THERMODYNAMICS-01

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1. INTRODUCTION

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

Thermodynamics	≡	Thermo + dynamics
Dynamics	≡	Study of change due to a driving force
Thermo	≡	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 DEFINITITIONS (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 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 defined value.

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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 propreties are non additive.
- * Ratio of two extensive property gives as intensive property.

Extensive Properties	Intensive Properties
Volume	Molar volume
Number of moles	Density
Mass	Refractive index
Free Energy (G)	Surface tension
Entropy (S)	Viscosity
Enthalpy (H)	Free energy per mole
Internal energy (E & U)	Specific heat
Heat capacity	Pressure
	Temperature
	Boilling 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 :

		В
(i)	If ϕ is state funct	ion, $\int_{A} d\phi = \phi_{B} - \phi_{A}$

- (ii) If ϕ is a state function, $\oint d\phi = 0$
- **2.5** Path function : Function which depend 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. Intenstive 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.
 Extenstive property : Mass, Volume, number of moles, Heat capacity, internal energy, enthalpy, entropy

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2.	Which of the following	gare state function & pa	th function ?				
	Pressure, Volume, Enthalpy, Work, Heat, Gibbs energy, temperature, Internal energy, Entropy						
Sol.	State function : Pressu	ure, volume , enthalpy,	Gibbs energy, temperature	e, Internal energy, Entropy			
	Path function : Work	, Heat					
3.	A state function is that :						
	(A) which is used in the	rmochemistry					
	(B) which obeys all law	s of thermodynamics					
	(C) quantity whose value	ue depends only upon th	e state of the system				
	(D) quantity which is us	ed in measuring thermal	change				
Ans.	(C)						
4.	Which amongst the foll	owing is an extensive pr	operty of the system -				
	(A) Temperature	(B) Volume	(C) Viscosity	(D) Refractive index			
Ans.	(B)						
5.	Which of the following	g is not a state function	of thermodynamic system	n -			
	(A) Internal energy(E)		(B) Free energy(G)				
	(C) Enthalpy(H)		(D) Work(W)				
Ans.	(D)						
6.	What is true for a cycl	lic process					
	(A) $W = 0$	$(B) \Delta E = 0$	$(\mathbf{C}) \Delta \mathbf{H} = 0$	(D) B & C both			
Ans.	(D)						
7.	The internal energy cha A to B by a reversible p in internal energy ?	inge when a system goe path and returns to state	s from state A to B is 40 kJ A by an irreversible path	/mole. If the system goes from what would be the net change [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.)

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(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.

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

However \boldsymbol{Q}_{net} or \boldsymbol{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.

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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.

$$W = \int_{V_1}^{V_2} P \cdot dV = -\int_{V_1}^{V_2} P_{ext} dV$$

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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 + cT².....)

General	values	of	C _v	&	C _p	for	an	ideal	gas	can	be	taken	as	follows.
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Atom	aiaita		nn		C	ν V		C _P	,	γ
Aton	lifetty	11 _{tr}	"Rot	Π _{Vib}		Incl. Vib	Excl. Vib	Incl. Vib	Excl. Vib	Incl. Vib
Mo	ono	3	0	0	$\frac{3}{2}R$	$\frac{3}{2}R$	$\frac{5}{2}R$	$\frac{5}{2}R$	$\frac{5}{3}$	$\frac{5}{3}$
Γ	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.

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

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.

 $\mathbf{H} = \mathbf{U} + \mathbf{P}\mathbf{V}$

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

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 $\Delta H \& \Delta U$:

The difference between $\Delta H \& \Delta U$ 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

 $\Delta H = \Delta U + (\Delta n_{o})RT$

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 $U_2 - U_1 = q + w$

 $\Delta \mathbf{U} = \mathbf{q} + \mathbf{w}$

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 # II

- 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)	$H_2O(g)$	\longrightarrow	$H_2O(\ell)$
(ii)	$H_2O(s)$	\longrightarrow	$H_2O(g)$
(iii)	$H_2O(\ell)$	\longrightarrow	$H_2O(s)$
(iv)	CaCO ₃ (s)	\longrightarrow	$CaO(s) + CO_2(g)$
(i) +	+ , (ii) –, (iii) –	, (iv) –	

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Ans.

