विध्न विचारत भीरु जन, नहीं आरम्भे काम, विपति देख छोड़े तुरंत मध्यम मन कर श्याम।
पुरुष सिंह संकल्प कर, सहते विपति अनेक, ‘बना‘ न छोड़े ध्येय को, रघुबर राखे टेक।।

रचितः मानव धर्म प्रणेता
सद्गुरु श्री रणछोड़दासजी महाराज

STUDY PACKAGE

This is TYPE 1 Package
please wait for Type 2

Subject : CHEMISTRY

Topic : THERMODYNAMICS

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7. 34 Yrs. Que. from IIT-JEE
8. 10 Yrs. Que. from AIEEE

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THE KEY

The subject of ***Thermodynamics*** deals basically with the interaction of one body with another in terms of quantities of heat & work. It may be *defined* as the branch of science which deals with energy changes associated with various physical & chemical processes. The entire formulation of thermodynamics is based on a few (Three) fundamental laws which have been established on the basis of human experience of the experimental behaviour of macroscopic aggregates of matter collected over a long period of time. ***Thermochemistry*** is the branch of physical chemistry which deals with the thermal or heat changes caused by chemical reactions. It is based on first law of thermodynamics. There are two laws of thermochemistry:

(a) Lavoisier & Laplace law (b) Hess's law.

TERMS & CONVENTIONS

A number of terms & conventions are used in thermodynamics.

A ***System*** is defined as that part of the universe which is at the moment under investigation.

Universe less the system is defined as ***Surroundings***. The actual or imaginary surface that separates the system from the surroundings is called the ***Boundary***.

TYPES OF SYSTEMS:

A system is said to be ***Isolated*** if it cannot exchange matter and energy with the surroundings (coffee in a thermos flask).

A system is said to be ***Closed*** if it can exchange energy but not matter. Coffee in a closed stainless steel flask is an example. A system is said to be ***Open*** if it can exchange matter and energy both. A thermo flask or a steel flask if not closed is an example. A system is said to be homogeneous when it is completely uniform throughout, made up of one phase only, pure liquid. solid, gas.

A system is said to be heterogeneous if it consists of two or more phases, liquid in contact with vapour.

STATE OF A SYSTEM :

The state of a system is defined by a particular set of its measurable properties. For example, we can describe the state of a gas by quoting its pressure (P) , volume (V) and temperature (T) etc.

Variables like P, V , T are *State Functions* OR *State Variables* because their values depend only on the state of a system and not on how the state was reached.

State variables can be intensive or extensive. An intensive variable (eg. temperature, pressure, concentration) is one whose value is independent of the size of the system. An extensive variable (eg. volume , mass, surface area is one whose value is proportional to the size of the system.

Extensive Properties (Depend upon quantity of Matter present and are additive)	**Intensive Properties (Do not depend upon quantity of Matter present and are non additive)**
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	Specific heat
Heat capacity	Pressure
	Temperature
	Boiling point, freezing point etc

THERMODYNAMIC PROCESS :

A thermodynamic process involves change of a system from one state to another state.

TYPES:

A process is called ***Isothermal***, if the temperature of the system remains constant during the change. It is carried out in a thermostat and in such a process the exchange of energy between the system and surroundings takes place. In such a process dT = 0 & dE = 0.

A process is called ***Adiabatic***, if the system does not exchange energy with surroundings. Such a process is carried out in perfectly insulated containers. During it the temperature of the system may change. In such a process dQ = 0.

A process carried out at a constant pressure is called an **isobaric** process. In such a process dP = 0.

A process in which the volume of the system remains constant is called an **isochoric** process, whereby dV = 0.

CYCLIC PROCESS :

When a system undergoes a number of different processes and finally returns to its initial state.

$\Delta E = 0$ & $\Delta H = 0$.

REVERSIBLE PROCESS : (QUASI-STATIC)

A process which is carried out so slowly that the system and the surroundings are always in equilibrium is known as a ***Reversible Process***. If this condition does not hold good, the process is said to be, ***Irreversible***.

In a reversible process the driving force is infinitesimally larger than the opposing force. If the driving force is made infinitely smaller than opposing force, the system can be brought back without producing any permanent change.

A process which proceeds of its own i.e. without any external help, is called as ***Spontaneous Process*** (or a natural process).

Internal Energy (Intrinsic Energy) E – Every system having some quantity of matter is associated with a definite amount of energy, called internal energy.

$E = E_{Translational} + E_{Rotational} + E_{vibrational} + E_{Bonding} + E_{Electronic} + ...$

It is a state function & is an extensive property.

$\Delta E = E_{final} - E_{initial}$; $\Delta E = q_v$

ZEROTH LAW OF THERMODYNAMICS

It states that, two systems in thermal equilibrium with a third system, are also in thermal equilibrium with each other.

FIRST LAW OF THERMODYNAMICS

It is law of conservation of energy. Mathematically, this law is written as :

$\Delta E = q + w$, where ΔE is change in internal energy of the system and is a state function, q is the transfer of heat from / to the system and w is the work involved (either done on the system or by the system) . 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.

TYPES OF WORK :

Two TYPES of work normally come across in chemistry. These are *Electrical Work* in system involving ions, while the *Mechanical Work* is involved when a system changes its volume in the, presence of an externally applied pressure (i.e. pressure volume work). It is especially important in system containing gases.

If a system expands from a volume V_1 to V_2 at constant pressure P, then the first law equation becomes,
$\Delta E = q - P\,\Delta V$ $(\Delta V = V_2 - V_1)$ ....(1)

For a process carried at constant volume A B = q (heat absorbed at constant volume)

Work = Intensity factor X capacity factor
w – by the system (Expansion) negative
w – on the system (compression) positive
q → absorbed by the system positive
q → given out by the system negative
Work done in irreversible process (Expansion) $w = -P_{Ext}\,\Delta V$

Work done in isothermal reversible process $w = -2.303\,nRT \log \frac{V_2}{V_1}$

(maximum work) (Expansion) $= -2.303\,nRT \log \frac{P_1}{P_2}$

work done is adiabatic reversible process $w = \frac{nR}{\gamma - 1}[T_2 - T_1]$

$$\gamma = \frac{C_P}{C_V} = \text{Poisson's ratio}$$

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 :

$H = E + PV$ (By definition) or $\Delta H = \Delta E + P\,\Delta V + V\Delta P$
or $\Delta H = \Delta E + P\,\Delta V$ (at constant pressure) combining with first law. Equation (1) becomes
$\Delta H = q_p$

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.
The difference between ΔH & ΔE becomes significant only when gases are involved (insignificant in solids and liquids) and is given by: $\Delta H = \Delta E + (\Delta n)\,RT$, where Δn is the INCREASE in the number of moles of the gases involved (i.e. Total number of moles of product gases less the total number of moles of reactant gases).

FACTORS AFFECTING ΔH OF THE REACTIONS ARE :

(i) Temperature
(ii) Physical states of reactants & products
(iii) Allotropic forms of elements &
(iv) Pressure & volume (in case of gases)

Two Types of Reactions may be distinguished :

(i) **Exothermic Reactions :** For these ΔH is negative, which implies that
$\sum H$ (products) $<$ $\sum H$ (reactants)

(ii) **Endothermic Reactions :** For these ΔH is positive, which implies that
$\sum H$ (products) $>$ $\sum H$ (reactants)

HESS'S LAW OF CONSTANT HEAT SUMMATION :

According to Hess's law (a consequence of first law), if a set of reactants is converted into a set of product by more than one sequence of reactions, the total enthalpy change will be the same for every sequence.

As such, the chemical equations can be treated ordinary algebraic expressions and can be added or subtracted to yield the required equation. The corresponding enthalpy changes are also manipulated in the same way to obtain the enthalpy change for the desired equation.

APPLICATIONS OF HESS'S LAW :

It helps us in Calculation of :

(i) Heat of formation (ΔH_f) of many substances which cannot be synthesised directly from their elements.
(ii) Bond energies.
(iii) Enthalpy changes of slow reactions and
(iv) Enthalpy of transformation, say from one allotropic form to the other.

