

THERMODYNAMICS-01

1. INTRODUCTION

Thermodynamics is concerned with energy and its transformation in various forms in different physical and chemical processes.

Thermodynamics \equiv Thermo + dynamics

Dynamics \equiv Study of change due to a driving force

Thermo \equiv Thermal which is related to temperature or energy.

The laws of thermodynamics deal with energy changes of macroscopic systems involving a large number of molecules rather than microscopic systems containing a few molecules. Thermodynamics is not concerned about how and at what rate these energy transformations are carried out, but is based on initial and final states of a system undergoing the change. Laws of thermodynamics apply only when a system is in equilibrium or moves from one equilibrium state to another equilibrium state. Macroscopic properties like pressure and temperature do not change with time for a system in equilibrium state.

2. SOME BASIC DEFINITIONS (Thermodynamic terms)

2.1 SYSTEM :

The macroscopic part of the universe under study is called a **system**. Rest of the universe outside the system is called **surroundings**. The actual or imaginary surface that separates the system from the surroundings is called the **boundary**.

However, the entire universe other than the system is not affected by the changes taking place in the system. Therefore, for all practical purposes, the surroundings are that portion of the remaining universe which can interact with the system. Usually, the region of space in the neighbourhood of the system constitutes its surroundings.

2.1.1 Types of boundary :

- (i) Real or imaginary
- (ii) Rigid (fixed) or movable (flexible)
- (iii) Permeable (allow mass transfer) or impermeable (does not allow mass transfer).
- (iv) Diathermal (allow heat transfer) or Adiabatic (does not allow heat transfer).

2.1.2 Types of systems :

- (i) **Isolated system** : A system is said to be isolated if it cannot exchange both matter and energy with the surroundings. Example : coffee in a thermos flask.
- (ii) **Closed system** : A system is said to be closed if it can exchange energy but not matter. Example : Coffee in a closed stainless steel flask.
- (iii) **Open system** : A system is said to be open if it can exchange matter and energy. Example : A thermos flask or a steel flask if not closed.

Note : A perfectly isolated system is only a theoretical system.

2.2 State of system : A system is called in a particular state where all the macroscopic properties of the system have definite value.

2.3 Properties of system : The state of a system is defined by a particular set of its measurable quantities called properties. They can be categorised into extensive and intensive properties.

Intensive property is one whose value is independent of the size (or mass) of the system. An extensive property is one whose value depends on the size (or mass) of the system.

* Extensive properties are additive but intensive properties are non additive.

* Ratio of two extensive property gives an intensive property.

Extensive Properties

Volume
 Number of moles
 Mass
 Free Energy (G)
 Entropy (S)
 Enthalpy (H)
 Internal energy (E & U)
 Heat capacity

Intensive Properties

Molar volume
 Density
 Refractive index
 Surface tension
 Viscosity
 Free energy per mole
 Specific heat
 Pressure
 Temperature
 Boiling point, freezing point etc

- 2.4 State function or state variable :** Variables like P, V, T are State Functions or State Variables because their values depend only on the present state of a system and not on how the state was reached

Condition for a function to be a state function :

(i) If ϕ is state function, $\int_A^B d\phi = \phi_B - \phi_A$

(ii) If ϕ is a state function, $\oint d\phi = 0$

- 2.5 Path function :** Function which depends on the path, i.e. how the process is carried out e.g. work & heat.

- 2.6 Thermodynamic process :** A thermodynamic process involves change of a system from one state to another state.

EXERCISE-I

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

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

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

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

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

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

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

Path function : Work, Heat

3. A state function is that :

- (A) which is used in thermochemistry
- (B) which obeys all laws of thermodynamics
- (C) quantity whose value depends only upon the state of the system
- (D) quantity which is used in measuring thermal change

Ans. (C)

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

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

Ans. (B)

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

- (A) Internal energy(E)
- (B) Free energy(G)
- (C) Enthalpy(H)
- (D) Work(W)

Ans. (D)

6. What is true for a cyclic process [E = internal energy]

- (A) $W = 0$
- (B) $\Delta E = 0$
- (C) $\Delta H = 0$
- (D) B & C both

Ans. (D)

7. The internal energy change when a system goes from state A to B is 40 kJ/mole. If the system goes from A to B by a reversible path and returns to state A by an irreversible path what would be the net change in internal energy ? [AIEEE-2003]

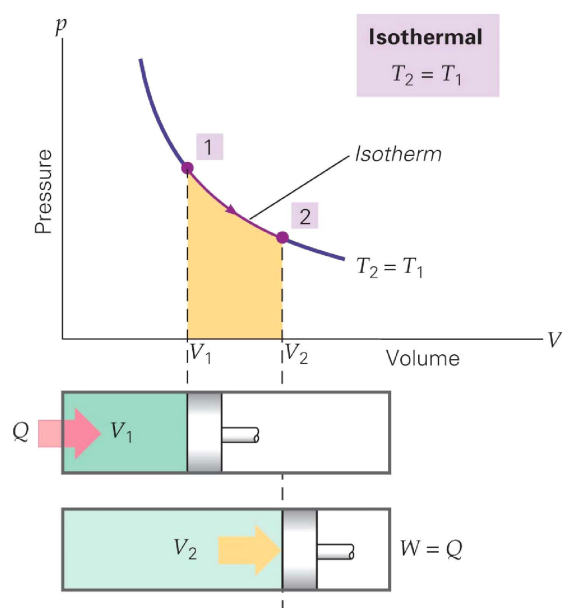
- (A) < 40 kJ
- (B) Zero
- (C) 40 kJ
- (D) > 40 kJ

Ans.(B)

Type of process :

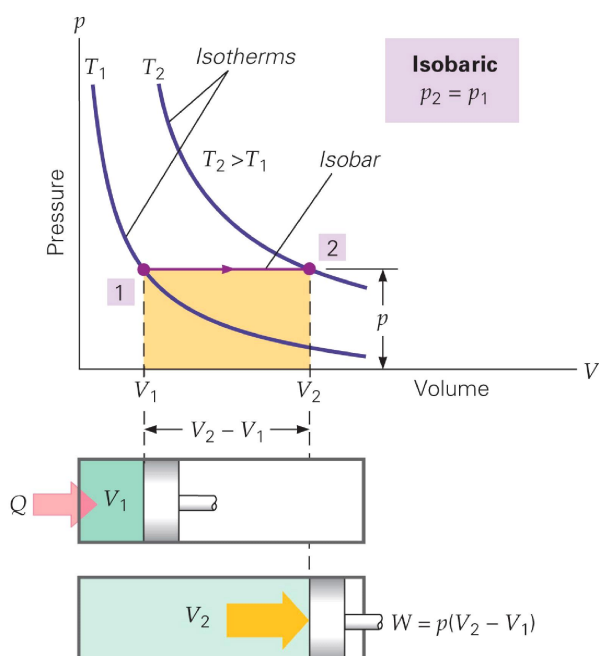
(i) Isothermal process :

A process in which temperature of the system remains constant is called isothermal process.



(ii) Isobaric process :

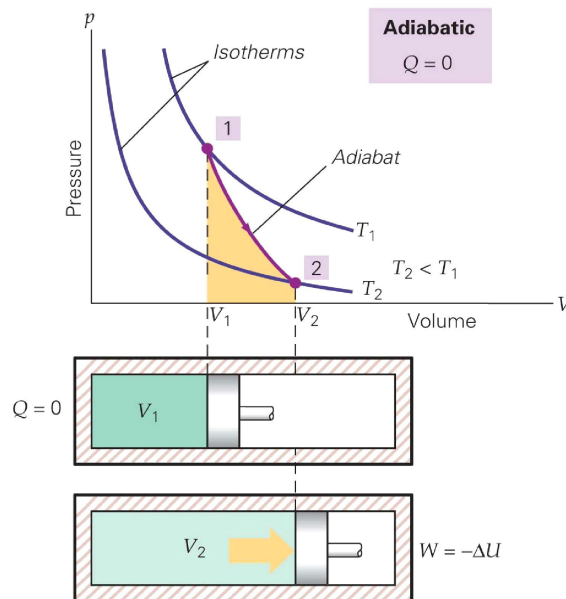
A process in which pressure of the system remains constant is called isobaric process. Temperature and volume of the system may change.



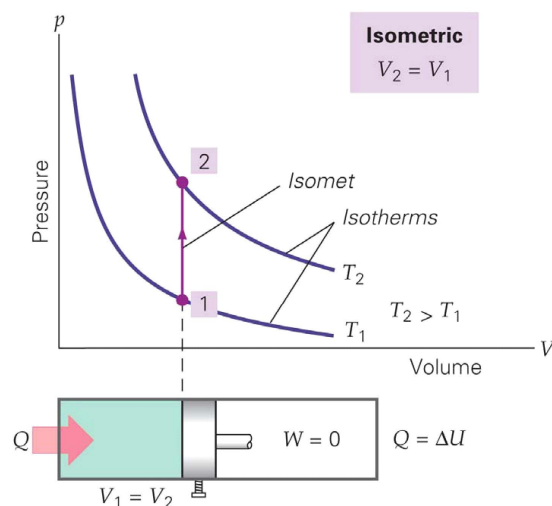
Ex. All the reactions or processes taking place in open vessel like boiling of water in open vessel, burning of charcoal, melting of wax take place at constant pressure (1 atm.)

(iii) Adiabatic process :

A process in which no heat exchange takes place is called adiabatic process. Adiabatic process occurs in systems with insulated walls.

**(iv) Isochoric process :**

The process for which volume of the system remains constant is called isochoric process i.e., Heating of gas in closed or rigid vessel.

**(v) Cyclic process :** It is combination of two or more process in which the final state of system, becomes identical to the initial. The net change in all thermodynamic properties of system must be zero.

$$\Delta T = \Delta P = \Delta V = \Delta H = \Delta S = \Delta G \dots\dots = 0$$

However Q_{net} or W_{net} may or may not be zero.

(vi) Reversible or Irreversible process : If the initial state may be received just by reversing the direction of process at any state, process is called reversible. In irreversible process the initial state can never be achieved just by reversing the direction of process.

