

**1. INTRODUCTION:****1.1 What is Thermodynamics and why is it useful ?**

Thermodynamics is the branch of science that describes the behavior of matter and the transformation between different forms of energy on a macroscopic scale. Thermodynamics describes a system in terms of its bulk properties.

**1.2 The laws of Thermodynamics :**

The law's of thermodynamics is the law of observation. No one has ever observed that anything goes in contrary to thermodynamics law. So we elevate this observation to the status of thermodynamic law. The real justification of this comes when things we derive using this law turns out to be true that is verified by experiments.

**1.3 Application of Thermodynamics :**

- (i) It provides relationship between heat, work and measurable properties of matter.
- (ii) It predicts direction of natural change - like what circumstances are best for rusting of iron.
- (iii) It predicts up to what extent a chemical reaction can proceed in forward direction.

**Example:** How much ammonia ( $\text{NH}_3$ ) can be formed from  $\text{N}_2$  and  $\text{H}_2$  in a closed container.

- (iv) It help in understanding why different phases of matter exist and provide simple relationship between various measurable properties of system (thermo dynamical variables):

**1.4 Salient features of Thermodynamics :**

During study of this chapter you will observe that mostly you will be dealing with macroscopic properties (bulk properties) like pressure, volume, temperature density of system. This is because thermodynamics is macroscopic science and it do not concern's with detailed microscopic make up of the system.

**1.5 Limitations :**

- (1) It tells us whether a given chemical reaction will take place or not under the given set of conditions but doesn't tell us anything about the rate of reaction.
- (2) It tells us about the initial and final properties of the system but doesn't tell us anything about the path or mechanism followed by the system.

**2. BASIC DEFINITIONS:****2.1 System :** Part of universe under investigation is called system. System can be classified as

- (a) Homogeneous system : System consist of single phase. Eg: Pure solid, a pure liquid a solution, or a mixture of gases.
- (b) Heterogeneous system : A system consisting of many phases. Eg: System of two immiscible liquids, two or more solids, a liquid in contact with its vapour etc. are example of heterogeneous system.

**2.2 Surrounding :** Anything outside the system is called surrounding.

**2.3 Boundary :** The interface between system and surrounding is called boundary. Across boundary energy and mass are transferred between system and surrounding. Boundary can be real or hypothetical. Boundary are classified as :

- (a) Permeable : It allows exchange of matter and energy between system and surrounding.
- (b) Impermeable : It allows only exchange of energy between system and surrounding.
- (c) Adiabatic wall : The heat exchange is not allowed between system and surrounding.
- (d) Diathermic wall : The heat can be exchanged across the wall.

**2.3.1 Classification of system on the basis of boundaries:**

- (i) Open system : A system which is enclosed by permeable boundaries so it can exchange both energy and matter with surrounding. Eg: Living systems( any living organism) are open systems, air in an open room ; water flow in pipe.
- (ii) Closed system : A system which is enclosed by impermeable boundaries it can exchange only energy with surrounding. Eg. : any matter in a closed container ; Heating of water in closed container.
- (iii) Isolated system : A system which cannot exchange matter or energy with surrounding. Eg. : 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).

**2.4 Phase:** By the term phase we mean a homogeneous physically distinct part of a system which is bounded by a surface and can be separated out mathematically from the other parts of the system.

**2.5 The state of a system :**

We specify the state of a system, a sample of material by specifying the values of all the variables describing the system. If the system is a sample of a pure substance this would mean specifying the values of the temperature,  $T$ , the pressure,  $p$ , the volume,  $V$ , and the number of moles of the substance,  $n$ .

**2.5.1 State variables:** To define a thermodynamic states of a system, we have to specify the values of certain measurable quantities. These are called thermodynamic variable or state variable.

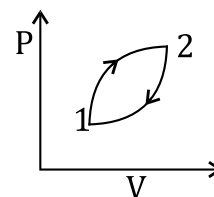
A system can be completely defined by four variables namely pressure, temperature, volume and composition. A system is said to be in a certain definite state when all of its properties have definite value. **Between two fixed states the change in the value of state function is same irrespective of the path followed between two states.**

**Differential of a state function integrated over a cyclic path** returns zero.

In other words summation of change in state function in a cyclic process is equal to zero. If  $\oint dX = 0 \Rightarrow X$  is a state function (property of state function)

Note that if  $X$  is a state function,  $dX$  is called **definite quantity**

**Example :**  $T, V, P$  and  $U$  (internal energy),  $H$  (enthalpy) are state variables.



### 2.5.2 Path function :

Quantities which are dependent on the path/way the system has achieved a particular state.

Path functions are also called **indefinite quantities** since between two fixed state the value of path function is not fixed.

Eg: Heat, work, Heat capacities (Molar heat capacities, specific heat capacities etc.).

These quantities are defined when there is a process going on.

These cannot have any definite (particular) value in any particular state of the system.

### 2.6 Extensive and Intensive variables :

Properties which depend on the amount of the substance (or substances) present in the system are called extensive properties. Eg. mass, volume, heat capacity, internal energy, entropy, Gibb's free energy ( $G$ ), surface area etc. These properties will change with change in the amount of matter present in the system. It is important to note that the total value of an extensive property of a system is equal to the sum of the values of different parts into which the system is divided.

**Intensive properties :** Properties which are independent of the amount of substance (or substances) present in the system are called intensive properties, e.g. pressure, density, temperature, viscosity, surface tension, refractive index, emf, chemical potential, sp. heat etc, These are intensive properties.

An extensive property can be converted into intensive property by defining it per unit of another extensive property.

**Ex.** Concentration = mole/volume

Density = mass / volume

heat capacity = heat absorbed / rise in temperature

While mole, mass, heat are extensive properties, concentration, density and heat capacity are intensive properties.

### ❑ EXAMPLE BASED ON BASIC DEFINITION :

1. Which one is not a state function :-

(A) internal energy (B) volume (C) heat (D) enthalpy

**Ans. (C)**

2. When no heat energy is allowed to enter or leave the system, it is called :-

(A) isothermal process

(B) reversible process

(C) adiabatic process

(D) irreversible process

**Ans. (C)****3.** Which is the intensive property :-

(A) temperature

(B) viscosity

(C) density (D) all

**Ans. (D)****4.** A thermodynamic state function is :-

(A) one which obeys all the law of thermodynamics

(B) a quantity which is used in measuring thermal changes

(C) one which is used in thermochemistry

(D) a quantity whose value depends only on the state of system

**Ans. (D)****5.** A system is changed from state A to state B by one path and from B to A by another path. If  $\Delta E_1$  and  $\Delta E_2$  are the corresponding changes in internal energy, then :-(A)  $\Delta E_2 + E_2 = +ve$ (B)  $\Delta E_1 + \Delta E_2 = -ve$ (C)  $\Delta E_1 + \Delta E_2 = 0$ 

(D) none of the above

**Ans. (C)****6.** A well stoppered thermos flask contains some ice cubes. This is an example of a :-

(A) closed system

(B) open system

(C) isolated system

(D) non-thermodynamics system

**Ans. (C)****2.7 Thermodynamic equilibrium :**

Thermodynamic generally deals the equilibrium state of the system in which the state variable are uniform and constant throughout the whole system.

The term thermodynamic equilibrium implies the existence of three different types of equilibria in the system. These are :

**(i) Mechanical equilibrium :** When there is no macroscopic movement within the system itself or of the system with respect to surroundings, the system is said to be in a state of mechanical equilibrium.

**(ii) Chemical equilibrium :** When the system consists of more than one substance and the composition of the system does not vary with time, the system is said to be in chemical equilibrium. The chemical composition of a system at equilibrium must be uniform and there should be no net chemical reaction taking place.

- (iii) **Thermal equilibrium** : When the temperature throughout the entire system is the same as that of the surroundings then the system is said to be in thermal equilibrium.

## 2.8 Equation of state :

An equation that relates the variables T, P, V, and n to each other is called the "equation of state." The most general form for an equation of state is.

$$f(P, V, T, n) = 0.$$

### The ideal gas equation of state :

The best known equation of state for a gas is the "ideal gas equation of state". It is usually written in the form,

$$PV = nRT$$

This equation contains a constant, R, called the gas constant.

### The Vander Walls equation of state for real gases :

The Vander Walls equation of state is,

$$\left( p + a \frac{n^2}{V^2} \right) (V - nb) = nRT$$

Notice that the Vander Walls equation of state differs from the ideal gas by the addition of two adjustable parameters, a, and b (among other things).

**Note :** Equation of state for liquid and solids are also defined empirically.

**2.9 Thermodynamic Process :** Anything which changes state of system is called Thermodynamic process. Usually as a result of heat and work interactions change of state take place. e.g. isothermal process

### 2.9.1 Some thermodynamic processes :

- (1) **Isothermal process** : A process in which temperature of the system remains constant is called isothermal process. That is  $T = \text{constant}$

$$T_i = T_f$$

$$\Delta T = 0$$

- (2) **Isobaric process** : A process in which pressure of the system remains constant is called isobaric process. Temperature and volume of the system may change. That is

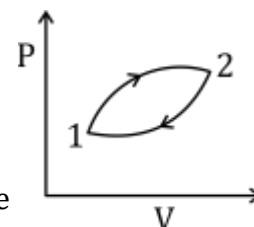
$$P = \text{constant}$$

$$P_i = P_f$$

$$\Delta P = 0$$

All the reactions or processes taking place in open vessel like boiling of water in open vessel, burning of charcoal, melting of wax take place at constant pressure (1 atm.)

- (3) **Adiabatic process** : A process in which no heat exchange takes place is called adiabatic process. Adiabatic process occurs in isolated systems.
- (4) **Isochoric process** : The process for which volume of the system remains constant is called isochoric process i.e., Heating of gas in closed vessel.
- (5) **Poly tropic processes** : It is defined as a process in which  $PV^n = \text{constant}$
- (6) **Cyclic process** : If a system after completing a series of different process returns to its initial state then overall process is called cyclic process.



In cyclic process all the state variables remain constant because initial state becomes final state in cyclic process.

Ex.  $\Delta H = 0, \Delta E = 0, \Delta P.E. = 0$

**2.9.2 Path of a process** : The exact sequence of steps through which system changes state is called path of a process. Eg: All of the above mentioned processes can be performed in two ways, **reversibly and irreversibly**

- **Reversible process**: When the difference between driving force and opposing force is very small and the process is carried out infinitesimally slowly, then the process is called reversible process

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

A reversible process is also called quasi static process. During a reversible process, the system and surrounding remain in equilibrium throughout the process.

The reversible processes are idealized processes which cannot be actually carried out, but nevertheless they are very important because they help in calculation of change in state function in the process. In other words the reversible processes are **hypothetical processes**.

**A quasi static process is the one in which system remain infinitesimally closer to the state of equilibrium throughout the process.**

**Irreversible process:**

- 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 ;  $F_{\text{driving}} - F_{\text{opposing}} = \Delta F$
- 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.

### Reversible Process

- (1) Driving force is infinitesimally small.
- (2) PV work is done across pressure difference  $dP$
- (3) A reversible heat transfer take place across temperature difference  $dT$
- (4) It is an ideal process.
- (5) It takes infinite time for completion of process.
- (6) It is an imaginary process and can not be realised in actual practice
- (7) Throughout the process, the system remain infinitesimally closer to state of equilibrium and exact path of process can be drawn

### Irreversible Process

- (1) Driving force is large and finite.
- (2) PV work is done across pressure difference  $\Delta P$
- (3) across temperatur difference  $\Delta T$  across temperatur difference  $\Delta T$
- (4) It is a real process.
- (5) It takes finite time for completion of process.
- (6) It is a natural process and occurs in particular direction under given set of conditions.
- (7) The system is far removed from state of equilibrium and exact path of process is indeterminate.

## 2.10 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 flows due to temperature gradient while work is done due to imbalance of **generalized force**. Due to imbalance of generalized force (intensive property) generalized displacement (extensive property) is produced. The product of generalized force and generalized displacement is work.

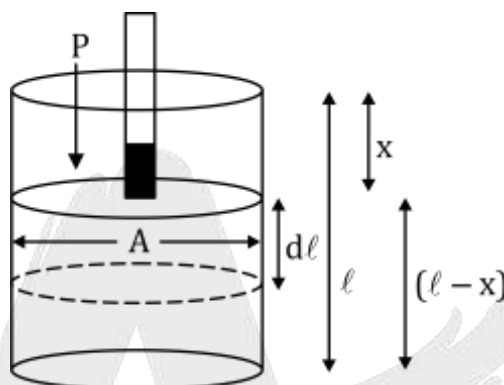
Work done on the system can reversible and irreversible depending on magnitude of imbalance of generalized force.

Heat is also transferred between system and surrounding in two ways – reversible and irreversible.

Reversible heating means heating an object from  $T_i$  to  $T_f$  using infinite heat reservoirs.

Irreversible heat transfer means heat transfer across temp difference  $\Delta T$ .

**2.10.1 PV-WORK** Consider a cylinder fitted with a frictionless piston, which enclosed  $n$  mole of an ideal gas. Let an external force  $F$  pushes the piston inside producing displacement in piston. Let distance of piston from a fixed point is  $x$  and distance of bottom of piston at the same fixed point is  $l$ . This means the volume of cylinder =  $(l - x)A$  where  $A$  is area of cross section of piston.



- For a small displacement  $dx$  due to force  $F$ , work done on the system.

$$\text{Also } P = \frac{F}{A}$$

$$F = PA$$

$$dW = PA \cdot dx$$

$$V = (\ell - x) A$$

$$\Rightarrow dV = -A \cdot dx$$

$$\Rightarrow dW = -P_{\text{ext}} \cdot dV$$

**Note:** During expansion  $dV$  is positive and hence sign of  $w$  is negative since work is done by the system and negative sign representing decrease in energy content of system. During compression, the sign of  $dV$  is negative which gives positive value of  $w$  representing the increase in energy content of system during compression.

### 2.10.2 Difference between heat and work :

When a gas is supplied some heat, its molecules move faster and with greater randomness in different directions. But when work is done on the same system gas molecules are compressed and move initially in direction of force as they get condensed.

So heat is random form of energy while work is organised form of energy.

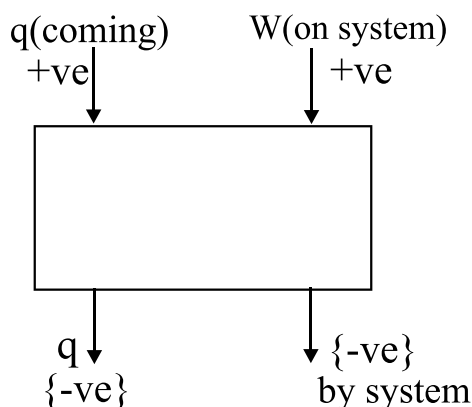
### 2.11 SIGN CONVENTIONS:

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 (Compression of gas) = Positive



7. Find the work done when one mole of ideal gas in 10L container at 1 atm. is allowed to enter a evacuated bulb of capacity 100 L.

**Ans.** Zero

**Sol.**  $W = -P\Delta V$

But since gas enters the vacuum bulb and pressure in vacuum is zero. This type of expansion is called **free expansion** and work done is zero.

8. Find the work done when 1 mole of gas expands from 1 litre to 5 litre against constant atmospheric pressure.

**Ans.** - 4 Latm

**Sol.**  $W = -P\Delta V = -1(5 - 1) = -4 \text{ Latm.}$

9. Find the work done when 18 ml of water is getting vapourised at 373 K in open vessel (Assume the ideal behaviour of water vapour).

**Ans.** - 30 Latm

**Sol.**  $PV = nRT$  [V in litre and T in Kelvin]

$$PV = 1 \times 0.0821 \times 373$$

$$PV = 30 \quad [P = 1\text{atm.}]$$

$$V = 30 \text{ litre}$$

$$W = -P\Delta V$$

$$= -1(30 - V_{\text{gas}}) \quad [18 \text{ ml is negligible as compared to 30 litre}]$$

$$= -1 \times 30 = -30 \text{ Latm.}$$

## 2.12 INTERNAL ENERGY (U):

The internal energy of the gas confined in a container is defined relative to a coordinate system fixed on the container. Viewed at a microscopic level, the internal energy can take on a number of forms such as.

- The kinetic energy of the molecules.
- The potential energy of the constituents of the system ; for example, a crystal consisting of dipolar molecules will experience a change in its potential energy as an electric field is applied to the system.
- The internal energy stored in the form of molecular vibrations and rotations.
- The internal energy stored in the form of chemical bonds that can be released through a chemical reaction.

The total of all these forms of energy for the system of interest is given the symbol  $U$  and is called the internal energy.

Hence total internal energy of a system can be written as

$$U = U_{\text{translational}} + U_{\text{rotational}} + U_{\text{vibrational}} + U_{\text{intermolecular}} + U_{\text{electronic}} + U_{\text{relativistic}}$$

of these  $U_{\text{relativistic}}$  and  $U_{\text{electronic}}$  is unaffected by ordinary heating. So basically the kinetic energy terms and  $U_{\text{intermolecular}}$  accommodate heat provided to the system. For an ideal gas,  $U_{\text{intermolecular}}$  is equal to zero, because of absence of intermolecular force of attraction in ideal gas.  $U_{\text{intermolecular}}$  have large and negative value in solids and liquids.

For an ideal gas  $U$  is only function of temperature e.g.  $U = f(T) + \text{Constant}$

Due to absence of pressure or volume terms in ideal gas internal energy,  $U$  is independent of pressure and volume of theoretical ideal gas

### DO YOURSELF - 1

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
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
3. Calculate the work done by 0.1 mole of a gas at  $27^{\circ}\text{C}$  to double its volume at constant pressure ( $R = 2 \text{ cal mol}^{-1} \text{ K}^{-1}$ )
4. At  $25^{\circ}\text{C}$ , 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 ?

5. Calculate the number of kJ necessary to raise the temperature of 60 g of aluminium from 35°C to 55°C. Molar heat capacity of Al is 24 mole<sup>-1</sup>K<sup>-1</sup>.
6. 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 energy.
7. Two litre of N<sub>2</sub> at 0°C and 5 atm pressure are expanded isothermally against a constant external pressure of 1 atm until the pressure of gas reaches 1 atm. Assuming gas to be ideal, calculate work of expansion.

### 3. FIRST LAW OF THERMODYNAMICS (FLOT) :

It is based on law of conservation of energy that Energy of total universe is always conserved.

or

**Total energy of an isolated system is always conserved.**

If a system is present in particular thermodynamic state say 'A' it has fixed amount of internal energy  $U_A$ . Suppose by a process the system is taken from state

A to state B. In the process 'q' heat is absorbed by system and w work is done on the system. Thus at the state 'B' total internal energy of system ( $U_B$ ) become

$$U_B = U_A + q + w.$$

$$U_B - U_A = q + w$$

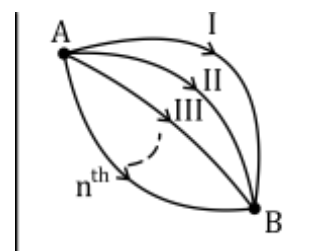
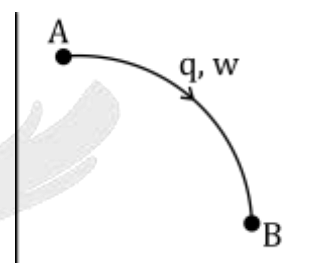
$$\Rightarrow \Delta U = q + w$$

Here q, w are heat and work involve in respective processes.

This is mathematical statement of first law.

First law of thermodynamics states that energy is conserved. Direct consequence of this statement is U is state function. This implies between any two fixed state, there can be infinite process or path, but  $\Delta U$  in all process will remain the same. (Property of a function of state)

Consider a system taken from state A to B by nth different paths.



- Note that heat and work involve in all the process are different but  $\Delta U$  is same. This mean heat and work are indefinite quantities while  $\Delta U$  is a definite quantity.

$\Rightarrow$  Some other statement of first law :

$$\sum_{\text{cyclic process}} \Delta U = 0 \text{ or } \oint dU = 0$$

{Integral of dU over cyclic path is zero.}

- **First law of thermodynamics applied to close system involving only PV work.**

For system involving only PV work first law mathematical statement can be written in differential form as :

$$\boxed{dU = dq - PdV}$$

- 10.** During 200J work done on the system, 140 J of heat is given out. Calculate the change in internal energy.

**Ans.** +60J

**Sol.**  $w = 200 \text{ J}; \quad q = -140 \text{ J};$

$q = \Delta U + (-w);$  where  $-w$  is work done by the system

$$\Delta U = q + w$$

$$\Delta U = -140 + 200 = +60\text{J}$$

- 11** A gas absorbs 200 J of heat and expands against the external pressure of 1.5 atm from a volume of 0.5 litre. Calculate the change in internal energy.

**Sol.**  $w = -P\Delta V = -1.5 \times (1.0 - 0.5) = -0.75 \text{ litre atm}$

$$= -0.75 \times 101.3 \text{ J} = -75.975 \text{ J}$$

$$1 \text{ litre atm} = 101.3 \text{ J}$$

$$\text{Now, } \Delta U = 200 - 75.975 = +124.025 \text{ J}$$

- 12.** A gas expands against a variable pressure given by  $P = \frac{20}{V}$  bar. During expansion from volume of 1 litre to 10 litre, the gas undergoes a change in internal energy of 400 J. Heat absorbed by the gas during expansion (in kJ) :

**Ans.** 5

**Sol.**  $W = \int_1^{10} Pdv = -20 \int_1^{10} \frac{dv}{V} = -20[\ln(V)]_1^{10} = -20 \ln(10) = -4605 \text{ J}$

$$\Delta q = \Delta U - W$$

$$= 400 - (-4605) = 5005 \text{ J} \gg 5 \text{ kJ.}$$

#### 4. CALCULATION OF DIFFERENT QUANTITIES IN FIRST LAW OF THERMODYNAMICS :

##### 4.1 Heat exchange at constant pressure ( $q_p$ ):

Chemical reactions are generally carried out at constant pressure (atmospheric pressure) so it has been found useful to define a new state function Enthalpy (H) as :

$$H = U + PV \text{ (By definition).....(1)}$$

$$\text{or } \Delta H = \Delta U + \Delta(PV)$$

$$\text{or } \Delta H = \Delta U + P\Delta V \text{ (at constant pressure) combining with first law. Equation (1) becomes}$$

$$\Delta H = q_p \text{ (That is at constant pressure heat exchange is equal to change in enthalpy)}$$

#### 4.2 Heat exchange at constant volume ( $q_v$ ) :

For an isochoric process in a system involving only PV work,

$$\Delta U = q_v$$

This result is valid for all the substance under isochoric conditions (when only PV work is involved) and also from the previous article it is clear that

$$\Delta H = q_p$$

This result is valid for all the substance involving isobaric process (when only PV work is involved)

Hence heat exchanged at constant pressure and volume are important **Definite quantities**

#### 4.3 Heat capacity:

The heat capacity of a system may be defined as the amount of heat required to raise the temperature of the system by one degree.

If  $\delta q$  is the small quantity of heat added to the system, let the temperature of the system rises by  $dT$ , then heat capacity  $C$  of the system is given by

$$C = \frac{dq}{dT} \quad \text{.....(i)}$$

In case of gases we have two types of heat capacity i.e. heat capacity at constant volume and heat capacity at constant pressure.

##### 4.3.1 Heat capacity at constant volume ( $C_v$ ) :

Molar heat capacity at constant volume is defined by the relation

$$C_v = \frac{dq_v}{dT} \quad \text{.....(ii)}$$

For first law of thermodynamics

$$dU = dq - dw$$

$$\text{But } dw = P dV$$

$$\therefore dU = dq - P dV \quad \text{....(iii)}$$

At constant volume

$$dU = dq_v$$

$\therefore$  Heat capacity at constant volume  $C_v$  is given by

$$C_v = \frac{dq_v}{dT} = \left( \frac{\partial U}{\partial T} \right)_v$$

or 
$$C_v = \left( \frac{\partial U}{\partial T} \right)_v \quad \dots (iv)$$

It may be defined as the rate of change of internal energy with temperature at constant volume.

#### 4.3.2 Heat capacity at constant pressure ( $C_p$ ) :

When pressure is maintained constant, equation (i) takes the form

$$C_p = \frac{\delta q_p}{dT} \quad \dots (v)$$

From first law of thermodynamics

At constant pressure

$$\delta q_p = (dU + PdV) = dH$$

$$[H = U + PV \text{ At constant } P, dH = dU + PdV]$$

$\therefore \delta q_p = dH \quad \dots (vi)$

Heat capacity at constant pressure  $C_p$  is given by

$$C_p = \frac{\delta q_p}{dT} = \left( \frac{\partial H}{\partial T} \right)_p$$

or 
$$C_p = \left( \frac{\partial H}{\partial T} \right)_p \quad \dots (vii)$$

It is the rate of change of enthalpy with temperature at constant pressure.

Hence heat capacity of a system at constant volume  $C_v$  is equal to the increase in internal energy of the system per degree rise of temperature at constant volume. Similarly heat capacity at constant pressure  $C_p$  is numerically equal to the increase in enthalpy of the system per degree rise of temperature.

For 1 mole of an ideal gas, heat capacity at constant pressure i.e.  $C_p$  is greater than the heat capacity at constant volume i.e.,  $C_v$

$$C_p > C_v$$

These are called molar heat capacities

i.e., 
$$C_p = \left( \frac{\partial H}{\partial T} \right)_p$$

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

**Note:** For ideal gases, since  $U$  and  $H$  are only function of temperature, hence subscript  $P$  and  $V$  from  $C_p$  and  $C_v$  equation can be dropped, which means



$$C_p = \left( \frac{\partial H}{\partial T} \right)_p = \left( \frac{\partial H}{\partial T} \right) \text{ with means } C_p = \left( \frac{\partial H}{\partial T} \right)$$

Hence for any process involving ideal gas  $dH = C_p dT$

similarly for change in internal energy involving ideal gas, the subscript V from the expression of  $C_v$  can be dropped. Hence,  $dU = nC_v dT$  for all process involving ideal gases.

Hence  $\Delta H$  and  $\Delta U$  is equal to zero for isothermal process involving ideal gases.

**Note:** The relation  $dH = C_p dT$  valid for any substance other than ideal gas only in isobaric process.

The relation  $dU = C_v dT$  valid for any substance other than ideal gas only in isochoric process.

- 13.** Find the amount of heat required (in terms of "a") to raise the temperature of 1 mole substance from 3 K to 5 K. At low temperatures.  $C_p = aT^3 \text{ J K}^{-1} \text{ mol}^{-1}$ .

**Ans.** 136 a

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

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

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

#### 4.4 DEGREE OF FREEDOM(f) AND EQUI-PARTITION PRINCIPLE :

According to Law of equi-partition of energy (i) each translation and rotational degree of freedom in a molecule contributes  $\frac{1}{2}RT$  to the thermal energy of one mole of a gas, and

(ii) each vibrational degree of freedom in a molecule contributes  $RT$  to the thermal energy of one mole of a gas.

**The degrees of freedom** in a molecule are given by the **number of coordinates** required to locate all the mass points (atoms) in a molecule. If a molecule contains only one atom (as in a monatomic gas), it has three degrees of freedom corresponding to translational motion in the three independent spatial directions X, Y and Z. If a molecule contains N atoms, each atom contributes these three degrees of freedom, so the molecule has a total of  $3N$  degrees of freedom. Since three coordinates (degree of freedom) are required to represent the translational motion of the molecule, the remaining  $(3N - 3)$  coordinates represent what are called the **internal degrees of freedom**. If the molecule is linear, it has two rotational degrees of freedom; for a non-linear molecule, there are three rotational degrees of freedom. The remaining degrees of freedom, that is  $3N - 5$  for linear and  $3N - 6$  non - linear molecules are the vibrational degrees of freedom. Table list the degrees of freedom for several molecule.

Type	Molecule	Trans	Rot	Vib	Total
Monoatomic	He	3	0	0	3
Diatomic	N <sub>2</sub>	3	2	1	6
Triatomic linear	CO <sub>2</sub>	3	2	4	9
non-linear	H <sub>2</sub> O	3	3	3	9

In a monatomic molecule  $\bar{E} = 3RT/2$  in agreement with the simple model. For a diatomic molecule, there are three translational, two rotational (because the molecule is linear) and one vibrational degrees of freedom making a total of six. the thermal energy per mole would, therefore, be,

$$\bar{E} = \left(\frac{3}{2}RT\right)_{\text{trans}} + \left(\frac{2}{2}RT\right)_{\text{rot}} + (1RT)_{\text{vib}}$$

$$\text{and } \bar{C}_V = 3R/2 + R + R = 7R/2 = 7 \text{ cal deg}^{-1} \text{ mol}^{-1}$$

Table shows that the observed values of  $\bar{C}_V$  for diatomic molecules deviate greatly from the predicted values, The fact that the value of  $5 \text{ cal deg}^{-1} \text{ mol}^{-1}$  (which is close to  $5R/2$ ) is most common for simple diatomic molecules shows that vibration degrees of freedom are active only at very high temperature.