CONVENTIONAL VALUES OF MOLAR ENTHALPIES :

It is not possible to determine the absolute value of enthalpy of a substance and further it also depends on the conditions under which its determination is carried out. It is therefore necessary to choose some standard conditions for reporting the enthalpy data.

Conventionally, the enthalpy of every element in its most stable state of aggregation at 1 atm. (101.325 k Pa) and 298 K is assigned a zero value.

Based on the above convention, the relative values of "Standard molar enthalpies" ($\Delta H°$) of other substances are obtained and it is obvious that in terms of ΔH_f^o values, the enthalpy change of any reaction is given as :

$$\Delta H° = \sum \Delta H_f^o \text{ (products)} - \sum \Delta H_f^o \text{ (reactants)}$$

i.e. $$\Delta H° = \left(\begin{matrix} \textit{sum of standard enthalpies} \\ \textit{of formation of product} \end{matrix}\right) - \left(\begin{matrix} \textit{sum of standard enthalpies} \\ \textit{of formation of reactants} \end{matrix}\right)$$

Reactions are frequently classified according to type of thermochemical purpose and the enthalpies of reactions are given different names.

A balanced chemical equation which expresses the heat changes taking place in a reaction as well as the physical states of various reactants and products is known as a thermochemical equation.

Heat capacity $C = \dfrac{dq}{dT}$; $C_V = \left(\dfrac{\partial E}{\partial T}\right)_V$; $Cp = \left(\dfrac{\partial H}{\partial T}\right)_P$

$q = C (T_2 - T_1)$ for 1 mole; $q = nC (T_2 - T_1)$ for n moles

Kirchoffs Equation: $\dfrac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_P$; $\dfrac{\Delta E_2 - \Delta E_1}{T_2 - T_1} = \Delta C_V$

Trouton's Rule : Entropy of vaporization of non-associated or non-dissociated liquid is constant & may be taken as about 87.3 J $k^{-1}mol^{-1}$.

Thermochemical Equations : An equation which indicates the amount of heat change in the reaction. These can be added, subtracted or multiplied whenever required.

The various named Enthalpies are defined as the Enthalpy change when ....

Enthalpy of reaction : "quantities of substances indicated in the balanced equation react completely to form the product."

Enthalpy of formation : “one mole of the substance is formed directly from its constituent elements."

Enthalpy of combustion : “one mole of the substance undergoes complete combustion” (it is always negative)

Calorific Value : “it is the amount of heat given out by complete combustion of unit weight of a solid or liquid or unit volume of a gas”.

Enthalpy of solution : “one mole of the substance is completely dissolved in a large excess of the given solvent under given conditions of temperature and pressure”.

Enthalpy of neutralisation : “one gram equivalent of an acid is neutralised by one gram equivalent of a base in fairly dilute solution” .

Enthalpy of hydration : “one mole of an anhydrous (or a partly hydrated salt) combines with the required number of mole of water to form a specific hydrate”.

Enthalpy of sublimation : “one mole of a solid is directly converted into its vapour at a given temperature below its melting point” .

Enthalpy of fusion : “one mole of the solid substance is completely converted into the liquid state at its melting point” .

Enthalpy of vaporisation : “one mole of a substance is converted from the liquid state to its vapour state at its boiling point”.

Resonance Energy = Observed heat of formation - Calculated heat of formation

BOND ENTHALPIES’ (BOND ENERGIES) :

The bond enthalpy of a diatomic molecule (H_2, $C1_2$, O_2) is equal to its dissociation energy and is defined as “the enthalpy change involved in breaking the bond between atoms of a gaseous molecule” (Bond breaking is an endothermic process). Average bond enthalpy (energy) is the average value of bond energy obtained from molecules that contain more than one bond of that type.

$$\text{Av. BE} = \frac{\Delta H_f \text{ of molecules}}{\text{no. of bonds}}$$

BE is an additive property.

SECOND LAW OF THERMODYNAMICS

The essence of first law is that all physical and chemical processes take place in such a manner that the total energy of the universe remain constant.

However, it is observed that all processes have a natural direction ,i.e. a direction in which they take place spontaneously. First law fails to answer this. Another feature of the spontaneous processes is that they proceed only until an equilibrium is achieved.

The direction of a spontaneous process and that it eventually reaches equilibrium, can be understood on the basis of entropy concept introduced through the second law of thermodynamics.

ENTROPY AND SPONTANEITY:

Entropy (denoted by S) in s state function. When the state of a system changes, entropy also changes.

The change of entrops ΔS is defined by, $\Delta S = \frac{q_{rev}}{T}$, where q_{rev} means that the heat is being supplied "Isothermally " and "Reversibly" (JK^{-1}).

One can think entropy as a measure of the degree of randomness or disorder in a system. The greater the disorder, in a system, the higher is the entropy.
A useful form of 2nd law of thermodynamics is :
"The entropy of the universe increases in the course of every spontaneous (natural) change".

OR

"For a spontaneous process in an isolated system, the change in entropy is positive".

When a system is in equilibrium the entropy is maximum. So mathematically

$$\Delta S = 0 \quad \text{(at equilibrium)}$$

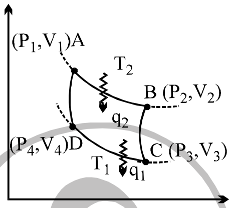
SECOND LAW :

Statements :

(i) No cyclic engine is possible which take heat from one single source and in a cycle completely convert it into work without producing any change in surrounding.

(ii) Efficiency of Carnot engine working reversibly is maximum.

Carnot cycle



AB – Iso. Rev.Exp. $\qquad w_{AB} = -nRT_2 \ln \frac{V_2}{V_1}$

BC – Ada. Rev. Exp. $\qquad w_{BC} = C_V (T_1 - T_2)$

CD – Iso. Rev. Comp. $\qquad w_{CD} = -nRT_1 \ln \left(\frac{V_4}{V_3}\right)$

DA – Iso. Rev. Comp. $\qquad w_{DA} = C_V (T_2 - T_1)$

$$\text{Carnot efficiency } \eta = \frac{-w_{Total}}{q_2} = \frac{T_1 - T_2}{T_2} = \frac{q_1 + q_2}{q_2}$$

CARNOT CYCLE :

$$\frac{q_1}{T_1} + \frac{q_2}{T_2} = 0 \text{ for rev. cycle}$$

$$\text{Irreversible engine } \frac{q_1}{T_1} + \frac{q_2}{T_2} < 0$$

$$\oint \frac{q_{rev}}{T} = 0 \Rightarrow \frac{q_{rev}}{T} \text{ is a state function.}$$

$$\Delta S = \int \frac{dq_{rev}}{T}$$

Also $\quad \Delta S_{syt} + \Delta S_{surr} = 0 \qquad$ for rev. process
$\qquad \Delta S_{syt} + \Delta S_{surr} > 0 \qquad$ for irrev. process
$\Rightarrow \quad \Delta S_{syt} + \Delta S_{surr} \geq 0 \qquad$ (In general)

ENTROPY CHANGE (General Expression):

$$\Delta S = nC_V\, ln\, \frac{T_2}{T_1} + nR\, ln\, \frac{V_2}{V_1}$$

Change in state function for various processes.
Reversible irreversible isothermal expansion and contraction : (ideal gas)

$$\Delta E = 0;\ \Delta H = 0;\ \Delta S = nR\, ln\, \frac{V_2}{V_1}$$

Isobaric heating or cooling :

$$\Delta E = C_V\, \Delta T$$
$$\Delta H = C_P\, \Delta T = q_P$$
$$\Delta S = nC_P\, ln\left(\frac{T_2}{T_1}\right)$$

Isochoric heating or cooling :

$$\Delta E = C_V\, \Delta T = q_V$$
$$\Delta H = C_P\, \Delta T$$
$$\Delta S = nC_V\ \ ln\left(\frac{T_2}{T_1}\right)$$

Adiabatic process :

$$\Delta E = C_V\, \Delta T$$
$$\Delta H = C_P\, \Delta T$$
$$\Delta S = nC_V\, ln\frac{T_2}{T_1} + nR\, ln\, \frac{V_2}{V_1} \text{ for irreversible process}$$

$\Delta S = 0$ for reversible adiabatic compression and expansion.

