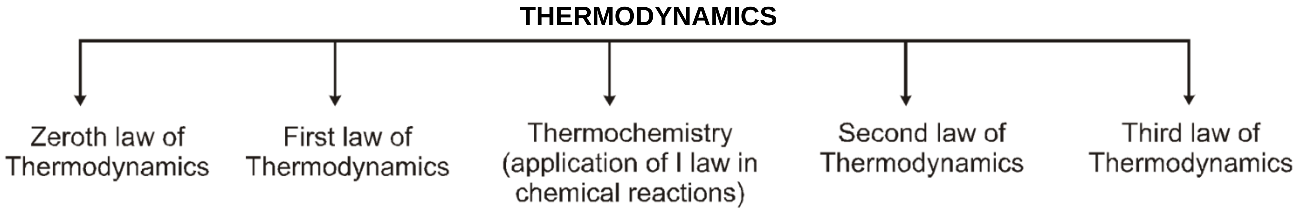
Thermodynamics & Thermochemistry

Section (A) : Basic definition

Introduction :

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



Application of thermodynamics :

In chemistry using thermodynamics

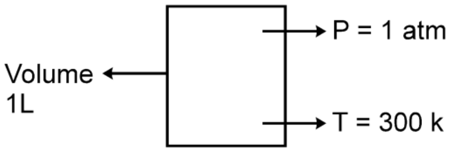
- We can predict feasibility of the reaction that is if two substances are mixed then the reaction between them will takes place or not.
- If reaction does take place then what are the energy changes involved during the reaction.
- If in a chemical reaction, equilibrium is going to get attained then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

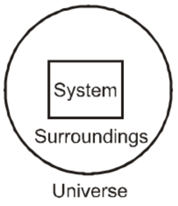
Limitations of Thermodynamics :

- 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.

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) or diathermic(conducting).

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

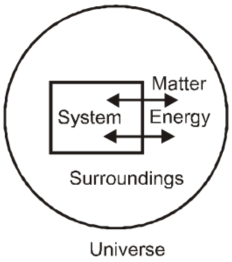
- **Closed system :** System which can exchange only energy but cannot exchange matter with the surrounding is called closed system.

  E.g : any matter in a closed container.

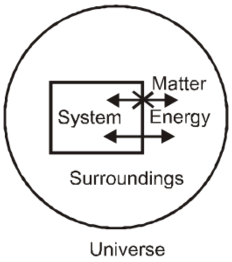
- **Isolated system :** System which cannot exchange energy and matter both with the surroundings.

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).

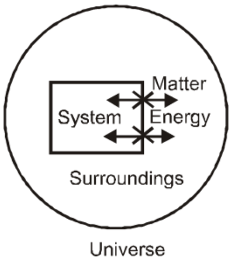
❍ Whole of universe is a perfect isolated system.



Open System



Close System



Isolated system

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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.

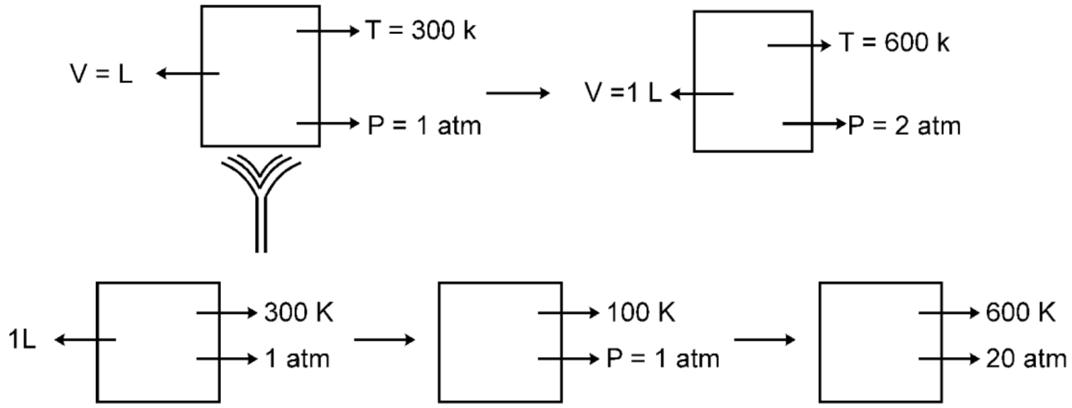
State function :

- 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 be a state function but distance travelled by the object will be a path function.

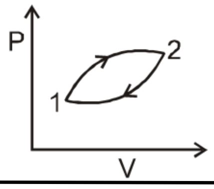
for any thermodynamic system,

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.

Eg. 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.

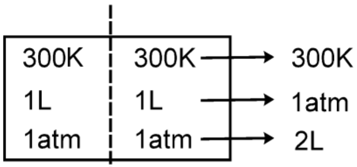
Intensive properties :

- 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)

Solved Examples

Ex-1. Categorize these property into state and path function

(a) Internal energy (b) Volume (c) Heat (d) Enthalpy

(e) Temperature (f) Work (g) Molar heat capacity

Sol. State function : (a) (b) (d) (e) ; Path function : (c) (f) (g)

Ex-2. Categorize these property into extensive and intensive property

(a) Temp (b) Internal energy (c) Heat (d) Density

(e) Molar volume (f) molar enthalpy (g) viscosity

Sol. Extensive Property : (b) (c) ; Intensive Property : (a) (d) (e) (f) (g)

● Thermodynamic equilibrium :

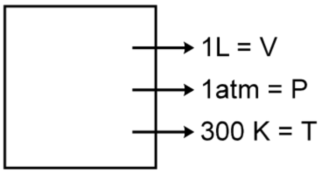
● When there is no change in any observable or measurable property of a system with time then the system is said to be in thermodynamic equilibrium.

● Thermodynamic equilibrium consist of three types of equilibrium.

(a) Mechanical equilibrium

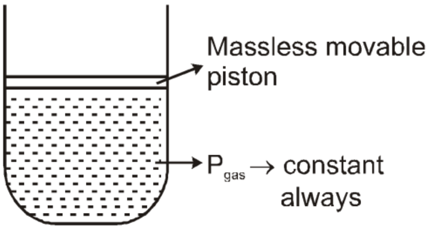
(b) Thermal equilibrium

(c) Chemical equilirbrium



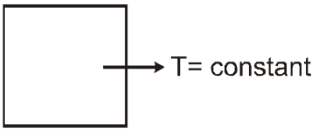
● **Mechanical equilibrium :**

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.