#### 4.5 RELATIONSHIP BETWEEN $C_P$ AND $C_V$ FOR IDEAL GAS :

Hence transfer of heat at constant volume brings about a change in the internal energy of the system whereas that at constant pressure brings about a change in the enthalpy of the system.

from the first law  $dH = dU + d(PV)$  for a differential change in state

$$\text{if only ideal gas is involved } PV = nRT \quad dU = nC_V dT \quad \text{and} \quad dH = nC_P dT$$

substituting these results we get

$$nC_P dT = nC_V dT + nR dT$$

$$C_P = C_V + R \text{ valid only for ideal gas}$$

relationship between  $C_P$  and  $C_V$  for real gases, liquid and solids is beyond the scope of JEE syllabus.

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 <sub>2</sub> ; O <sub>2</sub> ; H <sub>2</sub>
3.	Linear polyatomic	5	$\frac{5R}{2}$	$\frac{7R}{2}$	$\frac{7}{5}$	CO <sub>2</sub> ; HCl
4.	Non-Linear polyatomic	6	$\frac{6R}{2}$	$\frac{8R}{2}$	$\frac{8}{6}$	H <sub>2</sub> O ; NH <sub>3</sub> ; CH <sub>4</sub>

\* In above table vibrational degree of freedom is assumed to be inactive

14. 10 dm<sup>3</sup> of O<sub>2</sub> at 101.325 kPa and 298 K is heated to 348 K. Calculate the heat absorbed,  $\Delta H$  and  $\Delta U$  of this process at

(a) at constant pressure

(b) at constant volume

Given :  $C_p/\text{JK}^{-1} \text{mol}^{-1} = 25.72 + 0.013 (T/\text{K}) - 3.86 \times 10^{-6} (T/\text{K})^2$

Assume ideal behaviour.

Sol. Amount of the gas,  $n = \frac{PV}{RT}$

$$\text{or } n = \frac{(101.325)(10)}{(8.314)(298)} = 0.409 \text{ mol.}$$

(a) constant pressure

$$q_p = \Delta H = n \int_{T_1}^{T_2} C_p dT$$

Here  $T_2 = 348 \text{ K}$ ,  $T_1 = 298 \text{ K}$

$$\text{or } q_p = 0.409 \left[ (25.72)(T_2 - T_1) + 0.013 \left( \frac{T_2^2}{2} - \frac{T_1^2}{2} \right) - (3.83 \times 10^{-6}) \left( \frac{T_2^3}{3} - \frac{T_1^3}{3} \right) \right]$$

$$\text{or } q_p = 0.409 \times 1475.775 = 603.59 \text{ J}$$

Ans.  $\Delta U = \Delta H - \Delta(PV)$

$$= \Delta H - P\Delta V - V\Delta P$$

at constant pressure

$$\Delta U = \Delta H - P\Delta V = \Delta H - nR\Delta T$$

$$= 603.59 - 0.409 \times 8.314 \times 50$$

$$= 433.57 \text{ J}$$

Ans. (b) At constant volume

$$q_p = \Delta H = \int_{T_1}^{T_2} nC_v dT = \int_{T_1}^{T_2} nC_p dT = \int_{T_1}^{T_2} nC_p dT - \int_{T_1}^{T_2} nR dT$$

$$= 603.59 - 170.02 = 433.57 \text{ J}$$

**Ans.**  $\Delta H = \Delta U + \Delta (PV) = \Delta U + nR\Delta T = 603.59 \text{ J}$

## DO YOURSELF - 2

- 10 g of argon gas is compressed isothermally and reversibly at a temperature of  $27^\circ\text{C}$  from 10 L to 5L. Calculate enthalpy change ( $\Delta H$ ) for this process  $R = 2.0 \text{ cal K}^{-1} \text{ mol}^{-1}$ . ( $\log_{10} 2 = 0.30$ , Atomic mass of Ar = 40)
- 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 ( $\Delta U$ ) = 40 L-atm. The change in enthalpy of the process in L-atm ;  
(A) 43 (B) 57 (C) 42 (D) 21
- 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
- Calculate the work done when 1 mol of zinc dissolves in hydrochloric acid at 273 K in :  
(a) an open beaker  
(b) a closed beaker at 300 K.

## 5. CALCULATION OF WORK FOR DIFFERENT TYPE OF PROCESS ON AN IDEAL GAS :

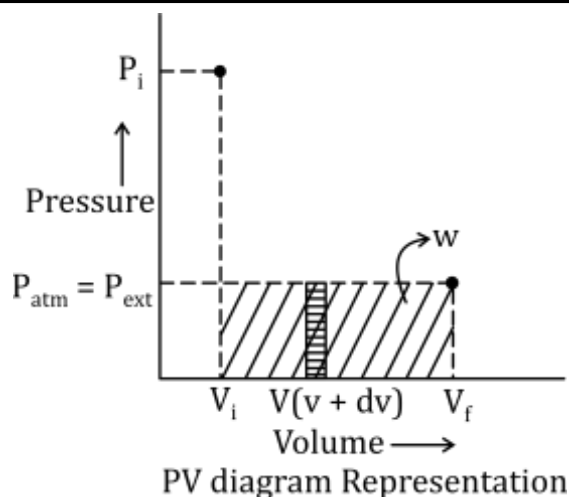
## 5.1 ISOTHERMAL PROCESS :

## 5.1.1 Work done in Irreversible isothermal expansion:

- (a) **Process involving only one step:** If external pressure over the piston is abruptly changed from the equilibrium value, the mechanical equilibrium of system is disturbed and piston rushes out

This type of PV-work is irreversible PV- work. To calculate irreversible PV-work law of conservation of energy is used. Suppose as a result of difference in pressure a piston moves out and in the process volume increase by  $\Delta V$ ,

$$w_{\text{irr}} = - P_{\text{ext.}} \Delta V$$



(b) Process involving two steps:

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

$$P_{\text{ext}_1} = (P_{\text{atm}} + m_2 g/A)$$

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

$$P_{\text{ext}_1} V_1 = P_i V_i \text{ (isothermal)}$$

Now, if second mass  $m_2$  is also removed then expansion

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

$$\text{So, } P_{\text{ext}_2} = P_{\text{atm}}$$

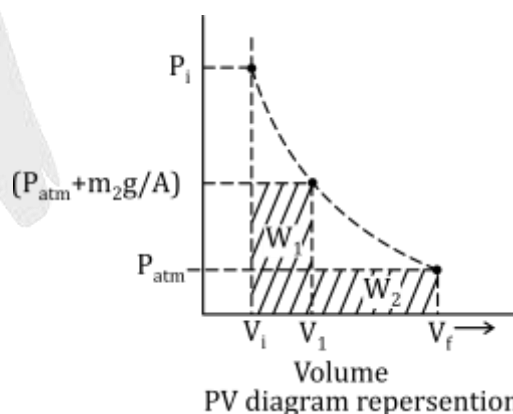
work done in expansion from  $V_i$  to  $V_1$

$$W_1 = - (P_{\text{atm}} + m_2 g/A) (V_i - V_1)$$

& work done in expansion from  $V_1$  to  $V_f$

$$W_2 = - P_{\text{atm}} (V_f - V_1)$$

$$\text{Total work} = W_1 + W_2$$



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.

### 5.1.2 Work done in reversible isothermal expansion

Take an ideal gas in a cylinder fitted with a frictionless piston. The cylinder is put in a large constant temperature bath and pressure over the piston is changed infinitesimally slowly.

If external pressure is decreased by infinitesimal small value, piston will go up by infinitesimal distance 'dx' and temperature of gas inside piston decreases by dT (due to kinetic energy transfer of molecule to piston). To maintain thermal equilibrium infinitesimally small heat dq will enter into the system. If the process is continued for infinite steps, the path of process is an isotherm on P-V graph.

If the gas is expanded from initial volume  $V_1$  to final volume  $V_2$  by gradually changing external pressure infinite steps, process is called reversible isothermal process.

During reversible process :

$$P_{\text{ext}} = P_{\text{int}} \pm dP$$

$$P_{\text{ext}} = P_{\text{int}} = \frac{nRT}{V} \text{ for an ideal gas}$$

$$\text{because } P_{\text{int}} = P_{\text{ideal}} = \frac{nRT}{V}$$

$$dw_{\text{rev, isothermal}} = -PdV$$

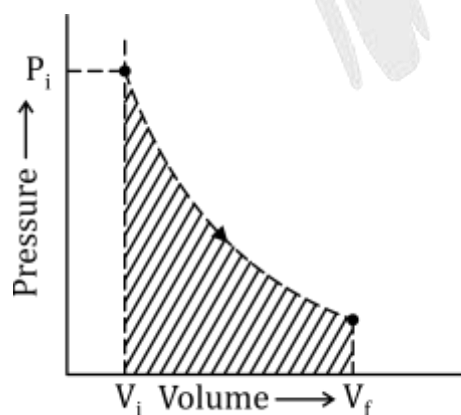
$$\int dw = -\int \frac{nRT}{V} dV$$

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

Work = Area under the P-V diagram

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

$$W = -ve$$



PV Diagram representation

**Note :** If process takes place in  $n$  steps and  $n \rightarrow \infty$  then process will be like reversible compression.



### 5.1.3 Work done in Irreversible isothermal expansion:

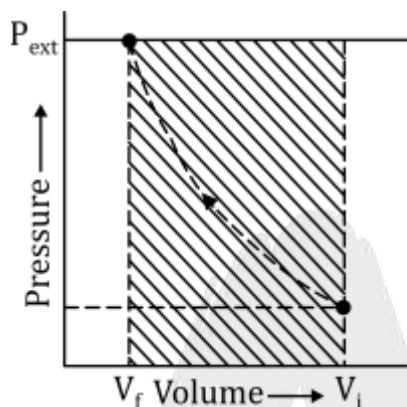
#### (a) Single step compression :

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

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

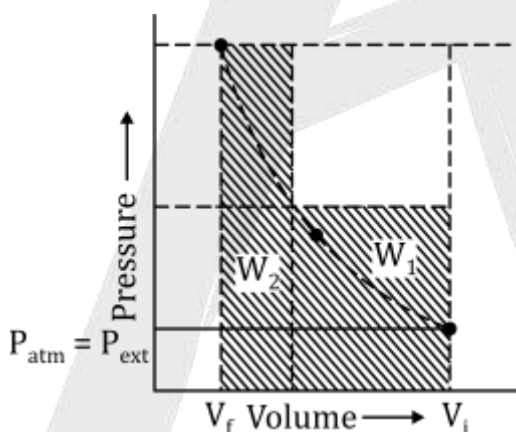
so, to calculate total work done on the gas

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



#### (b) 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 against external pressure of ( $P_{\text{atm}} + m_1g/A$ )

$$\text{So, } W_1 = -(P_{\text{atm}} + m_1g/A) (V_1 - V_i)$$

$$\text{Similarly, } W_2 = -(P_{\text{atm}} + m_0g/A) (V_f - V_1)$$

### 5.1.4 Reversible isothermal compression of an ideal gas

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

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

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

### Conclusion :

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

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

Output – work done by engine/machine/system

Input – work done by system on a surrounding

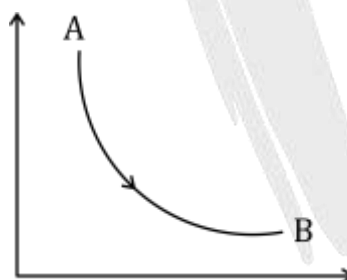
- ♦ **If expansion/compression takes place against constant external pressure then it is irreversible.**
- ♦ **If there is sudden change then the process is irreversible.**

### Reversible and irreversible isothermal process.

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

**Reversible process :** If a process operates in 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  $A \rightarrow B$  work =  $w$ , heat =  $Q$  then if for the process  $B \rightarrow A$ , work =  $-w$ , heat =  $-Q$  then the process is reversible.



If the reversible isothermal expansion is reversed by gradually increasing the pressure the system will return to initial state retracing its path. This means the path of a reversible process can be exactly reversed if conditions are reversed.

- Work done by the system during reversible isothermal expansion is maximum possible work obtainable from system under similar conditions.
- If the external pressure is constant in an isothermal process, the process is irreversible.

## 5.2 ISOCHORIC PROCESS :

Since  $dv = 0$

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

### 5.3 ISOBARIC PROCESS :

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

So,  $w = -P_{\text{ext}} (V_f - V_i)$  (for both reversible and irreversible process)

**5.4 Stoppered expansion (kind of an irreversible expansion):** In this expansion, the gas is allowed to expand against constant external pressure but the piston is stopped at certain volume when system gradually attains equilibrium. In this type of expansion, the  $P_{\text{external}}$  and  $P_{\text{final}}$  are different. The stoppered expansion will help you realize that there can be infinite irreversible path's connection for any two given state at same temperature. (the same can be said about reversible paths)

the work done during stoppered expansion can be given by

$$w = -P_{\text{ext}} \left( \frac{nRT_f}{P_f} - \frac{nRT_i}{P_i} \right) \quad \text{where } P_{\text{ext}} \text{ and } P_f \text{ are different}$$

### 6. ADIABATIC PROCESS :

In an adiabatic process, no loss or gain of heat takes place i.e.,  $q = 0$ .

**6.1 Reversible adiabatic process :** For a reversible adiabatic process  $dq = 0$ .

From first law, we have,

$$dq = dU + dw$$

Since  $dq = 0$

$$\therefore dU = -dw$$

For an ideal gas,

$$dU = C_v dT$$

$$\therefore C_v dT = -dw = -pdV$$

$$\text{or, } C_v dT = - (nRT/V) dV$$

$$\text{or, } C_v dT/T + nR dV/V = 0$$

Integrating the above equation between  $T_1$  and  $T_2$  and  $V_1$  and  $V_2$ , the initial and final temperature and volumes, we have,

$$\int_{T_1}^{T_2} C_v \frac{dT}{T} + nR \int_{V_1}^{V_2} \frac{dV}{V} = 0$$

$$\text{or } C_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} = 0$$

Here  $C_v$  is assumed to be independent of temperature.

But,  $C_p - C_v = nR$

Hence, from we get

$$C_v \ln \frac{T_2}{T_1} + (C_p - C_v) \ln \frac{V_2}{V_1} = 0$$

$$\text{or, } \ln \frac{T_2}{T_1} = \frac{C_p - C_v}{C_v} \ln \frac{V_1}{V_2}$$

we put,  $C_p/C_v = \gamma$

Equation may therefore be written as,

$$(\gamma - 1) \ln \frac{V_2}{V_1} + \ln \frac{T_2}{T_1} = 0$$

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

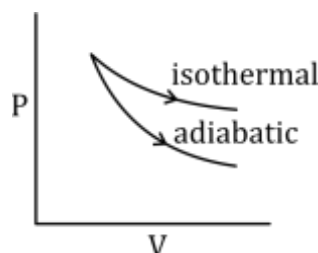
$$\text{or } (T_1 V_1)^{\gamma-1} = (T_2 V_2)^{\gamma-1} = \text{constant}$$

For an ideal gas,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\text{or } \frac{T_1}{T_2} = \frac{P_2 V_2}{P_1 V_1}$$

$$\therefore P_1 V_1^\gamma = P_2 V_2^\gamma = \text{constant}$$



In general, for a reversible adiabatic expansion

$$P V^\gamma = \text{constant}$$

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

$$T P^{1-\gamma/\gamma} = \text{constant}$$

work done is given by either  $w = nC_v(T_2 - T_1)$  or rearranging it gives  $w = (P_2 V_2 - P_1 V_1) / \gamma - 1$

For an isothermal expansion,  $PV = \text{constant}$ . but for an reversible adiabatic expansion  $PV^\gamma = \text{constant}$  differentiating both  $PV$  and  $PV^{\gamma-1}$  with respect to  $V$  we get for isothermal process  $dP/dV = -P/V$  while for adiabatic process  $dP/dV = -\gamma(P/V)$  since  $\gamma$  is always  $>1$  slope of  $P$   $V$  curve is more negative in case of adiabatic process.

In figure, pressure and volume are plotted for isothermal and adiabatic cases. It is evident that a given pressure fall produces a lesser volume increase in the adiabatic case, because the temperature also falls during the adiabatic expansion.

**6.2 The irreversible adiabatic process:** Suppose an ideal gas is confined in a adiabatic container fitted with friction less piston. If the thermodynamic equilibrium of system is disturbed by changing external pressure suddenly by finite value and let the system come to equilibrium the process is irreversible adiabatic process. The work done ( $w$ ) is given by

$$\Delta U = w = -P_{\text{ext}}(V_f - V_i)$$

$$\Delta U = nC_v(T_f - T_i)$$

$$\Rightarrow nC_v(T_f - T_i) = -P_{\text{ext}}(V_f - V_i)$$

$$nC_v(T_f - T_i) = -P_{\text{ext}}\left(\frac{nRT_f}{P_f} - \frac{nRT_i}{P_i}\right)$$

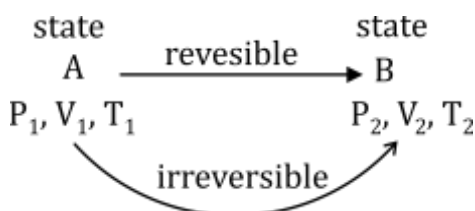
solving this equation for  $T_f$

now  $w = \Delta U = nC_V(T_2 - T_1)$

$$w = \left[ \frac{P_f V_f - P_i V_i}{\gamma - 1} \right]$$

### 6.3 Comparison of reversible and irreversible adiabatic process :

**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 steps are linked by an adiabatic reversible and irreversible path then

$$w_{\text{rev.}} = \Delta U_{\text{rev.}}$$

But as  $u$  is a state function

$$\therefore \Delta U_{\text{rev.}} = \Delta U_{\text{irrev.}} \Rightarrow w_{\text{irrev.}} = w_{\text{rev.}}$$

as work is a path function.

If we assume that

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

$$\Rightarrow \text{It implies that } \Delta U_{\text{rev.}} \neq \Delta U_{\text{irrev.}}$$

$\Rightarrow$  Two steps A and B can never lie both on a reversible as well as irreversible adiabatic path.

$\Rightarrow$  There lies only one unique adiabatic path linkage between two steps A and B.

#### 6.3.1 Adiabatic Expansion (single step Vs Infinite steps)

Single step means irreversible process

Infinite steps means reversible process

In adiabatic compression process,

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

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

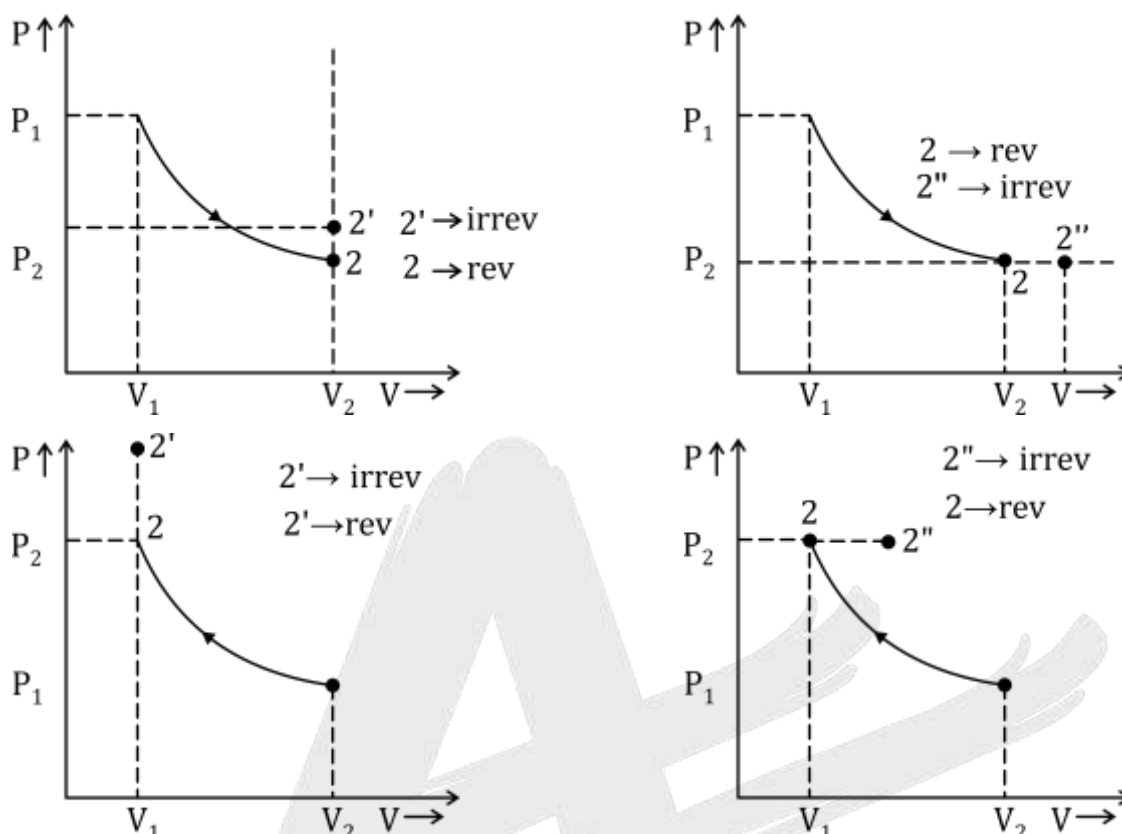
$$(P_2)_{\text{rev.}} < (P_2)_{\text{irrev}} \quad (\text{If volume change are same})$$

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

#### 6.3.2 Adiabatic Expansion (single step Vs two steps)

If the expansion is carried out in two steps then work done in two steps by the gas > work done in one step by the gas. So,  $\Delta U_{\text{two steps}} > \Delta U_{\text{single step}}$

$T_f$  in two steps  $< T_f$  in single step because decrease in internal energy in two step is  $>$  decrease in internal energy in one step.



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,  $\Delta U_{\text{two stage}} > \Delta U_{\text{single stage}}$

- $T_f$  in two stage  $< T_f$  in single stage because decrease in internal energy in two stage is  $>$  decrease in internal energy in one stage.

#### 6.4 Comparison of isothermal and adiabatic process :

Starting from same state, if system is allowed to expand to same final pressure,

$$|W_{\text{rev, isothermal}}| > |W_{\text{rev, adiabatic}}|.$$

In reversible isothermal process, heat is entering from surrounding, while in adiabatic process, work is done on the expansion of internal energy of system.

Starting from same initial state, if system is compressed to same final pressure,  $W_{\text{rev, adia}} > W_{\text{rev, iso}}$ .

During adiabatic compression, the work done is getting stored in the system, and temperature of system increases, the gas become less and less compressible, and greater work is required to compress the system.

15. 1 mole of  $\text{CO}_2$  gas at 300 K is expanded under reversible adiabatic condition such that its volume becomes 27 times. (a) What is the final temperature ? (b) What is work done ?

Given  $\gamma = 1.33$  and  $C_v = 25.08 \text{ J mol}^{-1} \text{ K}^{-1}$  for  $\text{CO}_2$ .

Ans.  $T_2 = 100 \text{ K}$ ,  $w = - 5.016 \text{ KJ}$



**Sol.** (a)  $T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$

$$300 \times V^{4/3-1} = T_2 \times 27V^{4/3-1}$$

$$T_2 = 100 \text{ K}$$

(b)  $\Delta E = q + W$

For reversible adiabatic process,

$$q = 0$$

$$\Delta E = W$$

$$W = n C_v \Delta T$$

$$W = 1 \times 25.08 \times (100 - 300) = -5.016 \text{ kJ}$$

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

**Ans.** 72

**Sol.**  $q = 0, \Delta U = W$

$$nC_v(T_2 - T_1) = -P_{\text{ext}}(V_2 - V_1)$$

$$\frac{3}{2} nR (T_2 - 30) = -2 \left( \frac{nRT_2}{2} - \frac{nR \times 30}{1} \right)$$

$$\frac{3}{2} (T_2 - 30) = (60 - T_2) \quad T_2 = 42 \text{ K}$$

$$W = n C_v(T_2 - T_1) = 2 \times \frac{3}{2} \times 2 (42 - 30) = 72 \text{ cal.}$$

- 17.** Two moles of He gas ( $\gamma = 5/3$ ) are initially at temp  $27^\circ\text{C}$  and occupy a volume of 20 L. The gas is first expanded at constant pressure until its volume is doubled. Then it undergoes and reversible adiabatic change, until the volume become 110 lit, then find final temperature.

(Given  $\left(\frac{4}{11}\right)^{2/3} = \frac{1}{2}$ )

**Ans.** 300K

**Sol.** 1<sup>st</sup> process is isobaric

volume become double so, T is also become double

So, for adiabatic  $T_i = 2 \times 300 = 600$

$$V_i = 40$$

$$T_f = ?, V_f = 110$$

for adiabatic

$$P_1 V_1^\gamma = \text{constant} = T V^{\gamma-1} = \text{constant}$$

$$T_i V_i^{5/3-1} = T_f V_f^{2/3}$$

$$600 \times (40)^{2/3} = T_f \times (40)^{2/3} = T_f \times (110)^{2/3}$$

$$T_f = 300 \text{ K}$$

## 7. POLYTROPIC PROCESS:

A process described by  $PV^n = C$  is called polytropic process. where  $n$  is a real number. Work done for polytropic process :

$$dw = -PdV$$

Let us suppose an ideal gas is undergoing poly tropic process

$$dw = -PdV$$

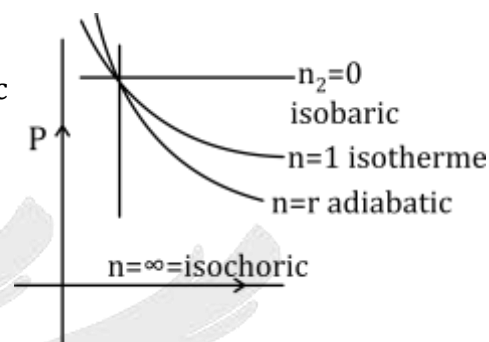
$$\int dw = \int_{V_1}^{V_2} \frac{C}{V^n} dV$$

$$\Rightarrow w = \frac{-C}{(-n+1)} \left[ \frac{1}{V^{n-1}} \right]_{V_1}^{V_2}$$

$$= \frac{C}{(n-1)} \left( \frac{1}{V_2^{n-1}} - \frac{1}{V_1^{n-1}} \right)$$

$$w = \frac{C}{(n-1)} \left( \frac{P_2 V_2 - P_1 V_1}{C} \right)$$

$$\boxed{w = \left( \frac{P_2 V_2 - P_1 V_1}{n-1} \right)}$$



### 7.1 Heat capacity for polytropic process :

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

from first law

$$dq = dU + PdV \quad \dots\dots\dots(i)$$

$$\frac{dq}{dT} = \frac{nC_v dT}{dT} + \frac{nRT}{V} \cdot \frac{dV}{dT} \Rightarrow C = \frac{nC_v dT}{dT}$$

$$C = n C_v + \frac{nRT}{V} \left( \frac{dV}{dT} \right) \quad \dots\dots\dots(ii)$$

$$PV^n = k$$

$$V^n = \frac{k}{P} = \frac{kV}{n_g RT} \Rightarrow V^{(n-1)} = \frac{k}{n_g RT}$$

$$(n-1) V^{(n-2)} + dV = \frac{-RdT}{n_g RT^2}$$

$$\Rightarrow \frac{dV}{dT} = \frac{k}{(n-1) \left( \frac{k}{PV^2} \right) (PV) T}$$

$$\frac{dV}{dT} = - \left( \frac{V}{T} \right) \left( \frac{1}{n-1} \right) \quad \dots\dots\dots(iii)$$

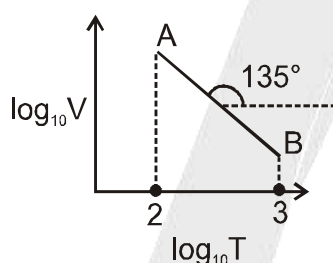
substituting (iii) in equation (ii)

$$C = n_g C_V + \frac{n_g R}{1-n}$$

from 1 mole gas

$$C = C_v + \frac{R}{1-n}$$

18. Three moles of an ideal diatomic gas undergoes a change in state from A to B reversibly as follows :



Which of the following statements is/are correct regarding the above process :

- (A) Work done on the gas is 2700 R
- (B) In the above process, pressure varies inversely with square of volume.
- (C) Heat supplied to the gas is 4050 R
- (D) Data insufficient for the calculation of work and heat supplied.