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- 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

 $H_{ideal gas} = f(T)$, 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
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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) $(U_1 + 150 J)$ (B) $(U_1 + 1050 J)$ (C) $(U_1 - 150 J)$ (D) $(U_1 - 1050 J)$

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 dm³ to 6 dm³ against a constant external pressure of 3 atm is -
 - (A) -608 J (B) +304 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 K = 41 kJ mol⁻¹ and R = 8.3 J mol⁻¹ 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)

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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 :-

(B) q = -208 J, w = -208 J

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

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

- (A) q = +208 J, w = -208 J
- (C) q = -208 J, w = +208 J

Ans. (A)

Sol. q = +208 Joule

for isothermal process

 $\Delta U = 0$

 \therefore from Ist law of thermodynamics

 $\Delta \mathbf{U} = \mathbf{q} + \mathbf{w}$

0 = q + w

 \Rightarrow w = -q = -208 Joule

9. CALCULATION OF q, w, $\Delta U \& \Delta H$ IN VARIOUS PROCESS :

9.1 ISOTHERMAL EXPANSION OR COMPRESSION OF IDEAL GAS :

For isothermal process : $\Delta T = 0$

 $\therefore \quad \Delta U = n.C_{p,m}.\Delta T = 0$ $\Delta H = n.C_{p,m}.\Delta T = 0$ and $q = \Delta U - w = -w$

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

9.1.1 Reversible process :

...

$$w_{rev.} = -\int_{V_1}^{V_2} P_{ext} \cdot dV = -\int_{V_1}^{V_2} (P \pm dP) \cdot dV = -\int_{V_1}^{V_2} P \cdot dV = -\int_{V_1}^{V_2} \frac{nRT}{V} \cdot dV$$
$$w_{rev.} = -nRT \cdot \ln \frac{V_2}{V_1} = -nRT \cdot \ln \frac{P_1}{P_2}$$

9.1.2 Irreversible process, against a constant external pressure :

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

9.1.3 Free expansion (or expansion in vacuum) :

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

9.1.4 Comparison of magnitude of work :

In expansion, magnitude of work = $-w_{exp}$ In compression, magnitude of work = w_{comp} Now, $w_{rev} - w_{irr} = (-P.dV) - (-P_{ext}.dV) = (P_{ext} - P).dV$ = -ve, always In expansion, $P_{ext} < P$ and dV = +ve

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

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

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

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

9.1.5 Graphical comparison :

(a) **Expansion** :











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

(b) Compression :





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- Ex.1 Two moles of an ideal gas undergoes isothermal expansion from 4 L to 20 L at 27°C. Calculate q, w, ΔU and ΔH , if the process is performed.
 - (i) reversibly
 - (ii) irreversibly, against a constant external pressure of 1atm.
 - (iii) as free expansion
- **Sol.** For isothermal process, $\Delta T = 0$. Hence,
 - $\Delta U = n.C_{v,m}.\Delta T = 0$ $\Delta H = n.C_{p,m}.\Delta T = 0$

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

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

(ii)
$$w = -P_{ext} \cdot (V_2 - V_1) = -1 \operatorname{atm}(20L - 4L) = -16L \operatorname{-atm} = -16 \times 101.3J = -1620.8J$$

 $q = -w = 1620.8J$
(iii) $w = 0$ and $q = 0$

9.2 ADIABATIC EXPANSION OR COMPRESSION OF IDEAL GAS :

$$q = 0$$

$$\therefore \quad \Delta \mathbf{U} = \mathbf{w} = \mathbf{n} \cdot \mathbf{C}_{\mathbf{v} \cdot \mathbf{m}} \cdot (\mathbf{T}_2 - \mathbf{T}_1)$$

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

The change in temperature may be calculated as

$$\mathbf{n} \cdot \int_{T_1}^{T_2} \mathbf{C}_{\mathbf{v},\mathbf{m}} \cdot \mathbf{dT} = -\int_{V_1}^{V_2} \mathbf{P}_{\mathrm{ext}} \cdot \mathbf{dV}$$

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

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

(b) If $C_{y,m}$ is temperature independent and the process is irreversible, then

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

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- (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.



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 0.1atm.
- (iii) as free expansion
- **Sol.**: For adiabatic process, q = 0

(i)
$$\mathbf{T} \cdot \mathbf{V}^{\gamma-1} = \text{constant} \implies \mathbf{T}_1 \cdot \mathbf{V}_1^{\gamma-1} = \mathbf{T}_2 \cdot \mathbf{V}_2^{\gamma-1}$$

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

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

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

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

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

- (iii) $\Delta U = w = 0$ 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.:
$$q = 0$$

 $\Delta U = w$
or, $n.C_{v,m}.(T_2 - T_1) = -P_{ext}.(V_2 - V_1)$
or, $n.\frac{3}{2}R(T_2 - T_1) = -P_2\left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1}\right)$
or, $\frac{3}{2}(T_2 - 300) = -\left(T_2 - 300 \times \frac{1}{12}\right) \implies T_2 = 190K$
or, $\Delta U = w = 5 \times \frac{3}{2}R \times (190 - 300) = -6859.05J$
and $\Delta H = \gamma.\Delta U = -11431.75J$