In the reversible process, the driving force is only infinitesimally greater than the opposing force. In the irreversible process, they differ largely.

A perfectly reversible process is a theoretical process because it takes infinite time but reversible processes are important because it results maximum efficiency in any machine. The actual process occurring in the machine is quasi static which may tend to reversible or irreversible process.

During irreversible process, one of the equation of state like $PV = nRT$, is valid. Such equation is valid only at initial & final state. However during reversible process such equation are valid throughout the process.

A process is reversible when the system throughout remain in thermodynamic equilibrium with the surrounding.

A system is said in thermodynamic equilibrium when it simultaneously satisfy the following equilibria.

- (a) **Thermal equilibrium:** Same temperature throughout (No heat transfer within the system)
- (b) **Mechanical equilibrium :** Same pressure or force throughout the system (No work should be performed by one part on the other)
- (c) **Material equilibrium :** No change in the composition of system with time. No mass transfer within the system.

If a system is in thermodynamic equilibrium there is no net energy or mass transfer within the system.

3. WORK

Thermodynamically, work may be defined as the form of energy which appears only when, there is some change in the boundary of the system. Such work is called mechanical or PV work.

Work may also be non-mechanical like electric work.

Presently, we will discuss only mechanical work.

- (i) It is not thermodynamic property of system.
- (ii) It depends on the quantity of system.
- (iii) Sign convention, work on system = (+)ve.

In physics, work is calculate from the force applied by system, but in chemistry due to external force.

$W = \int_{V_1}^{V_2} P \cdot dV = - \int_{V_1}^{V_2} P_{\text{ext}} dV$
<div style="display: flex; justify-content: space-around;"> Physics Chemistry </div>

4. HEAT

Heat is defined as the energy that flows into or out of a system because of a difference in temperature between the system and its surrounding.

According to IUPAC convention

heat lost by system is expressed with -ive sign

heat given to system is expressed with +ive sign

* $q_v = nC_{v,m} dT$

* $q_p = nC_{p,m} dT$

* $C_{p,m} - C_{v,m} = R$ (for ideal gas)

* C_v & C_p depends on temperature even for an ideal gas. ($C = a + bT + cT^2$)

General values of C_v & C_p for an ideal gas can be taken as follows.

Atomicity		n_{tr}	n_{Rot}	n_{Vib}	C_v		C_p		γ	
						Incl. Vib	Excl. Vib	Incl. Vib	Excl. Vib	Incl. Vib
Mono		3	0	0	$\frac{3}{2}R$	$\frac{3}{2}R$	$\frac{5}{2}R$	$\frac{5}{2}R$	$\frac{5}{3}$	$\frac{5}{3}$
Di		3	2	1	$\frac{5}{2}R$	$\frac{7}{2}R$	$\frac{7}{2}R$	$\frac{9}{2}R$	$\frac{7}{5}$	$\frac{9}{7}$
Tri	Linear	3	2	4	$\frac{5}{2}R$	$\frac{13}{2}R$	$\frac{7}{2}R$	$\frac{15}{2}R$	$\frac{7}{5}$	$\frac{15}{13}$
	Non Linear	3	3	3	$3R$	$6R$	$4R$	$7R$	$\frac{4}{3}$	$\frac{7}{6}$

5. INTERNAL ENERGY (E & U)

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

$$U = U_{\text{Kinetics}} + U_{\text{Potential}} + U_{\text{Electronic}} + U_{\text{nuclear}} + \dots$$

U is a state function & is an extensive property.

$$\Delta U = U_{\text{final}} - U_{\text{initial}}$$

For a given closed system

$$U = f(T, V)$$

$$dU = \left(\frac{\partial U}{\partial T} \right)_v dT + \left(\frac{\partial U}{\partial V} \right)_T dV$$

6. ENTHALPY

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.

$$H = U + PV$$

$$\Delta H = \Delta U + \Delta(PV)$$

at constant pressure

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

combining with first law.

$$\Delta H = q_p$$

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.

6.1 RELATIONSHIP BETWEEN ΔH & ΔU :

The difference between ΔH & ΔU becomes significant only when gases are involved (insignificant in solids and liquids)

$$\Delta H = \Delta U + \Delta(PV)$$

If substance is not undergoing chemical reaction or phase change.

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

In case of chemical reaction

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

7. ZEROth LAW OF THERMODYNAMICS

Two system in thermal equilibrium with a third system are also in thermal equilibrium with each other. It introduces temperature as a state function.

8. FIRST LAW OF THERMODYNAMICS

"Total energy of universe remains constant." It is law of conservation of energy.

Let us consider a system whose internal energy is U_1 . If the system is supplied with heat q , the internal energy of the system increases to $U_1 + q$. If work (w) is done on the system, the internal energy in the final state of the system, U_2 is given by

$$U_2 = U_1 + q + w$$

or $U_2 - U_1 = q + w$

$$\Delta U = q + w$$

According to IUPAC, heat added to the system and work done on the system are assigned positive values as both these modes increase the internal energy of the system.

EXERCISE -2

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

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

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

(a) $q = +20$ Joule. (b) $w = -40$ Joule.

(c) $w = +5$ Joule. (d) $q = -50$ Joule.

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

(a) $q = +10$ kJ

(b) $w = -20$ kJ

Ans. (a) $q = + 10$ kJ :

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

(b) $w = - 20$ kJ :

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

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

Initial state		Final state
(i) $\text{H}_2\text{O}(\text{g})$	\longrightarrow	$\text{H}_2\text{O}(\ell)$
(ii) $\text{H}_2\text{O}(\text{s})$	\longrightarrow	$\text{H}_2\text{O}(\text{g})$
(iii) $\text{H}_2\text{O}(\ell)$	\longrightarrow	$\text{H}_2\text{O}(\text{s})$
(iv) $\text{CaCO}_3(\text{s})$	\longrightarrow	$\text{CaO}(\text{s}) + \text{CO}_2(\text{g})$

Ans. (i) + , (ii) –, (iii) – , (iv) –

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

Sol. Because

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

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

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

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

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

Ans. (D)

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

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

Ans. (A)

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

- (A) $(U_1 + 150 \text{ J})$ (B) $(U_1 + 1050 \text{ J})$ (C) $(U_1 - 150 \text{ J})$ (D) $(U_1 - 1050 \text{ J})$

Ans. (A)

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

- (A) 32 J (B) 40 J (C) 48 J (D) –32 J

Ans. (A)

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

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

Ans. (A)

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

(A) -608 J (B) $+304 \text{ J}$ (C) -304 J (D) -6 J

Ans. (A)

19. Assuming that water vapour is an ideal gas, the internal energy change (ΔU) when 1 mol of water is vapourised at 1 bar pressure and 100°C , (Given : Molar enthalpy of vapourisation of water at 1 bar and $373 \text{ K} = 41 \text{ kJ mol}^{-1}$ 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) $41.00 \text{ kJ mol}^{-1}$

Ans.(3)

20. A piston filled with 0.04 mol of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37.0°C . As it does so, it absorbs 208 J of heat. The values of q and w for the process will be :- [JEE-MAIN-2013]

($R = 8.314 \text{ J/mol K}$) ($\ln 7.5 = 2.01$)

(A) $q = + 208 \text{ J}$, $w = - 208 \text{ J}$
 (B) $q = - 208 \text{ J}$, $w = - 208 \text{ J}$
 (C) $q = - 208 \text{ J}$, $w = + 208 \text{ J}$
 (D) $q = + 208 \text{ J}$, $w = + 208 \text{ J}$

Ans.(A)

Sol.

$q = + 208 \text{ Joule}$

for isothermal process

$$\Delta U = 0$$

\therefore from 1st law of thermodynamics

$$\Delta U = q + w$$

$$0 = q + w$$

$$\Rightarrow w = -q = -208 \text{ Joule}$$

9. CALCULATION OF q , w , ΔU & ΔH IN VARIOUS PROCESS :

9.1 ISOTHERMAL EXPANSION OR COMPRESSION OF IDEAL GAS :

For isothermal process : $\Delta T = 0$

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

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

$$\text{and } q = \Delta U - w = -w$$

Now, w depends on path (reversible or irreversible).

9.1.1 Reversible process :

$$w_{\text{rev.}} = - \int_{V_1}^{V_2} P_{\text{ext}} \cdot dV = - \int_{V_1}^{V_2} (P \pm dP) \cdot dV = - \int_{V_1}^{V_2} P \cdot dV = - \int_{V_1}^{V_2} \frac{nRT}{V} \cdot dV$$

$$\therefore w_{\text{rev.}} = -nRT \cdot \ln \frac{V_2}{V_1} = -nRT \cdot \ln \frac{P_1}{P_2}$$

9.1.2 Irreversible process, against a constant external pressure :

$$w_{\text{irr.}} = -P_{\text{ext}} \int_{V_1}^{V_2} dV = -P_{\text{ext}} (V_2 - V_1)$$

9.1.3 Free expansion (or expansion in vacuum) :

$P_{\text{ext}} = 0$ but $dV = \text{finite}$, Hence, $w = 0$

9.1.4 Comparison of magnitude of work :

In expansion, magnitude of work = $-w_{\text{exp}}$

In compression, magnitude of work = w_{comp}

Now, $w_{\text{rev}} - w_{\text{irr}} = (-P \cdot dV) - (-P_{\text{ext}} \cdot dV) = (P_{\text{ext}} - P) \cdot dV$
 $= -ve$, always

In expansion, $P_{\text{ext}} < P$ and $dV = +ve$

In compression, $P_{\text{ext}} > P$ and $dV = -ve$

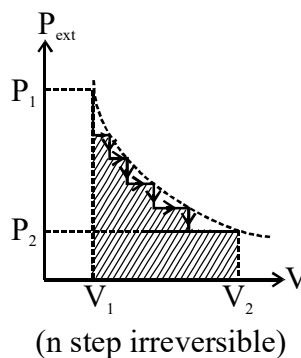
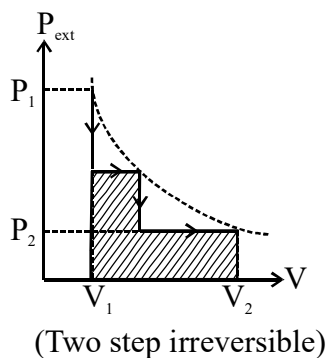
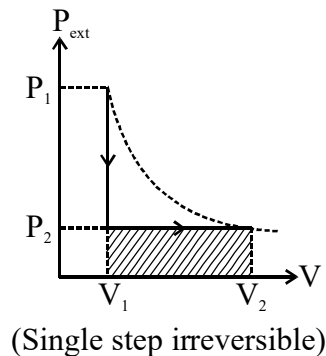
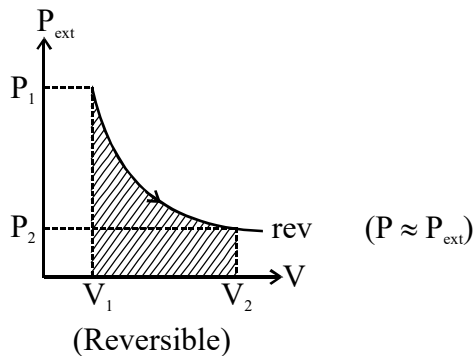
Hence, $w_{\text{rev}} < w_{\text{irr}}$ (Always, with proper sign).