● 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

$P_i = P_f$

$\Delta P = 0$

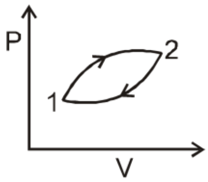
4. **Adiabatic process :** q = constant

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.

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

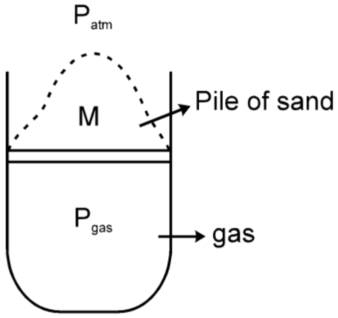
○ An ideal reversible process will take infinite time to get completed.

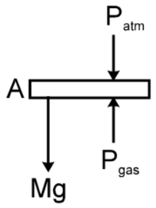
○ It is carried out infinitesimally slowly.

○ Strictly speaking there is no ideal reversible process in universe.

To get an idea of a reversible process we can consider the following system.

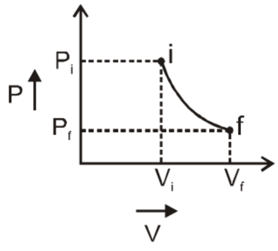
An ideal gas is enclosed in a container and a massless piston is put on the gas on which a pile of sand is placed having particles of negligible mass. To carry out a reversible expansion we will slowing decrease the mass of the sand lets say by removing the particles one by one, so the expansion of the 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

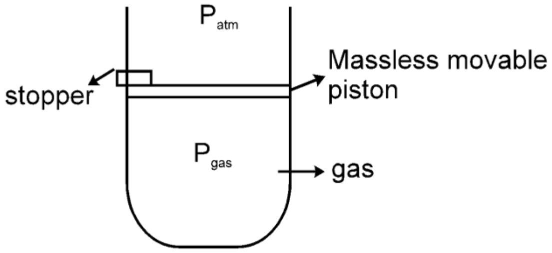
○ If during the process there is a finite difference in driving force and opposing force so that process takes place with a finite rate ; $F_{driving} - F_{opposing} = \Delta F$

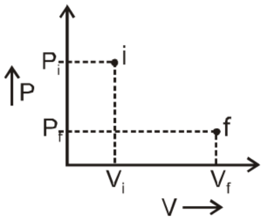
○ Irreversible processes will get completed in finite time.

○ 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 :

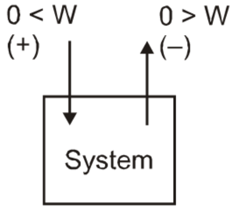
These are two ways by which a system can interact or can exchange energy with its surroundings.
(i) Heat & (ii) Work
Heat & Work both are forms of energy.

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) ; Rodiation (vacuum)

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

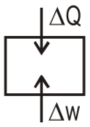
- ## IUPAC Sign convention about Heat and Work

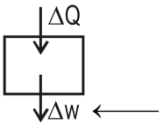


Any energy given to system is taken positive so heat given to system = positive
heat given out from system / taken out from system = Negative
Work done on the system = Positive

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 :





In Physics

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

Work done on the system = +ve
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

WORK (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 units 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 $\Delta K_{piston} = 0$

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

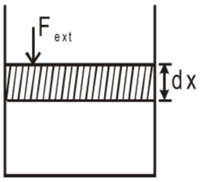
as the external pressure is always defined hence for all processes work can be calculated using

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

Work : $dW = F_{ext}\, dx$

P-V Work :

Assuming that under an external force F_x, the piston moves down by a distance 'dx'.



$$dW = \frac{F_{ext}}{A}(A \quad dx) \quad \Rightarrow \quad dW = P_{ext}\,(dV)$$

As the work done in the above case by the external agent is +ve and as the expression conveys otherwise, hence a -ve sign is introduced.

$$dW = -P_{ext}.\, dV$$

- **Calculation of work for different type of process for an ideal gas.**

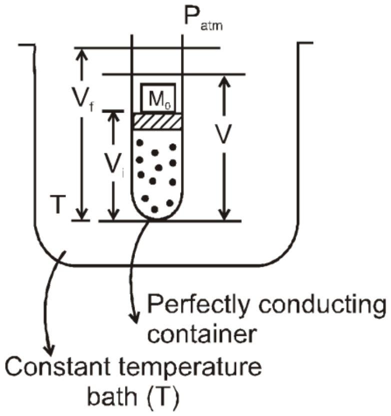
  (1) Isothermal expansion : There are many ways in which a gas can be expanded isothermally.

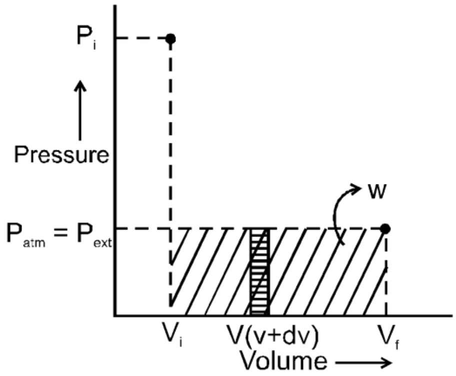
- **Work done in irreversible isothermal expansion**

  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 initally 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

$$V \longrightarrow (V + dv)$$

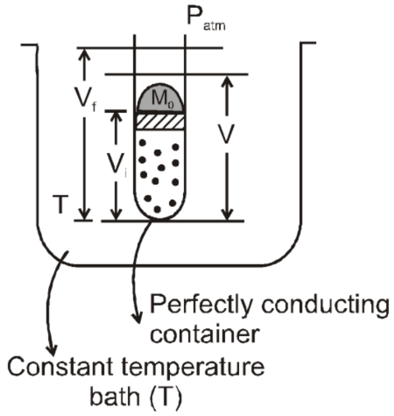
$dw = -P_{ext}.dv$ (IUPAC sign convention)

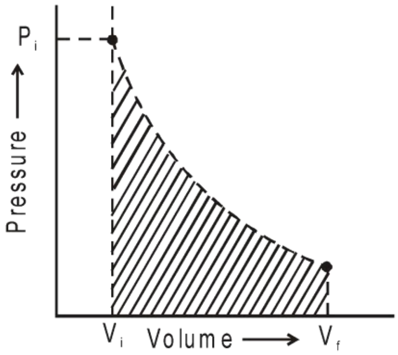
so $W = \int dw = -\int_{V_i}^{V_f} P_{ext}.dv$

