THERMODYNAMICS Ist LAW

CONTENTS

Particulars **Page No.**

JEE (ADVANCED) SYLLABUS

First law of thermodynamics; Internal energy, work and heat, pressure-volume work; Enthalpy

JEE (MAIN) SYLLABUS

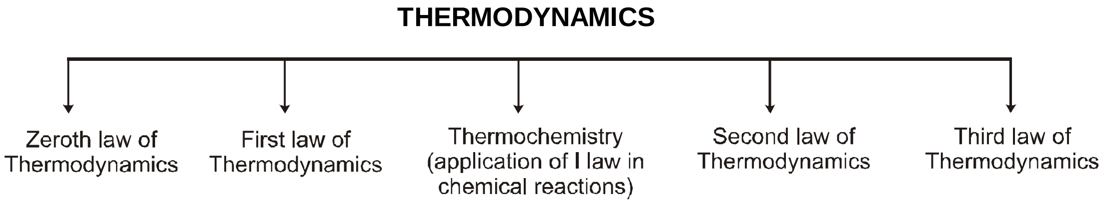
Thermal equilibrium, zeroth law of thermodynamics, concept of temperature. Heat, work and internal energy. First law of thermodynamics.

Thermodynamics Ist Law

Thermodynamics

Introduction :

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



Application of thermodynamics :

In chemistry using thermodynamics

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

Limitations of Thermodynamics :

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

SOLVED EXAMPLE

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

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

Which of these reaction will attain equilibrium earlier ?

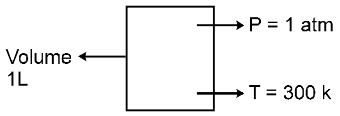
Sol. We cannot predict, because value of equilibrium constant has no relation with time taken to attain equilibrium.

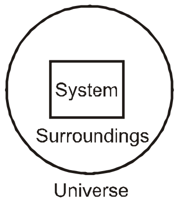
❖ More the equilibrium constant K, more will be the concentration of products at equilibrium state.

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

Terms to be used in Thermodynamics :

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





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

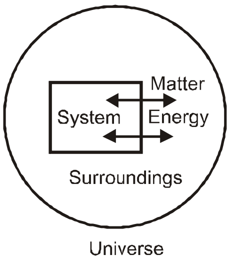
- **Surrounding :** Rest of the universe.
- **Universe :** Universe = System + Surroundings
- **Boundary :** Anything which separates system & surroundings is called boundary.
  - Boundary can be real or imaginary.
  - Boundary can be flexible or rigid
    e.g. - air in a flexible balloon (flexible boundary)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

Types of system :

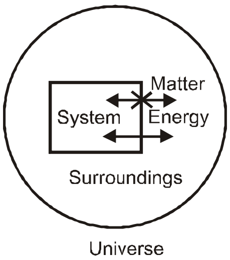
- **Open system :** System which can exchange energy & matter both with the surroundings.
  e.g. : Living systems(any living organism) are open systems, air in an open room ; water flow in pipe.
- **Closed system :** System which can exchange only energy but cannot exchange matter with the surroundings is called closed system.
  e.g. : any matter in a closed container ; Heating of water in closed container.
- **Isolated system :** System which cannot exchange energy and matter both with the surroundings.

  e.g. : Water in thermos flask.(Though not a perfectly isolated system but can be taken as, for small interval of time as the energy exchanges are negligible) ; Hot tea in thermos (few time).

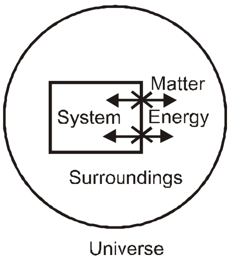
  ❍ Whole of universe is a perfect isolated system.



Open System



Close System



Isolated system

State of a system :

- It means the condition in which the system is present.
- It can be specified/defined by measuring/ specifying some observable/measurable properties of the system like pressure, volume, temperature, amount of substance, elasticity, heat capacity etc.

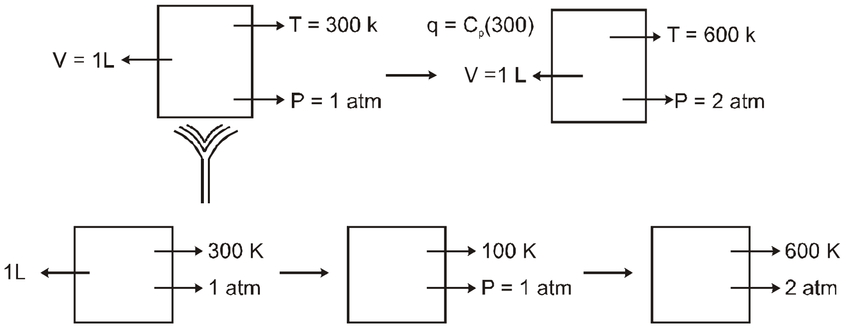
  e.g. For an ideal gaseous system state of the system can be defined by specifying volume, temperature and pressure.
- We may have to specify more properties of the system depending on the complexity of the system.

State function (State variables) :

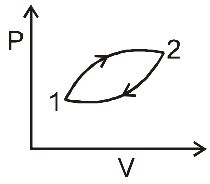
- Property of a system which is dependent only on the state of the system i.e. it is a point function
- It is independent of the path adopted to attain a particular state.

  e.g. In Mechanics, Displacement of any object will a state function but distance travelled by the object will be a path function.
  For any thermodynamic system,
  Temperature, Pressure, Volume, Total internal energy (E or U), Enthapy(H), Gibbs free energy (G), Entropy (S) are all state functions.

e.g.



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



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

$$\oint dx = 0$$

- State variables can be extensive or intensive.
- Change in state function are not state function.
  Eq. ΔT, ΔV, ΔP, ΔH, ΔG, ΔV, etc are not state function.

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

- **Types of properties**

Extensive properties :

- Functions or properties of the system which are dependent on mass or on size of the system are called Extensive Properties **.**
- Extensive functions are additive in nature (The addition of the volumes of the two parts equals the volume of the whole of the room.)

e.g. Volume, Mass, Total heat capacity, Total internal energy (E), Enthalpy(H), Gibbs Free Energy(G), Entropy(S) ; moles etc.

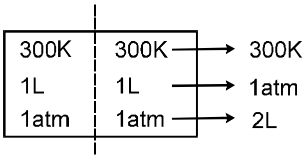
Intensive properties :

- Functions or properties which are not mass dependent or size dependent are called intensive function.
- Intensive properties are not additive in nature.

eg. Temperature, pressure, molar heat capacity, specific heat capacity, density,concentration, vapour pressure; B.P. ; F.P. ; Viscosity ; pH etc.

How to identify extensive or intensive properties

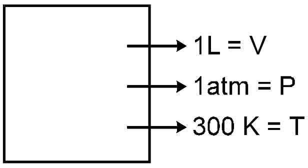
If a system in a particular state is divided into two equal or unequal parts, the properties which have value equal to the original value of that property for the whole of the system is called an **Intensive property.** While the properties which have values different from the values for whole of the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



Room is divided into two equal halves

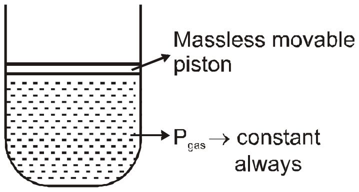
- For example consider air in a room at temp of 300K, 1 atm pressure. Now, if the room is divided by some boundary (imaginary or real) into two parts (equal or unequal) then in these two parts :
  - ❍ The temperature, pressure, density of the gas, concentration of gaseous molecules etc. will have the same value as that of for whole of the system. (intensive)
  - ❍ While the vol7ume of two parts, mass of gas in two parts, total energy of the gaseous molecules in the two parts, entropy the two parts etc. will be different from the values of these properties as for the whole of the system initially. (extensive)

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

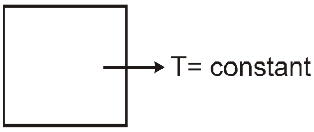


  - **Mechanical equilibrium :**

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



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



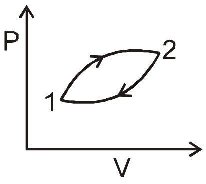
  - **Chemical equilibrium :** There should not be any concentration gradient of any of the species in the system.

- **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.
   $\Delta V = 0$
   $\Delta H = 0$



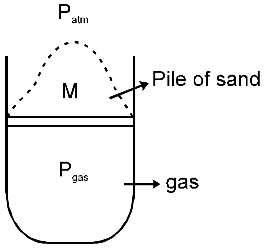
- **Types of thermodynamics processes on basis of the way the processes are carried out :**
- **Reversible process :**

  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.

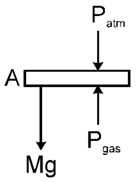
$$F_{driving} - F_{opposing} = \Delta F \text{ and } \Delta F \to 0$$

  - 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.

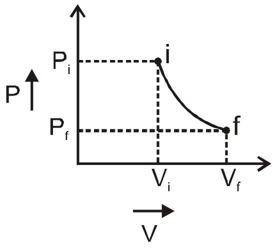
To get an idea of a reversible process we can consider the following system. An ideal gas is enclosed in a container and a massless piston is put on the gas on which a pile of sand is placed having particles of negligible mass. To carry out a reversible expansion we will slowing decrease the mass of 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

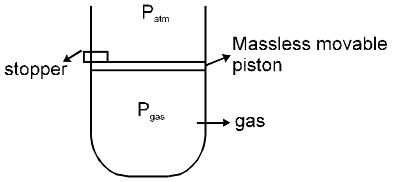
f – i : compression

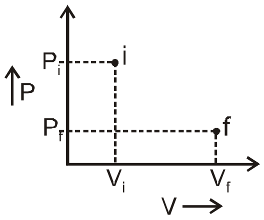
- **Irreversible process :** The process can not be reversed by a small change is known as irreversible.
  - If a process is carried out in such a manner so that the system is in thermodynamic equilibrium

    (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

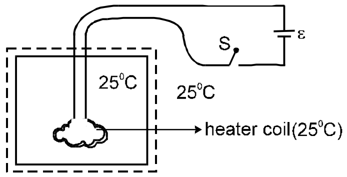
- **Modes of energy exchange :**

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) ; Radiation (vacuum)

Work : Energy transfer which is not heat or which is not because of temperature difference is called work.
Work can be of many types : Mechanical work, Electrical work, Magnetic work, Gravitational work etc.
❍ **The same energy transfer can be called work or can also be called heat depending on choice of the system.**
To understand this, consider a system shown below in which water is taken in a closed container at 25°C, the surroundings is also at temperature of 25°C and there is a heater coil in the dipped in the water which is connected to a battery through a switch S.Heater coil is also at 25°C initially.

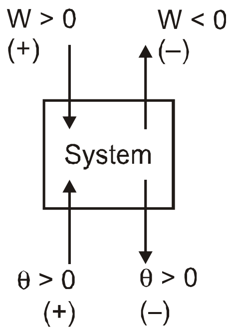


Now, there are two ways in which system can be chosen.

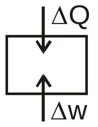
I–System : All contents of the container (water + Heater coil).
When switch is turned on there will be increment in the temperature of the system. Since the temperature of the surroundings was equal to temperature of the system so, heat can not flow but still there is increment in the energy of the system and hence, there is temperature increment. This must be because of electrical work done by the battery on the system not because of the heat transfer as initially temperatures were equal.
II–System : Water only is our system. Heater coil will be part of the surroundings.
In this case when switch is turned on the temperature of the heater coil will increase first so there will be a temperature difference between system & surroundings. Hence, this energy transfer will be called heat.

- **IUPAC Sign convention about Heat and Work**

Any energy given to system is taken positive so heat given to system = positive
heat taken out from system = Negative
Work done on the system = Positive
Work done by the system = Negative
The sign convention is different from physics, but the meaning always comes out to be same only in equation we have to use a different sign convention for work.
So if in any problem, w = – 10 J
It means system has done work of 10 Joule on surroundings.

