume ‘V’, the work done is slight expansion from

$V \longrightarrow (V + dV)$

$dw = -P_{ext} \,.\, dV$ (IUPAC sign convention)

So, $W = \int dw = -\int_{V_i}^{V_f} P_{ext}.dv = -P_{ext}(V_f - V_i)$

Only initial and final states can be located (as at intermediate stages pressure of the gas is not defined)

(ii) Two step isothermal expansion:

Mass M_0 is divided into two mass (may be equal or unequal)

$M_0 = (m_1 + m_2)$

Now, if m_1 only is removed, then the expansion of gas will take place against constant external pressure

$P_{ext_1} = (P_{atm} + m_2 g/A)$

and this expansion will take place only upto volume V_1 such that

$P_{ext_1} \,.\, V_1 = P_i V_i$ (isothermal)

Now, if second mass m_2 is also removed then expansion

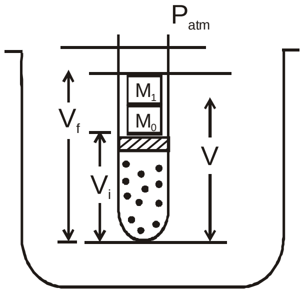
$V_1 \longrightarrow V_f$ will take place against constant pressure

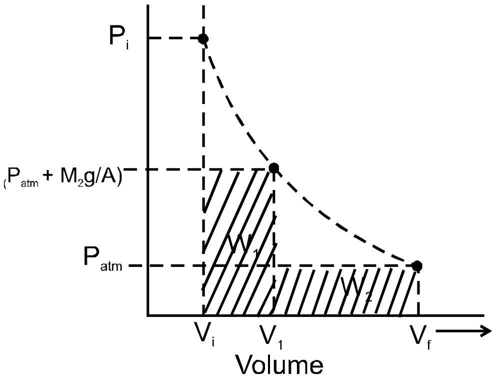
So, $P_{ext_2} = P_{atm}$

work done is expansion $V_i \longrightarrow V_1$; $W_1 = -(P_{atm} + M_2 g/A)(V_i - V_1)$

& work done is expansion $V_1 \longrightarrow V_f$; $W_2 = -P_{atm}(V_f - V_i)$

Total work = $W_1 + W_2$



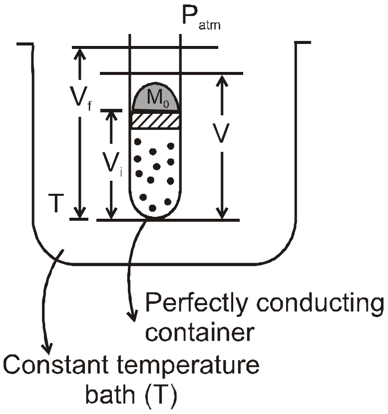


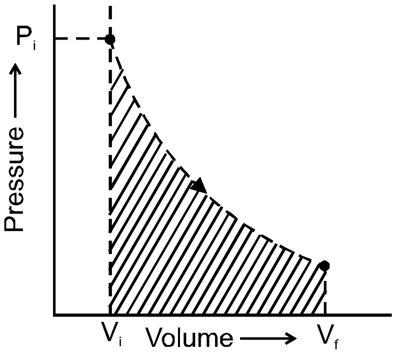
PV Diagram representation

- Work done in this irreversible expansion is greater than work done by gas during the single stage expansion of gas and so on for three step expansion we divide the mass m_0 into three masses m_1, m_2 and m_3 and remove these step by step and so on.

(iii) For n step expansion and n $\longrightarrow \infty$

If $n \to \infty$; Irreversible process becomes reversible process





PV Diagram representation

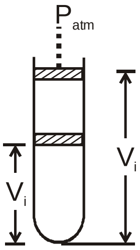
(B) Isothermal compression of ideal gas :

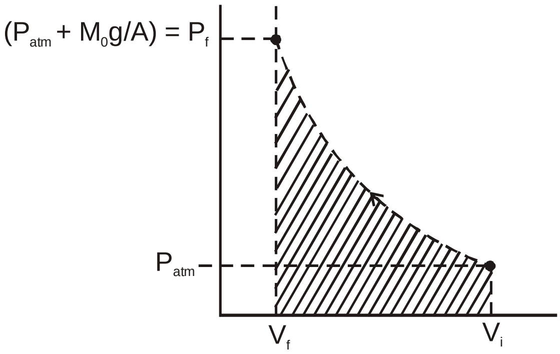
(a) Reversible isothermal compression of an ideal gas

This can be achieved by placing particles of sand one by one at a very slow take in the assembly which keeps the temperature of gas constant in this case the expression of work done will be exactly similar to as obtained in case of reversible expansion of gas

$W = -\, nRT \ln(V_f/V_i)$

This will automatically come out to be +ve as $V_f < V_i$





(b) Irreversible isothermal compression of an ideal gas

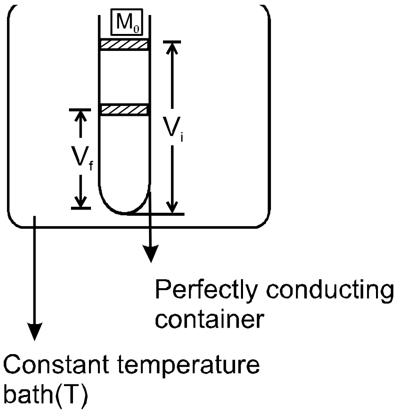
(i) Single step compression :

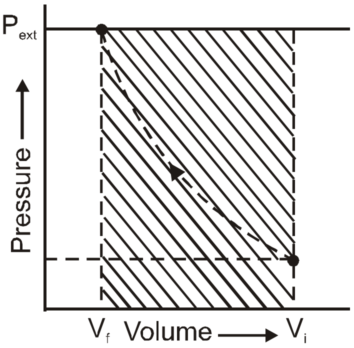
To compress gas a mass m_0 is suddenly placed on massless piston

$dw = -P_{ext}.\ dv = -(P_{atm} + m_0g/A)\ dv$

so, to calculate total work done on the gas

$W = \int dw = -\int_{V_i}^{V_f} P_{ext}.\ dv$; $\quad W = -P_{ext}(V_f - V_i)$





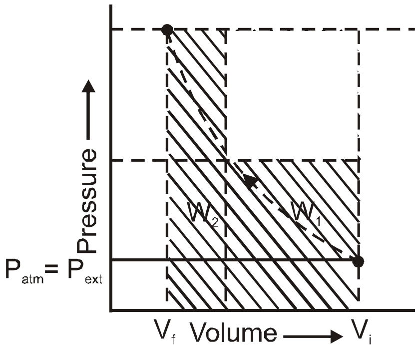
(ii) Two step compression :

Place mass m_0 in two fragments (m_1+m_2) the graphical representation will make the calculation of work done. If m_1 is placed first, then the first compression has taken place aganist external pressure of $(P_{atm} + m_1g/A)$

So, $\quad W_1 = -(P_{atm} + m_1\,g/A)(V_1 - V_i)$

$\quad$ Simlarly, $W_2 = -(P_{atm} + m_0\,g/A)(V_f - V_i)$

Note : If process takes place in n steps and n → ∞ then process will be like reversible compression.



Conclusion :

Whenever work is done on the gas then it will be minimum in case of reversible process.

Thats why different machines/engines are designed to work reversibly so maximum output can be obtained but minimum input is given to it.

$\left\{ \begin{array}{l} \text{output – work done by engine/machine/system} \\ \text{input – work done by system us a surrounding} \end{array} \right.$

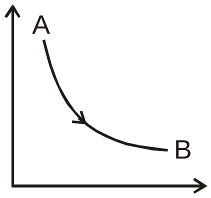
- ***If expansion/compression takes place against constant external pressure then it is irreversible.***
- ***If there is sudden change then the process is irreversible.***

Reversible and irreversible isothermal process.

- Except the infinite stage compression/expansion, all are irreversible.
- We can redefine reversible and irreversible as follows:

Reverssible process: If a process operates is such a fashion that when it is reversed back both the system as well as surroundings are restored to their initial position w.r.t. both work and heat, is known as reversible process.

If for the process A → B work = w, heat = Q then if for the process B → A, work = – w, heat = –Q then the process is reversible.



- If the external pressure is constant in isothermally process, process is irreversible.

Solved Examples

Ex-2. Calculate the work performed when 2 moles of hydrogen expand isothermally and reversibly at 25ºC form 15 to 50 litres.

Sol. We have, $W = -2.303\ n\ RT \log \frac{V_2}{V_1} = -2.303 \times 2 \times 2 \times 298 \times \log \frac{50}{15} = -1436$ calories.

Ex-3. If a gas at a pressure of 10 atm at 300 k expands against a constant external pressure of 2 atm from a vol. of 10 litres to 20 litres find work done ? [Isothermal process]

Sol. Process is irreversible

$$w = -\int_{10}^{20} 2dv = -2\ [20 - 10] = -20\ \text{L.atm}$$

1 litre atm = 101.3 J

---

2. ISOCHORIC PROCESS :

Since $dv = 0$

So, $w = 0$ (for both reversible and irreversible process)

3. ISOBARIC PROCESS :

Since $P = \text{constt.} = P_{ext}$

So, $w = -P_{ext}(v_f - v_i)$ (for both reversible and irreversible process)

Section (D) : Heat & Internal energy

Calculation of ΔE :

Internal Energy (E, also denoted by U) :

Every system having some quantity of matter is associated with a definite amount of energy, called internal energy.

- It is the sum of all forms of energies present in the system.

  $E = E_{Translational} + E_{Rotational} + E_{Vibrational} + E_{bonding} + ...$

  $\Delta E = E_{Final} - E_{Initial}$.

- **Thermodynamic definition of an ideal gas :**
  - For a gas the internal energy is directly proportional to its absolute temperature then the gas is termed as an ideal gas.

    so $\left(\frac{\partial E}{\partial V}\right)_T = 0$, $\left(\frac{\partial E}{\partial P}\right)_T = 0$

    $\Delta E = q_v$, heat supplied to a gas at constant volume, since all the heat supplied goes to increase the internal energy of the gas.
  - It is an extensive property & a state function. It is exclusively a function of temperature.

    If $\Delta T = 0$; $\Delta E = 0$ as well.
  - With change in temperature only kinetic energy changes.
- **Degree of freedom :** The total no of modes on which a molecule of an ideal gas can exchange energy during collisons is known as its degrees of freedom.

  Translational degree of freedom = 3 (for all type of gases.)

  Rotational degree of freedom

  = 0 – monoatomic gases
  = 2 – diatomic or linear polyatomic gases
  = 3 – non-linear polyatomic gases.

  If “f” is initial degree of freedom for that gas.

  f = 3 for monoatomic
  = 5 for diatomic or linear polyatomic
  = 6 for non - linear polyatomic

Law of equipartion of energy :

Energy equal to $\frac{1}{2}$kT is associated with each degree of freedom per ideal gas molecule

Where k is Boltzmann constant

$$E/\text{molecule} = f \times \frac{1}{2}kT \quad \Rightarrow \quad E/\text{mole} = \frac{f}{2}RT \quad \text{when } (R = k \times N_A)$$

∴ For n moles,

$$E = \frac{f}{2}nRT \text{ only for ideal gas.} \quad \Rightarrow \quad \Delta E = \frac{f}{2}nR\Delta T$$

Calculation of Heat (q)

- Heat is a path function and is generally calculated indirectly using Ist law of thermodynamics.
- First calculate ΔE and W & then q or heat can be calculated if heat capacity of any process is given to us.

❍ Total Heat Capacity (C_T)

Heat required to raise the temperature of system by 1ºC under the given process is known as total heat capacity.

Mathematically, $C_T = \frac{dq}{dT}$ J/ºC

- It is extensive properties and path function.

So, $dq = C_T dT$

on integrating $\boxed{q = \int C_T dT}$

❍ Molar heat capacity (C)

Heat required to raise temperature of 1 mole of a subtance by 1ºC

Mathematically, $C = \frac{dq}{ndT}$ J mole^{-1} K^{-1}

So, $dq = nCdT$

$q = \int nCdT = nC\Delta T$

C is intensive path function.

C_p is molar heat capacity at constant pressure

C_V is molar heat capacity at constant volume

C_p and C_V are intensive but not a path function

❍ Specific heat capacity (s) :

Heat required to raise temperature of unit mass (generally 1 g) of a substance by 1ºC.

$$S = \frac{dq}{mdT} \text{ Jg}^{-1}\text{ K}^{-1}$$

So, $dq = msdT$

$q = \int dq = \int ms \ dT = ms\Delta T$

S is intensive path function

S_P is specific heat capacity at constant pressure

S_V is specific heat capacity at constant volume

S_P & S_V are intensive but not a path function

Total heat capacity, molar heat capacity & specific heat capacity of a process on a substance are related as

$$C_T = nC = ms \quad \& \quad C = Ms$$

Where m – weight of substance, M – molar mass of substance, n – no. of moles of the substance

For	isothermal process	$C = \pm\infty$	For	isobaric process	$C = C_p$
For	isochoric process	$C = C_v$	For	adiabatic process	$C = 0$

Heat capacity can have value from –∞ to +∞ depending on the process.

Note :

(1) Heat capacity is a path function and different type of heat capacities are defined

(2) Remember heat capacity of a substance is not fixed it is dependent on type of process which is being performed on that substance.

Solved Examples

Ex-4. During an expansion of ideal gas the work done by gas is 100 J and the heat capacity of process is found to be +2 J/ºC. Find ΔE of gas if the final temperature of gas is 25ºC higher than its initial temperature.

Sol. $\Delta E = q + W$

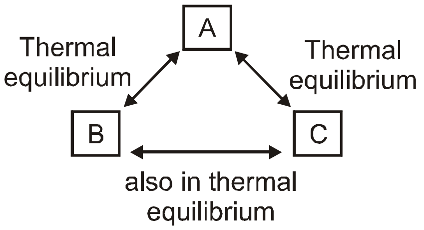
$q = 2 \times 25 = 50$ J & $W = -100$ J

$\Delta E = 50 - 100 = -50$ J

Section (E) : First law of thermodynamics

Zeroth Law of Thermodynamics (ZLOT) :

- If two systems are in thermal equilibrium with third system, then they are also in thermal equilibrium with each other.



(All three are in thermal equilibrium with each other.)

First Law of Thermodynamics (FLOT) :

Law of energy conservation :

Energy of total universe is always conserved.

or

Total energy of an isolated system is always conserved.

or

Hence absolute value of E can never be calculated only change in value of E can be calculated for a particular process.

Mathematical form of First Law of thermodynamics.

