

THERMODYNAMICS & THERMOCHEMISTRY

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JEE(Advanced) Syllabus

First law of thermodynamics; Internal energy, work and heat, pressure-volume work; Enthalpy; Second law of thermodynamics, Entropy, Free energy, Criterion of spontaneity; Heat of reaction, fusion and vapourization, Hess's law.

JEE(Main) Syllabus

Thermal equilibrium, Zeroth law of thermodynamics, concept of temperature. Heat, work and internal energy. First law of thermodynamics. Second law of thermodynamics: reversible and irreversible processes. Carnot engine and its efficiency.



Thermodynamics & Thermochemistry

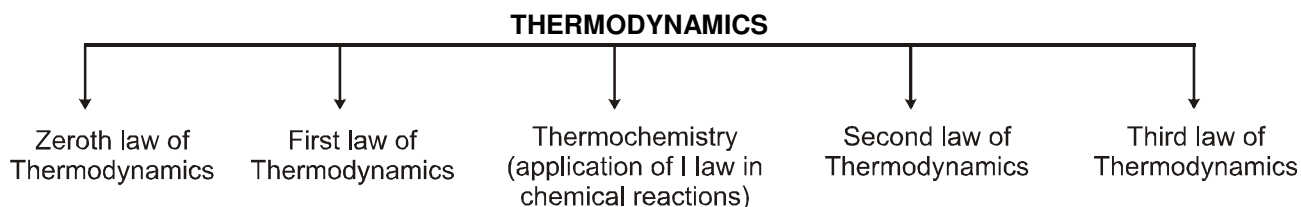
1. THERMODYNAMICS

Thermodynamics Ist Law

Section (A) : Basic definitions

Introduction:

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



Application of thermodynamics:

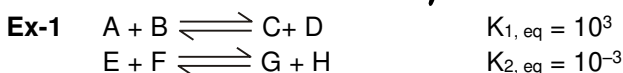
In chemistry using thermodynamics

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

Limitations of thermodynamics:

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

Solved Examples



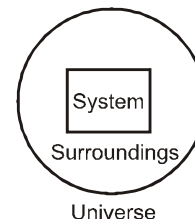
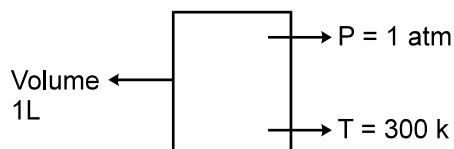
Which of these reaction will attain equilibrium earlier ?

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

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

Terms to be used in thermodynamics:

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



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

- **Surrounding** : Rest of the universe.
- **Universe** : Universe = System + Surroundings

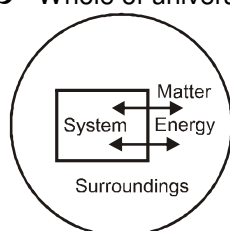




- **Boundary** : Anything which separates system & surroundings is called boundary.
 - Boundary can be real or imaginary.
 - Boundary can be flexible or rigid
e.g. air in a flexible balloon (flexible boundary) while air in a room (fixed boundary).
 - Boundary can be adiabatic (non-conducting; $\Delta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

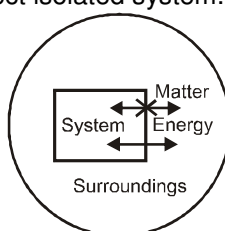
Types of system :

- **Open system**: System which can exchange energy & matter both with the surroundings.
e.g. : Living systems(any living organism) are open systems, air in an open room; water flow in pipe.
- **Closed system**: System which can exchange only energy but cannot exchange matter with the surroundings is called closed system.
e.g. : any matter in a closed container ; Heating of water in closed container.
- **Isolated system**: System which cannot exchange energy and matter both with the surroundings.
e.g. : Water in thermos flask.(Though not a perfectly isolated system but can be taken as, for small interval of time as the energy exchanges are negligible) ; Hot tea in thermos (few time).
 - Whole of universe is a perfect isolated system.



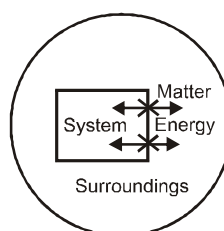
Universe

Open System



Universe

Close System



Universe

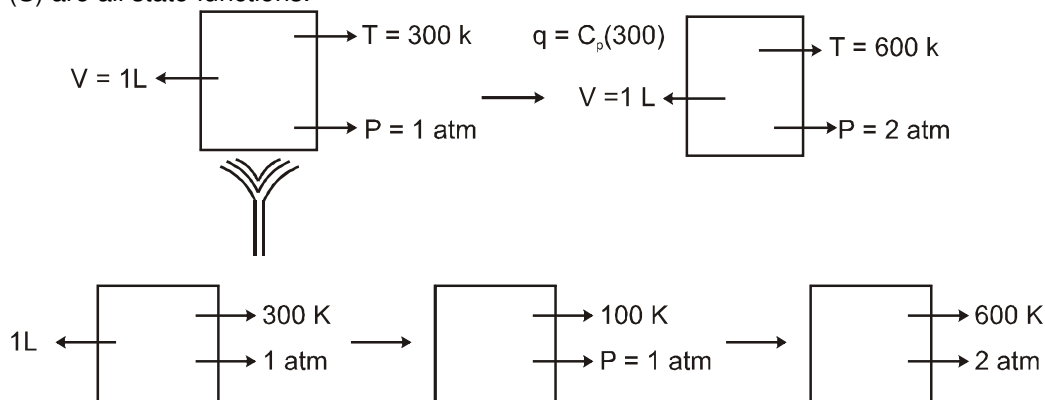
Isolated system

- **State of a system:**
 - It means the condition in which the system is present.
 - It can be specified/defined by measuring/ specifying some observable/measurable properties of the system like pressure, volume, temperature, amount of substance, elasticity, heat capacity etc.
e.g. For an ideal gaseous system state of the system can be defined by specifying volume, temperature and pressure.
 - We may have to specify more properties of the system depending on the complexity of the system.

State function (State variables) :

- Property of a system which is dependent only on the state of the system i.e. it is a point function
- It is independent of the path adopted to attain a particular state.
e.g. In Mechanics, Displacement of any object will a state function but distance travelled by the object will be a path function.
For any thermodynamic system,
Temperature, Pressure, Volume, Total internal energy (E or U), Enthapy(H), Gibbs free energy (G), Entropy (S) are all state functions.

e.g.



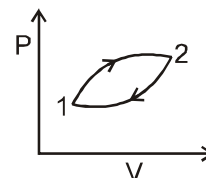


In the above example the final temperature, pressure, and the volume will be same in both the above ways but the work involved and the heat exchanged during the processes will be different.

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

$$\oint dx = 0$$

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



● Path function :

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

● Types of properties

Extensive properties :

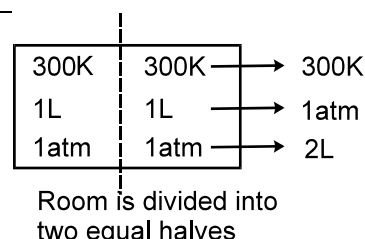
- Functions or properties of the system which are dependent on mass or on size of the system are called Extensive Properties.
- Extensive functions are additive in nature (The addition of the volumes of the two parts equals the volume of the whole of the room.)
e.g. Volume, Mass, Total heat capacity, Total internal energy (E), Enthalpy(H), Gibbs Free Energy(G), Entropy(S) ; moles etc.

Intensive properties :

- Functions or properties which are not mass dependent or size dependent are called intensive function.
- Intensive properties are not additive in nature.
eg. Temperature, pressure, molar heat capacity, specific heat capacity, density, concentration, vapour pressure; B.P. ; F.P. ; Viscosity ; pH etc.

How to identify extensive or intensive properties

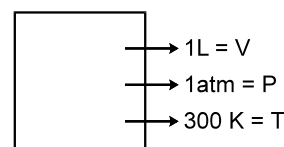
If a system in a particular state is divided into two equal or unequal parts, the properties which have value equal to the original value of that property for the whole of the system is called an **Intensive property**. While the properties which have values different from the values for whole of the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



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

● Thermodynamic equilibrium:

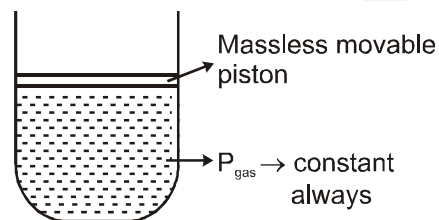
- When there is no change in any observable or measurable property of a system with time then the system is said to be in thermodynamic equilibrium.
- Thermodynamic equilibrium consist of three types of equilibrium.
 - Mechanical equilibrium
 - Thermal equilibrium
 - Chemical equilibrium





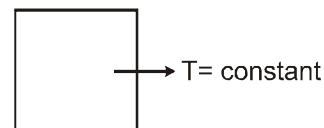
- **Mechanical equilibrium:**

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



- **Thermal equilibrium:** There should not be any temperature gradient (difference).

Temperature may have different values at different places/locations in a system but it should remain constant with time.



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

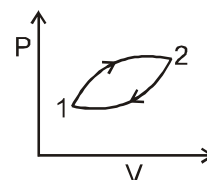
Section (B) : Thermodynamics processes & graph

- **Types of thermodynamic process on basis of state/conditions**

Thermodynamic process : Any method/process by which system can change its state from one state of thermodynamic equilibrium to another state of thermodynamic equilibrium.

There can be infinite type of thermodynamic processes, out of these the following are important ones:

1. **Isothermal process :** $T = \text{constant}$
 $T_i = T_f$
 $\Delta T = 0$
2. **Isochoric process :** $V = \text{constant}$
 $V_i = V_f$
 $\Delta V = 0$
3. **Isobaric process :** $P = \text{constant}$
 $P_i = P_f$
 $\Delta P = 0$
4. **Adiabatic process :** $q = \text{constant}$
or heat exchange with the surrounding = 0 (zero)
5. **Cyclic Process :** A system undergoes a series of changes and comes back to the initial state.
 $\Delta V = 0$
 $\Delta H = 0$



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

- **Reversible process :**

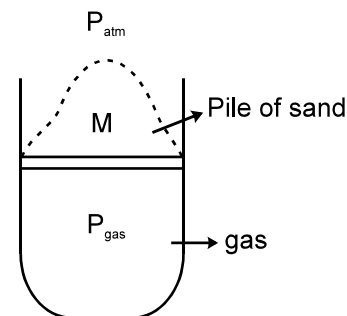
The process that can be reversed by a very small change is known as reversible process.

- If a process is carried out in such a manner so that the system is always in thermodynamic equilibrium at every stage of the process.
- If the process is carried out such that the difference in driving force and opposing force is infinitesimally small so that process takes place at infinitesimally slow rate.

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

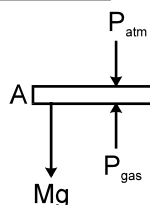
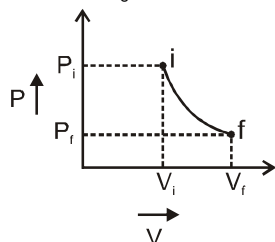
- An ideal reversible process will take infinite time to get completed.
- It is carried out infinitesimally slowly.
- Strictly speaking there is no ideal reversible process in universe.

To get an idea of a reversible process we can consider the following system an ideal gas is enclosed in a container and a massless piston is put on the gas on which a pile of sand is placed having particles of negligible mass. To carry out a reversible expansion we will slowly decrease the mass of the sand let's say by removing the particles one by one, so the expansion of the gas will take place at infinitesimally small rate and we can always assume the system to be in thermodynamic equilibrium. So, the expansion will be of reversible type.





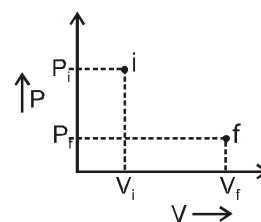
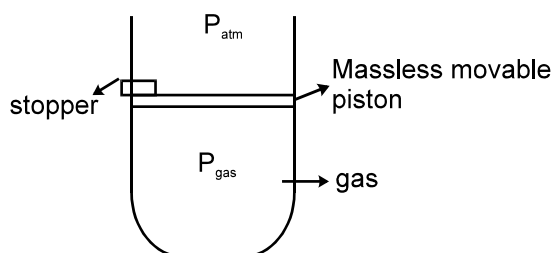
FBD of piston

For piston to be in equilibrium : $P_{\text{gas}} = P_{\text{atm}} + Mg/A$ 

Sign : i – f : expansion
f – i : compression

- **Irreversible process:** The process can not be reversed by a small change is known as irreversible.
 - If a process is carried out in such a manner so that the system is in thermodynamic equilibrium.
 - (I) Only at initial & final state of the process but not at the intermediate stages.
 - (II) System may be in thermodynamic equilibrium state at some finite number of intermediate stages only - for example - n step irreversible expansion of a gas.
 - If during the process there is a finite difference in driving force and opposing force so that process takes place with a finite rate; $F_{\text{driving}} - F_{\text{opposing}} = \Delta F$.
 - Irreversible processes will get completed in finite time.
 - At intermediate stages of the irreversible process, different state function such as pressure, temperature etc. are not defined.
 - All real process are irreversible.

Consider the above system. If the stopper placed over the piston is removed, then the piston will move with almost infinite acceleration and will keep moving to a position where the pressure of the gas becomes equal to the external pressure. Since the process will get completed in finite time and there was a finite difference between the driving force and the opposing force so, process is irreversible. During the process, the pressure of the gas can not be defined as it will be having different values at different locations.



Sign : i – f : expansion
f – i : compression

● Modes of energy exchange:

These are two ways by which a system can interact or can exchange energy with its surroundings.

(i) Heat & (ii) Work

Heat & Work both are forms of energy.

Heat: When the energy transfer across a boundary as a result of temperature difference between system & surroundings is known as heat.

● Modes of heat transfer: Conduction (solids); Convection (fluids); Radiation (vacuum)

Work: Energy transfer which is not heat or which is not because of temperature difference is called work.



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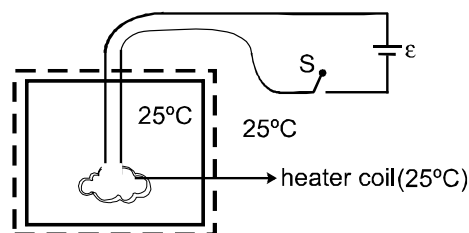
ADVTDS - 5



Work can be of many types: Mechanical work, Electrical work, Magnetic work, Gravitational work etc.

○ **The same energy transfer can be called work or can also be called heat depending on choice of the system.**

To understand this, consider a system shown below in which water is taken in a closed container at 25°C , the surroundings is also at temperature of 25°C and there is a heater coil in the dipped in the water which is connected to a battery through a switch S. Heater coil is also at 25°C initially. Now, there are two ways in which system can be chosen.



I-System: All contents of the container (water + Heater coil).

When switch is turned on there will be increment in the temperature of the system. Since the temperature of the surroundings was equal to temperature of the system so, heat can not flow but still there is increment in the energy of the system and hence, there is temperature increment. This must be because of electrical work done by the battery on the system not because of the heat transfer as initially temperatures were equal.

II-System: Water only is our system. Heater coil will be part of the surroundings.

In this case when switch is turned on the temperature of the heater coil will increase first so there will be a temperature difference between system & surroundings. Hence, this energy transfer will be called heat.

● IUPAC Sign convention about Heat and Work

Any energy given to system is taken positive so heat given to system = positive

heat taken out from system = Negative

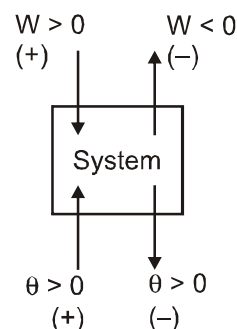
Work done on the system = Positive

Work done by the system = Negative

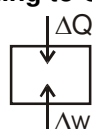
The sign convention is different from physics, but the meaning always comes out to be same only in equation we have to use a different sign convention for work.

So if in any problem, $w = -10 \text{ J}$

It means system has done work of 10 Joule on surroundings.



According to Chemistry :



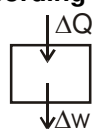
$$\Delta U = \Delta Q + \Delta W$$

IUPAC convention of Heat

1. Heat given to the system = +ve

3. Work done on the system = +ve

According to Physics :



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

2. Heat coming out of the system = -ve

4. Work done by the system = -ve

Section (C) : Work calculation

WORK DONE (w) :

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

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

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

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

1 litre. atm = 101.3 Joules = 24.206 cal



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

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

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

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

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

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

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

1. ISOTHERMAL PROCESS :

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

(a) **Isothermal reversible expansion :**

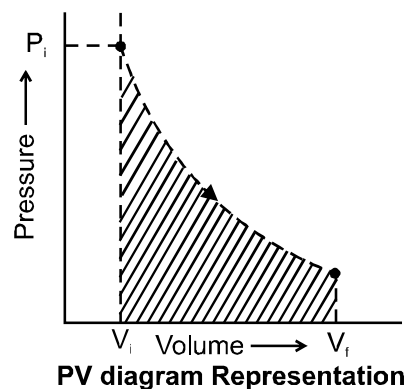
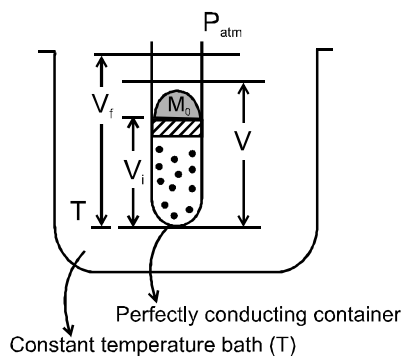
$$P_{\text{ext}} = P_0 + \frac{mg}{A} = P_{\text{gas}} = P \text{ (always)}$$

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

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

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

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



Work = Area under the P–V diagram

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

$$W = -ve$$

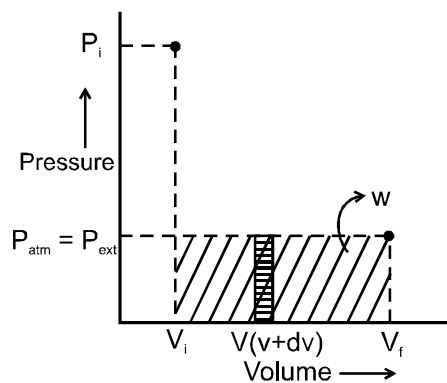
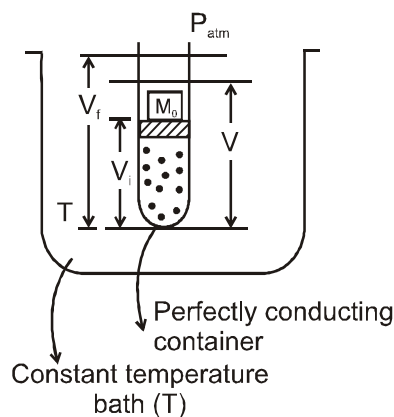
(b) **Irreversible isothermal expansion :**

(i) **Single step isothermal expansion**

We are assuming expansion against atmospheric pressure which need not be the case in a given problem.

A mass equal to m_0 is placed on piston initially to maintain equilibrium.