Now, as magnitude of work in expansion is $-w_{\text{exp}}$, hence, $(-w_{\text{rev, exp}}) > (-w_{\text{irr, exp}})$, i.e., magnitude of work is greater when expansion is reversible.

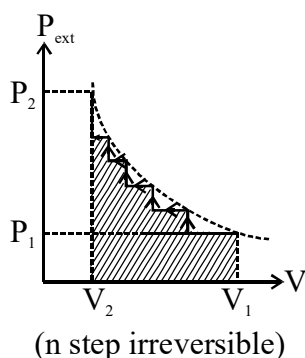
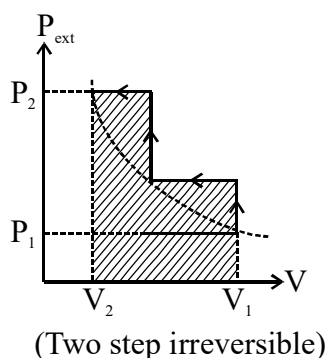
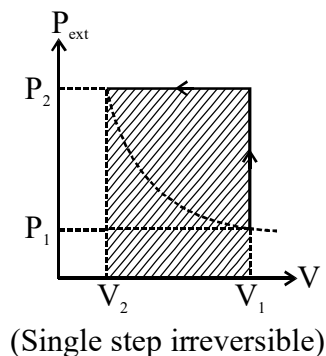
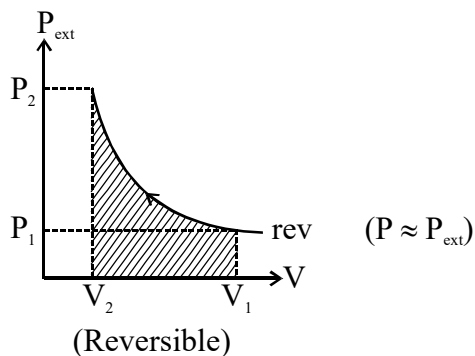
And, as magnitude of work in compression is w_{comp} , hence, $(w_{\text{rev, comp}}) < (w_{\text{irr, comp}})$, i.e., magnitude of work is greater when compression is irreversible.

9.1.5 Graphical comparison :

(a) Expansion :



$(-w_{\text{exp}}) : \text{Rev} > n \text{ step} > \dots > 2 \text{ step} > \text{single step}$

(b) Compression :

$$(w_{\text{comp}}) : \text{Rev} < n \text{ step} < \dots < 2 \text{ step} < \text{single step}$$

Ex.1 Two moles of an ideal gas undergoes isothermal expansion from 4L to 20L at 27°C. Calculate q , w , ΔU and ΔH , if the process is performed.

(i) reversibly

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

(iii) as free expansion

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

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

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

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

$$\text{and } q = -w = 8028.52 \text{ J}$$

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

$$= -16 \times 101.3 \text{ J} = -1620.8 \text{ J}$$

$$q = -w = 1620.8 \text{ J}$$

$$(iii) \quad w = 0 \text{ and } q = 0$$

9.2 ADIABATIC EXPANSION OR COMPRESSION OF IDEAL GAS :

$$q = 0$$

$$\therefore \Delta U = w = n.C_{v,m}.(T_2 - T_1)$$

$$\text{and } \Delta H = n.C_{p,m}.(T_2 - T_1)$$

The change in temperature may be calculated as

$$n \cdot \int_{T_1}^{T_2} C_{v,m} \cdot dT = - \int_{V_1}^{V_2} P_{\text{ext}} \cdot dV$$

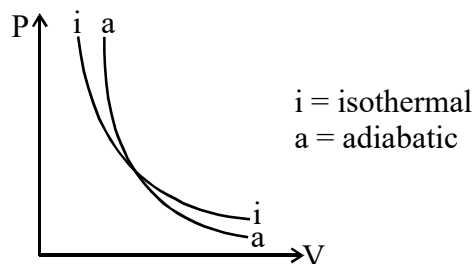
- (a) If $C_{v,m}$ is temperature independent and the process is reversible, then
 $T \cdot V^{\gamma-1} = \text{constant}$

or, $P \cdot V^{\gamma} = \text{constant}$

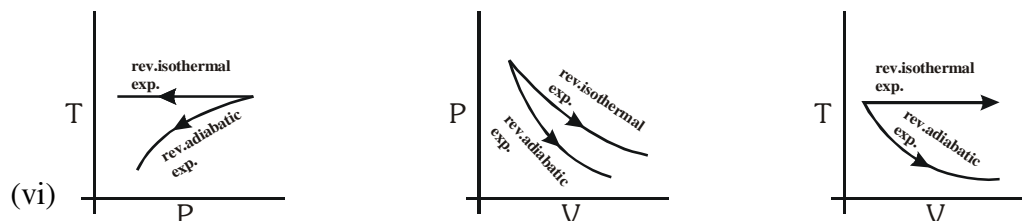
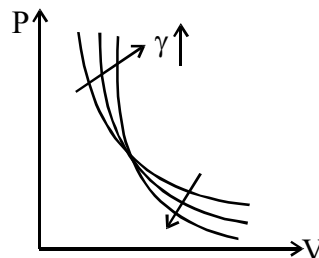
or, $T^{\gamma} P^{1-\gamma} = \text{constant}$

- (b) If $C_{v,m}$ is temperature independent and the process is irreversible, then
 $n \cdot C_{v,m} \cdot (T_2 - T_1) = -P_{\text{ext}} \cdot (V_2 - V_1)$

- (i) The temperature of ideal gas decreases in adiabatic expansion (except free expansion, which is isothermal too) and the temperature of ideal gas increases in adiabatic compression.
- (ii) The final temperature of gas is always higher in irreversible process (expansion or compression) relative to reversible process, for the same change in volume.
- (iii) Just like isothermal process, the magnitude of work is maximum when expansion is reversible and compression is irreversible (single step).
- (iv) Work in reversible isothermal and adiabatic processes may be compared graphically.



- (v) Work in reversible adiabatic process may be compared graphically.



Comparison of reversible adiabatic expansion and reversible isothermal expansion on TP, PV and TV diagram

Ex.2. Two moles of an ideal monoatomic gas undergoes adiabatic expansion from 5L, 127°C to 40L. Calculate q , ΔU , w and ΔH , if the process is performed.

- (i) reversibly
- (ii) irreversibly, against a constant external pressure of 0.1 atm.
- (iii) as free expansion

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

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

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

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

$$\Delta H = \gamma \Delta U = -12471 \text{ J}$$

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

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

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

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

Ex.3. Five moles of an ideal monoatomic gas undergoes adiabatic expansion from 12 atm to 1 atm, against a constant external pressure of 1 atm. If the initial temperature of gas is 27°C, calculate the final temperature. Also calculate q , ΔU , w and ΔH .

Sol. : $q = 0$

$$\Delta U = w$$

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

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

$$\text{or, } \frac{3}{2}(T_2 - 300) = - \left(T_2 - 300 \times \frac{1}{12} \right) \Rightarrow T_2 = 190 \text{ K}$$

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

$$\text{and } \Delta H = \gamma \cdot \Delta U = -11431.75 \text{ J}$$

9.3 ISOBARIC PROCESS FOR AN IDEAL GAS :

$$q = \Delta H = n \cdot C_{v,m} \cdot \Delta T$$

$$\therefore \Delta U = n \cdot C_{v,m} \cdot \Delta T$$

$$w = -P \cdot (V_2 - V_1) = -nR \cdot \Delta T$$

Ex.4. One mole of an ideal diatomic undergoes isobaric expansion from 27°C to 87°C . Calculate q , ΔU , w and ΔH .

Sol. : $q = \Delta H = n.C_{v,m}.\Delta T = 1 \times \frac{7}{2}R \times 60 = 1745.94 \text{ J}$

$$\Delta U = \frac{\Delta H}{\gamma} = 1247.1 \text{ J}$$

and $w = -nR.\Delta T = -1 \times 8.314 \times 60 = -498.84 \text{ J}$

9.4 ISOCHORIC PROCESS FOR AN IDEAL GAS :

$$w = 0$$

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

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

Ex.5. Ten moles of an ideal gas ($\gamma = 1.2$) is heated from 27°C to 47°C at constant volume. Calculate q , ΔU , w and ΔH .