9.3 ISOBARIC PROCESS FOR AN IDEAL GAS : $q = \Delta H = n.C_{v,m}.\Delta T$ $\therefore \Delta U = n.C_{v,m}.\Delta T$

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

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

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

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

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

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

or,

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

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

9.5 POLYTROPIC PROCESS FOR AN IDEAL GAS :

$$\Delta U = n.C_{ym}.\Delta T$$

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

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

 $P.V^{x} = constant$

 $T.V^{x-1} = constant$

where x = polytropic index

$$w_{rev} = \frac{P_2 V_2 - P_1 V_1}{1 - x} = -\frac{nR(T_2 - T_1)}{1 - x} \qquad (x \neq 1)$$
$$= -nRT \cdot ln \frac{V_2}{V_1} \qquad (x = 1)$$

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 SATE :

Solid iquid

Liquid Gas

Solid cas

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

 $\Delta \mathbf{U} = \mathbf{q} + \mathbf{w}$

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

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

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

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

EXERCISE # III

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. (ln5 = 1.6)

Ans. w = -3.99 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, $\Delta U \& \Delta H$. Calculate the corresponding value of all if the above process is carried out reversibly. (ln2 = 0.7)

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

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	Р	V	Т			
1						
2						
3						



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Step	Name of process	q	W	ΔU	ΔH
А					
В					
С					
overall					

	Table -1						
	State	Р	V	Т			
Ans.	1	1 atm	22.4	273			
	2	2 atm	22.4	546			
	3	1 atm	44.8	546			

Name of process	q	W	$\Delta \mathbf{E}$	ΔH
Isochoric	3/2 R (273)	0	3/2 R (273)	5/2 R(273)
Isothermal	546 R ln 2	-546 Rln2	0	0
Isobaric	-5/2 R(273)	R(273)	-3/2 R (273)	-5/2 R(273)
	Name of process Isochoric Isothermal Isobaric	Name of process q Isochoric 3/2 R (273) Isothermal 546 R ln 2 Isobaric -5/2 R(273)	Name of process q w Isochoric 3/2 R (273) 0 Isothermal 546 R ln 2 -546 Rln2 Isobaric -5/2 R(273) R(273)	Name of process q w ΔE Isochoric 3/2 R (273) 0 3/2 R (273) Isothermal 546 R ln 2 -546 Rln2 0 Isobaric -5/2 R(273) R(273) -3/2 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	Р	V	Т		
1					
2					
3					



Step	Name of process	q	W	ΔU	ΔH
А					
В					
С					
	cyclic				

		Table-1							
	State	Р	V	Т					
Ans.	1	1 atm	22.4	273					
	2	1	44.8	546					
	3	0.5	44.8	273					

Step	Name of process	q	W	$\Delta \mathbf{E}$	$\Delta \mathbf{H}$
А	Isobaric	5/2 R (273)	-R(273)	3/2 R (273)	5/2 R(273)
В	Isochoric	– 3/2 R (273)	0	– 3/2 R (273)	- 5/2 R (273)
С	Isothermal	– 273 R ln2	273 R ln2	0	0
	Cyclic	R(273) – 273 Rln2	$-R(273)+273R \ln 2$	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.

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

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) $(T_{f})_{rev} = (T_{f})_{irrev}$

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

 $(4) (T_{f})_{irrev} > (T_{f})_{rev}$

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]
 - $\left(2\right)$ 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)

Ans. (1)