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



PV diagram Representation

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

In this case, the pressure of the gas will not be defined as the sudden expansion has taken place so all the molecules of sample will not get the information of expansion simultaneously, there will be a time gap and hence, there will be a **state of turbulence**. From some intermediate state of volume ' V ', the work done is slight expansion from

$V \longrightarrow (V + dV)$

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

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

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

(ii) Two step isothermal expansion:

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

$$M_0 = (m_1 + m_2)$$

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

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

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

$$P_{ext_1} \cdot V_1 = P_i V_i \text{ (isothermal)}$$

Now, if second mass m_2 is also removed then expansion

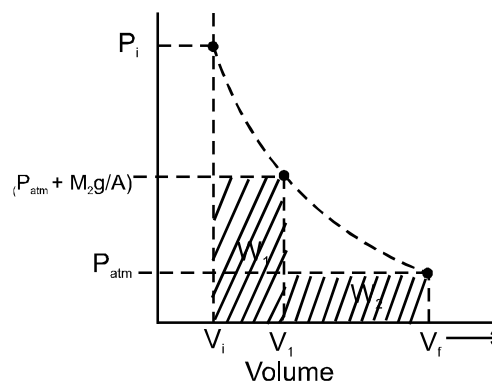
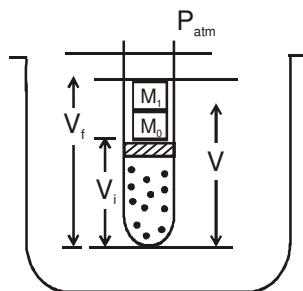
$V_1 \longrightarrow V_f$ will take place against constant pressure

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

$$\text{work done is expansion } V_i \longrightarrow V_1 ; \quad W_1 = -(P_{atm} + M_2g/A) (V_1 - V_i)$$

$$\& \text{ work done is expansion } V_1 \longrightarrow V_f ; \quad W_2 = -P_{atm} (V_f - V_1)$$

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

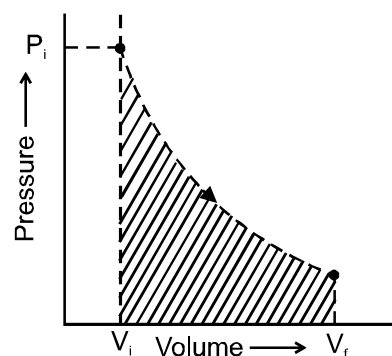
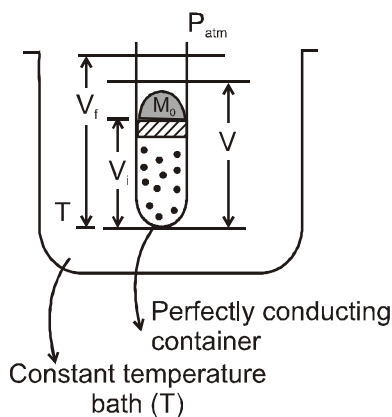


PV Diagram representation

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

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

If $n \rightarrow \infty$; Irreversible process becomes reversible process



PV Diagram representation

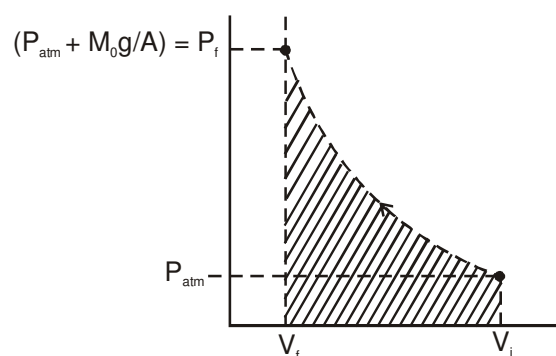
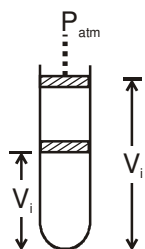
(B) Isothermal compression of ideal gas :

(a) Reversible isothermal compression of an ideal gas

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

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

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



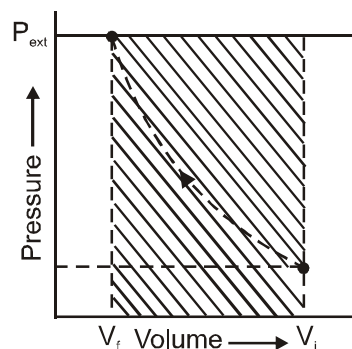
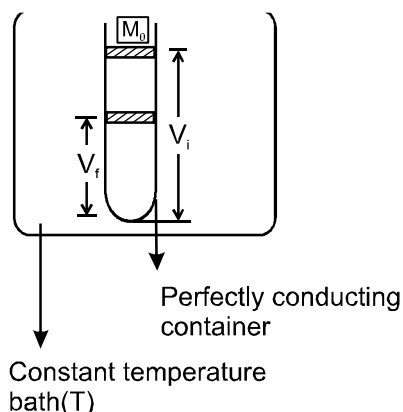
**(b) Irreversible isothermal compression of an ideal gas****(i) Single step compression :**

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

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

so, to calculate total work done on the gas

$$W = \int dw = -\int_{V_i}^{V_f} P_{\text{ext}} \cdot dv ; \quad W = -P_{\text{ext}} (V_f - V_i)$$

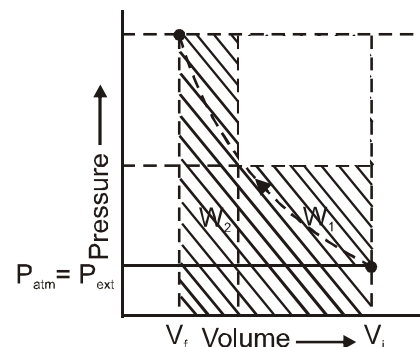
**(ii) Two step compression :**

Place mass m_0 in two fragments ($m_1 + m_2$) the graphical representation will make the calculation of work done. If m_1 is placed first, then the first compression has taken place against external pressure of $(P_{\text{atm}} + m_1g/A)$

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

$$\text{Similarly, } W_2 = -(P_{\text{atm}} + m_2g/A) (V_f - V_1)$$

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

**Conclusion :**

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

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

- { output – work done by engine/machine/system
- { input – work done by system on a surrounding

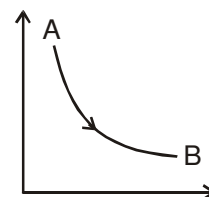
- **If expansion/compression takes place against constant external pressure then it is irreversible.**
- **If there is sudden change then the process is irreversible.**

Reversible and irreversible isothermal process.

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

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

If for the process $A \rightarrow B$ work = w , heat = Q then if for the process $B \rightarrow A$, work = $-w$, heat = $-Q$ then the process is reversible.



- If the external pressure is constant in isothermal process, process is irreversible.



Solved Examples

Ex-2. Calculate the work performed when 2 moles of hydrogen expand isothermally and reversibly at 25°C from 15 to 50 litres.

Sol. We have, $W = -2.303 n RT \log \frac{V_2}{V_1} = -2.303 \times 2 \times 2 \times 298 \times \log \frac{50}{15} = -1436$ calories.

Ex-3. If a gas at a pressure of 10 atm at 300 K expands against a constant external pressure of 2 atm from a vol. of 10 litres to 20 litres find work done? [Isothermal process]

Sol. Process is irreversible

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

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

2. ISOCHORIC PROCESS :

Since $dv = 0$

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

3. ISOBARIC PROCESS :

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

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

Section (D) : Heat & Internal energy

Calculation of ΔE :

Internal Energy (E, also denoted by U) :

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

- It is the sum of all forms of energies present in the system.

$$E = E_{\text{Translational}} + E_{\text{Rotational}} + E_{\text{Vibrational}} + E_{\text{bonding}} + \dots$$

$$\Delta E = E_{\text{Final}} - E_{\text{Initial}}$$

● Thermodynamic definition of an ideal gas :

- For a gas the internal energy is directly proportional to its absolute temperature then the gas is termed as an ideal gas.

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

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

- It is an extensive property & a state function. It is exclusively a function of temperature.

If $\Delta T = 0$; $\Delta E = 0$ as well.

- With change in temperature only kinetic energy changes.

● Degree of freedom : The total no of modes on which a molecule of an ideal gas can exchange energy during collisions is known as its degrees of freedom.

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

Rotational degree of freedom

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

If "f" is initial degree of freedom for that gas.

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



● Law of equipartition of energy :

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

Where k is Boltzmann constant

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

∴ For n moles,

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

● Calculation of Heat (q)

- Heat is a path function and is generally calculated indirectly using 1st law of thermodynamics.
- First calculate ΔE and W & then q or heat can be calculated if heat capacity of any process is given to us.

○ Total Heat Capacity (C_T)

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

$$\text{Mathematically, } C_T = \frac{dq}{dT} \text{ J/}^\circ\text{C}$$

- It is extensive properties and path function.

$$\text{So, } dq = C_T dT$$

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

○ Molar heat capacity (C)

Heat required to raise temperature of 1 mole of a substance by 1°C

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

$$\text{So, } dq = nC dT$$

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

C is intensive path function.

C_p is molar heat capacity at constant pressure

C_v is molar heat capacity at constant volume

C_p and C_v are intensive but not a path function

○ Specific heat capacity (s) :

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

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

$$\text{So, } dq = ms dT$$

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

S is intensive path function

S_p is specific heat capacity at constant pressure

S_v is specific heat capacity at constant volume

S_p & S_v are intensive but not a path function

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

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

Where m – weight of substance, M – molar mass of substance, n – no. of moles of the substance





For isothermal process

$$C = \pm\infty$$

For isobaric process

$$C = C_p$$

For isochoric process

$$C = C_v$$

For adiabatic process

$$C = 0$$

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

- (1) Heat capacity is a path function and different type of heat capacities are defined
- (2) Remember heat capacity of a substance is not fixed it is dependent on type of process which is being performed on that substance.

Solved Examples

Ex-4. During an expansion of ideal gas the work done by gas is 100 J and the heat capacity of process is found to be $+2 \text{ J/}^\circ\text{C}$. Find ΔE of gas if the final temperature of gas is 25°C higher than its initial temperature.

Sol. $\Delta E = q + W$

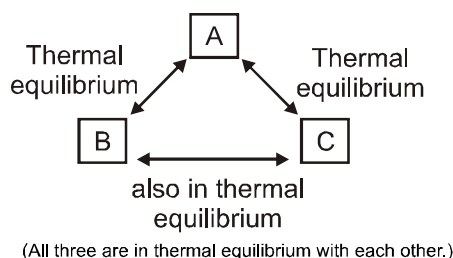
$$q = 2 \times 25 = 50 \text{ J} \text{ \& } W = -100 \text{ J}$$

$$\Delta E = 50 - 100 = -50 \text{ J}$$

Section (E) : First law of thermodynamics

Zeroth Law of Thermodynamics (ZLOT) :

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



First Law of Thermodynamics (FLOT) :

Law of energy conservation :

Energy of total universe is always conserved.

or

Total energy of an isolated system is always conserved.

or

Hence absolute value of E can never be calculated only change in value of E can be calculated for a particular process.

Mathematical form of First Law of thermodynamics.

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

$$E_2 = E_1 + q + w$$

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

Application of First Law

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

Since

$$\Delta W = -P\Delta V$$

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



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

4. Adiabatic process :

$dQ = 0$ (no heat changed b/w system and surrounding)
 $dU = dQ + dW$

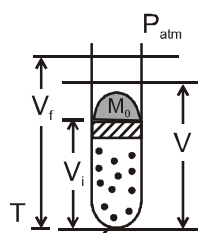
$$\Rightarrow nC_v dT = -PdV \quad \Rightarrow \quad \int nC_v dT = \int -\frac{nRT}{V} \cdot dV$$

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

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

$$T_2 V_2^{\gamma-1} = T_1 V_1^{\gamma-1} \quad \text{or} \quad T V^{\gamma-1} = \text{constant}$$

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



Perfectly non-conducting container

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

Operation of adiabatic process

(a) Reversible Adiabatic

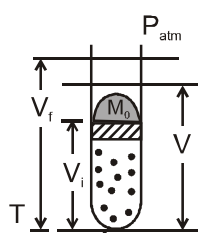
- Operation wise adiabatic process and isothermal process are similar hence all the criteria that is used for judging an isothermal irreversible processes are applicable to adiabatic process.
- Also, volume in case of isothermal volume is more than that of adiabatic at constant pressure and no of moles,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

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

$$\therefore w = - \int \frac{K}{V^\gamma} \cdot dv,$$

$$\Rightarrow W = -K \left[\frac{V_2^{-\gamma+1} - V_1^{-\gamma+1}}{(1-\gamma)} \right] = \frac{P_2 V_2^\gamma \cdot V_2^{1-\gamma} - P_1 V_1^\gamma \cdot V_1^{1-\gamma}}{\gamma-1}$$

$$\Rightarrow \text{Work done} = \frac{P_2 V_2 - P_1 V_1}{\gamma-1} \quad (\text{as } K = P_2 V_2^\gamma = P_1 V_1^\gamma)$$



Perfectly non-conducting container

(b) Irreversible Adiabatic

Adiabatic irreversible expansion -

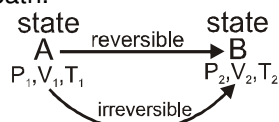
$$W = \int -P_{\text{ext.}} \cdot dv = -P_{\text{ext}} (V_2 - V_1)$$

$$\text{and } \int du = \int dw$$

$$\therefore W = \Delta u$$

$$W = nC_v (T_2 - T_1) = \frac{nR(T_2 - T_1)}{\gamma-1} = \frac{P_2 V_2 - P_1 V_1}{\gamma-1}$$

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

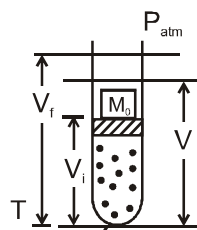


If the two states are linked by an adiabatic reversible and irreversible path then

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

But as u is a state function

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



Perfectly non-conducting container



as work is a path function.
If we assume that

$$W_{\text{irrev.}} = W_{\text{rev.}} \Rightarrow \text{It implies that}$$

$$\Delta U_{\text{rev.}} \neq \Delta U_{\text{irrev.}} \quad \text{Which again is a contradiction as } U \text{ is a state function.}$$

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

○ Comparison of Adiabatic Expansion (single stage Vs Infinite stage)

Single stage means irreversible process

Infinite stage means reversible process

In adiabatic compression process,

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

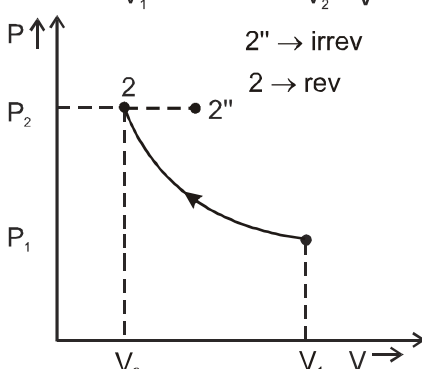
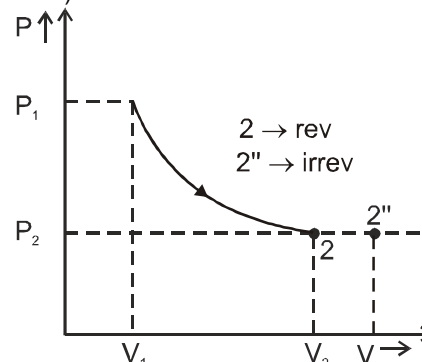
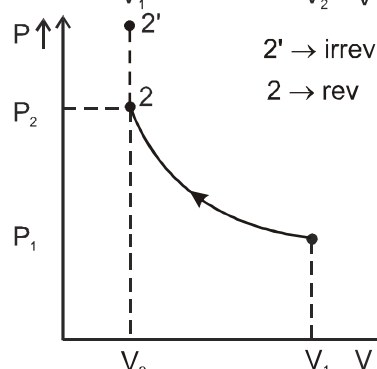
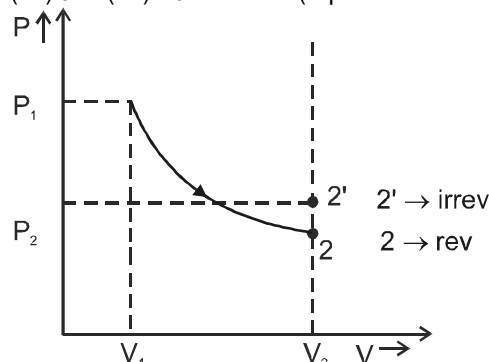
$$\therefore (T_2)_{\text{rev.}} < (T_2)_{\text{irrev}}$$

$$(P_2)_{\text{rev.}} < (P_2)_{\text{irrev}}$$

(If volume change are same)

$$(V_2)_{\text{rev.}} < (V_2)_{\text{irrev}}$$

(If pressure change are same)



● Comparison of single stage Vs two stage expansion(adiabatic).

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

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

○ Adiabatic Irreversible process (calculation of state parameters)

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

P_1, V_1, T_1

P_2, V_2, T_2

$$W = \frac{nR(T_2 - T_1)}{\gamma - 1} = \frac{P_2 V_2 - P_1 V_1}{\gamma - 1} = -P_{\text{ext.}} (V_2 - V_1), \quad \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

● Free expansion :

Always going to be irreversible and since $P_{\text{ext}} = 0$

$$\text{So, } dW = -P_{\text{ext.}} dV = 0$$

If no heat is supplied $q = 0$

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



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ADVTDS - 15



Section (G) : Enthalpy

Calculation of C_p and C_v

(a) Constant volume process (Isochoric)

$$dU = dq + dw$$

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

$$\therefore dU = (nC_v dT)_v$$

$$dU = nC_v dT$$

C_v is Specific molar heat capacity at constant volume.

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

(b) Constant pressure process (Isobaric) :

$$dU = dQ + dW$$

$$dU = dQ - PdV$$

$$\Rightarrow dQ = dU + PdV \quad \dots\dots\dots (i)$$

Defining a new thermodynamic function

$$H \equiv \text{Enthalpy}$$

- It is a state function and extensive property
- It is mathematically defined as :

$$H = U + PV$$

as $dH = dU + d(PV)$

as $P = \text{constant}$

$$dH = dU + PdV \quad \dots\dots\dots (ii)$$

from equation (i) & (ii)

$$\therefore dH = (dq)_p \quad \text{only at constant pressure.}$$

Heat given at constant pressure = Change in enthalpy

$$dH = (nC_p dT)_p$$

$$dH = nC_p dT$$

● Relation between C_p and C_v for an ideal gas

$$H = U + PV$$

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

for an ideal gas

$$PV = nRT$$

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

$$nC_p dT = nC_v dT + nRdT$$

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

Table # 1 At Normal temperature

S.No.	Gas	Degree of freedom	$C_{v,m} \left(\frac{fR}{2} \right)$	$C_{p,m} \left(\frac{f+2}{2} R \right)$	$\gamma = \left(\frac{f+2}{f} \right)$	Examples
1.	Monoatomic	3	$\frac{3R}{2}$	$\frac{5R}{2}$	$\frac{5}{3}$	He; Ne
2.	Diatomic	5	$\frac{5R}{2}$	$\frac{7R}{2}$	$\frac{7}{5}$	N ₂ ; O ₂ ; H ₂
3.	Linear polyatomic	5	$\frac{5R}{2}$	$\frac{7R}{2}$	$\frac{7}{5}$	CO ₂ ; HCl
4.	Non-Linear polyatomic	6	$\frac{6R}{2}$	$\frac{8R}{2}$	$\frac{8}{6}$	H ₂ O; NH ₃ ; CH ₄

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





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

Case - I

For an ideal gas undergoing a process.

the formula to be used are

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

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

$$W = - \int P_{\text{ext}} \cdot dV$$

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

$$du = dq + dw$$

Solved Examples

Ex-5. Calculate the maximum work done when pressure on 10 g of hydrogen is reduced from 20 atm to 1 atm at a constant temperature of 273 K. The gas behaves ideally. Will there be any change in internal energy? Also, calculate 'q'.

Sol. We have, $W = -2.303 nRT \log \frac{P_1}{P_2}$

$$n = \text{number of moles of hydrogen} = \frac{\text{wt. in grams}}{\text{mol. wt.}} = \frac{10}{2} = 5 \text{ moles.}$$

$$\text{Thus, } W = -2.303 \times 5 \times 2 \times 273 \times \log \frac{20}{1} = -8180 \text{ calories.}$$

Further, the change in state of the system at constant temperature will not change internal energy i.e., $\Delta U = 0$.

$$\text{Again, } q = \Delta U - W = 0 - (-8180) = 8180 \text{ calories.}$$

Case - II

For solids and liquid system :

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

$$dH = nC_p dT \neq \left(\frac{f}{2} + 1 \right) nR dT \quad (\text{as it is not an ideal gas})$$

$$W = - \int P_{\text{ext}} \cdot dV$$

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

$$dU = dq + dw$$

Solved Examples

Ex-6. A liquid of volume of 100 L and at the external pressure of 10 atm—Lt the liquid is confined inside an adiabatic bath. External pressure of the liquid is suddenly increased to 100 atm and the liquid gets compressed by 1 L against this pressure then find,

(i) work (ii) ΔU (iii) ΔH

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

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

$$\Rightarrow 100 = \Delta U$$

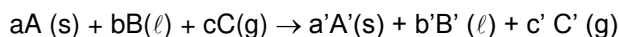
$$\Delta H = \Delta U + (P_1 V_2 - P_1 V_1)$$

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

$$= 100 + 100 \times 89 = 9000 \text{ lit atm.}$$

$$1 \text{ L. atm} = 101.3 \text{ Joule.}$$



**Case - III****For chemical reactions :**

$$\begin{aligned} W &= -\int P_{\text{ext.}} dV = \int -P_{\text{ext.}} (V_f - V_i) \\ &= -P_{\text{ext.}} [(V_{A'}(s) + (V_{B'}(\ell) + (V_{C'}(g) - (V_A(s) + (V_B(\ell) + (V_C(g)))] \\ \therefore W &= -P_{\text{ext.}} [V_{C'}(g) - V_C(g)] \\ &= -P_{\text{ext.}} \left[\frac{n'_c RT}{P_{\text{ext.}}} - \frac{n_c RT}{P_{\text{ext.}}} \right] = - \frac{P_{\text{ext.}} (n'_c - n_c) RT}{P_{\text{ext.}}} \\ W &= -(n'_c - n_c) RT \\ \therefore W &= -\Delta n_g RT \\ dU &= dq + dw \\ \text{if at constant pressure} \\ dq &= dH \\ \therefore dU &= dH - pdV \\ dU &= dH - \Delta n_g RT \\ \therefore dH &= dU + \Delta n_g RT \end{aligned}$$

Solved Examples

Ex-7. For the combustion of 1 mole of liquid benzene at 25°C, the heat of reaction at constant pressure is given by, $C_6H_6(\ell) + 7\frac{1}{2}O_2(g) \rightarrow 6CO_2(g) + 3H_2O(\ell)$; $\Delta H = -780980$ cal.

What would be the heat of reaction at constant volume?

Sol. We have, $\Delta H = \Delta E + \Delta n_g RT$
 Here, $\Delta n_g = 6 - 7.5 = -1.5$.
 Thus, $\Delta E = \Delta H - \Delta n_g RT = -780980 - (-1.5) \times 2 \times 298 = -780090$ calories.

Section (H) : Phase transition

Case - IV During phase transformation.

Phase transitions generally take place at constant pressure (unless specified) and at constant temperature. So, $\Delta T = 0$.

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

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

Hence, $\Delta H \neq 0$.

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

To calculate W , use $dW = -P_{\text{ext.}} dV$ and then calculate ΔE using 1st law of thermodynamics.