If a system is initially in a particular state in which its total internal energy is E_1. Now q amount of heat is given to it and w amount of work is done on it so that in new state its total internal energy becomes E_2. Then according to 1st Law of thermodynamics.

$$E_2 = E_1 + q + w$$

so $\Delta E = (E_2 - E_1) = q + w$

Application of First Law

$\Delta U = \Delta Q + \Delta W$ Since $\Delta W = -P\Delta V$

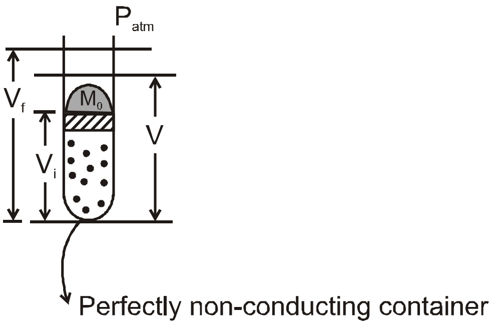
$\Delta U = \Delta Q - P\Delta V$

Section (F) : Adiabatic, isothermal, polytropic & free expansion processes

4. Adiabatic process :

dQ = 0 (no heat changed b/w system and surrounding

$$dU = dQ + dW$$



$$\Rightarrow \quad nC_V\, dT = -PdV \quad \Rightarrow \quad \int nc_V dT = \int -\frac{nRT}{V}.dv$$

$$\Rightarrow \quad \int_{T_1}^{T_2} \frac{C_v.dT}{T} = -\int_{V_1}^{V_2} \frac{R}{V}.\,dV \quad \Rightarrow \quad C_V \ln\frac{T_2}{T_1} = -R\ln\frac{V_2}{V_1}$$

$$\ln\frac{T_2}{T_1} = \ln\left(\frac{V_2}{V_1}\right)^{-R/c_v} \quad \Rightarrow \quad \left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

$$T_2 V_2^{\gamma-1} = T_1 V_1^{\gamma-1} \quad \text{or} \quad TV^{\gamma-1} = \text{constant}$$

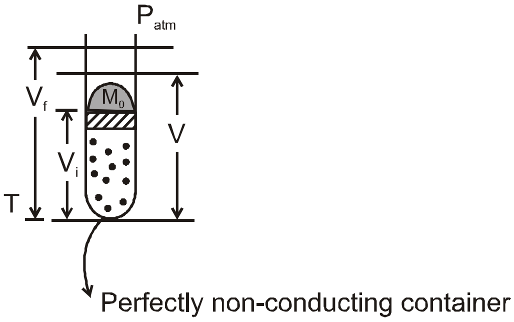
$$PV^{\gamma} = \text{constant}$$

- This is only valid when the quantity PV^{γ} or $TV^{\gamma-1}$ is constant only for a quasi-static or reversible process.
- For irreversible adiabatic process these equations are not applicable.

Operation of adiabatic process

(a) Reversible Adiabatic

- Operation wise adiabatic process and isothermal process are similar hence all the criteria that is used for judging an isothermal irreversible processes are applicable to adiabatic process.
- Also, volume in case of isothermal volume is more than that of adiabatic at constant pressure and no of moles, $V \propto T$



$$w = -\int P_{ext.}\, dv \text{, but} \qquad P_{ext} = P_{int} = \frac{K}{V^{\gamma}}$$

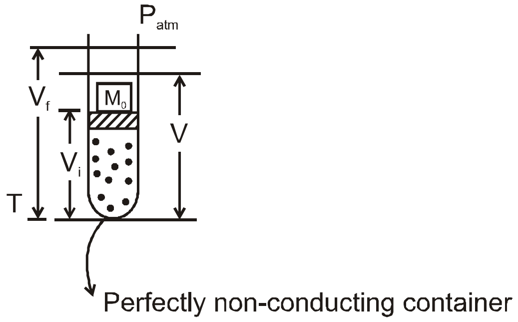
$$\therefore \quad w = -\int \frac{K}{V^{\gamma}}.\,dv\,,$$

$$\Rightarrow \quad W = -K\,\frac{\left[V_2^{-\gamma+1} - V_1^{-\gamma+1}\right]}{(1-\gamma)} = \frac{P_2V_2^{\gamma}.V_2^{1-\gamma} - P_1V_1^{\gamma}.V_1^{1-\gamma}}{\gamma-1}$$

$$\Rightarrow \quad \text{Work done} = \frac{P_2V_2 - P_1V_1}{\gamma-1} \qquad (\text{as } K = P_2V_2^{\gamma} = P_1V_1^{\gamma})$$

(b) Irreversible Adiabatic

- **Adiabatic irreversible expansion –**



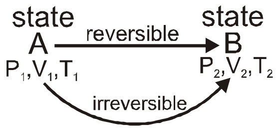
$$W = \int -P_{ext.}dv \quad = -P_{ext}(V_2 - V_1)$$

and $\int du = \int dw$

$$\therefore \quad W = \Delta u$$

$$W = nC_v(T_2 - T_1) = \frac{nR(T_2 - T_1)}{\gamma-1} = \frac{P_2V_2 - P_1V_1)}{\gamma-1}$$

Note: If two states A and B are connected by a reversible path then they can never be connected by an irreversible path.



If the two states are linked by an adiabatic reversible and irreversible path then

$$w_{rev.} = \Delta u_{rev.}$$

But as u is a state function

$$\therefore \quad \Delta u_{rev.} = \Delta u_{irrev.} \Rightarrow \quad w_{irrev.} = w_{rev.}$$

as work is a path function.

If we assume that

$$w_{irrev.} = w_{rev.} \quad \Rightarrow \quad \text{It implies that}$$

$\Delta u_{rev.} \neq \Delta u_{irrev.}$ Which again is a contradiction as U is a state function.

- Two states A and B can never lie both on a reversible as will as irreversible adiabatic path.
- There lies only one unique adiabatic path linkage between two states A and B.

❍ Comparison of Adiabatic Expansion (single stage Vs Infinite stage)

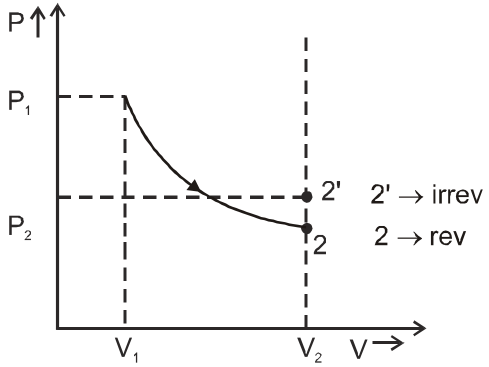
Single stage means irreversible process
Infinite stage means reversible process
In adiabatic compression process,

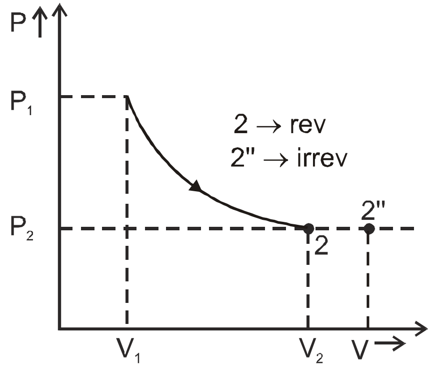
$(W_{gas})_{rev} < (W_{gas})_{irrev} \Rightarrow \Delta u_{rev.} < \Delta u_{irrev.}$

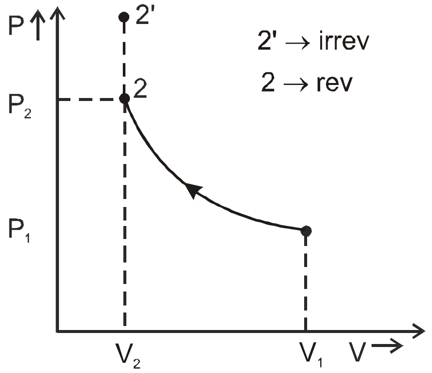
$\therefore$ $(T_2)_{rev.} < (T_2)_{irrev}$

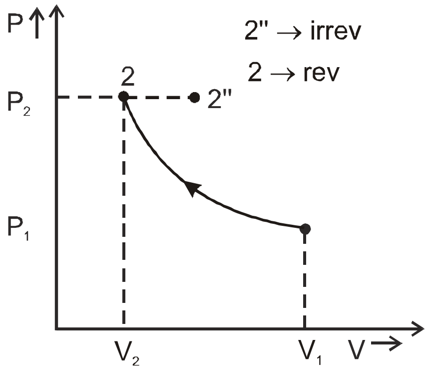
$(P_2)_{rev.} < (P_2)_{irrev}$ (If volume change are same)

$(V_2)_{rev.} < (V_2)_{irrev}$ (If pressure change are same)









- **Comparison of single stage Vs two stage expansion(adiabatic).**
  If the expansion is carried out in two stages then work done in two stage by the gas > work done in one stage by the gas. So, $\Delta U_{\text{two stage}} > \Delta U_{\text{single stage}}$
  $\therefore$ T_f in two stage < T_f in single stage because decrease in internal energy in two stage is > decrease in internal energy in one stage.

❍ Adiabatic Irreversible process (calculation of state parameters)

$$\text{State A} \xrightarrow{\text{irrev}} \text{State B}$$

P_1,V_1,T_1 $\qquad$ P_2,V_2,T_2

$$W = \frac{nR(T_2 - T_1)}{\gamma - 1} = \frac{P_2V_2 - P_1V_1}{\gamma - 1} = -P_{ext.}(V_2 - V_1) \ , \ \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

- **Free expansion :**
  Always going to be irrerversible and since $P_{ext} = 0$
  So, $dW = -P_{ext}.dV$
  $= 0$
  If no heat is supplied q = 0
  then $\Delta E = 0$ So, $\Delta T = 0$.

Section (G) : Enthalpy

Calculation of C_p and C_v

(a) Constant volume process (Isochoric)

$dU = dq + dw$

$\therefore$ $dU = (dq)_v$ (Heat given at constant volume = change in internal energy)

$\therefore$ $dU = (nCdT)_v$

$dU = nC_v dT$

C_v is Specific molar heat capacity at constant volume.

$$C_v = \frac{1}{n}.\frac{dU}{dT} = \frac{1}{n}\frac{d\ \ (fnRT)/2}{dT} = \frac{fR}{2}$$

(b) Constant pressure process (Isobaric) :

$dU = dQ + dW$

$dU = dQ - PdV$

$\Rightarrow$ $dQ = dU + PdV$ .... (i)

Defining a new thermodynamic function

$H \equiv$ Enthalpy

- It is a state function and extensive property
- It is mathematically defined as :

$H = U + PV$

as $dH = dU + d\,(Pv)$

as $P =$ constant

$dH = dU + PdV$ .... (ii)

from equation (i) & (ii)

$\therefore$ $dH = (dq)_p$ only at constant pressure.

Heat given at constant pressure = Change in enthalpy

$dH = (nCdT)_p$

$dH = nC_p\,dT$

Relation between C_p and C_v for an ideal gas

$H = U + PV$

$\therefore$ $dH = dU + d(PV)$

for an ideal gas

$PV = nRT$

$d(PV) = d(nRT) = nRdT$

$nC_p\,dT = nC_v dT + nRdT$

$\Rightarrow$ $\mathbf{C_p - C_v = R}$ only for ideal gas $\Rightarrow$ Mayer's Relationship

Table # 1 At Normal temperature

S.No.	**Gas**	**Degree of freedom**	**$C_{v,m}\left(\frac{fR}{2}\right)$**	**$C_{p,m}\left(\frac{f+2}{2}\right)R$**	**$\gamma = \left(\frac{f+2}{f}\right)$**	**Examples**
1.	Monoatomic	3	$\frac{3R}{2}$	$\frac{5R}{2}$	$\frac{5}{3}$	He; Ne
2.	Diatomic	5	$\frac{5R}{2}$	$\frac{7R}{2}$	$\frac{7}{5}$	N_2; O_2; H_2
3.	Linear polyatomic	5	$\frac{5R}{2}$	$\frac{7R}{2}$	$\frac{7}{5}$	CO_2; HCl
4.	Non-Linear polyatomic	6	$\frac{6R}{2}$	$\frac{8R}{2}$	$\frac{8}{6}$	H_2O; NH_3; CH_4

Note : At high temperature vibrational degree of freedom is also included.

Calculation of ΔH, ΔU, work, heat etc.

Case - I **For an ideal gas undergoing a process.**

the formula to be used are

$$dU = nC_v dT = \frac{f}{2} nRdT$$

$$dH = nC_p dT = \left(\frac{f}{2}+1\right) nRdT$$

$$W = -\int P_{ext}.\ dV$$

$$dH = dU + d(PV)$$

$$du = dQ + dw$$

Solved Examples

Ex-5. Calculate the maximum work done when pressure on 10 g of hydrogen is reduced from 20 atm to 1 atm at a constant temperature of 273 K. The gas behaves ideally. Will there be any change in internal energy? Also, calculate 'q'.

Sol. We have, $W = -2.303\, nRT \log \frac{P_1}{P_2}$

$$n = \text{number of moles of hydrogen} = \frac{\text{wt. in grams}}{\text{mol. wt.}} = \frac{10}{2} = 5 \text{ moles.}$$

Thus, $W = -2.303 \times 5 \times 2 \times 273 \times \log \frac{20}{1} = -8180$ calories.

Further, the change in state of the system at constant temperature will not change internal energy i.e., $\Delta U = 0$.

Again, $q = \Delta U - W = 0 - (-8180) = 8180$ calories.

Case - II **For solids and liquid system :**

$$dU = nC_v dT \neq \frac{f}{2} nRdT \qquad \text{(as it is not an ideal gas)}$$

$$dH = nC_p\, dT \neq \left(\frac{f}{2}+1\right) nRT \text{ (as it is not an ideal gas)}$$

$$W = -\int P_{ext}.\ dV$$

$$\Delta H = \Delta U + (P_2V_2 - P_1V_1)$$

$$dU = dq + dw$$

Solved Examples

Ex-6. A liquid of volume of 100 L and at the external pressure of 10 atm–Lt the liquid is confined inside an adiabatic bath. External pressure of the liquid is suddenly increased to 100 atm and the liquid gets compressed by 1 L against this pressure then find,

(i) work (ii) ΔU (iii) ΔH

Sol. Work done = $-100 \times -1 = 100$ L. atm

$\Delta q = 0 \quad \Delta w = \Delta U$

$\Rightarrow \quad 100 = \Delta U$

$\Delta H = \Delta U + (P_1V_2 - P_1V_1)$

$= 100 + (100 \times 99 - 100 \times 10)$

$= 100 + 100 \times 89 = 9000$ lit atm.