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10. SUMMARY

Process	Expression	Expression	Expression ΔU		Work on
	for w	for q			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	P-(atm)→ P-(at
Irreversible isothermal	$w = -P_{ext} (V_2 - V_1)$ $= -P_{ext} \left(\frac{nRT}{P_2} - \frac{nRT}{P_1} \right)$	$\mathbf{q} = \mathbf{P}_{\text{ext}} \left(\mathbf{V}_2 - \mathbf{V}_1 \right)$	0	0	P-(atm) P-(a
Isobaric process	$w = -P_{ext} (V_2 - V_1)$ $= - nR\Delta T$	$\mathbf{q} = \Delta \mathbf{H} = \mathbf{n} \mathbf{C}_{\mathbf{P}} \Delta \mathbf{T}$	$\Delta \mathbf{U} = \mathbf{n} \mathbf{C}_{\mathbf{V}} \Delta \mathbf{T}$	$\Delta \mathbf{H} = \mathbf{n} \mathbf{C}_{\mathbf{p}} \Delta \mathbf{T}$	P-(atm)→
Isochoric process	$\mathbf{w} = 0$	$\mathbf{q} = \Delta \mathbf{U} = \mathbf{n} \mathbf{C}_{\mathbf{V}} \Delta \mathbf{T}$	$\Delta \mathbf{U} = \mathbf{n} \mathbf{C}_{\mathbf{V}} \Delta \mathbf{T}$	$\Delta \mathbf{H} = \mathbf{n} \mathbf{C}_{\mathbf{P}} \Delta \mathbf{T}$	P. P. V
Reversible	$\mathbf{w} = \mathbf{n}\mathbf{C}_{\mathbf{V}}(\mathbf{T}_2 - \mathbf{T}_1)$	$\mathbf{q} = 0$	$\Delta U = nC_V \Delta T$	$\Delta H = nC_P \Delta T$	
adiabatic process	$=\frac{\mathbf{P}_2\mathbf{V}_2-\mathbf{P}_1\mathbf{V}_1}{\gamma-1}$	PV^{γ} =constant $TV^{\gamma-1}$ =constant $TP^{1-\gamma/\gamma}$ =constant			P ₁ Isotherm Adiabatic V ₁ V ₂
Irreversible	$\mathbf{w} = \mathbf{n}\mathbf{C}_{\mathbf{V}}(\mathbf{T}_2 - \mathbf{T}_1)$	$\mathbf{q} = 0$	$\Delta U = nC_V \Delta T$	$\Delta \mathbf{H} = \mathbf{n}\mathbf{C}_{\mathbf{P}}\Delta\mathbf{T}$	▲P Rev
adiabatic process	$=\frac{\mathbf{P}_2\mathbf{V}_2-\mathbf{P}_1\mathbf{V}_1}{\gamma-1}$	$nC_{v}(T_{2}-T_{1}) =$ $-P_{ext}\left(\frac{nRT_{2}}{P_{2}}-\frac{nRT_{1}}{P_{1}}\right)$			$ \begin{array}{c c} & & & \\ \hline \\$
Polytropic	$w = \frac{P_2 V_2 - P_1 V_1}{n - 1}$ $w = \frac{R(T_2 - T_1)}{(n - 1)}$	$q = \int_{T_1}^{T_2} C_V dT$ $w = \frac{R(T_2 - T_1)}{(n-1)}$	$\Delta \mathbf{U} = \mathbf{n} \mathbf{C}_{\mathbf{V}} \Delta \mathbf{T}$	$\Delta \mathbf{H} = \mathbf{n} \mathbf{C}_{\mathbf{P}} \Delta \mathbf{T}$	$ \begin{array}{c} $
Cyclic Process	Area encolsed in PV-diagram For clockwise –ive For anticlockwise +ive	$\mathbf{q} = -\mathbf{w}$	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 12.48JK⁻¹ mol⁻¹. [JEE 2000]

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

$$\mathbf{T}_{1}\mathbf{V}_{1}^{\gamma-1} - \mathbf{T}_{2}\mathbf{V}_{2}^{\gamma-1}$$
$$\mathbf{T}_{2} = \mathbf{T}_{1}\left(\frac{\mathbf{V}_{1}}{\mathbf{V}_{2}}\right)^{\gamma-1}$$

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

$$T_{2} = 189.2 \text{ Kelvin.}$$

$$n = \frac{P_{1}V_{1}}{RT_{1}} = \frac{(1)(1.25)}{(0.0821)(300)} = 0.507$$

$$\Delta H = nC_{p.m} \ (T_{2} - T_{1})$$

$$= 0.0507 \ (20.78) \ (189.2 - 300)$$

= -116.732 Joule.

- 2. Which of the following statement is false ?
 - (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]

(B) 42.3

(D) Not defined, because pressure is not constant

- (A) 40.0
- (C) 44.0
- Ans. (C)

$$\Delta \mathbf{H} = \Delta \mathbf{U} + \mathbf{P}_2 \mathbf{Y}_2 - \mathbf{P}_1 \mathbf{Y}_1$$
$$\Delta \mathbf{H} = 30 + 20 - 6$$
$$= 44$$

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 .

$$0 + w = \Delta U$$

$$\Delta U = -P_{ext} (Y_2 - V_1)$$

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

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

$$\Delta H = \Delta U + P_2 Y_2 - P_1 Y_1$$

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

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[JEE 2001]

[JEE 2004]

 $\Delta H = 0.1 + \left[\frac{100(99) - (1)(100)}{1000}\right]$ $\Delta H = 0.1 + 9.8$ $\Delta H = 9.9 \text{ bar. litre}$ $\Delta H = 990 \text{ Joules}$

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

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

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

Ans. (C)

$$-P_{ext} (V_2 - V_1) = nC_{v.m.} (T_2 - T_1)$$
$$-1(2 - 1) = 1 \left(\frac{3}{2}R\right) (T_2 - T)$$
$$T_2 = T - \frac{2}{3R}$$

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)

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

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

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

$$= \frac{3}{2}R + \frac{R}{2} = \frac{4R}{2}$$
Among the following, the

(A) Internal energy

Among the following, the state function(s) is (are)

[JEE 2009]

(C) Reversible expansion work

(B) Irreversible expansion work

(D) Molar enthalpy

Ans. (A,D)

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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.
 - (b) When 1 mole of gas expands from 1 litre to 5 litre against constant one atmospheric pressure.
- 2. Find the work done in atm-litre when 18 mL of water is getting vapourised at 373 K in open vessel.