Solved Examples

Ex-8. Calculate q , W , ΔE and ΔH when 100 g of $CaCO_3$ is converted into its aragonite form given density of calcite = 2 g/cc and density of aragonite = 2.5 g/cc

Sol. $CaCO_3 \rightleftharpoons CaCO_3$
 Calcite Aragonite $\Delta H = 2$ kJ/mole
 Generally for solid \rightarrow Solid
 solid \rightarrow Liquid
 solid \rightarrow Liquid
 transitions $W \ll q$ So, $\Delta E \approx q = \Delta H$
 while for gaseous conversion for example
 Solid \rightarrow gas
 Liquid \rightarrow gas
 $q = \Delta H \neq \Delta E$, as W will be significant



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

Thermodynamics IInd & IIIrd Law

Section (A) : Introduction about entropy

● IInd Law of thermodynamics :

Requirement : Ist law insufficient to Explain

Neutralization, Melting of ice $> 0^\circ$

Combustion, Freezing of water $< 0^\circ$

Fall of water, Boiling of water $> 100^\circ \text{C}$

Cooling of a hot body, Free expansion of a gas, mixing of gases.

Spontaneous / Natural / Irreversible Processes :

If a system moves along in a direction on its own and system, surrounding interactions without the help of any external agency, then that direction is known as spontaneous direction and the process is known as a spontaneous process.

Limitation :

First law cannot predict the direction of any process. But in nature a process is found to have a specific direction at certain conditions.

1. Energy can be the factor : To achieve stability

* All exothermic processes are spontaneous.

* All endothermic processes are non spontaneous.

Exceptions

* melting of ice (above 0°C) although $\Delta H > 0$, $\Delta E > 0$

* Vaporization of water (above 100°C) $\Delta H > 0$, $\Delta E > 0$

* Spreading of ink in water $\Delta H = 0$, $\Delta E = 0$

* Mixing of two gases

* Endothermic solution of salt $\Delta H > 0$, $\Delta E > 0$

2. It is observed that nature tries to distribute energy and matter uniformly (randomization)

Second law of thermodynamics :

Entropy of the universe is constantly increasing.

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0 \text{ for a spontaneous process.}$$

Where (S) = entropy is the measure of randomness or disorder. It is a state function and extensive property.

Mathematically

$$ds = \frac{dq_{\text{rev}}}{T} \text{ or } \Delta S = \int \frac{dq_{\text{rev}}}{T}, \quad \frac{dq}{T} \text{ is state function only for reversible process}$$

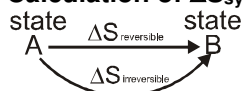
$$dS \propto dq_{\text{rev}}, \quad dS \propto \frac{1}{T}$$

At Higher T - entropy is already high. Therefore, heat addition will not introduce much change in the entropy.



Section (B) : Entropy Calculation

- **Calculation of ΔS_{system}**

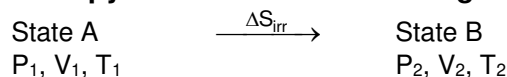


As 'S' is a state function. Hence ' ΔS ' will also be a state function.

$$\therefore \Delta S_{\text{irrev}} = \Delta S_{\text{rev}}$$

$$\Delta S = \int_A^B \frac{dq_{\text{rev}}}{T} \text{ reversible path}$$

- **Entropy calculation for an ideal gas undergo in a process.**



As 'S' is a state function. So, ΔS will not depend upon path

$$\Delta S_{\text{irrev}} = \Delta S_{\text{rev, system}} = \int_A^B \frac{dq_{\text{rev}}}{T} \text{ rev path.}$$

from the first law

$$dU = dQ + dw$$

$$dQ = dU - dw$$

for reversible path

$$dq = dq_{\text{rev}}$$

$$dq_{\text{rev}} = dU + P_{\text{gas}} dV \quad \{P_{\text{ext}} = P_{\text{gas}} \text{ reversible}\}$$

$$\Delta S_{\text{rev, system}} = \int_A^B \frac{dU + P_{\text{gas}} dV}{T}$$

for an ideal gas

$$\frac{P_{\text{gas}}}{T} = \frac{nR}{V} \quad \& \quad du = nc_v dT$$

$$\therefore \Delta S_{\text{sys}} = \int_{T_1}^{T_2} \frac{nc_v dT}{T} + \int_{V_1}^{V_2} \frac{nR dV}{V}$$

$$\therefore \Delta S_{\text{system}} = nC_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

- **Calculation of $\Delta S_{\text{surrounding}}$** : As the surrounding is an infinite heat reservoir hence, no. amount of heat given to the surrounding can cause turbulence in it, hence all heat exchanges with surroundings are considered to be reversible.

$$\Delta S_{\text{surrounding}} = \int \frac{dq_{\text{surrounding}}}{T}$$

For surrounding T is constant

$$\therefore \Delta S_{\text{surr}} = \frac{1}{T} \int dq_{\text{surr}} = \frac{q_{\text{surrounding}}}{T}$$

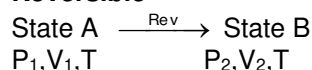
But according to the law of conservation of energy

$$Q_{\text{surr}} = -Q_{\text{system}}$$

$$\therefore \Delta S_{\text{surr}} = \frac{-q_{\text{system}}}{T}$$

- **Isothermal process :**

(a) **Reversible**





$$\Delta S_{\text{system}} = nC_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

Since $T_1 = T_2$

$$\Delta S_{\text{system}} = nR \ln \frac{V_2}{V_1}$$

$$\Delta S_{\text{surrounding}} = -\frac{q_{\text{system}}}{T}$$

$du = dq + dw$ (since $T_1 = T_2$. So, $du = 0$)

$$\therefore dq = -dw$$

$$\therefore q = -w \text{ as } w = -nRT \ln \frac{V_2}{V_1}$$

$$q = nRT \ln \frac{V_2}{V_1}$$

$$\therefore \Delta S_{\text{sys.}} = \frac{-nRT \ln \frac{V_2}{V_1}}{T} = -nR \ln \frac{V_2}{V_1}$$

$$\begin{aligned} \Delta S_{\text{universe}} &= \Delta S_{\text{system}} + \Delta S_{\text{surr}} \\ &= nR \ln \frac{V_2}{V_1} - nR \ln \frac{V_2}{V_1} = 0 \end{aligned}$$

(b) Irreversible

State A $\xrightarrow{\text{irrev}}$ State B
 P_1, V_1, T P_2, V_2, T

$$\Delta S_{\text{system}} = nR \ln \frac{V_2}{V_1}$$

$$\Delta S_{\text{Surrounding}} = -\frac{q_{\text{system}}}{T}$$

q_{system} is calculated using FLOT

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

$$\therefore \Delta S_{\text{surrounding}} = \frac{-P_{\text{ext}}(V_2 - V_1)}{T}$$

$$\begin{aligned} \Delta S_{\text{universe}} &= nR \ln \frac{V_2}{V_1} - \frac{-P_{\text{ext}}(V_2 - V_1)}{T} \\ &= \frac{1}{T} \left[\left(nRT \ln \frac{V_2}{V_1} \right) - P_{\text{ext}} (V_2 - V_1) \right] = \frac{1}{T} [W_{\text{irrev}} - W_{\text{rev}}] > 0 \end{aligned}$$

As irreversible work of gas is more than reversible work.

● **Adiabatic Process (Isoentropic process)**

(a) Reversible Adiabatic

State A $\xrightarrow{\text{rev}}$ State B
 P_1, V_1, T_1 P_2, V_2, T_2

$$\Delta S_{\text{system}} = nC_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

$TV^{\gamma-1} = \text{constant}$

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

$$(\Delta S)_{\text{system}} = nC_v \ln \left(\frac{V_1}{V_2} \right)^{\gamma-1} + nR \ln \frac{V_2}{V_1} = 0$$

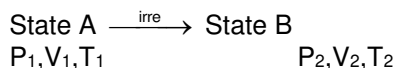




$$\Delta S_{\text{surr}} = -\frac{q_{\text{sys}}}{T} = 0 \quad (q_{\text{sys}} = 0)$$

$$\therefore \Delta S_{\text{universe}} = 0 + 0 = 0$$

(b) Irreversible Adiabatic



Using irreversible adiabatic process it is not possible to reach same state B which was reached by reversible adiabatic.

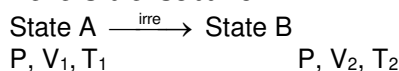
$$\Delta S_{\text{system}} = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} > 0 \quad [(T_2)_{\text{irrev}} > (T_2)_{\text{rev}}]$$

$$\Delta S_{\text{surr}} = -\frac{q_{\text{sys}}}{T} = 0 \quad \text{as } q = 0$$

For irreversible expansion the decrease in temperature will be lesser as work done is lesser hence, decrease in entropy due to fall in temperature will be lesser in case of irreversible expansion. Hence, net entropy would increase.

● **Isobaric process :**

(a) Reversible Isobaric



$$\Delta S_{\text{sys}} = \int \frac{dq_{\text{rev}}}{T} = \int \frac{nC_p dT}{T} = nC_p \ln \frac{T_2}{T_1}$$

$$\Delta S_{\text{surrounding}} = \int \frac{dq_{\text{rev}}}{T} = \int_{T_1}^{T_2} \frac{-dq_{\text{sys}}}{T} = -nC_p \ln \frac{T_2}{T_1}$$

$$\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \Delta S_{\text{surrounding}} = 0$$

(b) Irreversible Isobaric

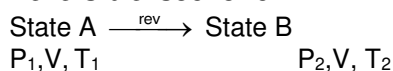
$$\Delta S_{\text{sys}} = \int \frac{dq_{\text{rev}}}{T} = \int_{T_1}^{T_2} \frac{nC_p dT}{T} = nC_p \ln \frac{T_2}{T_1}$$

$$\Delta S_{\text{surrounding}} = \int \frac{dq_{\text{rev}}}{T} = \frac{-nC_p (T_2 - T_1)}{T_2}$$

$$\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \Delta S_{\text{surrounding}} > 0$$

● **Isochoric Process**

(a) Reversible Isochoric



$$\Delta S_{\text{sys}} = \int \frac{dq_{\text{rev}}}{T} = \int_{T_1}^{T_2} \frac{nC_V dT}{T} = nC_V \ln \frac{T_2}{T_1}$$

$$\Delta S_{\text{surrounding}} = \int \frac{dq_{\text{rev}}}{T} = \int_{T_1}^{T_2} \frac{-dq_{\text{sys}}}{T} = -nC_V \ln \frac{T_2}{T_1}$$

$$\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \Delta S_{\text{surrounding}} = 0$$

(b) Irreversible Isochoric

$$\Delta S_{\text{sys}} = \int \frac{dq_{\text{rev}}}{T} = \int_{T_1}^{T_2} \frac{nC_V dT}{T} = nC_V \ln \frac{T_2}{T_1}$$

$$\Delta S_{\text{surrounding}} = \frac{-nC_V (T_2 - T_1)}{T_2}$$

$$\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \Delta S_{\text{surrounding}} > 0$$



• Entropy Calculation for phase transformations

$$\Delta S_{\text{fusion}} = \int \frac{dq}{T} = \frac{1}{T} \int dq = \frac{Q}{T}$$

$$\text{For constant pressure } \Delta S_{\text{fus.}} = \frac{\Delta H_{\text{fus}}}{T}$$

$$\text{For constant volume } \Delta S_{\text{fus.}} = \frac{\Delta U_{\text{fusion}}}{T}$$

$$\Delta S_{\text{vap}} = \int \frac{dq}{T} = \frac{1}{T} \int dq = \frac{Q}{T}$$

$$\text{For constant Pressure, } \Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T}$$

$$\text{For constant Volume, } \Delta S_{\text{vap}} = \frac{\Delta U_{\text{vap}}}{T}$$

• Entropy Calculation solid or liquid systems:

(a) 'Cu' block kept in open atmosphere

$$\Delta S_{\text{system}} = \int_{T_1}^{T_2} \frac{msdT}{T} = m \ln \frac{T_2}{T_1}$$

$$\therefore \Delta S_{\text{surr}} = \int \frac{dq_{\text{surr}}}{T} = \frac{q_{\text{surr}}}{T_2}$$

$$\text{but } q_{\text{surr}} = -q_{\text{system}} = -ms(T_2 - T_1) = ms(T_1 - T_2)$$

$$\text{Hence, } \Delta S_{\text{surr}} = \frac{ms(T_1 - T_2)}{T_2}$$

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surr}}$$

$$\therefore \Delta S_{\text{universe}} = ms \ln \frac{T_2}{T_1} + \frac{ms(T_1 - T_2)}{T_2} > 0$$

(b) Two copper block kept in contact in thermostat

Two blocks are of same mass

$\Delta S_{\text{surr}} = 0$ (since no heat is lost to surrounding)

$\Delta S_{\text{system}} = \Delta S_A + \Delta S_B$

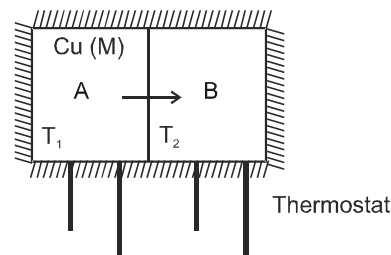
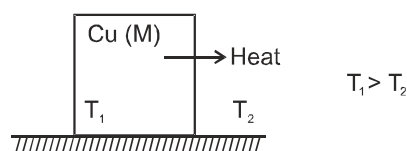
System will reach a common temperature (T_f)

and $T_1 > T_f > T_2$

$$\begin{aligned} \Delta S_{\text{system}} &= \int_{T_1}^{T_f} \frac{dq_A}{T} + \int_{T_2}^{T_f} \frac{dq_B}{T} \\ &= \int_{T_1}^{T_f} \frac{msdT}{T} + \int_{T_2}^{T_f} \frac{msdT}{T} = ms \left[\ln \frac{T_f}{T_1} + \ln \frac{T_f}{T_2} \right] \end{aligned}$$

$$\Delta S_{\text{system}} = ms \ln \frac{T_f^2}{T_1 T_2}$$

$$\text{Since } T_f = \frac{T_1 + T_2}{2} \quad \therefore \Delta S_{\text{system}} = ms \ln \frac{(T_1 + T_2)^2}{4T_1 T_2}$$



Solved Examples

Ex-9. (a) One mole of an ideal gas expands isothermally and reversibly at 25°C from a volume of 10 litres to a volume of 20 litres.

- What is the change in entropy of the gas?
- How much work is done by the gas?
- What is q (surroundings)?
- What is the change in the entropy of the surroundings?
- What is the change in the entropy of the system plus the surroundings?





(b) Also answer the questions opening a stopcock and allowing the gas to rush into an evacuated bulb of 10 L volume.

Sol. (a) (i) $\Delta S = 2.303 nR \log \frac{V_2}{V_1} = 2.303 \times 1 \times 8.314 \times \log \frac{20}{10} = 5.76 \text{ J/K.}$

(ii) $W_{\text{rev}} = -2.303nRT \log \frac{V_2}{V_1}$
 $= -2.303 \times 1 \times 8.314 \times 298 \times \log \frac{20}{10} = -1781 \text{ J.}$

(iii) For isothermal process, $\Delta U = 0$ and heat is absorbed by the gas,

$$q_{\text{rev}} = \Delta U - W = 0 - (-1781) = 1718 \text{ J.}$$

$$\therefore q_{\text{rev}} = 1718 \text{ J.} \quad (\because \text{process is reversible})$$

(iv) $\Delta S_{\text{surr}} = -\frac{1718}{298} = -5.76 \text{ J/K.}$

As entropy of the system increases by 5.76 J, the entropy of the surroundings decreases by 5.76J, since the process is carried out reversibly.

(v) $\Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0 \dots$ for reversible process

(b) (i) $\Delta S = 5.76 \text{ J/K}$, which is the same as above because S is a state function

(ii) $W = 0$ ($\because p_{\text{ext}} = 0$)

(iii) No heat is exchanged with the surroundings.

(iv) $\Delta S_{\text{surr}} = 0$.

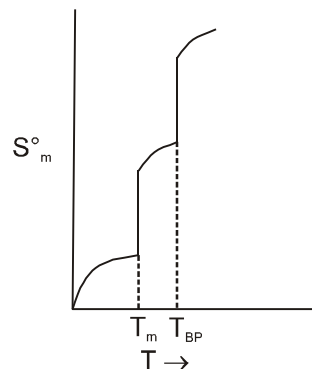
(v) The entropy of the system plus surroundings increases by 5.76 J/K, as we expect entropy to increase in an irreversible process.

● Third Law Of Thermodynamics :

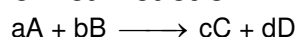
The entropy of perfect crystals of all pure elements & compounds is zero at the absolute zero of temperature.

Thus, absolute value of entropy unlike the absolute value of enthalpy for any pure substance can be calculated at any given temperature. In standard state (298 K, 1 atm), it is standard absolute entropy S° .

$$\Delta S = S_{T(K)} - S_{0(K)} = \int_0^T \frac{nCdT}{T}$$



● For chemical reaction



$$\Delta S^\circ_{\text{system}} = (\sum S^\circ_m n_i)_{\text{product}} - (\sum S^\circ_m n_i)_{\text{reactant}}$$

where S°_m = standard molar entropy. It can be calculated using third law of thermodynamics.

$$\Delta S_{\text{surr}} = \frac{-Q_{\text{system}}}{T} = \frac{-\Delta H_{\text{system}}}{T}$$

* For a perfectly crystalline substance at 0 K, entropy = 0

● For phase transformations

$$\Delta S_{\text{fusion}} = \int \frac{dp}{T} = \frac{1}{T} \int dp = \frac{Q}{T}$$

$$\text{for constant pressure } \Delta S_{\text{fus.}} = \frac{\Delta H_{\text{fus.}}}{T}$$

$$\text{for constant volume } \Delta S_{\text{fus.}} = \frac{\Delta U_{\text{fusion}}}{T}$$

$$\Delta S_{\text{vap}} = \int \frac{dQ}{T} = \frac{1}{T} \int dQ = \frac{Q}{T}$$

$$\text{for constant Pressure, } \Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T}$$

$$\text{for constant Volume, } \Delta S_{\text{vap}} = \frac{\Delta U_{\text{vap}}}{T}$$



Section (C) : Free energy

● **Gibb's free energy (G) :**

A system parameter to predict the spontaneity of chemical reaction was introduced by Gibb's so that entropy calculation for the surrounding need not be carried out.

It is a free energy at constant pressure.

$$G = H - TS$$

$$dG = dH - TdS - SdT$$

$$\& \quad H = U + PV$$

$$dH = dU + PdV + VdP \Rightarrow dG = dU + PdV + VdP - TdS - SdT$$

From 1st law of thermodynamics

$$dq = dU + PdV$$

& from 2nd law, $dq = TdS$

$$dG = dq + VdP - TdS - SdT$$

$$dG = -SdT + VdP$$

At constant temperature,

$$dG = VdP$$

For ideal gas, $V = \frac{nRT}{P}$

$$dG_m = V_m dP = \frac{RT}{P} dP$$

$$\int_1^2 dG_m = RT \int_{P_1}^{P_2} \frac{dP}{P}$$

$$G_{m_2} - G_{m_1} = RT \ln \frac{P_2}{P_1}$$

Where G_m is free energy for 1 mole

If G_{m_1} is free energy for 1 mole in standard state and G_{m_2} is free energy for one mole in any other state.

$$G_m - G_m^\circ = RT \ln \frac{P}{1} \quad \& \quad G - G^\circ = nRT \ln \frac{P}{1}$$

For the reaction, $aA(g) + bB(g) \rightleftharpoons C(g) + dD(g)$

$$(\Delta G)_{\text{reaction}} = (\Sigma \Delta G)_{\text{product}} - (\Sigma \Delta G)_{\text{reactant}}$$

$$(\Delta G)_{\text{reaction}} = G_C + G_D - G_A - G_B$$

$$G_C - G_C^\circ = cRT \ln \frac{P_C}{1} \Rightarrow G_C = G_C^\circ + cRT \ln P_C$$

$$\text{Similarly, } G_D = G_D^\circ + dRT \ln P_D ; \quad G_A = G_A^\circ + aRT \ln P_A, \quad G_B = G_B^\circ + bRT \ln P_B$$

$$(\Delta G)_{\text{reaction}} = (G_C^\circ + cRT \ln P_C) + (G_D^\circ + dRT \ln P_D) - (G_A^\circ + aRT \ln P_A) - (G_B^\circ + bRT \ln P_B)$$

$$= (\Delta G)^\circ_{\text{reaction}} + RT \ln \frac{P_C^c \cdot P_D^d}{P_A^a \cdot P_B^b}$$

$$\Delta G_{\text{reaction}} = \Delta G^\circ_{\text{reaction}} + RT \ln Q$$

Gibb's Helmholtz Equation :

$$dG = VdP - SdT$$

At constant Pressure

$$dG = -SdT \Rightarrow \left(\frac{dG}{dT} \right)_P = -S \quad \& \quad \left(\frac{\partial \Delta G}{\partial T} \right)_P = -\Delta S$$

$$\& \quad G = H - TS \Rightarrow \frac{G - H}{T} = -S$$

$$\frac{G - H}{T} = \left(\frac{\partial G}{\partial T} \right)_P$$

$$G = H + T \left(\frac{\partial G}{\partial T} \right)_P$$



$$\Delta G = \Delta H + T \left(\frac{\partial \Delta G}{\partial T} \right)_P$$

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

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$$

$$\Delta S_{\text{surr}} = \frac{-Q_{\text{system}}}{T} = \frac{-\Delta H_{\text{system}}}{T}$$

$$T \Delta S_{\text{univ}} = T \Delta S_{\text{system}} - \Delta H_{\text{system}}$$

Introducing a new thermodynamic function G = Gibb's free energy (State function and an extensive property)

$$G_{\text{system}} = H_{\text{system}} - TS_{\text{system}}$$

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

$$\Delta G_{\text{system}} = \Delta H_{\text{system}} - T \Delta S_{\text{system}} \dots\dots\dots (ii)$$

Comparing equation (i) and (ii)

$$\Delta G_{\text{system}} = -T \Delta S_{\text{universe}}$$

New criteria of spontaneity :

- (i) If ΔG_{system} is $(-ve) < 0 \Rightarrow$ process is spontaneous
- (ii) If ΔG_{system} is $> 0 \Rightarrow$ process is non spontaneous
- (iii) If $\Delta G_{\text{system}} = 0 \Rightarrow$ system is at equilibrium

So, at every temperature $\Delta G \neq 0$

ΔH_{system}	ΔS_{system}	$\Delta G_{\text{system}} = \Delta H_{\text{system}} - T \Delta S_{\text{system}}$
+ Ve	- Ve	+
- Ve	+ Ve	-
+ Ve	+ Ve	- Ve at high temperature
- Ve	- Ve	+ Ve at high temperature

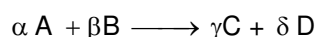
ΔG° = standard free energy change :

When the reactants under standard conditions gets converted into products which is also under standard condition, then the free energy change is known as ΔG° (it is a constant) for 1 mole at 1 bar.