**Ans. (ABC)**

**Sol.** From graph, slope = -1

$$\text{eq} = \log_{10} V + \log_{10} T = \text{constant}$$

$$VT = \text{constant or } PV^2 = \text{constant}$$

$$C = C_V + \frac{R}{1-n} \therefore C = \frac{5R}{2} + \frac{R}{1-2} = \frac{3R}{2}$$

$$\therefore q = nC \Delta T = 3 \times \frac{3R}{2} \times (1000-100) = 4050 R$$

$$\Delta U = nC_v \Delta T = 3 \times \frac{5R}{2} \times (1000 - 100) = 6750 R$$

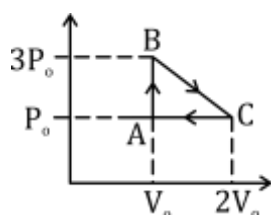
$$\therefore W = \Delta U - q = 6750 R - 4050 R = 2700 R$$

8. **Free expansion of ideal gas:** When ideal gas is allowed to expand against zero external pressure, the process is called free expansion.  $W=0$  for free expansion. During the free expansion, the ideal gas do not lose any energy, and hence temperature of ideal gas remain constant. Hence, free expansion of ideal gas is an example of isothermal, adiabatic irreversible process.

However if a real gas is allowed to expand in vacuum, the gas may be cooled or heated up depending upon temperature of the real gas. The temperature above which a gas hots up upon expansion is called inversion temperature.

S. No.	Process	w	q	$\Delta U$	$\Delta H$	Molar heat capacity
1.	Isochoric	0	$nC_{v,m}(T_f - T_i)$	$q_v$	$nC_{p,m}(T_f - T_i)$	$C_{v,m}$
2.	Isobaric	$-P_{\text{ext}}(V_2 - V_1)$	$nC_{p,m}(T_f - T_i)$	$q + w$	$nC_{p,m}(T_f - T_i)$	$C_{p,m}$
3.	Isothermal	$W_{\text{rev}} = -nRT \ln \left( \frac{V_f}{V_i} \right)$ $W_{\text{irrev}} = -P_{\text{ext}}(V_f - V_i)$	$-w$	0	0	$\pm \infty$
4.	Adiabatic	$\frac{P_f V_f - P_i V_i}{\gamma - 1}$	0	W	0	0
5.	Polytrophic	$\frac{P_f V_f - P_i V_i}{(n - 1)}$	$\Delta U - w$	$nC_{v,m}(T_2 - T_1)$	$nC_{p,m}(T_2 - T_1)$	$C_{v,m} + \frac{R}{1 - \gamma}$

19. One mole of ideal monoatomic gas is carried through the reversible cyclic process as shown in figure. Calculate net heat absorbed by the gas in the path BC.



(1)  $\frac{1}{2} P^\circ V^\circ$

(2)  $\frac{7}{2} P^\circ V^\circ$

(3)  $2 P^\circ V^\circ$

(4)  $\frac{5}{2} P^\circ V^\circ$

Ans. (1)

Sol.  $\Delta U = q + w$

$$W_{BC} = \frac{1}{2} (2V^\circ - V^\circ) (P^\circ - 3P^\circ) + (2V^\circ - V^\circ) (0 - P^\circ) = -2P^\circ V^\circ$$

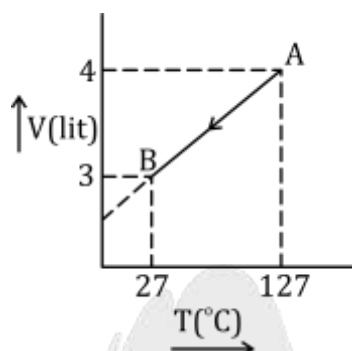
$$\Delta U = nC_V \Delta T = 1 \times \frac{3}{2} R \left( \frac{P^\circ 2V^\circ}{R} - \frac{3P^\circ V^\circ}{R} \right) = -\frac{3}{2} P^\circ V^\circ$$

$$q_{BC} = \Delta U - W = -\frac{3}{2} P^\circ V^\circ + 2P^\circ V^\circ = \frac{1}{2} P^\circ V^\circ$$

### DO YOURSELF - 2

- The temperature of the system decreases in an
  - Adiabatic compression
  - Isothermal compression
  - Isothermal expansion
  - Adiabatic expansion
- 1 mole of  $\text{NH}_3$  gas at  $27^\circ\text{C}$  is expanded in reversible adiabatic condition to make volume 8 times ( $\gamma = 1.33$ ). Final temperature and work done respectively are :
  - 150 K, 900 cal
  - 150 K, 400 cal
  - 250 K, 1000 cal
  - 200 K, 800 cal
- 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 :
  - $W_3 > W_1 > W_2$
  - $W_3 > W_2 > W_1$
  - $W_2 > W_1 > W_3$
  - $W_1 > W_2 > W_3$
- One mole of an ideal gas 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 :
  - 270 K
  - 273 K
  - 248.5 K
  - 200 K
- A piston freely move in a insulated cylinder from volume 5 lit to 10 lit then calculate work done & heat during this expansion.
- 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.

7. The work done in adiabatic compression of 2 mole of an ideal monoatomic gas by constant external pressure of 2 atm starting from initial pressure of 1 atm and initial temperature of 30 K ( $R = 2 \text{ cal/mol-degree}$ )
8. One mole of Ideal gas ( $C_{p,m} = 15 \text{ JK}^{-1} \text{ mole}^{-1}$ ) follow the process as shown in figure.



Predict the following :

- (i) Nature of process                      (ii) Calculate work done, Heat of process.

9. **Change in internal energy and enthalpy in chemical reactions :** Enthalpy and internal energy change in chemical reaction involve change in potential energy due to chemical change. During chemical change transformation of bonds take place. If the bonds in product are more stable, leading to decrease in potential energy of atom and molecules, the enthalpy and internal energies decreases. In the process surplus energy is liberated and process is called exothermic process. During endothermic chemical process which take place absorbing energy from surrounding, the potential energy of system of chemical substance increases.

Consider a chemical reaction



The internal energy change can be given as (Theoretically)

$$\Delta U = cU_c + dU_d - aU_a - bU_b$$

where  $U_a, U_b, U_c, U_d$  etc. are molar internal energy of respective species.

since absolute internal energies cannot be determine,  $U_i$  are determined with respect to internal energy of elements in their most stable state. The internal energies of elements in their most stable allotropic modification is arbitrary taken as zero at 298K and 1 atm pressure.

also,  $\Delta_r U = q_v$  for reaction taking place under constant volume and temperature condition.

For the similar reaction occurring at constant pressure and temperature, enthalpy change,  $\Delta H$  is given by

$$\Delta H = cH_c + dH_d - aH_a - bH_b$$

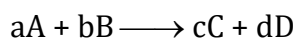


where  $H$  are enthalpies of respective species

however  $\Delta H$  is equal to heat exchange during chemical process at constant pressure and temperature.

$\Delta_r H = q_p$  for reaction taking place under constant pressure and temperature conditions

□ **Relationship between  $\Delta_r H$  and  $\Delta_r U$  in chemical reactions:** For a general chemical reaction given by



$$\Delta_r H = cH_c + dH_d - aH_a - bH_b \quad \dots\dots\dots (1)$$

$$\text{but } H_i = U_i + PV_i$$

Substituting the value of molar enthalpies of substance in equation (1) we get

$$\Delta_r H = cU_c + dU_d - aU_a - bU_b + P(cV_c + dV_d - aV_a - bV_b)$$

$$\Delta_r H = \Delta_r U + P(V_f - V_i) \quad \dots\dots\dots (2)$$

(a) If all the reactant and products are ideal gases  $V_c, V_d, V_a$  and  $V_b$  all are equal to molar volume of ideal

gas e.g.  $V = RT/P$  which on substitution in previous equation gives

$$\Delta_r H = \Delta_r U + (d + c - a - b)RT$$

$$\Delta_r H = \Delta_r U + \Delta n_g RT \quad \dots\dots\dots (3)$$

Where  $\Delta n_g$  is difference of stoichiometric coefficient of gaseous products and gaseous reactants.

(b) In case of liquid and solids present in chemical equations, their molar volumes can be ignored in comparison to molar volume of ideal gases and hence do not count stoichiometric coefficient of solid and liquids in  $\Delta n_g$ .

(c) In case of non ideal behaviour of gases, equation (2) should be used.

**20.** The internal energy change in the conversion of 1.0 mole of the calcite form of  $\text{CaCO}_3$  to the aragonite form is +0.21 kJ. Calculate the enthalpy change when the pressure is 1.0 bar; given that the densities of the solids are  $2.71 \text{ g cm}^{-3}$  and  $2.93 \text{ g cm}^{-3}$  respectively.

**Ans.**  $0.20972 \text{ kJ mol}^{-1}$

**Sol.**  $\Delta H = \Delta U + P\Delta V$

$$\text{Given } \Delta E = +0.21 \text{ kJ mol}^{-1} = 0.21 \times 10^3 \text{ J mol}^{-1}$$

$$P = \bar{1} = 1.0 \times 10^5 \text{ Pa}$$

$$\Delta V = V_{(\text{aragonite})} - V_{(\text{Calcite})}$$

$$= \left( \frac{100}{2.93} - \frac{100}{2.71} \right) \text{ cm}^3 \text{ mol}^{-1} \text{ of } \text{CaCO}_3$$

$$= -2.77 \text{ cm}^3 = -2.77 \times 10^{-6} \text{ m}^3$$

$$\therefore \Delta H = 0.21 \times 10^3 - 1 \times 10^5 \times 2.77 \times 10^{-6} = 209.72 \text{ J} = 0.20972 \text{ kJ mol}^{-1}$$

21. One mole of a non-ideal gas undergoes a change of state (2.0 atm, 3.0 L, 95 K)  $\longrightarrow$  (4.0 atm, 5.0 L, 245 K) with a change in internal energy,  $\Delta U = 30.0 \text{ L. atm}$ . Calculate change in enthalpy of the process in L. atm.

Ans. 44

Sol. (20 atm, 3.0 L, 95 K) (4.0 atm, 5.0 L, 245 K)

$$n = 1; \Delta U = 30.0 \text{ L. atm}$$

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

$$= 30 + (P_2V_2 - P_1V_1)$$

$$= 30 + (4 \times 5 - 2 \times 3) = 30 + 14 = 44 \text{ L. atm}$$

22. 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 energy.

Ans. 760 J

Sol.  $\Delta U = nC_vdT = n \times (T_2 - T_1)$

$$= (P_2V_2 - P_1V_1) = \times P(V_2 - V_1)$$

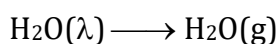
$$= \times 1 \times (5 - 2) = \times 101.325 = 760 \text{ J}$$

10. **Change in internal energy and enthalpy in phase transition :** At certain temperature under one atmospheric pressure, one phase changes into other phase by taking certain amount of Heat. The temperature at which this happens is called **transition temperature** and heat absorbed during the process is called Enthalpy of phase transition. Heat absorbed during transition is exchanged at constant pressure and temperature and it is significant to know that the process is reversible.

**Fusion:** Solid ice at 273K and 1 atm pressure reversibly changes into liquid water. Reversibly, isothermally and isobarically, absorbing heat known as latent heat of fusion or enthalpy of fusion.

**Vaporisation:** Water at 373K and 1 atm pressure changes into its vapors absorbing heat known as latent heat of vaporisation. The latent heat of vaporisation is heat exchanged isothermally, isobarically and reversibly to convert water into its vapour at boiling point.

Internal energy change of phase transitions involving gas phase has no practical significance because it is not possible to carry out  $\Delta U$  of phase transition directly through an experiment. However  $\Delta U$  of phase transition can be determined theoretically from experimentally obtained value of  $\Delta H$  of phase transition.



$$\Delta H_{\text{vaporisation}} = \Delta U_{\text{vaporisation}} + P(V_f - V_i)$$

$$\Delta H_{\text{vaporisation}} = \Delta U_{\text{vaporisation}} + \{RT/V\}\{V_g\}$$

ignoring volume of liquid as compared to molar volume of gas

$$\Rightarrow \Delta H_{\text{vap.}} = \Delta U_{\text{vap.}} + RT$$

where R is gas constant and T absolute temperature for condensed phase transitions like solid liquid transitions

$$H_{\text{vap.}} \approx \Delta U_{\text{vap.}}$$

23. What is  $\Delta U$  when 2.0 mole of liquid water vaporises at  $100^\circ\text{C}$  ? The heat of vaporisation ( $\Delta H_{\text{vap.}}$ ) of water at  $100^\circ\text{C}$  is  $40.66 \text{ kJmol}^{-1}$ .

**Ans.**  $\Delta U = 75.12 \text{ kJ}$

**Sol.**  $\Delta U = \Delta H - (P_2V_2 - P_1V_1) \quad (\ominus \quad V_2 \gg V_1)$

$$= \Delta H - (P_2V_2) \Rightarrow \Delta H - nRT$$

$$\Delta U = 40.66 \times 2 - \frac{2 \times 8.314 \times 373}{1000} = 75.12 \text{ kJ}$$

### ANSWER KEY

### DO YOURSELF - 1

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

**Sol.** State function depends on the state of the system and path function depends on path which a system follow.

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

**Sol.** Extensive property depends on size or mass of the system while intensive property is independent on size or mass of the system.

3.  $-60 \text{ cal.}$

**Sol.**  $\frac{V_1}{V_2} = \frac{T_1}{T_2} \Rightarrow \frac{V}{2V} = \frac{300}{T_2} \Rightarrow T_2 = 600 \Rightarrow \Delta T = 300$

$$w = -P\Delta V = nR\Delta T \quad ; \quad w = -0.1 \times 2 \times 300 = -60 \text{ cal.}$$

4.  $1.2 \times 10^3 \text{ J}$

**Sol.**  $w = -P_{\text{ext}}(V_2 - V_1) = -4(1 - 4) \text{ bar.L} = 1.2 \times 10^3 \text{ J}$

5.  $1.066 \text{ kJ}$

**Sol.**  $q = nC\Delta T = \left(\frac{60}{27}\right) \times 24 \times (55 - 35) = 1066 \text{ J} = 1.066 \text{ kJ}$

6. 760 J

**Sol.**  $\Delta U = nC_{vd}T = n \times \frac{fR}{2} (T_2 - T_1)$

$$= \frac{5}{2} nR \left( \frac{P_2 V_2}{nR} - \frac{P_1 V_1}{nR} \right) = \frac{5}{2} (P_2 V_2 - P_1 V_1) = \frac{5}{2} \times P(V_2 - V_1)$$

$$= \frac{5}{2} \times 1 \times (5 - 2) \times 101.325 = 760 \text{ J}$$

7. - 810.10 joule

**Sol.** Since the external pressure is greatly different from the pressure of  $N_2$  and thus, process is irreversible.

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

$$w = -1 \times (V_2 - V_1)$$

Given  $V_1 = 2 \text{ litre}$   $V_2 = ?$   $T = 273 \text{ K}$

$P_1 = 5 \text{ atm}$   $P_2 = 1 \text{ atm}$

$$\therefore P_1 V_1 = P_2 V_2$$

$$\therefore V_2 = \frac{2 \times 5}{1} = 10 \text{ litre}$$

$$\therefore w = -1 (10 - 2) = -8 \text{ litre atm}$$

$$\therefore = - \frac{8 \times 1.987}{0.0821} \text{ calorie} = - \frac{8 \times 1.987 \times 4.184}{0.0821} \text{ J} = -810.10 \text{ joule}$$

### DO YOURSELF - 2

1. Zero

**Sol.** For reversible isothermal compression,

$$\Delta U = 0$$

$$\Delta H = 0$$

2. (B)

**Sol.** When both P and V are changing

$$\Delta H = \Delta U + \Delta (PV) = \Delta U + (P_2 V_2 - P_1 V_1) = 40 + (20 - 3) = 57 \text{ L-atm}$$

3. (D)

**Sol.** In isothermal reversible process ideal gas has constant temperature and so  $\Delta U = 0$  and  $\Delta H = 0$ .

4. (a) - 2271.14 J (b) 0.

**Sol.** (a) From one mole of zinc, the no. of moles of  $H_2$  gas evolved = 1

Hence volume of hydrogen gas evolved = 22.4 litre (when  $P = 1$  atm and  $T = 273$  K)

$\therefore w = -P\Delta V = -1 \times 22.4 \text{ Latm}$

$$= -22.4 \times \frac{8.314}{0.082} \text{ J} = -2271.14 \text{ J}$$

(b) For a closed system  $P_{\text{ext}} = 0$ , therefore,  $w = 0$ .

### DO YOURSELF - 3

1. (D)

**Sol.** When a real gas is forced through a porous plug into a region of low pressure, it is found that due to expansion, the gas on the side of low pressure gets cooled.

The phenomenon of producing lowering of temperature when a gas is made to expand adiabatically from a region of high pressure into a region of low pressure is known as Joule-Thomson effect.

2. (A)

**Sol.**  $T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$  ;  $300 \times V^{1/3} = T_2 (8V)^{1/3}$  ;  $T_2 = 150$  K

$$W = nC_v (T_2 - T_1) = 1 \times 3 R (150 - 300) = 3 \times 2 (-150) = -900 \text{ cal}$$

3. (A)

4. (C)

**Sol.**  $q = 0$  ;  $\Delta U = w$

$$\Rightarrow nC_{v,m} (T_2 - T_1) = -P_{\text{ext}} \left[ \frac{nRT_2}{P_2} - \frac{nRT_1}{P_1} \right]$$

$$C_{v,m} [T_2 - T_1] = P_{\text{ext}} \cdot R \left[ \frac{T_1}{P_1} - \frac{T_2}{P_2} \right] ; \frac{5}{2} R [T_2 - 300] = 2 \times R \left[ \frac{300}{5} - \frac{T_2}{2} \right]$$

$$T_2 = 248.5 \text{ K}$$

5.  $w = 0$  ;  $q = 0$

**Sol.** process is of free expansion

so,  $w = 0$  ,  $q = 0$

6. - 2.6 J

**Sol.**  $\Delta U = q + w$

$$= 200 \text{ J} - 0.5 \text{ atm} (62 - 22)$$

$$= 200 \text{ J} - 2 \text{ L atm}$$

$$= 200 \text{ J} - 2 \times 101.3 \text{ J} (1 \text{ L atm} = 101.3 \text{ J})$$

$$= -2.6 \text{ J}$$

7. 72

Sol.  $q = 0, \Delta U = W$

$$nC_V(T_2 - T_1) = -P_{\text{ext}}(V_2 - V_1)$$

$$n \frac{3}{2} R (T_2 - 30) = -2 \left( \frac{nRT_2}{2} - \frac{nR \times 30}{1} \right)$$

$$\frac{3}{2} (T_2 - 30) = (60 - T_2) \quad T_2 = 42 \text{ K}$$

$$W = nC_V(T_2 - T_1) = 2 \times \frac{3}{2} \times 2 (42 - 30) = 72 \text{ cal.}$$

8. (i) Isobaric (ii)  $w = 830.865 \text{ J}, q = -150 \text{ J}$

Sol. (i)  $\left( \frac{PV}{nRT} \right)_A = \left( \frac{PV}{nRT} \right)_B$

$$\frac{P_A \times 4}{nR \times 400} = \frac{P_B \times 3}{nR \times 300} = \frac{P_A}{100} = \frac{P_B}{100}; \quad P_A = P_B$$

Hence process is isobaric.

$$(ii) W = -P_{\text{ext}}(V_2 - V_1) = - \left( \frac{nRT_A}{V_A} \right) (V_B - V_A) = - \left( \frac{1 \times 0.082 \times 300}{3} \right) (3 - 4) \times 101.325 \text{ J}$$

$$= 830.865 \text{ J}$$

$$q_{AB} = nC_P (T_2 - T_1) = 1 \times 15 \times (300 - 400) = -150 \text{ J}$$

## EXERCISE - (O-I)

## BASIC DEFINITIONS &amp; GRAPHS

- Out of boiling point (I), mole (II), pH (III) and density (IV), intensive properties are  
(A) I, II (B) I, II, III (C) I, III, IV (D) All of these
- 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.

## HEAT, INTERNAL ENERGY AND WORK CALCULATION

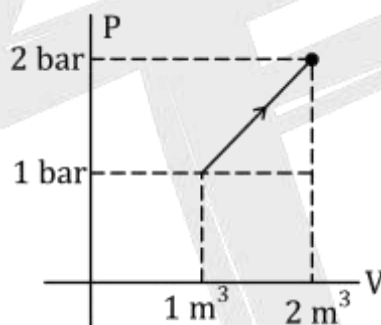
- Heat transfer during freezing of liquid in a system will be :  
(A)  $q = 0$  (B)  $q > 0$   
(C)  $q < 0$  (D)  $q > 0$  or  $q < 0$  (depending on the nature of liquid)
- Two moles of an ideal gas expand spontaneously into vacuum. The work done is :  
(A) Zero (B) 2 J (C) 4 J (D) 8 J
- $\text{H}_2\text{O(s)} \rightarrow \text{H}_2\text{O(l)}$   
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 be determined
- One mole of a gas occupying 3 dm<sup>3</sup> expands against a constant external pressure of 1 atm to a volume of 13 L. The work-done is :-  
(A) - 10 atm dm<sup>3</sup> (B) - 20 atm dm<sup>3</sup> (C) - 39 atm dm<sup>3</sup> (D) - 48 atm dm<sup>3</sup>
- A thermodynamic system goes from states (i)  $P_1, V$  to  $2P, V$  (ii)  $V$  to  $2V$ .  
at constant pressure  $P$  Then work done in the two cases is  
(A) Zero, Zero (B) Zero, - PV (C) - PV, Zero (D) -2PV, -PV

## FIRST LAW OF THERMODYNAMICS

- According to first law of thermodynamics (where  $q$  = heat supplied to system &  $W \rightarrow$  work done on the system) :  
(A)  $\Delta U = q - W$  (B)  $\Delta U = q + W$  (C)  $\Delta U = \Delta q + \Delta W$  (D)  $\Delta U = \Delta q + W$
- A system absorbs 600J of heat and work equivalent to 300 J on its surroundings. The change in internal energy is  
(A) 300 J (B) 400 J (C) 500 J (D) 600 J



10. A system undergoes a process which absorbed 0.5 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
11. If work done by the system is 300 J 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
12. 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)  $200 \times \frac{398}{308}$  J
13. A system has internal energy equal to  $U_1$  J, 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 :
14. What is  $\Delta U$  for the process described by figure? Heat supplied during the process  $q = 200$  kJ.



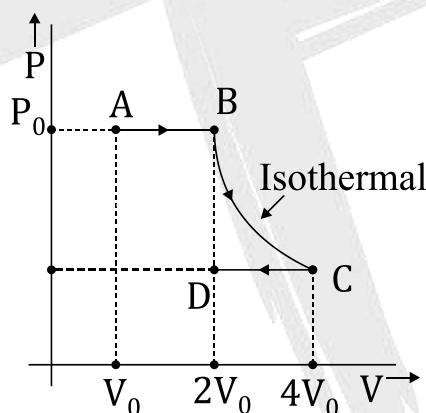
- (A) +50 kJ (B) -50 kJ (C) -150 kJ (D) + 150 kJ
15. What is the change in internal energy when a gas is compressed from 377 mL to 177 mL under a constant pressure of 1520 torr, while at the same time being cooled by removing 124 J heat ?  
 [Take : 1L atm = 100 J]  
 (A) -24 J (B) - 84 J (C) - 164 J (D) - 248 J
16. At 1 atm pressure freezing of  $n$  mole of water liquid ( $0^\circ\text{C}$ ) to ice ( $0^\circ\text{C}$ ) then heat transfer :  
 (A)  $n\Delta H_{\text{fusion}}$  (B)  $-n\Delta H_{\text{fusion}}$  (C)  $nC_{v,m}\Delta T$  (D)  $\Delta H_{\text{fusion}}$
17. For which reaction will  $\Delta H = \Delta U$  ?  
 (A)  $\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightarrow 2 \text{HBr}(\text{g})$  (B)  $\text{C}(\text{s}) + 2 \text{H}_2\text{O}(\text{g}) \rightarrow 2 \text{H}_2(\text{g}) + \text{CO}_2(\text{g})$   
 (C)  $\text{PCl}_5(\text{g}) \rightarrow \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$  (D)  $2 \text{CO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{CO}_2(\text{g})$

18. For a reaction,  $2X(s) + 2Y(s) \rightarrow 2C(l) + D(g)$   
The  $q_p$  at  $27^\circ\text{C}$  is  $-28 \text{ Kcal mol}^{-1}$ . The value of  $q_v$  is :  
(A)  $-27.4 \text{ Kcal mol}^{-1}$  (B)  $+27.4 \text{ Kcal mol}^{-1}$  (C)  $-28.6 \text{ Kcal mol}^{-1}$  (D)  $28.6 \text{ Kcal mol}^{-1}$
19. A mixture of 2 moles of carbon monoxide(g) and 1 mole of oxygen(g) in a closed vessel is ignited to get carbon dioxide(g), then :  
(A)  $\Delta H > \Delta U$  (B)  $\Delta H < \Delta U$  (C)  $\Delta H = \Delta U$  (D) Not definite
20. For the reaction  $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$ ,  $\Delta H$  is :  
(A)  $\Delta U + 2RT$  (B)  $\Delta U - 2RT$  (C)  $\Delta U + RT$  (D)  $\Delta U - RT$
21. A vessel contains 100 L 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 L. If the external pressure is 1 atm, and 202.6 Joules of heat were supplied then :  
(A)  $\Delta U = 0$ ,  $\Delta H = 0$  (B)  $\Delta U = +202.6 \text{ J}$ ,  $\Delta H = +202.6 \text{ J}$   
(C)  $\Delta U = -202.6 \text{ J}$ ,  $\Delta H = -202.6 \text{ J}$  (D)  $\Delta U = 0$ ,  $\Delta H = +202.6 \text{ J}$
22. Consider the reaction at 300 K,  
 $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$   $\Delta H = -185 \text{ kJ/mol}$   
Calculate  $\Delta U$  if 3 mole of  $H_2$  completely react with 3 mole of  $Cl_2$  to form HCl.  
(A) 0 (B)  $-185 \text{ kJ}$  (C)  $555 \text{ kJ}$  (D)  $-555 \text{ kJ}$
23. Ethyl chloride ( $C_2H_5Cl$ ), is prepared by reaction of ethylene with hydrogen chloride as,  
 $C_2H_4(g) + HCl(g) \longrightarrow C_2H_5Cl(g)$   $\Delta H = -72.3 \text{ kJ/mol}$   
What is the value of  $\Delta U$  (in kJ), if 70 g of ethylene and 73 g of HCl are allowed to react at 300 K.  
(A)  $-69.8$  (B)  $-180.75$  (C)  $-174.5$  (D)  $-139.6$
24. 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  $50 \text{ J/}^\circ\text{C}$ . Then the enthalpy change during the process is (1L atm  $\simeq 100 \text{ J}$ )  
(A)  $\Delta H = 15 \text{ kJ}$  (B)  $\Delta H = 15.7 \text{ kJ}$  (C)  $\Delta H = 14.4 \text{ kJ}$  (D)  $\Delta H = 14.7 \text{ kJ}$
25. The heat capacity of liquid water is  $75.6 \text{ J/mol}\cdot\text{K}$ , while the enthalpy of fusion of ice is  $6.0 \text{ kJ/mol}$ . What is the minimum number of ice cubes at  $0^\circ\text{C}$ , each containing 9.0 g of water, needed to cool 500 g of liquid water from  $20^\circ\text{C}$  to  $0^\circ\text{C}$  ?  
(A) 1 (B) 7 (C) 14 (D) 16

## THERMODYNAMIC PROCESSES

26. 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

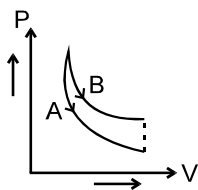
27. In an isothermal expansion of an ideal gas. Select wrong statement.
- (A) There is no change in the temperature of the gas  
 (B) There is no change in the internal energy of the gas  
 (C) The work done by the gas is equal to the heat supplied to the gas  
 (D) The work done by the gas is equal to the change in its internal energy
28. 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°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)  $-8.31 \times 10^7 \times 298 \times 2.303 \log 0.5$
29. 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
30. Work for the following process ABCD on a monoatomic gas is :