(Assume the ideal behaviour of water vapour).

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



- (c) If $U_D U_A = 40J$, find the heat absorbed in the process AD and DB if work done by system in ADB is 10 Joule.
- 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)
- 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)
- 8. 2 mole of an ideal gas undergoes isothermal compression along three different paths if it's initial state is (2 bar, 4 litre) in all three process.
 - (i) Reversible compression from till 20 bar.
 - (ii) A single stage compression against a constant external pressure of 20 bar
 - (iii) A two stage compression consisting initially of compression against a constant external pressure of 10 bar until $P_{gas}=P_{ext}$, followed by compression against a constant pressure of 20 bar until $P_{gas}=P_{ext}$. Calculate the work (in bar. L) for each of these processes and for which of the irreversible processes is the magnitude of the work greater ? [Given : R = 0.08 bar. L/mole.K]
- **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]
- **10.** Two mole of ideal diatomic gas ($C_{v,m} = 5/2 \text{ R}$) 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, $\Delta H \& \Delta U$.

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- 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.
- 12. 1 mole of 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 Jmol⁻¹K⁻¹ for CO₂.

- 13. Molar heat capacity of an ideal gas at constant volume is given by $C_v = (16.5 + 10^{-2} \text{ T}) \frac{\text{J}}{\text{K} \text{mol}}$. 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.
- 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 JK⁻¹ 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 Joule/mol.K r R = 0.0821 atm litre/mol.K]

D 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

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

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

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





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



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

D Problem based on polytropic process

19. For 1 mole of ideal monoatomic gas if $\frac{P}{V^2}$ = 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 =
$$0.0821 \frac{L - atm}{mole - k}$$
, 1 L-atm = 24 cal)

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.

D 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.
- 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 kJ mol⁻¹.
- 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 Δ H and Δ U for the reaction.

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.
- (b) Heat absorbed or released by the gas in each process.
- (c) The total work done by the gas during complete cycle. $(\ln 2 = 0.7)$
- 2. One mole of an ideal gas (not necessarily monoatomic) is subjected to the following sequence of steps.
 - (a) It is heated at constant volume from 298 K to 373 K
 - (b) It is expanded freely into a vacuum to double volume at 373 K.
 - (c) It is cooled reversibly at constant pressure to 298K. Calculate q, w, ΔU and ΔH for the overall process.
- 3. 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.
- 4. 3 dm³ 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 bar litre/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.
- 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.
- 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' :

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 In 2 = 0.7, R = 2 cal/K-mol]



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- 8. 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 (lwl) in cal. **[Use : ln2 = 0.70 ; R = 2 Cal/K.mol.]**
- **9.** How many times volume of diatomic gas should be expanded reversibly & adiabatically in order to reduce it's r.m.s velocity to half.

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).

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 (IWI) (in atm-litre) in this process.

[Use R = 0.08 atm litre/ mole. K]

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 SO₂ gas ($C_{p,m} = 4 R$) 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 cal/mol. K and R = 0.08 L. atm / mol K as per desire]



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. ($\mathbf{R} = 2$ cal/K-mol. ln 2 = 0.7)

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

$$P_{1} = 10 \text{ bar} \qquad V_{1} = \frac{1}{\ell n 10} \text{ litre} \qquad P_{1} \qquad P_{1} \qquad P_{2} \qquad P_{2} = 1 \text{ bar} \qquad V_{2} = \frac{4}{\ell n 10} \text{ litre} \qquad V_{1} \qquad V_{2} = V$$

Consisting of two isobaric and two isothermal processes. Calculate the net work in the entire cycle in litre bar.