At standard conditions :

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

= constant for a GIVEN REACTION



$$\Delta G^\circ = (\text{Gibb's energy of product}) - (\text{Gibb's energy of reactant})$$

$$\Delta G^\circ = \gamma G_{m,C}^\circ + \delta G_{m,D}^\circ - \alpha G_{m,A}^\circ - \beta G_{m,B}^\circ, \text{ where } G_m^\circ \text{ can not be calculated as } H_m^\circ \text{ cannot be calculated.}$$

Hence, we can convert this relation in to Gibb's energy of formation of substance.

$$\Delta G^\circ = \gamma \Delta G_{f,C}^\circ + \delta \Delta G_{f,D}^\circ - \alpha \Delta G_{f,A}^\circ - \beta \Delta G_{f,B}^\circ$$

ΔG_f° : standard Gibb's energy of formation.

$$\Delta G_f^\circ \text{ (elements in their standard states)} = 0$$

$$\Delta G^\circ = \Delta G_{f,\text{product}}^\circ - \Delta G_{f,\text{reactants}}^\circ$$

For a reaction in progress

$$\Delta G = \Delta G^\circ + RT \ln Q$$

Q is reaction quotient, $\Delta G > 0$ backward is feasible, $\Delta G < 0$ forward is feasible

At equilibrium $\Delta G = 0 \therefore Q = K \therefore \Delta G^\circ = -RT \ln K$ at equilibrium.



Solved Examples

Ex-10. K_a for CH_3COOH at 25°C is 1.754×10^{-5} . At 50°C , K_a is 1.633×10^{-5} . What are ΔH° and ΔS° for the ionisation of CH_3COOH ?

Sol. $(\Delta G^\circ)_{298} = -2.303RT \log K = -2.303 \times 8.314 \times 298 \times \log (1.754 \times 10^{-5}) = 27194 \text{ J.}$
 $(\Delta G^\circ)_{323} = 2.303 \times 8.314 \times 323 \times \log (1.633 \times 10^{-5}) = 29605 \text{ J.}$
 $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \Rightarrow \quad 27194 = \Delta H^\circ - 298 \Delta S^\circ$
 $29605 = \Delta H^\circ - 323 \Delta S^\circ \quad \Rightarrow \quad \Delta H^\circ = -1.55 \text{ kJ/mol} \quad \Rightarrow \quad \Delta S^\circ = -96.44 \text{ J/mol.K}$

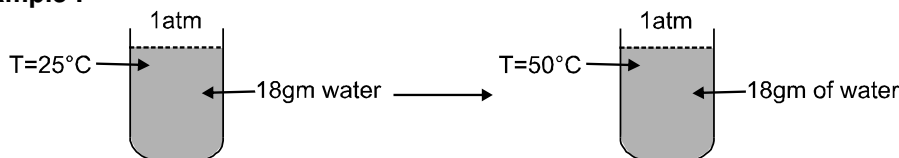
2. THERMOCHEMISTRY

Section (A) : Calculation ΔU , ΔH & W for chemical reaction

○ Enthalpy of a substance :

- Every substance has a fixed value of enthalpy under any particular state. Though, its exact value cannot be calculated but it has some finite fixed value.
- The enthalpy of one mole of a substance called molar enthalpy in any particular state can be assigned symbol
- $H_m(\text{substance})$: For example molar enthalpy of water vapours at 398 K and 1 atm pressure may be represented as $H_m(\text{H}_2\text{O}, \text{g}, 398 \text{ K}, 1 \text{ atm})$. In very simple words, enthalpy can be considered as heat constant (amount) of substance, and during reaction this heat is being released or absorbed.
- Molar enthalpy of substance under standard conditions is called standard molar enthalpy of a substance. Standard state of any substance means.
 - For a **GAS** standard state means ideal gas at 1 bar partial pressure at any give temperature.
 - For a **LIQUID** – pure liquid at one bar pressure at 1 bar pressure at any given temperature.
 - For a **PURE CRYSTALLINE SOLID** – pure crystalline solid at 1 bar pressure and at any given temperature
 - For any **SUBSTANCE or ION IN SOLUTION** – the species should be in unit molality (can also be taken as 1 M concentration), at one bar pressure and at any given temperature.
- Molar standard enthalpy of water vapours at 398 K will be represented as $H^\circ(\text{H}_2\text{O}, \text{g}, 398 \text{ K})$ and molar standard enthalpy of liquid water at 398 K will be represented as $H_m^\circ(\text{H}_2\text{O}, \text{l}, 398 \text{ K})$ (It is hypothetical but can be calculated).
- We cannot exactly calculate enthalpy content of a substance only the change in enthalpy can be calculated when substance is taken from one state to other.

For example :



Let enthalpy content initially be $H_{m,1}^\circ$ & finally enthalpy content be $H_{m,2}^\circ$

Then, $\Delta H^\circ = H_{m,2}^\circ - H_{m,1}^\circ$

= heat added at constant pressure to change temperature from 25°C to 50°C .

= $C_P \Delta T = (18 \text{ cal/mole } ^\circ\text{C}) (25^\circ\text{C}) = 450 \text{ cal}$

Solved Examples

Ex-11. Why does heat get released/absorbed during chemical reactions?

Sol. Because the reactants have a fixed enthalpy content before the reaction and when these are converted into the products which have a different enthalpy content. So, heat gets released or absorbed. Even if temperature of reactions remains constant yet due to change in bonding energies $\Delta E \neq 0$.

If $H_{\text{products}} > H_{\text{reactants}}$

Reaction should be endothermic as we have to give extra heat to reactants to get these converted into products and

if $H_{\text{products}} < H_{\text{reactants}}$



Reaction will be exothermic as extra heat content of reactants will be released during the reaction.

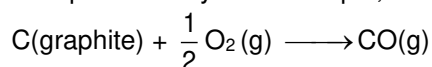
Enthalpy change of a reaction : $\Delta H_{\text{reaction}} = H_{\text{products}} - H_{\text{reactants}}$

$$\begin{aligned} \Delta H^{\circ}_{\text{reactions}} &= H^{\circ}_{\text{products}} - H^{\circ}_{\text{reactants}} \\ &= \text{positive} \quad - \quad \text{endothermic} \\ &= \text{negative} \quad - \quad \text{exothermic} \end{aligned}$$

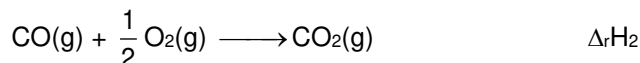
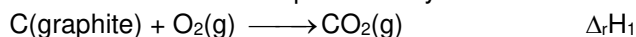
Section (B) : Basics & Kirchoff's law

○ Hess's Law of constant heat summation :

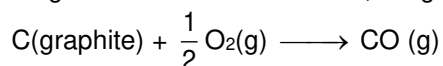
- The heat absorbed or evolved in a given chemical equation is the same whether the process occurs in one step or several steps.
- The chemical equation can be treated as ordinary algebraic expressions and can be added or subtracted to yield the required equation. The corresponding enthalpies of reactions are also manipulated in the same way so as to give the enthalpy of reaction for the desired chemical equation.
- Since $\Delta_r H$ stands for the change of enthalpy when reactants (substances on the left hand side of the arrow) are converted into products (substances on the right hand side of the arrow) at the same temperature and pressure, if the reaction is reversed (i.e., products are written on the left hand side and reactants on the right hand side), then the numerical value of $\Delta_r H$ remains the same, but **its sign changes**.
- The utility of Hess's law is considerable. In almost all the thermochemical numericals, Hess's law is used.
- One of the important applications of Hess's law is to determine enthalpy of reaction which is difficult to determine experimentally. For example, the value $\Delta_r H$ for the reaction



which is difficult to determine experimentally, can be estimated from the following two reactions for which $\Delta_r H$ can be determined experimentally.



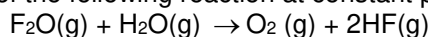
Subtracting the latter from the former, we get



Consequently, $\Delta_r H = \Delta_r H_1 - \Delta_r H_2$

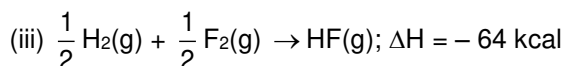
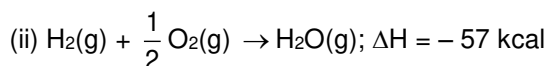
Solved Examples

Ex-12. Calculate heat of the following reaction at constant pressure,



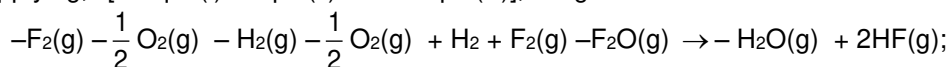
The heats of formation of $\text{F}_2\text{O}(\text{g})$, $\text{H}_2\text{O}(\text{g})$ and $\text{HF}(\text{g})$ are 5.5 kcal, -57kcal and -64 kcal respectively.

Sol. Given that (i) $\text{F}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{F}_2\text{O}(\text{g}); \Delta H = 5.5 \text{ kcal}$



F_2O and H_2O in eqns. (i) and (ii) and in the eqn. given in the problem are on the opposite sides, while HF in eqn. (iii) and in the eqn. given in the problem is on the same sides.

Thus applying, $[-\text{Eqn. (i)} - \text{Eqn. (ii)} + 2 \times \text{Eqn. (iii)}]$, we get



$$\Delta H = -5.5 - (-57) + 2 \times (-64)$$

or $\text{F}_2\text{O}(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{O}_2(\text{g}) + 2\text{HF}(\text{g}); \Delta H = -76.5 \text{ kcal}.$



○ Relation between energy and enthalpy of a reaction :

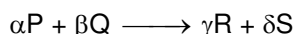
$$\Delta_r H = \Delta_r U + (\Delta \nu_g)RT$$

where $\Delta \nu_g$ is the change in the stoichiometric number of gaseous species in going from reactants to products.

It should be noted that while computing $\Delta \nu_g$ of a reaction, only the stoichiometric numbers of gaseous are counted and those of liquids and solids are completely ignored.

Kirchoff's equation (Variation of ΔH° with temperature)

Since the enthalpy (or standard enthalpy) of a substance is dependent on state of the substance, value of enthalpy of a substance changes with temperature and hence the enthalpy change of reaction is also dependent on temperature at which the reaction is being carried out. This change in enthalpy change (or ΔE of reaction is carried out at constant volume) is represented by **Kirchoff's Equations**.



at temperature T_1 let the standard enthalpy of reaction be ΔH_1° , then

$$\Delta H_1^\circ = \gamma H_m^\circ(R, T_1) + \delta H_m^\circ(S, T_1) - \alpha H_m^\circ(P, T_1) - \beta H_m^\circ(Q, T_1)$$

If the same reaction is carried out at temperature T_2 , then

$$\Delta H_2^\circ = \gamma H_m^\circ(R, T_2) + \delta H_m^\circ(S, T_2) - \alpha H_m^\circ(P, T_2) - \beta H_m^\circ(Q, T_2)$$

Then, the change in enthalpy (or difference in enthalpy at these two temperatures)

$$\Delta H^\circ = \Delta H_2^\circ - \Delta H_1^\circ = \gamma \{H_m^\circ(R, T_2) - H_m^\circ(R, T_1)\} + \delta \{H_m^\circ(S, T_2) - H_m^\circ(S, T_1)\} - \alpha \{H_m^\circ(P, T_2) - H_m^\circ(P, T_1)\} - \beta \{H_m^\circ(Q, T_2) - H_m^\circ(Q, T_1)\}$$

$H_m^\circ(R, T_2) - H_m^\circ(R, T_1) = C_{P,R}(T_2 - T_1)$ = Heat required at constant pressure to increase temperature of one mole of R from T_1 to T_2

Similarly

$$H_m^\circ(S, T_2) - H_m^\circ(S, T_1) = C_{P,S}(T_2 - T_1)$$

$$H_m^\circ(P, T_2) - H_m^\circ(P, T_1) = C_{P,P}(T_2 - T_1) \text{ and}$$

$$H_m^\circ(Q, T_2) - H_m^\circ(Q, T_1) = C_{P,Q}(T_2 - T_1)$$

$$\text{so } \Delta H^\circ = \Delta H_2^\circ - \Delta H_1^\circ = \gamma C_{P,R}(T_2 - T_1) + \delta C_{P,S}(T_2 - T_1) - \alpha C_{P,P}(T_2 - T_1) - \beta C_{P,Q}(T_2 - T_1)$$

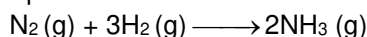
$$= [\gamma C_{P,R} + \delta C_{P,S} - \alpha C_{P,P} - \beta C_{P,Q}](T_2 - T_1) = \Delta C_P (T_2 - T_1)$$

$$\Delta C_P = \gamma C_{P,R} + \delta C_{P,S} - \alpha C_{P,P} - \beta C_{P,Q}$$

= Difference in molar heat capacities of products and reactants.

$$\text{so } \Delta H_2^\circ = \Delta H_1^\circ + \int \Delta C_P \cdot dT$$

For example for the reaction



$$\Delta H_2^\circ = \Delta H_1^\circ + \Delta C_P (T_2 - T_1)$$

$$\text{where } \Delta C_P = 2C_{P,NH_3} - C_{P,N_2} - 3C_{P,H_2}$$

$$* \text{ for a constant volume reaction, } \Delta E_2^\circ = \Delta E_1^\circ + \int \Delta C_V \cdot dT$$

Section (C) : Enthalpy of formation & combustion

○ Enthalpy of formation :

It is not possible to determine the absolute value of the molar enthalpy of a substance. However, based on the following convention, the relative values of standard molar enthalpies of formation of various substances can be built.

- "The standard enthalpy of formation of every element in its stable state of aggregation at one bar pressure and at specified temperature is assigned a zero value". The specified temperature is usually taken as 25°C.

A few examples are $\Delta H_f^\circ(O_2, g) = 0$

$$\Delta H_f^\circ(C, \text{graphite}) = 0$$

$$\Delta H_f^\circ(C, \text{diamond}) \neq 0$$

$$\Delta H_f^\circ(Br_2, \text{liquid}) = 0$$

$$\Delta H_f^\circ(S, \text{rhombic}) = 0$$

$$\Delta H_f^\circ(S, \text{monoclinic}) \neq 0$$

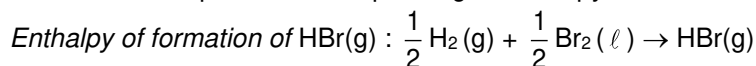
$$\Delta H_f^\circ(P, \text{white}) = 0$$

$$\Delta H_f^\circ(P, \text{black}) \neq 0$$

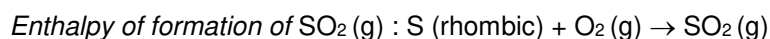
- "The standard enthalpy of formation of a compound is the change in the standard enthalpy when one mole of the compound is formed starting from the requisite amounts of elements in their stable state of aggregation".



The chemical equations corresponding to enthalpy of formation of few substances are given below.



$$\Delta H_f^\circ(\text{HBr, g}) = H_m^\circ(\text{HBr, g}) - \frac{1}{2} H_m^\circ(\text{H}_2, \text{g}) - \frac{1}{2} H_m^\circ(\text{Br}_2, \ell) \quad \dots(1)$$



$$\Delta H_f^\circ(\text{SO}_2, \text{g}) = H_m^\circ(\text{SO}_2, \text{g}) - H_m^\circ(\text{S, rhombic}) - H_m^\circ(\text{O}_2, \text{g}) \quad \dots(2)$$

But above equations cannot be for calculation of enthalpy of reaction as the molar enthalpies of different species can not be exactly known.

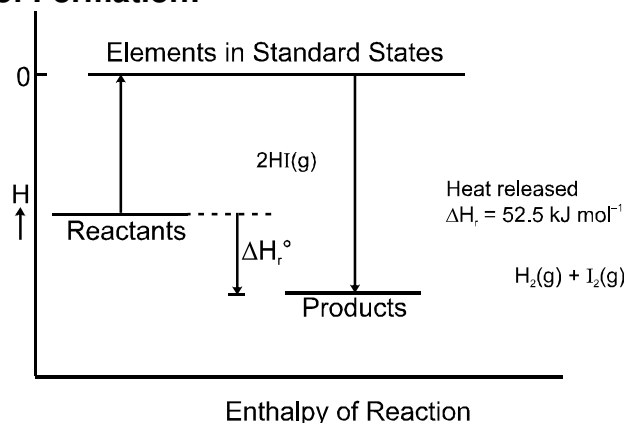
○ Enthalpy of Reaction from Enthalpies of Formation:

The enthalpy of reaction can be calculated by

$$\Delta H_r^\circ = \sum v_B \Delta H_f^\circ, \text{products} - \sum v_B \Delta H_f^\circ, \text{reactants}$$

v_B is the stoichiometric coefficient

above equation holds good for any reaction as the same reference state is used for reactants and products (shown in figure).



Solved Examples

Ex-13. Calculate the standard enthalpy of reaction $\text{ZnO(s)} + \text{CO(g)} \longrightarrow \text{Zn(s)} + \text{CO}_2(\text{g})$.

Given, $\Delta H_f^\circ(\text{ZnO, s}) = -350 \text{ KJ/mole}$, $\Delta H_f^\circ(\text{CO}_2, \text{g}) = -390 \text{ KJ/mole}$, $\Delta H_f^\circ(\text{CO, g}) = -110 \text{ KJ/mole}$.

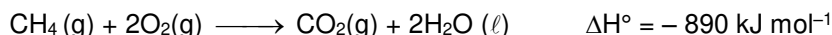
Sol. $\Delta H^\circ = \{\Delta H_f^\circ(\text{CO}_2, \text{g}) - (\Delta H_f^\circ(\text{ZnO, s}) + \Delta H_f^\circ(\text{CO, g}))\}$

$$\Delta H^\circ_{\text{reaction}} = -390 - (-350 - 110) = 70 \text{ KJ}$$

○ Enthalpy of Combustion :

- It is the enthalpy change when one mole of a compound combines with the requisite amount of oxygen to give products in their stable forms.

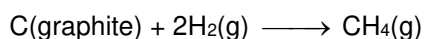
For example, the standard enthalpy of combustion of methane at 298 K is -890 kJ mol^{-1} . This implies the following reaction :



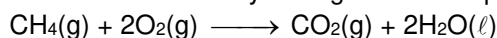
The standard enthalpy of combustion of methane at 298 K may be written as

$$\Delta H_c^\circ(\text{CH}_4, \text{g, 298 K}) = -890 \text{ kJ mol}^{-1}$$

- The data on the enthalpy of combustion can be determined experimentally.
- With the help of such data, we can determine the enthalpy of formation of a compound, which otherwise is difficult or impossible to determine experimentally. Consider for example, the enthalpy of formation of $\text{CH}_4(\text{g})$:



First of all, the combination of carbon and hydrogen does not occur readily. Secondly, if the reaction is even completed, the end product would not be pure methane. Therefore, the enthalpy of formation of methane can be determined indirectly through the enthalpy of combustion of methane :



$$\Delta H_c^\circ(\text{CH}_4, \text{g}) = \Delta H_f^\circ(\text{CO}_2, \text{g}) + 2\Delta H_f^\circ(\text{H}_2\text{O}, \ell) - \Delta H_f^\circ(\text{CH}_4, \text{g})$$

therefore $\Delta H_f^\circ(\text{CH}_4, \text{g}) = \Delta H_f^\circ(\text{CO}_2, \text{g}) + 2\Delta H_f^\circ(\text{H}_2\text{O}, \ell) - \Delta H_c^\circ(\text{CH}_4, \text{g})$

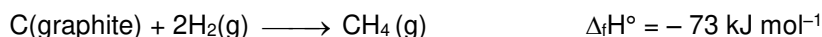
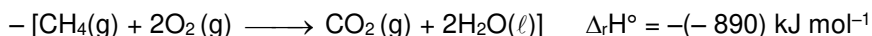
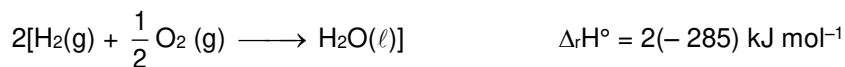
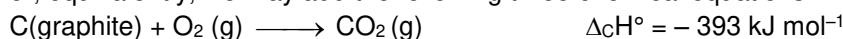


- The enthalpies of formation of CO_2 and H_2O can be determined experimentally by the combustion of carbon (graphite) and hydrogen. Thus, knowing the measured value of $\Delta H_c^\circ(\text{CH}_4, \text{g})$, the enthalpy of formation of CH_4 can be calculated. The value is

$$\Delta H_f^\circ(\text{CH}_4, \text{g}) = \Delta H_f^\circ(\text{CO}_2, \text{g}) + 2 \Delta H_f^\circ(\text{H}_2\text{O}, \ell) - \Delta H_c^\circ(\text{CH}_4, \text{g})$$

$$= [-393 + 2(-285) - (-890)] \text{ kJ mol}^{-1} = -73 \text{ kJ mol}^{-1}$$

or, equivalently, we may add the following three chemical equations.