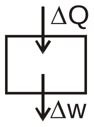


According to Chemistry :



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

According to Physics :

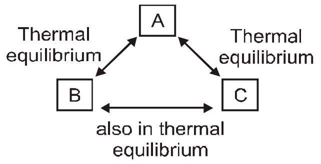


$\Delta U = \Delta Q - \Delta W$

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

Zeroth Law of Thermodynamics (ZLOT) :

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



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

First Law of Thermodynamics (FLOT) :

Law of energy conservation :
Energy of total universe is always conserved.
or
Total energy of an isolated system is always conserved.
or
Hence absolute value of E can never be calculated only change in value of E can be calculated for a particular process.

Mathematical form of First Law of thermodynamics.

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

$$E_2 = E_1 + q + w$$

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

Application of First Law

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

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

- **Calculation of different quantities in First Law of Thermodynamics (FLOT) :**

Calculation of ΔE :

Internal Energy (E, also denoted by U) :

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

- It is the sum of all forms of energies present in the system.
  $E = E_{Translational} + E_{Rotational} + E_{Vibrational} + E_{bonding} + ...$
  $\Delta E = E_{Final} - E_{Initial}$.
- **Thermodynamic definition of an ideal gas :**
- For a gas the internal energy is directly proportional to its absolute temperature then the gas is termed as an ideal gas.

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

$\Delta E = q_v$, heat supplied to a gas at constant volume, since all the heat supplied goes to increase the internal energy of the gas.

- It is an extensive property & a state function . It is exclusively a function of temperature.
  If $\Delta T = 0$; $\Delta E = 0$ as well.
- With change in temperature only kinetic energy changes.

- **Degree of freedom** → The total no of modes on which a molecule of an ideal gas can exchange energy during collisons is known as its degrees of freedom.

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

Rotational degree of freedom

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

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

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

- **Law of equipartion of energy :**

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

Where k is Boltzmann constant

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

∴ For n moles,

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

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

❍ Total Heat Capacity (C_T)

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

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

- It is extensive properties and path function.

So, $dq = C_T dT$

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

❍ Molar heat capacity (C)

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

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

So, $dq = nCdT$

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

C is intensive path function.

C_p is molar heat capacity at constant pressure

C_V is molar heat capacity at constant volume

C_p and C_V are intensive but not a path function

❍ Specific heat capacity (s) :

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

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

So, $dq = msdT$

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

S is intensive path function

S_P is specific heat capacity at constant pressure

S_V is specific heat capacity at constant volume

S_P & S_V are intensive but not a path function

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

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

Where m – weight of substance

M – molar mass of substance

n – no. of moles of the substance

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

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

Note :

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

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

SOLVED EXAMPLE

Ex.2 Represent the following observations in terms of proper IUPAC symbol?

(a) Heat absorbed by a system is 20 Joule.
(b) Work done by a system is 40 Joule.
(c) Work done on a system is 5 Joule.
(d) Heat given out by system is 50 Joule.

Ans. It is standard practice to represent both types of heat and work (in/out or on/by) by single symbols q and w -

(a) q = +20 Joule. (b) w = –40 Joule.
(c) w = +5 Joule. (d) q = –50 Joule.

Ex.3 For certain processes the heat and work exchanged between system and surrounding is given in standard format. Describe the physical interpretation of each observation.

(a) q = +10 kJ (b) w = –20 kJ

Ans. (a) q = + 10 kJ :

Since numerical value of q is positive, this shows heat is absorbed by the system from surrounding resulting in gain of energy by system.

(b) w = – 20 kJ :

Since numerical value of work is negative, this shows work is done by the system on surrounding resulting in loss of energy of system.

Ex.4 Predict sign of work done in following reactions at constant pressure.

	Initial state		**Final state**
(i)	$H_2O(g)$	$\longrightarrow$	$H_2O(\ell)$
(ii)	$H_2O(s)$	$\longrightarrow$	$H_2O(g)$
(iii)	$H_2O(\ell)$	$\longrightarrow$	$H_2O(s)$
(iv)	$CaCO_3(s)$	$\longrightarrow$	$CaO(s) + CO_2(g)$

Ans. (i) + , (ii) –, (iii) – , (iv) –

Ex.5 If work done by the system is 300 joule when 100 cal heat is supplied to it. The change in internal energy during the process is :-

(A) – 200 Joule (B) 400 Joule (C) 720 Joule (D) 120 Joule

Ans. (D)

Ex.6 A system has internal energy equal to U_1, 450 J of heat is taken out of it and 600 J of work is done on it. The final energy of the system will be -

(A) (U_1 + 150 J) (B) (U_1 + 1050 J) (C) (U_1 – 150 J) (D) (U_1 – 1050 J)

Ans. (A)

WORK DONE (w) :

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

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

Units :

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

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

1 litre. atm = 101.3 Joules = 24.206 cal

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

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

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

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

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

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

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

1. ISOTHERMAL PROCESS :

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

(a) Isothermal reversible expansion :

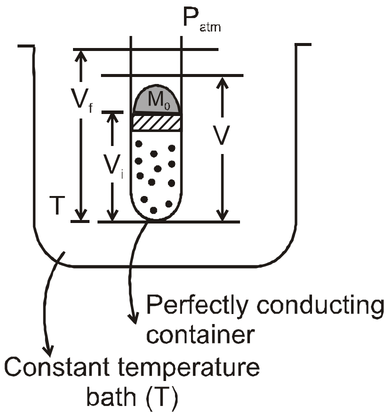
$$P_{ext} = P_0 + \frac{mg}{A} =z\ P_{gas} = P \text{ (always)}$$

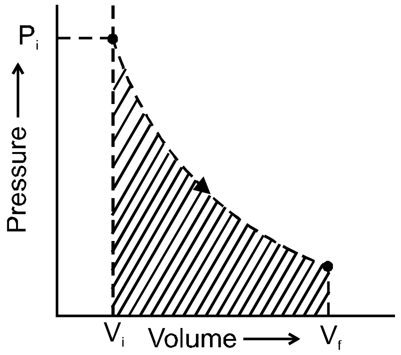
In reversible process, $P_{ext} = P_{gas}$ (thermodynamic equilibrium always)

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

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

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





PV diagram Representation

Work = Area under the P–V diagram

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

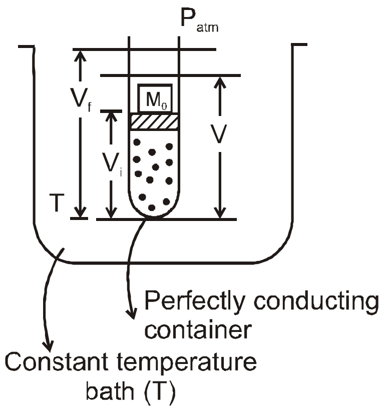
$$W = -ve$$

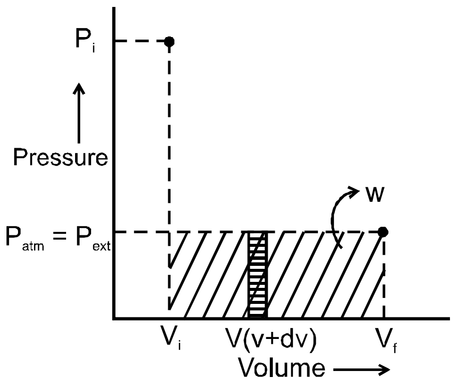
(b) Irreversible isothermal expansion :

(i) Single step isothermal expansion

We are assuming expansion against atmospheric pressure which need not be the case in a given problem. A mass equal to m_0 is placed on piston initially to maintain equilibrium.

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





PV diagram Representation

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

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

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

$V \longrightarrow (V + dV)$

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

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

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

(ii) Two step isothermal expansion :

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

$M_0 = (m_1 + m_2)$

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

$P_{ext_1} = (P_{atm} + m_2g/A)$

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

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

Now, if second mass m_2 is also removed then expansion

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

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

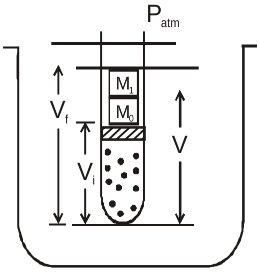
work done is expansion $V_i \longrightarrow V_1$

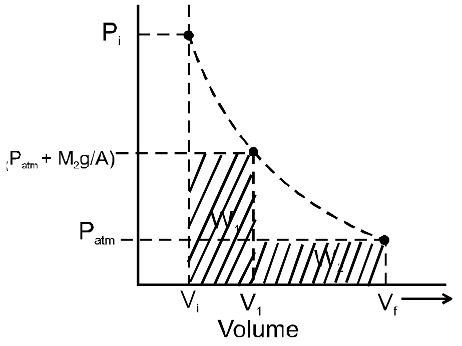
$W_1 = -(P_{atm} + M_2g/A)(V_i - V_1)$

& work done is expansion $V_1 \longrightarrow V_f$

$W_2 = -P_{atm}(V_f - V_i)$

Total work = $W_1 + W_2$



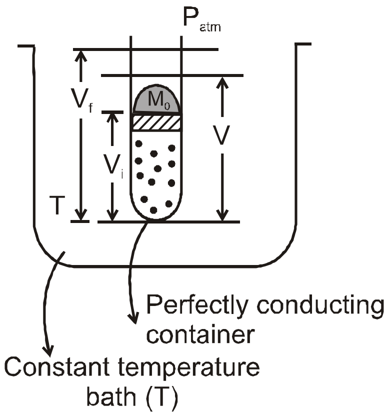


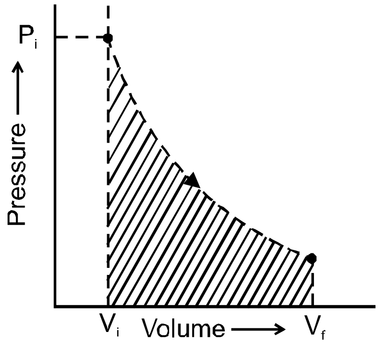
PV Diagram representation

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

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

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





PV Diagram representation

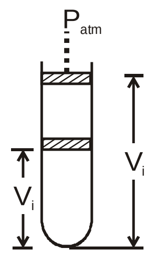
(B) Isothermal compression of ideal gas :

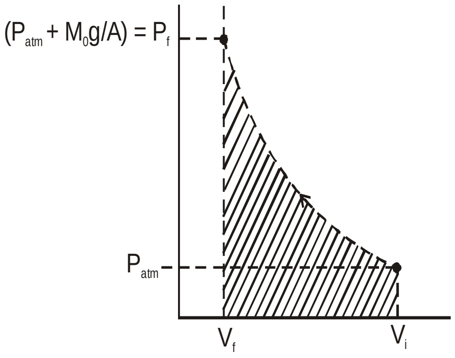
(a) Reversible isothermal compression of an ideal gas

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

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

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





(b) Irreversible isothermal compression of an ideal gas

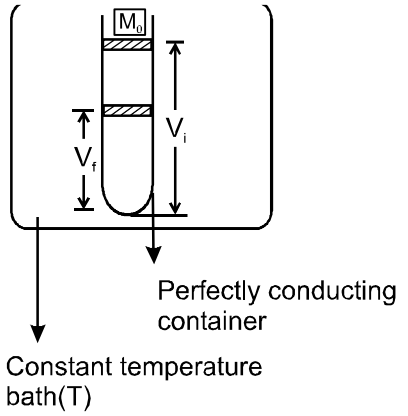
(i) Single step compression :

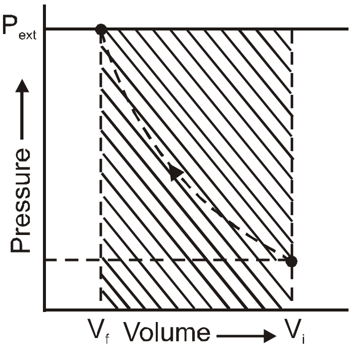
To compress gas a mass m_0 is suddenly placed on massless piston

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

so, to calculate total work done on the gas

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





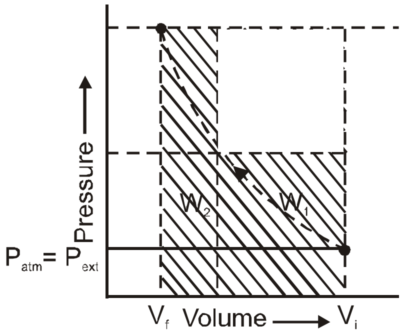
(ii) Two step compression :

Place mass m_0 in two fragments (m_1+m_2) the graphical representation will make the calculation of work done

If m_1 is placed first, then the first compression has taken place aganist external pressure of $(P_{atm} + m_1g/A)$

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

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



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

Conclusion :

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

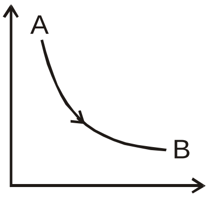
Thats why different machines/engines are designed to work reversibly so maximum output can be obtained but minimum input is given to it.