Sol. : $w = 0$

$$q = \Delta U = n.C_{v,m}.\Delta T = 2 \times \frac{R}{1.2-1} \times 20 = 200 R$$

$$\Delta H = \gamma.\Delta U = 240R$$

9.5 POLYTROPIC PROCESS FOR AN IDEAL GAS :

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

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

For ideal gas is reversible polytropic process and $C_{v,m}$ temperature independent,

$$P.V^x = \text{constant}$$

or, $T.V^{x-1} = \text{constant}$

where x = polytropic index

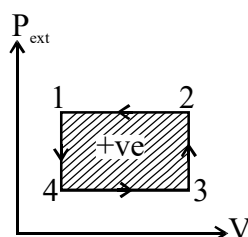
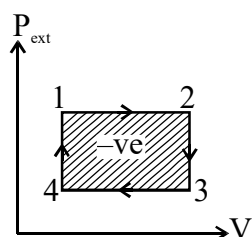
$$w_{\text{rev}} = \frac{P_2 V_2 - P_1 V_1}{1-x} = -\frac{nR(T_2 - T_1)}{1-x} \quad (x \neq 1)$$

$$= -nRT \cdot \ln \frac{V_2}{V_1} \quad (x = 1)$$

and $q = n.C_m.\Delta T$

The molar heat capacity, $C_m = C_{v,m} + \frac{P \cdot dV}{n \cdot dT} = C_{v,m} + \frac{R}{1-x}$

9.6 CYCLIC PROCESS :



9.7 CHANGE IN PHYSICAL STATE :

Solid \rightleftharpoons liquid

Liquid \rightleftharpoons Gas

Solid \rightleftharpoons Gas

Changes in physical state occurs at constant pressure and temperature conditions.

$$\Delta U = q + w$$

$$q = \Delta H = m.L$$

$$\text{and } w = -P(V_{\text{final state}} - V_{\text{initial state}})$$

Ex.6. 90 gm water is completely converted into steam at 100°C and 1 atm. Calculate q, ΔU, w and ΔH. Latent heat of vaporisation of water at 100°C is 540 cal/gm.

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

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

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

EXERCISE-3

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

Ans. $w = -3.99 \text{ kJ}$

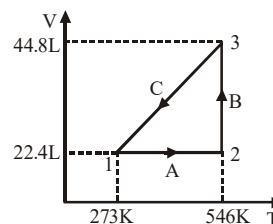
22. Five moles of an ideal gas at 300 K, expanded isothermally from an initial pressure of 4 atm to a final pressure of 1 atm against a constant external pressure of 1 atm. Calculate q, w, ΔU & ΔH. Calculate the corresponding value of all if the above process is carried out reversibly. ($\ln 2 = 0.7$)

Ans. $w_{\text{irr}} = -1125 \text{ R}$, $w_{\text{rev}} = -2100 \text{ R}$, $\Delta U = \Delta H = 0$, $q = -w$

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

Table-1			
State	P	V	T
1			
2			
3			

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



Ans.

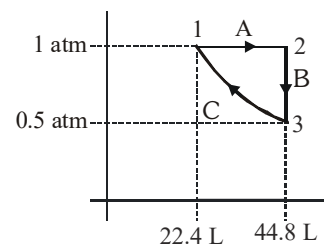
Table-1			
State	P	V	T
1	1 atm	22.4	273
2	2 atm	22.4	546
3	1 atm	44.8	546

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

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

Table-1			
State	P	V	T
1			
2			
3			

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



Ans.

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

Step	Name of process	q	w	ΔE	ΔH
A	Isobaric	$5/2 R (273)$	$-R (273)$	$3/2 R (273)$	$5/2 R (273)$
B	Isochoric	$-3/2 R (273)$	0	$-3/2 R (273)$	$-5/2 R (273)$
C	Isothermal	$-273 R \ln 2$	$273 R \ln 2$	0	0
	Cyclic	$R (273) - 273 R \ln 2$	$-R (273) + 273 R \ln 2$	0	0

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

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

Ans. -0.25

26. 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]

- (1) $T_f > T_i$ for reversible process but $T_f = T_i$ for irreversible process
- (2) $(T_f)_{\text{rev}} = (T_f)_{\text{irrev}}$
- (3) $T_f = T_i$ for both reversible and irreversible processes
- (4) $(T_f)_{\text{irrev}} > (T_f)_{\text{rev}}$

26. Ans.(4)

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

- (1) $q = -nRT \ln \frac{V_2}{V_1}$ (isothermal reversible expansion of an ideal gas)[JEE-MAINS(online)-2014]
- (2) For a system at constant volume, heat involved merely changes to internal energy.
- (3) $w = -nRT \ln \frac{V_2}{V_1}$ (isothermal reversible expansion of an ideal gas)
- (4) $\Delta U = 0$ (isothermal reversible expansion of a gas)

27. Ans.(1)

10. SUMMARY

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

11. LIMITATION OF FIRST LAW :

It can predict the change in energy as a result of change in state or vice-versa, but can not predict the natural direction of change (whether a change can happen on it's own or not).

MISCELLANEOUS PREVIOUS YEARS QUESTION

1. A sample of argon gas at 1 atm pressure and 27°C expands reversibly and adiabatically from 1.25 dm³ to 2.50 dm³. Calculate the enthalpy change in this process. $C_{v,m}$ for argon is 12.48 JK⁻¹ mol⁻¹

[JEE 2000]

Ans. $\Delta H \approx -115$ J

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

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

$$T_2 = 300 (1/2)^{8.3/12.48} \left[\gamma^{-1} \frac{R}{C_{\gamma,m}} \right]$$

$$T_2 = 189.2 \text{ Kelvin.}$$

$$n = \frac{P_1 V_1}{RT_1} = \frac{(1)(1.25)}{(0.0821)(300)} = 0.507$$

$$\begin{aligned} \Delta H &= n C_{p,m} (T_2 - T_1) \\ &= 0.507 (20.78) (189.2 - 300) \\ &= -116.732 \text{ Joule.} \end{aligned}$$

2. Which of the following statement is false ?

[JEE 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

Ans. (A)

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 (ΔU) = 30.0 L-atm. The change in enthalpy (ΔH) of the process in L-atm.

[JEE 2002]

- (A) 40.0
- (B) 42.3
- (C) 44.0
- (D) Not defined, because pressure is not constant

Ans. (C)

$$\Delta H = \Delta U + P_2 V_2 - P_1 V_1$$

$$\Delta H = 30 + 20 - 6$$

$$= 44$$

4. 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 ΔU and ΔH .

[JEE 2004]

Ans. $\Delta U = 10 \text{ J}$, $\Delta H = 990 \text{ J}$

$$0 + w = \Delta U$$

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

$$= -100 \left(\frac{-1}{1000} \right)$$

$$= 0.1 \text{ bar litre.}$$

$$\Delta H = \Delta U + P_2 V_2 - P_1 V_1$$

$$\Delta H = 0.1 + \left[\frac{100(99) - (1)(100)}{1000} \right]$$

$$\Delta H = 0.1 + 9.8$$

$$\Delta H = 9.9 \text{ bar. litre}$$

$$\Delta H = 990 \text{ Joules}$$

5. 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 2004]
- (A) 11.4 kJ (B) - 11.4 kJ (C) 0 kJ (D) 4.8 kJ

Ans. (C)

In isothermal process $\Delta T = 0$

$$\Delta H = nC_{v,m} \Delta T$$

$$\Delta H = 0$$

6. 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. [JEE 2005]
- (R = 0.0821 litre. atm K⁻¹ mol⁻¹)

(A) T (B) $\frac{T}{(2)^{\frac{5}{3}-1}}$ (C) $T - \frac{2}{3 \times 0.0821}$ (D) $T + \frac{2}{3 \times 0.0821}$

Ans. (C)

$$-P_{\text{ext}} (V_2 - V_1) = nC_{v,m} (T_2 - T_1)$$

$$-1(2 - 1) = 1 \left(\frac{3}{2} R \right) (T_2 - T)$$

$$T_2 = T - \frac{2}{3R}$$

7. The molar heat capacity of a monoatomic gas for which the ratio of pressure and volume is one.

- (A) $\frac{4}{2}R$ (B) $\frac{3}{2}R$ (C) $\frac{5}{2}R$ (D) zero [JEE 2006]

Ans. (A)

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

$$PV^{-1} = C$$

$$C_m = C_{v.m.} + \frac{R}{1 - (-1)}$$

$$= \frac{3}{2}R + \frac{R}{2} = \frac{4R}{2}$$

8. Among the following, the state function(s) is (are) [JEE 2009]

- (A) Internal energy (B) Irreversible expansion work
(C) Reversible expansion work (D) Molar enthalpy

Ans. (A,D)

EXERCISE # (S-I)

BASIC

1. Find the work done in each case :

- (a) When one mole of ideal gas in 10 litre container at 1 atm is allowed to enter an very large evacuated bulb of capacity 100 litre.

TE0001

- (b) When 1 mole of gas expands from 1 litre to 5 litre against constant one atmospheric pressure.

TE0002

2. Find the work done in atm-litre when 18 mL of water is getting vapourised at 373 K against 1atm pressure.

(Assume the ideal behaviour of water vapour).

TE0003

3. Find total degree of freedom and break up as translational, rotational or vibrational degree of freedom in following cases.

- (i) CO_2 (ii) SO_2 (iii) He (iv) NH_3

TE0004

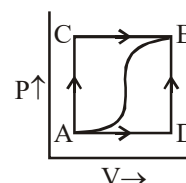
□ **Problems related to First law of thermodynamics :**

4. The gas is cooled such that it loses 65 J of heat. The gas contracts as it cools and work done on the system is equal to 20 J. What are q, w and ΔU ?

TE0005

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

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



TE0006

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

TE0007

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

TE0008

6. An ideal gas undergoes expansion from A(10 atm, 1 litre) to B(1 atm, 10 litre), first against 5 atm and then against 1 atm, isothermally. Calculate the amount of heat absorbed (in litre. atm)

TE0009

7. 2 moles of an ideal gas is compressed from (1 bar, 2L) to 2 bar isothermally. Calculate magnitude of minimum possible work involved in the change (in Joules). (Given : 1 bar L = 100 J) ($\ln 2 = 0.7$)

TE0010

8. 2 mole of an ideal gas undergoes isothermal compression along three different paths if its initial state is (2 bar, 4 litre) in all three process.