Gibb's function :

$$G = H - TS$$

at constant T and pressure

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

$\Delta G = (\Delta H - T\Delta S) \leq 0$ for rev. process.
$(-\Delta G)_{T,\, P}$ = work done by system max. non P – V

$$\frac{\Delta G}{T} = -\,(\Delta S_{syst} + \Delta S_{surr.})$$

$\Delta G < 0$ for spontaneous process
$\Delta G = 0$ for equilibrium.

GIBBS FREE ENERGY (G) AND SPONTANEITY:

A new thermodynamic (state) function G , the Gibbs free energy is defined as :

$G = H - TS$ or $\Delta G = \Delta H - T\,\Delta S$ (at constant temperature and pressure)

For a spontaneous reaction ΔG must be negative. The use of Gibbs free energy has the advantage that it refers to the system only (and not surroundings also as in entropy).

To summaries, the spontaneity of a chemical reaction is decided by two factors taken together:

(i) the enthalpy factor and (ii) the entropy factor.

The equation $\Delta G = \Delta H - T\,\Delta S$ takes both the factors into consideration.

The most favorable situation for a negative value of ΔG is a negative value of ΔH and a positive value of ΔS. However a large negative value of ΔH may outweigh an unfavorable ΔS value and a large value of ΔS may outweigh an unfavorable value of ΔH.

STANDARD FREE ENERGY CHANGE (ΔG°) :

The standard free energy change ΔG° is defined as the free energy change for a process at a specified temperature in which the reactants in their standard state are converted to the products in their standard state. It is denoted by ΔG°.

Like the standard enthalpy of formation of an element "the standard free energy of formation of an element in its standard state is zero". And so ;

$$\Delta G_r^o = \sum \Delta G_f^o \text{ (products)} - \sum \Delta G_f^o \text{ (reactants)}$$

The standard free energy change. ΔG° is related to the equilibrium constant k_{eq} by the relation;

$$\Delta G^\circ = -2.303\,RT \log k_{eq}.$$

It can be shown that free energy change for a process is equal to the maximum possible work that can be derived from the process i.e.

$\Delta G^\circ = W_{max}$ (for a reversible change at constant pressure and temperature)

In case of a galvanic cell, free energy change, ΔG is related to the electrical work done in the cell.

$\Delta G = -nFE_{cell}$, where E_{cell} = e.m.f. of the cell ; F = Faraday constant and

n = number of electrons being transferred in the chemical process

So $\Delta G = -nFE^o_{cell}$, where E^o_{cell} is the standard cell potential.

Clausius Claperyon's Equation : $\log \dfrac{p_2}{p_1} = \dfrac{\Delta H}{2.303R}\left[\dfrac{1}{T_1} - \dfrac{1}{T_2}\right]$ (For liquid ⇔ gas equilibrium)

p_1 & p_2 are vapour pressure at T_I & T_2

THIRD LAW OF THERMODYNAMICS

"At absolute zero, the entropy of a perfectly crystalline substance is taken as zero", which means that at absolute zero every crystalline solid is in a state of perfect order and its entropy should be zero.

By virtue of the third law, the absolute value of entropy (unlike absolute value of enthalpy) for any pure substance can be calculated at room temperature.

The standard absolute entropy of, a substance" So, is the entropy of the substance in its standard at 298K and 1 atm.

Absolute entropies of various substances have been tabulated and these value are used to calculate entropy changes for the reactions by the formula;

$$\Delta S^\circ = \sum S^\circ \text{ (products)} - \sum S^\circ \text{ (reactants)}$$

EXERCISE-I

First law : Heat (q), work (w) and ΔU, ΔH

Q.1 In which of the following changes at constant pressure is work done by system on surrounding? By the surrounding on system?

	Initial state		Final state
(i)	H_2O (g)	$\longrightarrow$	H_2O (l)
(ii)	H_2O (s)	$\longrightarrow$	H_2O (g)
(iii)	H_2O (l)	$\longrightarrow$	H_2O (s)
(iv)	$2H_2$(g) + N_2(g)	$\longrightarrow$	$2NH_3$ (g)
(v)	$CaCO_3$ (s)	$\longrightarrow$	CaO (s) + CO_2 (g)

Q.2 The gas is cooled and loses 65 J of heat. The gas contracts as it cools and work done on the system equal to 20 J is exchanged with the surroundings. What are q, w and ΔE ?

Q.3 The enthalpy change for the reaction of 50 ml of ethylene with 50.0 ml of H_2 at 1.5 atm pressure is ΔH = – 0.31 KJ. What is the ΔE.

Q.4 The enthalpy of combustion of glucose is – 2808 $KJmol^{-1}$ at 25°C. How many grams of glucose do you need to consume [Assume wt = 62.5 Kg].

(a) to climb a flight of stairs rising through 3M.

(b) to climb a mountain of altitude 3000 M?

Assume that 25% of enthalpy can be converted to useful work.

Q.5 What is ΔE when 2.0 mole of liquid water vaporises at 100°C ? The heat of vaporisation , ΔH vap. of water at 100°C is 40.66 $KJmol^{-1}$.

Q.6 If 1.0 k cal of heat is added to 1.2 L of O_2 in a cylinder of constant pressure of 1 atm, the volume increases to 1.5 L. Calculate ΔE and ΔH of the process.

Q.7 When the following reaction was carried out in a bomb calorimeter, ΔE is found to be – 742.7 kJ/mol of NH_2CN (s) at 298 K.

$$NH_2CN\ (s) + \frac{3}{2} O_2\ (g) \rightarrow N_2\ (g) + CO_2\ (g) + H_2O\ (l)$$

Calculate ΔH_{298} for the reaction.

Q.8 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 ΔE for the reaction.

Q.9 Water expands when it freezes. Determine amount of work in joules, done when a system consisting of 1.0 L of liquid water freezes under a constant pressure of 1.0 atm and forms 1.1 L of ice.

Q.10 Lime is made commercially by decomposition of limestone $CaCO_3$. What is the change in internal energy when 1.00 mole of solid $CaCO_3$ (V = 34.2 ml) absorbs 177.9 kJ of heat and decomposes at 25°C against a pressure of 1.0 atm to give solid CaO. (Volume = 16.9 ml) and CO_2 (g) (V = 24.4 L).

Q.11 One mole of solid Zn is placed in excess of dilute H_2SO_4 at 27 °C in a cylinder fitted with a piston. Find the value of ΔE, q and w for the process if the area of piston is 500 cm^2 and it moves out by 50 cm against a pressure of 1 atm during the reaction. The heat given to surrounding is 36.5 KJ.

$$Zn(s) + 2H^+\ (aq)\ 1\ Zn^{2+}\ (aq) + H_2(g)$$

Q.12 Two mole of ideal diatomic gas ($C_{V,m}$ = 5/2 R) at 300 K and 5 atm expanded irreversly & adiabatically to a final pressure of 2 atm against a constant pressure of 1 atm. Calculate q, w, ΔH & ΔV.

Q.13 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 cont. ext. pressure of 1 atm. Calculate q, w, ΔU & ΔH. Calculate the corresponding value of all if the above process is carried out reversibly.

Q.14 Calculate the max. work done by system in an irreversible (single step) adiabatic expansion of 1 mole of a polyatomic gas from 300K and pressure 10 atm to 1 atm.($\gamma = 1.33$).

Q.15 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 $C_V = 25.08$ J $mol^{-1}K^{-1}$ for CO_2.

Q.16 Three moles of a ideal gas at 200 K and 2.0 atm pressure undergo reversible adiabatic compression until the temperature becomes 250 K for the gas C_V is 27.5 JK^{-1} mol^{-1} in this temperature range. Calculate q, w, ΔU, ΔH and final V and final P.