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

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

Reversible and irreversible isothermal process.

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



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

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

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

SOLVED EXAMPLE

Ex.7 Two moles of an ideal gas undergoes isothermal expansion from 4 L to 20 L at 27°C. Calculate q, w, ΔU and ΔH, if the process is performed.

(i) reversibly

(ii) irreversibly, against a constant external pressure of 1atm.

(iii) as free expansion

Sol. For isothermal process, $\Delta T = 0$. Hence,

$\Delta U = n.C_{v,m}.\Delta T = 0$

$\Delta H = n.C_{p,m}.\Delta T = 0$

(i) $$w = -nRT \cdot \ln\frac{V_2}{V_1} = -2 \times 8.314 \times 300 \times \ln\frac{20}{4} = -8028.52J$$

and $q = -w = 8028.52$ J

(ii) $w = -P_{ext}.(V_2 - V_1) = -1$ atm(20L – 4L) = –16L-atm

= – 16 × 101.3J = – 1620.8J

$q = -w = 1620.8J$

(iii) $w = 0$ and $q = 0$

Ex.8 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]

So. Process is irreversible

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

1 litre atm = 101.3 J

---

2. ISOCHORIC PROCESS :

Since $dv = 0$

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

3. ISOBARIC PROCESS :

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

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

Calculation of C_p and C_v

(a) Constant volume process (Isochoric)

$dU = dq + dw$

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

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

$dU = nC_v dT$

C_v is Specific molar heat capacity at constant volume.

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

(b) Constant pressure process (Isobaric) :

$dU = dQ + dW$

$dU = dQ - PdV$

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

Defining a new thermodynamic function

$H \equiv$ Enthalpy

- It is a state function and extensive property

- It is mathematically defined as :

$H = U + PV$

as $dH = dU + d(Pv)$

as $P = \text{constant}$

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

$PV = nRT$

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

$nC_p\,dT = nC_vdT + nRdT$

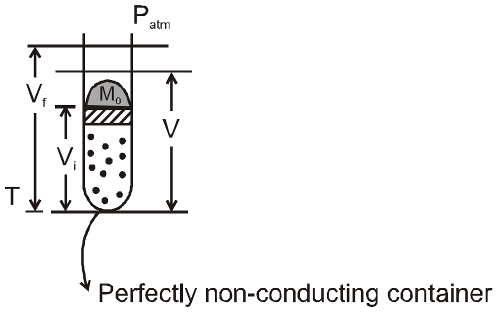
$\Rightarrow$ $\mathbf{C_p - C_v = R}$ only for ideal gas $\Rightarrow$ Mayer's Relationship

Table # 1 **At Normal temperature**

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

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

4. ADIABATIC PROCESS :



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

$dU = dQ + dW$

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

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

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

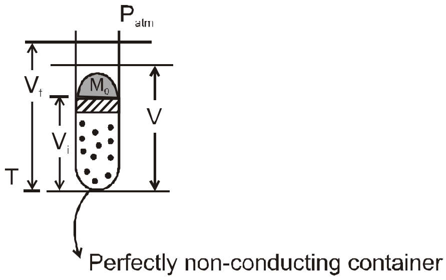
$$T_2V_2^{\gamma-1} = T_1V_1^{\gamma-1} \qquad \text{or} \qquad TV^{\gamma-1} = \text{constant}$$

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

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

Operation of adiabatic process

(a) Reversible Adiabatic



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

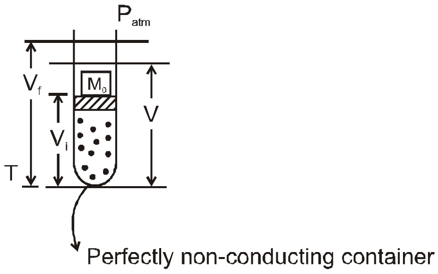
$$w = -\int P_{ext.}\,dv\,, \qquad \text{but} \qquad P_{ext} = P_{int} = \frac{K}{V^{\gamma}}$$

$$\therefore\ w = -\int \frac{K}{V^{\gamma}}.\,dv\,, \qquad \Rightarrow W = -K\,\frac{\left[V_2^{-\gamma+1} - V_1^{-\gamma+1}\right]}{(1-\gamma)} = \frac{P_2V_2^{\gamma}.V_2^{1-\gamma} - P_1V_1^{\gamma}.V_1^{1-\gamma}}{\gamma-1}$$

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

(b) Irreversible Adiabatic

- **Adiabatic irreversible expansion –**

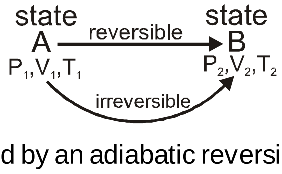


$$W = \int -P_{ext.}dv \quad = -P_{ext}(V_2 - V_1)\,, \qquad \text{and} \qquad \int du = \int dw$$

$$\therefore \qquad W = \Delta u$$

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

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



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

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

But as u is a state function

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

as work is a path function.

If we assume that

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

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

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

Comparison of Adiabatic Expansion (single stage Vs Infinite stage)

Single stage means irreversible process

Infinite stage means reversible process

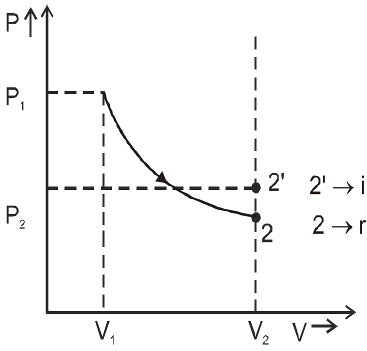
In adiabatic compression process,

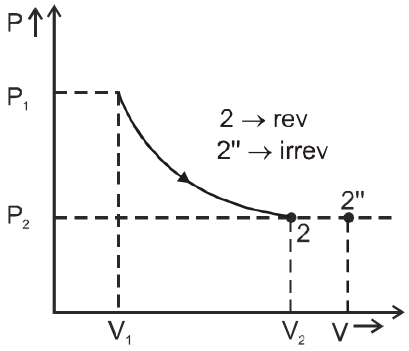
$(W_{gas})_{rev} < (W_{gas})_{irrev} \Rightarrow \Delta u_{rev.} < \Delta u_{irrev.}$

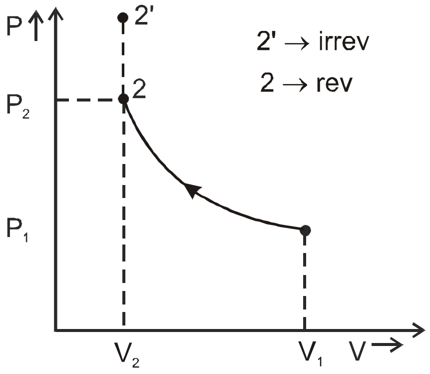
$\therefore \quad (T_2)_{rev.} < (T_2)_{irrev}$

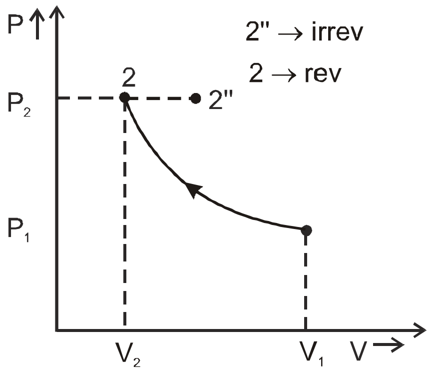
$(P_2)_{rev.} < (P_2)_{irrev}$ (If volume change are same)

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









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

❍ Adiabatic Irreversible process (calculation of state parameters)

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

P_1,V_1,T_1 P_2,V_2,T_2

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

- **Free expansion –**

  Always going to be irrerversible and since $P_{ext} = 0$

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

  $= 0$

  If no heat is supplied $q = 0$

  then $\Delta E = 0$ So, $\Delta T = 0$.

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

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

the formula to be used are

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

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

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

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

$$du = dQ + dw$$

SOLVED EXAMPLE

Ex.9. Two moles of an ideal monoatomic gas undergoes adiabatic expansion from 5L, 127°C to 40L. Calculate q, ΔU, w and ΔH, if the process is performed.

(i) reversibly

(ii) irreversibly, against a constant external pressure of 0.1atm.

(iii) as free expansion

Sol. : For adiabatic process, $q = 0$

(i) $T \cdot V^{\gamma-1} = \text{constant} \Rightarrow T_1 \cdot V_1^{\gamma-1} = T_2 \cdot V_2^{\gamma-1}$

$$\therefore\ T_2 = T_1\left(\frac{V_1}{V_2}\right)^{\gamma-1} = 400 \times \left(\frac{5}{40}\right)^{\frac{5}{3}-1} = 100\text{K}$$

Now, $w = \Delta U = nC_v\Delta T = -7482.6$ J

$\Delta H = \gamma\Delta U = -12471$ J

(ii) $\Delta U = w = -P_{ext}.(V_2 - V_1) = -0.1 \times (40 - 5) \times 101.3 = -354.55$J

and $\Delta H = \frac{5}{3} \cdot \Delta U = -590.92\text{J}$

(iii) $\Delta U = w = 0$

and $\Delta H = 0$

Ex.10. Five moles of an ideal monoatomic gas undergoes adiabatic expansion from 12 atm to 1 atm, against a constant external pressure of 1 atm. If the initial temperature of gas is 27°C, calculate the final temperature. Also calculate q, ΔU, w and ΔH.

Sol. : $q = 0$

$\Delta U = w$

or, $n.C_{v,m}.(T_2 - T_1) = -P_{ext}.(V_2 - V_1)$

or, $n.\frac{3}{2}R(T_2 - T_1) = -P_2\left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1}\right)$

or, $\frac{3}{2}(T_2 - 300) = -\left(T_2 - 300 \times \frac{1}{12}\right)$

$\Rightarrow$ $T_2 = 190K$

or, $\Delta U = w = 5 \times \frac{3}{2}R \times (190 - 300) = -6859.05J$

and $\Delta H = \gamma.\Delta U = -11431.75J$

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

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

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

Ex.11. A liquid of volume of 100 L and at the external pressure of 10 atm–Lt the liquid is confined inside an adiabatic bath. External pressure of the liquid is suddenly increased to 100 atm and the liquid gets compressed by 1L against this pressure then find,

(i) work (ii) ΔU (iii) ΔH

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

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

$\Rightarrow$ $100 = \Delta U$

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

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

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

1 L. atm = 101.3 Joule.

Case - III **For chemical reactions :**

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

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

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

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

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

$$= -P_{ext.}\left[\frac{n'_C RT}{P_{ext}} - \frac{n_C RT}{P_{ext}}\right] = -\frac{P_{ext.}(n'_C - n_C)RT}{P_{ext.}}$$

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

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

$dU = dq + dw$

if at constant pressure

$dq = dH$

$\therefore \quad dU = dH - pdV$

$dU = dH - \Delta ng RT$

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

SOLVED EXAMPLE

Ex.12. 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?

Solution : We have, $\Delta H = \Delta E + \Delta n_g RT$

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

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

Case - IV During phase transformation.

Phase transitions generally take place at constant pressure (unless specified) and at constant temperature.

So, $\Delta T = 0$

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

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

Also, during this phase transition $\Delta(PV) \neq 0$

Hence, $\Delta H \neq 0$.