$W = -P_{ext}(V_f - V_i)$

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

• Work done in reversible isothermal expansion





Let initial pressure of gas be Pi and initial mass of sand placed to keep equilibrium be m_0, so

$p_i = p_{atm} + \left(\frac{m_0 g}{A}\right)$ A = Area of cross section of piston

Now if a grain of sand is removed from the pile, the new external pressure will become

$P'_{ext} = P_{atm} + \frac{(An - dm)}{A} g$

or in other word

$P'_{ext} = P_g - dp$

It can be summarised that the process will operate such that the system will always be in equilibrium and at any stage of the process

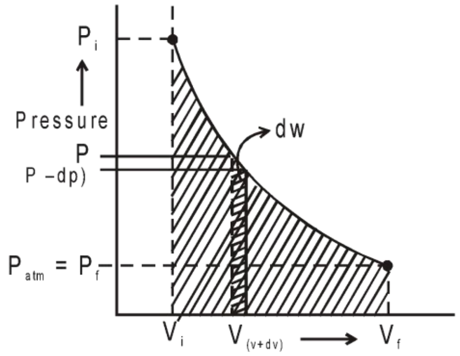
$P_{ext} = P_{gas} - dp$

$W_{ext} = -\int_{v_1}^{v_2} P_{ext}.dv = -\int_{v_1}^{v_2} (P_{gas} - dp)dv$

$= -\int_{v_1}^{v_2} (P_{gas}dv) = \int_{v_1}^{v_2} \frac{nRT}{V}dv = -$ nRT in

$\frac{v_1}{v_2}$

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



This process can also be repressnted in a PV digram as follows

Here we have assumed $P_f = P_{atm}$ need not become for a given problem the pressure of the gas at intermediate stages is defined and hence the process can be represented in "PV" diagram

(2) isothermal compression of an ideal gas :

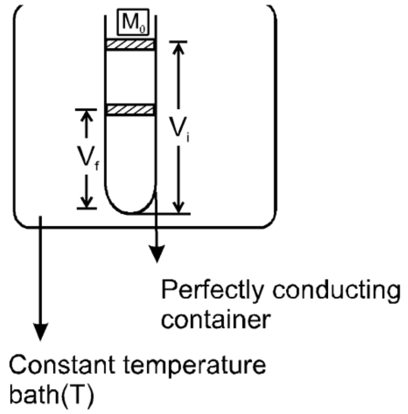
• Work done in irreversible isothermal compression

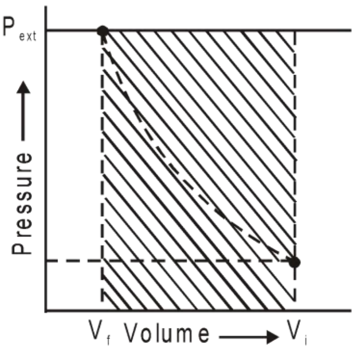
To compress gas a mass m_0 is suddenly placed on massless piston

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

so. to calculate total work done on the gas

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



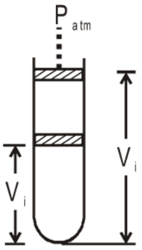


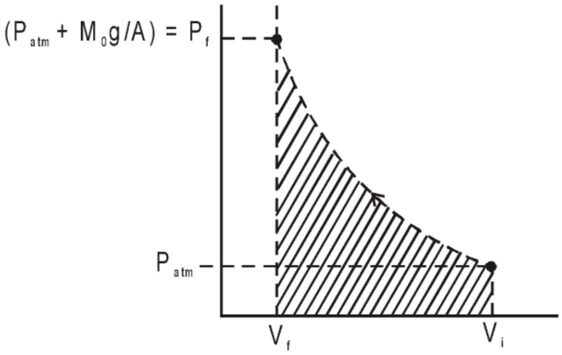
• Reversible isothermal compression of an ideal gas

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 $V_f < V_i$





Conclusion :

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

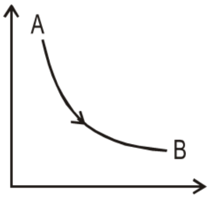
Thats why different machines/engines are designd to work reversibly so maximum output can be obtained but minimum input is given to it

$$\begin{cases}\text{output - work done by engine/machine/system}\\ \text{input - work done by system us a surrounding}\end{cases}$$

○ ***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 isothernally process, process is irreversible

Solved Examples

Ex-3. Calculate the work performed when 2 moles of hydrogen expand isothermally and reversibly at 25ºC form 15 to 50 litres.

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

Ex-4. 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

$$w = -\int_{10}^{20} 2dv = -[20-10]$$

$= -20$ J.

1 litre atm = 101.3 J

Thermodynamic definition of an ideal gas :

- If for a gas the internal energy is directly proportional to its absolute temperature then the gas is termed as an ideal gas.

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

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.

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

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

$\Delta E = q_v$, 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.

● **Degrees 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 degrees 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

U/molecule = f x $\frac{1}{2}$ KT

∴ U/mole = $\frac{f}{2}$ x KT ⇒ U/mole = $\frac{1}{2}$ RT

∴ For n moles = $\frac{f}{2}$ nRT

U = $\frac{f}{2}$ nRT only for ideal gas.

● 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.

● Heat capacity is a path function and different type of heat capacities are defined

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

---

○ Total Heat Capacity

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

Mathematically $C_T = \frac{\Delta q}{\Delta T} = \frac{dq}{dT}$ = J/ºC

● It is extensive properties and path function

So $dq = cdT$

on integrating $q = \int cdT$

❍ Molar heat capacity

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

Mathematically $C = \frac{\Delta q}{n\Delta T} = \frac{dq}{ndT}$ = J mole^{-1} K^{-1}

So. $dq = ncdT$

$q = \int ncdT = nc\Delta T$

for an ideal gas C_P and C_V are frequently used.