Q.17 A sample of a fluorocarbon was allowed to expand reversibly and adiabatically to twice its volume. In the expansion the temperature dropped from 298.15 K to 248.44 K. Assume the gas behaves perfectly. Estimate the value of $C_{V,m}$.

Q.18 Find the work done when one mole of the gas is expanded reversibly and isothermally from 5 atm to 1 atm at 25°C.

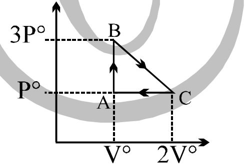
Q.19 One mole of ideal monoatomic gas is carried through the reversible cyclic process as shown in figure. Calculate.

(a) work done by the gas

(b) The heat exchanged by the gas in path CA and AB.

(c) Net heat absorbed by the gas in the path BC.

(d) The max. temperature attained by the gas during the cycle.



Q.20 One mole of an ideal monoatomic gas is carried through the 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.

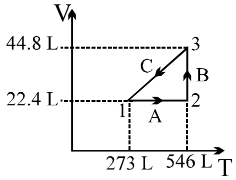
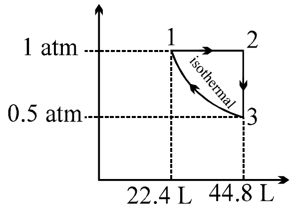


Table-1

State	P	V	T
1			
2			
3			

Step	Name of process	q	w	ΔE	ΔH
A					
B					
C					

Q.21 One mole of an ideal monoatomic gas is put through rev path as shown in figure. Fill in the balnk in the table given below:



State	P	V	T
1			
2			
3			

Step	Name of process	q	w	ΔE	ΔH
A					
B					
C					

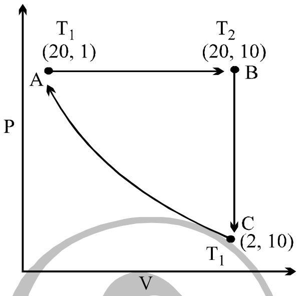
Q.22 One mole of a perfect monoatomic gas is put through a cycle consisting of the following three reversible steps :

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

(AB) Isobaric expansion to return the gas to the original volume of 10 litres with T going from T_1 to T_2.

(BC) Cooling at constant volume to bring the gas to the original pressure and temperature.

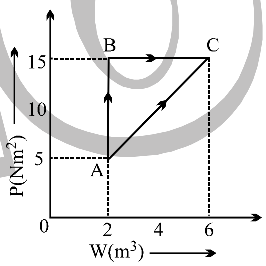
The steps are shown schematically in the figure shown.



(a) Calculate T_1 and T_2.

(b) Calculate ΔE, q and W in calories, for each step and for the cycle.

Q.23 The given figure shows a change of state A to state C by two paths ABC and AC for an ideal gas. Calculate the:

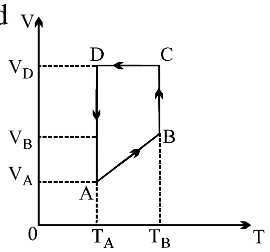


(a) Path along which work done is least.

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

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

Q.24 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.

Kirchoff's Rule : Variation of Enthalpy with Temperature

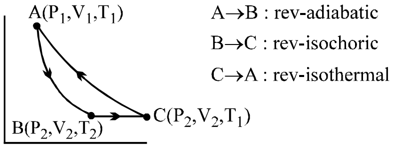
Q.25 The standard enthalpy of formation of water liquid is – 285.76 kJ at 298 K. Calculate the value of 373K. The molar heat capacities at constant pressure (C_P) in the given temperature range of H_2 (g), O_2(g) and H_2O (l) are respectively 38.83, 29.16 and 75.312 $JK^{-1}mol^{-1}$.

Q.26 Methan (Considered to be an ideal gas) initially at 25°C and 1 bar pressure is heated at constant pressure until the volume has doubled. The variation of the molart heat capacity with ansolute temperature is given by $C_P = 22.34 + 48.1 \times 10^{-3}\ T$

where C_P is in $JK^{-1}\ mol^{-1}$. Calculate molar (a) ΔH (b) ΔU.

Second law & Entropy change in thermodynamic processes

Q.27 One mole of monoatomic gas was taken through a cylic process as shown in figure.



Calculate $\sum\limits_{ABCA} \frac{dq_{rev}}{T}$.

Q.28 One mole of NaCl (s) on melting absorved 30.5 KJ of heat and its entropy is increased by 28.8 JK^{-1}. What is the melting point of sodium chloride?

Q.29 Oxygen is heated from 300 to 600 at a constant pressure of 1 bar. What is the increases in molar entropy? The molar heat capacity in JK^{-1} mol^{-1} for the O_2 is

$$C_P = 25.5 + 13.6 \times 10^{-3}\,T - 42.5 \times 10^{-7}\,T^2$$

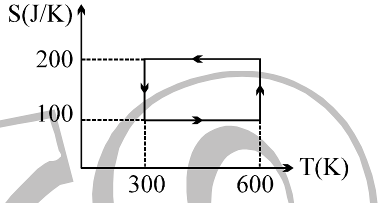
Q.30 A heat engine absorbs 760 kJ heat from a source at 380K. It rejects (1) 650 kJ, (ii) 560 kJ, (iii) 504 kJ of heat to sink at 280 K. State which of these represent a reversible, an irreversible and an impossible cycle.

Q.31 From the given T-S diagram of a reversible carnot engine, find

(i) work delivered by engine in each cycle

(ii) heat taken from the source in each cycle.

(iii) ΔS_{sink} in each cycle.



Gibb's Function

Q.32 Calculate the free energy change at 298 K for the reaction ;
$Br_2(l) + Cl_2(g) \longrightarrow 2\,BrCl(g)$. For the reaction $\Delta H^\circ = 29.3$ kJ & the entropies of $Br_2(l)$, $Cl_2(g)$ & $BrCl(g)$ at the 298 K are 152.3, 223.0, 239.7 J mol^{-1} K^{-1} respectively.

Q.33 Using the date given below , establish that the vaporization of $CCl_4(l)$ at 298 K to produce $CCl_4(g)$ at 1 atm pressure does not occur spontaneously .

Given : $CCl_4(l, 1\,atm) \longrightarrow CCl_4(g, 1\,atm)$; $\Delta S^\circ = 94.98\ JK^{-1}\ mol^{-1}$;

$\Delta H^\circ_f(CCl_4, g) = -106.7\ kJ\ mol^{-1}$ & $\Delta H^\circ_f(CCl_4, l) = -139.3\ kJ\ mol^{-1}$

Q.34 Animals operate under conditions of constant pressure and most of the processes that maintain life are electrical (in a broad sense). How much energy is available for sustaining this type of muscular and nervous activity from the combustion of 1 mol of glucose molecules under standard conditions at 37°C (blood temperature)? The entropy change is + 182.4 JK^{-1} for the reaction as stated.

$$\Delta H_{combustion\ [glucose]} = -2808\ KJ$$

Q.35 From the given table answer the following questions:

	CO(g)	CO_2(g)	H_2O(g)	H_2(g)
ΔH°_{298} (-KCal/mole)	–26.42	–94.05	–57.8	0
ΔG°_{298} (-KCal/mole)	–32.79	–94.24	–54.64	0
S°_{298} (-Cal/Kmole)	47.3	51.1	?	31.2

Reaction: $H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$

(i) Calculate $\Delta_r H^\circ_{298}$ (ii) Calculate $\Delta_r G^\circ_{298}$ (iii) Calculate $\Delta_r S^\circ_{298}$

(iv) Calculate $\Delta_r E^\circ_{298}$ (v) Calculate S°_{298} $[H_2O(g)]$

PROFICIENCY TEST

Q.1 Mark the following statement as True or False.