○ Measurement of Enthalpy of Combustion :

Enthalpy of combustion are usually measured by placing a known mass of the compound in a closed steel container (known as bomb calorimeter) which is filled with oxygen at about 30 bar pressure.

The calorimeter is surrounded by a known mass of water. The entire apparatus is kept in an insulated jacket to prevent heat entering into or leaving from the container, as shown in figure. The sample is ignited electrically to bring about the combustion reaction. The heat evolved is used in raising the temperature of water and the calorimeter.

If total heat capacity of calorimeter and all of its contents = C ,

rise in temperature = ΔT

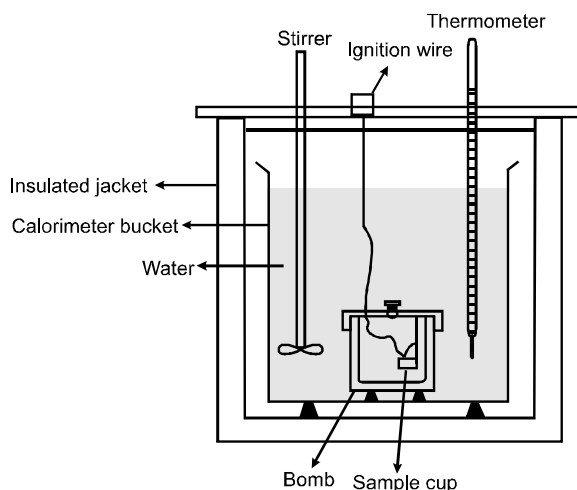
then heat released = $q = C\Delta T$ of this heat is because of mass m of substance then :

$$\text{due to 1 mole, heat released} = \left(\frac{M}{m}\right) q = \Delta E_c^\circ$$

(Constant volume reaction).

Now, ΔH_c° can be calculated by using $\Delta H_c^\circ = \Delta E_c^\circ + \Delta n_g RT$.

Where Δn_g is the change in stoichiometric number of gaseous species in the balanced chemical equation representing the combustion process.



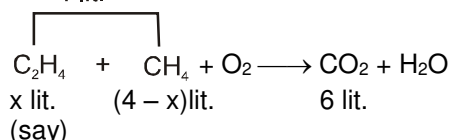
Bomb calorimeter to determine enthalpy of combustion

Solved Examples

Ex-14. A gas mixture of 4 litres of ethylene and methane on complete combustion at 25°C produces 6 litres of CO_2 . Find out the amount of heat evolved on burning one litre of the gas mixture. The heats of combustion of ethylene and methane are -1464 and -976 kJ mol^{-1} at 25°C . [IIT-1991]

4 lit.

Sol.



or x moles (4 - x) moles 6 moles

Applying POAC for C atoms,

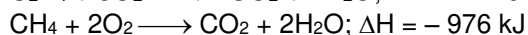
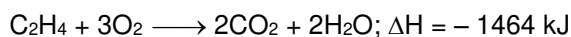
$$2 \times x + 1 \times (4 - x) = 1 \times 6 ; x = 2 \text{ lit.}$$

Thus, the volume of $\text{C}_2\text{H}_4 = 2 \text{ lit.}$, and volume of $\text{CH}_4 = 2 \text{ lit.}$

volume of C_2H_4 in a 1 litre mixture = $2/4 = 0.5 \text{ lit.}$

and volume of CH_4 in a 1 litre mixture = $1 - 0.5 = 0.5 \text{ lit.}$

Now, thermochemical reactions for C_2H_4 and CH_4 are



As ΔH values given are at 25°C , let us first calculate the volume occupied by one mole of any gas at 25°C (supposing pressure as 1 atm)

$$\text{Volume per mole at } 25^\circ\text{C} = \frac{298}{273} \times 22.4 = 24.4 \text{ lit.}$$

$$\text{Thus, heat evolved in the combustion of 0.5 lit. of } \text{C}_2\text{H}_4 = -\frac{1464}{24.4} \times 0.5 = -30 \text{ kJ}$$

$$\text{and heat evolved in the combustion of 0.5 lit. of } \text{CH}_4 = \frac{976}{24.4} \times 0.5 = -20 \text{ kJ.}$$

$$\therefore \text{ total heat evolved in the combustion of 1 litre of the mixture} = -30 + (-20) = -50 \text{ kJ.}$$

Section (D) : Bond enthalpy method & Resonance energy

○ Bond Enthalpies :

The **bond enthalpy** is the average of enthalpies required to dissociate the said bond present in different gaseous compounds into free atoms or radicals in the gaseous state. While **bond dissociation enthalpy** is the enthalpy required to dissociate a given bond of some specific compound. For example the enthalpy of dissociation of the O–H bond depends on the nature of molecular species from which the H atom is being separated. For example, in the water molecule.



However, to break the O–H bond in the hydroxyl radical required a different quantity of heat :



The bond enthalpy, ΔH_{OH} , is defined as the average of these two values, that is :

$$\Delta H_{\text{OH}} = \frac{501.87 \text{ kJ mol}^{-1} + 423.38 \text{ kJ mol}^{-1}}{2} = 462.625 \text{ kJ mol}^{-1}$$

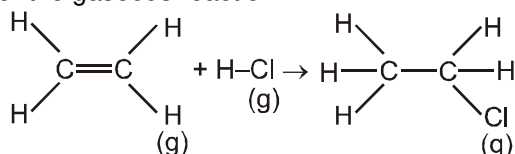
In the case of diatomic molecules, such as H_2 , the bond enthalpy and bond dissociation enthalpy are identical because each refers to the reaction.



Thus, the bond enthalpy given for any particular pair of atoms is the average value of the dissociation enthalpies of the bond for a number of molecules in which the pair of atoms appears.

○ Estimation of Enthalpy of a reaction from bond Enthalpies :

Let the enthalpy change for the gaseous reaction

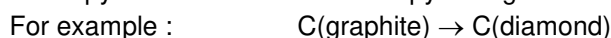


be required from the bond enthalpy data. This may be calculated as follows :

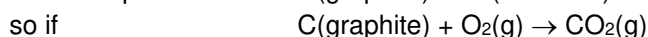
$$\begin{aligned} \Delta H &= \left(\text{Enthalpy required to break reactants into gaseous atoms} \right) - \left(\text{Enthalpy released to form products from the gaseous atoms} \right) \\ &= [4\Delta H_{\text{C-H}} + \Delta H_{\text{C=C}} + \Delta H_{\text{H-Cl}}]_{\text{R}} + [-5\Delta H_{\text{C-H}} - \Delta H_{\text{C-C}} - \Delta H_{\text{C-Cl}}]_{\text{P}} \\ &= (\Delta H_{\text{C=C}} + \Delta H_{\text{H-Cl}}) - (\Delta H_{\text{C-H}} + \Delta H_{\text{C-C}} + \Delta H_{\text{C-Cl}}) \end{aligned}$$

Enthalpy of Transition :

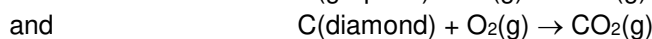
Enthalpy of transition is the enthalpy change when one mole of one allotropic form changes to another.



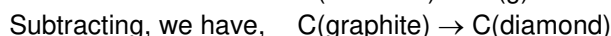
$$\Delta H_{\text{trs}}^\circ = 1.90 \text{ kJ mol}^{-1}$$



$$\Delta H_{\text{c}}^\circ = -393.51 \text{ kJ mol}^{-1}$$



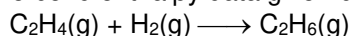
$$\Delta H_{\text{c}}^\circ = -395.41 \text{ kJ mol}^{-1}$$



$$\Delta H_{\text{trs}}^\circ = 1.90 \text{ kJ mol}^{-1}$$

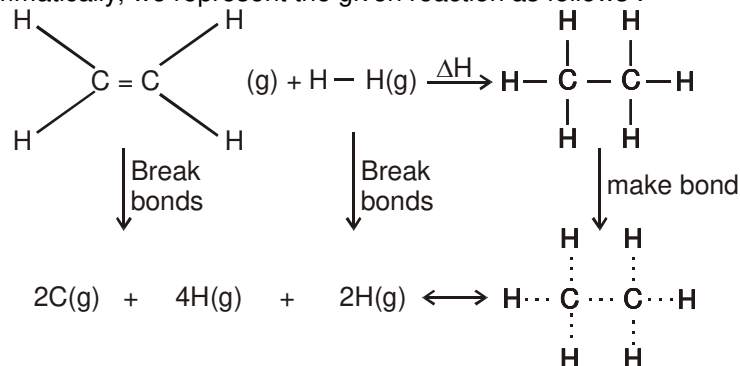
Solved Examples

Ex-15. Using the bond enthalpy data given below, calculate the enthalpy change for the reaction



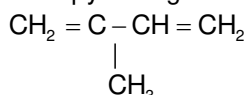
Data :	Bond	Bond enthalpy
	C – C	336 kJ mol ⁻¹
	C = C	606 kJ mol ⁻¹
	C – H	410 kJ mol ⁻¹
	H – H	431 kJ mol ⁻¹

Sol. Diagrammatically, we represent the given reaction as follows :



$$\begin{aligned}\Delta H_r &= (4\Delta H_{C-H} + \Delta H_{C=C} + \Delta H_{H-H}) - (6\Delta H_{C-H} + \Delta H_{C-C}) \\ &= (4 \times 410 + 606 + 431) - (6 \times 410 + 336) \\ &= 2677 - 2796 = -119 \text{ kJ/mol.}\end{aligned}$$

Ex-16. Using the bond enthalpy data given below, estimate the enthalpy of formation of gaseous isoprene



Data: Bond enthalpy of C – H bond = 413.38 kJ mol⁻¹
 Bond enthalpy of C – C bond = 347.69 kJ mol⁻¹
 Bond enthalpy of C = C bond = 615.05 kJ mol⁻¹
 Enthalpy of sublimation of carbon (graphite) = 718.39 kJ mol⁻¹
 Enthalpy of dissociation of H₂(g) = 435.97 kJ mol⁻¹

Sol. For isoprene, we have to form

2C – C bonds : 2C = C bonds and 8C – H bonds

Method-1 For which energy released is

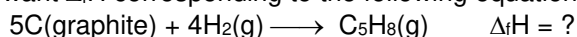
$$[2(+347.69) + 2(+615.05) + 8(+413.38)] \text{ kJ mol}^{-1} = 5\,232.52 \text{ kJ mol}^{-1}$$

that is, ΔH (from gaseous atoms) = + 5232.52 kJ mol⁻¹

The reaction corresponding to this is



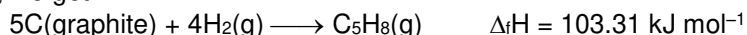
But we want $\Delta_f H$ corresponding to the following equation



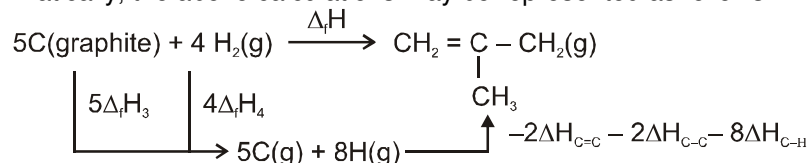
This can be obtained by the following manipulations :



Adding, we get



Method-2 Diagrammatically, the above calculations may be represented as follows.





Applying Hess's law, we get

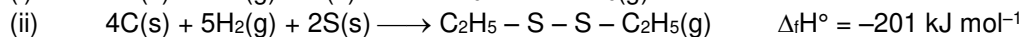
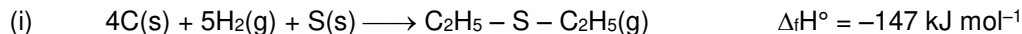
$$\begin{aligned}\Delta_f H &= 5\Delta_f H_3 + 4\Delta_f H_4 - 2\Delta_f H_{C=C} - 2\Delta_f H_{C-C} - 8\Delta_f H_{C-H} \\ &= (5 \times 718.39 + 4 \times 435.97 - 2 \times 615.05 - 2 \times 347.69 - 8 \times 413.38) \text{ kJ mol}^{-1} \\ \Delta_f H &= 103.31 \text{ kJ mol}^{-1}\end{aligned}$$

Ex-17. Find the bond enthalpy of S – S bond from the following data :

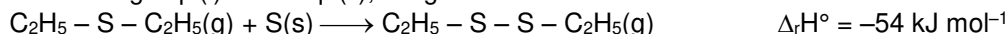


Sol. Given that

Method-1



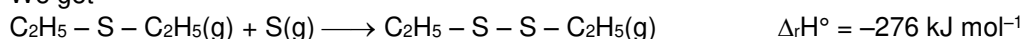
Subtracting Eq. (i) from Eq. (ii), we get



Adding to this, the following equation



We get

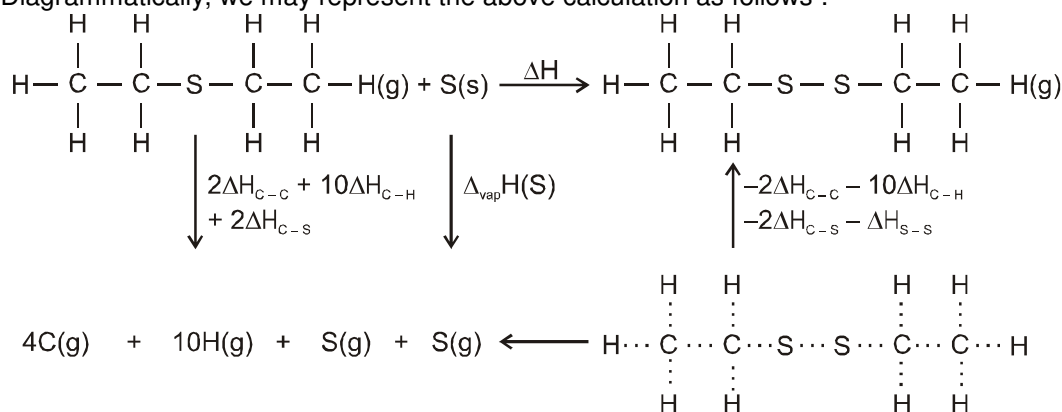


In the last equation 276 kJ of heat evolved because of the S–S bond formation.

Hence, the bond enthalpy of S – S is 276 kJ mol⁻¹.

Method-2

Diagrammatically, we may represent the above calculation as follows :



According to Hess's law :

$$\Delta_f H^\circ = \text{Enthalpy involved in bond breaking } \Delta_{\text{vap}} H^\circ(\text{S}) - \text{Enthalpy involved in bond making}$$

$$\begin{aligned}\Delta_f H^\circ &= [2\Delta_f H_{C-C} + 10\Delta_f H_{C-H} + 2\Delta_f H_{C-S} + \Delta_{\text{vap}} H^\circ(\text{S})] + [-2\Delta_f H_{C-C} - 10\Delta_f H_{C-H} - 2\Delta_f H_{C-S} - \Delta_f H_{S-S}] \\ &= \Delta_{\text{vap}} H^\circ(\text{S}) - \Delta_f H_{S-S}\end{aligned}$$

$$\begin{aligned}\text{or } \Delta_f H_{S-S} &= \Delta_{\text{vap}} H^\circ(\text{S}) - \Delta_f H^\circ \\ &= \Delta_{\text{vap}} H^\circ(\text{S}) - [\Delta_f H^\circ(\text{C}_2\text{H}_5 - \text{S} - \text{S} - \text{C}_2\text{H}_5) - \Delta_f H^\circ(\text{C}_2\text{H}_5 - \text{S} - \text{C}_2\text{H}_5)] \\ &= [222 - \{-201 - (-147)\}] \text{ kJ mol}^{-1} = 276 \text{ kJ mol}^{-1}\end{aligned}$$

○ Resonance energy :

Difference between energy of resonance hybrid and resonating structure in which resonance hybrid have lower energy because stabilised by resonance.

$$\Delta H^\circ_{\text{resonance}} = \Delta H^\circ_{f, \text{experimental}} - \Delta H^\circ_{f, \text{calculated}}$$

$$= \Delta H^\circ_{\text{combustion, calculated}} - \Delta H^\circ_{\text{combustion, experimental}}$$

Solved Examples

Ex-18. Calculate the heat of formation of benzene from the following data, assuming no resonance. Bond energies :

$$\text{C} - \text{C} = 83 \text{ kcal}, \text{C} = \text{C} = 140 \text{ kcal}, \text{C} - \text{H} = 99 \text{ kcal}$$

$$\text{Heat of atomisation of C} = 170.9 \text{ kcal}$$

$$\text{Heat of atomisation of H} = 52.1 \text{ kcal}$$



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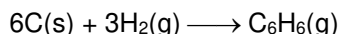
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ADVTDS - 34



Sol. We have to calculate ΔH for the reaction



For reactants :

Heat of atomisation of 6 moles of C = $6 \times 170.9 \text{ kcal}$

Heat of atomisation of 6 moles of H = $6 \times 52.1 \text{ kcal}$

For products :

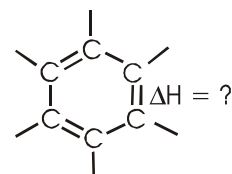
Heat of formation of 6 moles of C – H bonds = -6×99

Heat of formation of 3 moles of C–C = -3×83

Heat of formation of 3 moles of C = C bonds = -3×140

on adding, we get heat of formation of C_6H_6 , i.e.,

$$\Delta_f H = 6 \times 170.9 + 6 \times 52.1 - 6 \times 99 - 3 \times 83 - 3 \times 140 = -75 \text{ kcal}$$

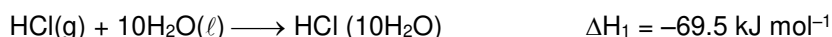


Section (E) : Enthalpy of solution & Born Haber's cycle

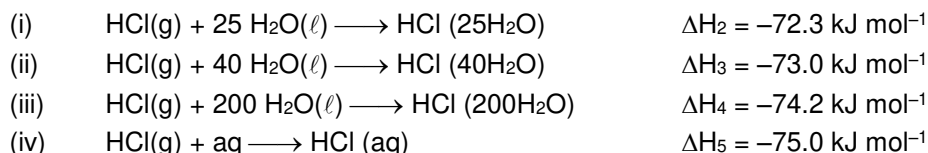
○ Integral enthalpy of solution

The integral enthalpy of solution at the given concentration is the enthalpy change when one mole of the solute is dissolved in a definite quantity of solvent to produce a solution of a desired concentration.

While recording integral enthalpies of solution it is a general practice to state the amount of the solvent in which 1 mole of solute is dissolved ; Thus



indicates that when 1 mole of hydrogen chloride gas is dissolved in 10 mol of water, there is an evolution of 69.5 kJ of heat. Other values are



Whenever amount of solvent is not specified then take its amount to be very large just like in equation no. (iv).

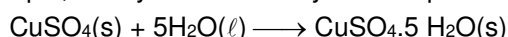
○ Enthalpy of Hydration :

Enthalpy of hydration is used in following two ways.

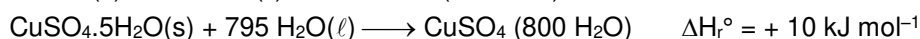
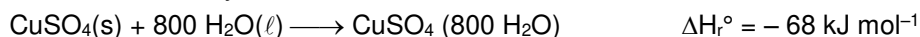
● Enthalpy of hydration of anhydrous or partially hydrated salts :

Enthalpy of hydration of a given anhydrous or partially hydrated salt is the enthalpy change when it combines with the requisite amount of water to form a new hydrated stable salt.

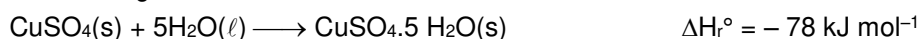
For example, the hydration of anhydrous cupric sulphate is represented by



There is a almost invariably a liberation of heat in such reactions, i.e. the value of ΔH is negative.



by subtraction, we get



● Enthalpy of hydration of gaseous ions.

Enthalpy of hydration of any gaseous ion is the enthalpy change when 1 mole of the gaseous ion is hydrated in large amount of water to form aqueous ion.

By convention, the standard enthalpy of formation of $\text{H}^+(\text{aq})$ is taken to be zero.