○ Specific heat capacity (s) :

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

$S = \frac{\Delta q}{m\Delta T} = \frac{dq}{mdT}$ = Jg^{-1} K^{-1}

so $dq = msdT$

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

We can define specific heat capacity at constant pressure and at constant volume.(**s_P & s_V**)

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

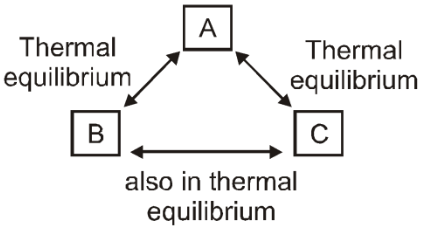
$C_T = nC = ms$ & $C = Ms$

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

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

Heat capacity can have value from $-\infty$ to $+\infty$ depending on the process.

Zeroth Law of Thermodynamics (ZLOT) :



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

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

Section (B) : First law of thermodynamics, calculations of ΔE, W & Q.

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

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

(1) Constant volume process (Isochoric)

$dU = dq + dw$

$dU = dq - pdV$

$\therefore dU = (dq)_v$

Heat given at constant volume = change in internal energy

$du = (dq)$

$\therefore dU = (nCdT)_v$

$dU = nC_vdT$

C_v is Specific molar heat capacity at constant volume.

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

(2) 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 $P = \text{constant}$ ⇒ $dH = dU + PdV$ .... (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

$PV = nRT$

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

$nC_p\, dT = nC_vdT + nRdT$

⇒ $C_p - C_v = R$ only for ideal gas ⇒ Mayer's Relationship

Section (C) : Calculation of ΔE, ΔH, w and q in different type of physical processes on an idel gas, solid and on liquids

● Calculation of ΔH, ΔU, work, heat etc.

Case - I For an ideal gas undergoing a process.

The formula to be used are

$$dU = nC_vdT = \frac{f}{2}nRdT$$

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

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

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

$$\Delta H = \Delta U + nR\,\Delta T$$

$$du = dQ + dw$$

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.

Solved Examples

Ex-5. Calculate the maximum work done when pressure on 10 g of hydrogen is reduced form 20 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 = number of moles of hydrogen = $\frac{\text{wt. in grams}}{\text{mol. wt.}} = \frac{10}{2}$ = 5 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 :**

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

$dH = nC_p\, dT \neq (f/2 + 1)\, nRT$ (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 it the is confined inside an adibatic 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

W = – 1

Sol. Work don = –100 × – 1 = 100 lit 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 lit atm = 101.3 Joule.

Case - III **For chemical reactions :**

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

$W = -\int P_{ext.}\ dv = \int -P_{ext.}\ (v_f - v_i)$

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

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

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

$W = -\,(n_{c'} - n_c)RT$

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

$dU = dq + dw$

If at constant pressure

$dq = dH$

$\therefore \quad dU = dH - pdV$

$dU = dH - \Delta ng\ RT$

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

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,

$$C_6H_6(\ell) + 7\frac{1}{2}O_2\ (g) \rightarrow 6CO_2\ (g) + 3H_2O\ (\ell);\ \Delta H = -780980\ \text{cal.}$$

What would be the heat of reaction at constant volume?

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

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

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

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 ΔU 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 U is summation of all type of energies so $\Delta U \neq 0$. 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 ΔU using Ist law of thermodynamics.

Solved Examples

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

Sol. $CaCO_3 \rightleftharpoons CaCO_3$

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

Generally for solid $\longrightarrow$ Solid

solid $\longrightarrow$ Liquid

solid $\longrightarrow$ Liquid

transitions $W << q$ so. $\Delta U \simeq q = \Delta H$

while for gaseous conversion for example

Solid $\longrightarrow$ gas

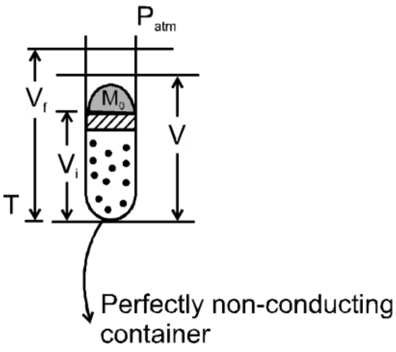
Liquid $\longrightarrow$ gas

$q = \Delta H \neq \Delta U$. as W will be significant.

ADIABATIC PROCESS :

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

$dU = dQ + dW$



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

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

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

$T_2 V_2^{\gamma-1} = T_1 V_1^{\gamma-1}$

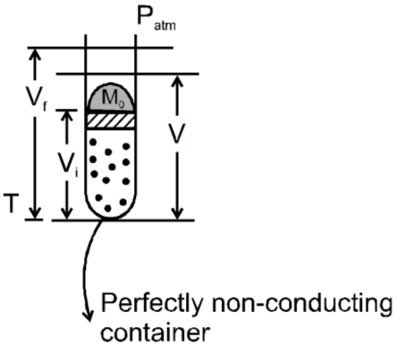
or $T V^{\gamma-1} = \text{constant}$

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

- 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

(1) 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 contant pressure and no of moles, $V \propto T$

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

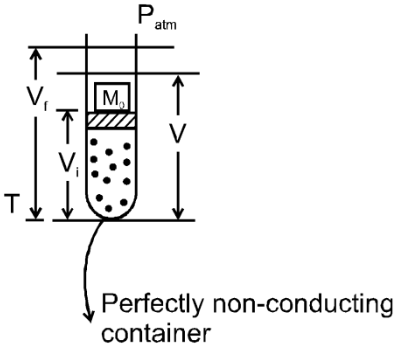
$\therefore\ w = -\int \frac{K}{V^{\gamma}}.\ dv$

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

$\Rightarrow$ work done $= \frac{P_2V_2 - P_1V_1}{\gamma-1}$ (as $K = P_2V_2^{\gamma} = P_1V_1^{\gamma}$)

(2) Irreversible Adiabatic

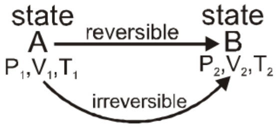
- **Adiabatic irreversible expansion**



W = $\int -P_{ext.} dv$ = – P_{ext} (V_2 – V_1) , or $\int du = \int dw$

∴ W = ΔU

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



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

∴ $\Delta U_{rev.} = \Delta U_{irrev.}$

⇒ $W_{irrev.} = W_{rev.}$

as work is a path function.

If we assume that

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

⇒ 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.
- In other words if two states A and B are connected by a reversible path then they can never be connected by an irreversible path.
- There lies only one unique adiabatic path linkage between two states A and B.