1. Pressure is an intensive property.
2. Like U and H, S is also a state function.
3. When a system undergoes a change at constant pressure, it is referred to an isothermal process.
4. A reversible process is always quasi-static.
5. The workdone by a gas during free expansion is equal to zero.
6. First law of T.D. is applicable to all processes irrespective to whether they are reversible or irreversible.
7. All spontaneous processes proceed in one direction only.
8. Whenever a system undergoes a cyclic change

$$\oint \frac{dQ}{T} \le 0$$

9. Positive value of ΔS_{system} during the process can be taken as sole criterion of spontaneity.
10. A real crystal has higher entropy than the ideal crystal.

Q.2 Fill in the blank with appropriate items:

1. According to IUPAC conventions work done on the surroundings is________ .
2. A system is said to be _______ if it can neither exchange matter nor energy with surrounding.
3. A carnot cycle uses only _______ thermal reservoir.
4. A carnot cycle consists of only _______ processes.
5. The efficiency of a carnot engine can be increased by_________ sink temperature when the source temperature is held constant.
6. For a reversible adiabatic process, S = constnat and hence it is called as an ______ process.
7. Entropy change of a system is determined by the ________ and ______ states only, irrespective of how the system has changed its states.
8. Solidification of liquid shows ________ in entropy.
9. When Fe(s) is dissolved in a aqueous HCl in a closed rigid vessel the work done is ______.
10. For Non-spontaneous process at constant T & P ΔG is _________.

EXERCISE-II

Q.1 Calculate workdone in adiabatic compression of one mole of an ideal gas (monoatomic) from an initial ressure of 1 atm to final pressure of 2 atm. Initial temperature = 300 K.

(a) If process is carried out reversible

(b) if process is carried out irreversible against 2 atm external pressure.

Compute the final volume reached by gas in two cases and describe the work graphically.

Q.2 1 mole of ice at 0°C and 4.6 mm Hg pressure is converted to water vapour at a constant temperature and pressure. Find ΔH and ΔE if the latent heat of fusion of ice is 80 cal/gm and latent heat of vaporisation of liquid water at 0°C is 596 cal per gram and the volume of ice in comparison of that water (vapour) is neglected.

Q.3 Two moles of an ideal gas ($\gamma = 5/3$) are initially at a temperature of 27°C and occupy a volume of 20 litre. The gas is first expanded at constant pressure until the volume is doubled. It then undergoes adiabatic change until the temperature returns to its initial value.

(a) Sketch the process on P – V diagram.

(b) What are final pressure and final volume of gas.

(c) What is the work done by the gas.

Q.4 20.0 dm^3 of an ideal gas (diatomic $C_{v,m} = 5R/2$) at 673 K and 0.7 MPa expands until pressure of the gas is 0.2 MPa. Calculate q, w, ΔU and ΔH for the process if the expansion is :

(i) Isothermal and reversible
(ii) Adiabatic and reversible
(iii) Isothermal and adiabatic
(iv) Against 0.2 MPa and adiabatic
(v) Against 0.2 MPa and isothermal.

Q.5 One mole of an ideal monoatomic gas ($C_{V,m} = 1.5$ R) is subjected to the following sequence of steps:

(a) The gas is heated reversibly at constant pressure of 101.325 kPa from 298 K to 373 K.

(b) Next, the gas is expanded reversibly and isothermally to double its volume.

(c) Finally, the gas is cooled reversibly and adiabatically to 308K.

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

Q.6 Calculate ΔS_f^o at 298 K of ; (i) NaCl(s) , (ii) NH_4Cl(s) & (iii) diamond.

The values of S^o of Na, Cl_2, NaCl, NH_4Cl, N_2, H_2, diamond & graphite are 51, 223, 72, 95, 192, 131, 2.43 & 5.69 JK^{-1} mol^{-1} respectively.

Q.7 One mole of an ideal gas is expanded isothermally at 298 K until its volume is tripled. Find the values of ΔS_{gas} and ΔS_{total} under the following conditions.

(i) Expansion is carried out reversibly.

(ii) Expansion is carried out irreversibly where 836.8J of heat is less absorbed than in (i)

(iii) Expansion is free.

Q.8 10 g of neon initially at a pressure of 506.625 kPa and temperature of 473 K expand adiabatically to a pressure of 202.65 kPa. Calculate entropy change of the system and total entropy change for the following ways of carrying out this expansion.

(i) Expansion is carried out reversibly.

(ii) Expansion occurs against a constant external pressure of 202.65 kPa.

(iii) Expansion is a free expansion.

Q.9 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.

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

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

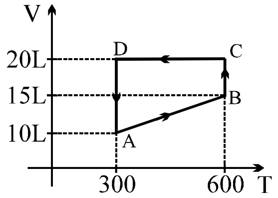
Q.10 Calculate the heat of vaporisation of water per gm at 25°C and 1 atm.

Given $\Delta H_f^o[H_2O(l)] = -285.57$ kJ/mol, $\Delta H_f^\circ[H_2O(g)] = -241.6$ kJ/mol.

Comment why ΔH_{vap} (25°C) > ΔH_{vap} (100°C).
Use data of **Q.20**

Q.11 Pressure over 1000 ml of a liquid is gradually increases from 1 bar to 1001 bar under adiabatic conditions. If the final volume of the liquid is 990 ml, calculate ΔU and ΔH of the process, assuming linear variation of volume with pressure.

Q.12 One mole monoatomic ideal gas was taken through process ABCD as shown in figure. Calculate



(i) w_{AB}, w_{BC}, w_{CD}, w_{DA}
(ii) q_{AB}, q_{BC}, q_{CD}, q_{DA}
(iii) ΔH_{AB}, ΔH_{BC}, ΔH_{CD}, ΔH_{DA}
[Use : $ln(3/2) = 0.40$; $ln(4/3) = 0.29$]

Q.13 One mole of ideal monoatomic gas was taken through reversible isochoric heating from 100 K to 1000 K. Calculate ΔS_{system}, ΔS_{surr}, and ΔS_{total} in
(i) when the process carried out reversibly
(ii) when the process carried out irreversibly (one step)

Q.14 Calculate the entropy of a substance at 600 K using the following data.
(i) Heat capacity of solid from 0 K to normal melting point 200 K
$C_{P,m}(s) = 0.035\,T$ $JK^{-1}mol^{-1}$.
(ii) Enthalpy of fusion = 7.5 KJ mol^{-1}, (iii)Enthalpy of vaporisation = 30 KJ mol^{-1}.
(iv) Heat capacity of liquid from 200 K to normal boiling point 300 K
$C_{P,m}(l) = 60 + 0.016\,T$ $JK^{-1}mol^{-1}$.
(v) Heat capacity of gas from 300 K to 600 K at 1 atm
$C_{P,m}(g) = 50.0$ $JK^{-1}mol^{-1}$.

Q.15(a) An ideal gas undergoes a single stage expansion against a constant opposing pressure from (P_1, V_1, T) to (P_2, V_2, T). What is the largest mass m which can be lifted through a height h in this expansion?
(b) The system in (a) restored to its initial state by a single stage compression. What is the smallest mass m' which must fall through the height h to restore the system?
(c) What is the net mass lowered through height h in the cyclic transformation in (a) and (b)?

Q.16 Calculate the free energy change in the freezing of 18 gm of water at 263.15 K, given that the vapour pressure of water and ice at 263.15 K are 0.287 Pa and 0.260 Pa, respectively.

Q.17 A 32 g sample of CH_4 gas initially at 101.325 kPa and 300K is heated to 550 K. $C_{P,m}/JK^{-1}mol^{-1} = 12.552 + 8.368 \times 10^{-2}\,T/K$. Assuming CH_4 behaves ideally, compute w, q . ΔU and ΔH for (a) an isobaric reversible process, and (b) an isochoric reversible process.

Q.18 Derive a mathematical expression for the work done on the surrounding when a gas that has the equation of state $PV = nRT - \frac{n^2a}{V}$ expands reversibly from V_i to V_f at constant temperature.

Q.19 For the reaction

$$FeCO_3\,(s) = FeO\,(g) + CO_2\,(g)$$

$\Delta_r G°/J\,mol^{-1} = 78073.4 - 60.33\,(T/K)\log(T/K) - 25.397\,(T/K) + 34.476 \times 10^{-3}\,(T/K)^2$
find $\Delta_r H°$ and $\Delta_r S°$ for the reaction at 25°C.