- (A)  $w = -2 P_0 V_0 \ln 2$ , (B)  $w = -2 P_0 V_0 \ln 2$ ,  
 (C)  $w = -P_0 V_0 (1 + \ln 2)$ , (D)  $w = -P_0 V_0 \ln 2$ ,
31. One mole of an ideal monoatomic gas expanded irreversibly in two stage expansion.
- State-1 (8.0 bar, 4.0 L, 300 K)  
 State-2 (2.0 bar, 16 L, 300 K)  
 State-3 (1.0 bar, 32 L, 300 K)
- Total heat absorbed by the gas in the process is :
- (A) 116 J (B) 40 J (C) 4000 J (D) 200 J

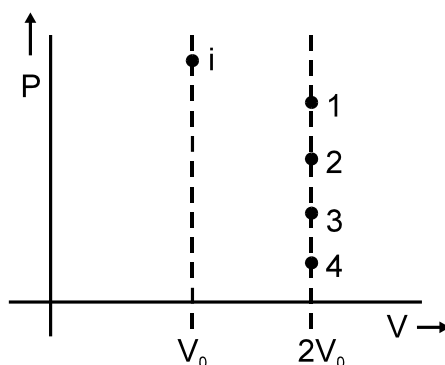
32. Which one of the following equations does not correctly represent the first law of thermodynamics for the given process in ideal gas ?  
(A) Isothermal process :  $q = -w$  (B) Cyclic process :  $q = -w$   
(C) Adiabatic process :  $\Delta U = q$  (D) Expansion of a gas into vacuum :  $\Delta U = q$
33. For an adiabatic process which of the following relations must be correct -  
(A)  $\Delta U = 0$  (B)  $P\Delta V = 0$  (C)  $q = 0$  (D)  $q = +W$
34. The temperature of an ideal gas increases in an :  
(A) adiabatic compression (B) adiabatic expansion  
(C) isothermal expansion (D) isothermal compression
35. When a gas is compressed adiabatically and reversibly, the final temperature is :  
(A) higher than the initial temperature (B) lower than the initial temperature  
(C) the same as initial temperature (D) dependent upon the rate of compression
36. One mole of an ideal gas ( $C_{v,m} = \frac{5}{2}R$ ) 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
37. 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
38. A gas ( $C_{v,m} = \frac{5}{2}R$ ) behaving ideally was allowed to expand reversibly and adiabatically from 1 L to 32 L. It's initial temperature was 327° C. The molar enthalpy change (in J/mole) for the process is :-  
(A) -1125 R (B) - 575 R (C) -1575 R (D) -75 R
39. One mole of ideal gas is allowed to expand reversibly and adiabatically from a temperature of 27°C. If the work done by the gas in the process is 3 kJ, the final temperature will be equal to ( $C_v = 20 \text{ J/K-mol}$ )  
(A) 100 K (B) 450 K (C) 150 K (D) 400 K
40. 1 mole of  $\text{NH}_3$  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

41. 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<sub>2</sub> respectively  
(C) O<sub>2</sub> and H<sub>2</sub> respectively (D) H<sub>2</sub> and He respectively
42. 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)  $W_1 > W_2 > W_3$
43. The magnitudes of enthalpy changes for irreversible adiabatic expansion of a gas from 1L to 2L is  $\Delta H_1$  and for reversible adiabatic expansion for the same expansion is  $\Delta H_2$ . Then
- (A)  $\Delta H_1 > \Delta H_2$   
(B)  $\Delta H_1 < \Delta H_2$   
(C)  $\Delta H_1 = \Delta H_2$   
(D)  $\Delta H_1 = \Delta U_1$  &  $\Delta H_2 = \Delta U_2$  where  $\Delta U_1$  &  $\Delta U_2$  are magnitudes of change in internal energy of gas in these expansions respectively.
44. An ideal gaseous sample at initial state i ( $P_0, V_0, T_0$ ) is allowed to expand to volume  $2V_0$  using two different processes. In the first process the equation of process is  $PV^2 = K_1$  and in second process the equation of the process is  $PV = K_2$ . Then,
- (A) work done in first process will be greater than work in second process (magnitude wise)  
(B) The order of values of work done can't be compared unless we know the value of  $K_1$  and  $K_2$ .  
(C) value of work done (magnitude) in second process is greater in above expansion irrespective of the value of  $K_1$  and  $K_2$ .  
(D) 1<sup>st</sup> process is not possible
45. There are two samples of same gas initially under similar initial state. Gases of both the samples are expanded. 1<sup>st</sup> sample using reversible isothermal process and 2<sup>nd</sup> sample using reversible adiabatic process till final pressures of both the samples becomes half of initial pressure, then
- (A) Final volume of 1<sup>st</sup> sample < final volume of 2<sup>nd</sup> sample  
(B) Final volume of 2<sup>nd</sup> sample < final volume of 1<sup>st</sup> sample  
(C) final volumes will be equal  
(D) Information is insufficient

46. If four identical samples of an ideal gas initially at similar state ( $P_0, V_0, T_0$ ) are allowed to expand to double their volumes by four different process.



I : by isothermal irreversible process

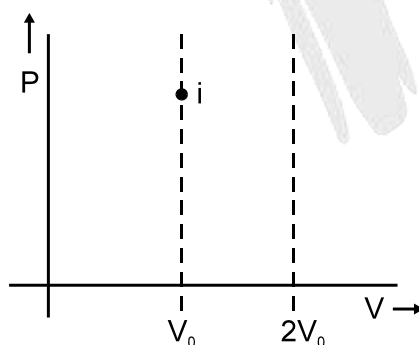
II : by reversible process having equation  $P^2 V = \text{constant}$

III : by reversible adiabatic process

IV : by irreversible adiabatic expansion against constant external pressure.

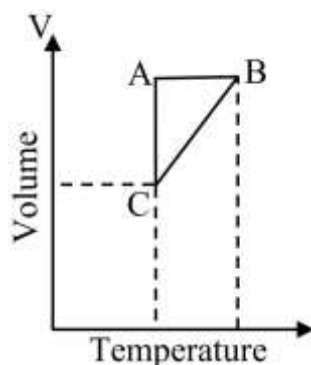
Then, in the graph shown the final state is represented by four different points then, the correct match can be

- (A) 1 - I, 2 - II, 3 - III, 4 - IV                      (B) 1 - II, 2 - I, 3 - IV, 4 - III  
(C) 2 - III, 3 - II, 4 - I, 1 - IV                      (D) 3 - II, 1 - I, 3 - IV, 4 - III
47. Two samples (initially under same states) of an ideal gas are first allowed to expand to double their volume using irreversible isothermal expansion against constant external pressure, then samples are returned back to their original volume first by reversible adiabatic process and second by reversible process having equation  $PV^2 = \text{constant}$  then

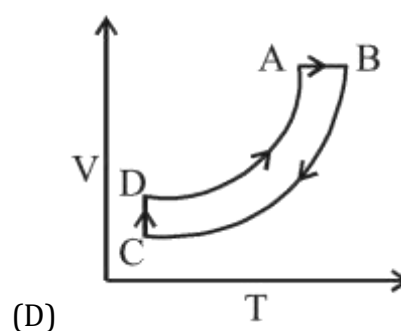
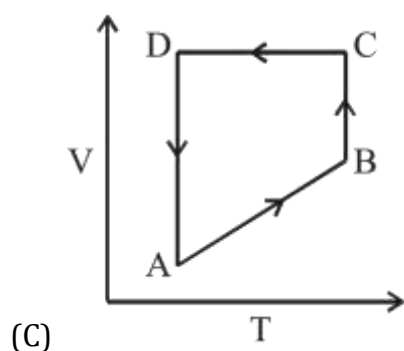
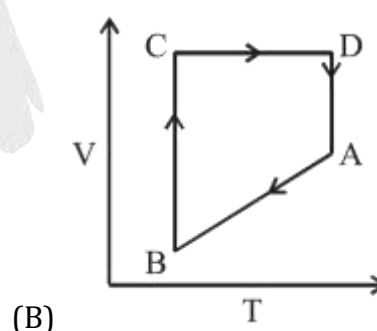
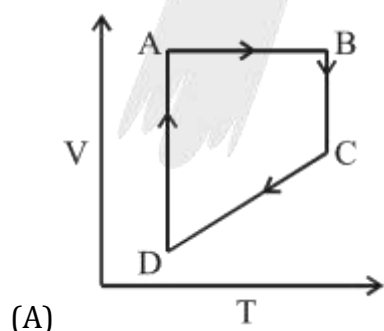
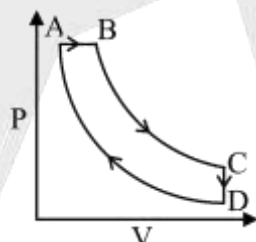


- (A) final temperature of both samples will be equal  
(B) final temperature of first sample will be greater than of second sample  
(C) final temperature of second sample will be greater than of first sample  
(D) none of these

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

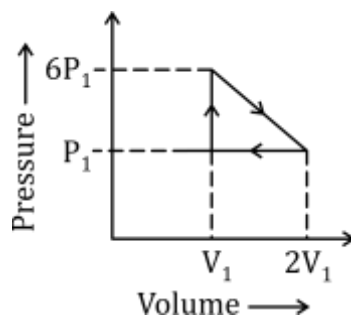


- (A) Isochoric, Isobaric, Isothermal (B) Isobaric, Isochoric, Isothermal  
(C) Isothermal, Isobaric, Isochoric (D) Isochoric, Isothermal, Isobaric
49. An ideal gas is taken around the cycle ABCDA as shown in figure. The net work done during the cycle is equal to :-  
(A) Zero (B) Positive (C) Negative (D) Can't be predicted
50. A cyclic process ABCD is shown in PV diagram for an ideal gas. which of the following diagram represents the same process?

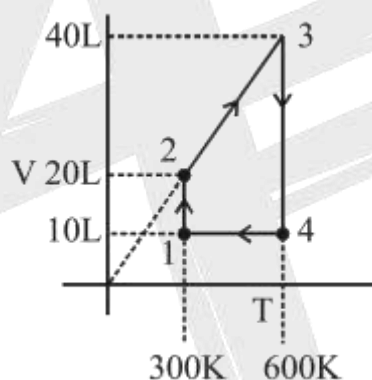




51. An ideal gas is taken around the cycle ABCA as shown in P-V diagram. The net work done by the gas during the cycle is equal to :



- (A)  $12P_1V_1$  (B)  $6P_1V_1$   
(C)  $5P_1V_1$  (D)  $P_1V_1$
52. What is the net work done when 1 mole of monoatomic ideal gas undergoes in a process described by 1, 2, 3, 4 in given V-T graph. (Use :  $R = 2\text{ cal/mole K}$ ,  $\ln 2 = 0.7$ )



- (A)  $-600\text{ cal}$  (B)  $-660\text{ cal}$  (C)  $+660\text{ cal}$  (D)  $+600\text{ cal}$

## EXERCISE – (S-I)

## BASIC DEFINITIONS &amp; GRAPHS

- How many of the following physical properties are extensive :
 

(i) Mass	(ii) Vapour pressure	(iii) Mole
(iv) Kinetic energy	(v) Internal energy	(vii) molarity
- How many of the following are state function :
 

(i) Internal energy	(ii) Heat	(iii) Enthalpy
(iv) Entropy	(v) Pressure	(vi) Temperature
(vii) Volume	(viii) Work	(ix) Specific heat capacity
(x) Molar heat capacity		

## HEAT, INTERNAL ENERGY AND WORK CALCULATION

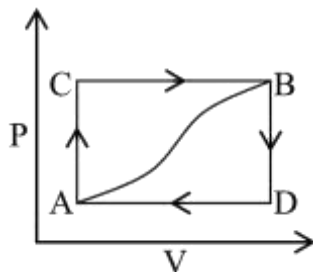
- Calculate the amount of heat (in kJ) necessary to raise the temperature of 60 g of aluminum from 35°C to 55°C. Molar heat capacity of Al is 36 mole<sup>-1</sup> K<sup>-1</sup>.
- Predict sign of work done in following reactions at constant pressure.
 

Initial state		Final state
(i) H <sub>2</sub> O(g)	→	H <sub>2</sub> O(l)
(ii) H <sub>2</sub> O(s)	→	H <sub>2</sub> O(g)
(iii) H <sub>2</sub> O(l)	→	H <sub>2</sub> O(s)
(iv) CaCO <sub>3</sub> (s)	→	CaO(s) + CO <sub>2</sub> (g)
- Water expands when it freezes. Determine amount of work, in joules, done 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.
- A sample of an ideal gas is expanded from 1 dm<sup>3</sup> to 3 dm<sup>3</sup> in a reversible process for which  $P = KV^3$ , with  $K = 1/5$  (atm/dm<sup>3</sup>), what is work done by gas (L atm)

## FIRST LAW OF THERMODYNAMICS

- 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.
- A gas expands from 2 L to 6 L against a constant pressure of 0.5 atm on absorbing 400 J of heat. Calculate the change in internal energy.
- 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 :
- A system works in a cyclic 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] :

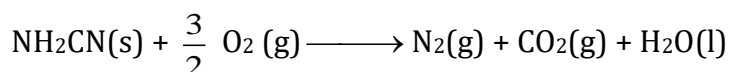
11. The gas is cooled such that it loses 65 J of heat. The gas contracts as it cools and work done on the system equal to 20 J. What are  $q$ ,  $w$  and  $\Delta U$  ?
12. When a system is taken from state A to state B along the path ACB, 80J of heat flows into the system and the system does 30J of work.



- (a) How much heat flows into the system along path ADB if the work done is  $-10\text{J}$  ?
- (b) When the system is returned from state B to A along the curved path, the work done on the system is  $20\text{J}$ . Does the system absorb or liberate heat, and how much ?
- (c) If  $U_D - U_A = 40\text{J}$ , find the heat absorbed in the process AD and DB. if the work done is  $-10\text{J}$  along path ADB.?
13. Lime is made commercially by decomposition of limestone,  $\text{CaCO}_3$ . What is the change in internal energy when 1.00 mole of solid  $\text{CaCO}_3$  ( $V = 34\text{ ml}$ ) absorbs  $180\text{ kJ}$  of heat and decomposes at certain temperature against a pressure of  $1.0\text{ bar}$  to give solid  $\text{CaO}$ . (Volume =  $16\text{ ml}$ ) and  $\text{CO}_2(\text{g})$  ( $V = 20\text{ L}$ ).

### ENTHALPY

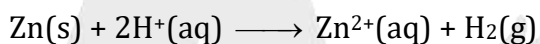
14. One mole of a non-ideal gas undergoes a change of state ( $2.0\text{ atm}, 3.0\text{ L}, 95\text{ K}$ )  $\rightarrow$  ( $4.0\text{ atm}, 5.0\text{ L}, 245\text{ K}$ ) with a change in internal energy,  $\Delta U = 30.0\text{ L atm}$ . Calculate change in enthalpy of the process in  $\text{L atm}$ .
15. If  $1.0\text{ kcal}$  of heat is added to  $1.2\text{ L}$  of  $\text{O}_2$  in a cylinder of constant pressure of  $1\text{ atm}$ , the volume increases to  $1.5\text{ L}$ . Calculate  $\Delta U$  and  $\Delta H$  of the process.
16. When the following reaction was carried out in a bomb calorimeter,  $\Delta U$  is found to be  $-742.7\text{ kJ/mol}$  of  $\text{NH}_2\text{CN}(\text{s})$  at  $300\text{ K}$ .



Calculate  $\Delta H_{300\text{K}}$  for the reaction. ( $R = 8\text{ J/mole-K}$ ).

17. What is  $\Delta U$  when  $2.0\text{ mole}$  of liquid water vaporises at  $100^\circ\text{C}$ ? The heat of vaporisation,  $\Delta H_{\text{vap}}$  of water at  $100^\circ\text{C}$  is  $40.66\text{ kJ mol}^{-1}$ .

18. At 500 kbar pressure, density of diamond and graphite are 3 g/cc and 2 g/cc respectively, at certain temperature 'T'. Find the value  $|\Delta H - \Delta U|$  (kJ/mole) for the conversion of 1 mole of graphite to 1 mole of diamond at temperature 'T' :
19. When 1 mole of ice melts at 0°C and at constant pressure of 1 atm. 1440 calories of heat are absorbed by the system. The molar volumes of ice and water are 0.0196 and 0.0180 L respectively. Calculate  $\Delta H$  and  $\Delta U$  for the reaction.
20. For the reaction,  $2A(g) + 3B(g) \longrightarrow 4C(g) + D(l)$  :  $\Delta H = -20$  KJ/mole  
Find the heat exchanged when 0.4 mole of A reacts with excess of B in a closed rigid container. The temperature is constant at 300 K. [R=8.3 J/K mole]
21. One mole of solid Zn is placed in excess of dilute  $H_2SO_4$  at 27°C in a cylinder fitted with a piston. Find the value of  $\Delta U$ , q and w for the process if the area of piston is 500 cm<sup>2</sup> and it moves out by 50 cm against a pressure of 1 atm during the reaction. The heat given to surrounding is 36.5 kJ.



### THERMODYNAMICS PROCESSES

22. Calculate the work done during isothermal reversible expansion of one mole ideal gas from 10 atm to 1 atm at 300 K.
23. Find the work done when one mole of the gas is expanded reversibly and isothermally from 5 atm to 1 atm at 25°C.
24. At 25°C, 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 ?
25. The valve on a cylinder containing initially 1 liters of an ideal gas at 7 atm and 25°C is opened to the atmosphere, whose the pressure is 760 torr and the temperature is 25°C. Assuming that the process is isothermal, how much work (in L.atm) is done on the atmosphere by the action of expansion ?
26. 10 g of argon gas is compressed isothermally and reversibly at a temperature of 27°C from 10 L to 5L. Calculate enthalpy change ( $\Delta H$ ) for this process  $R = 2.0$  cal K<sup>-1</sup> mol<sup>-1</sup>.  $\log_{10}2 = 0.30$  Atomic mass of Ar = 40
27. 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,  $\Delta U$  &  $\Delta H$ . Calculate the corresponding value of all if the above process is carried out reversibly.
28. 2 mole of an ideal gas undergoes isothermal compression along three different paths  
(i) Reversible compression from  $P_i = 2$  bar and  $V_i = 4$  L to  $P_f = 20$  bar  
(ii) A single stage compression against a constant external pressure of 20 bar, and

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

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 :  $R = 0.08 \text{ bar. L/mole.K}$ ]

**Magnitude of work is maximum in single stage compression**

29. Calculate the work done by 0.1 mole of a gas at  $27^\circ \text{C}$  to double its volume at constant pressure ( $R = 2 \text{ cal mol}^{-1} \text{ K}^{-1}$ )
30. A piston freely moves in an insulated cylinder from volume 5 L to 10 L then calculate work done & heat during this expansion.
31. 1 mole of  $\text{CO}_2$  gas at 300 K is expanded under reversible adiabatic condition such that its volume becomes 27 times. (a) What is the final temperature ? (b) What is work done ?  
Given  $\gamma = 1.33$  and  $C_V = 25.08 \text{ Jmol}^{-1} \text{ K}^{-1}$  for  $\text{CO}_2$ .
32. Three moles of an ideal gas at 200 K and 2.0 atm pressure undergo reversible adiabatic compression until the temperature becomes 250 K for the gas  $C_V$  is  $27.5 \text{ JK}^{-1} \text{ mol}^{-1}$  in this temperature range. Calculate  $q$ ,  $w$ ,  $\Delta U$ ,  $\Delta H$  and final  $V$  and final  $P$   
Given  $\left(\frac{5}{4}\right)^{1/0.3} = 2.1$ ,  $\left(\frac{5}{4}\right)^{13/3} = 2.61$
33. The work done in adiabatic compression of 2 mole of an ideal monoatomic gas by constant external pressure of 2 atm starting from initial pressure of 1 atm and initial temperature of 30 K ( $R = 2 \text{ cal/mol-K}$ )
34. 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  $q$ ,  $w$ ,  $\Delta H$  &  $\Delta U$ .
35. Calculate the work done by system in an irreversible (single step) adiabatic expansion of 1 mole of a polyatomic gas ( $\gamma = 4/3$ ) from 400 K and pressure 10 atm to 1 atm.
36. Two molar of He gas ( $\gamma = 5/3$ ) are initially at temp  $27^\circ \text{C}$  and occupy a volume of 20 L. The gas is first expanded at constant pressure until its volume is doubled. then it undergoes and reversible adiabatic change, until the volume become 110 L, then predict the value of  $T/100$   
(where  $T$  is the final temperature,  $= \left(\frac{4}{11}\right)^{2/3} = \frac{1}{2}$ )
37. The work done in adiabatic compression of 2 mole of an ideal monoatomic gas by constant external pressure of 2 atm starting from initial pressure of 1 atm and initial temperature of 30 K ( $R = 2 \text{ cal/mol-K}$ ).

PROBLEMS BASED ON POLYTROPIC

38. For 1 mole of ideal monoatomic gas if  $\frac{P}{V^2} = \text{constant}$  and initial temperature is 100 K. If gas is expanded from 1 L to 2 L then find in cal. (a) heat capacity (b) total heat absorbed (c) work done (d) change in internal energy.

(Assume  $R = 0.0821 \text{ L atm mole}^{-1} \text{ K}^{-1}$ ,  $1 \text{ Latm} = 24 \text{ cal}$ )

39.  $\frac{1}{22.4}$  mol of an ideal monatomic 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. ( $R = \frac{22.4}{273} \text{ L atm mole}^{-1} \text{ K}^{-1}$ ).

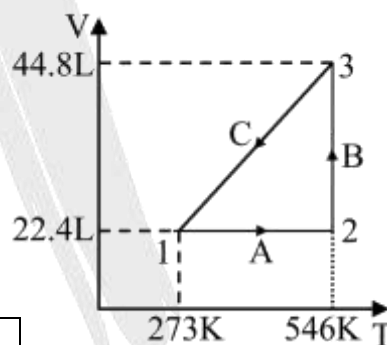
40. Draw the P-V diagram for the following cyclic processes

(A) Isothermal expansion from state A to B, isochoric pressure increases from B to C, isothermal contraction from C to D, isobaric contraction from D  $\rightarrow$  A.

(B) Isobaric expansion from A  $\rightarrow$  B, isochoric pressure increases from B  $\rightarrow$  C, isobaric compression from C  $\rightarrow$  D, isochoric pressure drop from D  $\rightarrow$  A.

41. 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			
Step	P	V	T
1			
2			
3			

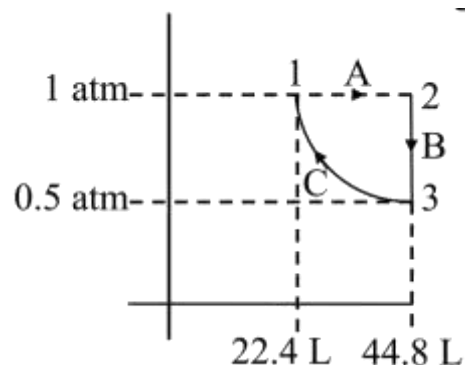


Step	Name of process	q	w	$\Delta U$	$\Delta H$
A					
B					
C					
overall					

42. 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			
Step	P	V	T
1			
2			
3			



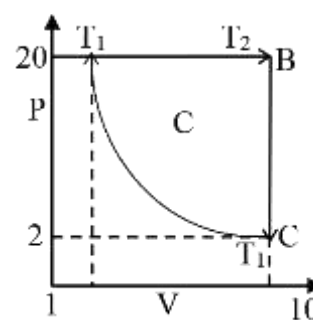
Step	Name of process	q	w	$\Delta U$	$\Delta H$
A					
B					
C					
	cyclic				

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

(C  $\longrightarrow$  A) Isothermal compression from 2 atm and 10 L to 20 atm and 1 L.

(A  $\longrightarrow$  B) Isobaric expansion to return the gas to the original volume of 10 L with T going from  $T_1$  to  $T_2$ .

(B  $\longrightarrow$  C) 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  $T_2$

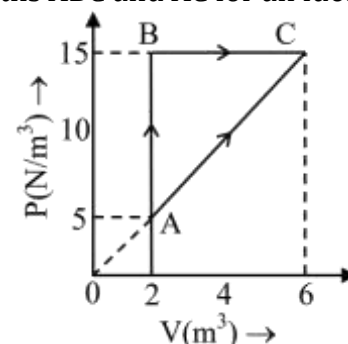
(b) Calculate  $\Delta U$ , q and w in calories, for each step and for the cycle.

44. 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.

(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 200 J.

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

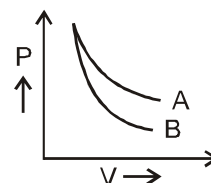




## EXERCISE-(O-II)

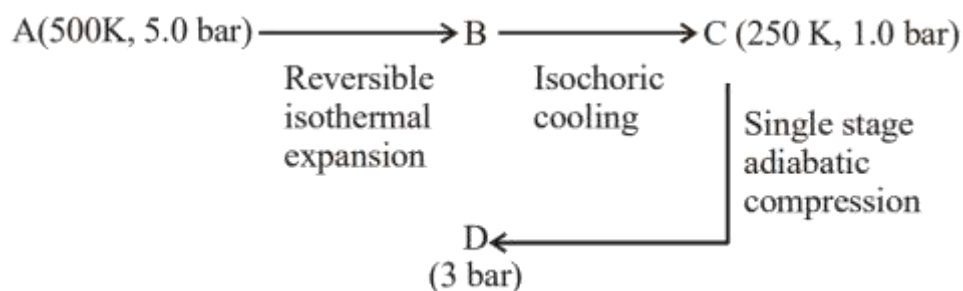
## ONE OR MORE THAN ONE MAY BE CORRECT

- Choose the correct statement(s) :
  - System and surrounding are always separated by a real or imaginary boundary.
  - Perfectly isolated system can never be created.
  - In a reversible process, energy change in each step can be reversed.
  - The value of  $\left(\gamma = \frac{C_p}{C_v}\right)$  remains constant for diatomic gas at all temperature
- Choose the correct statement(s) among the following :
  - Internal energy of  $H_2O$  remains constant during conversion of liquid into its vapour at constant temperature.
  - During fusion of ice into water enthalpy change and internal energy change are almost same at constant temperature.
  - Molar heat capacity of gases are temperature dependent.
  - During boiling of  $H_2O$  at 1 atm,  $100^\circ C$  kinetic energy of  $H_2O$  molecules increases.
- Which of the following statement is/are correct
  - Enthalpy can be written as  $H = f(V,T)$  for a substance ( no physical or chemical change)
  - Absolute value of enthalpy can't be determined
  - The heat absorbed during the isothermal expansion of an ideal gas against vacuum is zero
  - During compression of an ideal gas at constant pressure the temperature of gas decreases
- In an isothermal expansion of a gaseous sample, the correct relation is :  
 [The reversible and irreversible processes are carried out between same initial and final states.]
  - $w_{rev} > w_{irrev}$
  - $w_{irrev} > w_{rev}$
  - $q_{rev} < q_{irrev}$
  - $\Delta U_{rev} = \Delta E_{irrev}$
- During the isothermal expansion of an ideal gas :
  - The internal energy remains unaffected
  - The temperature remains constant
  - The enthalpy remains unaffected
  - The enthalpy increases
- 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 :
  - He and  $H_2$
  - $H_2$  and He
  - $SO_3$  and  $CO_2$
  - $N_2$  and Ar



7. 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  $PV^\gamma = \text{constant}$  will be valid (where P and V are gas variables)  
 (C)  $\Delta U + P_{\text{ext}}\Delta V = 0$   
 (D) Enthalpy of the gas remains unchanged.
8. 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)  $\frac{T_1 T_2 (P_1 V_1 + P_2 V_2)}{P_1 V_1 T_2 + P_2 V_2 T_1}$  (B)  $\frac{P_1 V_1 T_1 + P_2 V_2 T_2}{P_1 V_1 + P_2 V_2}$  (C)  $\frac{P_1 V_1 T_2 + P_2 V_2 T_1}{P_1 V_1 + P_2 V_2}$  (D)  $\frac{T_1 T_2 (P_1 V_1 + P_2 V_2)}{P_1 V_1 T_1 + P_2 V_2 T_2}$
9. Choose the correct statement(s) :
- (A) During adiabatic expansion of an ideal gas magnitude of work obtained is equal to  $\Delta H$  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,  $\Delta U$  is less in adiabatic expansion than in isobaric expansion if expansion starts with same initial state.
10. 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)  $E_4 > E_3$
11. Which statement is/are correct :-
- (A) Final temperature in reversible adiabatic expansion is lesser than in irreversible adiabatic expansion.  
 (B) When heat is supplied to an ideal gas in an isothermal process, kinetic energy of gas will increase  
 (C) When an ideal gas is subjected to adiabatic expansion it gets cooled  
 (D)  $w_{\text{adiabatic}} > w_{\text{isothermal}}$  in an ideal gas compression from same initial state to same final volume