Enthalpy of hydration of Cl^- gaseous ions will be represented by :





Section (F) : Enthalpy of neutralization

- The amount of heat released when one gram equivalent of an acid is neutralised by one gram equivalent of a base.

or

- The amount of heat released in formation of one mole of water when an acid is neutralised by a base.

or

- Enthalpy of neutralization is defined as the enthalpy change when one mole of H^+ in dilute solution combines with one mole of OH^- to give rise to undissociated water, i.e.



Remember :

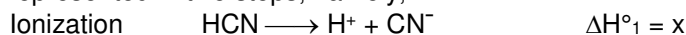
- For **Strong Acid + Strong Base**, heat of neutralisation is always equal to -13.7 kcal/mole or -57.1 kJ/mole .
- For any other combination of **acid and base** this heat is less than -13.7 kcal/mole or -57.1 kJ/mole .

○ Enthalpy of Ionization of Weak Electrolyte :

- Whenever a weak acid (or base) reacts with a strong base (or acid), the release of heat is less than 57.1 kJ mol^{-1} .
- It is because of the fact that these acids or bases are not completely ionized in solution. Some of the heat is consumed in ionizing these acids and bases this heat is known as enthalpy of ionization. Examples are :



The enthalpy of ionization can be calculated as follows. The neutralization of a weak acid, say HCN, may be represented in two steps, namely,



The complete reaction is obtained by adding the above two steps. Thus



Obviously, $\Delta H^\circ = \Delta H^\circ_1 + \Delta H^\circ_2$

$$\Delta H^\circ_1 = \Delta H^\circ - \Delta H^\circ_2 = [-12 - (-57.1)] = 45.1 \text{ kJ/mole}$$

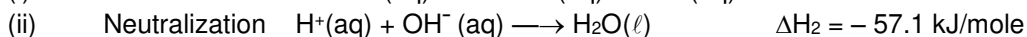
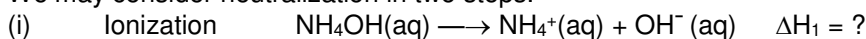
- Greater the enthalpy of ionization of any weak acid or weak base, weaker will be the acid or base.

Solved Examples

Ex-19. Enthalpy of neutralization of HCl by NaOH is -57.1 kJ/mol and by NH_4OH is -51.1 kJ/mol . Calculate the enthalpy of dissociation of NH_4OH .

Sol. Given that, $H^+(aq) + NH_4OH(aq) \longrightarrow NH_4^+(aq) + H_2O(l) \quad \Delta H = -51.1 \text{ kJ/mole}$

We may consider neutralization in two steps.



Thus, $\Delta H = \Delta H_1 + \Delta H_2$

Therefore, $\Delta H_1 = \Delta H - \Delta H_2 = -51.1 \text{ kJ/mol} + 57.1 \text{ kJ mol}^{-1} = 6.0 \text{ kJ/mol}$

Enthalpy of Precipitation :

Enthalpy of precipitation is the enthalpy change when one mole of a precipitate is formed.



Solved Examples

Ex-20. Calculate ΔH° for the reaction, $Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$ at $25^\circ C$.

Given $\Delta_f H^\circ(Ag^+, aq) = 105 \text{ kJ mol}^{-1}$, $\Delta_f H^\circ(Cl^-, aq) = -167 \text{ kJ mol}^{-1}$ and $\Delta_f H^\circ(AgCl, s) = -127 \text{ kJ mol}^{-1}$

Sol. For the reaction $Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$

We have
$$\Delta H^\circ = \Delta_f H^\circ(AgCl, s) - \Delta_f H^\circ(Ag^+, aq) - \Delta_f H^\circ(Cl^-, aq)$$

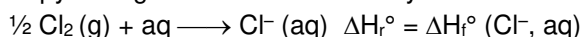
$$= [-127 - 105 - (-167)] \text{ kJ mol}^{-1} = -65 \text{ kJ mol}^{-1}$$





○ Enthalpy of Formation of ions :

The enthalpy change when one mole of hydrated ions is obtained from element in its standard state as.



By convention, the standard enthalpy of formation of $\text{H}^+(\text{aq})$ is taken to be zero.

We have seen that $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \longrightarrow \text{H}_2\text{O}(\ell) \quad \Delta_{\text{H}}^\circ = -57.1 \text{ kJ mol}^{-1}$

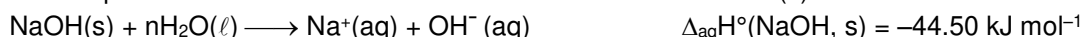
For this reaction, $\Delta_{\text{H}}^\circ = \Delta_{\text{H}}^\circ(\text{H}_2\text{O}, \ell) - \{\Delta_{\text{H}}^\circ(\text{H}^+, \text{aq}) + \Delta_{\text{H}}^\circ(\text{OH}^-, \text{aq})\}$

Hence, at 25°C , we get $\Delta_{\text{H}}^\circ(\text{H}^+, \text{aq}) + \Delta_{\text{H}}^\circ(\text{OH}^-, \text{aq}) = \Delta_{\text{H}}^\circ(\text{H}_2\text{O}, \ell) - \Delta_{\text{H}}^\circ$

so $\Delta_{\text{H}}^\circ(\text{OH}^-, \text{aq}) = \{-286.1 - (-57.1)\} \text{ kJ mol}^{-1} = -229.00 \text{ kJ mol}^{-1}$

- With the enthalpies of formation of these two ions, the enthalpy of formation of any other ion can be found from the enthalpies of formation and solution of its pure compound with H^+ or OH^- . For example, the enthalpy of formation of Na^+ can be calculated from the enthalpy of formation and enthalpy of infinite dilute solution of NaOH . The two values are :

- The chemical equation for the formation of infinite dilute solution of $\text{NaOH}(\text{s})$ is



Since there are equal amounts of water on both sides of the above equation, the two enthalpies give no net effect and thus

$$\Delta_{\text{aq}}\text{H}^\circ(\text{NaOH}, \text{s}) = \Delta_{\text{H}}^\circ(\text{Na}^+, \text{aq}) + \Delta_{\text{H}}^\circ(\text{OH}^-, \text{aq}) - \Delta_{\text{H}}^\circ(\text{NaOH}, \text{s})$$

$$\begin{aligned} \text{or } \Delta_{\text{H}}^\circ(\text{Na}^+, \text{aq}) &= \Delta_{\text{aq}}\text{H}^\circ(\text{NaOH}, \text{s}) - \Delta_{\text{H}}^\circ(\text{OH}^-, \text{aq}) + \Delta_{\text{H}}^\circ(\text{NaOH}, \text{s}) \\ &= [-44.50 - (-229.99) + (-425.61)] \text{ kJ mol}^{-1} = -240.12 \text{ kJ mol}^{-1} \end{aligned}$$

- Similarly, from $\text{NaCl}(\text{aq})$ or $\text{HCl}(\text{aq})$, the enthalpy of formation of $\text{Cl}^-(\text{aq})$ can be determined, and so on. The changes in enthalpy of any ionic reaction can then be found from these ionic enthalpies of formation and the usual enthalpies of formation of compounds.

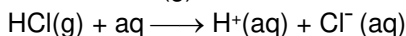
Solved Examples

Ex-21. The enthalpy of formation of $\text{H}_2\text{O}(\ell)$ is -285 kJ mol^{-1} and enthalpy of neutralization of a strong acid and a strong base is -55 kJ mol^{-1} . What is the enthalpy of formation of OH^- ions ?

Sol. Given that, $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \longrightarrow \text{H}_2\text{O}(\ell)$
 $\Delta_{\text{H}}^\circ \quad 0 \quad -285 \text{ kJ mol}^{-1}$
 $\Delta_{\text{neut}}\text{H} = \Delta_{\text{H}}^\circ(\text{H}_2\text{O}, \ell) - \Delta_{\text{H}}^\circ(\text{OH}^-, \text{aq})$

$$\begin{aligned} \text{Hence } \Delta_{\text{H}}^\circ(\text{OH}^-, \text{aq}) &= \Delta_{\text{H}}^\circ(\text{H}_2\text{O}, \ell) - \Delta_{\text{neut}}\text{H} \\ &= [-285 - (-55)] \text{ kJ mol}^{-1} = -230 \text{ kJ mol}^{-1} \end{aligned}$$

Ex-22. Calculate the enthalpy change when one mole of $\text{HCl}(\text{g})$ is dissolved in a very large amount of water at 25°C . The change in state is :



Given : $\Delta_{\text{H}}^\circ(\text{HCl}, \text{g}) = -92 \text{ kJ mol}^{-1}$ and $\Delta_{\text{H}}^\circ(\text{Cl}^-, \text{aq}) = -167 \text{ kJ mol}^{-1}$

Sol. For the reaction, $\text{HCl}(\text{g}) + \text{aq} \longrightarrow \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq})$

We have $\Delta_{\text{H}}^\circ = \Delta_{\text{H}}^\circ(\text{Cl}^-, \text{aq}) - \Delta_{\text{H}}^\circ(\text{HCl}, \text{g})$

$$\Delta_{\text{H}}^\circ = [-167 - (-92)] \text{ kJ mol}^{-1} = -75 \text{ kJ mol}^{-1}$$

MISCELLANEOUS SOLVED EXAMPLES

1. Find (in terms of "a") the amount of energy required to raise the temperature of a substance from 3 K to 5 K. At low temperatures. $C_P = aT^3$.

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

$$\begin{aligned} &= na \left[\frac{T^4}{4} \right]_3^5 = \frac{na}{4} [(5)^4 - (3)^4] \\ &= \frac{na[625 - 81]}{4} = 136 na. \end{aligned}$$

Ans. $q = 136 na$.





2. A thermally isolated vessel contains 100 g of water at 0°C. When air above the water is pumped out, some of the water freezes and some evaporates at 0°C itself. Calculate the mass of the ice formed such that no water is left in the vessel. Latent heat of vaporization of water at 0°C = 2.10×10^6 J/kg and latent heat of fusion of ice = 3.36×10^5 J/kg.

Sol. Total mass of the water = $M = 100$ g
 Latent heat of vaporization of water at 0°C
 $= L_1 = 21.0 \times 10^5$ J/Kg
 & Latent heat of fusion of ice = $L_2 = 3.36 \times 10^5$ J/Kg
 Suppose, the mass of the ice formed = m
 Then, the mass of water evaporated = $M - m$.
 Heat lost by the water in freezing = Heat taken by water in evaporation.
 Thus, $mL_2 = (M - m)L_1$ or $m = 86$ g.

Ans. 86.2 g

3. Work done in expansion of an ideal gas from 4 litre to 6 litre against a constant external pressure of 2.1 atm was used to heat up 1 mole of water at 293 K. If specific heat of water is $4.2 \text{ J g}^{-1} \text{ K}^{-1}$, what is the final temperature of water?

Sol. $W = -2.1 [6 - 4] = -2.1 \times 2$
 $= -4.2 \text{ atm} \times \text{lit.}$
 $= -4.2 \times 101.325 \text{ J}$

This work is used to heat up the water

Specific heat of $\text{H}_2\text{O} = 4.2 \frac{\text{J}}{\text{gram} \cdot \text{K}}$

Heat required for increasing temperature by 1°C of 1 mole = $4.2 \times 18 = 75.6 \text{ J}$

$4.2 \times 101.325 = 75.6 [T - 293]$

$5.63 = T - 293$

$T = 298.63 \text{ K}$

Ans. 298.63 K

4. 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/g and latent heat of vaporisation of liquid water at 0°C is 596 cal/g and the volume of ice in comparison to that of water (vapour) is neglected.

Sol. No. of mole = 1 mole

$T = 273 \text{ K}$.

$Pv = nRT$.

$\frac{4.6}{760} v = 1 \times 0.0821 \times 273$

$v = 3699 \text{ lit} \approx [3700 \text{ lit}]$

latent heat of fusion = 80 cal/gram Latent heat of vaporisation = 596 cal/gram

$\Delta H = 80 \times 18 + 596 \times 18 = [80 + 596] \times 18$

$\Delta H = 12168 \text{ cal}$

$\Delta H = \Delta E + P [V_2 - V_1]$

$12168 = \Delta E + \frac{4.6}{760} [3699] \times 24.24$

$\Rightarrow \Delta E = 12168 - \frac{4.6}{760} \times 3699 \times 24.24$

$= 12168 - 542.72 = 11625.28 \text{ cal.}$

Ans. 12168 cal, 11625.28 cal

5. For Ag, \bar{C}_p ($\text{JK}^{-1} \text{ mol}^{-1}$) is given by $24 + 0.006 T$. Calculate ΔH if 3 mol of silver are raised from 27°C to its melting point 927°C under 1 atm pressure.

Sol. $\Delta H = \int_{T_1}^{T_2} nC_p dT = \int_{T_1}^{T_2} 3(24 + .006T) dT = 3 [24 (T_2 - T_1) + \frac{1}{2} \times 0.006 (T_2^2 - T_1^2)]$

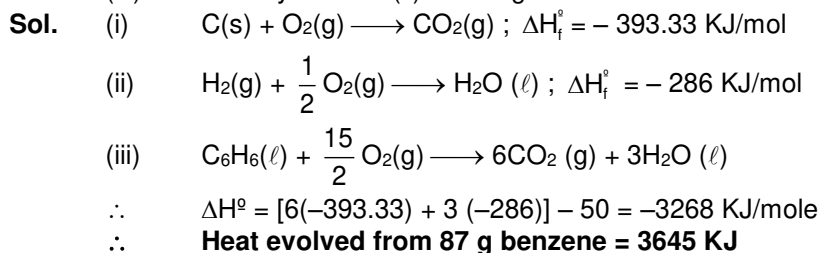
$= 3 \times 25650 = 76950 \text{ J}$

Ans. 76950 J



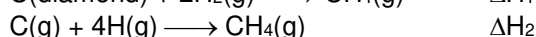
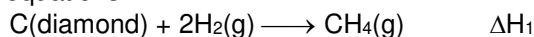
6. Calculate the amount of heat evolved during the complete combustion of 100 ml of liquid benzene from the following data.

- (i) 18 g of graphite on complete combustion evolve 590 KJ heat
- (ii) 15889 KJ heat is required to dissociate all the molecules of 1 litre water into H_2 and O_2 .
- (iii) The heat of formation of liquid benzene is 50 kJ/mol
- (iv) Density of $C_6H_6(l) = 0.87 \text{ g/ml}$



Ans. 3645 KJ

7. For the equations



Predict whether

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

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

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

(D) $\Delta H_1 = \Delta H_2 + \Delta_{\text{vap}}H(C) + \Delta_{\text{diss}}H(H_2)$

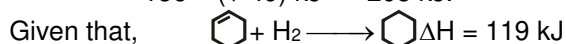
Ans. (B)

8. The standard molar enthalpies of formation of cyclohexane (l) and benzene (l) at 25°C are -156 and $+49 \text{ KJ mol}^{-1}$ respectively. The standard enthalpy of hydrogenation of cyclohexene (l) at 25° is -119 KJ mol^{-1} . Use these data to estimate the magnitude of the resonance energy of benzene.

Sol. Enthalpy of formation of 3 carbon-carbon double bonds

$$= \Delta H_f(\text{cyclohexene}) - \Delta H_f(\text{benzene})$$

$$= -156 - (+49) \text{ kJ} = -205 \text{ kJ.}$$



Theoretical enthalpy of formation of 3 double bonds in benzene ring

$$= 3 \times (-119) \text{ kJ} = -357 \text{ kJ.}$$

$$\therefore \text{resonance energy of benzene} = -357 - (-205) \text{ kJ} = -152 \text{ kJ mole}^{-1}$$

Ans. $-152 \text{ kJ mole}^{-1}$

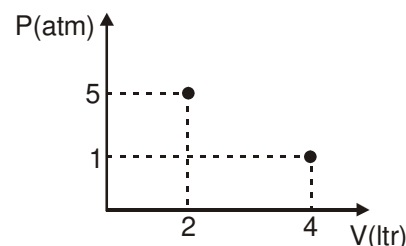
9. Following graph shows a single stage expansion process, then workdone by the system is

(A) -9104 J

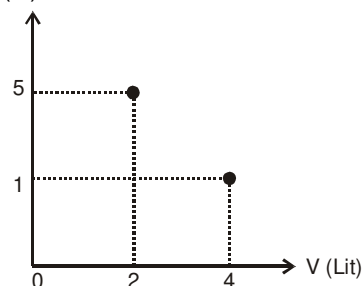
(B) -202.6 J

(C) -506 J

(D) -101.3 J



Sol.

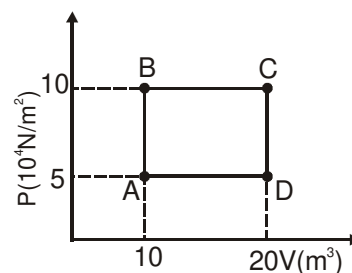


$$W = -P_{\text{ext}} (V_2 - V_1) = -1 \times 2 \times 101.325 \text{ J} = -202.6 \text{ J}$$

Ans. (B)



10. A sample of 2 kg of helium (assumed ideal) is taken through the process ABC and another sample of 2 kg of the same gas is taken through the process ADC. Then the temperature of the states A and B are (Given $R = 8.3 \text{ joules/mol K}$) :
- (A) $T_A = 120.5 \text{ K}$, $T_B = 120.5 \text{ K}$
 (B) $T_A = 241 \text{ K}$, $T_B = 241 \text{ K}$
 (C) $T_A = 120.5 \text{ K}$, $T_B = 241 \text{ K}$
 (D) $T_A = 241 \text{ K}$, $T_B = 482 \text{ K}$



Sol. $\frac{0.5 \times 10^5}{1.01 \times 10^5} \times 10 \times 10^3 = \frac{2 \times 1000}{2} \times 0.082 T_A$

$$\frac{1}{1.01} = 0.082 T_A$$

$$T_A = 120.5 \text{ K}$$

at constant volume

$$\frac{P_A}{T_A} = \frac{P_B}{T_B}$$

$$T_B = \frac{P_B \cdot T_A}{P_A} = \frac{10}{5} \times 120.5 = 241 \text{ K}.$$

Ans. (C)

11. In an isothermal expansion of a gaseous sample the correct relation is (consider w (work) with sign according to new IUPAC convention)
 [The reversible and irreversible processes are carried out between same initial and final states.]
 (A) $w_{\text{rev}} > w_{\text{irrev}}$ (B) $w_{\text{irrev}} > w_{\text{rev}}$ (C) $q_{\text{rev}} < q_{\text{irrev}}$ (D) can not be predicted

Ans. (B)

12. One mole of an ideal monoatomic gas is caused to go through the cycle shown in figure. Then, the change in the internal energy in expanding the gas from a to c along the path abc is :
- (A) $3 P_0 V_0$ (B) $6 RT_0$
 (C) $4.5 RT_0$ (D) $10.5 RT_0$

Sol. $Pv = nRT$ at point C
 $2P_0 \times 4V_0 = 1 \times RT_C$

$$T_C = \left[\frac{8P_0 V_0}{R} \right]$$

at point a

$$P_0 V_0 = 1 \times RT_0$$

$$T_0 = \frac{P_0 V_0}{R}; \quad T_C = 8 T_0$$

$$\text{Change in internal energy} = [nC_v dT]$$

$$\text{For path a to b} = 1 \times \frac{3}{2} R \times [3T_0] = \frac{9}{2} RT_0$$

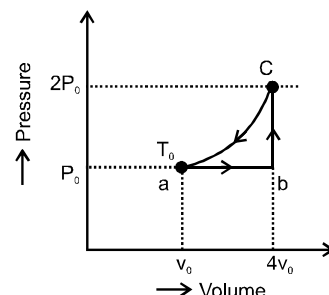
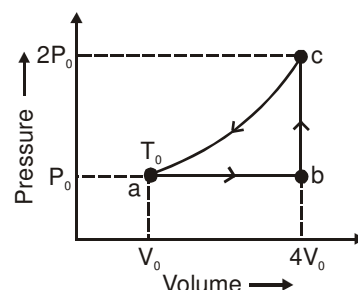
$$\text{For path b to c} = 1 \times \frac{3}{2} R \times [4T_0] = 6T_0 R$$

$$\text{Total change} = \frac{9}{2} RT_0 + 6RT_0 = \frac{21 RT_0}{2} = 10.5 RT_0.$$

So total change in internal energy

$$\Delta U = 10.5 RT_0$$

Ans. (D)



13. A certain mass of gas is expanded from (1L, 10 atm) to (4L, 5 atm) against a constant external pressure of 1 atm. If initial temperature of gas is 300 K and the heat capacity of process is $50 \text{ J/}^\circ\text{C}$. Then the enthalpy change during the process is (1L atm $\approx 100 \text{ J}$)
- (A) $\Delta H = 15 \text{ kJ}$ (B) $\Delta H = 15.7 \text{ kJ}$ (C) $\Delta H = 14.4 \text{ kJ}$ (D) $\Delta H = 14.7 \text{ kJ}$



Sol. $\Delta H = \Delta E + \Delta(PV)$ & $\Delta E = q + W = (50 \times 300 - 3 \times 100) \text{ J}$ [as $T_f = 2 \times 300 \text{ K} = 600 \text{ K}$] = 14.7 kJ
 $\Delta H = 14700 + 10 \times 100 = 15700 \text{ J} = 15.7 \text{ kJ}$.