1 L. atm = 101.3 Joule.

Case - III **For chemical reactions :**

$aA(s) + bB(\ell) + cC(g) \rightarrow a'A'(s) + b'B'(\ell) + c'C'(g)$

$W = -\int P_{ext.}\ dV = \int -P_{ext.}\ (V_f - V_i)$

$= -P_{ext.}\ [(V_{A'}(s) + (V_{B'}(\ell) + (V_{C'}(g) - (V_A(s) + (V_B(\ell) + (V_C(g))]$

$\therefore$ $W = -P_{ext.}\ [V_{C'}(g) - V_C(g)]$

$$= -P_{ext.}\left[\frac{n'_c\,RT}{P_{ext}} - \frac{n_c\quad RT}{P_{ext}}\right] = -\ \frac{P_{ext.}\quad (n'_c - n_c)RT}{P_{ext.}}$$

$W = -(n'_c - n_c)RT$

$\therefore$ $W = -\Delta n_g\ RT$

$dU = dq + dw$

if at constant pressure

$dq = dH$

$\therefore$ $dU = dH - pdV$

$dU = dH - \Delta ng\ RT$

$\therefore$ $dH = dU + \Delta ng\ RT$

Solved Examples

Ex-7. For the combustion of 1 mole of liquid benzene at 25ºC, the heat of reaction at constant pressure is given by, $C_6H_6(\ell) + 7\frac{1}{2}O_2\ (g) \rightarrow 6CO_2\ (g) + 3H_2O\ (\ell)$; $\Delta H = -780980$ cal.

What would be the heat of reaction at constant volume?

Sol. We have, $\Delta H = \Delta E + \Delta n_g\ RT$

Here, $\Delta n_g = 6 - 7.5 = -1.5$.

Thus, $\Delta E = \Delta H - \Delta n_g\ RT = -780980 - (-1.5) \times 2 \times 298 = -780090$ calories.

Section (H) : Phase transition

Case - IV During phase transformation.

Phase transitions generally take place at constant pressure (unless specified) and at constant temperature. So, $\Delta T = 0$.

But still ΔH and ΔE are non zero (different from process on an ideal gas)

Because during phase transitions though the kinetic energy of molecules of substance remains same but the potential energy gets modified or changed and since E is summation of all type of energies. So, $\Delta E \neq 0$. Also, during this phase transition $\Delta(PV) \neq 0$

Hence, $\Delta H \neq 0$.

Now, to calculate heat – generally latent heats of transitions are given and since process is taking place at constant pressure. So, $q = \Delta H$.

To calculate W, use $dW = -P_{ext}\ dV$ and then calculate ΔE using Ist law of thermodynamics.

Solved Examples

Ex-8. Calculate q, W, ΔE and ΔH when 100 g of $CaCO_3$ is converted into its aragonite form given density of calcite = 2 g/cc and density of aragonite = 2.5 g/cc

Sol. $CaCO_3 \rightleftharpoons CaCO_3$

Calcite Aragonite $\Delta H = 2$ kJ/mole

Generally for solid $\longrightarrow$ Solid

solid $\longrightarrow$ Liquid

solid $\longrightarrow$ Liquid

transitions $W << q$ So, $\Delta E \simeq q = \Delta H$

while for gaseous conversion for example

Solid $\longrightarrow$ gas

Liquid $\longrightarrow$ gas

$q = \Delta H \neq \Delta E$, as W will be significant

S.No.	Process	w	q	ΔU	ΔH	Molar heat capacity
1.	Isochoric	0	$nC_{v,m}(T_f - T_i)$	q_v	$nC_{p,m}(T_f - T_i)$	$C_{v,m}$
2.	Isobaric	$-P_{ext}(V_2 - V_1)$	$nC_{p,m}(T_f - T_i)$	q + w	$nC_{p,m}(T_f - T_i)$	$C_{p,m}$
3.	Isothemal	$W_{rev} = -nRT\ln\left(\frac{V_f}{V_i}\right)$ $W_{irrev} = -P_{ext}(V_f - V_i)$	–w	0	0	± ∞
4.	Adidatic	$\frac{P_fV_f - P_iV_i}{\alpha - 1}$	0	w	0	0
5.	Polytropic	$\frac{P_fV_f - P_iV_i}{(n-1)}$	$\Delta U - w$	$nC_{v,m}(T_2 - T_1)$	$nC_{p,m}(T_2 - T_1)$	$C_{v,m} + \frac{R}{1-\gamma}$

Thermodynamics IInd & IIIrd Law

Section (A) : Introduction about entropy

- **IInd Law of thermodynamics :**

Requirement : Ist law insufficient to Explain
Neutralization, Melting of ice > 0°
Combustion, Freezing of water < 0°
Fall of water, Boiling of water > 100° C
Cooling of a hot body, Free expansion of a gas, mixing of gases.

Spontaneous /Natural /Irreversible Processes :

If a system moves along in a direction on its own and system, surrounding interactions without the help of any external agency, then that direction is known as spontaneous direction and the process is knwon as a spontaneous process.

Limitation :

First law cannot predict the direction of any process. But in nature a process is found to have a specific direction at certain conditions.

1. Energy can be the factor : To achieve stability
* All exothermic processes are spontaneous.
* All endothermic processes are non spontaneous.

Exceptions

* melting of ice (above 0°C) although $\Delta H > 0$, $\Delta E > 0$
* Vaporization of water (above 100°C) $\Delta H > 0$, $\Delta E > 0$
* Spreading of ink in water $\Delta H = 0$, $\Delta E = 0$
* Mixing of two gases
* Endothermic solution of salt $\Delta H > 0$, $\Delta E > 0$

2. It is observed that nature tries to distribute energy and matter uniformaly (randomization)

Second law of thermodynamics :

Entropy of the universe is constantly inereasing.

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0$$ for a spontaneous process.

Where **(S)** = entropy is the measure of randomness or disorder. It is a state function and extensive property.

Mathematically

$ds = \frac{dq_{rev}}{T}$ or $\Delta S = \int \frac{dq_{rev}}{T}$, $\frac{dq}{T}$ is state function only for reversible process

$dS \propto dq_{rev}$, $dS \propto \frac{1}{T}$

At Higher T - entropy is already high. Therefore, heat addition will not introduce much change in the entropy.

Section (B) : Entropy Calculation

- **Calculation of ΔS_{system}**

$$\begin{tikzcd}
\text{state A} \arrow[r, "\Delta S_{\text{reversible}}"] \arrow[r, bend right, "\Delta S_{\text{irreversible}}"'] & \text{state B}
\end{tikzcd}$$

As 'S' is a state function. Hence 'ΔS' will also be a state function.

∴ $\Delta S_{irrev} = \Delta S_{rev}$

$$\Delta S = \int_A^B \frac{dq_{rev}}{T} \text{ reversible path}$$

- **Entropy calculation for an ideal gas undergo in a process.**

$$\begin{matrix} \text{State A} & \xrightarrow{\Delta S_{irr}} & \text{State B} \\ P_1, V_1, T_1 & & P_2, V_2, T_2 \end{matrix}$$

As 'S' is a state function.So, ΔS will not depend upon path

$$\Delta S_{irrev} = \Delta S_{rev,\ system} = \int_A^B \frac{dq_{rev}}{T} \text{ rev path.}$$

from the first law

$$dU = dQ + dw$$
$$dQ = dU - dw$$

for reversible path

$$dq = dq_{rev}$$
$$dq_{rev} = dU + P_{gas}\, dV \qquad \{P_{ext} = P_{gas} \text{ reversible}\}$$
$$\Delta S_{rev,\ system} = \int_A^B \frac{dU + P_{gas}\ \ dV}{T}$$

for an ideal gas

$$\frac{P_{gas}}{T} = \frac{nR}{V} \text{ \& } du = nc_V\, dT$$

∴ $$\Delta S_{sys} = \int_{T_1}^{T_2} \frac{nc_V\, dT}{T} + \int_{V_1}^{V_2} \frac{nRdV}{V}$$

∴ $$\Delta S_{system} = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

- **Calculation of $\Delta S_{surrounding}$:** As the surrounding is an infinite heat reservoir hence, no. amount of heat given to the surrounding can cause turbulance in it, hence all heat exhanges with surroundings are considered to be reversible.

$$\Delta S_{surrounding} = \int \frac{dq_{surrounding}}{T}$$

For surrounding T is constant

∴ $$\Delta S_{surr} = \frac{1}{T} \int dq_{surr} = \frac{q_{surrounding}}{T}$$

But according to the law of conservation of energy

$$q_{surr} = -\, q_{system}$$

∴ $$\Delta S_{surr} = \frac{-q_{system}}{T}$$

- ## Isothermal process :

(a) Reversible

$$\text{State A} \xrightarrow{\text{Rev}} \text{State B}$$

$P_1, V_1, T \qquad P_2, V_2, T$

$$\Delta S_{\text{system}} = nC_V \ell n \frac{T_2}{T_1} + nR \ell n \frac{V_2}{V_1}$$

Since $T_1 = T_2$

$$\Delta S_{\text{system}} = nR \ell n \frac{V_2}{V_1}$$

$$\Delta S_{\text{surrounding}} = -\frac{q_{\text{system}}}{T}$$

$du = dq + dw$ (since $T_1 = T_2$. So, $du = 0$)

$\therefore dq = -dw$

$\therefore q = -w$ as $w = -nRT \ell n \frac{V_2}{V_1}$

$$q = nRT \ell n \frac{V_2}{V_1}$$

$$\therefore \Delta S_{\text{sys.}} = \frac{-nRT \ell n \frac{V_2}{V_1}}{T} = -nR \ell n \frac{V_2}{V_1}$$

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surr}}$$

$$= nR \ell n \frac{V_2}{V_1} - nR \ell n \frac{V_2}{V_1} = 0$$

(b) Irreversible

$$\text{State A} \xrightarrow{\text{irrev}} \text{State B}$$

$P_1, V_1, T \qquad P_2, V_2, T$

$$\Delta S_{\text{system}} = nR \ell n \frac{V_2}{V_1}$$

$$\Delta S_{\text{Surrounding}} = \frac{-\ q_{\text{system}}}{T}$$

q_{system} is calculated using FLOT

$q_{\text{system}} = P_{\text{ext}}(V_2 - V_1)$

$$\therefore \Delta S_{\text{surrounding}} = \frac{-p_{\text{ext}}(V_2 - V_1)}{T}$$

$$\Delta S_{\text{universe}} = nR \ell n \frac{V_2}{V_1} - \frac{-p_{\text{ext}}(V_2 - V_1)}{T}$$

$$= \frac{1}{T}\left[(nRT \ \ell n \ \frac{V_2}{V_1}) - P_{\text{ext}} \ (V_2 - V_1)\right] = \frac{1}{T}[W_{\text{irrev}} - W_{\text{rev}}] > 0$$

As irreversible work of gas is more than reversible work.

- ## Adiabatic Process (Isoentropic process)

(a) Reversible Adiabatic

$$\text{State A} \xrightarrow{\text{rev}} \text{State B}$$

$P_1, V_1, T_1 \qquad P_2, V_2, T_2$

$$\Delta S_{\text{system}} = nC_V \ \ell n \frac{T_2}{T_1} + nR \ \ell n \ \frac{V_2}{V_1}$$

$TV^{\gamma-1} = \text{constant}$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

$$(\Delta S)_{system} = nC_V \ell n\left(\frac{V_1}{V_2}\right)^{\gamma-1} + nR\ell n\frac{V_2}{V_1} = 0$$

$$\Delta S_{surr} = -\frac{q_{sys}}{T} = 0\ (q_{sys} = 0) \qquad \therefore\ \Delta S_{universe} = 0 + 0 = 0$$

(b) Irreversible Adiabatic

State A $\xrightarrow{irre}$ State B

P_1,V_1,T_1 $\qquad\qquad$ P_2,V_2,T_2

Using irreversible adiabatic process it is not possible to reach same state B which was reached by reversible adiabatic.

$$\Delta S_{system} = nC_V\ \ell n\frac{T_2}{T_1} + nR\ \ell n\ \frac{V_2}{V_1} > 0 \quad [(T_2)_{irrev} > (T_2)_{rev}]$$

$$\Delta S_{surr} = -\frac{q_{\ sys}}{T} = 0 \qquad \text{as } q = 0$$

For irreversible expansion the decrease in temprature will be lesser as work done is lesser hence, decrease in entropy due to fall in temprature will be lesser in case of irrversible expansion. Hence, net entropy would increase.

• Isobaric process :

(a) Reversible Isobaric

State A $\xrightarrow{irre}$ State B

P, V_1, T_1 $\qquad\qquad$ P, V_2, T_2

$$\Delta S_{sys} = \int\frac{dq_{rev}}{T} = \int\frac{nC_p dT}{T} = nC_p\ell n\frac{T_2}{T_1}$$

$$\Delta S_{surrounding} = \int\frac{dq_{rev}}{T} = \int_{T_1}^{T_2}\frac{-dq_{sys}}{T} = -\ nC_p\ell n\frac{T_2}{T_1}$$

$$\Delta S_{universe} = \Delta S_{sys} + \Delta S_{surrounding} = 0$$

(b) Irreversible Isobaric

$$\Delta S_{sys} = \int\frac{dq_{rev}}{T} = \int_{T_1}^{T_2}\frac{nC_p dT}{T} = nC_p\ell n\frac{T_2}{T_1}$$

$$\Delta S_{surrounding}\ \int\frac{dq_{rev}}{T} = \frac{-nC_p\left(T_2 - T_1\right)}{T_2}$$

$$\Delta S_{universe} = \Delta S_{sys} + \Delta S_{surrounding} > 0$$

• Isochoric Process

(a) Reversible Isochoric

State A $\xrightarrow{rev}$ State B

P_1,V, T_1 $\qquad\qquad$ P_2,V, T_2

$$\Delta S_{sys} = \int\frac{dq_{rev}}{T} = \int_{T_1}^{T_2}\frac{nC_v dT}{T} = nC_v\ell n\frac{T_2}{T_1}$$

$$\Delta S_{surrounding} = \int\frac{dq_{rev}}{T} = \int_{T_1}^{T_2}\frac{-dq_{sys}}{T} = -\ nC_v\ell n\frac{T_2}{T_1}$$

$$\Delta S_{universe} = \Delta S_{sys} + \Delta S_{surrounding} = 0$$

(b) Irrversible Isochoric

$$\Delta S_{sys} = \int\frac{dq_{rev}}{T} = \int_{T_1}^{T_2}\frac{nC_v dT}{T} = nC_p\ell n\frac{T_2}{T_1}$$

$$\Delta S_{surrounding} = \frac{-nC_v\left(T_2 - T_1\right)}{T_2}$$

$$\Delta S_{universe} = \Delta S_{sys} + \Delta S_{surrounding} > 0$$

Entropy Calculation for phase transformations

$$\Delta S_{fusion} = \int \frac{dq}{T} = \frac{1}{T}\int dq = \frac{Q}{T}$$

For constant pressure $\Delta S_{fus.} = \dfrac{\Delta H_{fus}}{T}$

For constant volume $\Delta S_{fus.} = \dfrac{\Delta U_{fusion}}{T}$

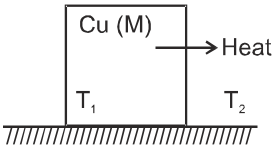
$$\Delta S_{vap} = \int \frac{dq}{T} = \frac{1}{T}\int dq = \frac{Q}{T}$$