❍ Adiabatic Irreversible process (calculation of state parameters)

State A $\xrightarrow{irrev}$ State B

P_1,V_1,T_1 P_2,V_2,T_2

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

- **Free expansion – Always going to be irrerversible and since P_{ext} = 0**

so ΔW = – P_{ext} . dV

= 0

If no. heat is supplied $q = 0$
then $\Delta U = 0$ so $\Delta T = 0$.

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	$\frac{P_fV_f - P_iV_i}{(n-1)}$	$\Delta U - w$	$nC_{v,m}(T_2 - T_1)$	$nC_{p,m}(T_2 - T_1)$	$C_{v,m} + \frac{R}{1-\gamma}$

Section (D) : II$_{nd}$ Law of thermodynamics: Basics of entropy, Entropy calculation for different types of physical process on an ideal gas, solid and liquid, chemical reaction

● II$_{nd}$ 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

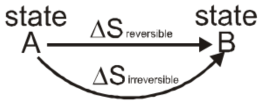
$ds = \frac{dq_{rev}}{T}$ or $\Delta S = \int \frac{dq_{rev}}{T}$, $\frac{dq}{T}$ is state function only for reversible process

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

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

● Entropy Calculation :

- **Calculation of ΔS_{system}**



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

$\therefore$ $\Delta S_{irrev} = \Delta S_{rev}$

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

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

State A $\xrightarrow{\Delta S_{irr}}$ State B

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

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

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

from the first law $dU = dQ + dw$

$dQ = dU - dw$

For reversible path $dq = dq_{rev}$

$dq_{rev} = dU + P_{gas}\, dV$ $\{P_{ext} = P_{gas}$ reversible$\}$

$$\Delta S_{rev,\ system} = \int_A^B \frac{dU + P_{gas}\ dV}{T}$$

For an ideal gas

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

$$\therefore \quad \Delta S_{sys} = \int_{T_1}^{T_2} \frac{nc_v\ dT}{T} + \int_{V_1}^{V_2} \frac{nRdV}{V}$$

$$\therefore \quad \Delta S_{system} = nc_v\, \ell n \frac{T_2}{T_1} + nR\, \ell n \frac{V_2}{V_1}$$

- **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

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

But according to the law of conservation of energy

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

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

- ## Isothermal process :

(a) Reversible

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

P_1, V_1, T P_2, V_2, T

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

Since $T_1 = T_2$

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

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

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

$\therefore$ dq = – dw

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

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

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

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

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

(b) Irreversible

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

P_1, V_1, T P_2, V_2, T

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

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

q_{system} is calculated using FLOT

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

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

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

$= \frac{1}{T}\left[(nRT\ \ \ell n\ \ \frac{V_2}{V_1}) - P_{ext}\ \ (V_2 - V_1)\right]$

$= \frac{1}{T}$ $[W_{irrev} - W_{rev}] > 0$

As irreversible work of gas is more than reversible work.

- ## Adiabatic Process (Isoentropic process)

(a) Reversible Adiabatic

State A $\xrightarrow{rev}$ State B

P_1, V_1, T_1 P_2, V_2, T_2

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

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

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

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

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

$\therefore \Delta S_{universe} = 0 + 0 = 0$

(b) Irreversible Adiabatic

State A $\xrightarrow{irre}$ State B

P_1, V_1, T_1 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.

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

$\Delta S_{surr} = -\frac{q_{\ sys}}{T} = 0$ 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.

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

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

- ### For chemical reaction

$aA + bB \longrightarrow cC + dD$

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

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 perfectly crystalline 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 $\Delta S_{fus.} = \dfrac{\Delta H_{fus}}{T}$

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

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

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

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

Section (E) : ΔG calculation, Spontanity of chemical reaction significance of ΔG and III$_{rd}$ Law of thermodynamics

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

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

for a spontaneous change

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

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

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

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 spontanity :

(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 $\Delta G \neq 0$

ΔG_{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

ΔG° = 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 ΔG^o (it is a contant) for 1 mole at 1 bar.

At standared conditions :

$\Delta G° = \Delta H° - T\Delta S°$

= constant for a GIVEN REACTION

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

$\Delta G°$ = (Gbb's energy of product) – (Gibb's energy of reactant)

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

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

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

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

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

For a reaction in progress

$\Delta G = \Delta G^o + RT \ln Q$

Q is reaction quotient , $\Delta G > 0$ backward is feasible , $\Delta G < 0$ forward is feasible

At equilibrium $\Delta G = 0$ $\therefore Q = K \therefore \Delta G^o = -RT \ln K$ 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.

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

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

$29605 = \Delta H^o - 323\, \Delta S^o$

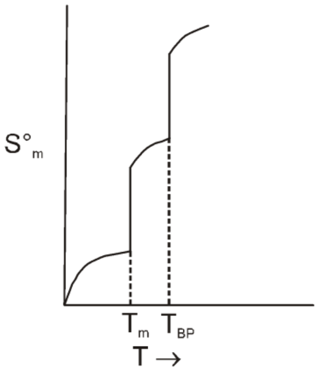
$\Delta H^o = -1.55$ kJ/mol

$\Delta S^o = -96.44$ J/mol.K

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^o .



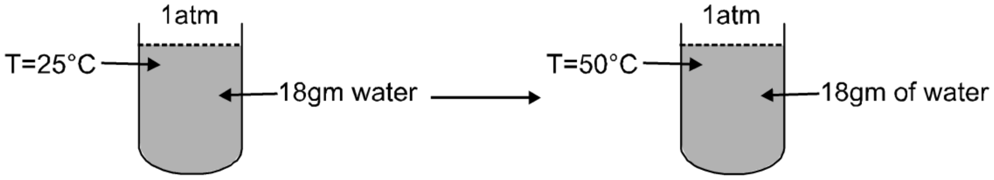
$\Delta S = S_{T(K)} - S_{0(K)} = \int_0^T \frac{nCdT}{T}$

Section (F) : Thermochemistry: Enthalpy contents and Kirchoff's equation

❍ 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, ΔH° = $H^0_{m,2} - H^0_{m,1}$

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 heat gets released or absorbed. Even if temperature of reactions remains constant yet due to change in bonding energies ΔE ≠ 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 : $\Delta H_{reaction} = H_{products} - H_{reactants}$

$\Delta H°_{reactions} = H°_{products} - H°_{reactants}$

= positive – endothermic

= negative – exothermic

❍ 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 find.