Q.20 Compute $\Delta_r G$ for the reaction $H_2O\,(l, 1\,atm, 323\,K) \rightarrow H_2O\,(g, 1\,atm, 323\,K)$
Given that : $\Delta_{vap}H$ at 373 K = 40.639 $kJmol^{-1}$, $C_P(H_2O, l) = 75.312\,J\,K^{-1}mol^{-1}$,
$C_p\,(H_2O, g) = 33.305\,J\,K^{-1}mol^{-1}$.

EXERCISE-III

Q.1 Out of boiling point (I), entropy (II), pH (III) and e.m.f. of a cell (IV) Intensive properties are:
(A) I, II (B) I,II, III (C) I, III, IV (D) All of these

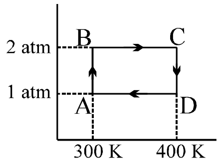
Q.2 Which has maximum internal energy at 298 K?
(A) helium gas (B) oxygen gas (C) ozone gas (D) equal

Q.3 Ethyl chloride (C_2H_5Cl), is prepared by reaction of ethylene with hydrogen chloride:

$$C_2H_4(g) + HCl\,(g) \longrightarrow C_2H_5Cl\,(g) \qquad \Delta H = -\,72.3 \text{ kJ}$$

What is the value of ΔE (in kJ), if 98 g of ethylene and 109.5 g of HCl are allowed to react at 300 K.
(A) – 64.81 (B) –190.71 (C) –209.41 (D) – 224.38

Q.4 Two moles of Helium gas undergo a reversible cyclic process as shown in figure. Assuming gas to be ideal, what is the net work involved in the cyclic process?



(A) –100 Rln4 (B) +100Rln4
(C) +200Rln4 (D) –200Rln4

Q.5 Benzene burns according to the following equation

$$2C_6H_6(l) + 15\,O_2\,(g) \longrightarrow 12\,CO_2\,(g) + 6H_2O(l) \qquad \Delta H^\circ = -6542 \text{ kJ}$$

What is the ΔE° for the combustion of 1.5 mol of benzene
(A) –3271 kJ (B) –9813 kJ (C) – 4906.5 kJ (D) None of these

Q.6 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 J/K mol)
(A) 100 K (B) 450 K (C) 150 K (D) 400 K

Q.7 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

Q.8 The maximum efficiency of a heat engine operating between 100°C and 25°C is
(A) 20% (B) 22.2% (C) 25% (D) none

Q.9 A heat engine operating between 227°C and 27°C absorbs 2 Kcal of heat from the 227°C reservoir reversibly per cycle. The amount of work done in one cycle is
(A) 0.4 Kcal (B) 0.8 Kcal (C) 4 Kcal (D) 8 Kcal

Q.10 A reversible heat engine A (based on carnot cycle) absorbs heat from a reservoir at 1000K and rejects heat to a reservoir at T_2. A second reversible engine B absorbs, the same amount of heat as rejected by the engine A, from the reservoir at T_2 and rejects energy to a reservoir at 360K.
If the efficiencies of engines A and B are the same then the temperature T_2 is
(A) 680 K (B) 640 K (C) 600 K (D) none

Q.11 For the reaction at 300 K

$$A(g) + B(g) \longrightarrow C(g)$$

$\Delta E = -3.0$ kcal ; $\Delta S = -10.0$ cal/K

value of ΔG is

(A) –600 cal (B) –6600 cal (C) –6000 cal (D) None

Q.12 The entropy change when two moles of ideal monoatomic gas is heat from 200 to 300°C reversibly and isochorically

(A) $\frac{3}{2}R\ln\left(\frac{300}{200}\right)$ (B) $\frac{5}{2}R\ln\left(\frac{573}{273}\right)$ (C) $3R\ln\left(\frac{573}{473}\right)$ (D) $\frac{3}{2}R\ln\left(\frac{573}{473}\right)$

Q.13 What is the free energy change (ΔG) when 1.0 mole of water at 100°C and 1 atm pressure is converted into steam at 100°C and 1 atm pressure?

(A) 80 cal (B) 540 cal (C) 620 cal (D) zero

Q.14 What is the free energy change (ΔG) when 1.0 mole of water at 100°C and 1 atm pressure is converted into steam at 100°C and 2 atm pressure?

(A) zero cal (B) 540 cal (C) 515.4 cal (D) none

Q.15 When two equal sized pieces of the same metal at different temperatures T_h (hot piece) and T_c(cold piece) are brought into contact into thermal contact and isolated from it's surrounding. The total change in entropy of system is given by

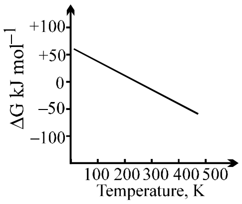
(A) $C_v\ln\frac{T_c + T_h}{2T_c}$ (B) $C_v\ln\frac{T_2}{T_1}$ (C) $C_v\ln\frac{(T_c + T_h)^2}{2T_h.T_c}$ (D) $C_v\ln\frac{(T_c + T_h)^2}{4T_h.T_c}$

Q.16 Pick out the correct statement among the following.

(A) $\Delta S_f^o\{He(g)\} > 0$ at 298 K (B) $\Delta S_f^o\{H_2O(g)\} > 0$ at 298 K

(C) S° of H_2 gas > 0 at 298 K (D) $\Delta G_f^o\{H_2(g)\} > 0$ at 298 K

Q.17 What can be concluded about the values of ΔH and ΔS from this graph?



(A) $\Delta H > 0, \Delta S > 0$ (B) $\Delta H > 0, \Delta S < 0$

(C) $\Delta H < 0, \Delta S > 0$ (D) $\Delta H < 0, \Delta S < 0$

Q.18 Which of the following statement(s) is/are incorrect:

Statement (a) : Reversible isothermal compression of an ideal gas represents the limiting minimum value of the workdone (|w|) by the surrounding on the system.

Statement (b) : In an irreversible process, the cyclic integral of work is not zero.

Statement (c) : For thermodynamic changes in adiabatic process $T^{\left(\frac{C_{p,m}}{R}\right)}.P =$ constant

Statement (d) : ΔS_{system} is zero for reversible adiabatic expansion of an ideal gas.

(A) Statement c (B) Statement a, b, c (C) Statement a, b, d (D) All

Q.19 9.0 gm ice at 0°C is mixed with 36 gm of water at 50°C in a thermally insulated container.
Using the following data, answer the question that follow
$C_P(H_2O) = 4.18\ Jg^{-1}K^{-1}$; ΔH_{fusion} (ice) = $335\ J\ g^{-1}$

(i) final temperature of water is
(A) 304.43 K (B) 296.97 K (C) 303.93 K (D) 287 K

(ii) ΔS_{ice} is
(A) 11.04 JK^{-1} (B) 3.16 JK^{-1} (C) 14.2 JK^{-1} (D) 7.84 JK^{-1}

(iii) ΔS_{water} is
(A) –12.64 JK^{-1} (B) –0.34 JK^{-1} (C) –5.42 JK^{-1} (D) 12.64 JK^{-1}

(iv) What is the total entropy change in the process?
(A) –1.56 JK^{-1} (B) –1.60 JK^{-1} (C) 1.56 JK^{-1} (D) 1.60 JK^{-1}

Q.20 Liquid water freezes at 273 K under external pressure of 1 atm. The process is at equilibrium
$H_2O\ (l)$ 1 H_2O (s) at 273 K & 1 atm.
However it was required to calculate the thermodynamic parameters of the fusion process occuring at same pressure & different temperature. Using the following data, answer the question that follow.

$d_{ice} = 0.9$ gm/cc ; $d_{H_2O(l)} = 1$ gm/cc ; $C_P[H_2O(s)] = 36.4\ JK^{-1}mol^{-1}$;
$C_P[H_2O(l)] = 75.3\ JK^{-1}mol^{-1}$; $\Delta H_{fusion} = 6008.2\ Jmol^{-1}$.