For constant Pressure, $\Delta S_{vap} = \dfrac{\Delta H_{vap}}{T}$

For constant Volume, $\Delta S_{vap} = \dfrac{\Delta U_{vap}}{T}$

Entropy Calculation solid or liquid systems:

(a) 'Cu' block kept in open atmosphere



$T_1 > T_2$

$$\Delta S_{system} = \int_{T_1}^{T_2} \frac{msdT}{T} = m\ell n\,\frac{T_2}{T_1}$$

$$\therefore \quad \Delta S_{surr} = \int \frac{dq_{surr}}{T} = \frac{q_{surr}}{T_2}$$

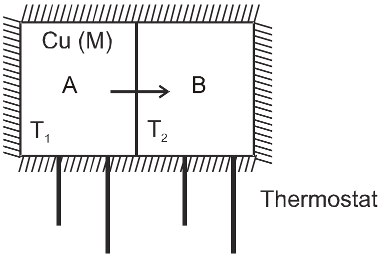
but $q_{surr} = -q_{system} = -ms(T_2 - T_1) = ms(T_1 - T_2)$

Hence, $\Delta S_{surr} = \dfrac{ms(T_1 - T_2)}{T_2}$

$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surr}$

$$\therefore \quad \Delta S_{universe} = ms\,\ell n\frac{T_2}{T_1} + \frac{ms(T_1 - T_2)}{T_2} > 0$$

(b) Two copper block kept in contact in thermostat



Two blocks are of same mass

$\Delta S_{surr} = 0$ (since no heat is lost to surrounding)

$\Delta S_{system} = \Delta S_A + \Delta S_B$

System will reach a common temperature (T_f)

and $T_1 > T_f > T_2$

$$\Delta S_{system} = \int_{T_1}^{T_f} \frac{dq_A}{T} + \int_{T_2}^{T_f} \frac{dq_B}{T}$$

$$= \int_{T_1}^{T_f} \frac{msdT}{T} + \int_{T_2}^{T_f} \frac{msdT}{T} = ms\left[\ell n\frac{T_f}{T_1} + \ell n\frac{T_f}{T_2}\right]$$

$$\Delta S_{system} = ms\ell n\frac{T_f^2}{T_1T_2}$$

Since $T_f = \dfrac{T_1 + T_2}{2}$ $\qquad \therefore \qquad \Delta S_{system} = ms\ell n\dfrac{(T_1 + T_2)^2}{4T_1T_2}$

Solved Examples

Ex-9. **(a)** One mole of an idal gas expands isothermally and reversibly at 25ºC from a volume of 10 litres to a volume of 20 litres.

(i) What is the change in entropy of the gas?
(ii) How much work is done by the gas?
(iii) What is q (surroundings)?
(iv) What is the change in the entropy of the surroundings?
(v) What is the change in the entropy of the system plus the surroundings?

(b) Also answer the questions opening a stopcock and allowing the gas to rush into an evacuated bulb of 10 L volume.

Sol. **(a)** (i) $\Delta S = 2.303\ nR \log \frac{V_2}{V_1} = 2.303 \times 1 \times 8.314 \times \log \frac{20}{10} = 5.76$ J/K.

(ii) $W_{rev} = -2.303nRT \log \frac{V_2}{V_1}$

$$= -2.303 \times 1 \times 8.314 \times 298 \times \log \frac{20}{10} = -1781 \text{ J.}$$

(iii) For isothermal process, $\Delta U = 0$ and heat is absorbed by the gas,

$q_{rev} = \Delta U - W = 0 - (-1718) = 1718$ J.

$\therefore$ $q_{rev} = 1718$ J. ($\therefore$ process is reversible)

(iv) $\Delta S_{surr} = -\frac{1718}{298} = -5.76$ J/K.

As entropy of the system increases by 5.76 J, the entropy of the surroundings decreases by 5.76J, since the process is carried out reversibly.

(v) $\Delta S_{sys} + \Delta S_{surr} = 0$..... for reversible process

(b) (i) $\Delta S = 5.76$ J/K, which is the same as above because S is a state function

(ii) W = 0 ($\because p_{ext} = 0$)

(iii) No heat is exchanged with the surroundings.

(iv) $\Delta S_{surr} = 0$.

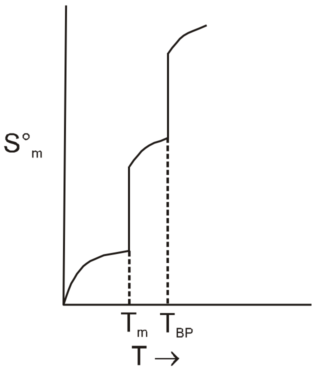
(v) The entropy of the system plus surroundings increases by 5.76 J/K, as we expect entropy to increase in an irreversible process.

- ## Third Law Of Thermodynamics :

The entropy of perfect crystals of all pure elements & compounds is zero at the absolute zero of temperature.

Thus, absolute value of entropy unlike the absolute value of enthalpy for any pure substance can be calculated at any given temperature. In standard state (298 K, 1 atm), it is standard absolute entropy S°.

$$\Delta S = S_{T(K)} - S_{0(K)} = \int_0^T \frac{nCdT}{T}$$



- ## For chemical reaction

$$aA + bB \longrightarrow cC + dD$$

$$\Delta S^o_{system} = (\Sigma\, S^0_m\, n_i)_{product} - (\Sigma\, S^0_m\, n_i)_{reactant}$$

where S^0_m = standard molar entropy. It can calculated using third law of thermodynamics.

$$\Delta S_{surr} = \frac{-Q_{system}}{T} = \frac{-\Delta H_{system}}{T}$$

* For a perfactly crystline substance at 0 K, entropy = 0

- ## For phase transformations

$$\Delta S_{fusion} = \int \frac{dp}{T} = \frac{1}{T}\int dp = \frac{Q}{T}$$

for constant pressure $\Delta S_{fus.} = \frac{\Delta H_{fus}}{T}$

for constant volume $\Delta S_{fus.} = \frac{\Delta U_{fusion}}{T}$

$$\Delta S_{vap} = \int \frac{dQ}{T} = \frac{1}{T} \int dQ = \frac{Q}{T}$$

for constant Pressure, $\Delta S_{vap} = \frac{\Delta H_{vap}}{T}$

for constant Volume, $\Delta S_{vap} = \frac{\Delta U_{vap}}{T}$

Section (C) : Free energy

- **Gibb's free energy (G) :**

A system parameter to predict the spontaneity of chemical reaction was introduced by Gibb's so that entropy calculation for the surrounding need not be carried out.

It is a free energy at constant pressure.

$G = H - TS$

$dG = dH - TdS - SdT$

& $H = U + PV$

$dH = dU + PdV + VdP \quad \Rightarrow \quad dG = dU + PdV + VdP - TdS - SdT$

From Ist law of thermodynamics

$dq = dU + PdV$

& from 2nd law, $dq = TdS$

$dG = dq + VdP - TdS - SdT$

$dG = -SdT + VdP$

At constant temperature,

$dG = VdP$

For ideal gas, $V = \dfrac{nRT}{P}$

$$dG_m = V_m dP = \frac{RT}{P} dP$$

$$\int_1^2 dG_m = RT \int_{P_1}^{P_2} \frac{dP}{P}$$

$$G_{m_2} - G_{m_1} = RT \ell n \frac{P_2}{P_1}$$

Where G_m is free energy for 1 mole

If G_{m_1} is free energy for 1 mole in standard state and G_{m_2} is free energy for one mole in any other state.

$$G_m - G°_m = RT\ln \frac{P}{1} \qquad \& \; G - G° = nRT\ell n \frac{P}{1}$$

For the reaction, $aA(g) + bB(g) \rightleftharpoons C(g) + dD(g)$

$(\Delta G)_{reaction} = (\Sigma \Delta G)_{product} - (\Sigma \Delta G)_{reactant}$

$(\Delta G)_{reaction} = G_C + G_D - G_A - G_B$

$$G_C - G°_C = cRT\ln \frac{P_C}{1} \quad \Rightarrow \quad G_C = G°_C + cRT\ln P_C$$

Similarly, $G_D = G°_D + dRT\ln P_D$; $G_A = G°_A + aRT\ln P_A$, $G_B = G°_B + bRT\ln P_B$

$$(\Delta G)_{reaction} = (G°_C + cRT\ln P_C) + (G°_D + dRT\ln P_D) - (G°_A + aRT\ln P_A) - (G°_B + bRT\ln P_B)$$

$$= (\Delta G)°_{reaction} + RT\ln \frac{P^c{}_C . P^d{}_D}{P^a{}_A . P^b{}_B}$$

$$\Delta G_{reaction} = \Delta G°_{reaction} + RT\ln Q$$

Gibb's Helmholtz Equation :

$dG = VdP - SdT$

At constant Pressure

$$dG = -SdT \quad \Rightarrow \quad \left(\frac{dG}{dT}\right)_P = -S \;\&\; \left(\frac{\partial \Delta G}{\partial T}\right)_P = -\Delta S$$

& $G = H - TS \quad \Rightarrow \quad \dfrac{G - H}{T} = -S$

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

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

$$\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_P$$

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

$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surrounding}$

$\Delta S_{surr} = \dfrac{-Q_{system}}{T} = \dfrac{-\Delta H_{system}}{T}$

$T\Delta S_{univ} = T\Delta S_{system} - \Delta H_{system}$

Introducing a new thermodyamic function G = Gibb's free energy (State function and an extensive property)

$G_{system} = H_{system} - TS_{system}$

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

$\Delta G_{system} = \Delta H_{system} - T\Delta S_{system}$ .... (ii)

Comparing equation (i) and (ii)

$\Delta G_{system} = -T\Delta S_{universe}$

New criteria of spontaneity :

(i) If ΔG_{system} is (–ve) < 0 ⇒ process is spontaneous

(ii) If ΔG_{system} is > 0 ⇒ process is non spontaneous

(iii) If ΔG_{system} = 0 ⇒ system is at equilibrium

So, at every temparature $\Delta G \neq 0$

ΔH_{system}	ΔS_{system}	$\Delta G_{system} = \Delta H_{system} - T\Delta S_{system}$
+ Ve	– Ve	+
– Ve	+ Ve	–
+ Ve	+ Ve	– Ve at high temprature
– Ve	– Ve	+ Ve at high temprature

ΔGº = standrad free energy change :

When the reactants under standrad conditions gets converted into products which is also under standared condition, then the free energy change is known as ΔGº (it is a constant) for 1 mole at 1 bar.

At standared conditions :

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

= constant for a GIVEN REACTION

$\alpha A + \beta B \longrightarrow \gamma C + \delta D$

ΔG° = (Gbb's energy of product) – (Gibb's energy of reactant)

$\Delta G^\circ = \gamma G^0_{m,C} + \delta G^0_{m,D} - \alpha G^0_{m,A} - \beta G^0_{m,B}$, where G^0_m can not be calculated as H^0_m cannot be calculated.

Hence, we can convert this relation in to Gibb's energy of formation of substance.

$\Delta G^\circ = \gamma \Delta G^0_{f,C} + \delta \Delta G^0_{f,D} - \alpha \Delta G^0_{f,A} - \beta \Delta G^0_{f,B}$

ΔG^0_f : standared Gibb's energy of formation.

ΔG^0_f (elements in their standard states) = 0

$\Delta G^\circ = \Delta G^0_{f,product} - \Delta G^0_{f,reactants}$

For a reaction in progress

$\Delta G = \Delta G^o + RT\, \ell n\, Q$

Q is reaction quotient , ΔG > 0 backward is feasible , ΔG < 0 forward is feasible

At equilibrium ΔG = 0 $\therefore$ Q = K $\therefore$ $\Delta G^o = -RT\, \ell n\, K$ at equilibrium.

Solved Examples

Ex-10. K_a for CH_3COOH at 25ºC is 1.754×10^{-5}. At 50ºC, K_a is 1.633×10^{-5}. What are ΔH^o and ΔS^o for the ionisation of CH_3COOH?

Sol. $(\Delta G^o)_{298} = -2.303RT \log K = -2.303 \times 8.314 \times 298 \times \log (1.754 \times 10^{-5}) = 27194$ J.

$(\Delta G^o)_{323} = 2.303 \times 8.314 \times 323 \times \log (1.633 \times 10^{-5}) = 29605$ J.

$\Delta G^o = \Delta H^o - T\Delta S^o \Rightarrow 27194 = \Delta H^o - 298\,\Delta S^o$

$29605 = \Delta H^o - 323\,\Delta S^o \Rightarrow \Delta H^o = -1.55$ kJ/mol $\Rightarrow \Delta S^o = -96.44$ J/mol.K

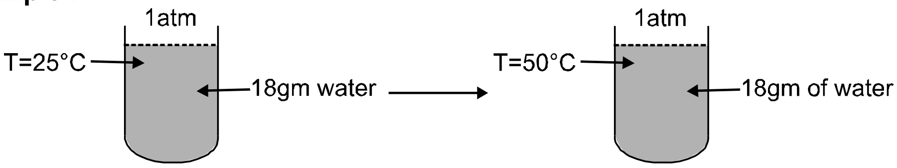
2. THERMOCHEMISTRY

Section (A) : Calculation ΔU, ΔH & W for chemical reaction

Enthalpy of a substance :

- Every substance has a fixed value of enthalpy under any particular state. Though, its exact value cannot be calculated but it has some finite fixed value.
- The enthalpy of one mole of a substance called molar enthalpy in any particular state can be assigned symbol
- H_m(substance) : For example molar enthalpy of water vapours at 398 K and 1 atm pressure may be represented as H_m (H_2O, g, 398 K, 1 atm). In very simple words, enthalpy can be considered as heat constant (amount) of substance, and during reaction this heat is being released or absorbed.
- Molar enthalpy of substance under standard conditions is called standard molar enthalpy of a substance. Standard state of any substance means.
  - For a **GAS** standard state means ideal gas at 1 bar partial pressure at any give temperature.
  - For a **LIQUID** – pure liquid at one bar pressure at 1 bar pressure at any given temperature.
  - For a **PURE CRYSTALLINE SOLID** – pure crystalline solid at 1 bar pressure and at any given temperature
  - For any **SUBSTANCE or ION IN SOLUTION** – the species should be in unit molality (can also be taken as 1M concentration), at one bar pressure and at any given temperature.
- Molar standard enthalpy of water vapours at 398 K will be represented as H°(H_2O, g , 398 K) and molar standard enthalpy of liquid water at 398 K will be represented as $H_m°$ (H_2O, l, 398 K)
  (It is hypothetical but can be calculated).
- We cannot exactly calculate enthalpy content of a substance only the change in enthalpy can be calculated when substance is taken from one state to other.

  For example :



Let enthalpy content initially be $H^0_{m,1}$ & finally enthalpy content be $H^0_{m,2}$

Then, $\Delta H° = H^0_{m,2} - H^0_{m,1}$

= heat added at constant pressure to change temperature from 25°C to 50°C.