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

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

SOLVED EXAMPLE

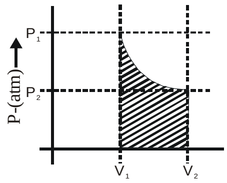
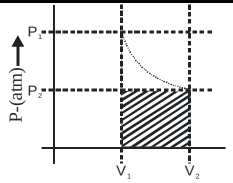
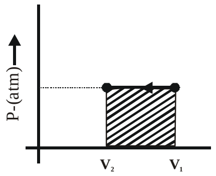
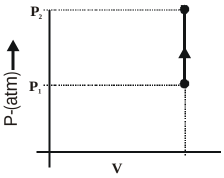
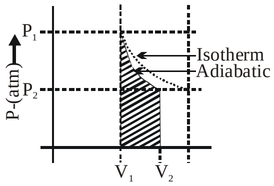
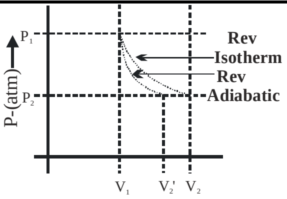
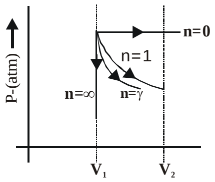
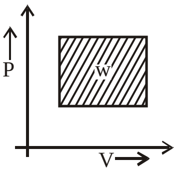
Ex.13. 90 gm water is completely converted into steam at 100°C and 1 atm. Calculate q, ΔU, w and ΔH. Latent heat of vaporisation of water at 100°C is 540 cal/gm.

Sol. : $\Delta H = m.L = 90 \times 540 = 48600$ cal

$$w = -P(V_{vap} - V_{water}) = -P.V_{vap} = -nRT = -\frac{90}{18} \times 2 \times 373 = -3730 \text{ cal}$$

$\Delta U = q + w = 48600 + (-3430) = 44870$cal

10. SUMMARY

Process	Expression for w	Expression for q	ΔU	ΔH	Work on PV-graph
Reversible isothermal	$w = -nRT\ln\frac{V_2}{V_1}$ $= -nRT\ln\frac{P_1}{P_2}$	$q = nRT\ln\left(\frac{V_2}{V_1}\right)$ $q = nRT\ln\left(\frac{P_1}{P_2}\right)$	**0 process**	**0**	
Irreversible isothermal	$w = -P_{ext}(V_2 - V_1)$ $= -P_{ext}\left(\frac{nRT}{P_2} - \frac{nRT}{P_1}\right)$	$q = P_{ext}(V_2 - V_1)$	**0**	**0**	
Isobaric process	$w = -P_{ext}(V_2 - V_1)$ $= -nR\Delta T$	$q = \Delta H = nC_P\Delta T$	$\Delta U = nC_V\Delta T$	$\Delta H = nC_P\Delta T$	
Isochoric process	**w = 0**	$q = \Delta U = nC_V\Delta T$	$\Delta U = nC_V\Delta T$	$\Delta H = nC_P\Delta T$	
Reversible adiabatic process	$w = nC_V(T_2 - T_1)$ $= \frac{P_2V_2 - P_1V_1}{\gamma - 1}$	**q = 0** PV^{γ}=constant $TV^{\gamma-1}$=constant $TP^{1-\gamma/\gamma}$=constant	$\Delta U = nC_V\Delta T$	$\Delta H = nC_P\Delta T$	
Irreversible adiabatic process	$w = nC_V(T_2 - T_1)$ $= \frac{P_2V_2 - P_1V_1}{\gamma - 1}$	**q = 0** $nC_v(T_2 - T_1) =$ $-P_{ext}\left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1}\right)$	$\Delta U = nC_V\Delta T$	$\Delta H = nC_P\Delta T$	
Polytropic	$w = \frac{P_2V_2 - P_1V_1}{n - 1}$ $w = \frac{R(T_2 - T_1)}{(n - 1)}$	$q = \int_{T_1}^{T_2} C_V dT$ $w = \frac{R(T_2 - T_1)}{(n - 1)}$	$\Delta U = nC_V\Delta T$	$\Delta H = nC_P\Delta T$	
Cyclic Process	**Area encolsed in PV-diagram** **For clockwise –ive** **For anticlockwise +ive**	**q = –w**	**0**	**0**	

MISCELLANEOUS SOLVED PROBLEMS (MSPs)

1. Which of the following are extensive and which are intensive properties ?

Temperature, boiling point, melting point, pressure , density , viscosity , surface tension, refractive index, molar volume, free energy/mole, specific heat, Specific volume , Mass , Volume , number of moles , Heat capacity, internal energy, enthalpy , entropy , ΔG, concentration, dipole moment, pH, gas constant, vapour pressure, specific gravity, E.M.F. of the dry cell, molarity, molality .

Sol. **Intensive property :** Temperature, (boiling point, melting point), pressure , density , viscosity, surface tension, refractive index, molar volume, free energy/mole, specific heat, Specific volume, concentration, dipole moment, pH, gas constant, vapour pressure, specific gravity, E.M.F. of the dry cell, molarity, molality.

Extensive property : Mass , Volume , number of moles , Heat capacity , internal energy, enthalpy, entropy

2. Which of the following are state function & path function ?

Pressure, Volume, Enthalpy, Work, Heat, Gibbs energy, temperature, Internal energy, Entropy

Sol. **State function :** Pressure, volume , enthalpy, Gibbs energy, temperature, Internal energy, Entropy

Path function : Work , Heat

3. A state function is that :

(A) which is used in thermochemistry

(B) which obeys all laws of thermodynamics

(C) quantity whose value depends only upon the state of the system

(D) quantity which is used in measuring thermal change

Ans. (C)

4. Which amongst the following is an extensive property of the system -

(A) Temperature (B) Volume (C) Viscosity (D) Refractive index

Ans. (B)

5. Which of the following is not a state function of thermodynamic system -

(A) Internal energy(E) (B) Free energy(G)

(C) Enthalpy(H) (D) Work(W)

Ans. (D)

6. What is true for a cyclic process

(A) W= 0 (B) Δ E = 0 (C) Δ H = 0 (D) B & C both

Ans. (D)

7. The internal energy change when a system goes from state A to B is 40 kJ/mole. If the system goes from A to B by a reversible path and returns to state A by an irreversible path what would be the net change in internal energy ?

(A) < 40 kJ (B) Zero (C) 40 kJ (D) > 40 kJ

Ans. (B)

8. Explain why variation of enthalpy for a process involving an ideal gas is given by $dH = nC_P dT$, irrespective of process ?

Sol. Because

$H_{\text{ideal gas}} = f(T)$, independent of pressure or volume

9. The heat capacity of a molecule depends upon complexity of the molecule. Explain ?

Sol. The heat capacity can be defined as energy needed to raise the temperature of a body by 1°C. The molecule which have large number of degree's of freedom requires larger quantity of heat to raise the temperature by 1°C. This is because energy supplied is distributed in each degree of freedom equally.

10. One mole of a gas absorbs 200J of heat at constant volume. Its temperature rises from 298 K to 308 K. The change in internal energy is :-

(A) 200 J (B) –200 J (C) $200 \times \frac{308}{298}$ J (D) $200 \times \frac{298}{308}$ J

Ans. (A)

11. The work done by a system is 8J when 40J heat is supplied to it. The change in internal energy of the system during the process :

(A) 32 J (B) 40 J (C) 48 J (D) –32 J

Ans. (A)

12. Two moles of an ideal gas expand spontaneously into vacuum. The work done is :–

(A) Zero (B) 2 J (C) 4 J (D) 8 J

Ans. (A)

13. The work done during the expansion of a gas from a volume of 4 dm^3 to 6 dm^3 against a constant external pressure of 3 atm is -

(A) –608 J (B) +304 J (C) –304 J (D) –6 J

Ans. (A)

14. Assuming that water vapour is an ideal gas, the internal energy change (ΔU) when 1 mol of water is vapourised at 1 bar pressure and 100°C, (Given : Molar enthalpy of vapourisation of water at 1 bar and 373 K = 41 kJ mol^{-1} and R = 8.3 J mol^{-1} K^{-1} will be) :-

(A) 4.100 kJ mol^{-1} (B) 3.7904 kJ mol^{-1} (C) 37.904 kJ mol^{-1} (D) 41.00 kJ mol^{-1}

Ans. **(C)**

15. A piston filled with 0.04 mol of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37.0°C. As it does so, it absorbs 208 J of heat. The values of q and w for the process will be :-
(R = 8.314 J/mol K) (In 7.5 = 2.01)

(A) q = + 208 J, w = – 208 J (B) q = – 208 J, w = – 208 J

(C) q = – 208 J, w = + 208 J (D) q = + 208 J, w = + 208 J

Ans. (A)

Sol. q = + 208 Joule

for isothermal process

$\Delta U = 0$

$\because$ from Ist law of thermodynamics

$\Delta U = q + w$

$0 = q + w$

$\Rightarrow$ $w = -q = -208$ Joule

16. Find the work done when one mole of the gas is expanded reversibly and isothermally from 5 atm to 1 atm at 27°C. (ln5 = 1.6)

Ans. w = –3.99 kJ

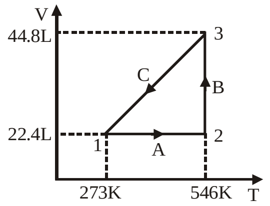
17. Five moles of an ideal gas at 300 K, expanded isothermally from an initial pressure of 4 atm to a final pressure of 1 atm against a constant external pressure of 1 atm. Calculate q, w, ΔU & ΔH. Calculate the corresponding value of all if the above process is carried out reversibly. (ln2 = 0.7)

Ans. $w_{irr} = -225\ R$, $w_{rev} = -210\ R$, $\Delta U = \Delta H = 0$, $q = -w$

18. One mole of an ideal monoatomic gas is carried through the reversible cycle of the given figure consisting of step A, B and C and involving state 1, 2 and 3. Fill in the blank space in the table given below assuming reversible steps.

Table-1

State	P	V	T
1			
2			
3			



Step	Name of process	q	w	ΔU	ΔH
A					
B					
C					
overall					

Ans.

Table-1

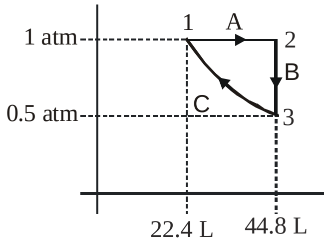
State	**P**	**V**	**T**
1	1 atm	22.4	273
2	2 atm	22.4	546
3	1 atm	44.8	546

Step	**Name of process**	**q**	**w**	**ΔE**	**ΔH**
A	Isochoric	3/2 R (273)	0	3/2 R (273)	5/2 R(273)
B	Isothermal	546 R ln 2	–546 Rln2	0	0
C	Isobaric	–5/2 R(273)	R(273)	–3/2 R (273)	–5/2 R(273)

19. One mole of an ideal monoatomic gas is put through reversible path as shown in figure. Fill in the blank in the tables given below.

Table-1

State	P	V	T
1			
2			
3			



Step	Name of process	q	w	ΔU	ΔH
A					
B					
C					
	cyclic				

Ans.

Table-1

State	P	V	T
1	1 atm	22.4	273
2	1	44.8	546
3	0.5	44.8	273

Step	Name of process	q	w	ΔE	ΔH
A	Isobaric	5/2 R (273)	–R(273)	3/2 R (273)	5/2 R(273)
B	Isochoric	– 3/2 R (273)	0	– 3/2 R (273)	– 5/2 R (273)
C	Isothermal	– 273 R ln2	273 R ln2	0	0
	Cyclic	R(273) – 273 Rln2	–R(273)+ 273R ln2	0	0

20. $\frac{1}{22.4}$ mol of an ideal monoatomic gas undergoes a reversible process for which $PV^2 = C$. The gas is expanded from initial volume of 1 L to final volume of 2 L starting from initial temperature of 273 K. Find the heat exchanged q during the process. Express your answer in litre atm.

$R = \frac{22.4}{273}$ L atm mole^{-1} degree^{-1}.