(i) The value of "ΔH_{fusion}" at 263 K & 1 atm will be
(A) +6008.2 J $mole^{-1}$ (B) 5619.2 J $mole^{-1}$ (C) –5619.2 J $mole^{-1}$ (D) 6619.2 J $mole^{-1}$

(ii) "ΔS_{fusion}" at 263 K & 1 atm will be
(A) 22.01 JK^{-1} mol^{-1} (B) 22.84 JK^{-1} mol^{-1} (C) 21.36 JK^{-1} mol^{-1} (D) 20.557 KJ^{-1} mol^{-1}

(iii) At 1 atm & at differnt temperature given below. Match the conditions & the temperature for the "fusion" process

	Condition		Temperature
(1)	Spontaneous	(a)	273 K
(2)	At equilibrium	(b)	260 K
(3)	Not feasible	(c)	280 K

(A) (1–c), (2–a), (3–b) (B) (1–b), (2–a), (3–c)
(C) (1–c), (2–b), (3–a) (D) (1–a), (2–b), (3–c)

(iv) For the fusion process at 263 K, match the conditions with the pressure

	Conditions		Pressure
(1)	Spontaneous	(a)	1 atm
(2)	At equilibrium	(b)	1054 atm
(3)	Not feasible	(c)	2000 atm

(A) (1–b), (2–c), (3–a) (B) (1–a), (2–b), (3–c)
(C) (1–c), (2–b), (3–a) (D) (1–a), (2–c), (3–b)

EXERCISE-IV

OBJECTIVE

Q.1 A process $A \longrightarrow B$ is difficult to occur directly instead it takes place in three successive steps.

$$\begin{tikzcd} C \arrow[r] & D \arrow[d] \\ A \arrow[u] & A \end{tikzcd}$$

$\Delta S\ (A \longrightarrow C) = 50$ e.u.
$\Delta S\ (C \longrightarrow D) = 30$ e.u.
$\Delta S\ (B \longrightarrow D) = 20$ e.u.

where e.u. is entropy unit.
Then the entropy change for the process $\Delta S\ (A \longrightarrow B)$ is
(A) +100 e.u. (B) –60 e.u. (C) –100 e.u. (D) + 60 e.u. **[JEE 2006]**

Q.2 The molar heat capacity of a monoatomic gas for which the ratio of pressure and volume is one.
(A) 4/2 R (B) 3/2 R (C) 5/2 R (D) zero **[JEE 2006]**

Q.3 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 temp. ($R = 0.0821$ litre. atm K^{-1} mol^{-1})

(A) T (B) $\dfrac{T}{(2)^{\frac{5}{3}-1}}$

(C) $T - \dfrac{2}{3 \times 0.0821}$ (D) $T + \dfrac{2}{3 \times 0.0821}$ **[JEE 2005]**

Q.4 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
(A) 11.4 kJ (B) –11.4 kJ
(C) 0 kJ (D) 4.8 kJ **[JEE 2004]**

Q.5 The enthalpy of vapourization of a liquid is 30 kJ mol^{-1} and entropy of vapourization is 75 J mol^{-1} K. The boiling point of the liquid at 1 atm is
(A) 250 K (B) 400 K
(C) 450 K (D) 600 K **[JEE 2004]**

Q.6 One mol 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.
(A) 40.0
(B) 42.3
(C) 44.0
(D) not defined, because pressure is not constant **[JEE 2002]**

Q.7 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 solution. **[JEE 2001]**

Q.8 Molar heat capacity of water in equilibrium with ice at constant pressure is
(A) zero (B) ∞
(C) 40.45 kJ K^{-1} mol^{-1} (D) 75.48 JK^{-1} mol^{-1} **[JEE 1997]**

SUBJECTIVE

Q.9 For the reaction,
$2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$; $\Delta H = -560$ kJ mol^{-1}
In one litre vessel at 500 K the initial pressure is 70 atm and after the reaction it becomes 40 atm at constant volume of one litre. Calculate change is internal energy. All the above gases show significant deviation from ideal behaviour. (1 L atm = 0.1 kJ) **[JEE 2006]**

Q.10 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 decreases by 1 ml. Find ΔU and ΔH **[JEE 2004]**

Q.11 Two moles of a perfect gas undergoes the following processes : **[JEE 2002]**
(a) a reversible isobaric expansion from (1.0 atm, 20.0 L) to (1.0 atm, 40.0 L);
(b) a reversible isochoric change of state from (1.0 atm, 40.0 L) to (0.5 atm, 40.0 L);
(c) a reversible isothermal compression from (0.5 atm, 40.0 L) to (1.0 atm, 20.0 L);
(i) Sketch with labels each of the processes on the same P-V diagram.
(ii) Calculate the total work (w) and the total heat change (q) involved in the above processes.
(iii) What will be the values of ΔU, ΔH and ΔS for the overall process ?

Q.12 Show that the reaction $CO\,(g) + \frac{1}{2}O_2\,(g) \longrightarrow CO_2\,(g)$ at 300 K is spontaneous and exothermic, when the standard entropy is – 0.094 kJ mol^{-1} K^{-1}. The standard Gibbs free energies of formation for CO_2 and CO are – 394.4 and – 137.2 kJ mol^{-1}, respectively. **[JEE 2001]**

Q.13 A sample of argon gas at 1 atm pressure and 27°C expands reversibly and adiabatically from 1.25 dm^3 to 2.50 dm^3. Calculate the enthalpy change in this process. $C_{v.m.}$ for argon is 12.48 JK^{-1} mol^{-1}. **[JEE 2000]**

ANSWER KEY

EXERCISE-I

Heat (q), work (w) and ΔU, ΔH (First Law)

Q.1 (i) w, (ii) – w, (iii) – w, (iv) w, (v) – w Q.2 $q = -65$ J ; $w = 20$ J; $\Delta E = -45$ J

Q.3 – 0.3024 kJ Q.4 (a) 0.47 gm, (b) 0.47 kg Q.5 $\Delta E = 75.11$ kJ

Q.6 $\Delta E = 0.993$ k cal, $\Delta H = 1$ k cal Q.7 – 741.5 kJ

Q.8 $\Delta H \cong \Delta E = 1440$ calories Q.9 – 10 J

Q.10 $q = 177.9$ kJ, $w = -2.5$ kJ ; $\Delta E = 175.4$ kJ

Q.11 DE = – 39.03 KJ/mole; q = – 36.5 KJ;w = – 2.53 KJ

Q.12 $\Delta U = w = -1247.1$; $\Delta H = -1745.94$ J

Q.13 $w_{irr} = -9353.25$, $w_{rev} = -17288.47$ J, $\Delta U = \Delta H = 0$ Q.14 – 1.683 kJ

Q.15 $T_2 = 100$ K ; W = 5.016 KJ

Q.16 $q = 0$; $w = \Delta U = 4.12$ KJ; $\Delta H = 5.37$ KJ; $V_f = 11.8$ dm^3; P = 5.21 atm

Q.17 $C_{V,m} = 31.6$ JK^{-1}mol^{-1} Q.18 $w = -3.988$ kJ

Q.19 $W = P_0V_0$; $q_{CA} = -\frac{5}{2}P°V°$; $q_{AB} = 3P°V°$; $q_{BC} = \frac{1}{2}P°V°$ $T_{max} = \frac{25}{8}\left(\frac{P°V°}{R}\right)$

Q.20

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	R ln 2	R ln 2	0	0
C	Isobaric	–5/2 R (273)	R (273)	–3/2 R (273)	–5/2 R (273)
	Cyclic	–R(273) + R ln 2	R(273)-R ln 2	0	0

Q.21

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	–R ln 2	R ln 2	0	0
	Cyclic	–R(273) + R ln 2	–R(273)–R ln 2	0	0

]

Q.22 (a) $T_1 = 243.60$ K; $T_2 = 2436.0$ K, (b) $\Delta E = 0$; $q = -w = +3262.88$ cal