- Reversible compression from till 20 bar.
- A single stage compression against a constant external pressure of 20 bar
- 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 : $R = 0.08 \text{ bar. L/mole.K}$]

TE0011

9. A monoatomic ideal gas undergoing irreversible adiabatic compression from 4L to 1L against 1 bar pressure. Calculate the enthalpy change of gas. (Given: 1 bar-L = 100 J)

TE0012

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

TE0013

11. 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.

TE0014

12. 1 mole of CO_2 gas at 300 K is expanded under reversible adiabatic condition such that its volume becomes 27 times.

- What is the final temperature ?
- What is work done ?

Given $\gamma = 1.33$ and $C_V = 25.08 \text{ Jmol}^{-1}\text{K}^{-1}$ for CO_2 .

TE0015

13. Molar heat capacity of an ideal gas at constant volume is given by $C_V = (16.5 + 10^{-2}T) \frac{\text{J}}{\text{K-mol}}$.

If 2 moles of this ideal gas are heated at constant volume from 300K to 400K. Then the change in internal energy (in kJ) will be approximately.

TE0016

14. Three moles of an ideal gas at 200 K and 2.0 atm pressure undergoes 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 , ΔU , ΔH and final V and final P .

Given $\left(\frac{5}{4}\right)^{1/0.3} = 2.1$, $\left(\frac{5}{4}\right)^{35.8/8.3} = 2.61$

[$R = 8.3 \text{ Joule/mol.K}$ or $R = 0.0821 \text{ atm litre/mol.K}$]

TE0017

❑ **Problem related to cyclic process**

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

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

(AB) Isobaric expansion to return the gas to the original volume of 10 litres with

T going from T_1 to T_2 . (BC) Cooling at constant volume to bring the gas to the original pressure and temperature. The steps are shown schematically in the figure shown.

(a) Calculate T_1 and T_2

TE0018

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

[Given : $\ln 10 = 2.3$, $R = 0.0821 \text{ atm.litre/mol.K}$ or $R = 2 \text{ cal/mol.K}$]

TE0019

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

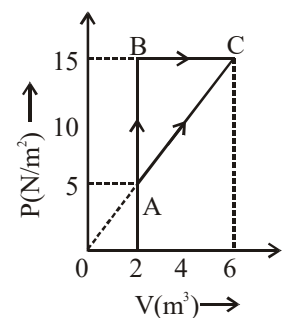
(a) Path along which magnitude of work done is least ABC or AC

TE0020

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

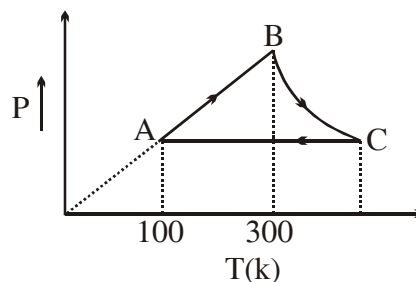
TE0021

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



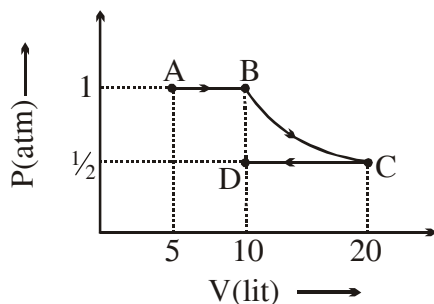
TE0022

17. Calculate the net work done in the following cycle for one mol of an ideal gas (in calorie), where in process BC, $PT = \text{constant}$. ($R = 2 \text{ cal/mol.K}$).



TE0023

18.



Calculate magnitude of total work done (in atm.lit) for the above process ABCD involving a monoatomic ideal gas.

[Given: $\ln 2 = 0.7$]

TE0024

❑ **Problem based on polytropic process**

19. 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 (a) heat capacity (b) total heat absorbed (c) work (d) change in internal energy.

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

TE0025

20. One mole of an ideal monoatomic gas undergoes expansion along a straight line on P-V curve from initial state A(3L, 8 atm) to final state B(7.5 L, 2 atm). Calculate q for the above process in L atm.

TE0026

❑ **Problems based on change in physical state :**

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

TE0027

22. What is ΔU when 2.0 mole of liquid water vaporises at 100°C ? The heat of vaporisation, ΔH_{vapour} of water at 100°C is $40.66 \text{ kJ mol}^{-1}$.

TE0028

23. When 1 mole of ice melt 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 litre respectively. Calculate ΔH and ΔU for the reaction.

TE0029

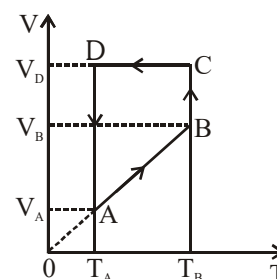
EXERCISE # (S-II)

1. A monoatomic ideal gas of two moles is taken through a reversible

cyclic process starting from A as shown in figure. The volume ratios

are $\frac{V_B}{V_A} = 2$ and $\frac{V_D}{V_A} = 4$. If the temperature T_A at A is 27°C , calculate:

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

**TE0030**

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

TE0031

- (c) The total work done by the gas during complete cycle. ($\ln 2 = 0.7$)

TE0032

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

- It is heated at constant volume from 298 K to 373 K
- It is expanded freely into a vacuum to double volume at 373 K.
- It is cooled reversibly at constant pressure to 298K.

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

TE0033

3. Derive a mathematical expression for the work done when n -mole 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 T .

TE0034

4. 3 dm^3 of an ideal monoatomic gas at 600 K and 32 bar expands until pressure of the gas is 1bar Calculate q , w , ΔU and ΔH for the process if the expansion is :

(Use : $R = 0.08 \text{ bar litre/mol-K} = 2 \text{ cal / mol-K}$)

- (i) Isothermal and reversible

TE0035

- (ii) Adiabatic and reversible

TE0036

- (iii) Isothermal and adiabatic

TE0037

- (iv) Against 1 bar and adiabatic

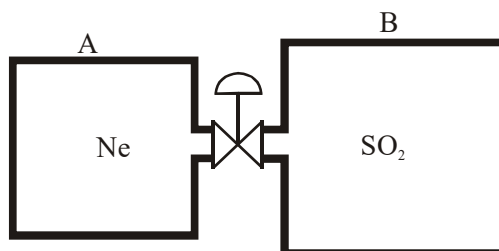
TE0038

- (v) Against 1 bar and isothermal.

TE0039

5. Pressure over 1000 mL of a liquid is gradually increased from 1 bar to 1001 bar under adiabatic conditions. If the final volume of the liquid is 990 mL, calculate ΔU and ΔH of the process, assuming linear variation of volume with pressure.
TE0040
6. At 500 kilobar 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' :
TE0041
7. 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 TK. The gas is then subjected to reversible isothermal expansion at TK 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 $\ln 2 = 0.7$, $R = 2$ cal/K-mol]
TE0042
8. One mole of an ideal gas at 300 K is heated at constant volume (V_1) until its 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.]
TE0043
9. How many times volume of diatomic gas should be expanded reversibly & adiabatically in order to reduce its r.m.s velocity to half.
TE0044
10. 0.5 mole each of two ideal gases A ($C_v = \frac{3}{2}R$) and B ($C_v = \frac{5}{2}R$) are taken in a container and expanded reversibly and adiabatically from $V = 1$ L to $V = 4$ L starting from initial temperature $T = 300$ K. Find $|\Delta H|$ for the process in (cal/mol).
TE0045
11. 0.50 mol of an ideal gas initially at a temperature of 300 K and at a pressure of 2 atm is expanded isothermally in three steps. In each step, the pressure is dropped suddenly and held constant until equilibrium is re-established. The pressure at each of the three stages of expansion are 1.6, 1.2 and 1 atm. Calculate the work done ($|W|$) (in atm -litre) in this process.
[Use $R = 0.08$ atm litre/ mole. K]
TE0046

12. Two rigid adiabatic vessels A and B which initially, contains two gases at different temperatures are connected by pipe line with valve of negligible volume. The vessel 'A' contains 2 moles Ne gas $\left(C_{p,m} = \frac{5}{2}R\right)$ at 300 K, vessel 'B' contains 3 moles of SO_2 gas ($C_{p,m} = 4R$) at 400 K. The volume of A & B vessel is 4 and 6 litre respectively. The final total pressure (in atm) when valve is opened and 12 Kcal heat supplied through it to vessels.
[Use : $R = 2 \text{ cal/mol. K}$ and $R = 0.08 \text{ L. atm / mol K}$ as per desire]



TE0047

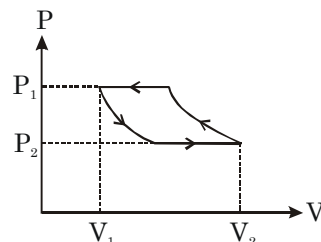
13. One mole of an ideal monoatomic gas initially at 1200 K and 64 atm is expanded to a final state at 300 K and 1.00 atm. To achieve change, a reversible path is constructed that involve an adiabatic expansion in the beginning followed by an isothermal expansion to the final state. Determine the magnitude of net work done by the gas, in cal. ($R = 2 \text{ cal/K-mol}$. $\ln 2 = 0.7$)

TE0048

14. An ideal gas is carried through a thermodynamic cycle.

$$P_1 = 2 \text{ bar} \quad V_1 = \frac{1}{\ln 10} \text{ litre}$$

$$P_2 = 1 \text{ bar} \quad V_2 = \frac{8}{\ln 10} \text{ litre}$$



Consisting of two isobaric and two isothermal processes. Calculate the net work in the entire cycle in litre bar. ($\log_{10}^2 = 0.3$)

TE0049

EXERCISE # (O-I)