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		EXERC	ISE # O-I	
		BA	ASIC	
1.	Out of boiling point	t (I), entropy (II), pH (III)	and density (IV), intens	sive properties are
	(A) I, II	(B) I, II, III	(C) I, III, IV	(D) All of these
2.	What is the change in	n internal energy when a ga	as is compressed from 37	77 ml to 177 ml under a constan
	$[Take \cdot (11 \text{ atm})]$	- 100 II	being cooled by remov	ving 124 J near ?
		= 100 J	(C) 164 I	(D) 249 I
2	(A) = 24 J	$(\mathbf{D}) = 64 \mathbf{J}$	(C) = 104 J	(D) = 248 J
э.	State 1	(8.0 hor 4.0 litre 2	OO K)	lage expansion.
	State-1	(8.0 bar, 4.0 litre, 3)	00 K)	
	State-2	(2.0 bar, 16)	0 K)	
	State-3	(1.0 bar, 32 litre, 30)	00 K)	
	Total heat absorbed	by the gas in the process	S 1S :	
	(A) 116J	(B) 40 J	(C) 4000 J	(D) None of these
4.	An ideal gas underg	goes isothermal expansion	from A(10 atm, $1l$) to	B(1 atm, 10 l) either by
	(I) Infinite stage exp	bansion or by	• .1 .11	
	(II) First against 5 a	tm and then against 1 atm	isothermally	
	Calculate $\frac{q_{I}}{q_{II}}$:			
	1	(D) 10 0 000	13	23.03
	(A) $\frac{13 \times 2.303}{13 \times 2.303}$	(B) 13×2.303	(C) $\frac{1}{23.03}$	(D) $-\frac{13}{13}$
5.	One mole of ideal g	as is allowed to expand re	versibly and adiabatical	ly from a temperature of 27°C.
	If the work done by	the gas in the process is	3 kJ, the final tempera	ture will be equal to -
	$(C_v = 20 \text{ J/K mol})$)		
	(A) 100 K	(B) 450 K	(C) 150 K	(D) 400 K
6.	For an adiabatic pro	ocess, which of the follow	ing relation must be con	rrect -
	$(A) \Delta U = 0$	$(B) P\Delta V = 0$	(C) $q = 0$	(D) $q = + W$
7.	A system containing	g ideal gas is expanded un	der adiabatic process	
	(A) Temperature inc	reases	(B) Internal energy	decreases
	(C) Internal energy in	ncreases	(D) None of these	
	(5)			
8.	A gas $\left(C_{v,m} = \frac{3}{2} R \right)$	behaving ideally was al	lowed to expand reven	rsibly and adiabatically from
	1 litre to 32 litre. It's in	iitial temperature was 327° C	C. The molar enthalpy cha	nge (in J/mole) for the process is :-
	(A) –1125 R	(B) - 575 R (C	C) $-1575 R$ (D)	None of these
9.	Two moles of an idea	al gas ($C_v = \frac{5}{2}R$) was comp	pressed adiabatically aga	ainst constant pressure of 2 atm,
	which was initially	at 350 K and 1 atm $nmax$	ure The work involved	in the process is equal to
	(A) 250 R	(B) 300 R	(C) 400 R	(D) 500 R
	(11) 250 K	(D) 500 K	(\mathbf{C}) TOU IX	(D) 500 K
		•		27

JEE-Chemistry

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10.	• A gas is expanded from volume V_1 to V_2 through three different process :						
	(a) Reversible adiaba	ttic (b) Reversib	le isothermal	(c) Irreversible adi	abatic		
	The correct statemen	ts is -					
	(A) $(T_f)_{Reversible Isother}$	$_{\rm rmal}$ > (T _f) _{Reversible} ;	$_{\rm adiabatic} > (T_{\rm f})_{\rm Irr}$	eversible adiabatic			
	(B) $(T_f)_{Reversible Isothe}$	$_{\rm rmal}$ > (T _f) _{Irreversible}	$_{adiabatic} > (T_f)$	Reversible adiabatic			
	(C) $W_{Reversible Isothermal} > W_{Irreversible adiabatic} > W_{reversible adiabatic}$						
	(D) $(P_f)_{\text{Reversible Isothermal}} > (P_f)_{\text{Reversible adiabatic}} > (P_f)_{\text{Irreversible adiabatic}}$						
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 in $300 \mathrm{K}$? $\mathrm{C_V}$ for the gas in						
	1.5 R. (R = 2 Cal / m)	nol/ K)					
	(A) 900 Cal	(B) 450 Cal	(C) 675 Ca	l (D) 33	1.57 Cal		
12.	For a process which	follows the equati	ion $PV^3 = C$, the	ne work done when	one mole of ideal gas was		
	taken from 1 atm to	$2\sqrt{2}$ atm starting	from initial ter	mperature of 300 K	is		
	(A) 300 R	(B) 150 R	(C) 600 R	(D) 900 R		
13.	What is the net work	done (w) when	1 mole of mor	noatomic ideal gas	40L 3 3		
	undergoes in a proce	ess described by 1	, 2, 3, 4 in giv	en V–T graph			
	Use : R = 2cal/mol	e K			V 20L		
	ln 2= 0.7				10L 1 4		
	(A) -600 cal		(B) – 660 cal	T 300K 600K		
	(C) + 660 cal		(D) + 600 cal	Λ Δ. Β		
14.	A cyclic process AB	CD is shown in P	V diagram fo	r an ideal gas.			
	which of the following	ng diagram represe	ents the same p	rocess?	P C		
				A .	v		
				Î C			
	$(A)_{V}$		(B) V \uparrow \downarrow A			
				В			
	D	>		\downarrow T			
	1			Ĩ			