= $C_P\Delta T$ = (18 cal/mole °C) (25°C) = 450 cal

Solved Examples

Ex-11. Why does heat get released/absorbed during chemical reactions?

Sol. Because the reactants have a fixed enthalpy content before the reaction and when these are converted into the products which have a different enthalpy content. So, heat gets released or absorbed. Even if temperature of reactions remains constant yet due to change in bonding energies $\Delta E \neq 0$.

If $H_{products} > H_{reactants}$

Reaction should be endothermic as we have to give extra heat to reactants to get these converted into products and

if $H_{products} < H_{reactants}$

Reaction will be exothermic as extra heat content of reactants will be released during the reaction.

Enthalpy change of a reaction : $\boxed{\Delta H_{reaction} = H_{products} - H_{reactants}}$

$$\begin{aligned} \Delta H^\circ_{reactions} &= H^\circ_{products} - H^\circ_{reactants} \\ &= \text{positive} \quad - \quad \text{endothermic} \\ &= \text{negative} \quad - \quad \text{exothermic} \end{aligned}$$

Section (B) : Basics & Kirchoff's law

❍ Hess's Law of constant heat summation :

- The heat absorbed or evolved in a given chemical equation is the same whether the process occurs in one step or several steps.
- The chemical equation can be treated as ordinary algebraic expressions and can be added or subtracted to yield the required equation. The corresponding enthalpies of reactions are also manipulated in the same way so as to give the enthalpy of reaction for the desired chemical equation.
- Since $\Delta_r H$ stands for the change of enthalpy when reactants (substances on the left hand side of the arrow) are converted into products (substances on the right hand side of the arrow) at the same temperature and pressure, if the reaction is reversed (i.e., products are written on the left hand side and reactants on the right hand side), then the numerical value of $\Delta_r H$ remains the same, but **its sign changes.**
- The utility of Hess's law is considerable. In almost all the thermochemical numericals, Hess's law is used.
- One of the important applications of Hess's law is to determine enthalpy of reaction which is difficult to determine experimentally. For example, the value $\Delta_r H$ for the reaction

$$\text{C(graphite)} + \frac{1}{2}O_2\text{(g)} \longrightarrow \text{CO(g)}$$

which is difficult to determine experimentally, can be estimated from the following two reactions for which $\Delta_r H$ can be determined experimentally.

$$\text{C(graphite)} + O_2\text{(g)} \longrightarrow CO_2\text{(g)} \qquad \Delta_r H_1$$

$$\text{CO(g)} + \frac{1}{2}O_2\text{(g)} \longrightarrow CO_2\text{(g)} \qquad \Delta_r H_2$$

Substracting the latter from the former, we get

$$\text{C(graphite)} + \frac{1}{2}O_2\text{(g)} \longrightarrow \text{CO (g)}$$

Consequently, $\Delta_r H = \Delta_r H_1 - \Delta_r H_2$

Solved Examples

Ex-12. Calculate heat of the following reaction at constant pressure,

$$F_2O(g) + H_2O(g) \rightarrow O_2\,(g) + 2HF(g)$$

The heats of formation of F_2O (g), H_2O(g) and HF (g) are 5.5 kcal, –57kcal and –64 kcal respectively.

Sol. Given that

(i) $F_2(g) + \frac{1}{2}O_2(g) \rightarrow F_2O(g);\ \Delta H = 5.5$ kcal

(ii) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g);\ \Delta H = -57$ kcal

(iii) $\frac{1}{2}H_2(g) + \frac{1}{2}F_2(g) \rightarrow HF(g);\ \Delta H = -64$ kcal

F_2O and H_2O in eqns. (i) and (ii) and in the eqn. given in the problem are on the opposite sides, while HF in eqn. (iii) and in the eqn. given in the problem is on the same sides.

Thus applying, [– Eqn. (i) –Eqn. (ii) + 2 × Eqn. (iii)], we get

$$-F_2(g) - \frac{1}{2}O_2(g) - H_2(g) - \frac{1}{2}O_2(g) + H_2 + F_2(g) - F_2O(g) \rightarrow -H_2O(g) + 2HF(g);$$

$$\Delta H = -5.5 - (-57) + 2 \times (-64)$$

or $F_2O(g) + H_2O(g) \rightarrow O_2(g) + 2HF(g);\ \Delta H = -76.5$ kcal.

❍ Relation between energy and enthalpy of a reaction :

$$\mathbf{\Delta_r H = \Delta_r U + (\Delta v_g)RT}$$

where Δv_g is the change in the stoichiocmetric number of gaseous species in going from reactants to products.

It should be noted that while computing Δv_g of a reaction, only the stoichiometric numbers of gaseous is counted and those of liquids and solids are completely ignored.

Kirchoff's equation (Variation of ΔH° with temprature)

Since the enthalpy (or standard enthalpy) of a substance is dependent on state of the substance, value of enthalpy of a substance changes with temperature and hence the enthalpy change of reaction is also dependent on temperaturte at which the reaction is being carried out. This change is enthalpy change (or ΔE of reaction is carried out at constant volume) is represented by **Kirchoff's Equations.**

$$\alpha P + \beta Q \longrightarrow \gamma R + \delta S$$

at temperature T_1 let the standard enthalpy of reaction be $\Delta H°_1$, then

$$\Delta H_1° = \gamma H°_m (R, T_1) + \delta H°_m (S, T_1) – \alpha H°_m (P, T_1) – \beta H°_m (Q, T_1)$$

If the same reaction is carried out at temperature T_2, then

$$\Delta H_2° = \gamma H°_m (R,T_2) + \delta H°_m (S, T_2) – \alpha H°_m (P, T_2) – \beta H°_m (Q, T_2)$$

Then, the change in enthalpy (or difference in enthalpy at these two temperatures)

$$\Delta H° = \Delta H_2° – \Delta H_1° = \gamma \{H_m° (R, T_2) – H_m° (R, T_1)\} + \{H_m° (\delta,T_2) – H_m° (\delta,T_1)\}$$
$$– \alpha \{H_m° (P, T_2) – H_m° (P, T_1)\} - \beta \{H_m° (Q, T_2) – H_m° (Q,T_1)\}$$

$H_m° (R, T_2) – H_m° (R, T_1) = C_{P, R} (T_2 – T_1)$ = Heat required at constant pressure to increase temperature of one mole of R from T_1 to T_2

Similarly

$$H_m°(S, T_2) – H_m° (S, T_1) = C_{P,S}(T_2 – T_1)$$
$$H_m°(P, T_2) – H_m° (P, T_1) = C_{P,P}(T_2 – T_1) \text{ and}$$
$$H_m°(Q, T_2) – H_m° (Q, T_1) = C_{P,Q}(T_2 – T_1)$$

so $\Delta H° = \Delta H_2° – \Delta H_1° = \gamma C_{P,R}(T_2 – T_1) + \delta C_{P,S}(T_2 – T_1) – \alpha C_{P,P}(T_2 – T_1) – \beta C_{P,Q}(T_2 – T_1)$

$$= [\gamma C_{P,R} + \delta C_{P,S} – \alpha C_{P,P} – \beta C_{P,Q}] (T_2 – T_1) = \Delta C_P (T_2 – T_1)$$

$$\Delta C_P = \gamma C_{P, R} + \delta C_{P,S} – \alpha C_{P,P} – \beta C_{P,Q}$$

= Difference in molar heat capacities of products and reactants.

so $\Delta H_2° = \Delta H_1° + \int \Delta C_P.dT$

For example for the reaction

$$N_2 (g) + 3H_2 (g) \longrightarrow 2NH_3 (g)$$

$$\Delta H_2° = \Delta H_1° + \Delta C_P (T_2 – T_1)$$

where $\Delta C_P = 2C_{P,\, NH_3} - C_{P,\, N_2} - 3C_{P,\, H_2}$

* for a constant volume reaction, $\Delta E_2^0 = \Delta E_1^0 + \int \Delta C_V \;.dT$

Section (C) : Enthalpy of formation & combustion

❍ Enthalpy of formation :

It is not possible to determine the absolute value of the molar enthalpy of a substance. However, based on the following convention, the relative values of standard molar enthalpies of formation of various substances can be built.

- "The standard enthalpy of formation of every element in its stable state of aggregation at one bar pressure and at specified temperature is assigned a zero value".The specified temperature is usually taken as 25°C.

  A few exmaples are $\Delta H_f° (O_2, g) = 0$

  $\Delta H_f°$ (C, graphite) = 0 $\Delta H_f°$ (C, diamond) ≠ 0

  $\Delta H_f°$ (Br_2, liquid) = 0

  $\Delta H_f°$ (S, rhombic) = 0 $\Delta H_f°$ (S, monoclinic) ≠ 0

  $\Delta H_f°$ (P, white) = 0 $\Delta H_f°$ (P, black) ≠ 0
- "The standard enthalpy of formation of a compound is the change in the standard enthalpy when one mole of the compound is formed starting from the requisite amounts of elements in their stable state of aggregation".

The chemical equations corresponding to enthalpy of formation of few substances are given below.

Enthalpy of formation of HBr(g) : $\frac{1}{2}H_2(g) + \frac{1}{2}Br_2(\ell) \rightarrow HBr(g)$

$$\Delta H_f°(HBr, g) = H_m^0(HBr, g) - \frac{1}{2}H_m^0(H_2, g) - \frac{1}{2}H_m^0(Br_2, \ell) \qquad ...(1)$$

Enthalpy of formation of $SO_2(g)$: S (rhombic) + $O_2(g) \rightarrow SO_2(g)$

$$\Delta H_f°(SO_2, g) = H_m^0(SO_2, g) - H_m^0(S, \text{rhombic}) - H_m^0(O_2, g) \qquad ...(2)$$

But above equations cannot be for calculation of enthalpy of reaction as the molar enthalpies of different species can not be exactly known.

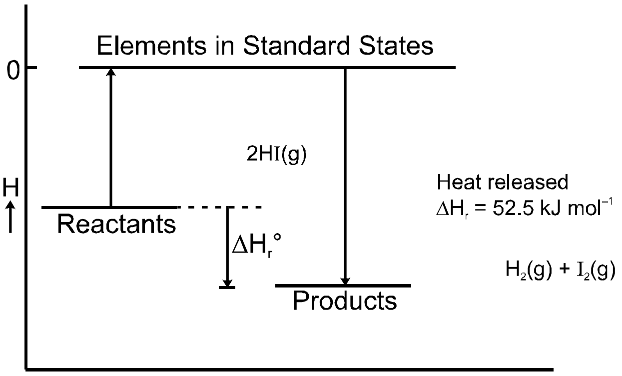
❍ Enthalpy of Reaction from Enthalpies of Formation:

The enthalpy of reaction can be calculated by

$$\Delta H_r° = \Sigma\, \nu_B\, \Delta H_f°{}_{,\text{products}} - \Sigma\, \nu_B\, \Delta H_f°{}_{,\text{reactants}}$$

ν_B is the stoichiometric coefficient

above equation holds good for any reaction as the same reference state is used for reactants and products (shown in figure).



Enthalpy of Reaction

Solved Examples

Ex-13. Calculate the standard enthalpy of reaction $ZnO(s) + CO(g) \longrightarrow Zn(s) + CO_2(g)$.

Given, $\Delta H_f°$ (ZnO, s) = – 350 KJ/mole, $\Delta H_f°$ (CO_2, g) = – 390 KJ/mole, $\Delta H_f°$ (CO, g) = – 110 KJ/mole.

Sol. $\Delta H° = \{\Delta H_f°(CO_2, g) - (\Delta H_f°(ZnO, s) + \Delta H_f°(CO, g))\}$

$\Delta H°_{\text{reaction}} = -390 - (-350 - 110) = 70$ KJ

❍ Enthalpy of Combustion :

- It is the enthalpy change when one mole of a compound combines with the requisite amount of oxygen to give products in their stable forms.

  For example, the standard enthalpy of combustion of methane at 298 K is – 890 kJ mol^{-1}. This implies the following reaction :

  $$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(□) \qquad \Delta H° = -890 \text{ kJ mol}^{-1}$$

  The standard enthalpy of combustion of methane at 298 K may be written as

  $$\Delta H_c°(CH_4, g, 298\text{ K}) = -890 \text{ kJ mol}^{-1}$$

- The data on the enthalpy of combustion can be determined experimentally.
- With the help of such data, we can determine the enthalpy of formation of a compound, which otherwise is difficult or impossible to determine experimentally. Consider for example, the enthalpy of formation of $CH_4(g)$:

  $$C(\text{graphite}) + 2H_2(g) \longrightarrow CH_4(g)$$

  First of all, the combination of carbon and hydrogen does not occur readily. Secondly, if the reaction is even completed, the end product would not be pure methane. Therefore, the enthalpy of formation of methane can be determined indirectly through the enthalpy of combustion of methane :

  $$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(□)$$

  $$\Delta H_C°(CH_4, g) = \Delta H_f°(CO_2, g) + 2\Delta H_f°(H_2O, □) - \Delta H_f°(CH_4, g)$$

  therefore $\Delta H_f°(CH_4, g) = \Delta H_f°(CO_2, g) + 2\Delta H_f°(H_2O, □) - \Delta H_C°(CH_4, g)$

- The enthalpies of formation of CO_2 and H_2O can be determined experimentally by the combustion of carbon (graphite) and hydrogen. Thus, knowing the mesured value of $\Delta H_C°(CH_4, g)$, the enthalpy of formation of CH_4 can be calculated. The value is

  $$\Delta H_f°(CH_4, g) = \Delta H_f°(CO_2, g) + 2\,\Delta H_f°(H_2O, □) - \Delta H_C°(CH_4, g)$$
  $$= [-393 + 2(-285) - (-890)] \text{ kJ mol}^{-1} = -73 \text{ kJ mol}^{-1}$$

or, equivalently, we may add the following three chemical equations.

$$C(graphite) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta_C H° = -393 \text{ kJ mol}^{-1}$$

$$2[H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(\ell)] \qquad \Delta_r H° = 2(-285) \text{ kJ mol}^{-1}$$

$$-[CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(\ell)] \qquad \Delta_r H° = -(-890) \text{ kJ mol}^{-1}$$

$$C(graphite) + 2H_2(g) \longrightarrow CH_4(g) \qquad \Delta_f H° = -73 \text{ kJ mol}^{-1}$$

❍ Measurement of Enthalpy of Combustion :

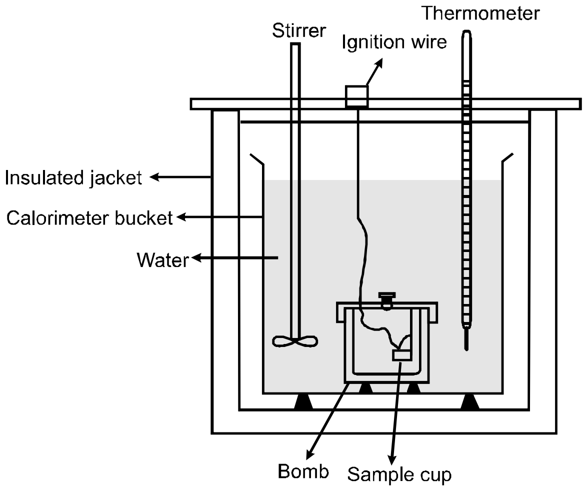
Enthalpy of combustion are usually measured by placing a known mass of the compound in a closed steel container (known as bomb calorimeter) which is filled with oxygen at about 30 bar pressure.