BASIC

1. Out of boiling point (I), entropy (II), pH (III) and density (IV), intensive properties are
 (A) I, II (B) I, II, III (C) I, III, IV (D) All of these
TE0050
2. 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
TE0051
3. One mole of an ideal monoatomic gas expanded irreversibly in two stage expansion.
 State-1 (8.0 bar, 4.0 litre, 300 K)
 State-2 (2.0 bar, 16litre, 300 K)
 State-3 (1.0 bar, 32 litre, 300 K)
 Total heat absorbed by the gas in the process is :
 (A) 116J (B) 40 J (C) 4000 J (D) None of these
TE0052
4. An ideal gas undergoes isothermal expansion from A(10 atm, 1l) to B(1 atm, 10 l) either by
 (I) Infinite stage expansion or by
 (II) First against 5 atm and then against 1 atm isothermally
 Calculate $\frac{q_I}{q_{II}}$
 (A) $\frac{1}{13 \times 2.303}$ (B) 13×2.303 (C) $\frac{13}{23.03}$ (D) $\frac{23.03}{13}$
TE0053
5. 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
TE0054
6. For an adiabatic process, which of the following relation must be correct -
 (A) $\Delta U = 0$ (B) $P \Delta V = 0$ (C) $q = 0$ (D) $q = + W$
TE0055

7. A system containing ideal gas is expanded under adiabatic process

- (A) Temperature increases (B) Internal energy decreases
(C) Internal energy increases (D) None of these

TE0056

8. A gas $\left(C_{v,m} = \frac{5}{2}R\right)$ behaving ideally was allowed to expand reversibly and adiabatically from 1 litre to 32 litre. Its 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) None of these

TE0057

9. 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

TE0058

10. A gas is expanded from volume V_1 to V_2 through three different process :

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

The correct statements is -

- (A) $(T_f)_{\text{Reversible Isothermal}} > (T_f)_{\text{Reversible adiabatic}} > (T_f)_{\text{Irreversible adiabatic}}$
(B) $(T_f)_{\text{Reversible Isothermal}} > (T_f)_{\text{Irreversible adiabatic}} > (T_f)_{\text{Reversible adiabatic}}$
(C) $W_{\text{Reversible Isothermal}} > W_{\text{Irreversible adiabatic}} > W_{\text{reversible adiabatic}}$
(D) $(P_f)_{\text{Reversible Isothermal}} > (P_f)_{\text{Reversible adiabatic}} > (P_f)_{\text{Irreversible adiabatic}}$

TE0059

11. What is the magnitude of work performed by one mole of an ideal gas when its volume increases eight times in irreversible adiabatic expansion if the initial temperature of the gas is 300 K ? C_v for the gas is $1.5 R$. ($R = 2 \text{ Cal / mol / K}$)

- (A) 900 Cal (B) 450 Cal (C) 675 Cal (D) 331.58 Cal

TE0060

12. For a process which follows the equation $PV^3 = C$, the work done when one mole of ideal gas was taken from 1 atm to $2\sqrt{2}$ atm starting from initial temperature of 300 K is

- (A) 300 R (B) 150 R (C) 600 R (D) 900 R

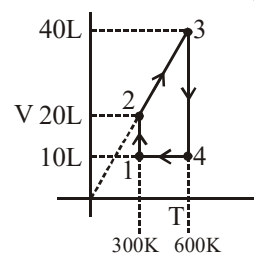
TE0061

13. What is the net work done (w) when 1 mole of monoatomic ideal gas undergoes in a process described by 1, 2, 3, 4 in given V-T graph

Use : $R = 2 \text{ cal/mole K}$

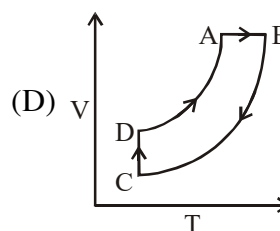
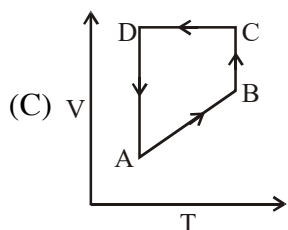
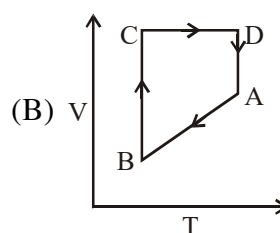
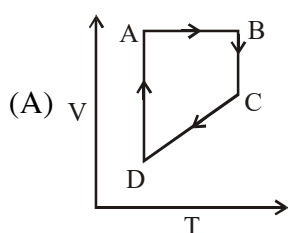
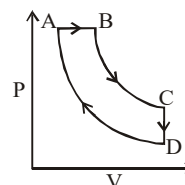
$\ln 2 = 0.7$

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



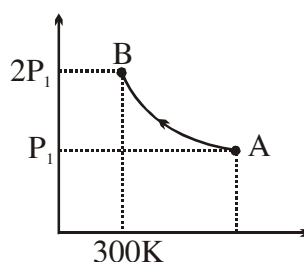
TE0062

14. A cyclic process ABCD is shown in PV diagram for an ideal gas. which of the following diagram represents the same process ?



TE0063

15. 2 moles of an ideal monoatomic gas is taken from state A to state B through a process AB in which $PT = \text{constant}$. The process can be represented on a P-T graph as follows:

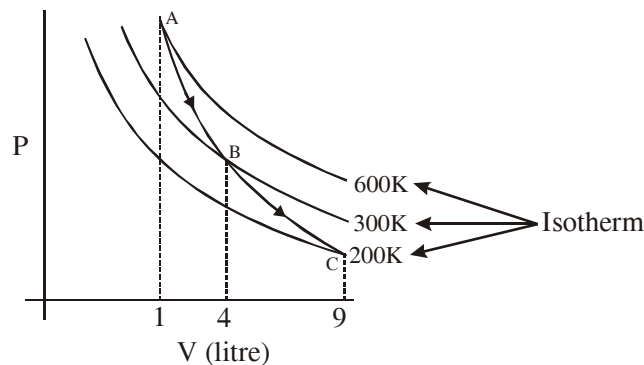


Select the incorrect option(s):

- (A) Heat evolved by the gas during process AB = $2100 R$
(B) Heat absorbed by the gas during process AB = $2100 R$
(C) $\Delta U = -900 R$
(D) $W = 1200R$

TE0064

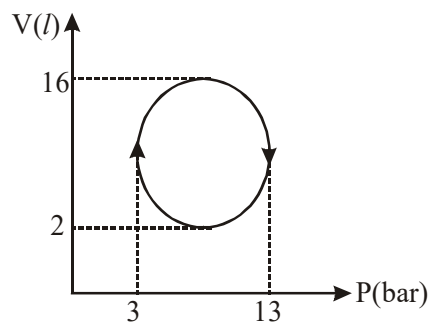
16. The given figure shows a polytropic process ABC for one mole of an ideal gas. Calculate the polytropic index (x) for the process-



- (A) $1/2$ (B) $-1/2$ (C) $3/2$ (D) None

TE0065

17. Work (in kJ) in the following cyclic process is

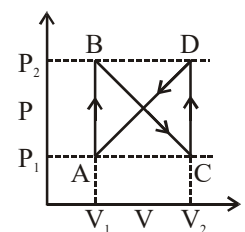


- (A) -11 (B) -11000 (C) 11 (D) 11000

TE0066

18. An ideal gas is taken around the cycle ABCDA as shown in figure. The net work done during the cycle is equal to :-

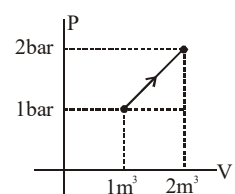
- (A) Zero
(B) Positive
(C) Negative
(D) We cannot predict



TE0067

19. What is ΔU for the process described by figure. Heat supplied during the process $q = 200$ kJ.

- (A) $+50$ kJ (B) -50 kJ
(C) -150 kJ (D) $+150$ kJ



TE0068

20. A diatomic ideal gas initially at 273 K is given 100 cal heat due to which system did 209 J work, Molar heat capacity (C_m) of gas for the process is [1 cal = 4.18 Joule]

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

TE0069

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

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

TE0070

22. An amount Q of heat is added to a monoatomic ideal gas in a process in which the gas performs a work $Q/2$ on its surrounding. The molar heat capacity of gas (in cal/K-mol) for the process is.

(A) 3R (B) 5R (C) 4R (D) 2R

TE0071

EXERCISE # (O-II)

❑ ONE OR MORE THAN ONE MAY BE CORRECT :

1. 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) $\frac{T_1 T_2 (P_1 V_1 + P_2 V_2)}{P_1 V_1 T_1 + P_2 V_2 T_2}$

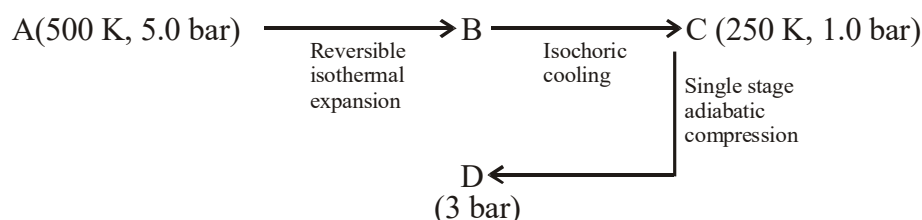
TE0072

2. The heat capacity of liquid water is 75.6 J/mol.K, while the enthalpy of fusion of ice is 6.0 kJ/mol. What is the smallest number of ice cubes at 0°C, each containing 9.0 g of water, needed to cool 500 g of liquid water from 20°C to 0°C ?

(A) 1 (B) 7 (C) 14 (D) 252

TE0073

3. 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) $\Delta U_{BC} = 375 R$

TE0074

4. A real gas is subjected to an adiabatic process from (2 bar, 40 lit., 300 K) to (4 bar, 30 lit., 300 K) against a constant pressure 4 bar the enthalpy change for the process is

(A) Zero (B) 6000 J (C) 8000 J (D) 80 J

TE0075

5. Which of the following statement is/are correct ?

- (A) Enthalpy can be written as $H = f(V, T)$ for a substance (no physical or chemical change)
(B) Absolute value of enthalpy can not be determined
(C) The heat absorbed during the isothermal expansion of an ideal gas against vacuum is zero
(D) During compression of an ideal gas at constant pressure the temperature of gas decreases.