Ans. –0.25

21. An ideal gas is allowed to expand both adiabatic reversibly and adiabatic irreversibly. If T_i is the initial temperature and T_f is the final temperature, which of the following statements is correct :-

(A) $T_f > T_i$ for reversible process but $T_f = T_i$ for irreversible process

(B) $(T_f)_{rev} = (T_f)_{irrev}$

(C) $T_f = T_i$ for both reversible and irreversible processes

(D) $(T_f)_{irrev} > (T_f)_{rev}$

Ans. (D)

22. Which of the following statements/relationships is not correct in thermodynamic changes ?

(A) $q = -nRT\,\ell n\frac{V_2}{V_1}$ (isothermal reversible expansion of an ideal gas)

(B) For a system at constant volume, heat involved merely changes to internal energy.

(C) $w = -nRT\ln\frac{V_2}{V_1}$ (isothermal reversible expansion of an ideal gas)

(D) $\Delta U = 0$ (isothermal reversible expansion of a gas)

Ans. (A)

Exercise # 1

✍ **Marked Questions may have for Revision Questions.**

PART - I : SUBJECTIVE QUESTIONS

Section (A) : Basic definitions

A-1.✍ Categorize these properties into state and path functions.

(a) Internal energy (b) Volume (c) Heat (d) Enthalpy
(e) Temperature (f) Work (g) Molar heat capacity

A-2.✍ Categorize these properties into extensive and intensive

(a) Temperature (b) Internal energy (c) Heat (d) Density
(e) Molar volume (f) molar enthalpy (g) viscosity

Section (B) : Thermodynamics processes & graph

Draw the P-V diagram for the following cyclic processes

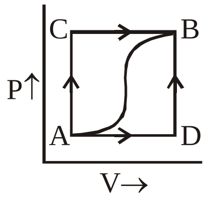
B-1. Isothermal expansion from state A to B, isochoric pressure increment from B to C, isothermal contraction from C to D, isobaric contraction from D → A.

B-2. Isobaric expansion from A → B, isochoric pressure increase from B → C, isobaric compression from C → D, isochoric pressure drop from D → A.

B-3. Isobaric expansion from A → B, isochoric pressure drop from B → C, isothermal compression C → A.

Section (C) : Work calculation

C-1. When a system is taken from state A to state B along the path ACB, 80J of heat flows into the system and the system does 30J of work.



(a) How much heat flows into the system along path ADB if the work done by the system is 10J ?

(b) When the system is returned from state B to A along the curved path,the work done on the system is 20J. Does the system absorb or liberate heat, and how much ?

(c) If $U_D - U_A = 40$J, find the heat absorbed in the process AD and DB if work done by system in ADB is 10 Joule.

C-2. Calculate the work done by 0.1 mole of a gas at 27^0 C to double its volume at constant pressure (R = 2 cal mol^{-1} K^{-1}) (R = 2 cal mol^{-1} K^{-1})

C-3. Calculate the work done during isothermal reversible expansion of one mole ideal gas from 10 atm to 1 atm at 300 K.

C-4.✍ At 25ºC, a 0.01 mole sample of a gas is compressed in volume from 4.0 L to 1.0 L at constant temperature. What is work done for this process if the external pressure is 4.0 bar ?

Section (D) : Heat & Internal energy

D-1. 2 mole of an ideal gas undergoes isothermal compression along three different paths if it's initial state is (2 bar, 4 litre) in all three process.

(i) Reversible compression from till 20 bar.

(ii) A single stage compression against a constant external pressure of 20 bar

(iii) A two stage compression consisting initially of compression against a constant external pressure of 10 bar until $P_{gas}=P_{ext}$, followed by compression against a constant pressure of 20 bar until $P_{gas}=P_{ext}$.

Calculate the work (in bar. L) for each of these processes and for which of the irreversible processes is the magnitude of the work greater ? [Given : R = 0.08 bar. L/mole.K]

D-2. Calculate the number of kJ necessary to raise the temperature of 60 g of aluminimum from 35ºC to 55ºC. Molar heat capacity of Al is 24 $mole^{-1}$ K^{-1}.

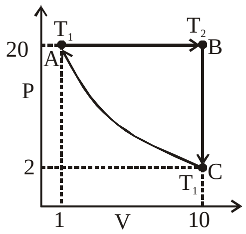
D-3. In a container, two mole of a diatomic ideal gas is allowed to expand against 1 atm pressure & volume change from 2 litre to 5 litre then calculate change in internal enrgy.

Section (E) : First law of thermodynamics

E-1. One mole of a perfect monoatomic gas is put through a cycle consisting of the following three reversible steps :

(CA) Isothermal compression from 2 atm and 10 litres to 20 atm and 1 litre.

(AB) Isobaric expansion to return the gas to the original volume of 10 litres with T going from T_1 to T_2. (BC) Cooling at constant volume to bring the gas to the original pressure and temperature. The steps are shown schematically in the figure shown.



(a) Calculate T_1 and T_2

(b) Calculate ΔU, q and w (in calories) for the cycle.

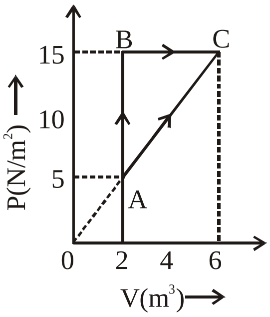
[Given : ln10 = 2.3, R = 0.821 atm.litre/mol-K or R = 2 cal/mol.K]

E-2. The given figure shows a change of state A to state C by two paths ABC and AC for an ideal gas. Calculate the :

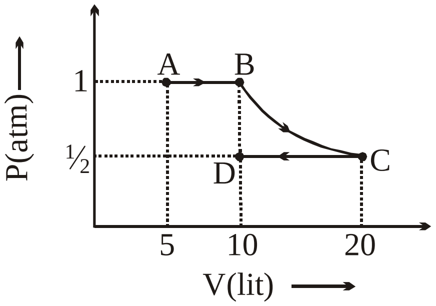
(a) Path along which magnitude of work done is least ABC or AC

(b) Internal energy at C if the internal energy of gas at A is 10 J and amount of heat supplied to change its state to C through the path AC is 200J.

(c) Amount of heat supplied to the gas to go from A to B, if internal energy change of gas from A to B is 10 J.



E-3.



Calculate magnitude of total work done (in atm.lit) for the above process ABCD involving a monoatomic ideal gas. **[Given : *l*n 2 = 0.7]**

E-4. The work done by a system is 8 joule, when 40 joule heat is supplied to it. What is the increase in internal energy of system.

E-5. A gas expands from 2 L to 6 L against a constant pressure of 0.5 atm on absorbing 200 J of heat. Calculate the change in internal energy.

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

F-1. Two mole of ideal diatomic gas ($C_{V,m}$ = 5/2 R) at 300K and 5 atm expanded irreversibly & adiabatically to a final pressure of 2 atm against a constant pressure of 1 atm. Calculate q, w, ΔH & ΔU.

F-2. Calculate the work done by system in an irreversible (single step) adiabatic expansion of 1 mole of a polyatomic gas (γ = 4/3) from 400 K and pressure 10 atm to 1 atm.

F-3. One mole of an ideal monoatomic gas $\left(\gamma = \frac{5}{3}\right)$ is mixed with one mole of a diatomic gas $\left(\gamma = \frac{7}{5}\right)$. ($\gamma$ denotes the ratio of specific heat at constant pressure, to that at constant volume) find γ for the mixture?

F-4. A piston freely move in a insulated cylinder from volume 5 lit to 10 lit then calculate work done & heat during this expansion.

Section (G) : Enthalpy

G-1. If 1.0 kcal of heat is added to 1.2 L of O_2 in a cylinder at constant pressure of 1 atm, the volume increases to 1.5 L. Calculate ΔU and ΔH of the process. (1 L- atm = 100 J)

G-2.✍ 10 g of argon gas is compressed isothermally and reversibly at a temperature of 27^0C from 10 L to 5L. Calculate enthalpy change (ΔH) for this process R = 2.0 cal K^{-1} mol^{-1}. $\log_{10}2 = 0.30$
Atomic mass of Ar = 40

Section (H) : Phase transition :

H-1. Water expands when it freezes. Determine amount of work done , in joules, when a system consisting of 1.0 L of liquid water freezes under a constant pressure of 1.0 atm and forms 1.1 L of ice.

H-2.✍ What is ΔU when 2.0 mole of liquid water vaporises at 100ºC ? The heat of vaporisation ($\Delta H_{vap.}$) of water at 100ºC is 40.66 KJmol^{-1}.

PART - II : OBJECTIVE TYPE QUESTIONS

Section (A) : Basic definitions

A-1.✍ Out of boiling point (I), entropy (II), pH (III) and e.m.f. of a cell (IV), intensive properties are :
(A) I, II (B) I, II, III (C) I, III, IV (D) All of the above

A-2.✍ Predict the total number of intensive properties :
(i) Free energy (ii) Critical density (iii) Viscosity (iv) Specific heat capacity
(v) molar heat capacity (vi) Kinetic energy (vii) Specific gravity (viii) Dielectric constant
(ix) pH
(A) 9 (B) 8 (C) 7 (D) 6

A-3. An ideal gas filled at pressure of 2 atm and temp of 300 K, in a balloon is kept in vacuum with in a large insulated container wall of balloon is punchtured then container temperature :
(A) Decreases (B) Increases (C) Remain constant (D) Unpredictable

A-4. Internal pressure of a perfect gas (ideal gas) is :
(A) Zero (B) infinite
(C) Calculated by PV = nRT (D) Can not say directally

Section (B) : Thermodynamics processes & graph

B-1. A gaseous system changes from state A (P_1, V_1, T_1) to B (P_2, V_2, T_2), B to C (P_3, V_3, T_3) and finally from C to A. The whole process may be called :

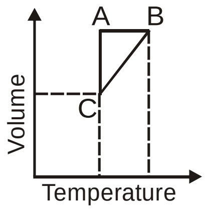
(A) Reversible process (B) Cyclic process (C) Isobaric process (D) Spontaneous process

B-2. A well stoppered thermoflask contains some ice cubes. This is an example of a-

(A) Closed system (B) Open system

(C) Isolated system (D) Non-thermodynamic system

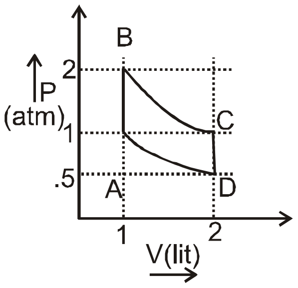
B-3. Five moles of a gas is put through a series of changes as shown graphicallay in a cyclic process the A $\rightarrow$ B, B $\rightarrow$ C and C $\rightarrow$ A respectively are

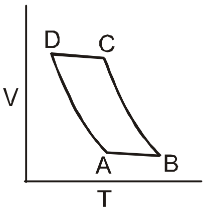


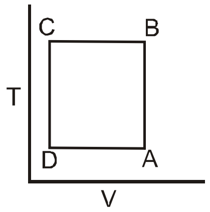
(A) Isochoric, Isobaric, Isothermal (B) Isobaric, Isochoric, Isothermal

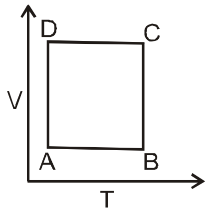
(C) Isothermal, Isobaric, Isochoric (D) Isochoric, Isothermal, Isobaric

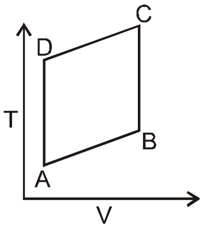
B-4. A cycle process ABCD is shown in P-V diagram for an ideal gas which of the diagram represent the same process.



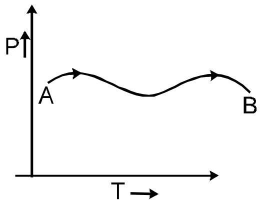
(A)


(B)


(C)


(D)


B-5. The P-T graph as given below was observed for a process on an ideal gas, which of the following statement is true.