- "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) : $\frac{1}{2} H_2(g) + \frac{1}{2} Br_2(l) \rightarrow HBr(g)$

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

Enthalpy of formation of SO_2 (g) : S (rhombic) + O_2 (g) → SO_2 (g)

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

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

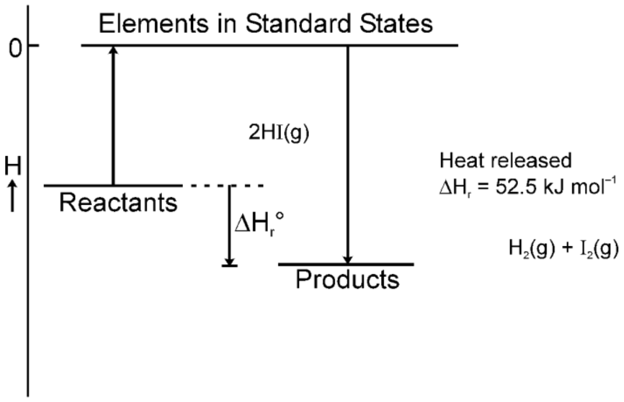
❍ Enthalpy of Reaction from Enthalpies of Formation:

The enthalpy of reaction can be calculated by

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

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-12. Calculate the standard enthalpy of reaction ZnO(s) + CO(g) $\longrightarrow$ Zn(s) + CO_2 (g).

Given, ΔH_f° (ZnO, s) = – 350 KJ / mole^{-1}
ΔH_f° (CO_2, g) = – 390 KJ / mole
ΔH_f° (CO, g) = – 110 KJ / mole

gy- $\Delta H^\circ = \{\Delta H_f^\circ(CO_2, g) - (\Delta H_f^\circ (ZnO, s) + \Delta H_f^\circ (CO, g))\}$
$\Delta H^\circ = \{-390 + 350 + 110\}$
ΔH° = 70 KJ/mole.

❍ 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

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

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

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

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

Substracting the latter from the former, we get

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

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

Solved Examples

Ex-13. 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) $F_2(g) + \frac{1}{2} O_2(g) \rightarrow F_2O(g)$; ΔH = 5.5 kcal

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

(iii) $\frac{1}{2} H_2(g) + \frac{1}{2} F_2(g) \rightarrow HF(g)$; ΔH = – 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

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

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

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

❍ 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^o 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 (G) : Enthalpy of combustion and neutralisation

❍ 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 :

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

  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 :

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

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

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

- 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

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

$$= [-393 + 2(-285) - (-890)] \text{ kJ mol}^{-1} = -73 \text{ kJ mol}^{-1}$$

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

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

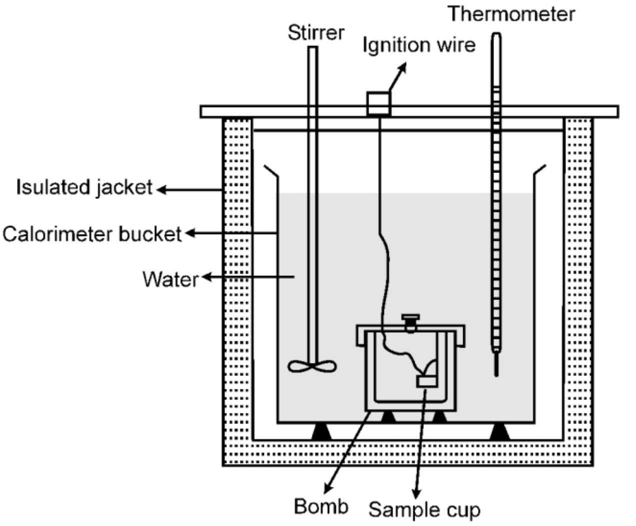
$$2[H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(\ell)] \qquad \Delta_r H° = 2(-285) \text{ kJ mol}^{-1}$$

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

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

❍ Measurement of Enthalpy of Combustion :

Enthalpies 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 calorimetre 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 calorimetre.



Bomb calorimeter to determine enthalpy of combustion

If total heat capacity of calorimeter and all of its contents = C, rise in temperature = ΔT then heat released = q = CΔT, this heat is because of m mass of substance.

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

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. $\overbrace{C_2H_4 \quad + \quad CH_4}^{3.67\text{ lit.}} + O_2 \rightarrow CO_2 + H_2O$

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

$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$; ΔH = – 1464 kJ

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$; ΔH = – 976 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 0.665 lit. of $C_2H_4 = -\frac{1464}{24.4} \times 0.5 = -30$ kJ

and heat evolved in the combustion of 0.335 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.

❍ 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

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

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

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

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

(iv) $HCl(g) + aq \longrightarrow HCl\ (aq)$ $\Delta H_5 = -75.0$ 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 to 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

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

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

$CuSO_4(s) + 800\ H_2O\ (\ell) \rightarrow CuSO_4\ (800\ H_2O)$ $\Delta H_r° = -68$ kJ mol^{-1}

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

by subtraction, we get $CuSO_4(s) + 5H_2O\ (\ell) \rightarrow CuSO_4.5\ H_2O(s)$ $\Delta H_r° = -78$ 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 :

$Cl^-(g) + aq. \longrightarrow Cl^-(aq)$ $\Delta H_{Hydration}$

❍ Enthalpy of Neutralisation :

- 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 :

- 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 :

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

$CH_3COOH + Na^+OH^- \rightarrow Na^+ + CH_3COO^- + H_2O$ $\Delta_rH° = -49$ 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-15. 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 Transition :

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

For example : $C(graphite) \rightarrow C(diamond)$ $\Delta H_{trs}^0 = 1.90$ kJ mol^{-1}

so if $C(graphite) + O_2(g) \rightarrow CO_2(g)$ $\Delta H_C^0 = -393.51$ kJ mol^{-1}

and $C(diamond) + O_2(g) \rightarrow CO_2(g)$ $\Delta H_C^0 = -395.41$ kJ mol^{-1}

Subtracting, we have, $C(graphite) \rightarrow C(diamond)$ $\Delta H_{trs}^0 = 1.90$ kJ mol^{-1}

Enthalpy of Precipitation :

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

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

Solved Examples

Ex-16. Calculate ΔH° 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.