The calorimeter is surrounded by a known mass of water. The entire apparatus is kept in an insulated jacket to prevent heat entering into or leaving from the container, as shown in figure. The sample is ignited electrically to bring about the combustion reaction. The heat evolved is used in raising the temperature of water and the calorimeter.

If total heat capacity of calorimeter and all of its contents = C,

rise in temperature = ΔT

then heat released = $q = C\Delta T$ of this heat is because of mass m of substance then :



Bomb calorimeter to determine enthalpy of combustion

due to 1 mole, heat released = $\left(\frac{M}{m}\right) q = \Delta E_C°$

(Constant volume reaction).

Now, $\Delta H_C°$ can be calculated by using $\Delta H_C° = \Delta E_C° + \Delta n_g RT$.

Where Δn_g is the change in stoichiometric number of gaseous species in the balanced chemical equation representing the combustion process.

Solved Examples

Ex-14. A gas mixture of 4 litres of ethylene and methane on complete combustion at 25ºC produces 6 litres of CO_2. Find out the amount of heat evolved on burning one litre of the gas mixture. The heats of combustion of ethylene and methane are – 1464 and –976 kJ mol^{-1} at 25ºC. **[IIT-1991]**

Sol. $\overbrace{C_2H_4 \quad + \quad CH_4}^{4\ lit.} + O_2 \longrightarrow CO_2 + H_2O$

x lit. (4 – x)lit. 6 lit.
(say)

or x moles (4 – x) moles 6 moles

Applying POAC for C atoms,

$2 \times x + 1 \times (4 - x) = 1 \times 6$; x = 2 lit.

Thus, the volume of C_2H_4 = 2 lit., and volume of CH_2 = 2 lit.

volume of C_2H_4 in a 1 litre mixture = 2/4 = 0.5 lit.

and volume of CH_4 in a 1 litre mixture = 1 –0.5 = 0.5 lit.

Now, thermochemical reactions for C_2H_4 and CH_4 are

$$C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O; \ \Delta H = -1464 \text{ kJ}$$

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O; \ \Delta H = -976 \text{ kJ}$$

As ΔH values given are at 25ºC, let us first calculate the volume occupied by one mole of any gas at 25ºC (supposing pressure as 1atm)

Volume per mole at 25ºC = $\frac{298}{273} \times 22.4 = 24.4$ lit.

Thus, heat evolved in the combustion of 0.5 lit. of $C_2H_4 = -\frac{1464}{24.4} \times 0.5 = -30$ kJ

and heat evolved in the combustion of 0.5 lit.of $CH_4 = \frac{976}{24.4} \times 0.5 = -20$ kJ.

∴ total heat evolved in the combustion of 1 litre of the mixture = –30 + (– 20) = – 50 kJ.

Section (D) : Bond enthalpy method & Resonance energy

❍ Bond Enthalpies :

The **bond enthalpy** is the average of enthalpies required to dissociate the said bond present in different gaseous compounds into free atoms or radicals in the gaseous state. While **bond dissociation enthalpy** is the enthalpy required to dissociate a given bond of some specific compound.for example the enthalpy of dissociation of the O–H bond depends on the nature of molecular species from which the H atom is being separated. For example, in the water molecule.

$H_2O(g) \longrightarrow H(g) + OH(g) \qquad \Delta H_r^o = 501.87 \text{ kJ mol}^{-1}$

However, to break the O–H bond in the hydroxyl radical required a different quantity of heat :

$OH(g) \longrightarrow O(g) + H(g) \qquad \Delta H_r^o = 423.38 \text{ kJ mol}^{-1}$

The bond enthalpy, ΔH_{OH}, is defined as the average of these two values, that is :

$$\Delta H_{OH} = \frac{501.87\text{mol}^{-1} + 423.38\text{kJmol}^{-1}}{2} = 462.625 \text{ kJ mol}^{-1}$$

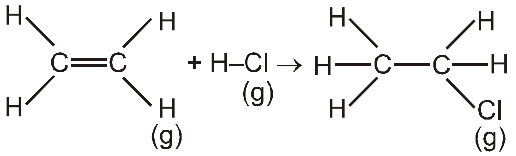
In the case of diatomic molecules, such as H_2, the bond enthalpy and bond dissociation enthalpy are identical because each refers to the reaction.

$H_2(g) \longrightarrow 2H(g) \qquad \Delta H_{H-H} = \Delta H_r^0 = 435.93 \text{ kJ mol}^{-1}$

Thus, the bond enthalpy given for any particular pair of atoms is the average value of the dissociation enthaplies of the bond for a number of molecules in which the pair of atoms appears.

❍ Estimation of Enthalpy of a reaction from bond Enthalpies :

Let the enthalpy change for the gaseous reaction



be required from the bond enthalpy data. This may be calculated as follows :

$$\Delta H = \begin{pmatrix}\text{Enthalpy required to break reactants} \\ \text{into gasesous atoms}\end{pmatrix} - \begin{pmatrix}\text{Enthalpy released to form products} \\ \text{from the gasesous atoms}\end{pmatrix}$$

$= [4\Delta H_{C-H} + \Delta H_{C=C} + \Delta H_{H-Cl}]_R + [-5\Delta H_{C-H} - \Delta H_{C-C} - \Delta H_{C-Cl}]_P$

$= (\Delta H_{C=C} + \Delta H_{H-Cl}) - (\Delta H_{C-H} + \Delta H_{C-C} + \Delta H_{C-Cl})$

Enthalpy of Transition :

Enthalpy of transition is the enthalpy change when one mole of one allotropic form changes to another.

For example :	C(graphite) → C(diamond)	$\Delta H_{trs}^o = 1.90 \text{ kJ mol}^{-1}$
so if	$C(graphite) + O_2(g) \rightarrow CO_2(g)$	$\Delta H_C^o = -393.51 \text{ kJ mol}^{-1}$
and	$C(diamond) + O_2(g) \rightarrow CO_2(g)$	$\Delta H_C^o = -395.41 \text{ kJ mol}^{-1}$
Subtracting, we have,	C(graphite) → C(diamond)	$\Delta H_{trs}^o = 1.90 \text{ kJ mol}^{-1}$

Solved Examples

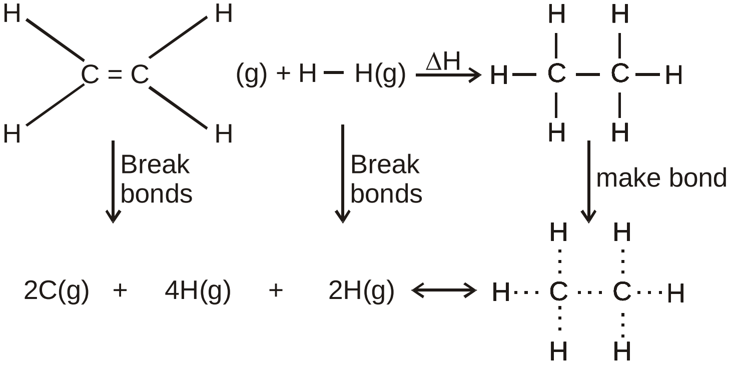
Ex-15. Using the bond enthalpy data given below, calculate the enthalpy change for the reaction

$C_2H_4(g) + H_2(g) \longrightarrow C_2H_6(g)$

Data :

Bond	Bond enthalpy
C – C	336 kJ mol^{-1}
C = C	606 kJ mol^{-1}
C – H	410 kJ mol^{-1}
H – H	431 kJ mol^{-1}

Sol. Diagrammatically, we represent the given reaction as follows :

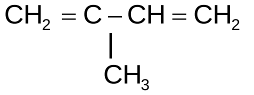


$\Delta H_r = (4\Delta H_{C-H} + \Delta H_{C=C} + \Delta H_{H-H}) - (6\Delta H_{C-H} + \Delta H_{C-C})$

$= (4 \times 410 + 606 + 431) - (6\times 410 + 336)$

$= 2677 - 2796 = - 119$ kJ/mol.

Ex-16. Using the bond enthalpy data given below, estimate the enthalpy of formation of gaseous isoprene



$CH_2 = C(CH_3) - CH = CH_2$

Data: Bond enthalpy of C – H bond = 413.38 kJ mol^{-1}
Bond enthalpy of C – C bond = 347.69 kJ mol^{-1}
Bond enthalpy of C = C bond = 615.05 kJ mol^{-1}
Enthalpy of sublimation of carbon (graphite) = 718.39 kJ mol^{-1}
Enthalpy of dissociation of $H_2(g)$ = 435.97 kJ mol^{-1}

Sol. For isoprene, we have to form

2C – C bonds ; 2C = C bonds and 8C – H bonds

Method-1 For which energy released is

$[2(+347.69) + 2(+615.05) + 8(+413.38)]$ kJ mol^{-1} = 5 232.52 kJ mol^{-1}

that is, ΔH (from gaseous atoms) = + 5232.52 kJ mol^{-1}

The reaction corresponding to this is

$5C(g) + 8H(g) \longrightarrow C_5H_8(g)$ $\quad \Delta_f H_1 = - 5232.52$ kJ mol^{-1}

But we want $\Delta_f H$ corresponding to the following equation

$5C(graphite) + 4H_2(g) \longrightarrow C_5H_8(g)$ $\quad \Delta_f H = ?$

This can be obtained by the following manipulations :

$5C(g) + 8H(g) \longrightarrow C_5H_8(g)$ $\quad \Delta_r H_2 = - 5232.52$ kJ mol^{-1}

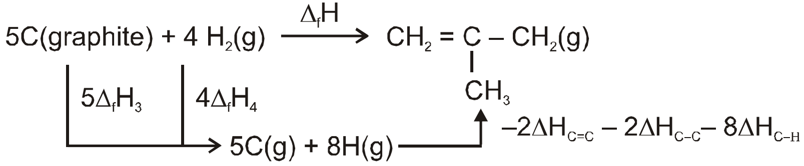
$5C(graphite) \longrightarrow 5C(g)$ $\quad \Delta_r H_3 = 5 \times 718.39$ kJ mol^{-1}

$4H_2(g) \rightarrow 8H(g)$ $\quad \Delta_r H_4 = 4 \times 435.97$ kJ mol^{-1}

Adding, we get

$5C(graphite) + 4H_2(g) \longrightarrow C_5H_8(g)$ $\quad \Delta_f H = 103.31$ kJ mol^{-1}

Method-2 Diagrammatically, the above calculations may be represented as follows.



Applying Hess's law, we get

$\Delta_f H \quad = 5\Delta H_3 + 4\Delta H_4 - 2\Delta H_{C=C} - 2\Delta H_{C-C} - 8\Delta H_{C-H}$

$= (5 \times 718.39 + 4 \times 435.97 - 2 \times 615.05 - 2 \times 347.69 - 8 \times 413.38)$ kJ mol^{-1}

$\Delta_f H$ = 103.31 kJ mol^{-1}

Ex-17. Find the bond enthalpy of S – S bond from the following data :

$C_2H_5 - S - C_2H_5(g)$ $\Delta_f H° = -147$ kJ mol^{-1}
$C_2H_5 - S - S - C_2H_5(g)$ $\Delta_f H° = -201$ kJ mol^{-1}
$S(g)$ $\Delta_f H° = 222$ kJ mol^{-1}

Sol. Given that

Method-1 (i) $4C(s) + 5H_2(g) + S(s) \longrightarrow C_2H_5 - S - C_2H_5(g)$ $\Delta_f H° = -147$ kJ mol^{-1}
(ii) $4C(s) + 5H_2(g) + 2S(s) \longrightarrow C_2H_5 - S - S - C_2H_5(g)$ $\Delta_f H° = -201$ kJ mol^{-1}

Subtracting Eq. (i) from Eq. (ii), we get

$C_2H_5 - S - C_2H_5(g) + S(s) \longrightarrow C_2H_5 - S - S - C_2H_5(g)$ $\Delta_r H° = -54$ kJ mol^{-1}

Adding to this, the following equation

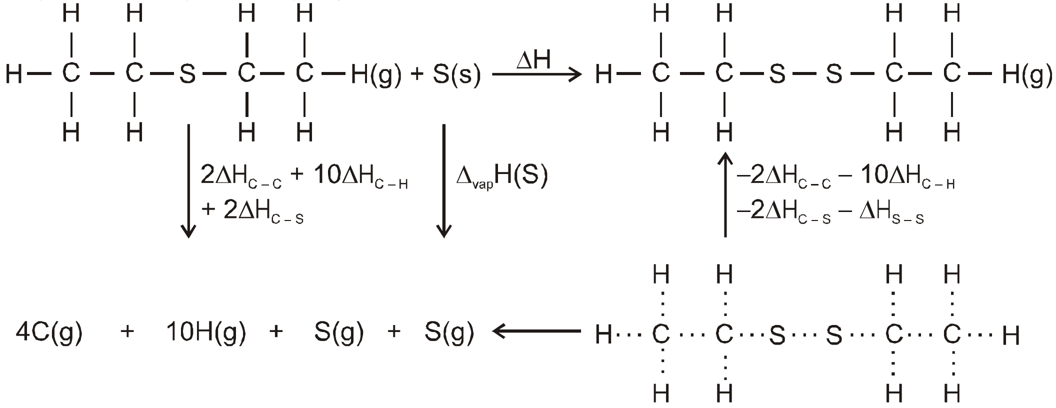
$S(g) \longrightarrow S(s)$ $\Delta_f H° = -222$ kJ mol^{-1}

We get

$C_2H_5 - S - C_2H_5(g) + S(g) \longrightarrow C_2H_5 - S - S - C_2H_5(g)$ $\Delta_r H° = -276$ kJ mol^{-1}

In the last equation 276 kJ of heat evolved because of the S–S bond formation.
Hence, the bond enthalpy of S – S is 276 kJ mol^{-1}.

Method-2 Diagrammatically, we may represent the above calculation as follows :



According to Hess's law :

$\Delta_r H°$ = Enthalpy involved in bond breaking $\Delta_{vap}H^o(s)$ – Enthalpy involved in bond making

$\Delta_r H° = [2\Delta H_{C-C} + 10\Delta H_{C-H} + 2\Delta H_{C-S} + \Delta_{vap}H(S)] + [-2\Delta H_{C-C} - 10\Delta H_{C-H} - 2\Delta H_{C-S} - \Delta H_{S-S}]$
$= \Delta_{vap}H°(S) - \Delta H_{S-S}$

or $\Delta H_{S-S} = \Delta_{vap}H°(S) - \Delta H°$
$= \Delta_{vap}H°(S) - [\Delta_f H°(C_2H_5 - S - S - C_2H_5] - \Delta_f H°(C_2H_5 - S - C_2H_5)]$
$= [222 - \{-201 - (-174)\}]$ kJ mol^{-1} = 276 kJ mol^{-1}

❍ Resonance energy :

Difference between energy of resonance hybrid and resonating structure in which resonance hybrid have lower energy because stabilised by resonance.