TE0076

6. Choose the correct statement(s)
- (A) During adiabatic expansion of an ideal gas, magnitude of work obtained is equal to ΔH of gas.
 (B) For same change in temperature of ideal gas through adiabatic process, magnitude of W will be same in reversible as well as irreversible process
 (C) During an adiabatic reversible expansion of an ideal gas, temperature of the system increases.
 (D) For same change in volume of ideal gas, ΔU is less in adiabatic expansion than in isobaric expansion if expansion starts with same initial state.

TE0077

7. Choose the correct statement(s) among the following -
- (A) Internal energy of H_2O remains constant during conversion of liquid into its vapour at constant temperature.
 (B) During fusion of ice into water, enthalpy change and internal energy change are almost same at constant temperature
 (C) Molar heat capacity of gases are temperature dependent
 (D) During boiling of H_2O at 1 atm, $100^\circ C$, average kinetic energy of H_2O molecules increases.

TE0078

8. 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) $E_4 > E_3$

TE0079

❑ **Assertion / reason :**

9. **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 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.

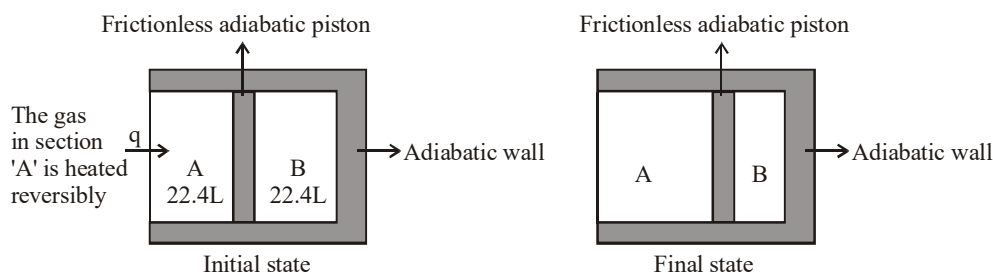
TE0080

10. **Statement-1 :** Due to adiabatic expansion, the temperature of an ideal gas always decreases.
Statement-2 : For an adiabatic process, $\Delta U = w$.
- (A) Statement-1 is true, statement-2 is true and statement-2 is 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.

TE0081

Paragraph for Q.11 to Q.13

A cylindrical container of volume 44.8 litres 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°C ideal gas occupy 22.4 litre.

11. What will be the final pressure in container B.

(A) 2 atm (B) 8 atm (C) 16 atm (D) 32 atm

TE0082

12. Final temperature in container A will be

(A) 1638 K (B) 6988 K (C) 3274 K (D) 51 K

TE0083

13. Change in enthalpy for section A in Kcal

(A) 48.3 (B) 80.53 (C) 4.83 (D) 8.05

TE0084

Paragraph for Q.14 to 16

As a result of the isobaric heating by $\Delta T = 72\text{K}$, one mole of a certain ideal gas obtains an amount of heat $Q = 1.60 \text{ kJ}$.

14. The work performed by the gas is -

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

TE0085

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

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

TE0086

16. The value of γ for the gas is -

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

TE0087

MATCH THE COLUMN :

17. Match Column-I with Column-II

Column-I (Ideal Gas)

- (A) Reversible isothermal process
 (B) Reversible adiabatic process
 (C) Irreversible adiabatic process
 (D) Irreversible isothermal process

Column-II (Related equations)

- (P) $W = 2.303 n RT \log(P_2/P_1)$
 (Q) $W = nC_{V,m} (T_2 - T_1)$
 (R) $W = -2.303nRT \log(V_2/V_1)$
 (S) $W = -\int_{V_i}^{V_f} P_{\text{ext.}} dV$

TE0088

18. Match the column

Column-I

- (A) Isothermal vaporisation of water at 100°C & 1 atm
 (B) Isothermal reversible expansion of an ideal gas
 (C) Adiabatic free expansion of ideal gas
 (D) Isochoric heating of an ideal gas

Column-II

- (P) $\Delta T = 0$
 (Q) $\Delta U = 0$
 (R) $\Delta H = 0$
 (S) $q = 0$
 (T) $w = 0$

TE0089

MATCH THE LIST :

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

Column-I

- (P) Isothermal process (reversible)
 (Q) Adiabatic process (reversible)
 (R) Isochoric process
 (S) Isothermal process (irreversible)

Column-II

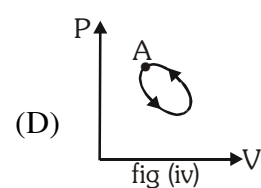
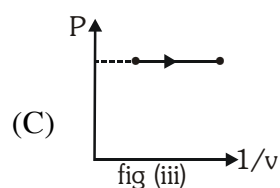
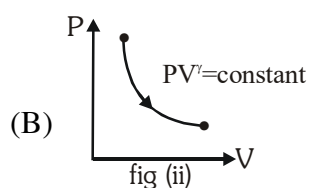
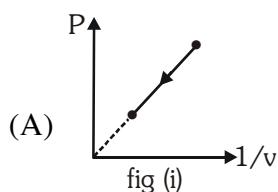
- (1) $q = 2.303 nRT \log \frac{P_1}{P_2}$
 (2) $PV^\gamma = \text{const.}$
 (3) $q = P_{\text{ext.}} (V_2 - V_1)$
 (4) Area under P-V curve is zero

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 |

TE0090

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



Column-I

- (P) In Fig (i)
(Q) In Fig (ii)
(R) In Fig (iii)
(S) In Fig (iv)

Column-II

- (1) Net heat is absorbed by the system
(2) Net work is done on the system
(3) Net heat is rejected by the system
(4) Net work is done by the system
(5) Net internal energy change is zero

Code:

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

TE0091

EXERCISE # (J-MAIN)

1. A piston filled with 0.04 mol of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37.0°C. As it does so, it absorbs 208 J of heat. The values of q and w for the process will be :- [JEE-MAIN-2013]

$$(R = 8.314 \text{ J/mol K}) (\ln 7.5 = 2.01)$$

- (1) $q = + 208 \text{ J}$, $w = - 208 \text{ J}$
 (2) $q = - 208 \text{ J}$, $w = - 208 \text{ J}$
 (3) $q = - 208 \text{ J}$, $w = + 208 \text{ J}$
 (4) $q = + 208 \text{ J}$, $w = + 208 \text{ J}$

TE0092

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

- (1) $q = -nRT \ln \frac{V_2}{V_1}$ (isothermal reversible expansion of an ideal gas) [JEE-MAINS(online)-2014]
 (2) For a system at constant volume, heat involved merely changes to internal energy.
 (3) $w = -nRT \ln \frac{V_2}{V_1}$ (isothermal reversible expansion of an ideal gas)
 (4) $\Delta U = 0$ (isothermal reversible expansion of a gas)

TE0093

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

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

TE0094

4. The enthalpy change on freezing of 1 mol of water at 5°C to ice at -5°C is :

$$(\text{Given } \Delta_{\text{fus}}H = 6 \text{ kJ mol}^{-1} \text{ at } 0^\circ\text{C}, C_p(\text{H}_2\text{O}, l) = 75.3 \text{ J mol}^{-1} \text{ K}^{-1}, C_p(\text{H}_2\text{O}, s) = 36.8 \text{ J mol}^{-1} \text{ K}^{-1})$$

[JEE-MAINS(online)-2017]

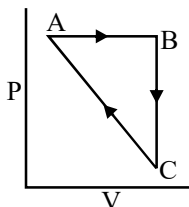
- (1) $-6.56 \text{ kJ mol}^{-1}$ (2) $-5.81 \text{ kJ mol}^{-1}$ (3) $-6.00 \text{ kJ mol}^{-1}$ (4) $-5.44 \text{ kJ mol}^{-1}$

TE0095

5. ΔU is equal to [JEE-MAINS(online)-2017]
 (1) Isochoric work (2) Isobaric work (3) Adiabatic work (4) Isothermal work

TE0096

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



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

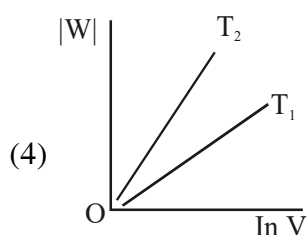
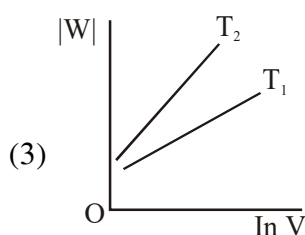
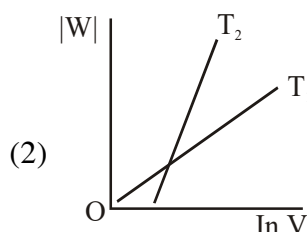
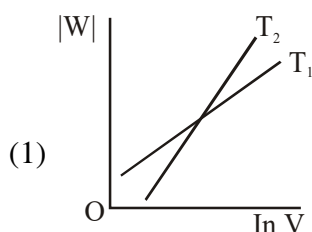
$$W_{AB} = -5 \text{ kJ mol}^{-1}, W_{CA} = 3 \text{ kJ mol}^{-1}$$

Heat absorbed by the system during process CA is :-

- (1) 18 kJ mol^{-1} (2) $+5 \text{ kJ mol}^{-1}$ (3) -5 kJ mol^{-1} (4) -18 kJ mol^{-1}

TE0097

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



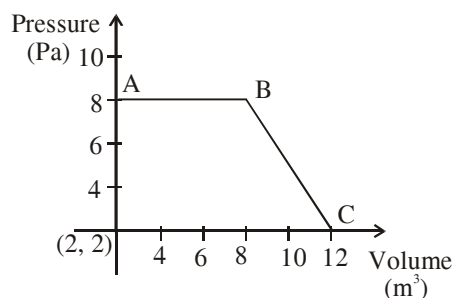
TE0098

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

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

TE0099

9. The magnitude of work done by a gas that undergoes a reversible expansion along the path ABC shown in the figure is _____. [JEE-MAINS(online)-2020]