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

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

We have seen that $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$ $\Delta_rH^0 = -57.1$ kJ mol^{-1}

For this reaction, $\Delta H_r^0 = \Delta H_f^0 (H_2O, l) - \{\Delta H_f^0 (H^+, aq) + \Delta H_f^0 (OH^-, aq)\}$

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

so $\Delta H_f^0 (OH^-, aq) = \{-286.1 - (-57.1)\}$ 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

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

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

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

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

$= [-44.50 - (-229.99) + (-425.61)]$ 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. These are recorded in Appendix-II. 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-17. 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, $H^+(aq) + OH^-(aq) \longrightarrow H_2O(\ell)$

$\Delta_f H$ 0 $-285\ \text{kJ mol}^{-1}$

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

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

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

Ex-18. 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 $\Delta_f H°\ (Cl^-, aq) = -167\ \text{kJ mol}^{-1}$

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

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

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

Section (H) : Bond Enthalpies and 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.

$H_2O(g) \rightarrow H(g) + OH(g)$ $\Delta H_r^0 = 501.87\ \text{kJ mol}^{-1}$

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

$OH(g) \rightarrow O(g) + H(g)$ $\Delta H_r^0 = 423.38\ \text{kJ mol}^{-1}$

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

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

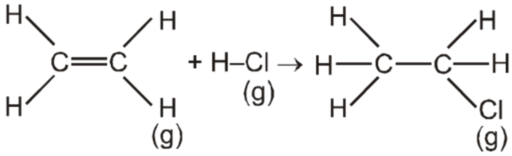
In the case of diatomic molecules, such as H_2, the bond enthalpy and bond dissociation enthalpy are identical because each refers to the reaction.

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

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 :

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

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

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

Solved Examples

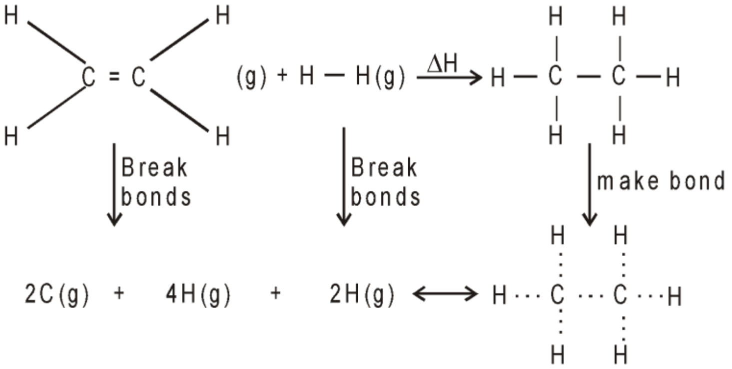
Ex-19. Using the bond enthalpy data given below, calculate the enthalpy change for the reaction

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

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}

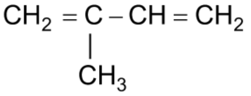
Sol. Diagrammatically, we represent the given reaction as follows :



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

$= (4 \times 410 + 606 + 431) - (6 \times 410 + 336) = 2677 - 2796 = -119$ kJ/mol.

Ex-20. Using the bond enthalpy data given below, estimate the enthalpy of formation of gaseous isoprene



$CH_2 = \underset{\displaystyle CH_3}{\underset{|}{C}} - CH = CH_2$

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) = +5 232.52 kJ mol^{-1}

The reaction corresponding to this is

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

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

$5C(\text{graphite}) + 4H_2(g) \rightarrow C_5H_8(g)$ $\quad \Delta_f H = ?$

This can be obtained by the following manipulations :

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

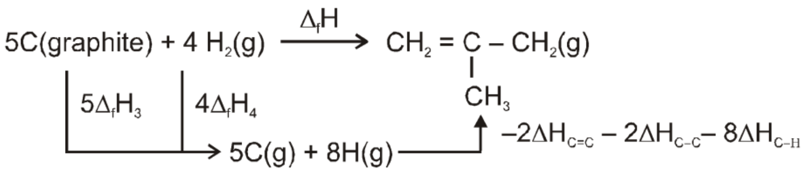
$5C(\text{graphite}) \rightarrow 5C(g)$ $\quad \Delta_r H_3 = 5 \times 718.39$ kJ mol^{-1}

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

Adding, we get

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

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



Applying Hess's law, we get

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

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

Δ_fH = 103.31 kJ mol^{-1}

Ex-21. Find the bond enthalpy of S – S bond from the following data :

$C_2H_5 - S - C_2H_5(g)$ $\Delta_fH° = -147$ kJ mol^{-1}

$C_2H_5 - S - S - C_2H_5(g)$ $\Delta_fH° = -201$ kJ mol^{-1}

$S(g)$ $\Delta_fH° = 222$ kJ mol^{-1}

Sol. Given that

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

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

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

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

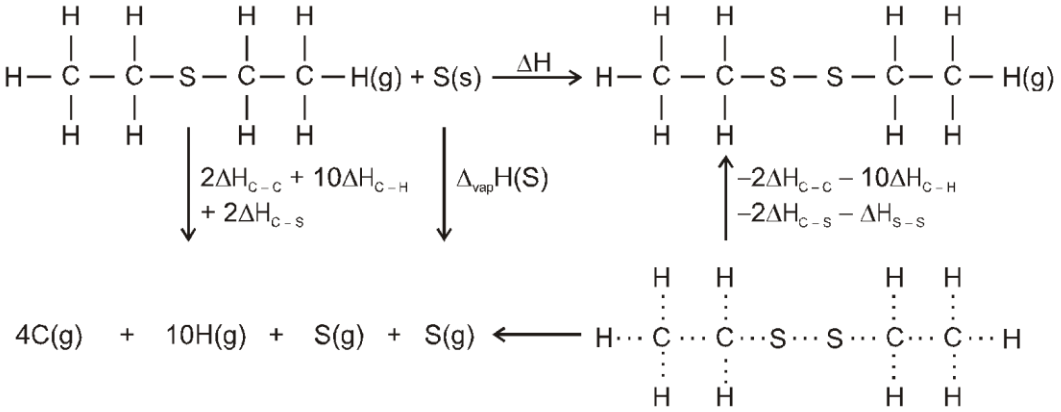
Adding to this, the following equation

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

We get $C_2H_5{-}S{-}C_2H_5(g) + S(g) \longrightarrow C_2H_5{-}S{-}S{-}C_2H_5(g)$ $\Delta_rH° = -276$ 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

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

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

= $\Delta_{vap}H°(S) - \Delta H_{S-S}$

or ΔH_{S-S} = $\Delta_{vap}H°(S) - \Delta H°$

= $\Delta_{vap}H°(S) - [\Delta_fH°(C_2H_5 - S - S - C_2H_5] - \Delta_fH°(C_2H_5 - S - C_2H_5)]$