12. Two moles of an ideal gas ( $C_{v,m} = \frac{3}{2} R$ ) is subjected to following change of state

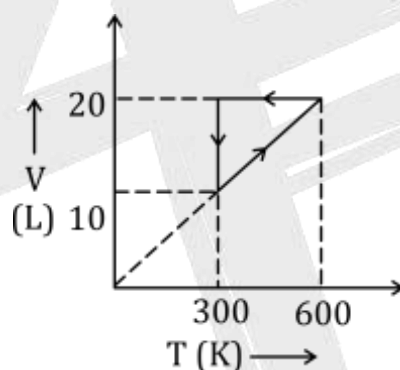


The correct statement is/are :

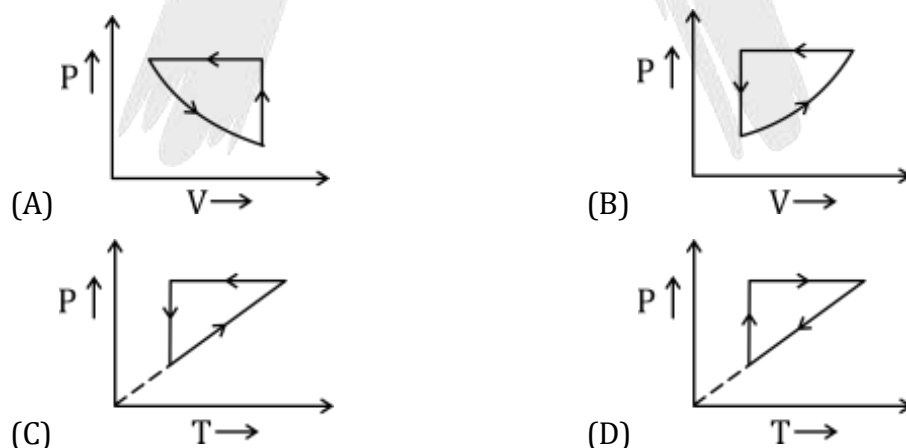
- (A) The pressure at B is 2.0 bar  
(B) The temperature at D is 450 K  
(C)  $\Delta H_{CD} = 1000 R$   
(D)  $\Delta U_{BC} = 375 R$

PARAGRAPH FOR Q.13 TO Q.14

One mol of ideal monoatomic gas undergo the state change as shown in the following graph ( $\ln 2 = 0.7$ )



13. Correct graph for the process in paragraph is -

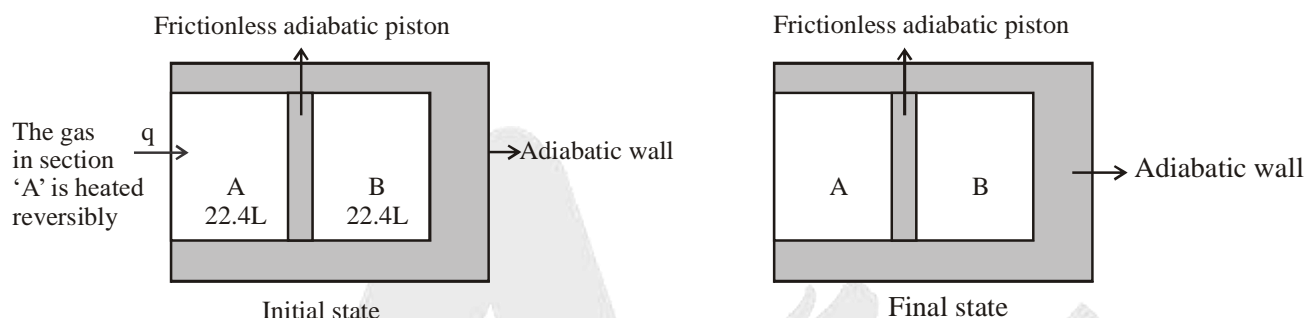


14. Efficiency of the cycle will be -

- (A) 50% (B) 25% (C) 13.63% (D) 12%

## PARAGRAPH FOR Q.15 TO Q.17

A cylindrical container of volume 44.8 L is containing equal no. of moles (in integer no.) of an ideal monoatomic gas in two sections A and B separated by an adiabatic frictionless piston as shown in figure. The initial temperature and pressure of gas in both section is 27.3K and 1 atm. Now gas in section 'A' is slowly heated till the volume of section B becomes  $(1/8)^{\text{th}}$  of initial volume



(Given:  $R = 2 \text{ cal/mol-K}$ ,  $C_{v,m}$  of monoatomic gas =  $\frac{3}{2} R$ . At 1 atm &  $0^\circ\text{C}$  ideal gas occupy 22.4 L.)

15. What will be the final pressure in container B.  
 (A) 2 atm                      (B) 8 atm                      (C) 16 atm                      (D) 32 atm
16. Final temperature in container A will be :  
 (A) 1638 K                      (B) 6988 K                      (C) 3274 K                      (D) 51 K
17. Change in enthalpy for section A in kcal :  
 (A) 48.3                      (B) 80.53                      (C) 4.83                      (D) 8.05
18. **Statement-1** : There is no change in enthalpy of an ideal gas during compression at constant temperature.  
**Statement-2** : Enthalpy of an ideal gas is a function of temperature and pressure.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is the correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

MATCH THE LIST :

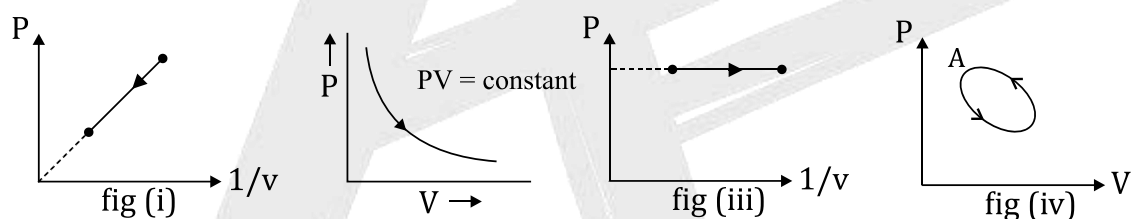
19. Match the following, and select the correct code :-

Column-I	Column-II
(P) Isothermal process (reversible)	(A) $q = 2.303 nRT \log \frac{P_1}{P_2}$
(Q) Adiabatic process (reversible)	(B) $PV^\gamma = \text{const.}$
(R) Isochoric process	(C) $q = P_{\text{ext.}} (V_2 - V_1)$
(S) Isothermal process (irreversible)	(D) Area under P-V curve is zero

Code:

	P	Q	R	S
(A)	2	1	4	3
(B)	1	2	4	3
(C)	2	1	3	4
(D)	1	2	3	4

20. The figures given below depict different processes for a given amount of an ideal gas.



Column-I	Column-II
(P) In Fig (i)	(A) Net heat is absorbed by the system
(Q) In Fig (ii)	(B) Net work is done on the system
(R) In Fig (iii)	(C) Net heat is rejected by the system
(S) In Fig (iv)	(D) Net work is done by the system
	(5) Net internal energy remains constant

Code:

	P	Q	R	S
(A)	1, 4, 5	4	2, 3	2, 3, 5
(B)	1, 4	4	2, 3	2, 5
(C)	1, 2, 4	2	1, 4	2, 3
(D)	1, 2	2	1, 4	3, 5

MATCH THE COLUMN :

21. Match Column-I with Column-II

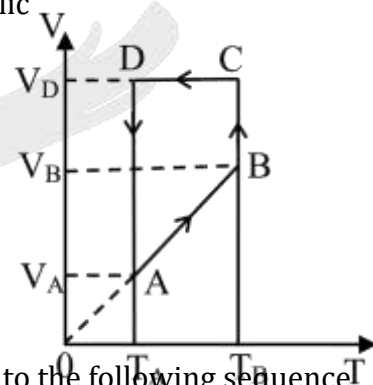
Column-I (Ideal Gas)	Column-II (Related equations)
(A) Reversible isothermal process	(P) $W = 2.303 nRT \log(P_2/P_1)$
(B) Reversible adiabatic process	(Q) $W = nC_{V,m} (T_2 - T_1)$
(C) Irreversible adiabatic process	(R) $W = -2.303nRT \log(V_2/V_1)$
(D) Irreversible isothermal process	(S) $W = - \int_{V_i}^{V_f}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

22. Match the column

Column-I	Column-II
(A) Isothermal vaporisation of water at 100°C & 1 atm	(P) $\Delta T = 0$
(B) Isothermal reversible expansion of an ideal gas	(Q) $\Delta U = 0$
(C) Adiabatic free expansion of ideal gas	(R) $\Delta H = 0$
(D) Isochoric heating of an ideal gas	(S) $q = 0$
	(T) $w = 0$

## EXERCISE- (S-II)

- The enthalpy change for the reaction of 50 ml of ethylene with 50.0 mL of  $H_2$  at 1.5 atm pressure is  $\Delta H = -0.31$  kJ. What is the  $\Delta U$ ?
- Derive a mathematical expression for the work done when a gas that has the equation of state  $PV = nRT - \frac{n^2 a}{V}$  expands reversibly from  $V_i$  to  $V_f$  at constant temperature.
- 3 dm<sup>3</sup> of an ideal monoatomic gas at 600 K and 32 bar expands until pressure of the gas is 1 bar. Calculate  $q$ ,  $w$ ,  $\Delta U$  and  $\Delta H$  for the process if the expansion is :  
(Use :  $R = 0.08$  Lbar / mol-K,  $= 2$  cal / mol-K)  
(i) Isothermal and reversible (ii) Adiabatic and reversible  
(iii) Isothermal and adiabatic (iv) Against 1 bar and adiabatic  
(v) Against 1 bar and isothermal.
- 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.
- 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  $q$ ,  $w$ ,  $\Delta U$  and  $\Delta H$  for the overall process.
- One mole of an ideal gas at 300 K is heated at constant volume ( $V_1$ ) until it's temperature is doubled, then it is subjected to isothermal reversible expansion till it reaches the original pressure. Finally the gas is cooled at constant pressure till system reached to the half of original volume ( $V_1/2$ ). Determine total work done ( $|w|$ ) in cal.  
[Use :  $\ln 2 = 0.70$  ;  $R = 2$  Cal/K.mol.]
- 2 mole of ideal monoatomic gas was subjected to reversible adiabatic compression from initial state of  $P = 1$  atm and  $T = 300$  K till the pressure is  $4\sqrt{2}$  atm and temperature is  $T$  K. The gas is then subjected to reversible isothermal expansion at  $T$  K till the internal pressure is one atm. The gas is now isobarically cooled to attain initial state. Find  $W_{Net}$  (in calorie) for whole process.  
[Use  $\ln 2 = 0.7$ ]





8. How many times volume of diatomic gas should be expanded reversibly & adiabatically in order to reduce its r.m.s velocity to half.  
**Fill your answer as sum of digits (excluding decimal places) till you get the single digit answer.**
9. Pressure over 1000 mL of a liquid is gradually increases from 1 bar to 1001 bar under adiabatic conditions. If the final volume of the liquid is 990 mL, calculate  $\Delta U$  and  $\Delta H$  of the process, assuming linear variation of volume with pressure.

A

## EXERCISE (JEE-MAINS)

1. 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 ? [AIEEE-2003]  
(A) < 40 kJ (B) Zero (C) 40 kJ (D) > 40 kJ
2. Consider the reaction :  $\text{N}_2 + 3\text{H}_2 \longrightarrow 2\text{NH}_3$  carried out at constant temperature and pressure, if  $\Delta H$  and  $\Delta U$  are the enthalpy and internal energy changes for the reaction, which of the following expressions is true ? [AIEEE-2005]  
(A)  $\Delta H = \Delta U$  (B)  $\Delta H = 0$  (C)  $\Delta H > \Delta U$  (D)  $\Delta H < \Delta U$
3. 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:- [AIEEE-2006]  
(A)  $T_f > T_i$  for reversible process but  $T_f = T_i$  for irreversible process  
(B)  $(T_f)_{\text{rev}} = (T_f)_{\text{irrev}}$   
(C)  $T_f = T_i$  for both reversible and irreversible processes  
(D)  $(T_f)_{\text{irrev}} > (T_f)_{\text{rev}}$
4. Assuming that water vapour is an ideal gas, the internal energy change ( $\Delta U$ ) when 1 mol of water is vapourised at 1 bar pressure and  $100^\circ\text{C}$ , (Given : Molar enthalpy of vapourisation of water at 1 bar and 373 K =  $41 \text{ kJ mol}^{-1}$  and  $R = 8.3 \text{ J mol}^{-1} \text{ K}^{-1}$  will be) :- [AIEEE-2007]  
(A)  $4.100 \text{ kJ mol}^{-1}$  (B)  $3.7904 \text{ kJ mol}^{-1}$   
(C)  $37.904 \text{ kJ mol}^{-1}$  (D)  $41.00 \text{ kJ mol}^{-1}$
5. The value of enthalpy change ( $\Delta H$ ) for the reaction  
 $\text{C}_2\text{H}_5\text{OH(l)} + 3\text{O}_{2(\text{g})} \rightarrow 2\text{CO}_{2(\text{g})} + 3\text{H}_2\text{O(l)}$   
at  $27^\circ\text{C}$  is  $-1366.5 \text{ kJ mol}^{-1}$ . The value of internal energy change for the above reaction at this temperature will be :- [AIEEE-2011]  
(A)  $-1371.5 \text{ kJ}$  (B)  $-1369.0 \text{ kJ}$   
(C)  $-1364.0 \text{ kJ}$  (D)  $-1361.5 \text{ kJ}$
6. The difference between the reaction enthalpy change ( $\Delta_r H$ ) and reaction internal energy change ( $\Delta_r U$ ) for the reaction : [JEE MAIN (online)- 2012]  
 $2\text{C}_6\text{H}_6(\text{l}) + 15\text{O}_2(\text{g}) \rightarrow 12\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l})$  at 300 K is ( $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ )  
(A)  $0 \text{ J mol}^{-1}$  (B)  $2490 \text{ J mol}^{-1}$   
(C)  $-2490 \text{ J mol}^{-1}$  (D)  $-7482 \text{ J mol}^{-1}$

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

[JEE MAIN (online)- 2014]

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

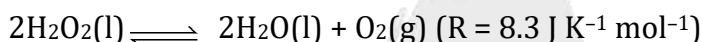
(B) For a system at constant volume, heat involved merely changes to internal energy.

(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)

8. If 100 mole of  $\text{H}_2\text{O}_2$  decompose at 1 bar and 300K, the work done (kJ) by one mole of  $\text{O}_2(\text{g})$  as it expands against 1 bar pressure is :

[JeeMain(online) 2016]



(A) 498.00

(B) 249.00

(C) 124.50

(D) 62.25

9.  $\Delta U$  is equal to :

[JEE MAIN-2017]

(A) Adiabatic work (B) Isothermal work (C) Isochoric work (D) Isobaric work

10. For a reaction,  $\text{A}(\text{g}) \rightarrow \text{A}(\text{l})$ ;  $\Delta H = -3RT$ . The correct statement for the reaction is :

[Jee Main(online) 2017]

(A)  $|\Delta H| > |\Delta U|$

(2)  $\Delta H = \Delta U \neq 0$

(C)  $|\Delta H| < |\Delta U|$

(D)  $\Delta H = \Delta U = 0$

11. A gas undergoes change from A to state B. In this process, the heat absorbed and work done by the gas is 5J and 8 J, respectively. Now gas is brought back to A by another process of during which 3 J of heat is evolve. In this reverse process of B to A :-

[Jee Main(online) 2017]

(A) 10 J of the work will be done by the surrounding on gas.

(B) 6 J of the work will be done by the surrounding on gas.

(C) 10 J of the work will be done by the gas.

(D) 6 J of the work will be done by the gas.

12. An ideal gas undergoes a cyclic process as shown in figure.

[JeeMain(online) 2018]

$$\Delta U_{BC} = -5 \text{ kJ mol}^{-1}, q_{AB} = 2 \text{ kJ mol}^{-1}$$

$$W_{AB} = -5 \text{ kJ mol}^{-1}, W_{CA} = 3 \text{ kJ mol}^{-1}$$

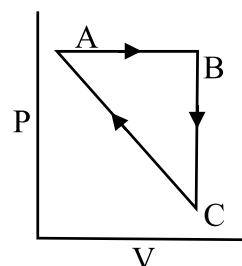
Heat absorbed by the system during process CA is :-

(A)  $18 \text{ kJ mol}^{-1}$

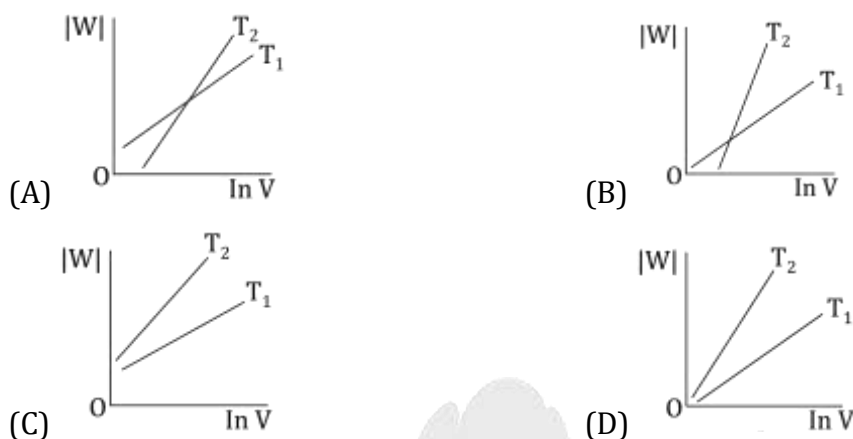
(B)  $+5 \text{ kJ mol}^{-1}$

(C)  $-5 \text{ kJ mol}^{-1}$

(D)  $-18 \text{ kJ mol}^{-1}$



13. 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 (Jan.) 2019]

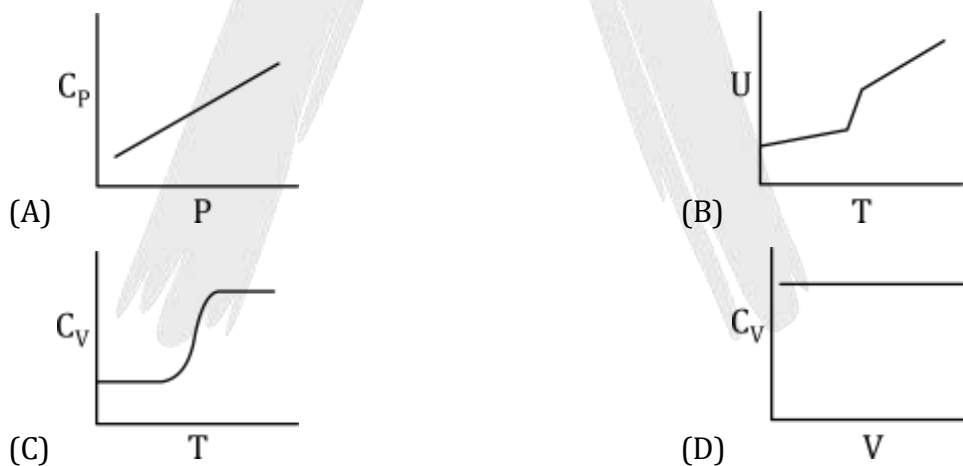


14. An ideal gas undergoes isothermal compression from  $5 \text{ m}^3$  to  $1 \text{ m}^3$  against a constant external pressure of  $4 \text{ Nm}^{-2}$ . Heat released in this process is used to increase the temperature of 1 mole of Al. If molar heat capacity of Al is  $24 \text{ J mol}^{-1} \text{ K}^{-1}$ , the temperature of Al increases by :

[Jee-Main (Jan.) 2019]

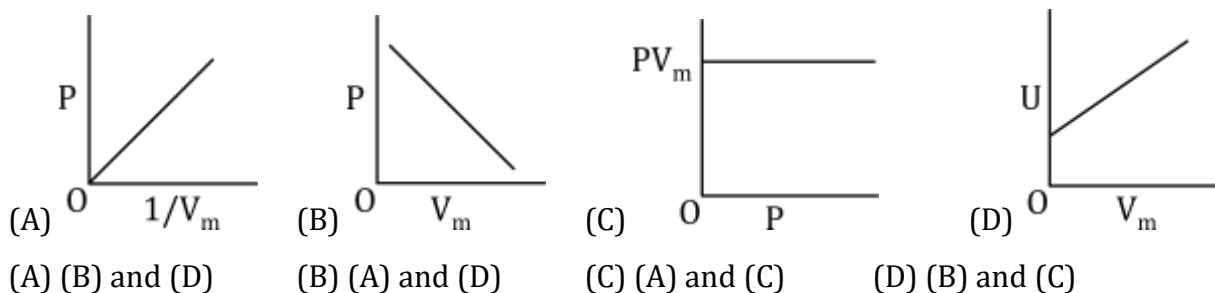
- (A)  $\frac{3}{2} \text{ K}$  (B)  $2 \text{ K}$  (C)  $1 \text{ K}$  (D)  $\frac{2}{3} \text{ K}$

15. For a diatomic ideal gas in a closed system, which of the following plots does not correctly describe the relation between various thermodynamic quantities? [Jee-Main (Jan.) 2019]



16. The combination of plots which does not represent isothermal expansion of an ideal gas is:

[Jee-Main (Jan.) 2019]



17. For silver,  $C_p(\text{J K}^{-1} \text{mol}^{-1}) = 23 + 0.01T$ . If the temperature (T) of 3 moles of silver is raised from 300 K to 1000 K at 1 atm pressure, the value of  $\Delta H$  will be close to :

[Jee-Main (Apr.) 2019]

- (A) 16 kJ (B) 13 kJ (C) 62 kJ (D) 21 kJ

18. 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 (Apr.) 2019]

- (A) Cyclic process :  $\Delta U = -w$  (B) Cyclic process :  $q = -w$   
(C) Isochoric process :  $\Delta U = q$  (D) Isothermal process :  $q = -w$

19. 5 moles of an ideal gas at 100 K are allowed to undergo reversible compression till its temperature becomes 200 K. If  $C_v = 28 \text{ J K}^{-1} \text{mol}^{-1}$ , calculate  $\Delta U$  and  $\Delta pV$  for this process.

 $(R = 8.0 \text{ J K}^{-1} \text{mol}^{-1})$ 

[Jee-Main (Apr.) 2019]

- (A)  $\Delta U = 14 \text{ J}$ ;  $\Delta(pV) = 0.8 \text{ J}$  (B)  $\Delta U = 2.8 \text{ kJ}$ ;  $\Delta(pV) = 0.8 \text{ J}$   
(C)  $\Delta U = 14 \text{ kJ}$ ;  $\Delta(pV) = 18 \text{ kJ}$  (D)  $\Delta U = 14 \text{ kJ}$ ;  $\Delta(pV) = 4 \text{ kJ}$

20. Among the following, the set of parameters that represents path functions, is :

[Jee-Main (Apr.) 2019]

- (A)  $q + w$  (B)  $q$  (C)  $w$  (D)  $H - TS$   
(A) (B) and (C) (B) (A) and (D) (C) (A), (B) and (C) (D) (B), (C) and (D)

21. During compression of a spring the work done is 10kJ and 2kJ escaped to the surroundings as heat. The change in internal energy,  $\Delta U$  (in kJ) is:

[Jee-Main (Apr.) 2019]

- (A) 8 (B) -8 (C) 12 (D) -12

22. An ideal gas is allowed to expand from 1 L to 10 L against a constant external pressure of 1 bar. The work done in kJ is:

[Jee-Main (Apr.) 2019]

- (A) -9.0 (B) -0.9 (C) -2.0 (D) + 10.0

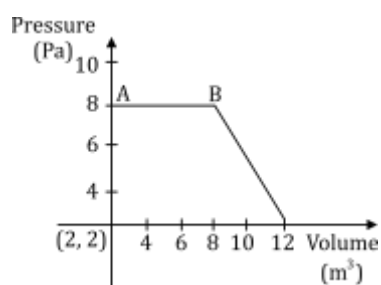
23. The difference between  $\Delta H$  and  $\Delta U$  ( $\Delta H - \Delta U$ ), when the combustion of one mole of heptane (I) is carried out at a temperature T, is equal to :

[Jee-Main (Apr.) 2019]

- (A)  $4 RT$  (B)  $-4 RT$  (C)  $-3 RT$  (D)  $3 RT$

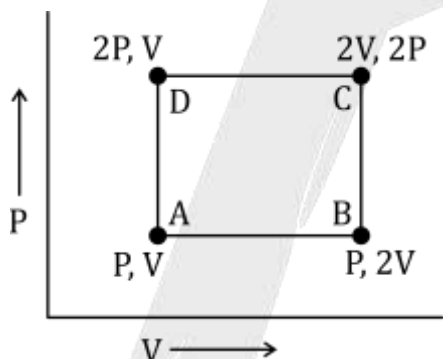
24. The magnitude of work done by a gas that undergoes a reversible expansion along the path A BC ?

[Jee Main, 2020]

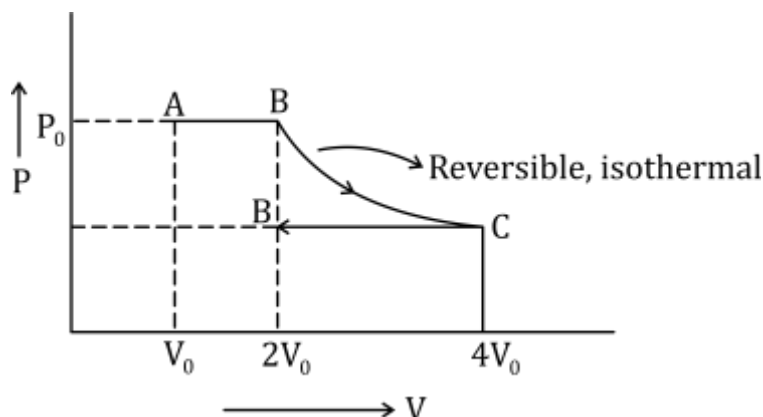


shown in the figure is \_\_\_\_\_.