15. 2 moles of an ideal monoatomic gas is taken from state A to state B through a process AB in which PT = 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) $\Delta U = -900 \text{ R}$
- (D) W = 1200R

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





17. Work in the following cyclic process is



Е





- heat capacity (C_m) of gas for the process is [1 cal = 4.18 Joule]
 - (B) $\frac{5}{2}$ R (C) $\frac{5}{4}$ R (A) $\frac{3}{2}$ R (D) 5R
- 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 (C) $\frac{7}{2}$ (B) 3R (D) 4R

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. Tahe molar heat capacity of gas (in cal/K-mol) for the process is.

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

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

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 ?

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) $\Delta H_{CD} = 1000 \text{ R}$	(D) $\Delta U_{\rm BC} = 375 \ {\rm R}$

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

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.
- **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.

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- 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 capicity of gases are temperature dependent
 - (D) During boiling of H_2O at 1 atm, 100°C, average kinetic energy of H_2O molecules increases.
- 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) $E_4 > E_3$

□ 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.
- 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.

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)th of initial volume.



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11.	Wha	at will be the final	l pressure in container B).			
	(A)	2 atm	(B) 8 atm	(C)	16 atm	(D) 32 atm	
12.	2. Final temperature in container A will be						
	(A)	1638 K	(B) 6988 K	(C)	3274 K	(D) 51 K	
13.	Cha	Change in enthalpy for section A in Kcal					
	(A)	48.3	(B) 80.53	(C) -	4.83	(D) 8.05	
			Paragrah for	Q.14 t	to 16		
	As a of h	result of the isobate $Q = 1.60 \text{ kJ}.$	aric heating by $\Delta T = 72K$	K, one m	ole of a certain	i ideal gas obtains an a	amount
14.	The	work performed b	by the gas is -				
	(A)	8.60 kJ	(B) 0.60 kJ	(C)	16.60 kJ	(D) 4.60 kJ	
15.	The	increment of its in	nternal energy (in kJ) is	-			
	(A)	1.0	(B) 1.6	(C)	2.2	(D) 2.0	
16.	The	value of γ for the	gas is -				
	(A)	0.6	(B) 1.4	(C)	1.6	(D) 1.5	
			MATCH THE	COLU	J MN :		
17.	Mat	ch Column-I with	Column-II				
		Column-I (Idea	al Gas)		Column-II (Related equations)		
	(A)	Reversible isothe	ermal process	(P)	W = 2.303 r	$1 \text{ RT } \log(\text{P}_2/\text{P}_1)$	
	(B)	Reversible adiab	patic process	(Q)	$W = nC_{V,m} ($	$T_2 - T_1$)	
	(C)	Irreversible adia	batic process	(R)	W = -2.3031	$hRT \log(V_2/V_1)$	
	(D)	Irreversible isoth	nermal process	(S)	$W = -\int_{V_i}^{V_f} P_{ext.} dt$	V	
18.	Mat	ch the column					
	Column–I		Coh	ımn–II			
	(A)	Isothermal vapo	risation of water at	(P)	$\Delta T = 0$		
 12. 13. 13. 14. 15. 16. 17. 18. 18. 		100°C & 1 atm					
	(B)	Isothermal rever	sible expansion	(Q)	$\Delta U = 0$		
		of an ideal gas					
	(C)	Adiabatic free e	xpansion of ideal gas	(R)	$\Delta H = 0$		
	(D)	Isochoric heatin	g of an ideal gas	(S)	q = 0		
				(T)	w = 0		
			•				33

JEE-Chemistry

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)

Code:

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

Column-II

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

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)

Code:

	Р	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

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 remains constant

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 J, w = -208 J

(2) q = -208 J, w = -208 J

- (3) q = -208 J, w = +208 J
- (4) q = +208 J, w = +208 J
- 2. Which of the following statements/relationships is not correct in thermodynamic changes?