= $[222 - \{-201 - (-174)\}]$ kJ mol^{-1} = 276 kJ mol^{-1}

Resonance Energy :

$\Delta H^\circ_{\text{resonance}} = \Delta H^\circ_{\text{f, experimental}} - \Delta H^\circ_{\text{f, calclulated}}$

$= \Delta H^\circ_{\text{c, calclulated}} - \Delta H^\circ_{\text{c, experimental}}$

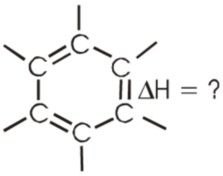
Solved Examples

Ex-22. 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, $6C (s) + 3H_2(g) \rightarrow C_6 H_6 (g)$

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.,

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

1025.4 312.6 – 594 –3 × 140

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. $q = \int ncp \cdot dT = \int naT^3 \cdot dT$

$= na\left[\frac{T^4}{4}\right]_3^5 = \frac{na}{4}[(5)^4 - (3)^4] = \frac{na\,[625 - 81]}{4}$

q = **136 na. Ans.**

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 × 2 = – 4.2 atm × lit. = – 4.2 × 101. 325 J

This work is used to heat up the water

Specific heat of H_2O = 4.2 J/g.K

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

4.2 × 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 × 0.0821 × 273

v = 3699 lit ≈ [3700 lit]

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

ΔH = 80 × 18 + 596 × 18 = [80 + 596] × 18

ΔH = 12168 cal

$\Delta H = \Delta E + \frac{4.6}{760} P [V_2 - V_1]$

12168 = ΔE + [3699] × 24.24

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

= 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 × 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 (ℓ) = 0.87 g/mℓ

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

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

(iii) $C_6H_6(\ell) + \frac{15}{2} O_2(g) \rightarrow 6CO_2(g) + 3H_2O(\ell)$

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

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

7. For the equations

$C(diamond) + 2H_2(g) \rightarrow CH_4(g)$ ΔH_1 ;

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

Predict whether

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

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

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

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

Ans. (3)

8. The standard molar enthalpies of formation of cyclohexane (l) and benzene (l) at 25º C 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 () – ΔH_f ()

= –156 – (+ 49) kJ = –205 kJ.

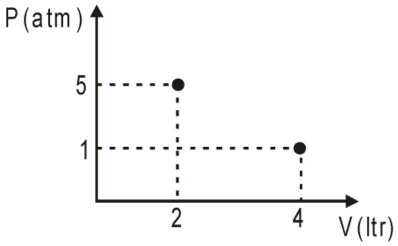
Given that,  + $H_2 \longrightarrow$  $\Delta H = 119$ kJ

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

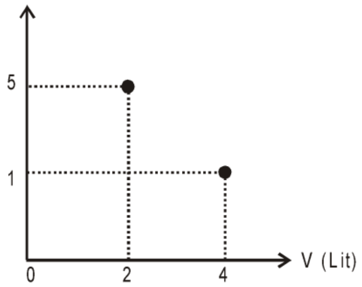


(1) – 9104 J

(2) – 202.6 J

(3) – 506 J

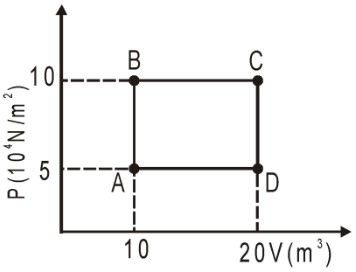
(4) – 101.3 J



Sol. **(2)**

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



(1) $T_A = 120.5$ K, $T_B = 120.5$ K
(2) $T_A = 241$ K, $T_B = 241$ K
(3) $T_A = 120.5$ K, $T_B = 241$ K
(4) $T_A = 241$ 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

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

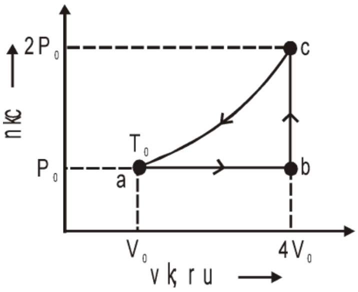
$T_B = \frac{P_B.T_A}{P_A} = \frac{10}{5} \times 120.5 = 241$ K. **Ans. (3)**

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.]

(1) $w_{rev} > w_{irrev}$ (2) $w_{irrev} > w_{rev}$ (3) $q_{rev} < q_{irrev}$ (4) can not be predicted

Ans. (2)

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 :



(1) $3\, P_0V_0$ (2) $6\, RT_0$ (3) $4.5\, RT_0$ (4) $10.5\, RT_0$

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. (4)**

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)

(1) $\Delta H = 15$ kJ (2) $\Delta H = 15.7$ kJ (3) $\Delta H = 14.4$ kJ (4) $\Delta H = 14.7$ 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 (2)**

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 $mol^{-1}K^{-1}$].

(1) 0 (2) $R\ell n\ (24.6)$ (3) $R\ \ell n\ (2490)$ (4) $R\ell n\ (24.6)$

Sol. $\Delta S = nR\ \ell n \left(\frac{V_f}{V_i}\right) = R\ell n \left(\frac{P_i}{P_f}\right) = R\ \ell n \left(\frac{300R}{1L \times 1\ \ atm}\right) = R\ell n\ (24.6)$ **Ans. (2)**

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 :

(1) 0.42 J/K-mol (2) 0.14 J/K-mol (3) 4.2 J/K-mol (4) 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. (2)**

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 ?

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

(1) 298 K (2) 668 K (3) 966 K

(4) 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. (3)**

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

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

(1) 21.471 KJ/mol (2) 145.688 KJ/mol (3) 65.488 KJ/mol (4) 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. (3)**

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 ?

(1) 1294.0 cals, 11247 cals (2) 921.4 cals, 11074 cals

(3) 1025.6 cal, 12474.3 cals (4) 1129.3 cals, 10207 cals

Sol. Mole of $H_2O = 1.39$

$Pv = nRT$

$1 \times v = 1.39 \times 0.082 \times 373$

$v = 42.51$ lit

$w = P_{ext.}\, dv = 1 \times [42.51]$ atm × lit. $= 42.80 \times 101.325$ J $= \dfrac{42.80 \times 101.325}{4.2} = 1025.6$ 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. (3)**