$\Delta H°_{\text{resonance}} = \Delta H°_{\text{f, experimental}} - \Delta H°_{\text{f, calclulated}}$
$= \Delta H°_{\text{combustion, calclulated}} - \Delta H°_{\text{combustion, experimental}}$

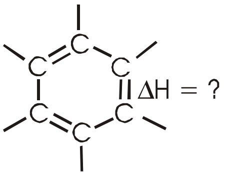
Solved Examples

Ex-18. Calculate the heat of formation of benzene from the following data, assuming no resonance. Bond energies :

C – C = 83 kcal, C = C = 140 kcal, C – H = 99 kcal
Heat of atomisation of C = 170 .9 kcal
Heat of atomisation of H = 52.1 kcal

Sol. We have to calculate ΔH for the reaction

$6C(s) + 3H_2(g) \longrightarrow C_6H_6(g)$



For reactants :

Heat of atomisation of 6 moles of C = 6 × 170.9 kcal
Heat of atomisation of 6 moles of H = 6 × 52.1 kcal

For products :

Heat of formation of 6 moles of C – H bonds = – 6 × 99

Heat of formation of 3 moles of C–C = – 3 × 83

Heat of formation of 3 moles of C$=$C bonds = –3 × 140

on adding, we get heat of formation of C_6H_6,i.e.,

$\Delta_f H = 6 \times 170.9 + 6 \times 52.1 - 6 \times 99 - 3 \times 83 - 3 \times 140 = -75$ kcal

---

Section (E) : Enthalpy of solution & Born Haber's cycle

❍ Integral enthalpy of solution

The integral enthalpy of solution at the given concentration is the enthalpy change when one mole of the solute is dissolved in a definite quantity of solvent to produce a solution of a desired concentration. While recording integral enthalpies of solution it is a general practice to state the amount of the solvent in which 1 mole of solute is dissolved ; Thus

$$HCl(g) + 10H_2O(\ell) \longrightarrow HCl\ (10H_2O) \qquad \Delta H_1 = -69.5 \text{ kJ mol}^{-1}$$

indicates that when 1 mole of hydrogen chloride gas is dissolved in 10 mol of water, there is an evolution of 69.5 kJ of heat. Other values are

(i) $HCl(g) + 25\ H_2O(\ell) \longrightarrow HCl\ (25H_2O)$ $\Delta H_2 = -72.3 \text{ kJ mol}^{-1}$

(ii) $HCl(g) + 40\ H_2O(\ell) \longrightarrow HCl\ (40H_2O)$ $\Delta H_3 = -73.0 \text{ kJ mol}^{-1}$

(iii) $HCl(g) + 200\ H_2O(\ell) \longrightarrow HCl\ (200H_2O)$ $\Delta H_4 = -74.2 \text{ kJ mol}^{-1}$

(iv) $HCl(g) + aq \longrightarrow HCl\ (aq)$ $\Delta H_5 = -75.0 \text{ kJ mol}^{-1}$

Whenever amount of solvent is not specified then take its amount to be very large just like in equation no. (iv).

❍ Enthalpy of Hydration :

Enthalpy of hydration is used in following two ways.

- Enthalpy of hydration of anhydrous or partially hydrated salts :

Enthalpy of hydration of a given anhydrous or partially hydrated salt is the enthalpy change when it combines with the requisite amount of water to form a new hydrated stable salt.

For example, the hydration of anhydrous cupric sulphate is represented by

$$CuSO_4(s) + 5H_2O(\ell) \longrightarrow CuSO_4.5\ H_2O(s)$$

There is a almost invariably a liberation of heat in such reactions, i.e. the value of ∆H is negative.

$$CuSO_4(s) + 800\ H_2O(\ell) \longrightarrow CuSO_4\ (800\ H_2O) \qquad \Delta H_r^\circ = -68 \text{ kJ mol}^{-1}$$

$$CuSO_4.5H_2O(s) + 795\ H_2O(\ell) \longrightarrow CuSO_4\ (800\ H_2O) \qquad \Delta H_r^\circ = +10 \text{ kJ mol}^{-1}$$

by subtraction, we get

$$CuSO_4(s) + 5H_2O(\ell) \longrightarrow CuSO_4.5\ H_2O(s) \qquad \Delta H_r^\circ = -78 \text{ kJ mol}^{-1}$$

- Enthalpy of hydration of gaseous ions.

Enthalpy of hydration of any gaseous ion is the enthalpy change when 1 mole of the gaseous ion is hydrated in large amount of water to form aqeous ion.

By convention, the standard enthalpy of formation of $H^+(aq)$ is taken to be zero.

Enthalpy of hydration of Cl^- gaseous ions will be represented by :

$$Cl^-(g) + aq. \longrightarrow Cl^-(aq) \qquad \Delta H_r^\circ = \Delta H_f^\circ\ (Cl^-, aq)$$

Section (F) : Enthalpy of neutralization

- The amount of heat released when one gram equivalent of an acid is neutralised by one gram equivalent of a base.

or

- The amount of heat released in formation of one mole of water when an acid is neutralised by a base.

or

- Enthalpy of neutralization is defined as the enthalpy change when one mole of H^+ in dilute solution combines with one mole of OH^- to give rise to undissociated water, i.e.

$H^+(aq) + OH^-(aq) \longrightarrow H_2O(\ell)$ $\Delta H = -57.1$ kJ/mole $= -13.7$ kcal/mol

Remember :

- For **Strong Acid + Strong Base**, heat of neutralisation is always equal to –13.7 kcal/mole or –57.1 kJ/mole.
- For any other combination of **acid and base** this heat is less than –13.7 kcal/mole or –57.1 kJ/mole.

❍ Enthalpy of Ionization of Weak Electrolyte :

- Whenever a weak acid (or base) reacts with a strong base (or acid), the release of heat is less than 57.1 kJ mol^{-1}.
- It is because of the fact that these acids or bases are not completely ionized in solution. Some of the heat is consumed in ionizing there acids and bases this heat is known as enthalpy of ionization. Examples are :

$HCN + Na^+OH^- \longrightarrow Na^+ + CN^- + H_2O$ $\Delta_rH° = -12$ kJ mol^{-1}

$CH_3COOH + Na^+OH^- \longrightarrow Na^+ + CH_3COO^- + H_2O$ $\Delta_rH° = -49$ kJ mol^{-1}

The enthalpy of ionization can be calculated as follows. The neutralization of a weak acid, say HCN, may be represented in two steps, namely,

Ionization $HCN \longrightarrow H^+ + CN^-$ $\Delta H°_1 = x$

Neutralization $H^+ + OH^- \longrightarrow H_2O$ $\Delta H°_2 = -57.1$ kJ/mole

The complete reaction is obtained by adding the above two steps. Thus

$HCN + OH^- \longrightarrow H_2O + CN^-$ $\Delta H° = -12$ kJ/mole

Obviously, $\Delta H° = \Delta H°_1 + \Delta H°_2$

$\Delta H°_1 = \Delta H° - \Delta H°_2 = [-12 - (-57.1)] = 45.1$ kJ/mole

- **Greater the enthalpy of ionization of any weak acid or weak base, weaker will be the acid or base.**

Solved Examples

Ex-19. Enthalpy of neutralization of HCl by NaOH is –57.1 kJ/mol and by NH_4OH is –51.1 kJ/mol. Calculate the enthalpy of dissociation of NH_4OH.

Sol. Given that, $H^+(aq) + NH_4OH(aq) \longrightarrow NH_4^+(aq) + H_2O(\ell)$ $\Delta H = -51.1$ kJ/mole

We may consider neutralization in two steps.

(i) Ionization $NH_4OH(aq) \longrightarrow NH_4^+(aq) + OH^-(aq)$ $\Delta H_1 = ?$

(ii) Neutralization $H^+(aq) + OH^-(aq) \longrightarrow H_2O(\ell)$ $\Delta H_2 = -57.1$ kJ/mole

Thus, $\Delta H = \Delta H_1 + \Delta H_2$

Therefore, $\Delta H_1 = \Delta H - \Delta H_2 = -51.1$ kJ/mol $+ 57.1$ kJ $mol^{-1} = 6.0$ kJ/mol

---

Enthalpy of Precipitation :

Enthalpy of precipitation is the enthalpy change when one mole of a precipitate is formed.

For example : $BaCl_2(aq.) + Na_2SO_4(aq) \rightarrow BaSO_4(s) + 2NaCl(aq)$ $\Delta_rH^0 = -24.27$ kJ mol^{-1}

Solved Examples

Ex-20. Calculate $\Delta H°$ for the reaction, $Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$ at 25°C.

Given $\Delta_fH°(Ag^+, aq) = 105$ kJ mol^{-1}, $\Delta_fH°(Cl^-, aq) = -167$ kJ mol^{-1} and $\Delta_fH°(AgCl, s) = -127$ kJ mol^{-1}

Sol. For the reaction $Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$

We have $\Delta H° = \Delta_fH°(AgCl, s) - \Delta_fH°(Ag^+, aq) - \Delta_fH°(Cl^-, aq)$

$= [-127 - 105 - (-167)]$ kJ $mol^{-1} = -65$ kJ mol^{-1}

❍ Enthalpy of Formation of ions :

The enthalpy change when one mole of hydrated ions is obtained from element in its standard state as.

$\frac{1}{2} Cl_2 (g) + aq \longrightarrow Cl^- (aq)$ $\Delta H_r° = \Delta H_f° (Cl^-, aq)$

By convention, the standard enthlpy of formation of $H^+(aq)$ is taken to be zero.

We have seen that $H^+ (aq) + OH^-(aq) \longrightarrow H_2O(l)$ $\Delta_r H^o = -57.1$ kJ mol^{-1}

For this reaction, $\Delta H_r^o = \Delta H_f^o(H_2O,l) - \{\Delta H_f^o(H^+, aq) + \Delta H_f^o(OH^-,aq)\}$

Hence, at 25ºC, we get $\Delta H_f^o(H^+, aq) + \Delta H_f^o(OH^-, aq) = \Delta H_f^o(H_2O, l) - \Delta H_r^0$

so $\Delta H_f^o(OH^- ,aq) = \{-286.1 - (-57.1)\}$ kJ $mol^{-1} = -229.00$ kJ mol^{-1}

- With the enthalpies of formation of these two ions, the enthalpy of formation of any other ion can be found from the enthalpies of formation and solution of its pure compound with H^+ or OH^-. For example, the enthalpy of formation of Na^+ can be calculated from the enthalpy of formation and enthalpy of infinite dilute solution of NaOH. The two values are :
- The chemical equation for the formation of infinite dilute solution of NaOH(s) is

$NaOH(s) + nH_2O(\square) \longrightarrow Na^+(aq) + OH^-(aq)$ $\Delta_{aq}H°(NaOH, s) = -44.50$ kJ mol^{-1}

Since there are equal amounts of water on both sides of the above equation, the two enthalpies give no net effect and thus

$\Delta_{aq}H°(NaOH, s) = \Delta_f H°(Na^+, aq) + \Delta_f H°(OH^-, aq) - \Delta_f H°(NaOH, s)$

or $\Delta_f H° (Na+, aq) = \Delta_{aq}H° (NaOH, s) - \Delta_f H°(OH°, aq) + \Delta_f H°(NaOH, s)$

$= [-44.50 - (-229.99) + (-425.61)]$ kJ $mol^{-1} = -240.12$ kJ mol^{-1}

- Similarly, from NaCl(aq) or HCl(aq), the enthalpy of formation of $Cl^-(aq)$ can be determined, and so on. The changes in enthalpy of any ionic reaction can then be found from these ionic enthalpies of formation and the usual enthalpies of formation of compounds.

Solved Examples

Ex-21. The enthalpy of formation of $H_2O(l)$ is –285 kJ mol^{-1} and enthalpy of neutralization of a strong acid and a strong base is –55 kJ mol^{-1}. What is the enthalpy of formation of OH^- ions ?

Sol. Given that, $H^+(aq) + OH^-(aq) \longrightarrow H_2O(\square)$

$\Delta_f H$ 0 –285 kJ mol^{-1}

$\Delta_{neut}H = \Delta_f H(H_2O, \square) - \Delta_f H(OH^-, aq)$

Hence $\Delta_f H (OH^-, aq) = \Delta_f H(H_2O, \square) - \Delta_{neut}H$

$= [-285 - (-55)]$ kJ $mol^{-1} = -230$ kJ mol^{-1}

Ex-22. Calculate the enthalpy change when one mole of HCl(g) is dissolved in a very large amount of water at 25°C. The change in state is : $HCl(g) + aq \longrightarrow H^+(aq) + Cl^-(aq)$

Given : $\Delta_f H (HCl, g) = -92$ kJ mol^{-1} and $\Delta_f H° (Cl^-, aq) = -167$ kJ mol^{-1}

Sol. For the reaction, $HCl(g) + aq \longrightarrow H^+(aq) + Cl^-(aq)$

We have $\Delta H° = \Delta_f H°(Cl^-,aq) - \Delta_f H°(HCl, g)$

$\Delta H° = [-167 - (-92)]$ kJ $mol^{-1} = -75$ kJ mol^{-1}

MISCELLANEOUS SOLVED EXAMPLES

1. Find (in terms of *"a"*) the amount of energy required to raise the temperature of a substance from 3 K to 5 K. At low temperatures. $C_P = aT^3$.

Sol. $q = \int nC_p \cdot dT = \int naT^3 \cdot dT$

$$= na\left[\frac{T^4}{4}\right]_3^5 = \frac{na}{4}[(5)^4 - (3)^4]$$

$$= \frac{na[625-81]}{4} = 136 \text{ na.}$$

Ans. q = 136 na.

2. A thermally isolated vessel contains 100 g of water at 0°C. When air above the water is pumped out, some of the water freezes and some evaporates at 0°C itself. Calculate the mass of the ice formed such that no water is left in the vessel. Latent heat of vaporization of water at 0°C = 2.10×10^6 J/kg and latent heat of fusion of ice = 3.36×10^5 J/kg.

Sol. Total mass of the water = M = 100 g

Latent heat of vaporization of water at 0°C

$= L_1 = 21.0 \times 10^5$ J/Kg

& Latent heat of fusion of ice $= L_2 = 3.36 \times 10^5$ J/Kg

Suppose, the mass of the ice formed = m

Then, the mass of water evaporated = M – m.

Heat lost by the water in freezing = Heat taken by water in evaporation.