Q.23 (a) AC, (b) 170 J, (c) 10 J

Q.24 (a) 600 K, (b) $q_{AB} = 3000$ cal; $q_{BC} = 1663$ cal; $q_{CD} = -1800$ cal; $q_{DA} = -1663$ cal; Total Q = 1200 cal, (c) W = –1200 cal

Kirchoff's Rule : Variation of Enthalpy with Temperature

Q.25 ΔH^o_{373} (H_2O (l)) = – 284.11 kJ Q.26 (a) 13.064 kJ mol^{-1}, (b) 10.587 kJ mol^{-1}

Second law & Entropy change in thermodynamic processes

Q.28 T = 1059 K Q.29 21.18 JK^{-1} mol^{-1} Q.30 (i) irreversible, (ii) reversible, (iii) impossible

Q.31 (i) 30 kJ, (ii) + 60 kJ, (iii) 100 J/K

Gibb's Function

Q.32 – 1721.8 J Q.33 $\Delta G^o = 4.3 \text{ kJ mol}^{-1} > 0$ Q.34 – 2864.5 KJ

Q.35 (i) – 9.83 Kcal/mole; (ii) – 6.81 Kcal/mole, (iii) – 10.13 Cal / Kmole, (iv) –9.83 Kcal/mole, (v) + 45.13 Cal/ K mole

PROFICIENCY TEST

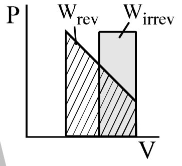
Q.1

1.	T	2.	T	3.	F	4.	T	5.	T
6.	T	7.	T	8.	T	9.	F	10.	T

Q.2

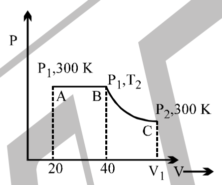
1.	negative	2.	isolated	3.	two	4.	reversible
5.	decresing	6.	isentropic	7.	Initial, final	8.	decrease
9.	zero	10.	positive				

EXERCISE II



Q.1 (a) $T_2 = 395.8$; $V_2 = 16.24$ L; $W_{rev} = 1194.72$ J,
(b) $V_2^1 = 17.24$ L ; $T_2^1 = 420$ K , $W_{irrev} = 1496.52$ J

Q.2 $\Delta H = 12168$ calories; $\Delta E = 11623$ calories



Q.3 (a) , (b) $P_2 = 0.435$ atm $V_1 = 113.13$ litre, (c) $W_T = –3000$ cal

Q.4 (i) $q = – w = 17.54$ kJ , $\Delta U = 0$ and $\Delta H = 0$; (ii) $q = 0$, $w = \Delta U = –10.536$ kJ and $\Delta H = –14.75$kJ
(iii) $q = 0$, $w = 0$, $\Delta U = 0$ and $\Delta H = 0$ (iv) $q = 0$; $\Delta U = w = – 7.14$ KJ; $\Delta H = – 9.996$ KJ,
(v) $q = –w = 10.0$ KJ, $\Delta U = \Delta H = 0$

Q.5 (a) $q = \Delta H = 1558.88$, $\Delta U = 935.33$; $w = – P(\Delta U) = – 623.55 \text{ J mol}^{-1}$
(b) $w = – 2149.7$; ΔU & $\Delta H = 0$, $q = – w$
(c) $q = 0$, $w = – 810.62$, $\Delta H = – 1351.03 \text{ Jmol}^{-1}$
for overall process $q = 3708.59$; $w = – 3583.88$, $\Delta U = 124.71$; $\Delta H = 207.85$

Q.6 (i) −90.5 (ii) −374.5 (iii) −3.26 (all in $\text{J mol}^{-1} \text{K}^{-1}$)

Q.7 (i) $\Delta S_{gas} = – \Delta S_{surr}$ and $\Delta S_{total} = 0$, (ii) $\Delta S_{total} = 2.808 \text{ J K}^{-1}$ (iii) $\Delta S_{total} = \Delta S_{sys} = 9.134 \text{ J K}^{-1}$

Q.8 (i) $\Delta S_{sys} = 0$; $\Delta S_{surr} = 0$ and $\Delta S_{total} = 0$, (ii) $\Delta S_{surr} = 0$; $\Delta S_{total} = \Delta S_{sys} = 0.957 \text{ JK}^{-1}$
(iii) $\Delta S_{sys} = \Delta S_{total} = 3.81 \text{ JK}^{-1}$

Q.9 ΔU & $\Delta H = 0$; $w = 623.55$; $q = – 623.55 \text{ J mol}^{-1}$

Q.10 ΔH_{vap}(25°C) = 43.97 kJ/mol = 2.433 kJ/gm, ΔH_{vap} (100°C) = 40.62 kJ/mol (given)

Q.11 $\Delta U = 501$ J ; $\Delta H = 99.5$ kJ

Q.12 (i) $w_{AB} = – 1496.52$ J, $w_{BC} = – 1446.63$ Joule, $w_{CD} = 0$, $w_{DA} = 1728.84$ Joule ;
(ii) $q_{AB} = 5237.82$ Joule, $q_{BC} = 1446.63$ Joule, $q_{CD} = – 3741.3$ Joule, $q_{DA} = 1728.84$ Joule;
(iii) $\Delta H_{AB} = 6235.5$ Joule, $\Delta H_{BC} = 0$, $\Delta H_{CD} = – 6235.5$ Joule, $\Delta H_{DA} = 0$ Joule

Q.13 (i) Rev. Process $\Delta S_{syst} = \frac{3}{2} R \ln 10$; $\Delta S_{surr} = -\frac{3}{2} R \ln 10$

(ii) Irr Process $\Delta S_{sys} = \frac{3}{2} R \ln 10$; $\Delta S_{surr} = \frac{3}{2} R\,(0 - 9)$; $\Delta S_{total} = \frac{3}{2} R\,(1.403)$

Q.14 $205.08\ JK^{-1}\ mol^{-1}$

Q.15 (a) $m = \frac{nRT}{gh}\left(1 - \frac{P_2}{P_1}\right)$, (b) $m' = \frac{nRT}{gh}\left(\frac{P_1}{P_2} - 1\right)$, (c) $m' - m = \frac{nRT}{gh}\left(\frac{(P_1 - P_2)^2}{P_1 P_2}\right)$

Q.16 $-216.198\ J\ mol^{-1}$

Q.17 (a) $q_P = \Delta H = 24.058$ kJ , $w = -4.157$ kJ , $\Delta U = 19.90$ kJ ; (b) $\Delta U = 19.90$ kJ ; $\Delta H = 24.058$; $w = 0$

Q.18 $w = -nRT\, ln \frac{V_f}{V_i} - n^2 a\left(\frac{1}{V_f} - \frac{1}{V_i}\right)$

Q.19 $\Delta_r H^\circ = 82.801\ kJ\ mol^{-1}$, $\Delta_r S^\circ = 180.33\ J\ K^{-1}\ mol^{-1}$

Q.20 $\Delta_r G = 5.59\ kJ\ mol^{-1}$

EXERCISE III

Q.1	C	Q.2	C	Q.3	C	Q.4	A	Q.5	D	Q.6	C	Q.7	D
Q.8	A	Q.9	B	Q.10	C	Q.11	A	Q.12	C	Q.13	D	Q.14	C
Q.15	D	Q.16	C	Q.17	A	Q.18	A	Q.19	(i) B (ii) C (iii) A (iv) C				
Q.20	(i) B (ii) D (iii) A (iv) C												

EXERCISE IV

Q.1	D	Q.2	A	Q.3	C	Q.4	C
Q.5	B	Q.6	C	Q.7	A	Q.8	B

Q.9 –557 kJ/mol

Q.10 $\Delta U = 0.1$ litre atm, $\Delta H = 9.9$ litre atm

Q.11 (ii) $-W = q = 620.77$ J, (iii) $\Delta H = 0$, $\Delta U = 0$, $\Delta S = 0$

Q.12 $\Delta H^\circ = -285.4$ kJ/mol, $\Delta G^\circ = -257.2$ kJ/mol

Q.13 $\Delta H = -114.52$ J