(1) q= -nRT $ln \frac{V_2}{V_2}$ (isothermal reversible expansion of an ideal gas) [Jee-Main_(Online)-2014]

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

- (3) w = -nRT ln $\frac{V_2}{V}$ (isothermal reversible expansion of an ideal gas)
- (4) $\Delta U = 0$ (isothermal reversible expansion of a gas)
- 3. A gas undergoes change from state A to state B. In this process, the heat absorbed and work done by the gas is 5 J and 8 J, respectively. Now gas is brought back to A by another process during which 3 J of heat is evolved. In this reverse process of B to A:-[Jee-Main_(Online)-2017]
 - (1) 10 J of the work will be done by the surrounding on gas.
 - (2) 6 J of the work will be done by the surrounding on gas.
 - (3) 10 J of the work will be done by the gas.
 - (4) 6 J of the work will be done by the gas.
- 4. The enthalpy change on freezing of 1 mol of water at 5°C to ice at –5°C is: [Jee-Main_(Online)-2017] (Given Δ_{fus} H = 6 kJ mol⁻¹ at 0°C, C_p(H₂O, *l*) = 75.3 J mol⁻¹ K⁻¹, C_p(H₂O, s) = 36.8 J mol⁻¹ K⁻¹) (1) -6.56 kJ mol-1 (2) -5.81 kJ mol⁻¹ $(3) - 6.00 \text{ kJ mol}^{-1}$ (4) -5.44 kJ mol⁻¹
- 5. ΔU is equal to

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

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



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

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

Heat absorbed by the system during process CA is :-

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

(4) -18 kJ mol⁻¹

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[Jee-Main_(Online)-2017]

(4) Isothermal work

[Jee-Main (Online)-2018]



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



8. An ideal gas undergoes isothermal compression from 5 m³ to 1 m³ against a constant external pressure of 4 Nm⁻². Heat released in this process is used to increase the temperature of 1 mole of Al. If molar heat capacity of Al is 24 J mol⁻¹ K⁻¹, the temperature of Al increases by **[JEE-MAINS(online)-2019]**

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

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EXERCISE # J-ADVANCED

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 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]



- 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 nd N to K
- 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
- 4. An ideal gas in thermally insulated vessel at internal pressure = P_1 , volume = V_1 and absolute temperature = T_1 expands irrversibly 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]



JEE-Chemistry

- An ideal gas is expanded from (p_1, V_1, T_1) to (p_2, V_2, T_2) under different conditions. The correct 5. 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
- A reversible cyclic process for an ideal gas is shown below. Here, P, V and T are pressure, volume 6. 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 $\Delta H_{CA} > \Delta U_{CA}$

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Thermodynamics-01

ANSWER-KEY

EXERCISE # S-I

1.	Ans. (a) $W = -P\Delta V$ (b) $W = -P\Delta V =$	-1(5	(-1) = -4 litre-a	tm.			
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) + $60J$ (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) 4	0 bar.L				
9.	Ans. (500 J)						
10.	Ans. $\Delta U = w = -1050 R$; $\Delta H = -14$	70 R	, q = 0				
11.	Ans. 2244.78 Joule						
12.	Ans. $T_2 = 100K$; w = -5.016 kJ						
13.	Ans. (7)						
14.	Ans. $q = 0$, $w = \Delta U = 4.125$ kJ; ΔH	[= 5.	372 kJ ; $V_f = 12$	1.8 dm ³ ; P = 5.22 atm			
15.	Ans. (a) $T_1 = 243.60 \text{ K}$; $T_2 = 2436 \text{ I}$	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. $\Delta E = 75.12 \text{ kJ}$						
23.	Ans. $\Delta H \cong \Delta U = 1440$ calories						
	EXERCISE # S-II						
1.	Ans. (a) 600 K, (b) 3 kcal, 1.680 kca	l, –1.	8 kcal, – 1.680 k	ccal (c) –1.2 kcal			
2.	Ans. $\Delta U \& \Delta H = 0$; w = 623.55 J ;	$\mathbf{q} = \mathbf{r}$	-623.55 J				
3.	Ans. $\mathbf{w} = -\mathbf{n}\mathbf{R}\mathbf{T} \ln \frac{\mathbf{V}_{f}}{\mathbf{V}_{i}} - n^{2}a\left(\frac{1}{\mathbf{V}_{f}} - \frac{1}{\mathbf{V}_{i}}\right)$						
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/m	ole			
7.	Ans. –1200 cal	8.	Ans. 60 cal				
9.	Ans. (32)	10.	Ans. (-900 calo	rioes)			
11.	Ans. 7.4 atm litre	12.	Ans. 35 atm				
13.	Ans. 3120	14.	Ans. (6)				
	-						

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			EXERCI	SE #	0-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)				
			EXERCIS	SE #	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.	7. Ans.(A) \rightarrow (P,R,S) ; (B) \rightarrow (Q,S) ; (C) \rightarrow (Q,S) ; (D) \rightarrow (S)						
18.	Ans.(A) \rightarrow (P);	(B) →	(P,Q,R) ; $(C) \rightarrow (P,Q,R)$	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)
	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)				

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