25. At constant volume, 4 mol an ideal gas when heated from 300 K to 500 K changes its internal energy by 5000 J. The molar heat capacity at constant volume is \_\_\_\_\_. [Jee Main, 2020]  
Multiply your answer with 100
26. For one mole of an ideal gas, which of these statements must be true? [Jee Main, 2020]  
(a)  $U$  and  $H$  each depends only on temperature  
(b) Compressibility factor  $z$  is not equal to 1  
(c)  $C_{P,m} - C_{V,m} = R$   
(d)  $dU = C_v dT$  for any process  
(A) (a) and (c) (B) (b), (c) and (d) (C) (a), (c) and (d) (D) (c) and (d)
27. A system does 200 J of work and at the same time absorbs 150 J of heat. The magnitude of the change in internal energy is J. (Nearest integer) [Jee Main, 2021]
28. At 25°C, 50 g of iron reacts with HCl to form  $FeCl_2$ . The evolved hydrogen gas expands against a constant pressure of 1 bar. The work done by the gas during this expansion is J. (Round off to the Nearest Integer).  
[Given :  $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ . Assume, hydrogen is an ideal gas]  
[Atomic mass of Fe is 55.85u] [Jee Main, 2021]
29. An ideal monoatomic gas traverses the cycle ABCD as shown below in the figure. The work done during the cycle is  $xPV$ . The value of  $x$  is. (Nearest integer) [Jee Main, 2021]



30. The work done by an ideal monoatomic gas when it is taken along the path ABCD as shown in the figure is  $xP_0 V_0$ . The value of  $(-x)$  is. (Nearest integer) [ $\ln 2 = 0.69$ ] [Jee Main, 2021]



31. Among the following the number of state variable is \_\_\_\_\_. [JEE Main, July 2022]  
 Internal energy (U)  
 Volume (V)  
 Heat (q)  
 Enthalpy (H)
32. 2.2 g of nitrous oxide ( $\text{N}_2\text{O}$ ) gas is cooled at a constant pressure of 1 atm from 310 K to 270 K causing the compression of the gas from 217.1 mL to 167.75 mL. The change in internal energy of the process,  $\Delta U$  is '-x' J. The value of 'x' is \_\_\_\_\_. [Nearest integer]  
 (Given: atomic mass of N = 14 g mol<sup>-1</sup> and of O = 16 g mol<sup>-1</sup>.  
 Molar heat capacity of  $\text{N}_2\text{O}$  is 100 JK<sup>-1</sup> mol<sup>-1</sup>) [JEE Main, June 2022]
33. Match List-I with List-II [JEE Main, June 2022]

	List-I		List-II
(A)	Spontaneous process	(I)	$\Delta H < 0$
(B)	Process with $\Delta P = 0$ , $\Delta T = 0$	(II)	$\Delta G_{\text{T.P.}} < 0$
(C)	$\Delta H_{\text{reaction}}$	(III)	Isothermal and isobaric process
(D)	Exothermic process	(IV)	[Bond energies of molecules in reactants] - [Bond energies of product molecules]

Choose the correct answer from the options given below:

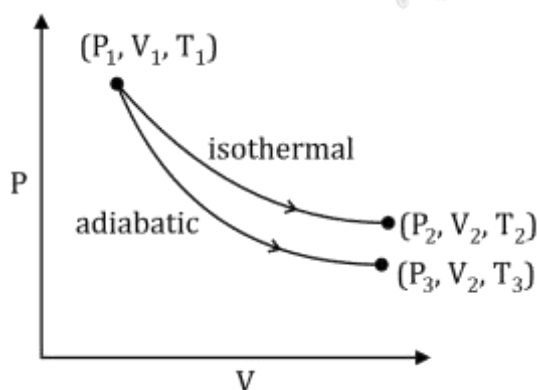
- (A) (A) - (III), (B) - (II), (C) - (IV), (D) - (I)      (B) (A) - (II), (B) - (III), (C) - (IV), (D) - (I)  
 (C) (A) - (II), (B) - (III), (C) - (I), (D) - (IV)      (D) (A) - (II), (B) - (I), (C) - (III), (D) - (IV)



## EXERCISE (JEE-ADVANCED)

1. A sample of argon gas at 1 atm pressure and 27°C expands reversibly and adiabatically from 1.25 dm<sup>3</sup> to 2.50 dm<sup>3</sup>. Calculate the enthalpy change in this process.  $C_{v,m}$  for argon is 12.48 JK<sup>-1</sup> mol<sup>-1</sup> [JEE Adv. 2000]
2. Which of the following statement is false ? [JEE Adv. 2001]
  - (A) Work is a state function
  - (B) Temperature is a state function
  - (C) Change of state is completely defined when initial and final states are specified.
  - (D) Work appears at the boundary of the system
3. One mole of non-ideal gas undergoes a change of state (2.0 atm, 3.0 L, 95 K) to (4.0 atm, 5.0 L, 245 K) with a change in internal energy ( $\Delta U$ ) = 30.0 Latm. The change in enthalpy ( $\Delta H$ ) of the process in Latm. [JEE Adv. 2002]
  - (A) 40.0
  - (B) 42.3
  - (C) 44.0
  - (D) Not defined, because pressure is not constant
4. Two moles of a perfect gas undergoes the following process. [JEE Adv. 2002]
  - (a) A reversible isobaric expansion from (1.0 atm, 20.0 L) to (1.0 atm, 40.0 L);
  - (b) A reversible isochoric change of state from (1.0 atm, 40.0 L) to (0.5 atm, 40.0 L);
  - (c) A reversible isothermal compression from (0.5 atm, 40.0 L) to (1.0 atm, 20.0 L);
  - (i) Sketch with labels each of the processes on the same P-V diagram.
  - (ii) Calculate the total work ( $w$ ) and the total heat change ( $q$ ) involved in the above processes.
  - (iii) What will be the values of  $\Delta U$ ,  $\Delta H$  and  $\Delta S$  for the overall process ?
5.  $C_{vc}$  value of He is always but  $C_v$  value of H<sub>2</sub> is at low temperature and moderate temperature and more than at higher temperature. Explain in two or three lines. [JEE Adv. 2003]
6. One mole of a liquid (1 bar, 100 ml) is taken in an adiabatic container and the pressure increases steeply to 100 bar. Then at a constant pressure of 100 bar, volume decrease by 1 ml. Find  $\Delta U$  and  $\Delta H$ . [JEE Adv. 2004]
7. Two mole of an ideal gas is expanded isothermally and reversibly from 1 litre to 10 litre at 300 K. The enthalpy change (in KJ) for the process is :- [JEE Adv. 2004]
  - (A) 11.4 kJ
  - (B) - 11.4 kJ
  - (C) 0 kJ
  - (D) 4.8 kJ
8. One mole of monoatomic ideal gas expands adiabatically at initial temp. T against a constant external pressure of 1 atm from one litre to two litre. Find out the final temperature. ( $R = 0.0821$  litre. atm K<sup>-1</sup> mol<sup>-1</sup>) [JEE Adv. 2005]
  - (A) T
  - (B)  $\frac{T}{(2)^{\frac{5}{3}-1}}$
  - (C)  $T - \frac{2}{3 \times 0.0821}$
  - (D)  $T + \frac{2}{3 \times 0.0821}$

9. For the reaction,  
 $2\text{CO(g)} + \text{O}_2 \longrightarrow 2\text{CO}_2\text{(g)}; \quad \Delta H = -560 \text{ kJ mol}^{-1}$   
 In one litre vessel at 500 K the initial pressure is 70 atm and after the reaction it becomes 40 atm at constant volume of one litre. Calculate change in internal energy. All the above gases show significant deviation from ideal behaviour. (1 L atm = 0.1 kJ) [JEE Adv. 2006]
10. The molar heat capacity of a monoatomic gas for which the ratio of pressure and volume is one. [JEE Adv. 2006]  
 (A)  $\frac{4}{2} R$  (B)  $\frac{3}{2} R$  (C)  $\frac{5}{2} R$  (D) zero
11. Among the following, the state function(s) is (are) [JEE Adv. 2009]  
 (A) Internal energy  
 (B) Irreversible expansion work  
 (C) Reversible expansion work  
 (D) Molar enthalpy
12. Among the following, extensive property is (properties are) [JEE Adv.-2010]  
 (A) molar conductivity (B) electromotive force  
 (C) resistance (D) heat capacity
13. One mole of an ideal gas is taken from a to 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 close to the ratio  $w_d / w_s$  is – [JEE Adv. 2010]
14. 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 Adv. 2012]

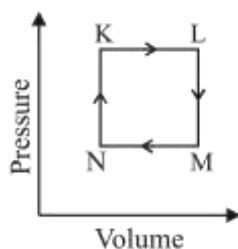


- (A)  $T_1 = T_2$  (B)  $T_3 > T_1$   
 (C)  $w_{\text{isothermal}} > w_{\text{adiabatic}}$  (D)  $\Delta U_{\text{isothermal}} > \Delta U_{\text{adiabatic}}$

## Paragraph for Question 15 and 16

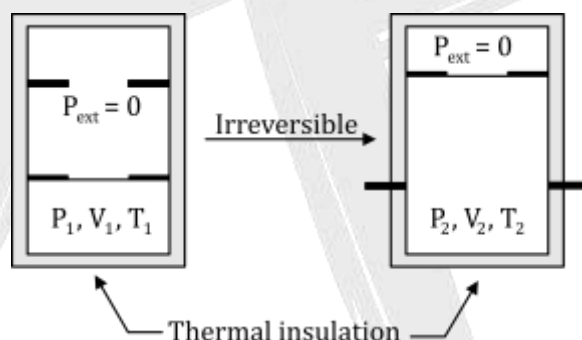
A fixed mass 'm' of a gas is subjected to transformation of states from K to L to M to N and back to K as shown in the figure.

[JEE Adv. 2013]



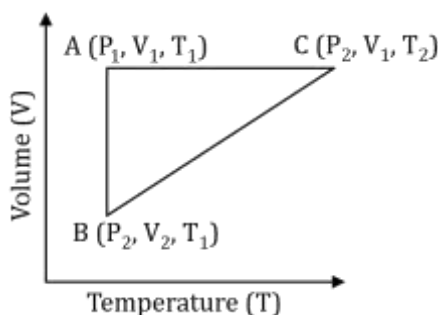
15. The pair of isochoric processes among the transformation of states is  
 (A) K to L and L to M (B) L to M and N to K  
 (C) L to M and M to N (D) M to N and N to K
16. The succeeding operations that enable this transformation of states are  
 (A) Heating, cooling, heating, cooling (B) cooling, heating, cooling, heating  
 (C) Heating, cooling, cooling, heating (D) Cooling, heating, heating, cooling
17. An ideal gas in 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 Adv. 2014]



- (A)  $q = 0$  (B)  $T_2 = T_1$  (C)  $P_2 V_2 = P_1 V_1$  (D)  $P_2 V_2^\gamma = P_1 V_1^\gamma$
18. 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 Adv. 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 is (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.

19. 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 Adv. 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  $\Delta H_{CA} > \Delta U_{CA}$
20. In thermodynamics, the  $P - V$  work done is given by [JEE Adv. 2020]

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

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.

ANSWER KEY

EXERCISE - (O-I)

BASIC DEFINITIONS & GRAPHS

- |         |         |         |         |         |         |         |
|---------|---------|---------|---------|---------|---------|---------|
| 1. (C)  | 2. (D)  | 3. (C)  | 4. (A)  | 5. (B)  | 6. (A)  | 7. (B)  |
| 8. (B)  | 9. (A)  | 10. (B) | 11. (D) | 12. (A) | 13. (A) | 14. (A) |
| 15. (B) | 16. (B) | 17. (A) | 18. (C) | 19. (B) | 20. (B) | 21. (D) |
| 22. (D) | 23. (D) | 24. (B) | 25. (C) | 26. (D) | 27. (D) | 28. (B) |
| 29. (A) | 30. (A) | 31. (C) | 32. (C) | 33. (C) | 34. (A) | 35. (A) |
| 36. (C) | 37. (D) | 38. (C) | 39. (C) | 40. (A) | 41. (B) | 42. (A) |
| 43. (B) | 44. (C) | 45. (B) | 46. (B) | 47. (C) | 48. (A) | 49. (A) |
| 50. (C) | 51. (C) | 52. (C) |         |         |         |         |

EXERCISE - (S-I)

- |  |   |                                       |  |
|--|---|---------------------------------------|--|
| 1. (D)   | 2. (6)  | 3. (1.6 kJ)                           | 4. ((i) w, (ii) -w, (iii) - w, (iv) - w) |
| 5. (- 10 J)  | 6. (- 4 L-atm)  | 7. (32 J)                             | 8. (200 J)                               |
| 10. (+ 24 cal)   | 11. (- 45 J)  | 12. (60 J, -70 J or 10 J)             | 13. (178 KJ)                             |
| 14. (44)   | 15. (+0.993 kcal, 1 kcal)                                 | 16. (-741.5 kJ/mol)                   |  |
| 17. ( $\Delta U = 75.11$ kJ)   | 18. (100 KJ/mole)   |                                       |  |
| 19. ( $\Delta H = \Delta U = 1440$ calories)   | 20. (- 3.5 kJ)  |                                       |  |
| 21. ( $\Delta E = -39.03$ kJ/mole; $q = -36.5$ kJ; $w = -2.53$ kJ)   |   |                                       |  |
| 22. (- 5744.14 J)  |   |                                       |  |
| 23. ( $w = -3.988$ kJ)   | 24. ( $1.2 \times 10^3$ J)                                | 25. (6 L-atm)                         | 26. (0)                                  |
| 27. (+17459.4)   |   |                                       |  |
| 28. ((i) 18.424 bar.L; (ii) 72 bar.L; (iii) 40 bar.L)  |   |                                       |  |
| 29. (- 60 cal.)  | 30. ( $W = 0$ ; $q = 0$ )                                 | 31. ( $T_2 = 100K$ ; $w = -5.016$ kJ) |  |
| 32. ( $q = 0$ , $w = \Delta U = 4.12$ kJ; $\Delta H = 5.37$ kJ; $V_f = 11.8$ dm <sup>3</sup> ; $P = 5.21$ atm) |   |                                       |  |
| 33. (72)   | 34. ( $\Delta U = w = -1247.1$ ; $\Delta H = -1745.94$ J) | 35. (2245 Joule)                      |  |
| 36. (3K)   | 37. (72)  |                                       |  |
| 38. ((A) $\frac{11}{6}R$ , (B) 2566.66 cal (C) - 448 cal (D) 2118.66 cal)                                      |   |                                       |  |
| 39. (- 0.25)   |   |                                       |  |

41. Step	Name of process	q	w	$\Delta U$	$\Delta H$
A	Isochoric	$3/2 R (273)$	0	$3/2 R (273)$	$5/2 R(273)$
B	Isothermal	$546 R \ln 2$	$-546 R \ln 2$	0	0
C	Isobaric	$-5/2 R(273)$	$R(273)$	$-3/2 R (273)$	$-5/2 R(273)$

42.	Step	Name of process	q	w	$\Delta E$	$\Delta H$
	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	$-273 R \ln 2$	$273 R \ln 2$	0	0
		Cyclic	$R(273) - 273 R \ln 2$	$-R(273) + 273 R \ln 2$	0	0
43.	((a) $T_1 = 243.60 \text{ K}$ ; $T_2 = 2436 \text{ K}$ , (b) $\Delta U = 0$ ; $q = -w = +3262 \text{ cal}$ )					
44.	((a) AC, (b) 170 J, (c) 10 J)					

EXERCISE- (O-II)

1. (ABC) 2. (BC) 3. (ABCD) 4. (BD) 5. (ABC) 6. (BCD)
7. (BD) 8. (A) 9. (BD) 10. (BD) 11. (ACD) 12. (ABC) 13. (D)
14. (D) 15. (D) 16. (A) 17. (B) 18. (C) 19. (B) 20. (A)
21. (A→PRS, B→QS, C→QS, D→S)
22. (A→P, B→PQR, C→PQRST, D→T)

EXERCISE- (S-II)

1. (- 0.3024 kJ)
2. ( $w = -nRT \ln - n^2 a$ )
3. ((i)  $w = -8400 \text{ cal}$ ,  $q = 8400 \text{ cal}$ ,  $\Delta U = \Delta H = 0$ .  
(ii)  $w = -2700 \text{ cal}$ ,  $q = 0 \text{ cal}$ ,  $\Delta U = -2700$ ,  $\Delta H = -4500 \text{ cal}$   
(iii)  $w = 0 \text{ cal}$ ,  $q = 0 \text{ cal}$ ,  $\Delta U = 0$ ,  $\Delta H = 0$ .  
(iv)  $w = -1395 \text{ cal}$ ,  $q = 0$ ,  $\Delta U = -1395 \text{ cal}$ ,  $\Delta H = -2325 \text{ cal}$   
(v)  $w = -2325 \text{ cal}$ ,  $q = 2325 \text{ cal}$ ,  $\Delta U = 0$ ,  $\Delta H = 0$ )
4. ((a) 600 K, (b) 3 kcal, 1.658 kcal, -1.8 kcal, -1.658 kcal (c) 1.2 kcal)
5. ( $\Delta U$  &  $\Delta H = 0$ ;  $w = 623.55$ ;  $q = -623.55 \text{ mol}^{-1}$ )
6. (60 cal)
7. ( $-1.2 \times 10^3$  or  $-1.19 \times 10^3$  (taking  $R = 1.98$ ))
8. (38)  
 $U_{\text{rms}} = u$   $T \propto U_{\text{rms}}^2 =$  In reversible adiabatic process
9. ( $\Delta U = 501 \text{ J}$ ;  $\Delta H = 99.5 \text{ kJ}$ )

EXERCISE (JEE-MAINS)

- |          |               |          |           |           |          |               |
|----------|---------------|----------|-----------|-----------|----------|---------------|
| 1. (B)   | 2. (D)        | 3. (D)   | 4. (C)    | 5. (C)    | 6. (D)   | 7. (A)        |
| 8. (A)   | 9. (A)        | 10. (A)  | 11. (B)   | 12. (B)   | 13. (B)  | 14. (D)       |
| 15. (A)  | 16. (A)       | 17. (C)  | 18. (A)   | 19. (D)   | 20. (A)  | 21. (A)       |
| 22. (B)  | 23. (B)       | 24. (48) | 25. (625) | 26. (C)   | 27. (50) | 28. (-2218 J) |
| 29. (pV) | 30. (-RTln 2) |          | 31. (3)   | 32. (195) | 33. (B)  |               |

EXERCISE -(JEE Advance)

- |                |          |                  |   |
|----------------|----------|------------------|---|
| 1. (-115.41 J) | 2. (A)   | 3. (C)           | 6. $\Delta U = 0.1 \text{ L atm}, \Delta H = 9.9 \text{ L atm}$ |
| 7. (C)         | 8. (C)   | 9. (-557 KJ/mol) | 10. (A) 11. (AD)  |
| 12. (CD)       | 13. (B)  | 14. (AD)         | 15. (B) 16. (C) 17. (ABC)                                       |
| 18. (ABD)      | 19. (BC) | 20. (ABC)        |   |



## SOLUTION

## EXERCISE - (O-I)

1. Intensive property B.P., pH, density
2. Enthalpy, internal energy and volume all are extensive properties
3. When liquid is freezes heat is given by system  $q < 0$
4.  $w = 0$   
for vacuum  $P_{\text{ext}} = 0$
5.  $\text{H}_2\text{O (s)} \longrightarrow \text{H}_2\text{O (l)}$   
 $\Delta V < 0$  so  $w > 0$
6.  $w = -1 \times (13 - 3)$   
 $= -10 \text{ atm dm}^3$
7. (i)  $P_1, V \longrightarrow 2P, V$   
vol. is constant so,  $w = 0$   
(ii)  $P, V \longrightarrow P, 2V$   
 $w = -P \times (2V - V) = -PV$
8. If work done on sys is  $w$   
 $\Delta U = q + w$   
If work done by sys is  $w$   
 $\Delta U = q - w$
9.  $q = +600 \text{ J}$  &  $w = -300 \text{ J}$   
 $\Delta U = q + w = 300 \text{ J}$
10.  $q = 0.5 \text{ kJ}$   
 $\Delta U = 300 \text{ J} = 0.3 \text{ kJ}$   
 $\Delta U = q + w$   
 $w = 0.3 - 0.5 = -0.2 \text{ kJ}$   
 $-200 = -1 \times \Delta V \times 100 \Delta V = 2$
12.  $q_v = \Delta U = +200 \text{ J}$
13.  $q = -450 \text{ J}$   
 $w = +600 \text{ J}$   
 $\Delta U = 150 \text{ J}$   
 $U_2 - U_1 = 150$   
 $U_2 = 150 + U_1$
14.  $q = +200 \text{ kJ}$

$$|w| = 1 \times 1 + \frac{1}{2} \times 1 \times 1 = 1.5 \text{ bar m}^3 = \frac{1.5 \times 10^3 \times 100}{10^3} = 150 \text{ kJ}$$

$$w = -150 \text{ kJ} \quad (\text{expansion})$$

$$\Delta U = q + w = 200 - 150 = +50 \text{ kJ}$$

15.  $q = -124 \text{ J}$

$$w = \frac{-2 \times (177 - 377)}{1000} = \frac{+2 \times 200}{1000} \times 100 = +40 \text{ J}$$

$$\Delta U = -84 \text{ J}$$

16.  $\text{H}_2\text{O}(\text{l}) \longrightarrow \text{H}_2\text{O}(\text{s}) \quad -\Delta H_{\text{fusion}}$

at constant P

$$q = \Delta H = -n\Delta H_{\text{fusion}}$$

17.  $\Delta H = \Delta U$

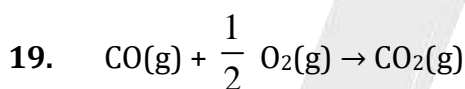
$$\text{if } \Delta n_g RT = 0 \Rightarrow \Delta n_g = 0$$

18.  $q_p = \Delta H = -28 \text{ kcal mol}^{-1}$

$$q_v = \Delta U$$

$$\Delta H = \Delta U + \frac{1 \times 2 \times 300}{1000}$$

$$-28 = \Delta U + 0.6 \Rightarrow \Delta U = -28.6 \text{ kcal mol}^{-1}$$



$$\Delta n_g = -0.5$$

$$\Delta H = \Delta U + \Delta n_g RT$$

$$\Delta H < \Delta U$$



$$\Delta n_g = -2$$

$$\Delta H = \Delta U - 2RT$$

21.  $q = \Delta H = 202.6 \text{ J}$

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

$$202.6 = \Delta U + 1 \times 2 \times 101.3 \Rightarrow \Delta U = 0$$

22.  $\Delta n_g = 0$

$$\Delta H = \Delta U = -185 \text{ kJ/mol} \quad (\text{for 1 mole H}_2)$$

$$= -185 \times 3 = -555 \text{ kJ} \quad (\text{for 3 mole H}_2)$$



$$2.5 \text{ mol} \quad 2 \text{ mol}$$

(LR)

$$\Delta H = \Delta U + \Delta n g R T$$

$$-72.3 = \Delta U + \frac{1 \times 8.314 \times 300}{1000}$$

$$\Delta U = -72.3 - 2.5 = -74.8 \text{ kJ}$$

for 2 mol HCl

$$\Delta U = -74.8 \times 2 = -149.6 \text{ kJ}$$

$$24. \quad \frac{1 \times 10}{300} = \frac{4 \times 5}{T_2}$$

$$T_2 = 600 \text{ K}$$

$$q = C \Delta T = \frac{50 \times 300}{1000} = +15 \text{ kJ}$$

$$w = \frac{-1 \times 3 \times 100}{1000} = -0.3 \text{ kJ}$$

$$\Delta U = q + w = 14.7 \text{ kJ}$$

$$\Delta H = 14.7 + \frac{10 \times 100}{1000} = +15.7 \text{ kJ}$$

25. Heat given by water = Heat taken by ice

$$\frac{500}{18} \times 75.6 \times 20 = n \times \frac{9}{18} \times 6 \times 10^3$$

$$n = 14$$

26. For isothermal  $\Delta T = 0$

$$\Delta U = 0 \text{ and } \Delta H = 0$$

27.  $\Delta T = 0, \Delta U = 0$

28.  $w = -1 \times R \times 298 \ln 2$

$$= -298 R \ln 2$$

$$= -298 \times 8.31 \times 2.303 \log 2 \times 10^7 \text{ ergs.}$$

29. For isochoric process

$$\Delta V = 0, w = 0 \text{ and } q = \Delta U$$

30. For process BC

$$w_{BC} = -2 P_0 V_0 \ln \frac{4V_0}{2V_0}$$

$$= -2 P_0 V_0 \ln 2$$

$$w_{CP} = \frac{-P_0}{2} \times (2V_0 - 4V_0) = + P_0 V_0$$

$$w_{AB} = - P_0 \times (2V_0 - V_0) = - P_0 V_0$$

$$w_{net} = - 2 P_0 V_0 \ln 2$$

31. I  $\longrightarrow$  II  $\longrightarrow$  III
- |       |       |       |
|-------|-------|-------|
| 8 bar | 2 bar | 1 bar |
| 4 L   | 16 L  | 32 L  |
| 300 K | 300 K | 300 K |

Process I  $\rightarrow$  II and II  $\rightarrow$  III are isothermal

$$\text{So } \Delta U = 0 ; q = -w$$

$$w_{I \rightarrow II} = -2 \times (16 - 4) = -2 \times 12 = -24 \text{ bar-L}$$

$$w_{II \rightarrow III} = -1 \times (32 - 16) = -1 \times 16 = -16 \text{ bar-L}$$

$$w_{net} = -40 \text{ bar-L} = -4000 \text{ J}$$

$$q = -w = +4000 \text{ J}$$

32. for isothermal process  $\Delta T = 0$  so  $q = -w$

for cyclic process

$$\Delta U = 0 \text{ (state function)}$$

for adiabatic process  $q = 0$  so  $\Delta U = w$

for free expansion  $w = 0$

33. for adiabatic  $q = 0$

34. In adiabatic compression  $T_f > T_i$

$$36. n \times \frac{5}{2} R \times (T_f - 300) = -2 \times \left( \frac{T_f}{2} - \frac{300}{5} \right) \times nR$$

$$3.5 T_f = 870$$

$$T_f = \frac{870}{3.5} = 248.57 \text{ K}$$

$$37. n \times \frac{5}{2} R \times (T_f - 350) = -2 \times \left( \frac{T_f}{2} - \frac{350}{1} \right) \times nR$$

$$2.5 T_f - 875 = -T_f + 700$$

$$3.5 T_f = 1575$$

$$T_f = 450 \text{ K}$$

$$w = 1 \times \frac{5}{2} R \times (450 - 350) = 2.5 R \times 100 = 250 R$$

38.  $T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1}$

$$\frac{T_f}{T_i} = \left( \frac{V_i}{V_f} \right)^{\gamma-1} \Rightarrow \frac{T_f}{600} = \left( \frac{1}{32} \right)^{\frac{2}{5}} = \frac{1}{4}$$

$$T_f = 150 \text{ K}$$

$$\Delta H = n C_p \Delta T = 1 \times \frac{7}{2} R \times (150 - 600) = -1575 R$$

39.  $w = n C_v \Delta T$

$$-3 \times 1000 = 1 \times 20 \times (T_f - 300)$$

$$T_f = +150 \text{ K}$$

40.  $T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1}$

$$\frac{T_f}{T_i} = \left( \frac{V_i}{V_f} \right)^{\gamma-1}$$

$$\frac{T_f}{300} = \left( \frac{1}{8} \right)^{4/3-1} = \frac{1}{2}$$

$$T_f = 150 \text{ K}$$

$$w = n C_v \Delta T$$

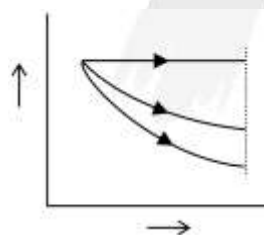
$$= 1 \times 3R \times (150 - 300)$$

$$= -450 R = -900 \text{ cal}$$

41.  $|\text{slope}| = |-\gamma P/V|$

$$\text{slope} \propto \gamma$$

$$\gamma_{\text{He}} > \gamma_{\text{H}_2}$$



42.

I – isobaric, II – isothermal and III – adiabatic

$$w_3 > w_1 > w_2 \text{ (area under the curve)}$$

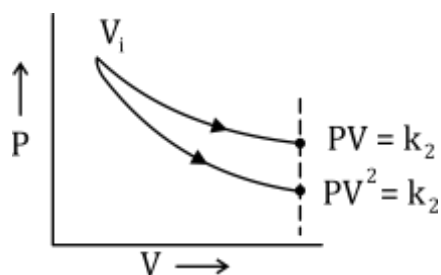
43. For same initial volume to same final volume through adiabatic reversible and adiabatic irreversible

$$T_f \text{ irrev} > T_f \text{ rev}$$

$$\Delta T \text{ rev} > \Delta T \text{ irrev}$$

$$\Delta H_2 > \Delta H_1 \text{ (magnitude)}$$

44.  $PV^x = k \Rightarrow \text{slope} = \left| -x \frac{P}{V} \right|$



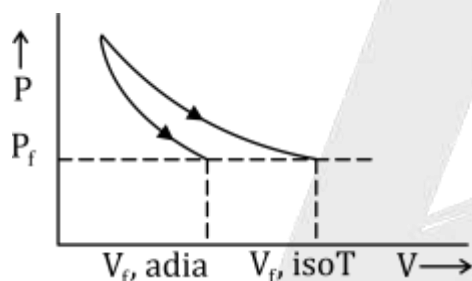
$PV^2 = k_1$  (process I)

$PV = k_2$  (process II)

$|w_2| > |w_1|$  (area under the curve)

45.  $PV = k$  (isothermal)

$PV^g = k$  (adiabatic)



In case of expansion

for isothermal  $T_f = T_i$  and for adiabatic  $T_f < T_i$

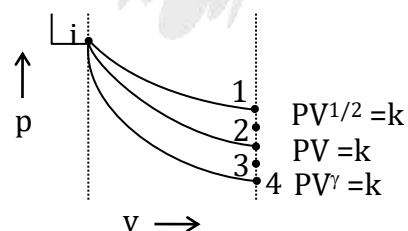
if  $P_f$  is same, then  $V_f$  will be greater for the process which has more  $T_f$ .

46. I - isothermal reversible ( $PV = K$ )

II -  $PV^{1/2} = \text{const.}$

III -  $PV^g = \text{const.}$

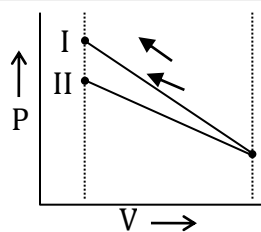
IV - Irreversible adiabatic



point 3 is for irreversible adiabatic because same final volume so  $(P_f)_{\text{irrev}} > (P_f)_{\text{rev}}$

47.  $PV^g = k$  (process I)

$PV^2 = k$  (process II)



$$(P_f)_{II} > (P_f)_I \text{ so } (T_f)_{II} > (T_f)_I$$

48.  $A \rightarrow B$  vol. const.  $\rightarrow$  isochoric

$A \rightarrow C$  Temp const.  $\rightarrow$  isothermal

$C \rightarrow A$  pressure const.  $\rightarrow$  isobaric

49. Process AB and CD volume is constant so  $w = 0$

amount of work done in process BC and DA is equal but sign is opposite.