(A) w = +ve, ΔH = +ve (B) w = –ve, ΔH = – ve

(C) w = –ve, ΔH = + ve (D) w = +ve, ΔH = –ve

B-6. In a laboratory, liquid in a thermally insulated container is stirred for one hr, by a mechanical linkage to a in surrounding, for this process :

(A) $W < 0; q = 0$ (B) $W < 0; q > 0$ (C) $W < 0; q > 0$ (D) $W > 0 ; q = 0$

Section (C) : Work Calculation

C-1. A thermodynamic system goes from states (i) P_1, V to $2P_1$, V (ii) P, V_1 to P, $2V_1$. Then work done in the two cases is

(A) Zero, Zero (B) Zero, $-PV_1$ (C) $-PV_1$, Zero (D) $-PV_1, -P_1V_1$

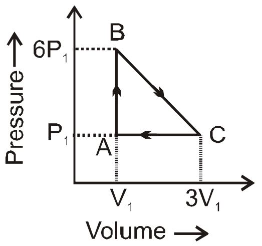
C-2. The work done in ergs for the reversible expansion of one mole of an ideal gas from a volume of 10 litres to 20 litres at 25^{0}C is :

(A) $-2.303 \times 298 \times 0.082 \log 2$ (B) $-298 \times 10^7 \times 8.31 \times 2.3031 \log 2$

(C) $-2.303 \times 298 \times 0.082 \log 0.5$ (D) $-8.31 \times 10^7 \times 298 \times 2.303 \log 0.5$

C-3. An ideal gas is taken around the cycle ABCA as shown in P-V diagram.

The net work done by the gas during the cycle is equal to :



(A) $12P_1V_1$ (B) $6P_1V_1$

(C) $5P_1V_1$ (D) P_1V_1

Section (D) : Heat & Internal energy

D-1. Freezing up liquid in a system then :

(A) $q = 0$ (B) $q > 0$

(C) $q < 0$ (D) $q > 0$ or $q < 0$ (depending on the nature of liquid)

D-2. One mole of an ideal monoatomic gas expanded irreversibly in two stage expansion.

State-1 (8.0 bar, 4.0 litre, 300 K)
State-2 (2.0 bar, 16litre, 300 K)
State-3 (1.0 bar, 32 litre, 300 K)

Total heat absorbed by the gas in the process is :

(A) 116J (B) 40 J (C) 4000 J (D) None of these

D-3. An ideal gas undergoes isothermal expansion from A(10 atm, 1l) to B(1 atm, 10 l) either by

(I) Infinite stage expansion or by

(II) First against 5 atm and then against 1 atm isothermally

Calculate $\frac{q_I}{q_{II}}$:

(A) $\frac{1}{13\times 2.303}$ (B) 13×2.303 (C) $\frac{13}{23.03}$ (D) $\frac{23.03}{13}$

D-4. Two moles of an ideal gas ($C_V = \frac{5}{2}R$) was compressed adiabatically against constant pressure of 2 atm, which was initially at 350 K and 1 atm pressure. The work involve in the process is equal to -

(A) 250 R (B) 300 R (C) 400 R (D) 500 R

D-5. A gas is expanded from volume V_1 to V_2 through three different process :

(a) Reversible adiabatic (b) Reversible isothermal (c) Irreversible adiabatic

The correct statements is -

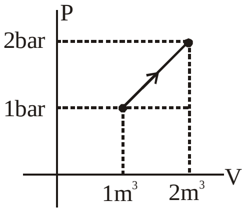
(A) $(T_f)_{\text{Reversible Isothermal}} > (T_f)_{\text{Reversible adiabatic}} > (T_f)_{\text{Irreversible adiabatic}}$

(B) $(T_f)_{\text{Reversible Isothermal}} > (T_f)_{\text{Irreversible adiabatic}} > (T_f)_{\text{Reversible adiabatic}}$

(C) $W_{\text{Reversible Isothermal}} > W_{\text{Irreversible adiabatic}} > W_{\text{reversible adiabatic}}$

(D) $(P_f)_{\text{Reversible Isothermal}} > (P_f)_{\text{Reversible adiabatic}} > (P_f)_{\text{Irreversible adiabatic}}$

D-6. What is ΔU for the process described by figure. Heat supplied during the process q = 200 kJ.



(A) +50 kJ (B) –50 kJ

(C) –150 kJ (D) + 150 kJ

D-7. For an ideal monoatomic gas during any process T = kV, find out the molar heat capacity of the gas during the process. (Assume vibrational degree of freedom to be active)

(A) $\frac{5}{2}R$ (B) 3R (C) $\frac{7}{2}$ (D) 4R

Section (E) : First law of thermodynamics

E-1. A system absorb 600J of heat and work equivalent to 300J on its surroundings. The change in internal energy is

(A) 300 J (B) 400 J (C) 500 J (D) 600 J

E-2. In an isochoric process the increase in internal energy is

(A) Equal to the heat absorbed (B) Equal to the heat evolved

(C) Equal to the work done (D) Equal to the sum of the heat absorbed and work done

E-3.✍ In an isothermal expansion of an ideal gas. Select wrong statement :

(A) there is no change in the temperature of the gas

(B) there is no change in the internal energy of the gas

(C) the work done by the gas is equal to the heat supplied to the gas

(D) the work done by the gas is equal to the change in its internal energy

E-4. A system undergoes a process which absorbed 5 kJ of heat and undergoing an expansion against external pressure of 1 atm, during the process change in internal energy is 300 J. Then predict the change in volume (lit.)

(A) 1 (B) 2 (C) 3 (D) 4

E-5.✍ When two moles of Hydrogen atoms join together to form a mole of hydrogen molecules in a rigid vessel

$$H\,(g) + H\,(g) \longrightarrow H_2\,(g)$$

(A) w < 0 (B) ΔU = negative

(C) q_{system} = positive (D) $q_{\text{surroundin}}$ = negative

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

F-1. The temperature of the system decreases in an

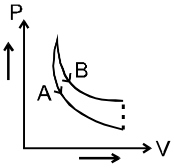
(A) Adiabatic compression (B) Isothermal compression

(C) Isothermal expansion (D) Adiabatic expansion

F-2. 1 mole of NH_3 gas at 27°C is expanded in reversible adiabatic condition to make volume 8 times ($\gamma = 1.33$). Final temperature and work done respectively are :

(A) 150 K, 900 cal (B) 150 K, 400 cal (C) 250 K, 1000 cal (D) 200 K, 800 cal

F-3.✍ In figure, A and B are two adiabatic curves for two different gases. Then A and B corresponds to :



(A) Ar and He respectively (B) He and H_2 respectively

(C) O_2 and H_2 respectively (D) H_2 and He respectively

F-4. If W_1 ; W_2 & W_3 are magnitude of work done of an ideal gas in isothermal, adiabatic & isobaric reversible expansion process from same initial stage to same final volume. Then correct order will be :

(A) $W_3 > W_1 > W_2$ (B) $W_3 > W_2 > W_1$ (C) $W_2 > W_1 > W_3$ (D) $W_1 > W_2 > W_3$

Section (G) : Enthalpy

G-1. One mole of non-ideal gas undergoes a change of state (1.0 atm, 3.0 L, 200 K) to (4.0 atm, 5.0 L, 250 K) with a change in internal energy (ΔU) = 40 L-atm. The change in enthalpy of the process in L-atm ;

(A) 43 (B) 57 (C) 42 (D) None of these

G-2. For the isothermal expansion of an ideal gas

(A) U and H increases (B) U increases but H decreases

(C) H increases but U decreases (D) U and H are unaltered

G-3. A vessel contains 100 litres of a liquid X. Heat is supplied to the liquid in such a fashion that, Heat given = change in enthalpy. The volume of the liquid increases by 2 litres. If the external pressure is one atm, and 202.6 Joules of heat were supplied then, [U - total internal energy]

(A) $\Delta U = 0$, $\Delta H = 0$ (B) $\Delta U = +202.6J$, $\Delta H = +202.6$ J

(C) $\Delta U = -202.6J$, $\Delta H = -202.6J$ (D) $\Delta U = 0$, $\Delta H = +202.6J$

Section (H) : Phase transition

H-1.✍_ $H_2O(s) \to H_2O(\ell)$

This phase transition is carried out at constant temp and pressure then work done during the process :

(A) W < 0 (B) W > 0 (C) W = 0 (D) can't detamined

$H_2O(s) \to H_2O(\ell)$

H-2. At 1 atm pressure freezing of n mole of water liquid (0ºC) to ice(0ºC) then heat transfer :

(A) $n\Delta H_{fusion}$ (B) $-n\,\Delta H_{fusion}$ (C) $nC_{v,m}\Delta T$ (D) ΔH_{fusion}

PART - III : MATCH THE COLUMN

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1. Match Column-I with Column-II

	Column–I (Ideal Gas)		Column-II (Related equations)
(A)	Reversible isothermal process	(P)	$W = 2.303\ n\ RT\ \log(P_2/P_1)$
(B)	Reversible adiabatic process	(Q)	$W = nC_{V,m}(T_2-T_1)$
(C)	Irreversible adiabatic process	(R)	$W = -2.303nRT\ \log(V_2/V_1)$
(D)	Irreversible isothermal process	(S)	$W = -\int_{V_i}^{V_f} P_{ext.}dV$

2.✍

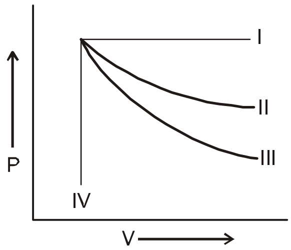
Column I	Column II
(A) A process carried out infinitesimally slowly	(p) Adiabatic
(B) A process in which no heat enters or leaves the system	(q) $\Delta E = 0$, $\Delta H = 0$
(C) A process carried out at constant temperature	(r) Reversible
(D) Cyclic process	(s) Isothermal

Exercise # 2

PART - I : ONLY ONE OPTION CORRECT TYPE

1. In which one of the following sets, all the properties belong to same category (all extensive or all intensive)?

(A) Mass, volume, pressure (B) Temperature, pressure, volume
(C) Heat capacity, density, entropy (D) Enthalpy, internal energy, volume.

2. 

The plots between P and V which represent isochoric and isobaric process respectively :

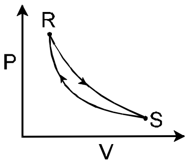
(A) I, II (B) IV, I (C) I, IV (D) II, III

3. Match the enteries of column I with appropriate entries of column II and choose the correct option out of the four options (A), (B), (C) and (D).

Column I	Column II
(X) Isothermal	(p) $\Delta T = 0$
(Y) Isobaric	(q) $\Delta V = 0$
(Z) Adiabatic	(r) $\Delta P = 0$
(W) Isochoric	(s) $q = 0$

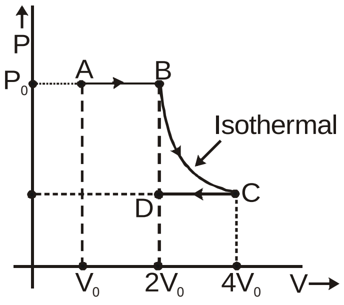
(A) X–p, Y–q, Z-r, W-x (B) X–p, Y–r, Z-s, W-q (C) X–s, Y–p, Z-r, W-q (D) X–s, Y–p, Z-q, W-r

4. Consider the cyclic process R → S → R as shown in the Fig. You are told that one of the path is adiabatic and the other one isothermal. Which one of the following is(are) true?



(A) Process R → S is isothermal (B) Process S → R is adiabatic
(C) Process R → S is adiabatic (D) Such a graph is not possible

5. Work for the following process ABCD on a monoatomic gas is :



(A) $w = -2P_0V_0 \ln 2$, (B) $w = -2P_0V_0 \ln 2$,
(C) $w = -P_0V_0(1+\ln 2)$, (D) $w = -P_0V_0 \ln 2$,

6. 50 L of a certain liquid is confined in a piston system at the external pressure 100 atm. This pressure is suddenly released and liquid is expanded against the constant atmospheric pressure, volume of the liquid increases by 1 L and the final pressure on the liquid is 10 atm. Find the workdone.

(A) 1L.atm (B) 5 L.atm (C) 500 L.atm (D) 50 L.atm

7. Which one of the following equations does not correctly represent the first law of thermodynamics for the given process in ideal gas ?