Thus, $mL_2 = (M - m) L_1$ or m = 86 g. **Ans.** 86.2 g

3. Work done in expansion of an ideal gas from 4 litre to 6 litre against a constant external pressure of 2.1 atm was used to heat up 1 mole of water at 293 K. If specific heat of water is 4.2 J g^{-1} K^{-1}, what is the final temperature of water ?

Sol. $W = -2.1 [6 - 4] = -2.1 \times 2$

$= -4.2$ atm × lit.

$= -4.2 \times 101.325$ J

This work is used to heat up the water

Specific heat of $H_2O = 4.2 \dfrac{J}{\text{gram} \cdot K.}$

Heat required for increasing temperature by 1°C of 1 mole = 4.2 × 18 = 75.6 J

$4.2 \times 101.325 = 75.6 [T - 293]$

$5.63 = T - 293$

T = 298.63 K **Ans.** 298.63 K

4. 1 mole of ice at 0°C and 4.6 mm Hg pressure is converted to water vapour at a constant temperature and pressure. Find ΔH and ΔE if the latent heat of fusion of ice is 80 cal/g and latent heat of vaporisation of liquid water at 0°C is 596 cal/g and the volume of ice in comparison to that of water (vapour) is neglected.

Sol. No. of mole = 1 mole

T = 273 K.

Pv = nRT.

$$\frac{4.6}{760} v = 1 \times 0.0821 \times 273$$

v = 3699 lit ≈ [3700 lit]

latent heat of fusion = 80 cal/gram Latent heat of vaporisation = 596 cal/gram

$\Delta H = 80 \times 18 + 596 \times 18 = [80 + 596] \times 18$

$\Delta H = 12168$ cal

$\Delta H = \Delta E + P [V_2 - V_1]$

$$12168 = \Delta E + \frac{4.6}{760} [3699] \times 24.24$$

$$\Rightarrow \quad \Delta E = 12168 - \frac{4.6}{760} \times 3699 \times 24.24$$

$= 12168 - 542.72 = 11625.28$ cal. **Ans.** 12168 cal, 11625.28 cal

5. For Ag, $\bar{C}_P$ (JK^{-1} mol^{-1}) is given by 24 + 0.006 T. Calculate ΔH if 3 mol of silver are raised from 27°C to its melting point 927°C under 1 atm pressure.

Sol. $$\Delta H = \int_{T_1}^{T_2} nC_p dT = \int_{T_1}^{T_2} 3(24 + .006T)dT = 3 [24 (T_2 - T_1) + \frac{1}{2} \times 0.006 (T_2^2 - T_1^2)]$$

$= 3 \times 25650 = 76950$ J **Ans.** 76950 J

6. Calculate the amount of heat evolved during the complete combustion of 100 ml of liquid benzene from the following data.

(i) 18 g of graphite on complete combustion evolve 590 KJ heat

(ii) 15889 KJ heat is required to dissociate all the molecules of 1 litre water into H_2 and O_2.

(iii) The heat of formation of liquid benzene is 50 kJ/mol

(iv) Density of C_6H_6 (□) = 0.87 g/m□

Sol. (i) $C(s) + O_2(g) \longrightarrow CO_2(g)$; $\Delta H_f^{\circ} = -393.33$ KJ/mol

(ii) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O$ (□) ; $\Delta H_f^{\circ} = -286$ KJ/mol

(iii) C_6H_6(□) + $\frac{15}{2}O_2(g) \longrightarrow 6CO_2\,(g) + 3H_2O$ (□)

∴ $\Delta H^{o} = [6(-393.33) + 3\,(-286)] - 50 = -3268$ KJ/mole

∴ **Heat evolved from 87 g benzene = 3645 KJ** **Ans.** 3645 KJ

7. For the equations

$C(\text{diamond}) + 2H_2(g) \longrightarrow CH_4(g)$ ΔH_1

$C(g) + 4H(g) \longrightarrow CH_4(g)$ ΔH_2

Predict whether

(A) $\Delta H_1 = \Delta H_2$

(B) $\Delta H_1 > \Delta H_2$

(C) $\Delta H_1 < \Delta H_2$

(D) $\Delta H_1 = \Delta H_2 + \Delta_{vap}H(C) + \Delta_{diss}H(H_2)$

Ans. (B)

8. The standard molar enthalpies of formation of cyclohexane (l) and benzene (l) at 25ºC are – 156 and + 49 KJ mol^{-1} respectively. The standard enthalpy of hydrogenation of cyclohexene (l) at 25º is –119 kJ mol^{-1}. Use these data to estimate the magnitude of the resonance energy of benzene.

Sol. Enthalpy of formation of 3 carbon-carbon double bonds

= ΔH_F()– $\Delta\ H_f$ ()

= –156 – (+ 49) kJ = –205 kJ.

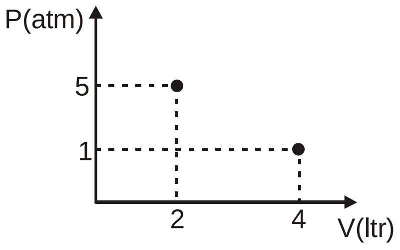
Given that, + $H_2 \longrightarrow$ ΔH = 119 kJ

Theoretical enthalpy of formation of 3 double bonds in benzene ring

= 3 × (–119) kJ = – 357 kJ.

∴ resonance energy of benzene = – 357 – (–205) kJ = –152 kJ $mole^{-1}$ **Ans.** –152 kJ $mole^{-1}$

9. Following graph shows a single stange expansion process, then workdone by the system is



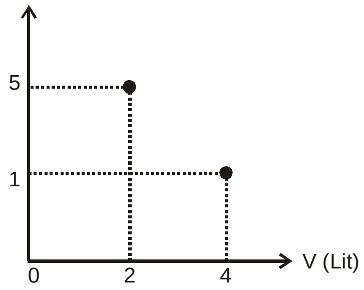
(A) – 9104 J

(B) – 202.6 J

(C) – 506 J

(D) – 101.3 J

Sol.

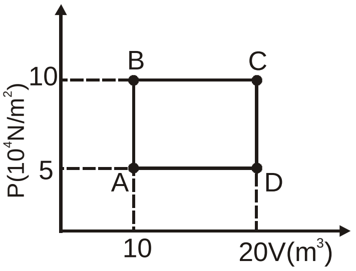


Ans. (B)

$W = -P_{ext}(V_2 - V_1) = -1 \times 2 \times 101.325\ J = -202.6\ J$

10. A sample of 2 kg of helium (assumed ideal) is taken through the process ABC and another sample of 2 kg of the same gas is taken through the process ADC. Then the temperature of the states A and B are (Given R = 8.3 joules/mol K) :

(A) $T_A = 120.5$ K, $T_B = 120.5$ K
(B) $T_A = 241$ K, $T_B = 241$ K
(C) $T_A = 120.5$ K, $T_B = 241$ K
(D) $T_A = 241$ K, $T_B = 482$ K



Sol. $\frac{0.5\times10^5}{1.01\times10^5} \times 10 \times 10^3 = \frac{2\times1000}{2} \times 0.082\ T_A$

$\frac{1}{1.01} = 0.082\ T_A$

$T_A = 120.5$ K

at constant volume

$$\frac{P_A}{T_A} = \frac{P_B}{T_B}$$

$T_B = \frac{P_B.T_A}{P_A} = \frac{10}{5} \times 120.5 = 241$ K. **Ans. (C)**

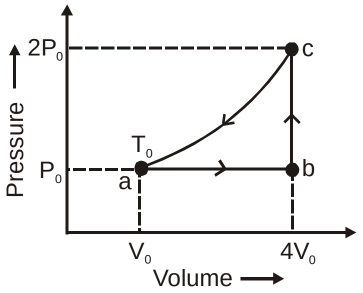
11. In an isothermal expansion of a gaseous sample the correct relation is (consider w (work) with sign according to new IUPAC convention)
[The reversible and irreversible processes are carried out between same initial and final states.]

(A) $w_{rev} > w_{irrev}$ (B) $w_{irrev} > w_{rev}$ (C) $q_{rev} < q_{irrev}$ (D) can not be predicted

Ans. (B)

12. One mole of an ideal monoatomic gas is caused to go through the cycle shown in figure. Then, the change in the internal energy in expanding the gas from a to c along the path abc is :

(A) $3\ P_0V_0$ (B) $6\ RT_0$
(C) $4.5\ RT_0$ (D) $10.5\ RT_0$



Sol. Pv = nRT at point C

$2P_0 \times 4v_0 = 1 \times RT_C$

$T_C = \left[\frac{8P_0V_0}{R}\right]$

at point a

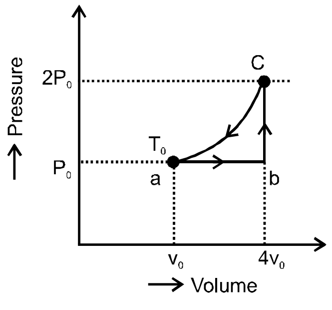
$P_0V_0 = 1 \times RT_0$

$T_0 = \frac{P_0V_0}{R}$; $T_C = 8\ T_0$

Change in internal energy = $[nC_VdT]$

For path a to b = $1 \times \frac{3}{2} R \times [3T_0] = \frac{9}{2} RT_0$

For path b to c = $1 \times \frac{3}{2} R \times [4T_0] = 6T_0\ R$



Total change = $\frac{9}{2} RT_0 + 6RT_0 = \frac{21\ RT_0}{2} = 10.5\ RT_0$.

So total change in internal energy

$\Delta U = 10.5\ RT_0$ **Ans. (D)**

13. A certain mass of gas is expanded from (1L, 10 atm) to (4L, 5 atm) against a constant external pressure of 1 atm. If initial temperature of gas is 300 K and the heat capacity of process is 50 J/°C. Then the enthalpy change during the process is (1L atm $\simeq$ 100 J)

(A) $\Delta H = 15$ kJ (B) $\Delta H = 15.7$ kJ (C) $\Delta H = 14.4$ kJ (D) $\Delta H = 14.7$ kJ

Sol. $\Delta H = \Delta E + \Delta(PV)$ & $\Delta E = q + W = (50 \times 300 - 3 \times 100)$ J [as $T_f = 2 \times 300$ K = 600 K] = 14.7 kJ

$\Delta H = 14700 + 10 \times 100 = 15700$ J = 15.7 kJ. **Ans (B)**

14. One mole of an ideal monoatomic gas expands isothermally against constant external pressure of 1 atm from initial volume of 1L to a state where its final pressure becomes equal to external pressure. If initial temperature of gas is 300 K then total entropy change of system in the above process is :
[$R = 0.082$ L atm mol^{-1} K^{-1} = 8.3 J $mol^{-1}K^{-1}$].

(A) 0 (B) $R\ell n$ (24.6) (C) $R\ \ell n$ (2490) (D) 3/2 $R\ell n$ (24.6)

Sol. $\Delta S = nR\ \ell n\left(\frac{V_f}{V_i}\right) = R\ell n\left(\frac{P_i}{P_f}\right) = R\ \ell n\left(\frac{300R}{1\,L \times 1\,atm}\right) = R\ell n\ (24.6)$ **Ans. (B)**

15. For a perfectly crystalline solid $C_{p.m.} = aT^3$, where a is constant. If $C_{p.m.}$ is 0.42 J/K–mol at 10 K, molar entropy at 10 K is :

(A) 0.42 J/K-mol (B) 0.14 J/K-mol (C) 4.2 J/K-mol (D) zero

Sol. $0.42 = a(10)^3 \Rightarrow a = 0.42 \times 10^{-3}$

$S_m = \int_0^{10} \frac{C_{p.m.}}{T} dT = \int_0^{10} aT^2 = \frac{a}{3}[10^3 - 0] = \frac{0.42}{3} = 0.14\ \ J/K - mol$ **Ans. (B)**

16. Given the following data :

Substance	ΔH° (kJ/mol)	S°(J/mol K)	ΔG° (kJ/mol)
FeO(s)	– 266.3	57.49	– 245.12
C (Graphite)	0	5.74	0
Fe(s)	0	27.28	0
CO(g)	– 110.5	197.6	– 137.15

Determine at what temperature the following reaction is spontaneous ?

$FeO(s) + C(Graphite) \longrightarrow Fe(s) + CO(g)$

(A) 298 K (B) 668 K (C) 966 K

(D) ΔG° is +ve, hence the reaction will never be spontaneous

Sol. $FeO(s) + C(graphite) \longrightarrow Fe(s) + CO(g)$

(1) $\Delta H = 0 + [-110.5] - (-266.3)$
$= -110.5 + 266.3$
$= +155.8$ kJ/mole

(2) $\Delta S = 27.28 + 197.6 - 57.49 - 5.74 = 161.65$ J/mole

(3) $\Delta G = \Delta H - T\Delta S = 0 = 155.8 - T \times 161.65 \times 10^{-3}$
$T \times 161.65 \times 10^{-3} = 155.8 \Rightarrow T = 963.8$ K **Ans. (C)**

17. If ΔH_f^o for Ag^+ (infinitely diluted), NO_3^- (infinitely diluted), Cl^- (infinitely diluted) and AgCl(s) are 105.579, –207.36, –167.159 and –127.068 respectively. Calculate the enthalpy change for the reaction

$AgNO_3(aq.) + HCl(aq.) \longrightarrow AgCl(s) + HNO_3\ (aq.)$

(A) 21.471 KJ/mol (B) 145.688 KJ/mol (C) –65.488 KJ/mol (D) None

Sol. $\Delta H^o_{reaction} = [\Delta H_f\ (AgCl) + \Delta H_f\,(H^+) + \Delta H_f(NO_3^-)] - [\Delta H^o_f\ (Ag^+)] + \Delta H^o_f\ (NO_3^-) + \Delta H^o_f\ (Cl^-) + \Delta H^o_f\ (H^+)]$
$= -127.068 - [105.579 - 167.159] = -65.488$ KJ / mol. **Ans. (C)**

18. What is the work done against the atmosphere when 25 grams of water vaporizes at 373 K against a constant external pressure of 1 atm ? Assume that steam obeys perfect gas laws. Given that the molar enthalpy of vaporization is 9.72 kcal/mole, what is the change of internal energy in the above process ?

(A) 1294.0 cal, 11247 cal (B) 921.4 cal, 11074 cal
(C) 1025.6 cal ; 12474.3 cal (D) 1129.3 cal, 10207 cal

Sol. Mole of H_2O = 1.39
$Pv = nRT$
$1 \times v = 1.39 \times 0.082 \times 373 \Rightarrow v = 42.51$ lit

$w = P_{ext.}\ dv = 1 \times [42.80]$ atm × lit. $= 42.80 \times 101.325$ J $= \frac{42.80 \times 101.325}{4.2} = 1025.6$ cal

$\Delta H = \Delta U + [P\Delta v]. = 12470.6$ cal.
$\Delta U = \Delta H - P\Delta v = 13500 - 1025.6 = 12474.3$ cal **Ans. (C)**