So  $w_{\text{net}} = 0$

51.  $|w|$  = Area enclosed

$$= \frac{1}{2} \times 2V_1 \times 5P_1$$

$$= 5 P_1 V_1$$

52.  $W_{1 \rightarrow 2} = -300 R \ln 2$

$$W_{2 \rightarrow 3} = -R \times (600 - 300) = -300 R$$

$$W_{3 \rightarrow 4} = -600 R \ln \frac{10}{40} = +1200 R \ln 2$$

$$W_{4 \rightarrow 1} = 0$$

$$W_{\text{net}} = 900 R \ln 2 - 300 R$$

$$= 300 R = 660 \text{ cal}$$



## EXERCISE - (S-I)

- Extensive properties: mass, mole, KE, internal energy  
Intensive properties: Vapour pressure and molarity
- State function : U, H, S, P, T, V  
Path function : q, w, molar heat capacity, Specific heat capacity
- $q = \frac{60}{27} \times 36 \times 20 = 1.6 \text{ kJ}$
- If vol. decreases then work will be done on system and w will be +ve and vice versa

(i) $\Delta V = -ve$	(ii) $\Delta V = +ve$	(iii) $\Delta V = +ve$	(iv) $\Delta V = +ve$ ,
$w = +ve$	$w = -ve$	$w = -ve$	$w = -ve$

(i) w, (ii) -w, (iii) -w, (iv) -w

- $w = -P\Delta V$   
 $w = -1 \times (1.1 - 1.0) = -0.1 \text{ L-atm} = -10 \text{ J}$

- $w = - \int P_{\text{ext}} dV$   
 $= - \int_1^3 K V^3 dV = -K \times \left[ \frac{V^4}{4} \right]_1^3 = -\frac{1}{5} \times \frac{1}{4} \times 80 = -4 \text{ L-atm}$

- $w = -8 \text{ J}$   
 $q = +40 \text{ J}$   
 $\Delta U = q + w = 32 \text{ J}$

- $q = +400 \text{ J}$   
 $w = -0.5 \times (6 - 2) = -2 \text{ L-atm} = -200 \text{ J}$   
 $\Delta U = q + w = 200$

- $q = +50 \text{ J}$        $\Delta U = +60 \text{ J}$   
 $\Delta U = q + w$   
 $w = +10 \text{ J}$

- $\Delta U = 0$ ,       $q = +84 - 60 = +24 \text{ cal}$   
 $\Delta U = q + w$   
 $w = -q = -24 \text{ cal}$   
 $|w| = +24 \text{ cal}$

- $q = -65 \text{ J}$        $w = +20 \text{ J}$   
 $\Delta U = q + w = -65 + 20 = -45 \text{ J}$

- $q_{AB} = +80 \text{ J}$ ,  $w_{AB} = -30 \text{ J}$   
 $\Delta U_{AB} = q_{AB} + w_{AB} = +50 \text{ J}$

$$(a) \Delta U_{ACB} = \Delta U_{ADB} = + 50 \text{ J}$$

$$\Delta U_{ADB} = q_{ADB} + w_{ADB}$$

$$+ 50 = q_{ADB} - 10 \Rightarrow q_{ADB} = 60 \text{ J}$$

$$(b) \Delta U_{BA} = -50 \text{ J} \quad w_{BA} = + 20 \text{ J}$$

$$q_{BA} = - 50 - 20 = -70 \text{ J}$$

$$(c) \Delta U_{AB} = \Delta U_{AD} + \Delta U_{DB}$$

$$50 = 40 + \Delta U_{DB} \Rightarrow \Delta U_{DB} = 10 \text{ J}$$

$$w_{ADB} = w_{AD} + w_{DB}$$

$$w_{AD} = -10 \text{ J} \text{ \& } w_{DB} = 0$$

$$q_{AD} = \Delta U_{AD} - w_{AD} = + 40 + 10 = 50 \text{ J}$$

$$q_{DB} = \Delta U_{DB} - w_{DB} = 10 \text{ J}$$

13.  $q = + 180 \text{ kJ}$

$$w = -1 \times (20) = -20 \text{ L-atm} = \frac{-20 \times 100}{1000} = -2 \text{ kJ}$$

$$\Delta U = 180 - 2 = + 178 \text{ kJ}$$

14.  $\Delta U = 30 \text{ L-atm}$

$$\Delta H = \Delta U + (P_2V_2 - P_1V_1) = 30 + 14 = 44 \text{ L-atm}$$

15.  $q = + 0.1 \text{ kcal}$

$$w = -1 \times (1.5 - 1.2) = -0.3 \text{ L-atm} = -30 \text{ J} = \frac{-30}{4.2 \times 1000} = -0.00723 \text{ kcal}$$

$$\Delta U = q + w = + 0.993 \text{ kcal}$$

$$\Delta H = \Delta U + P\Delta V = + 0.993 + 0.007 = 1 \text{ kcal}$$

16.  $\Delta U = - 742.7 \text{ kJ/mol}$

$$\Delta H = \Delta U + \Delta n_g RT$$

$$= -742.7 + \frac{0.5 \times 8 \times 300}{1000} = -742.7 + 1.2 = -741.5 \text{ kJ/mol}$$

17.  $\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{O}(g), \Delta H = 40.66 \text{ kJ mol}^{-1}$

$$\Delta H = \Delta U + \Delta n_g RT$$

$$40.66 = \Delta U + \frac{1 \times 8.314 \times 373}{1000}$$

$$\Delta U = + 37.55 \text{ (for 1 mole H}_2\text{O)}$$

$$= + 37.55 \times 2 \text{ (for 2 mole H}_2\text{O)} = + 75.11 \text{ kJ}$$

18.  $d_{\text{diamond}} = 3\text{g/ml}, d_{\text{graphite}} = 2\text{g/ml}$

$$P = 500 \text{ Kbar, Temperature} = T$$

Graphite  $\rightarrow$  Diamond

$$(1\text{mol}) \quad (1\text{mol})$$

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

$$(\Delta H - \Delta U) = P(V_2 - V_1)$$

$$= 500 \times 10^{-3} \left( \frac{m}{d_2} - \frac{m}{d_1} \right) = 500 \times 10^{-3} \left( \frac{12}{2} - \frac{12}{3} \right) \times 10^{-3} \times 100 = 500 \times 10^{-3} (6 - 4) \times 0.1 = 100 \text{ kJ}$$

19.  $q = + 1440 \text{ cal}$

$$w = + 1 \times 0.0016$$

$$= + 0.0016 \text{ L-atm} = 0.0384 \text{ cal}$$

$$\Delta U = 1440.0384 \text{ cal}$$

$$\text{for solid and liquid } \Delta H \approx \Delta U = 1440.0384 \text{ cal}$$

20. at const. vol.  $q = \Delta U$

$$\Delta H = \Delta U + \Delta nRT$$

$$\Delta U = -20 - (-1) \times \frac{8.3 \times 300}{1000}$$

$$= -17.5 \text{ kJ (for 2 mole of A)}$$

$$\Delta U = \frac{-17.5}{2} \times 0.4 \text{ (for 0.4 mole of A)} = -3.5 \text{ KJ}$$

$$q = \Delta U = -3.5 \text{ kJ}$$

21.  $w = -P\Delta V$

$$= -1 \times \frac{500 \times 50}{1000} = -25 \text{ L-atm} = \frac{-25 \times 101.3}{1000} = -2.53 \text{ kJ}$$

$$q = \Delta H = -36.5 \text{ kJ}$$

$$\Delta H = \Delta U + \Delta nRT$$

$$-36.5 = \Delta U + 1 \times 8.314 \times 300/1000$$

$$\Delta U = -36.5 - 2.5 = -39 \text{ kJ}$$

22.  $w = -nRT \ln P_1/P_2$

$$= -1 \times 8.314 \times 300 \ln \frac{10}{1} = -8.314 \times 300 \times 2.303 = -5744.14 \text{ J}$$

23.  $w = -nRT \ln P_1 / P_2$

$$= -1 \times R \times 298 \ln 5 = -298 R \ln 5 = -3.994 \text{ kJ}$$

24.  $w = -P_{\text{ext}} (V_2 - V_1)$

$$= -4 \times (1 - 4) = +12 \text{ L-atm} = \frac{12 \times 100}{1000} = 1.2 \text{ kJ}$$

25.  $P_1 V_1 = P_2 V_2$  ( for isothermal process)

$$7 \times 1 = 1 \times V_2 \Rightarrow V_2 = 7$$

$$w = -1 \times (7 - 1) = -6 \text{ L-atm}$$

$$w_{\text{surr}} = +6 \text{ L-atm}$$

26.  $\Delta H = n C_P \Delta T$

$$\text{for isoT process } \Delta T = 0 \Rightarrow \Delta H = 0$$

27. For isoT process  $\Delta T = 0$

If carried out irreversibly

$$\Delta U = n C_V \Delta T = 0, \quad \Delta H = n C_P \Delta T = 0$$

$$w_{\text{irrev}} = -P_{\text{ext}} \times \left( \frac{1}{P_2} - \frac{1}{P_1} \right) \times n \times R \times T = -1 \times \left( \frac{1}{1} - \frac{1}{4} \right) \times 5 \times 8.314 \times 300$$

$$= -\frac{3}{4} \times 5 \times 8.314 \times 300 = -9353.25 \text{ J}$$

$$q_{\text{irrev}} = -w_{\text{irrev}} = +9353.25 \text{ J}$$

If carried out reversibly

$$\Delta U = n C_V \Delta T = 0, \quad \Delta H = n C_P \Delta T = 0$$

$$w_{\text{rev}} = -nRT \ln \frac{V_1}{V_2} = -5 \times 8.314 \times 300 \ln \frac{4}{1} = -17459.4$$

$$q_{\text{rev}} = -w_{\text{rev}} = +17459.4$$

28. (i) If carried out reversibly

$$w = -nRT \ln \frac{V_1}{V_2} = -8 \ln 2/20 = +8 \ln 10 = +18.424 \text{ bar-L}$$

(ii) If carried out irreversibly

$$w = P_{\text{ext}} (V_2 - V_1) = -20 (0.4 - 4)$$

$$= +20 \times 3.6 \text{ bar-L} = +72 \text{ bar-L}$$

$$(iii) \quad w = -10 (0.8 - 4) - 20 (0.4 - 0.8)$$

$$= +10 \times 3.2 + 20 \times 0.4 = 32 + 8 = 40 \text{ bar-L}$$

29.  $w = -P_{\text{ext}} \Delta V = -nR(T_2 - T_1)$

$$= -0.1 \times 2 \times (600 - 300) = -0.1 \times 2 \times 300 = -60 \text{ cal.}$$

30. for free expansion

$$P_{\text{ext}} = 0 \text{ so, } w = 0$$

31.  $\gamma = \frac{4}{3}$

$$T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1} \text{ p } \frac{T_f}{T_i} = \left( \frac{V_i}{V_f} \right)^{\gamma-1}$$

$$\frac{T_f}{300} = \left( \frac{1}{27} \right)^{\frac{4}{3}-1} = \left( \frac{1}{27} \right)^{\frac{1}{3}} = \frac{1}{3} \Rightarrow T_f = 100 \text{ K}$$

$$w = 1 \times 25.08 (100 - 300) = -25.08 \times 200 \text{ J} = -5.016 \text{ kJ}$$

32. For reversible adiabatic process  $q = 0$

$$\Delta U = w = nC_{V,m} \Delta T = 3 \times 27.5 \times (250 - 200) = 4.125 \text{ kJ}$$

$$\Delta H = nC_{P,m} \Delta T = 3 \times 35.814 \times (250 - 200) = 5.3721 \text{ kJ}$$

$$T_i^\gamma P_i^{\gamma-1} = T_f^\gamma P_f^{\gamma-1} \Rightarrow \left( \frac{T_i}{T_f} \right)^\gamma = \left( \frac{P_f}{P_i} \right)^{1-\gamma}$$

$$\left( \frac{250}{200} \right)^\gamma = \left( \frac{P_f}{2} \right)^{1-\gamma} \Rightarrow \left( \frac{5}{4} \right)^{1.3} = \left( \frac{P_f}{2} \right)^{0.3}$$

$$P_f = 2 \times \left( \frac{5}{4} \right)^{\frac{1.3}{0.3}} = 2 \times 2.61 = 5.22$$

$$\frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f} \text{ p } 3 \times 0.0821 = \frac{5.22 \times V_f}{250} \text{ p } V_f = 11.8 \text{ L}$$

33.  $\Delta U = w$

For irreversible adiabatic process

$$nC_{V,m} \Delta T = -P_{\text{ext}} (V_2 - V_1)$$

$$n \times \frac{3}{4} R (T_2 - 30) = -2 \times \left( \frac{T_2}{2} - \frac{30}{1} \right) \times nR \text{ p } T_2 = 42 \text{ K}$$

$$w = nC_{V,m} \Delta T = 2 \times \frac{3}{2} R \times (42 - 30) = 36 R = 72 \text{ cal}$$

34. For irreversible adiabatic process  $q = 0$

$$nC_{V,m} \Delta T = -P_{\text{ext}} (V_2 - V_1)$$

$$n \times \frac{5}{2} R \times (T_f - 300) = -1 \times \left( \frac{T_f}{2} - \frac{300}{5} \right) \times nR \Rightarrow T_f = 270 \text{ K}$$

$$w = \Delta U = nC_{V,m} \Delta T = 2 \times \frac{5}{2} R \times (270 - 300) = -5R \times 30 = -1247.1 \text{ J}$$

$$\Delta H = nC_p\Delta T = 2 \times \frac{7}{2} R \times (270 - 300) = -7R \times 30 = -210 R = -1745.94 \text{ J}$$

35. For irreversible adiabatic process  $q = 0$

$$\Delta U = w$$

$$n \times 3R \times (T_f - 400) = -1 \times \left( \frac{T_f}{1} - \frac{400}{10} \right) \times nR \Rightarrow T_f = 310 \text{ K}$$

$$w = 1 \times 3R \times (310 - 400) = -270 R = -2244.78 \text{ J}$$

36. A  $\xrightarrow{P_{\text{const.}}}$  B  $\longrightarrow$  C

300 K	600 K	T = ?
20 L	40 L	110 L

$$T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1}$$

$$300 \times (40)^{\gamma-1} = T_f \times (110)^{\gamma-1}$$

$$\frac{T_f}{300} = \left( \frac{40}{110} \right)^{\gamma-1} \Rightarrow \frac{T_f}{600} = \left( \frac{4}{11} \right)^{\frac{2}{3}}$$

$$T_f = \frac{600}{2} = 300 \text{ K} \Rightarrow \frac{T_f}{100} = 3 \text{ K}$$

37. For irreversible adiabatic process

$$nC_v\Delta T = -P_{\text{ext}}(V_2 - V_1)$$

$$n \times \frac{3}{2} R \times (T_f - 30) = -2 \times \left( \frac{T_f}{2} - \frac{30}{1} \right) \times nR$$

$$1.5 T_f - 45 = -T_f + 60 \Rightarrow 2.5 T_f = 105$$

$$T_f = \frac{105}{2.5} = 42 \text{ K}$$

$$w = 2 \times \frac{3}{2} R \times 12 = 36 R = 72 \text{ cal}$$

38.  $PV^{-2} = K$

On comparing with  $PV^x = K \Rightarrow x = -2$

$$T_i V_i^{x-1} = T_f V_f^{x-1}$$

$$\frac{T_f}{100} = \left(\frac{1}{2}\right)^{-2-1} \Rightarrow \frac{T_f}{100} = \left(\frac{1}{2}\right)^{-3} \Rightarrow T_f = 800 \text{ K}$$

$$q = nC\Delta T$$

$$C = C_v - \frac{R}{x-1} = \frac{3R}{2} - \frac{R}{-3} = \frac{3R}{2} + \frac{R}{3} = \frac{11}{6} R$$

$$q = \frac{11}{6} R \times 700 = 2566.66 \text{ cal}$$

$$\Delta U = 1 \times \frac{3}{2} R \times 700 = 2100 \text{ cal}$$

$$w = \frac{nR\Delta T}{x-1} = -\frac{1 \times R \times 700}{3} = -466.66 \text{ cal}$$

39.  $PV^2 = k$

On comparing with  $PV^x = K \Rightarrow x = 2$

$$T_i V_i^{x-1} = T_f V_f^{x-1}$$

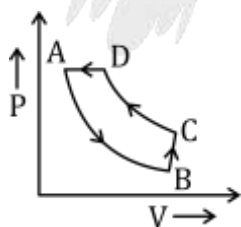
$$\frac{T_f}{T_i} = \left(\frac{V_i}{V_f}\right)^{x-1} \Rightarrow \frac{T_f}{273} = \left(\frac{1}{2}\right)^{2-1} = \frac{1}{2}$$

$$T_f = \frac{273}{2} = 136.5 \text{ K}$$

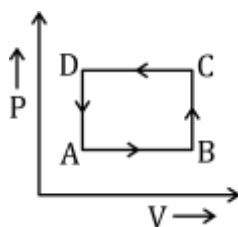
$$q = nC\Delta T$$

$$C = C_v - \frac{R}{x-1} = \frac{3}{2} R - \frac{R}{2-1} = \frac{3}{2} R - R = \frac{R}{2}$$

$$q = \frac{1}{22.4} \times \frac{R}{2} \times (136.5 - 273) = -\frac{1}{22.4} \times \frac{R}{2} \times \frac{273}{2} = -0.25 \text{ L-atm}$$



40. (A)



(B)

41. (i) In process A vol. is constant so it is ischoric process

$$\Delta V = 0 ; \text{ so } w = 0$$

$$q = \Delta U = nC_v\Delta T = 1 \times \frac{3}{2} R \times 273 = \frac{3}{2} R \times 273$$



$$\Delta H = nC_p\Delta T = 1 \times \frac{5}{2} R \times 273$$

(ii) In process B, Temp is constant, so it is isothermal process.

$$\Delta T = 0 ; \text{ so } \Delta U = nC_v\Delta T = 0 \text{ \& } \Delta H = nC_p\Delta T = 0$$

$$q = -w = + 1 \times R \times 546 \ln 2 = -546 R \ln 2$$

$$q = + 546 R \ln 2$$

(iii) In process C, pressure is constant because  $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

$$\Delta U = nC_v\Delta T = 1 \times \frac{3}{2} R \times (546 - 273) = -\frac{3}{2} R \times 273$$

$$q = \Delta H = nC_p\Delta T = 1 \times \frac{5}{2} R \times (546 - 273) = -\frac{5}{2} R \times 273$$

$$w = -nR(T_2 - T_1) = + R \times 273 = + 273R$$

42.  $n = 1$

At point - 1

$$P = 1 \text{ atm and } V = 22.4 \text{ L So } T = 273K$$

At point - 2

$$P = 1 \text{ atm and } V = 44.8 \text{ L So } T = 546K \text{ So}$$

At point - 3

$$P = 0.5 \text{ atm and } V = 44.8 \text{ L So } T = 273K$$

Step-A isobaric process

$$q = \Delta H = nC_p\Delta T = 1 \times \frac{5}{2} R \times 273$$

$$\Delta U = nC_v\Delta T = 1 \times \frac{3}{2} R \times 273$$

$$w = -nR(T_2 - T_1) = -R \times (546 - 273) = -273R$$

Step-B vol. is const. isochoric process

$$w = 0$$

$$q = \Delta U = nC_v\Delta T = -1 \times \frac{3}{2} R \times 273$$

$$\Delta H = nC_p\Delta T = -1 \times \frac{5}{2} R \times 273$$

Step-C  $P_1V_1 = P_2V_2$

so, it is isoT process

$$\Delta U = 0; \quad \Delta H = 0$$

$$w = -1 \times R \times 273 \ln \frac{1}{2} = +273 R \ln 2$$

$$q = -w = -273 R \ln 2$$

43. (a)  $T_1 = \frac{PV}{nR} = \frac{26 \times 1}{1 \times 0.0821} = 243.6 \text{ K}$

in process AB, pressure is constant so  $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

$$\text{So } T_2 = 2436 \text{ K}$$

(b) AB isobaric process (P is constant)

$$\Delta U = nC_v \Delta T = 1 \times \frac{3}{2} R \times 2192.4$$

$$q = nC_p \Delta T = 1 \times \frac{5}{2} R \times 2192.4$$

$$w = -1 \times R \times 2192.4 = -2192.4 R$$

BC isochoric process (V is constant)

$$w = 0$$

$$q = \Delta U = -\frac{3}{2} R \times 2192.4$$

CA isothermal process (Temp. is constant)

$$\Delta T = 0 \Rightarrow \Delta U = nC_v \Delta T = 0,$$

$$w = -R \times 243.6 \ln \frac{1}{10} = +243.6 R \ln 10$$

$$q = -w = -243.6 R \ln 10$$

for overall process  $\Delta U = 0$  so  $q = -w$

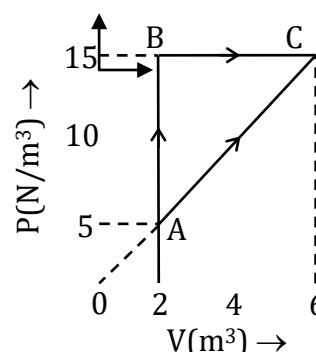
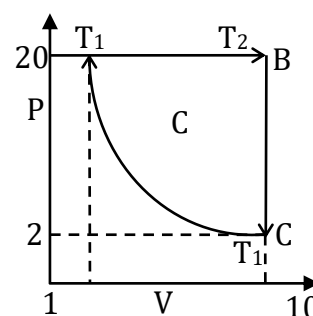
$$w = 243.6 R \ln 10 - 2192.4 R = -1631.3 R = -3262 \text{ cal}$$

44. (a)  $W_{AB} = 0$

$$W_{BC} = -P \Delta V = -15 \times 4 = -60 \text{ L-atm}$$

$$W_{AC} = -\left(5 \times 4 + \frac{1}{2} \times 10 \times 4\right) = -40 \text{ L-atm}$$

(b)  $\Delta U_{AC} = q_{AC} + w_{AC} = 200 - 40 = 160$



$$U_C - U_A = + 160$$

$$U_C = 160 + 10 = 170 \text{ J}$$

(c)  $\Delta U_{AB} = + 10 \text{ J}$

$$W_{AB} = 0$$

$$q = \Delta U = + 10 \text{ J}$$

A

EXERCISE-(O-II)

1.  $C_p$  &  $C_v$  are temperature dependent
2.  $H_2O(l) \longrightarrow H_2O(g)$   
At constant temperature  
KE = constant but PE increase so DU increase  
 $H_2O(s) \longrightarrow H_2O(l)$   
 $\Delta H \gg \Delta U$  for solid and liquid volume change is negligible.  
 $C_p$  and  $C_v$  are temperature dependent.
3. For any substance  
 $H = f(V,T) = f(P,T) = f(P,V)$   
For vacuum  $P_{ext} = 0, w = 0$   
If process is carried out isothermally in vacuum  $\Delta T = 0, \Delta U = 0, q = 0$   
For isobaric compression  $V \propto T \Rightarrow V^-, T^-$
4. For isotropic process if starting from same  $V_i$  and to same  $V_f$   
 $Q_{Tf, irrev} = T_{f, rev}$   
 $\Delta U_{rev} = \Delta U_{irrev}$   
 $|W_{rev}| > |W_{irrev}|$   
 $W_{rev} < W_{irrev}$  (with sign)  
 $w = -q$   
 $q_{rev} > q_{irrev}$
5. For isothermal process  
 $\Delta T = 0, \Delta H = 0, \Delta U = 0$
6.  $|\text{Slope}|_B > |\text{Slope}|_A$   
For adiabatic process  
 $|\text{Slope}| = \left| -\gamma \frac{P}{V} \right|$   
Slope of the curve will be more for the gas has higher value of  $\gamma$ .
7. In adiabatic expansion  
 $T_f < T_i$   
 $PV_\gamma = K$  (Valid only for rev. adiabatic)  
For irrev. Adiabatic  $\Delta U = w = -P_{ext} \Delta V$   
 $\Delta U = P_{ext} \Delta V = 0$   
 $\Delta H < 0$

8.  $n_1 C_V (T_f - T_1) + n_2 C_V (T_f - T_2) = 0$

$$\frac{P_1 V_1}{RT_1} (T_f - T_1) + \frac{P_2 V_2}{RT_2} (T_f - T_2) = 0$$

$$T_f \left( \frac{P_1 V_1}{RT_1} + \frac{P_2 V_2}{RT_2} \right) = \frac{P_1 V_1}{R} + \frac{P_2 V_2}{R}$$

$$T_f = \frac{T_1 T_2 (P_1 V_1 + P_2 V_2)}{P_1 V_1 T_1 + P_2 V_2 T_2}$$

9. For adiabatic process

$$W = \Delta U$$

For adiabatic rev and irrev. process.

$$\text{If } T_{f \text{ rev}} = T_{f \text{ irrev}} \text{ then from } W = n C_V \Delta T \Rightarrow W_{\text{rev}} = W_{\text{irrev}}$$

For rev. adiabatic expansion Temperature of system decreases.