(A) Isothermal process : q = – w (B) Cyclic process : q = – w

(C) Adiabatic process : ΔE = q (D) Expansion of a gas into vacuum : ΔE = q

8.✍ One mole of an ideal gas $\left(C_{v,m} = \frac{5}{2}R\right)$ at 300 K and 5 atm is expanded adiabatically to a final pressure of 2 atm against a constant pressure of 2 atm. Final temperature of the gas is :

(A) 270 K (B) 273 K (C) 248.5 K (D) 200 K

9. The magnitudes of enthalpy changes for irreversible adiabatic expansion of a gas from 1L to 2L is ΔH_1 and for reversible adiabatic expansion for the same expansion is ΔH_2. Then

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

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

(C) $\Delta H_1 = \Delta H_2$, enthalpy being a state function ($\Delta H_1 = \Delta H_2$½

(D) $\Delta H_1 = \Delta E_1$ & $\Delta H_2 = \Delta E_2$ where ΔE_1 & ΔE_2 are magnitudes of change in internal energy of gas in these expansions respectively.

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

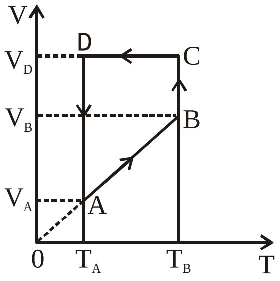
(A) ΔH = 15 kJ (B) ΔH = 15.7 kJ (C) ΔH = 14.4 kJ (D) ΔH = 14.7 kJ

11. An insulated container of gas has two chambers separated by an insulating partition. One of the chambers has volume V_1 and contains ideal gas at pressure P_1 and temperature T_1. The other chamber has volume V_2 and contains same ideal gas at pressure P_2 and temperature T_2. If the partition is removed without doing any work on the gas, the final equilibrium temperature of the gas in the container will be :-

(A) $\frac{T_1T_2(P_1V_1+P_2V_2)}{P_1V_1T_2+P_2V_2T_1}$ (B) $\frac{P_1V_1T_1+P_2V_2T_2}{P_1V_1+P_2V_2}$ (C) $\frac{P_1V_1T_2+P_2V_2T_1}{P_1V_1+P_2V_2}$ (D) $\frac{T_1T_2(P_1V_1+P_2V_2)}{P_1V_1T_1+P_2V_2T_2}$

PART - II : NUMERICAL TYPE QUESTIONS

1. A monoatomic ideal gas of two moles is taken through a reversible cyclic process starting from A as shown in figure. The volume ratios are $\frac{V_B}{V_A} = 2$ and $\frac{V_D}{V_A} = 4$. If the temperature T_A at A is 27°C, calculate:



(a) The temperature of the gas at point B.

(b) Heat absorbed or released by the gas in each process.

(c) The total work done by the gas during complete cycle. (ln2 = 0.7)

2. One mole of an ideal gas (not necessarily monoatomic) is subjected to the following sequence of steps.

(a) It is heated at constant volume from 298 K to 373 K

(b) It is expanded freely into a vacuum to double volume at 373 K.

(c) It is cooled reversibly at constant pressure to 298K.

Calculate q, w, ΔU and ΔH for the overall process.

3. How many statements are false ?

(i) Thermodynamics is concerned with total energy of the system.

(ii) Ist law of thermodynamics can be applied on the individual particle enclosed in vessel.

(iii) Many thermodynamic properties can not be measured absolutely, so change in thermodynamic property is required for calculation.

(iv) Feasibility of any chemical reaction can not be explained by thermodynamics.

(v) When surrounding is always in equilibrium with the system, the process called reversible.

(vi) Thermodynamics predict the time of attain the equilibrium.

4.✍ How many of the following physical properties are extensive :

(i) Free energy (ii) vapour pressure (iii) mole
(iv) Kinetic energy (v) Entropy (vi) Internal energy
(vii) Enthalpy (viii) specific heat capacity (ix) Coefficient of viscosity
(x) Total heat capacity

5.✍ How many of the following are state function :

(i) Internal energy (ii) Heat (iii) Enthalpy (iv) Entropy
(v) Pressure (vi) Temp. (vii) volume (viii) Work
(ix) specific heat capacity (x) molar heat capacity

6. Two moler of He gas (γ =5/3) are initially at temp 27ºC and occupy a volume of 20 litres. The gas is first expanded at constant pressure until its volume is doubled. then it undergoes and reversible adiabatic change, unit the volume become 110 lit, then predict the value of T/100 (where T is the final temperature, $\left(\frac{4}{11}\right)^{2/3}=\frac{1}{2}$)

7. A sample of an ideal gas is expanded from 1dm^3 to 3 dm^3 in a reversible process for which P = KV^3 , with K = 1/5 (atm/dm^3), what is work done by gas (L atm)

8. The valve on a cylinder containing initially 1 liters of an ideal gas at 7 atm and 25ºC is opened to the atmosphere, Whose the pressure is 760 torr and the temperature is 25ºC. Assuming that the process is isothermal, how much work (in L.atm) is done on the atmosphere by the action of expansion ?

9. A system is provided 50 joule of heat and the change in internal energy during the process is 60 J. Magnitude of work done on the system is :

10. A system works in a cylic process. It absorbs 20 calories of heat and rejects 60 J of heat during the process. The magnitude of work done (J) is [1 calorie = 4.2 J] :

11. The work done in adiabatic compression of 2 mole of an ideal monoatomic gas by constant external pressure of 2 atm starting from intial pressure of 1 atm and initial temperature of 30 K (R = 2 cal/mol-degree)

12.✍ One mole of a non-ideal gas undergoes a change of state (2.0 atm, 3.0 L, 95 K) $\rightarrow$ (4.0 atm, 5.0 L, 245 K) with a change in internal energy, ΔU=30.0 L. atm. Calculate change in enthalpy of the process in L. atm.

PART - III : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

1. Choose the correct statement(s) :-

(A) During adiabatic expansion of an ideal gas, magnitude of work obtained is equal to ΔH of gas.

(B) For same change in temperature of ideal gas through adiabatic process, magnitude of W will be same in reversible as well as irreversible process.

(C) During an adiabatic reversible expansion of an ideal gas, temperature of the system increases.

(D) For same change in volume of ideal gas, ΔU is less in adiabatic expansion than in isobaric expansion if expansion starts with same intial state.

2. Suppose that the volume of a certain ideal gas is to be doubled by one of the following processes :

(A) isothermal expansion (B) adiabatic expansion

(C) free expansion in insulated condition (D) expansion at constant pressure.

If E_1, E_2, E_3 and E_4 respectively are the changes in average kinetic energy of the molecules for the above four processes, then-

(A) $E_2 = E_3$ (B) $E_1 = E_3$ (C) $E_1 > E_4$ (D) $E_4 > E_3$

3. In an isothermal expansion of a gaseous sample, the correct relation is : (consider w (work) with sign according to new IUPAC convention)

[The reversible and irreversible processes are carried out between same initial and final states.]

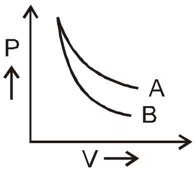
(A) $w_{rev} > w_{irrev}$ (B) $w_{irrev} > w_{rev}$ (C) $q_{rev} < q_{irrev}$ (D) $\Delta E_{rev} = \Delta E_{irrev}$

4. During the isothermal expansion of an ideal gas :

(A) The internal energy remains unaffected (B) The temperature remains constant

(C) The enthalpy remains unaffected (D) The enthalpy increases

5.✍ P-V plot for two gases (assuming ideal) during adiabatic processes are given in the figure. Plot A and plot B should correspond respectively to :



(A) He and H_2 (B) H_2 and He (C) SO_3 and CO_2 (D) N_2 and Ar

6. An ideal gas undergoes adiabatic expansion against constant external pressure. Which of the following is incorrect :

(A) Temperature of the system decreases.

(B) The relation PV^{γ} = constant will be valid (where P and V are gas variables)

(C) $\Delta E + P_{ext}\Delta V = 0$

(D) Enthalpy of the gas remains unchanged.

7.✍ For the sublimation of a solid at 1 atm, which of the following may be correct

(A) $\Delta U > 0$ at low temperature (B) $q > 0$

(C) $\Delta U < 0$ at high temperature (D) $\Delta H > 0$

PART - IV : COMPREHENSION

Read the following passage carefully and answer the questions.

Comprehension # 1

As a result of the isobaric heating by ΔT = 72K, one mole of a certain ideal gas obtains an amount of heat Q = 1.60 kJ.

1. The work performed by the gas is -

(A) 8.60 kJ (B) 0.60 kJ (C) 16.60 kJ (D) 4.60 kJ

2. The increment of its internal energy (in kJ) is -

(A) 1.0 (B) 1.6 (C) 2.2 (D) 2.0

3. The value of γ for the gas is -

(A) 0.6 (B) 1.4 (C) 1.6 (D) 1.5

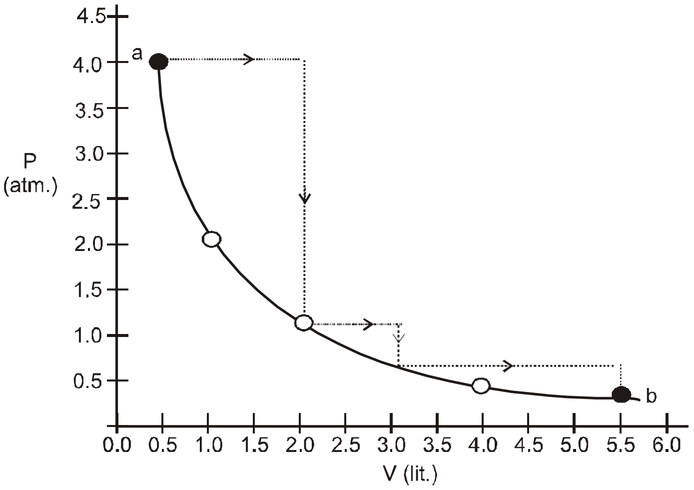
Exercise # 3

PART - I : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

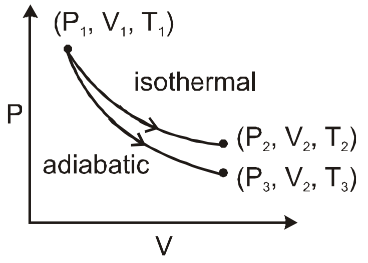
1.* Among the following, the intensive property is (properties are) : **[JEE 2010, 3/163]**

(A) molar conductivity (B) electromotive force (C) resistance (D) heat capacity

2. One mole of an ideal gas is taken from **a** and **b** along two paths denoted by the solid and the dashed lines as shown in the graph below. If the work done along the solid line path is w_s and that along the dotted line path is w_d, then the integer closest to the ratio w_d / w_s is : **[JEE 2010, 3/163]**

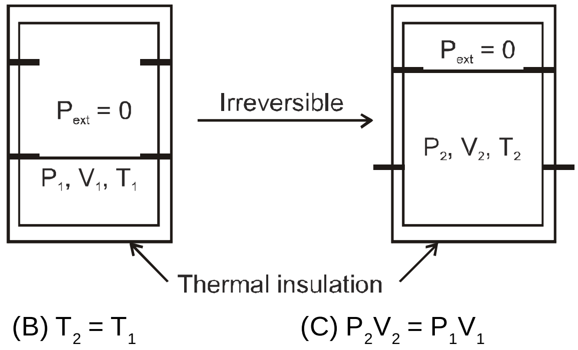


3.* The reversible expansion of an ideal gas under adiabatic and isothermal conditions is shown in the figure. Which of the following statement(s) is (are) correct ? **[JEE 2012, 4/136]**



(A) $T_1 = T_2$ (B) $T_3 > T_1$ (C) $w_{isothermal} > w_{adiabatic}$ (D) $\Delta U_{isothermal} > \Delta U_{adiabati}$]

4.* An ideal gas in a thermally insulated vessel at internal pressure = P_1, volume = V_1 and absolute temperature = T_1 expands irreversibly against zero external pressure, as shown in the diagram. The final internal pressure, volume and absolute temperature of the gas are P_2, V_2 and T_2, respectively. For this expansion, **[JEE(Advanced) 2014, 3/120]**



(A) $q = 0$ (B) $T_2 = T_1$ (C) $P_2V_2 = P_1V_1$ (D) $P_2V_2^{\gamma} = P_1V_1^{\gamma}$

5. An ideal gas is expanded from (p_1, V_1, T_1) to (p_2, V_2, T_2) under different conditions. The correct statement(s) among the following is(are) **[JEE 2017]**

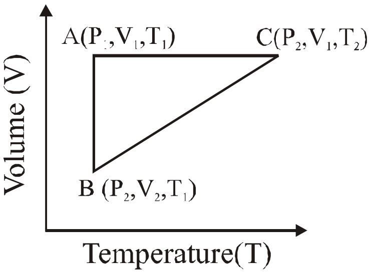
(A) The work done on the gas is maximum when it is compressed irreversibly from (p_2,V_2) to (p_1,V_1) against constant pressure p_1

(B) The work done by the gas is less when it is expanded reversibly from V_1 to V_2 under adiabatic conditions as compared to that when expanded reversibly from V_1 to V_2 under isothermal conditions.