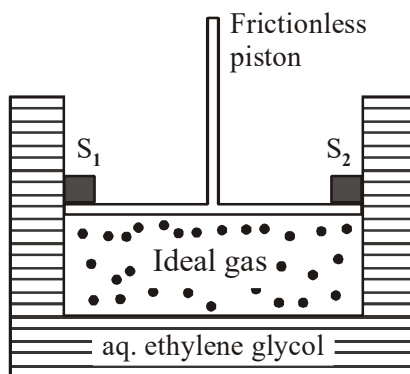
TE0100

10. At constant volume, 4 mol of 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-MAINS(online)-2020]

TE0101

11. A cylinder containing an ideal gas (0.1 mol of 1.0 dm^3) is in thermal equilibrium with a large volume of 0.5 molal aqueous solution of ethylene glycol at its freezing point. If the stoppers S_1 and S_2 (as shown in the figure) are suddenly withdrawn, the volume of the gas in litres after equilibrium is achieved will be _____. (Given, $K_f(\text{water}) = 2.0 \text{ K kg mol}^{-1}$, $R = 0.08 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$)

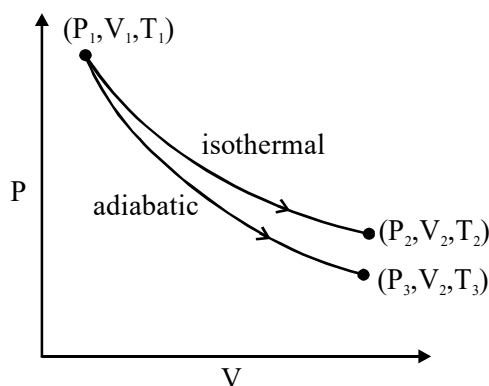
[JEE-MAINS(online)-2020]



TE0102

EXERCISE # (J-ADVANCED)

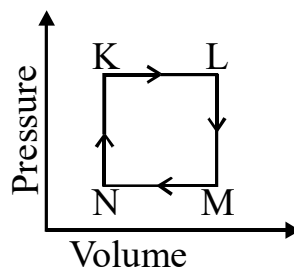
1. The reversible expansion of an ideal gas under adiabatic and isothermal conditions is shown in the figure. Which of the following statement(s) is (are) correct ? [JEE 2012]



- (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 2 and 3

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 2013]

**TE0103**

2. 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

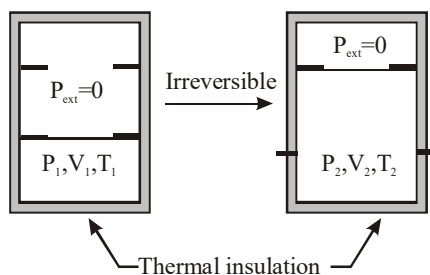
TE0104

3. 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

TE0105

4. 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 2014]



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

TE0106

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

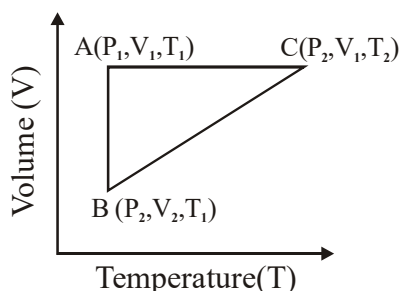
[JEE 2017]

- (A) The work done on the gas is maximum when it is compressed irreversibly from (p_2, V_2) to (p_1, V_1) against constant pressure p_1
 (B) The work done by the gas is less when it is expanded reversibly from V_1 to V_2 under adiabatic conditions as compared to that when expanded reversibly from V_1 to V_2 under isothermal conditions.
 (C) The change in internal energy of the gas (i) zero, if it is expanded reversibly with $T_1 = T_2$, and (ii) positive, if it is expanded reversibly under adiabatic conditions with $T_1 \neq T_2$
 (D) If the expansion is carried out freely, it is simultaneously both isothermal as well as adiabatic

TE0107

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

[JEE 2018]



The correct option(s) is (are)

- (A) $q_{AC} = \Delta U_{BC}$ and $w_{AB} = P_2 (V_2 - V_1)$ (B) $w_{BC} = P_2 (V_2 - V_1)$ and $q_{BC} = \Delta H_{AC}$
 (C) $\Delta H_{CA} < \Delta U_{CA}$ and $q_{AC} = \Delta U_{BC}$ (D) $q_{BC} = \Delta H_{AC}$ and $\Delta H_{CA} > \Delta U_{CA}$

TE0108

ANSWER KEY

EXERCISE # (S-I)

1. Ans. (a) 0 (b) $W = -P\Delta V = -1(5 - 1) = -4$ litre-atm.
2. Ans. -3.1 kJ
3. Ans. (i) 9, 3, 2, 4 (ii) 9, 3, 3, 3 (iii) 3, 3, 0, 0 (iv) 12, 3, 3, 6
4. Ans. $q = -65$ J; $w = 20$ J; $\Delta U = -45$ J
5. Ans. (a) $+60$ J (b) -70 J (c), $+50$ J, $+10$ J
6. Ans. (13)
7. Ans. (140)
8. Ans. (i) 18.42 bar.L; (ii) 72 bar.L; (iii) 40 bar.L
9. Ans. (500 J)
10. Ans. $\Delta U = w = -150$ R, $\Delta H = -210$ R, $q = 0$. Ans. 2244.78 Joule
12. Ans. $T_2 = 100$ K; $w = -5.016$ kJ
13. Ans. (4)
14. Ans. $q = 0$, $w = \Delta U = 4.125$ kJ; $\Delta H = 5.372$ kJ; $V_f = 11.8$ dm³; $P = 5.22$ atm
15. Ans. (a) $T_1 = 243.60$ K; $T_2 = 2436$ K, (b) $\Delta U = 0$; $q = -w = 3264.24$ cal
16. Ans. (a) AC, (b) 170 J, (c) 10 J
17. Ans. $[-800$ cal]
18. Ans. (7)
19. Ans. (a) $\frac{11}{3}$ cal /K-mol. (b) 2566.67 cal (c) -466.67 cal (d) 2100 cal
20. Ans. (9)
21. Ans. -10.13 J
22. Ans. $\Delta E = 75.12$ kJ
23. Ans. $\Delta U \approx \Delta H = 1440$ calories

EXERCISE # (S-II)

1. Ans. (a) 600 K, (b) 3 kcal, 1.680 kcal, -1.8 kcal, -1.680 kcal (c) $w = -1.2$ kcal
2. Ans. ΔU & $\Delta H = 0$; $w = 623.55$ J ; $q = -623.55$ J
3. Ans. $w = -nRT \ln \frac{V_f}{V_i} - n^2 a \left(\frac{1}{V_f} - \frac{1}{V_i} \right)$
4. Ans. (i) $w = -8400$ cal , $q = 8400$ cal , $\Delta U = \Delta H = 0$.
 (ii) $w = -2700$ cal , $q = 0$ cal , $\Delta U = -2700$, $\Delta H = -4500$ cal
 (iii) $w = 0$ cal , $q = 0$ cal , $\Delta U = 0$, $\Delta H = 0$.
 (iv) $w = -1395$ cal $q = 0$, $\Delta U = -1395$ cal , $\Delta H = -2325$ cal
 (v) $w = -2325$ cal $q = 2325$ cal , $\Delta U = 0$, $\Delta H = 0$
5. Ans. $\Delta U = 501$ J; $\Delta H = 99.5$ kJ

6. Ans. 100 KJ/mole
7. Ans. -1200 cal
8. Ans. 60 cal
9. Ans. (32)
10. Ans. (900 calories)
11. Ans. 7.4 atm litre
12. Ans. 35 atm
13. Ans. 3120
14. Ans. (1.8 bar-litre)

EXERCISE # (O-I)

- | | | | |
|-------------|--------------|-------------|-------------|
| 1. Ans.(C) | 2. Ans.(B) | 3. Ans.(C) | 4. Ans.(D) |
| 5. Ans.(C) | 6. Ans.(C) | 7. Ans.(B) | 8. Ans.(C) |
| 9. Ans.(D) | 10. Ans. (B) | 11. Ans.(D) | 12. Ans.(B) |
| 13. Ans.(C) | 14. Ans.(C) | 15. Ans.(B) | 16. Ans.(C) |
| 17. Ans.(C) | 18. Ans.(A) | 19. Ans.(A) | 20. Ans.(D) |
| 21. Ans.(A) | 22. Ans.(A) | | |

EXERCISE # (O-II)

- | | | | |
|---|----------------|-----------------|---------------|
| 1. Ans. (A) | 2. Ans.(C) | 3. Ans. (A,B,C) | 4. Ans. (C) |
| 5. Ans. (A,B,C,D) | 6. Ans. (B, D) | 7. Ans. (B,C) | 8. Ans. (B,D) |
| 9. Ans. (C) | 10. Ans. (D) | 11. Ans. (D) | 12. Ans. (A) |
| 13. Ans. (B) | 14. Ans. (B) | 15. Ans.(A) | 16. Ans. (C) |
| 17. Ans. (A) → (P,R,S) ; (B) → (Q, S) ; (C) → (Q,S) ; (D) → (S) | | | |
| 18. Ans. (A)-P; (B)-P,Q,R ; (C)-P,Q,R,S,T ; D-T | | | |
| 19. Ans. (B) | 20. Ans. (A) | | |

EXERCISE # (J-MAIN)

- | | | | |
|-----------------|-----------------|-------------------------|-------------|
| 1. Ans. (1) | 2. Ans. (1) | 3. Ans. (2) | 4. Ans. (1) |
| 5. Ans. (3) | 6. Ans. (2) | 7. Ans. (2) | 8. Ans. (2) |
| 9. Ans. (48.00) | 10. Ans. (6.25) | 11. Ans. (2.17 to 2.23) | |

EXERCISE # (J-ADVANCED)

- | | | | |
|-----------------|---------------|-------------|----------------|
| 1. Ans. (A,D) | 2. Ans. (B) | 3. Ans. (C) | 4. Ans.(A,B,C) |
| 5. Ans. (A,B,D) | 6. Ans. (B,C) | | |