Ans (B)

- 14.** One mole of an ideal monoatomic gas expands isothermally against constant external pressure of 1 atm from initial volume of 1L to a state where its final pressure becomes equal to external pressure. If initial temperature of gas is 300 K then total entropy change of system in the above process is :
 [R = 0.082 L atm mol⁻¹ K⁻¹ = 8.3 J mol⁻¹ K⁻¹].

(A) 0 (B) $R \ln(24.6)$ (C) $R \ln(2490)$ (D) $\frac{3}{2} R \ln(24.6)$

Sol. $\Delta S = nR \ln\left(\frac{V_f}{V_i}\right) = R \ln\left(\frac{P_i}{P_f}\right) = R \ln\left(\frac{300R}{1 \text{ L} \times 1 \text{ atm}}\right) = R \ln(24.6)$

Ans. (B)

- 15.** For a perfectly crystalline solid $C_{p,m} = aT^3$, where a is constant. If $C_{p,m}$ is 0.42 J/K-mol at 10 K, molar entropy at 10 K is :

(A) 0.42 J/K-mol (B) 0.14 J/K-mol (C) 4.2 J/K-mol (D) zero

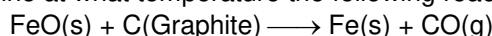
Sol. $0.42 = a(10)^3 \Rightarrow a = 0.42 \times 10^{-3}$
 $S_m = \int_0^{10} \frac{C_{p,m}}{T} dT = \int_0^{10} \frac{aT^3}{T} dT = \frac{a}{3} [10^3 - 0] = \frac{0.42}{3} = 0.14 \text{ J/K-mol}$

Ans. (B)

- 16.** Given the following data :

Substance	ΔH° (kJ/mol)	S° (J/mol K)	ΔG° (kJ/mol)
FeO(s)	-266.3	57.49	-245.12
C (Graphite)	0	5.74	0
Fe(s)	0	27.28	0
CO(g)	-110.5	197.6	-137.15

Determine at what temperature the following reaction is spontaneous ?



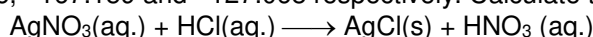
- (A) 298 K (B) 668 K (C) 966 K
 (D) ΔG° is +ve, hence the reaction will never be spontaneous

Sol. $\text{FeO(s)} + \text{C(graphite)} \longrightarrow \text{Fe(s)} + \text{CO(g)}$

- (1) $\Delta H = 0 + [-110.5] - (-266.3)$
 $= -110.5 + 266.3$
 $= +155.8 \text{ kJ/mole}$
 (2) $\Delta S = 27.28 + 197.6 - 57.49 - 5.74 = 161.65 \text{ J/mole}$
 (3) $\Delta G = \Delta H - T\Delta S = 0 = 155.8 - T \times 161.65 \times 10^{-3}$
 $T \times 161.65 \times 10^{-3} = 155.8 \Rightarrow T = 963.8 \text{ K}$

Ans. (C)

- 17.** If ΔH_f° for Ag^+ (infinitely diluted), NO_3^- (infinitely diluted), Cl^- (infinitely diluted) and AgCl(s) are 105.579, -207.36, -167.159 and -127.068 respectively. Calculate the enthalpy change for the reaction



- (A) 21.471 KJ/mol (B) 145.688 KJ/mol (C) -65.488 KJ/mol (D) None

Sol. $\Delta H_{\text{reaction}}^\circ = [\Delta H_f^\circ(\text{AgCl}) + \Delta H_f^\circ(\text{H}^+) + \Delta H_f^\circ(\text{NO}_3^-)] - [\Delta H_f^\circ(\text{Ag}^+) + \Delta H_f^\circ(\text{NO}_3^-) + \Delta H_f^\circ(\text{Cl}^-) + \Delta H_f^\circ(\text{H}^+)]$
 $= -127.068 - [105.579 - 167.159] = -65.488 \text{ KJ/mol}$

Ans. (C)

- 18.** What is the work done against the atmosphere when 25 grams of water vaporizes at 373 K against a constant external pressure of 1 atm ? Assume that steam obeys perfect gas laws. Given that the molar enthalpy of vaporization is 9.72 kcal/mole, what is the change of internal energy in the above process ?

- (A) 1294.0 cal, 11247 cal (B) 921.4 cal, 11074 cal
 (C) 1025.6 cal ; 12474.3 cal (D) 1129.3 cal, 10207 cal

Sol. Mole of $\text{H}_2\text{O} = 1.39$

$$Pv = nRT$$

$$1 \times v = 1.39 \times 0.082 \times 373 \Rightarrow v = 42.51 \text{ lit}$$

$$w = P_{\text{ext.}} dv = 1 \times [42.80] \text{ atm} \times \text{lit.} = 42.80 \times 101.325 \text{ J} = \frac{42.80 \times 101.325}{4.2} = 1025.6 \text{ cal}$$

$$\Delta H = \Delta U + [P\Delta v] = 12470.6 \text{ cal.}$$

$$\Delta U = \Delta H - P\Delta v = 13500 - 1025.6 = 12474.3 \text{ cal}$$

Ans. (C)



THERMODYNAMICS 1st LAW

Exercise-1

Marked Questions may have for Revision Questions.

PART - I : SUBJECTIVE QUESTIONS

Section (A) : Basic definitions

- A-1.** Categorize these properties into state and path functions.
 (a) Internal energy (b) Volume (c) Heat (d) Enthalpy
 (e) Temperature (f) Work (g) Molar heat capacity
- A-2.** Categorize these properties into extensive and intensive
 (a) Temperature (b) Internal energy (c) Heat (d) Density
 (e) Molar volume (f) molar enthalpy (g) viscosity
- A-3.** Identify the state functions and path functions.
 (a) The potential energy of a book in shelf.
 (b) The heat evolved when a cube of sugar is oxidized to $\text{CO}_{2(g)}$ and $\text{H}_2\text{O}_{(g)}$.
 (c) The work accomplished in burning a litre of gasoline.

Section (B) : Thermodynamics processes & graph

Draw the P-V diagram for the following cyclic processes

- B-1.** Isothermal expansion from state A to B, isochoric pressure increment from B to C, isothermal contraction from C to D, isobaric contraction from D \rightarrow A.
- B-2.** Isobaric expansion from A \rightarrow B, isochoric pressure increase from B \rightarrow C, isobaric compression from C \rightarrow D, isochoric pressure drop from D \rightarrow A.
- B-3.** Isobaric expansion from A \rightarrow B, isochoric pressure drop from B \rightarrow C, isothermal compression C \rightarrow A.

Section (C) : Work calculation

- C-1.** Calculate the work done by 0.1 mole of a gas at 27°C to double its volume at constant pressure (in isobaric process) ($R = 2 \text{ cal mol}^{-1} \text{ K}^{-1}$)
- C-2.** Calculate the work done during isothermal reversible expansion of one mole ideal gas from 10 atm to 1 atm at 300 K.
- C-3.** At 25°C , a 0.01 mole sample of a gas is compressed in volume from 4.0 L to 1.0 L at constant temperature. What is work done for this process if the external pressure is 4.0 bar ?

Section (D) : Heat & Internal energy

- D-1.** Calculate the heat necessary to raise the temperature of 60 g of aluminium from 35°C to 55°C . Molar heat capacity of Al is $24 \text{ mole}^{-1} \text{ K}^{-1}$.
- D-2.** In a container, two mole of a diatomic ideal gas is allowed to expand against 1 atm pressure & volume change from 2 litre to 5 litre isobarically then calculate change in internal energy.

Section (E) : First law of thermodynamics

- E-1.** The work done by a system is 8 joule, when 40 joule heat is supplied to it. What is the increase in internal energy of system.
- E-2.** A gas expands from 2 L to 6 L against a constant pressure of 0.5 atm on absorbing 200 J of heat. Calculate the change in internal energy.



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

- F-1.** One mole of an ideal monoatomic gas $\left(\gamma = \frac{5}{3}\right)$ is mixed with one mole of a diatomic gas $\left(\gamma = \frac{7}{5}\right)$. (γ denotes the ratio of specific heat at constant pressure, to that at constant volume) find γ for the mixture ?
- F-2.** A piston freely move in a insulated cylinder from volume 5 lit to 10 lit then calculate work done & heat during this expansion.

Section (G) : Enthalpy

- G-1.** If 1.0 kcal of heat is added to 1.2 L of O_2 in a cylinder at constant pressure of 1 atm, the volume increases to 1.5 L. Calculate ΔU and ΔH of the process. (1 L-atm = 100 J, 1 cal = 4.2 J)
- G-2.** 10 g of argon gas is compressed isothermally and reversibly at a temperature of $27^\circ C$ from 10 L to 5L. Calculate enthalpy change. Assume ideal behaviour (ΔH) for this process $R = 2.0 \text{ cal K}^{-1} \text{ mol}^{-1}$. $\log_{10} 2 = 0.30$ (Atomic mass of Ar = 40)

Section (H) : Phase transition

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

PART - II : ONLY ONE OPTION CORRECT TYPE

Section (A) : Basic definitions

- A-1.** Warming ammonium chloride with sodium hydroxide in a test tube is an example of :
(A) Closed system (B) Isolated system (C) Open system (D) None of these
- A-2.** Out of boiling point (I), entropy (II), pH (III) and e.m.f. of a cell (IV), intensive properties are :
(A) I, II (B) I, II, III (C) I, III, IV (D) All of the above
- A-3.** In which case bodies become hot due to mechanical energy losses
(i) Rub our hands for sometime (ii) Two vehicles collide with each other
(iii) Aeroplane crash (iv) Sliding of legs on roof surface
(v) Transfer of energy from hot body to cold body
(A) 5 (B) 4 (C) 3 (D) 2
- A-4.** Predict the total number of intensive properties :
(i) Free energy (ii) Critical density (iii) Viscosity (iv) Specific heat capacity
(v) molar heat capacity (vi) Kinetic energy (vii) Specific gravity (viii) Dielectric constant
(ix) pH
(A) 9 (B) 8 (C) 7 (D) 6
- A-5.** An ideal gas filled at pressure of 2 atm and temp of 300 K, in a balloon is kept in vacuum with in a large insulated container. Wall of balloon is punctured then container temperature :
(A) Decreases (B) Increases (C) Remain constant (D) Unpredictable

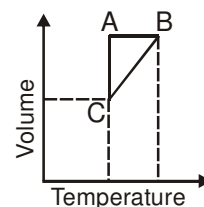
Section (B) : Thermodynamics processes & graph

- B-1.** A gaseous system changes from state A (P_1, V_1, T_1) to B (P_2, V_2, T_2), B to C (P_3, V_3, T_3) and finally from C to A. The whole process may be called :
(A) Reversible process (B) Cyclic process
(C) Isobaric process (D) Spontaneous process
- B-2.** A well stoppered thermos flask contains some ice cubes. This is an example of a-
(A) Closed system (B) Open system
(C) Isolated system (D) Non-thermodynamic system

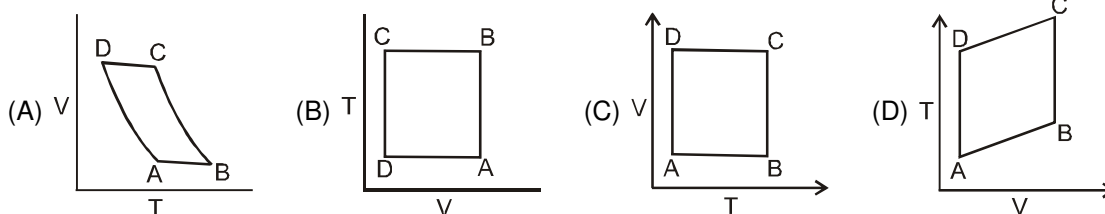
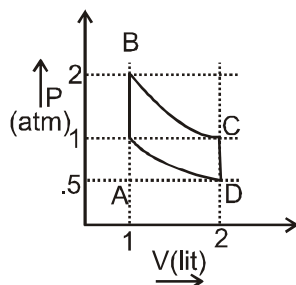


- B-3.** Five moles of a gas is put through a series of changes as shown graphically in a cyclic process the $A \rightarrow B$, $B \rightarrow C$ and $C \rightarrow A$ respectively are

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

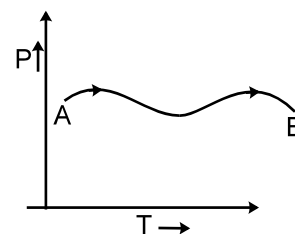


- B-4.** A cyclic process ABCD is shown in P-V diagram for an ideal gas. Which of the diagram represent the same process.



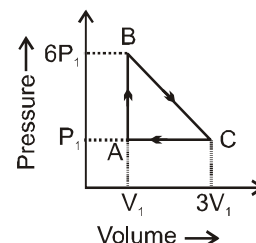
- B-5.** The P-T graph as given below was observed for a process on an ideal gas, which of the following statement is true.

(A) $w = +ve$, $\Delta H = +ve$
 (B) $w = -ve$, $\Delta H = -ve$
 (C) $w = -ve$, $\Delta H = +ve$
 (D) $w = +ve$, $\Delta H = -ve$



Section (C) : Work Calculation

- C-1.** A thermodynamic system goes from states (i) P_1, V to $2P_1, V$ (ii) P, V_1 to $P, 2V_1$. Then work done in the two cases is
 (A) Zero, Zero (B) Zero, $-PV_1$ (C) $-PV_1$, Zero (D) $-PV_1$, $-P_1V_1$
- C-2.** The work done in ergs for the reversible expansion of one mole of an ideal gas from a volume of 10 litres to 20 litres at 25°C is :
 (A) $-2.303 \times 298 \times 0.082 \log 2$ (B) $-298 \times 10^7 \times 8.31 \times 2.303 \log 2$
 (C) $-2.303 \times 298 \times 0.082 \log 0.5$ (D) $-8.31 \times 10^7 \times 298 \times 2.303 \log 0.5$
- C-3.** An ideal gas is taken around the cycle ABCA as shown in P-V diagram. The net work done by the gas during the cycle is equal to :
 (A) $12P_1V_1$
 (B) $6P_1V_1$
 (C) $5P_1V_1$
 (D) P_1V_1



Section (D) : Heat & Internal energy

- D-1.** For freezing of liquid in a system :
 (A) $q = 0$ (B) $q > 0$
 (C) $q < 0$ (D) $q > 0$ or $q < 0$ (depending on the nature of liquid)



- D-2.** For 2 mole of an ideal gas; the relation between C_p & C_v (non-molar) are :
 (A) $C_p - C_v = 2R$ (B) $C_v - C_p = 2R$ (C) $C_p - C_v = R$ (D) $C_v - C_p = R$

Section (E) : First law of thermodynamics

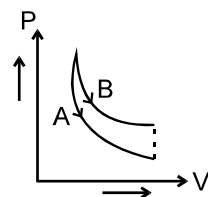
- E-1.** A system absorb 600J of heat and does work equivalent to 300J on its surroundings. The change in internal energy is
 (A) 300 J (B) 400 J (C) 500 J (D) 600 J
- E-2.** In an isochoric process the increase in internal energy is
 (A) Equal to the heat absorbed (B) Equal to the heat evolved
 (C) Equal to the work done (D) Equal to the sum of the heat absorbed and work done
- E-3.** In an isothermal expansion of an ideal gas. Select wrong statement :
 (A) there is no change in the temperature of the gas
 (B) there is no change in the internal energy of the gas
 (C) the work done by the gas is equal to the heat supplied to the gas
 (D) the work done by the gas is equal to the change in its internal energy
- E-4.** A system undergoes a process which absorbed 0.5 kJ of heat and undergoing an expansion against external pressure of 1 atm, during the process change in internal energy is 300 J. Then predict the change in volume (lit.)
 (A) 1 (B) 2 (C) 3 (D) 4
- E-5.** When two moles of Hydrogen atoms join together to form a mole of hydrogen molecules in a closed rigid vessel with diathermic walls.

$$2H(g) \longrightarrow H_2(g)$$

 (A) $w < 0$ (B) $\Delta U = \text{negative}$ (C) $q_{\text{system}} = \text{positive}$ (D) $q_{\text{surrounding}} = \text{negative}$

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

- F-1.** The temperature of the system decreases in an
 (A) Adiabatic compression (B) Isothermal compression
 (C) Isothermal expansion (D) Adiabatic expansion
- F-2.** 1 mole of NH_3 gas at $27^\circ C$ is expanded in reversible adiabatic condition to make volume 8 times ($\gamma = 1.33$). Final temperature and work done respectively are :
 (A) 150 K, 900 cal (B) 150 K, 400 cal (C) 250 K, 1000 cal (D) 200 K, 800 cal
- F-3.** In figure, A and B are two adiabatic curves for two different gases. Then A and B corresponds to :
 (A) Ar and He respectively
 (B) He and H_2 respectively
 (C) O_2 and H_2 respectively
 (D) H_2 and He respectively



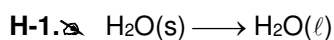
Section (G) : Enthalpy

- G-1.** One mole of non-ideal gas undergoes a change of state (1.0 atm, 3.0 L, 200 K) to (4.0 atm, 5.0 L, 250 K) with a change in internal energy (ΔU) = 40 L-atm. The change in enthalpy of the process in L-atm ;
 (A) 43 (B) 57 (C) 42 (D) None of these
- G-2.** For the isothermal expansion of an ideal gas
 (A) U and H increases (B) U increases but H decreases
 (C) H increases but U decreases (D) U and H are unaltered
- G-3.** A vessel contains 100 litres of a liquid X. Heat is supplied to the liquid in such a fashion that, Heat given = change in enthalpy. The volume of the liquid increases by 2 litres. If the external pressure is one atm, and 202.6 Joules of heat were supplied then, [U - total internal energy]
 (A) $\Delta U = 0$, $\Delta H = 0$ (B) $\Delta U = + 202.6 J$, $\Delta H = + 202.6 J$
 (C) $\Delta U = - 202.6 J$, $\Delta H = - 202.6 J$ (D) $\Delta U = 0$, $\Delta H = + 202.6 J$





Section (H) : Phase transition



This phase transition is carried out at constant temp and pressure then work done during the process :
 (A) $W < 0$ (B) $W > 0$ (C) $W = 0$ (D) can't be determined

H-2. At 1 atm pressure n mole of water (0°C) is frozen to ice (0°C) then heat transfer is :

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

PART - III : MATCH THE COLUMN

1. Match the column:

	Column-I		Column-II
(A)	Reversible isothermal expansion of an ideal gas	(p)	$w = -2.303 nRT \log \left(\frac{V_2}{V_1} \right)$
(B)	Reversible adiabatic compression of an ideal gas	(q)	$PV^\gamma = \text{constant}$
(C)	Irreversible adiabatic expansion of an ideal gas	(r)	$w = \frac{nR}{(\gamma - 1)} (T_2 - T_1)$
(D)	Irreversible isothermal compression of an ideal gas	(s)	$\Delta H = 0$

2. Match the column:

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

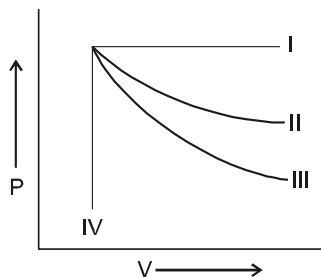
Exercise-2

PART - I : ONLY ONE OPTION CORRECT TYPE

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

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

2.



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

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

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

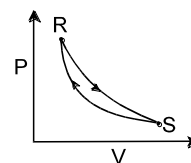
	Column-I		Column-II
(X)	Isothermal	(p)	$\Delta T = 0$
(Y)	Isobaric	(q)	$\Delta V = 0$
(Z)	Adiabatic	(r)	$\Delta P = 0$
(W)	Isochoric	(s)	$q = 0$

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



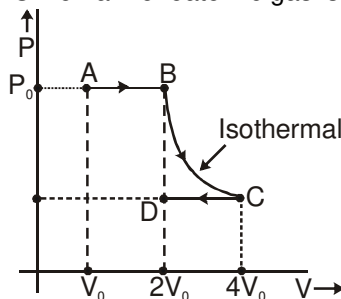


4. Consider the cyclic process $R \rightarrow S \rightarrow R$ as shown in the Fig. You are told that one of the path is adiabatic and the other one isothermal. Which one of the following is(are) true?



- (A) Process $R \rightarrow S$ is isothermal
(B) Process $S \rightarrow R$ is adiabatic
(C) Process $R \rightarrow S$ is adiabatic
(D) Such a graph is not possible

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



- (A) $w = -2 P_0 V_0 \ln 2$,
(B) $w = -2 P_0 V_0 \ln 4$,
(C) $w = -P_0 V_0 (1 + \ln 2)$,
(D) $w = -P_0 V_0 \ln 2$,
6. 50 L of a certain liquid is confined in a piston system at the external pressure 100 atm. This pressure is suddenly released and liquid is expanded against the constant atmospheric pressure, volume of the liquid increases by 1 L and the final pressure on the liquid is 10 atm. Find the workdone.
(A) 1 L.atm (B) 5 L.atm (C) 500 L.atm (D) 50 L.atm
7. Which one of the following equations does not correctly represent the first law of thermodynamics for the given process in ideal gas ?
(A) Isothermal process : $q = -w$ (B) Cyclic process : $q = -w$
(C) Adiabatic process : $\Delta E = q$ (D) Expansion of a gas into vacuum : $\Delta E = q$
8. One mole of an ideal gas $\left(C_{v,m} = \frac{5}{2}R\right)$ at 300 K and 5 atm is expanded adiabatically to a final pressure of 2 atm against a constant pressure of 2 atm. Final temperature of the gas is :
(A) 270 K (B) 273 K (C) 248.5 K (D) 200 K
9. The magnitudes of enthalpy changes for irreversible adiabatic expansion of a gas from 1L to 2L is ΔH_1 and for reversible adiabatic expansion for the same expansion is ΔH_2 . Then
(A) $\Delta H_1 > \Delta H_2$
(B) $\Delta H_1 < \Delta H_2$
(C) $\Delta H_1 = \Delta H_2$, enthalpy being a state function ($\Delta H_1 = \Delta H_2$)
(D) $\Delta H_1 = \Delta E_1$ & $\Delta H_2 = \Delta E_2$ where ΔE_1 & ΔE_2 are magnitudes of change in internal energy of gas in these expansions respectively.