(C) The change in internal energy of the gas (i) zero, if it is expanded reversibly with $T_1 = T_2$, and (ii) positive, if it is expanded reversibly under adiabatic conditions with $T_1 \neq T_2$

(D) If the expansion is carried out freely, it is simultaneously both isothermal as well as adiabatic

6. A reversible cyclic process for an ideal gas is shown below. Here, P , V and T are pressure , volume and temperature , respectively. The thermodynamic parameters q, w, H and U are heat, work, enthalpy and internal energy, respectively. **[JEE 2018]**



The correct option(s) is (are)

(A) $q_{AC} = \Delta U_{BC}$ and $w_{AB} = P_2 (V_2 - V_1)$

(B) $w_{BC} = P_2 (V_2 - V_1)$ and $q_{BC} = \Delta H_{AC}$

(C) $\Delta H_{CA} < \Delta U_{CA}$ and $q_{AC} = \Delta U_{BC}$

(D) $q_{BC} = \Delta H_{AC}$ and $\Delta H_{CA} > \Delta U_{CA}$

7. In thermodynamics, the P-V work done is given by **[JEE 2020]**

$$w = -\int dV\, P_{ext}$$

For a system undergoing a particular process, the work done is ,

$$w = -\int dV\left(\frac{RT}{V-b} - \frac{a}{V^2}\right)$$

This equation is applicable to a

(A) System that satisfies the van der Waals equation of state.

(B) Process that is reversible and isothermal.

(C) Process that is reversible and adiabatic.

(D) Process that is irreversible and at constant pressure.

PART - II : JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS)

1. A piston filled with 0.04 mol of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37.0ºC. As it does so, it absorbs 208 J of heat. The values of q and w for the process will be: (R = 8.314 J/mol K) (ln 7.5 = 2.01) **[JEE 2013, (MAIN), 4/120]**

(1) q = +208 J, w = – 208 J

(2) q = –208 J, w = – 208 J

(3) q = –208 J, w = + 208 J

(4) q = +208 J, w = + 208 J

2. Which of the following statements/relationships is not correct in thermodynamic changes ?

(1) $q = -nRT \, \ell n \frac{V_2}{V_1}$ (isothermal reversible expansion of an ideal gas) **[JEE-MAIN_(ONLINE)-2014]**

(2) For a system at constant volume, heat involved merely changes to internal energy.

(3) $w = -nRT \ln \frac{V_2}{V_1}$ (isothermal reversible expansion of an ideal gas)

(4) $\Delta U = 0$ (isothermal reversible expansion of a gas)

3. A gas undergoes change from state A to state B. In this process , the heat absorbed and work done by the gas is 5 J and 8 J, respectively. Now gas is brought back to A by another process during which 3 J of heat is evolved. In this reverse process of B to A:- **[JEE-MAIN_(ONLINE)-2017]**

(1) 10 J of the work will be done by the surrounding on gas.
(2) 6 J of the work will be done by the surrounding on gas.
(3) 10 J of the work will be done by the gas.
(4) 6 J of the work will be done by the gas.

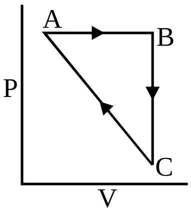
4. The enthalpy change on freezing of 1 mol of water at 5°C to ice at –5°C is:
(Given $\Delta_{fus}H = 6$ kJ mol^{-1} at 0°C, $C_P(H_2O, l) = 75.3$ J mol^{-1} K^{-1}, $C_P(H_2O, s) = 36.8$ J mol^{-1} K^{-1}) **[JEE-MAIN_(ONLINE)-2017]**

(1) –6.56 kJ mol^{-1} (2) –5.81 kJ mol^{-1} (3) –6.00 kJ mol^{-1} (4) –5.44 kJ mol^{-1}

5. ΔU is equal to **[JEE-MAIN_(ONLINE)-2017]**

(1) Isochoric work (2) Isobaric work (3) Adiabatic work (4) Isothermal work

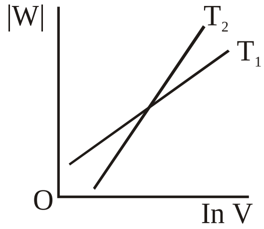
6. An ideal gas undergoes a cyclic process as shown in figure. **[JEE-MAIN_(ONLINE)-2018]**

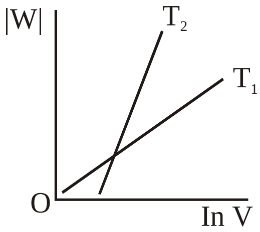


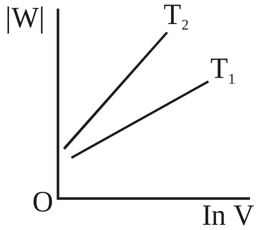
$\Delta U_{BC} = -5$ kJ mol^{-1}, $q_{AB} = 2$ kJ mol^{-1} $W_{AB} = -5$ kJ mol^{-1}, $W_{CA} = 3$ kJ mol^{-1}
Heat absorbed by the system during process CA is :-

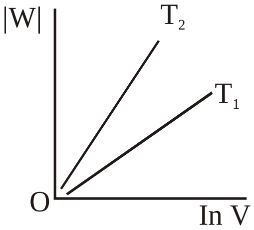
(1) 18 kJ mol^{-1} (2) +5 kJ mol^{-1} (3) –5 kJ mol^{-1} (4) –18 kJ mol^{-1}

7. Consider the reversible isothermal expansion of an ideal gas in a closed system at two different temperatures T_1 and T_2 ($T_1 < T_2$). The correct graphical depiction of the dependence of work done (w) on the final volume (V) is: **[JEE-MAIN_(ONLINE)-2019]**

(1)


(2)


(3)


(4)


8. An ideal gas undergoes isothermal compression from 5 m^3 to 1 m^3 against a constant external pressure of 4 Nm^{-2}. Heat released in this process is used to increase the temperature of 1 mole of Al. If molar heat capacity of Al is 24 J mol^{-1} K^{-1}, the temperature of Al increases by **[JEE-MAINS(ONLINE)-2019]**

(1) $\frac{3}{2}$K (2) $\frac{2}{3}$K (3) 1 K (4) 2 K

9. Which one of the following equations does not correctly represent the first law of thermodynamics for the given processes involving an ideal gas ? (Assume non-expansion work is zero) **[JEE(MAIN) 2019 ONLINE April. 4/120]**

(1) Cyclic process : q = – w (2) Isothermal process : q = – w
(3) Adiabatic process : $\Delta U = -w$ (4) Isochoric process : $\Delta U = q$

10. For silver, $C_p(JK^{-1}mol^{-1}) = 23 + 0.01T$. If the temperature (T) of 3 moles of silver is raised from 300K to 1000 K at 1 atm pressure, the value of ΔH will be close to **[JEE(MAIN) 2019 ONLINE April. 4/120]**

(1) 21 kJ (2) 16 kJ (3) 13 kJ (4) 62 kJ

11. The internal energy change (in J) when 90g of water undergoes complete evaporation at 100ºC is ____
(Given : ΔH_{vap} for water at 373 K = 41 kJ/mol, R = 8.314 JK^{-1} mol^{-1})
[JEE-MAINS SEPT. (ONLINE)-2020]

ANSWER KEY

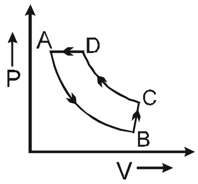
EXERCISE # 1

PART - I

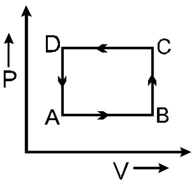
A-1. State function : (a) (b) (d) (e) ; Path function : (c) (f) (g)

A-2. Extensive Property : (b) (c) ; Intensive Property : (a) (d) (e) (f) (g)

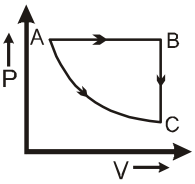
B-1.



B-2.



B-3.



C-1. (a) + 60J (b) –70 J (c), + 50 J, + 10 J,

C-2. –60 cal.

C-3. – 5744.4 J

C-4. 1.2×10^3 J

D-1. (i) 18.42 bar.L; (ii) 72 bar.L; (iii) 40 bar.L

D-2. 1.066 kJ

D-3. 760 J

E-1. (a) T_1 = 243.60 K; T_2 = 2436 K, (b) $\Delta U = 0$; q = –w = 3264.24 cal

E-2. (a) AC, (b) 170 J, (c) 10 J

E-3. 7

E-4. 32 J

E-5. – 2.6 J

F-1. $\Delta U = w = -1050$ R ; $\Delta H = -1470$ R , q = 0

F-2. 2244.78 Joule

F-3. $\frac{3}{2}$

F-4. W = 0 ; q = 0

G-1. ΔU = 4170 J, ΔH = 1 kcal

G-2. Zero

H-1. – 10.13 J

H-2. ΔU = 75.12 kJ

PART - II

A-1.	(C)	**A-2.**	(C)	**A-3.**	(C)	**A-4.**	(A)	**B-1.**	(B)
B-2.	(C)	**B-3.**	(A)	**B-4.**	(C)	**B-5.**	(C)	**B-6.**	(D)
C-1.	(B)	**C-2.**	(B)	**C-3.**	(C)	**D-1.**	(C)	**D-2.**	(C)
D-3.	(D)	**D-4.**	(D)	**D-5.**	(B)	**D-6.**	(A)	**D-7.**	(A)
E-1.	(A)	**E-2.**	(A)	**E-3.**	(D)	**E-4.**	(B)	**E-5.**	(B)
F-1.	(D)	**F-2.**	(A)	**F-3.**	(B)	**F-4.**	(A)	**G-1.**	(B)
G-2.	(D)	**G-3.**	(D)	**H-1.**	(B)	**H-2.**	(B)		

PART - III

1. (A) → (P,R,S); (B) → (Q, S); (C) → (Q,S); (D) → (S)

2. (A – r) ; (B – p) ; (C – s) ; (D – q)

EXERCISE # 2

PART - I

1.	(D)	**2.**	(B)	**3.**	(B)	**4.**	(D)	**5.**	(A)
6.	(A)	**7.**	(C)	**8.**	(C)	**9.**	(B)	**10.**	(B)
11.	(A)								

PART - II

1. (a) 600 K, (b) 3 kcal, 1.680 kcal, –1.8 kcal, – 1.680 kcal (c) –1.2 kcal

2. ΔU & $\Delta H = 0$; w = 623.55 J ; q = –623.55 J

3.	4	**4.**	7	**5.**	6	**6.**	3	**7.**	4
8.	6	**9.**	10	**10.**	24	**11.**	72	**12.**	44

PART - III

1.	(BD)	**2.**	(BD)	**3.**	(BD)	**4.**	(ABC)	**5.**	(BCD)
6.	(BD)	**7.**	(ABCD)						

PART - IV

1.	(B)	**2.**	(A)	**3.**	(C)

EXERCISE # 3

PART - I

1.	(AB)	**2.**	2	**3.***	(AD)	**4.**	(ABC)	**5.**	(ABD)
6.	(BC)	**7.**	(ABC)						

PART - II

1.	(1)	**2.**	(1)	**3.**	(2)	**4.**	(1)	**5.**	(3)
6.	(2)	**7.**	(2)	**8.**	(2)	**9.**	(3)	**10.**	(4)

11. 189000.00 to 190000.00