For same change in volume in adiabatic and isobaric expansion

$$T_{f \text{ isobaric}} = T_{f \text{ adiabatic}}$$

10. If volume is doubled then

$$\text{For isoT expansion } T_i = T_f$$

$$\text{For adiabatic expansion } T_i < T_f$$

$$\text{For free expansion } T_i = T_f$$

$$\text{For isobaric expansion } T_f > T_i$$

$$T_{f \text{ adiabatic}} < T_{f \text{ isoT}} = T_{f \text{ free expansion}} < T_{f \text{ isobaric}}$$

$$E_4 > E_3 = E_2 > E_1$$

11. For adiabatic process

$$q = 0$$

$$\Delta U = W$$

$$Q \quad W = -ve \quad \text{so } \Delta U = -ve$$

$$\Delta T = -ve$$

(D) For same change in volume during compression

$$(T_f)_{\text{adi.}} > (T_f)_{\text{iso.}}$$

12. At point B  $\Rightarrow T = 500 \text{ K}$

Process BC is isochoric

$$\text{So } \frac{P_B}{T_B} = \frac{P_C}{T_C}$$

$$\frac{P_B}{500} = \frac{1}{250} \Rightarrow P_B = 2 \text{ bar}$$

$$\Delta U_{BC} = nC_V \Delta T_{BC} = 2 \times \frac{3}{2} R \times (250 - 500) = -750 R$$

$$\Delta V = -P_{\text{ext}}(V_2 - V_1)$$

$$n \times \frac{3}{2} R \times (T_f - 250) = -3 \times \left( \frac{T_f}{3} - \frac{250}{1} \right) \times nR$$

$$2.5 T_f = 1125 \Rightarrow T_f = 450 K$$

$$\Delta H_{CD} = nC_P \Delta T = 2 \times \frac{5}{2} R \times 200 = 1000 R$$

14.  $n = - \frac{W_{\text{sys}}}{Q_{\text{supplied}}} \times 100$

$$q_{AB} = \Delta H = nC_P \Delta T = +750 R$$

$$q_{BC} = \Delta U = nC_V \Delta T = -450 R$$

$$q_{CA} = -300 R \ln 2$$

$$W_{AB} = -1 \times R \times (600 - 300) = -300 R$$

$$W_{BC} = 0$$

$$W_{CA} = +300 R \ln 2$$

$$W_{\text{net}} = 300 R \ln 2 - 300 R = -300 R \times 0.3$$

$$n = \frac{300 R \times 0.3}{750 R} \times 100 = 12\%$$

PARAGRAPH FOR Q.15 TO Q.17

15. Sec. B is adiabatic

$$P_i V_i^\gamma = P_f V_f^\gamma$$

$$\frac{P_f}{P_i} = \left( \frac{V_i}{V_f} \right)^\gamma$$

$$\frac{P_f}{1} = (8)^{5/3} \Rightarrow P_f = 32 \text{ atm}$$

16.  $\frac{P_f V_f}{T_f} = \frac{P_i V_i}{T_i}$

$$\frac{32 \times 22.4 \times 15 / 8}{T_f} = \frac{1 \times 22.4}{27.3}$$

$$T_f = 32 \times \frac{15}{8} \times 27.3 = 1638 K$$

17.  $\Delta H = nC_P \Delta T = 0.1 \times \frac{5}{2} R \times 1610.7 = 80.53 \text{ Kcal}$

18. If  $\Delta T = 0 \Rightarrow \Delta H = 0$

For ideal gas  $H = f(T)$

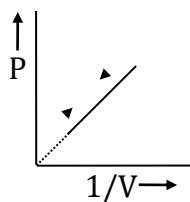
19. For rev. isoT

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

For rev. adiabatic  $PV^\gamma = K$

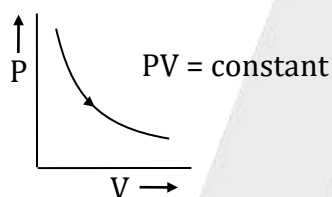
For isochoric process  $\Delta V = 0, W = 0$

For irrev. Isothermal  $q = -W = P_{\text{ext}} (V_2 - V_1)$



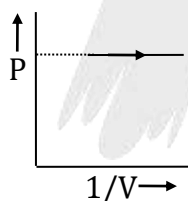
20. (i)

For isoT expansion  $W = -ve, q = +ve, \Delta U = 0$



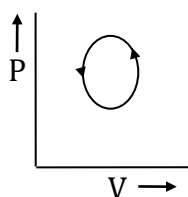
(ii)

isothermal expansion  $W < 0, \Delta T = 0, \Delta U = 0, q > 0$



(iii)

For isobaric compression  $\Delta T < 0, W > 0, q < 0$



(iv)

For cyclic process  $\Delta U = 0$ ,  $W = +ve$ ,  $q = -ve$

21. For rev. isoT

$$W = nRT \ln \frac{V_2}{V_1} = -nRT \ln \frac{P_1}{P_2}$$

For rev. adiabatic/irrev. adiabatic

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

$$\text{For irrev. IsoT } W = -\int_{V_1}^{V_2} P_{\text{ext}} dV = -P_{\text{ext}}(V_2 - V_1)$$

22. (A) For isothermal vaporisation of water

$$\Delta T = 0, \Delta U > 0, q > 0, \Delta H > 0, W < 0$$

(B) isoT rev. expansion

$$\Delta T = 0, \Delta U = 0, \Delta H = 0, W < 0, q > 0$$

(C) Adiabatic free expansion

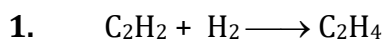
$$q = 0, P_{\text{ext}} = 0, W = 0, \Delta U = 0, \Delta T = 0, \Delta H = 0$$

(D) Isochoric heating

$$\Delta V = 0, W = 0, \Delta T > 0, \Delta U > 0, \Delta H > 0, q > 0$$



EXERCISE- (S-II)



$$V_i \quad 50 \text{ ml} \quad 50 \text{ ml} \quad 0$$

$$V_f \quad 0 \quad 0 \quad 50 \text{ ml}$$

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

$$= -0.31 - \frac{1.5 \times (-50 \times 10^{-3}) \times 100}{1000} = -0.31 + 75 \times 10^{-4} = -0.31 + 0.0075 = -0.3025 \text{ kJ}$$

2.  $PV = nRT - \frac{n^2 a}{V}$

$$P = \frac{nRT}{V} - \frac{n^2 a}{V^2}$$

$$dW = -PdV$$

$$W = - \int_{V_i}^{V_f} \left( \frac{nRT}{V} - \frac{n^2 a}{V^2} \right) dV$$

$$= -nRT \ln \left( \frac{V_f}{V_i} \right) - n^2 a \left( \frac{1}{V_f} - \frac{1}{V_i} \right)$$

3. Mole of gas

$$n = \frac{PV}{RT} = \frac{3 \times 22}{0.08 \times 600} = 2$$

(i) For isothermal reversible process  $\Rightarrow \Delta T = 0, \Delta H = 0, \Delta U = 0$

$$W = -2 \times 2.303 \times 2 \times 600 \log \frac{32}{1} = -8290.8 \text{ Cal}$$

$$q = -W = +8290.8 \text{ Cal}$$

(ii) Rev. adiabatic  $\Rightarrow q = 0,$

$$T_i^\gamma P_i^{1-\gamma} = T_f^\gamma P_f^{1-\gamma}$$

$$\frac{T_f}{T_i} = \left( \frac{P_i}{P_f} \right)^{\frac{1-\gamma}{\gamma}} \Rightarrow \frac{T_f}{600} = \left( \frac{32}{1} \right)^{\frac{-2}{5}} = (B)^{-2}$$

$$T_f = \frac{600}{4} = 150 \text{ K}$$

$$\Delta U = W = nC_V \Delta T = 2 \times \frac{3}{2} R \times (150 - 600) = -3R \times 450 = -2700 \text{ Cal}$$

$$\Delta H = nC_P \Delta T = 2 \times \frac{5}{2} R \times (150 - 600) = -5R \times 450 = -4500 \text{ Cal}$$

(iii) isoT and adiabatic  $\Rightarrow$  Free expansion

$$\Delta T = 0, U = 0, w = 0, q = 0, \Delta H = 0$$

(iv) For irrev. adiabatic

$$nC_V (T_f - T_i) = -P_{\text{ext}}(V_2 - V_1)$$

$$n \times \frac{3}{2} R \times (T_f - 600) = -1 \times \left( \frac{T_f}{1} - \frac{600}{32} \right) \times nR$$

$$T_f = 367.5 \text{ K}$$

$$q = 0, W = \Delta U = 2 \times \frac{3}{2} R \times (367.5 - 600) = -1395 \text{ Cal}$$

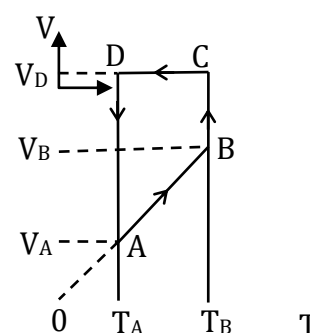
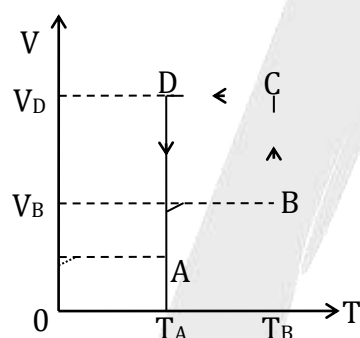
$$\Delta H = 2 \times \frac{5}{2} R \times (367.5 - 600) = -2325 \text{ Cal}$$

(v) For irrev. isoT

$$\Delta T = 0, \Delta U = \Delta H = 0$$

$$W = -1 \times \left( \frac{1}{1} - \frac{1}{32} \right) \times 2 \times 2 \times 600 = -2325 \text{ Cal}$$

$$q = +2325 \text{ Cal}$$



4.

$$\text{GIVEN: } n=2; \frac{V_B}{V_A} = 2; \frac{V_D}{V_A} = 4 \text{ and } T_A = 300 \text{ K}$$

(A) For process AB  $\Rightarrow P = \text{constant} \Rightarrow V \propto T$

$$\frac{V_A}{T_A} = \frac{V_B}{T_B} \Rightarrow \frac{V_B}{V_A} = \frac{T_B}{T_A}$$

$$2 \times 300 = T_B \Rightarrow T_B = 600 \text{ K}$$

$$\Rightarrow T_B = T_C = 600 \text{ K}$$

$$\Rightarrow T_A = T_D = 300 \text{ K}$$

$$(B) Q_{AB} = nC_P \Delta T = 2 \times \frac{5}{2} \times R \times (600 - 300) = 3000 \text{ cal} = 3 \text{ kcal}$$

$$BC \Rightarrow T = \text{constant} \Rightarrow Q_{BC} = -W_{BC} = nRT \ln \frac{V_C}{V_B} = 2 \times R \times 600 \times \ln 2$$

$$= 2 \times 2 \times 600 \times 0.69 = 1.658 \text{ cal}$$

$$CD \Rightarrow V = \text{constant} \Rightarrow Q_{CD} = nC_v \Delta T = 2 \times \frac{3R}{2} \times (300 - 600) = -3 \times 2 \times 300 = -1.8 \text{ kcal}$$

$$DA \Rightarrow T = \text{constant} \Rightarrow Q_{DA} = -W_{DA} = nRT \left( \frac{V_A}{V_D} \right) = 2 \times R \times \ln \left( \frac{1}{4} \right) = -2 \times 2 \times 300 \times 2 \times 0.69$$

$$= -1.658 \text{ kcal}$$

$$\begin{aligned} \text{(C)} \quad W_{\text{NET}} &= W_{AB} + W_{BC} + W_{CD} + W_{DA} \\ &= -nR(T_B - T_A) + (-Q_{BC}) + 0 + (-Q_{DA}) \\ &= \frac{-2 \times 2 \times 300}{1000} - 1.658 + 1.658 \\ &= -1.2 \text{ kcal} \end{aligned}$$

Work done by gas = 1.2 kcal

5. Given process is cyclic

Hence for overall process  $\Delta H = \Delta U = 0 \Rightarrow q = -W$

$$W = W_A + W_B + W_C$$

$$W_A = 0 \text{ (Volume Constant)}$$

$$W_B = 0 \text{ (free expansion)}$$

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

$$= -P \left( \frac{nRT_2}{P} - \frac{nRT_1}{P} \right) = -nR(T_2 - T_1) = -nR(298 - 373)$$

$$= +1 \times 8.314 \times 75 = 623.55 \text{ J}$$

$$W = 623.55 \text{ J}$$

$$q = -W = -623.55 \text{ J}$$

6. (I)  $T_1 = 300 \text{ K}, V_i = V, P_1 = P$

$$T_2 = 600 \text{ K}, V_2 = V, P_2 = 2P$$

$$W_{1-2} = 0$$

(II)  $T_2 = 600 \text{ K}, P_2 = 2P, V_2 = V$

$$T_3 = 600 \text{ K}, P_3 = P, V_3 = 2V$$

$$W_{2-3} = -1 \times R \times 600 \ln \left( \frac{2V}{V} \right) = -600R \ln 2$$

(II)  $P_3 = P, V_3 = 2V, T_3 = 600 \text{ K},$

$$P_4 = P, V_4 = V/2, T_4 = 600 \text{ K}$$

$$\frac{T_3}{V_3} = \frac{T_4}{V_4} \Rightarrow \frac{T_4}{600} = \frac{V_1/2}{2V_1} \Rightarrow T_4 = 150 \text{ K}$$

$$W_{3-4} = -nR(T_f - T_i) = -1 \times R(150 - 600) = 450 \text{ R}$$

7.  $C_v = \frac{3R}{2}, C_p = \frac{5R}{2} \quad n=2$

**Process -1** Reversible adiabatic compression

$$P_1 = 1 \text{ atm}, T_1 = 300 \text{ K}$$

$$P_2 = 4\sqrt{2} \text{ atm}, T_2 = T$$

$$P_1^{1-\gamma} T_1^\gamma = P_2^{1-\gamma} T_2^\gamma$$

$$\frac{T_f}{T_i} = \left( \frac{P_i}{P_f} \right)^{\frac{1-\gamma}{\gamma}} \quad \text{P} \quad \frac{T_f}{300} = \left( \frac{1}{4\sqrt{2}} \right)^{\frac{-2}{5}}$$

$$T_f = (300)^{1.67} \times (4\sqrt{2})^{\frac{2}{5}} = 600 \text{ K}$$

$$W = \frac{nR(T_2 - T_1)}{\gamma - 1} = \frac{2 \times R(600 - 300)}{\frac{5}{3} - 1} = 900 \text{ R}$$

**Process - 2** Reversible Isothermal

$$W = -nRT \ln \frac{P_i}{P_f} = -2 \times R \times 600 \ln \frac{4\sqrt{2}}{1} = -3000 \times R \ln 2$$

**Process - 3** Isobaric

$$W = -nR(T_f - T_i) = -2R(300 - 600) = 600R$$

$$W_{\text{net}} = 900 \text{ R} + (-3000 \times R \ln 2) + 600R = -600R$$

8.  $(V_{\text{rms}})_1 = \sqrt{\frac{3RT_1}{M}}$

$$(V_{\text{rms}})_2 = \sqrt{\frac{3RT_2}{M}}$$

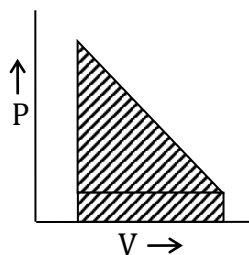
$$\Rightarrow (V_{\text{rms}})_2 = \frac{(V_{\text{rms}})_1}{2} \Rightarrow T_2 = \frac{T_1}{4}$$

Reversible adiabatic expansion

$$T_1 V_1^{g-1} = T_2 V_2^{g-1}$$

$$T_1 V_1^{g-1} = \frac{T_1}{4} V_2^{g-1} \Rightarrow \left( \frac{V_2}{V_1} \right)^{g-1} = 4$$

$$\left(\frac{V_2}{V_1}\right) = (4)^{\frac{1}{\gamma-1}} = (4)^{5/2} \Rightarrow V_2 = 32V_1$$



9.

$$W = \left(\frac{1}{2} \times 10 \times 10^{-3} \times 1000 \times 100\right) + (1 \times 10 \times 10^{-3} \times 100) = 501 \text{ J}$$

$$\Delta U = W = 501 \text{ J}$$

$$\Delta H = \Delta U + (P_2V_2 - P_1V_1) = 501 + [(1001 \times 990 \times 10^{-3} \times 100) - (1 \times 1000 \times 10^{-3} \times 100)] = 99.5 \text{ KJ}$$

## EXERCISE (JEE-MAINS)

- 1.
- $\Delta U$
- is state function

$$\Delta U_{AB} = +40 \text{ kJ/mol}$$

$$\Delta U_{BA} = -40 \text{ kJ/mol}$$

- 2.
- $\Delta n_g < 0$

$$\Delta H = \Delta U + \Delta n_g RT$$

$$\Delta H < \Delta U$$

- 3.
- $T_{f \text{ irrev}} > T_{f \text{ rev}}$

- 4.
- $\text{H}_2\text{O(l)} \rightleftharpoons \text{H}_2\text{O(g)}$

$$\Delta n_g = 1$$

$$\Delta H = \Delta U + \Delta n_g RT$$

$$41 = \Delta U + \frac{1 \times 8.3 \times 373}{1000}$$

$$\Delta U = +37.9041 \text{ kJ mol}^{-1}$$

- 5.
- $\text{C}_2\text{H}_5\text{OH(l)} + 3\text{O}_2\text{(g)} \longrightarrow 2\text{CO}_2\text{(g)} + 3\text{H}_2\text{O(l)}$

$$\Delta n_g = -1$$

$$\Delta H = \Delta U + \Delta n_g RT$$

$$-1366.5 = \Delta U - \frac{1 \times 8.314 \times 300}{1000}$$

$$\Delta U = -1366.5 + 2.4942 = -1364.0058 \text{ kJ}$$

- 6.
- $2\text{C}_6\text{H}_6\text{(l)} + 15\text{O}_2\text{(g)} \longrightarrow 12\text{CO}_2\text{(g)} + 6\text{H}_2\text{O(l)}$

$$\Delta n_g = -3$$

$$\Delta H = \Delta U + \Delta n_g RT$$

$$\Delta H - \Delta U = \Delta n_g RT$$

$$= \frac{-3 \times 8.314 \times 300}{1000} = -7482.6 \text{ J mol}^{-1}$$

7. For rev. isothermal process

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

$$\Delta U = 0$$

- 8.
- $W = -\Delta n_g RT = -1 \times 8.3 \times 300 \text{ J} = -2.49 \text{ kJ}$

9. For adiabatic process

$$q = 0, \Delta U = W$$

- 10.
- $\Delta n_g = -1$

$$\Delta H = \Delta U + \Delta n_g RT$$

$$|\Delta U| > |\Delta H|$$

11.  $q_{AB} = +5J$

$$W_{AB} = -8J$$

$$\Delta U_{AB} = q_{AB} + W_{AB} = -3J$$

$$\Delta U_{BA} = +3J$$

$$q_{BA} = -3J$$

$$W_{BA} = \Delta U_{BA} - q_{BA} = +6J$$

12.  $\Delta U = \Delta U_{AB} + \Delta U_{BC} + \Delta U_{CA} = 0$

$$\Delta U_{AB} = -5 + 2 = -3 \text{ kJ mol}^{-1}$$

$$-5 - 3 + \Delta U_{CA} = 0$$

$$\Delta U_{CA} = +8 \text{ kJ mol}^{-1}$$

$$q_{CA} = \Delta U_{CA} - W_{CA} = 8 - 3 = +5 \text{ kJ mol}^{-1}$$

14.  $W = -4 \times (1 - 5) = +16J$

$$q = C_m \Delta T$$

$$16 = 1 \times 24 \times \Delta T \quad \Delta T = \frac{2}{3} K$$

15.  $C_p$  is defined at constant P only.

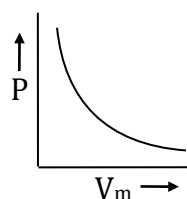
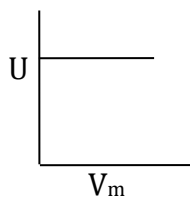
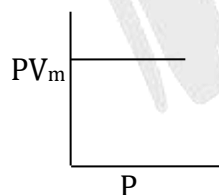
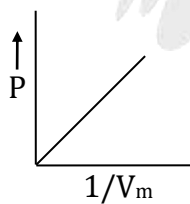
$$U = f(T)$$

$C_v$  is defined at constant V only.

$$C_p \text{ and } C_v = f(T)$$

16. For isoT process

$$PV_m = \text{Constant}$$



$$17. \quad \Delta H = \int_{T_2}^{T_1} nC_p dT = \int_{300}^{1000} 3(23 + 0.01T) dT = 61950 \text{ J} = 62 \text{ kJ}$$

18. For adiabatic process

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

19. 5 mole ideal gas is given,

$$C_{w,m} = 28 \text{ J K}^{-1} \text{ mol}^{-1}, R = 8 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$100 \text{ K} \longrightarrow 200 \text{ K}$$

$$\Delta U = nC_{v,m}dT = 5 \times 28 \times 100$$

$$= 14000 \text{ J}$$

$$= 14 \text{ kJ}$$

$$\Delta (PV) = P_2V_2 - P_1V_1$$

$$= nRT_2 - nRT_1$$

$$= 5 \times 8 \times 100 = 4 \text{ kJ}$$

20. Both work (w) and heat (q) are state function.

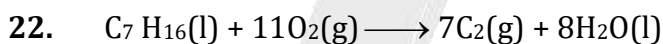
21. From 1<sup>st</sup> law of thermodynamics

$$\Delta U = q + w$$

$$w = 10 \text{ kJ (work is done on spring)}$$

$$q = -2 \text{ kJ (Heat rejected into surrounding)}$$

$$\Delta U = -2 + 10 = 8 \text{ kJ}$$



$$\Delta_{ng} = 7 - 11 = -4$$

$$\Delta H = \Delta U + \Delta_{ng}RT$$

$$\Delta H = \Delta U = -4RT$$

23. As process is Irreversible

$$\Rightarrow w = -P_{\text{ext}} (dv)$$

$$= -1 \times 9$$

$$= -9 \text{ lit. bar}$$

$$24. \quad |W| = \frac{1}{2}(6 + 10) \times 6 = 48 \text{ J}$$

$$25. \quad \Delta U = nC_v\Delta T$$

$$5000 = 4 \times C_v(500 - 300)$$

$$C_v = 6.25 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\text{Final ans} = 6.25 \times 100 = 625 \text{ J K}^{-1} \text{ mol}^{-1}$$

26. For ideal Gas



$$\# U = f(T), H = f(T)$$

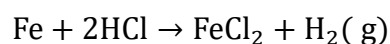
$$\# Z = 1$$

$$\# C_P - C_V = R$$

$$\# dU = C_V dT$$

28.  $T = 298 \text{ K}, R = 8.314 \frac{\text{J}}{\text{molK}}$

→ Chemical reaction is



$$50 \text{ g P} = 1 \text{ bar}$$

$$= \frac{50}{55.85} \text{ mol}$$

→ Work done for 1 mol gas

$$\rightarrow -P_{\text{ext}} \times \Delta V$$

$$= \Delta n g R T$$

$$= -1 \times 8.314 \times 298 \text{ J}$$

→ Work done for  $\frac{50}{55.85}$  mol of gas

$$= -1.8314 \times 298 \times \frac{50}{55.85} \text{ J}$$

$$= -2218.059 \text{ J};$$

$$= -2218 \text{ J}$$

29. The work done during the cyclic process is equal to the area enclosed by the curve of the process.

$$\text{Area enclosed by the rectangle} = \text{length} \times \text{width} = (2p - p) \times (2V - V) = pV$$

30. At A and D the temperatures of the gas will be equal, so

$$\Delta E = 0, \Delta H = 0$$

$$\text{Now } W = W_{AB} + W_{BC} + W_{CD}$$

Now,

for process AB is isobaric, so

$$\text{work} = -P_{\Delta} V$$

$$\text{work} = -P_{\Delta} V$$

$$= -P_0(2V_0 - V_0)$$

$$= -P_0V_0$$

along BC, as it is an isothermal process,

$$W = -RT \ln \left( \frac{4V_0}{2V_0} \right)$$

$$= -RT \ln 2$$

Along BC volume is doubled and as it is isothermal process so pressure must be halved.

Pressure at C is  $0.5 \times P_0$

Along CD,

$$W = -0.5 \times P_0(2V_0 - 4V_0)$$

$$= P_0V_0$$

So,

Total work done,

$$W = W_{AB} + W_{BC} + W_{CD}$$

$$= -P_0V_0 + (-RT \ln 2) + (+P_0V_0)$$

$$= -RT \ln 2$$

31. Internal energy, volume enthalpy are state variable.

$$32. \text{ N}_2\text{O moles} = \frac{2.2}{44} = \frac{1}{20}$$

$$\Delta H = nC_p\Delta T = \frac{1}{20} \times 100(-40) = -200\text{J}$$

$$\Delta U = q_p + w$$

$$w = -P_{\text{ext.}} \Delta V$$

$$W = -1 \frac{(167.75 - 217.1)}{1000} \times 101.3\text{J}$$

$$w = +5\text{J}$$

$$\Delta U = -200 + 5 = -195\text{J}$$

33. (A) For a spontaneous process  $\Delta G_{T,P} < 0$

(B)  $\Delta P = 0 \rightarrow$  Isobaric process;  $\Delta T = 0 \rightarrow$  Isothermal process

(C)  $\Delta H_{\text{reaction}} = (\Sigma \text{ Bond energies of reactants}) - (\Sigma \text{ bond energies of products})$

(D)  $\Delta H < 0$  is for exothermic reaction

EXERCISE (JEE-ADVANCED)

1.  $T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1}$

$$300 \times (1.25)^{\gamma-1} = T_f \times (2.5)^{\gamma-1}$$

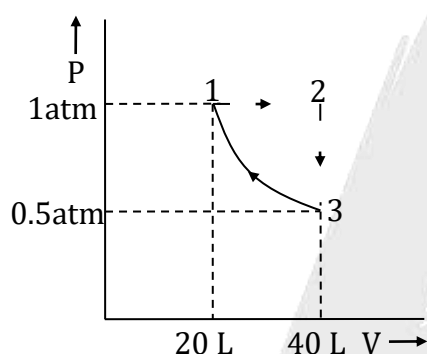
$$T_f = 300 \times \left( \frac{1.25}{2.5} \right)^{\gamma-1}$$

$$= \frac{300}{2^{2/3}} = 188.5 \text{ K}$$

$$\Delta H = n C_p \Delta T = 0.05 \times 20.8 \times (188.5 - 300) = -115.41 \text{ J}$$

2. Work is path function.

3.  $\Delta H = \Delta U + P_2 V_2 - P_1 V_1 = 30 + (5 \times 4 - 3 \times 2) = 30 + 14 = +44 \text{ L-atm}$



4.

$$W_{\text{net}} = w_1 + w_2 + w_3$$

$$= -1 \times 20 + 0 + 20 \ln 2 = 20(\ln 2 - 1) = -20 \times 0.307 \text{ L-atm} = -6.14 \text{ L-atm}$$

$$q = -w = +6.14 \text{ L-atm}$$

for cyclic process  $\Delta H = 0$ ,  $\Delta U = 0$ ,  $\Delta S = 0$

5. He molecule is monoatomic so it just has three degree of freedom at all temperature but  $H_2$  is diatomic molecule at higher temperature vibrational degree of freedom is also considered.

6. For adiabatic

$$\Delta U = W$$

$$W = -P \Delta V$$

$$= 100 \times 10^{-3}$$

$$= +0.1 \text{ bar-L}$$

$$\Delta H = \Delta U + P_2 V_2 - P_1 V_1$$

$$= +0.1 + (100 \times 99 - 1 \times 100) \times 10^{-3}$$

$$= +9.9 \text{ bar-L}$$

7.  $\Delta H = n C_p \Delta T$

For isoT  $\Delta T = 0$

8. For irrev. adiabatic

$$nC_v \Delta T = -P_{\text{ext}}(V_2 - V_1)$$

$$1 \times \frac{3}{2} R(T_f - T) = -1 \times (2 - 1)$$

$$T_f = T - \frac{2}{3 \times 0.0821}$$

9.  $\Delta H = \Delta U + V\Delta P$

$$-560 = \Delta U + 1 \times (40 - 70) \times 0.1$$

$$-560 = \Delta U - 3$$

$$\Delta U = -557 \text{ kJ mol}^{-1}$$

10.  $PV^{-1} = K$

$$C = \frac{3}{2} R - \frac{R}{-2} = \frac{3}{2} R + \frac{R}{2} = 2R$$

11. State function -  $\Delta U, \Delta H$

path function -  $W$

12. Intensive properties : molar conductivity, EMF

Extensive properties : Resistance , Heat capacity

$$13. W_s = -2.303RT \log \frac{V_2}{V_1} = -2.303 \times \log \frac{5.5}{0.5}$$

$$= -4.606 \log 1.1 = -4.8 \text{ L-atm}$$

$$W_d = -4 \times \frac{3}{2} + (-1 \times 1) = + \left( -\frac{2}{3} \times \frac{5}{2} \right) = -\frac{26}{3} \text{ L-atm} \quad \frac{W_d}{W_s} = 1.8 \gg 2.0$$

14.  $T_1 = T_2 > T_3$

$$T_1 > T_3$$

$W_{\text{isoT}} < W_{\text{adia}}$  (with sign)

$\Delta U_{\text{isoT}} > \Delta U_{\text{adia}}$ .

### Paragraph for Question 15 and 16

15. Isochoric process  $\Rightarrow$  vol. constant

16.  $KL \rightarrow P$  constant

$V, T$

$LM - V$  constant

$P, T$

$MN - P$  constant

$V, T$

NK - V constant

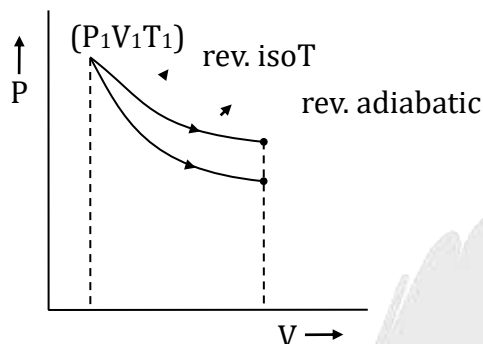
P, T

17. For free expansion

$$w = 0, q = 0 \quad \Delta T = 0$$

$$T_1 = T_2$$

$$P_1V_1 = P_2V_2$$



18.

(A) During irrev. compression maximum work is done on the gas.

(B) For expansion of ideal gas from same  $V_i$  to same  $V_f \Rightarrow |W_{\text{isotherm}}| > |W_{\text{adia}}|$

(C) If  $T_1 = T_2 \Rightarrow \Delta T = 0, \Delta U = 0$

For rev. adiabatic expansion  $T_2 < T_1 \Rightarrow \Delta U = -ve$

(D) For free expansion

$$P_{\text{ext}} = 0, w = 0$$

If it is carried out isothermally  $\Delta U = 0, q = 0$

it is adiabatic also

19. A-C isochoric process

A-B isotherm process

B-C isobaric process

$$q_{AC} = \Delta U_{AC} = nC_v(T_2 - T_1) = \Delta U_{BC}$$

$$w_{AB} = -nRT_1 \ln \frac{V_2}{V_1}$$

$$w_{BC} = -P_2(V_1 - V_2) = P_2(V_2 - V_1)$$

$$q_{BC} = \Delta H_{BC} = nC_p(T_2 - T_1) = \Delta H_{AC}$$

$$\Delta U_{CA} = nC_v(T_1 - T_2)$$

$$\Delta H_{CA} < \Delta U_{CA}$$

20.  $w = - \int P_{\text{ext.}} dV$

From van der waal equation of state for one mole gas.

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

$$P = \left[ \frac{RT}{V - b} - \frac{a}{V^2} \right]$$

For reversible process

$$P_{\text{ext.}} = P_{\text{gas}}$$

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

So, process is not applicable only for irreversible process.

Hence Ans, A, B, C.

A