PART - II : SINGLE AND DOUBLE VALUE INTEGER TYPE

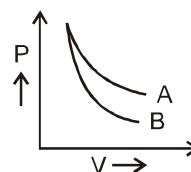
1. How many statements are false ?
(i) Thermodynamics is concerned only with total energy of the system.
(ii) 1st law of thermodynamics can be applied on the individual particle enclosed in vessel.
(iii) Many thermodynamic properties can not be measured absolutely, so change in thermodynamic property is required for calculation.
(iv) Feasibility of any chemical reaction can not be explained by thermodynamics.
(v) When surrounding is always in equilibrium with the system, the process called reversible.
(vi) Thermodynamics predict the time of attain the equilibrium.



2. How many of the following physical properties are extensive :
- | | | | |
|-------------------------------|----------------------|-------------------------|-------------------------------|
| (i) Free energy | (ii) vapour pressure | (iii) mole | (iv) Kinetic energy |
| (v) Entropy | (vi) Internal energy | (vii) Enthalpy | (viii) specific heat capacity |
| (ix) Coefficient of viscosity | | (x) Total heat capacity | |
3. How many of the following are state function :
- | | | | |
|-----------------------------|-------------------------|----------------|--------------|
| (i) Internal energy | (ii) Heat | (iii) Enthalpy | (iv) Entropy |
| (v) Pressure | (vi) Temp. | (vii) volume | (viii) Work |
| (ix) specific heat capacity | (x) molar heat capacity | | |
4. Two moles of He gas ($\gamma = 5/3$) are initially at temp 27°C and occupy a volume of 20 litres. The gas is first expanded at constant pressure until its volume is doubled. Then it undergoes reversible adiabatic change, until the volume become 110 lit, then predict the value of $T/100$ (where T is the final temperature, $\left(\frac{4}{11}\right)^{2/3} = \frac{1}{2}$)
5. A sample of an ideal gas is expanded from 1 dm^3 to 3 dm^3 in a reversible process for which $P = KV^3$, with $K = 1/5$ (atm/ dm^3), what is work done by gas (L atm).
6. The valve on a cylinder containing initially 1 liters of an ideal gas at 7 atm and 25°C is opened to the atmosphere, Whose the pressure is 760 torr and the temperature is 25°C . Assuming that the process is isothermal, how much work (in L.atm) is done on the atmosphere by the action of expansion ?
7. The work done (in Cal) in adiabatic compression of 2 mole of an ideal monoatomic gas by constant external pressure of 2 atm starting from intial pressure of 1 atm and initial temperature of 30 K ($R = 2$ cal/mol-degree)
8. One mole of a non-ideal gas undergoes a change of state ($2.0\text{ atm}, 3.0\text{ L}, 95\text{ K}$) \rightarrow ($4.0\text{ atm}, 5.0\text{ L}, 245\text{ K}$) with a change in internal energy, $\Delta U = 30.0\text{ L. atm}$. Calculate change in enthalpy of the process in L. atm.

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

1. Which of the following properties of a system are intensive ?
- | | |
|----------------------------|--|
| (A) color | (B) kinetic energy per mole |
| (C) X (where $X = U + H$) | (D) specific volume (volume per unit mass) |
2. Choose the correct statement :
- (A) system and surrounding are always separated by a real or imaginary boundary.
 (B) perfectly isolated system can never be created.
 (C) in reversible process, energy change in each step can be reversed.
 (D) irreversible process is also called quasi-equilibrium state.
3. In an isothermal expansion of a gaseous sample, the correct relation is : (consider w (work) with sign according to new IUPAC convention)
 [The reversible and irreversible processes are carried out between same initial and final states.]
- | | | | |
|---|---|---|---|
| (A) $w_{\text{rev}} > w_{\text{irrev}}$ | (B) $w_{\text{irrev}} > w_{\text{rev}}$ | (C) $q_{\text{rev}} < q_{\text{irrev}}$ | (D) $\Delta E_{\text{rev}} = \Delta E_{\text{irrev}}$ |
|---|---|---|---|
4. During the isothermal expansion of an ideal gas :
- | | |
|--|--------------------------------------|
| (A) The internal energy remains unaffected | (B) The temperature remains constant |
| (C) The enthalpy remains unaffected | (D) The enthalpy increases |
5. P-V plot for two gases (assuming ideal) during adiabatic processes are given in the figure. Plot A and plot B should correspond respectively to :
- | |
|-------------------------------------|
| (A) He and H_2 |
| (B) H_2 and He |
| (C) SO_3 and CO_2 |
| (D) N_2 and Ar |





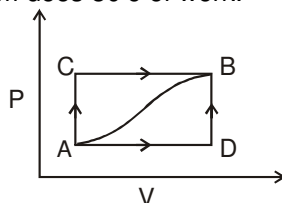
6. An ideal gas undergoes adiabatic expansion against constant external pressure. Which of the following is incorrect :
 (A) Temperature of the system decreases.
 (B) The relation $PV^\gamma = \text{constant}$ will be valid (where P and V are gas variables)
 (C) $\Delta E + P_{\text{ext}}\Delta V = 0$
 (D) Enthalpy of the gas remains unchanged.
7. For the sublimation of a solid at 1 atm, which of the following may be correct
 (A) $\Delta U > 0$ at low temperature
 (B) $q > 0$
 (C) $\Delta U < 0$ at high temperature
 (D) $\Delta H > 0$

PART - IV : COMPREHENSION

Read the following passage carefully and answer the questions.

Comprehension

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



- How much heat flows into the system along path ADB if the work done by the system is 10 J :
 (A) 40 J (B) 60 J (C) 80 J (D) 100 J
- When the system is returned from state B to A along the curved path, the work done on the system is 20 J. Does the system absorb or liberate heat and by how much ?
 (A) -70 J ; heat is liberated. (B) -60 J ; heat is liberated.
 (C) +70 J ; heat is absorbed. (D) +60 J ; heat is absorbed.
- If $E_D - E_A = +40\text{J}$, the heat absorbed in the processes AD and DB are respectively :
 (A) $q_{AD} = 30\text{ J}$ and $q_{DB} = -90\text{ J}$ (B) $q_{AD} = +60\text{ J}$ and $q_{DB} = 0\text{ J}$
 (C) $q_{AD} = -30\text{ J}$ and $q_{DB} = 90\text{ J}$ (D) $q_{AD} = +50\text{ J}$ and $q_{DB} = 10\text{ J}$

Exercise-3

* Marked Questions may have more than one correct option.

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

- The given reaction

$$2\text{CO} + \text{O}_2 \longrightarrow 2\text{CO}_2$$

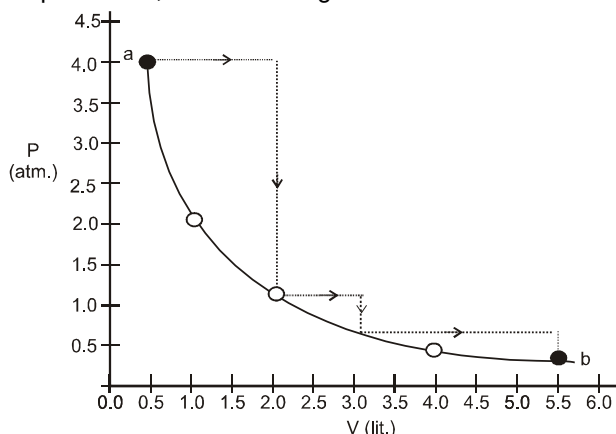
$$\text{2moles} \quad \text{1 mole}$$

$$\Delta H = -560\text{ kJ}$$
 is carried out in one litre container, if the pressure in the container gets changes from 70 atm to 40 atm as reaction gets completed. Calculate ΔU of the reaction. [1L atm = 0.1 kJ] [JEE 2006, 6/184]
- * Among the following, the state function(s) is(are) : [JEE 2009, 4/160]
 (A) Internal energy (B) Irreversible expansion work
 (C) Reversible expansion work (D) Molar enthalpy
- * Among the following, the intensive property is (properties are) : [JEE 2010, 3/163]
 (A) molar conductivity (B) electromotive force
 (C) resistance (D) heat capacity



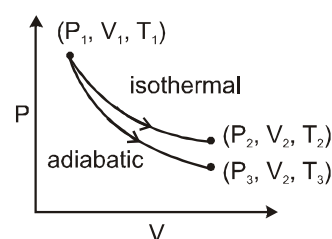


4. One mole of an ideal gas is taken from **a** and **b** along two paths denoted by the solid and the dashed lines as shown in the graph below. If the work done along the solid line path is w_s and that along the dotted line path is w_d , then the integer closest to the ratio w_d / w_s is : **[JEE 2010,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

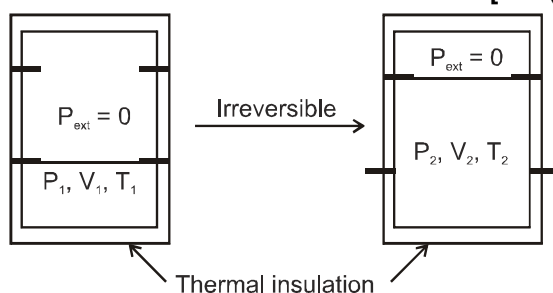


- 5.* The reversible expansion of an ideal gas under adiabatic and isothermal conditions is shown in the figure. Which of the following statement(s) is (are) correct ? **[JEE 2012, 4/136]**

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



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



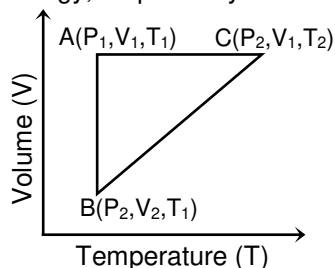
- (A) $q = 0$ (B) $T_2 = T_1$ (C) $P_2 V_2 = P_1 V_1$ (D) $P_2 V_2^\gamma = P_1 V_1^\gamma$

- 7.* An ideal gas is expanded from (p_1, V_1, T_1) to (p_2, V_2, T_2) under different conditions. The correct statement(s) among the following is (are) **[JEE(Advanced) 2017, 4/122]**

- (A) 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
 (B) The change in internal energy of the gas is (i) zero, if it is expanded reversibly with $T_1 = T_2$, and (ii) positive, if it is expanded reversibly under adiabatic conditions with $T_1 \neq T_2$
 (C) If the expansion is carried out freely, it is simultaneously both isothermal as well as adiabatic
 (D) 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



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



The correct option(s) is (are)

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

- [JEE(Advanced) 2018, 4/120]
 (B) $W_{BC} = P_2 (V_2 - V_1)$ and $q_{BC} = \Delta H_{AC}$
 (D) $q_{BC} = \Delta H_{AC}$ and $\Delta H_{CA} > \Delta U_{CA}$

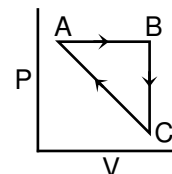
PART - II : JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS)

JEE-MAIN OFFLINE PROBLEMS

- 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 vapourization of water at 1 bar and $373\text{ K} = 41\text{ kJ mol}^{-1}$ and $R = 8.3\text{ J mol}^{-1}\text{ K}^{-1}$) will be : [AIEEE 2007, 3/120]
 (1) $37.904\text{ kJ mol}^{-1}$ (2) 41.00 kJ mol^{-1} (3) 4.100 kJ mol^{-1} (4) $3.7904\text{ kJ mol}^{-1}$
- 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 : ($R = 8.314\text{ J/mol K}$) ($\ln 7.5 = 2.01$) [JEE 2013, (Main), 4/120]
 ($R = 8.314\text{ J/mol K}$) ($\ln 7.5 = 2.01$)
 (1) $q = +208\text{ J}$, $w = -208\text{ J}$ (2) $q = -208\text{ J}$, $w = -208\text{ J}$
 (3) $q = -208\text{ J}$, $w = +208\text{ J}$ (4) $q = +208\text{ J}$, $w = +208\text{ J}$
- ΔU equal to : [JEE(Main) 2017, 4/120]
 (1) Isobaric work (2) Adiabatic work (3) Isothermal work (4) Isochoric work

JEE-MAIN ONLINE PROBLEMS

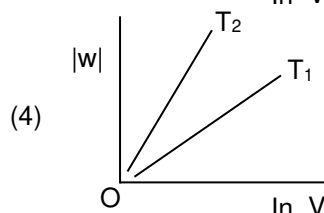
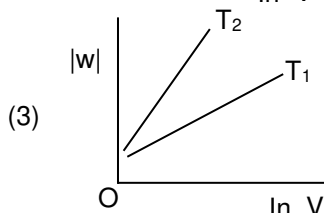
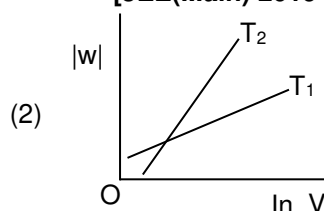
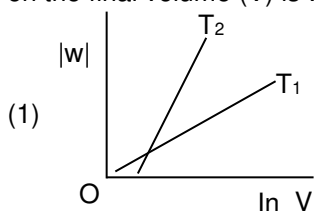
- If 100 mole of H_2O_2 decompose at 1 bar and 300 K , the work done (kJ) by one mole of $\text{O}_2(\text{g})$ as it expands against 1 bar pressure is : [JEE(Main) 2016 Online (10-04-16), 4/120]
 $2\text{H}_2\text{O}_2(\text{l}) \rightleftharpoons 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$ ($R = 8.3\text{ J K}^{-1}\text{ mol}^{-1}$)
 (1) 498.00 (2) 62.25 (3) 124.50 (4) 249.00
- 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) 2017 Online (09-04-17), 4/120]
 (1) 10 J of the work will be done by the surrounding on gas.
 (2) 10 J of the work will be done by the gas.
 (3) 6 J of the work will be done by the surrounding on gas.
 (4) 6 J of the work will be done by the gas.
- An ideal gas undergoes a cyclic process as shown in Figure. [JEE(Main) 2018 Online (15-04-18), 4/120]
 $\Delta U_{BC} = -5\text{ kJ mol}^{-1}$, $q_{AB} = 2\text{ kJ mol}^{-1}$
 $W_{AB} = -5\text{ kJ mol}^{-1}$, $W_{CA} = 3\text{ kJ mol}^{-1}$
 Heat absorbed by the system during process CA is :
 (1) -5 kJ mol^{-1} (2) $+5\text{ kJ mol}^{-1}$
 (3) 18 kJ mol^{-1} (4) -18 kJ mol^{-1}





4. 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) 2019 Online (09-01-19), 4/120]



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

[JEE(Main) 2019 Online (10-01-19), 4/120]

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

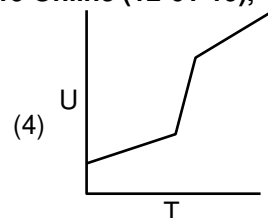
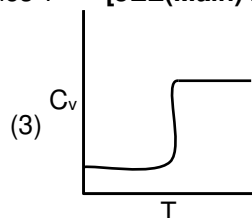
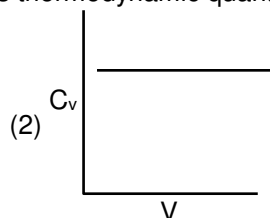
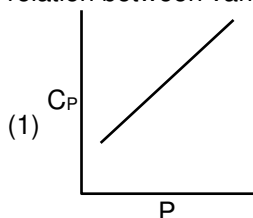
(2) $\frac{2}{3} \text{ K}$

(3) 1 K

(4) 2 K

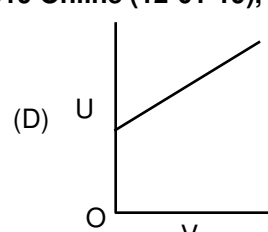
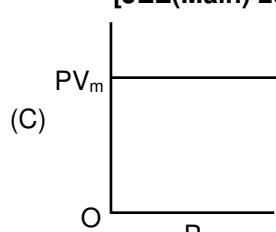
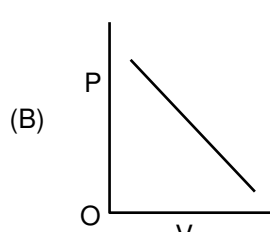
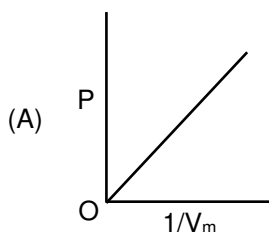
6. For a diatomic ideal gas in a closed system, which of the following plots does not correctly describe the relation between various thermodynamic quantities ?

[JEE(Main) 2019 Online (12-01-19), 4/120]



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

[JEE(Main) 2019 Online (12-01-19), 4/120]



(1) (B) and (C)

(2) (A) and (C)

(3) (A) and (D)

(4) (B) and (D)

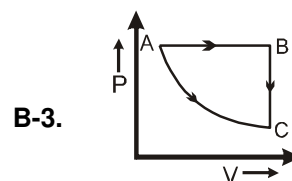
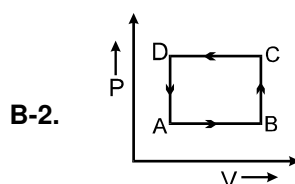
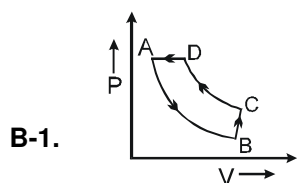


Answers

EXERCISE - 1

PART - I

- A-1.** State function : (a) (b) (d) (e) ; Path function : (c) (f) (g)
A-2. Extensive Property : (b) (c) ; Intensive Property : (a) (d) (e) (f) (g)
A-3. (a) Potential energy is state function.
 (b) Heat is a path function because a part of it may be used in work.
 (c) Work is not a state function.



- C-1.** 60 cal. **C-2.** -5744.4 J **C-3.** $1.2 \times 10^3 \text{ J}$ **D-1.** 1.066 kJ
D-2. 760 J **E-1.** 32 J **E-2.** -2.6 J **F-1.** $\frac{3}{2}$
F-2. $W = 0 ; q = 0$ **G-1.** $\Delta U = 4170 \text{ J}, \Delta H = 1 \text{ kcal}$ **G-2.** Zero **H-1.** $\Delta U = 75.12 \text{ kJ}$

PART - II

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

PART - III

1. $(A - p, s) ; (B - q, r) ; (C - r) ; (D - s)$ 2. $(A - r) ; (B - p) ; (C - s) ; (D - q)$

EXERCISE - 2

PART - I

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

PART - II

1. 4 (i, ii, iv, vi) 2. 7 (i, iii, iv, v, vi, vii, x) 3. 6 (i, iii, iv, v, vi, vii)
 4. 3 5. 4 6. 6 7. 72 8. 44

**PART - III**

- | | | | | |
|----------|-----------|---------|----------|----------|
| 1. (ABD) | 2. (ABC) | 3. (BD) | 4. (ABC) | 5. (BCD) |
| 6. (BD) | 7. (ABCD) | | | |

PART - IV

- | | | |
|--------|--------|--------|
| 1. (B) | 2. (A) | 3. (D) |
|--------|--------|--------|

EXERCISE – 3**PART – I**

1. $\Delta H = \Delta U + \Delta(PV)$
so, $\Delta U = \Delta H - \Delta(PV) = -560 - [40 - 70] \text{ (L atm)} = (-560 + 30 \times 0.1) \text{ kJ} = -557 \text{ kJ}.$
- | | | | | |
|----------|---------|------|---------|----------|
| 2. (AD) | 3. (AB) | 4. 2 | 5. (AD) | 6. (ABC) |
| 7. (ACD) | 8. (BC) | | | |

PART – II**JEE-MAIN OFFLINE PROBLEMS**

- | | | |
|--------|--------|--------|
| 1. (1) | 2. (1) | 3. (2) |
|--------|--------|--------|

JEE-MAIN ONLINE PROBLEMS

- | | | | | |
|--------|--------|--------|--------|--------|
| 1. (3) | 2. (3) | 3. (2) | 4. (4) | 5. (2) |
| 6. (1) | 7. (4) | | | |





THERMODYNAMICS IInd & IIIrd LAW

Exercise-1

PART - I : SUBJECTIVE QUESTIONS

Section (A) : Introduction about entropy

- A-1.** The entropy of a gas increases on its expansion. Why ?
- A-2.** Entropy of the solutions is higher than that of pure liquid. Why ?
- A-3.** What are the signs of ΔS for the system and for the surrounding in each of the following processes ?
 (a) Water boils in a teakettle on a hot stove.
 (b) Ice in an ice cube tray, left on a table melts.
 (c) A cup of coffee is reheated in a microwave oven.
- A-4.** State the second law of thermodynamics.
- A-5.** Write statement of IIIrd law of thermodynamics ?
- A-6.** State the thermodynamic condition of spontaneous occurrence of a process ?
- A-7.** If ΔH for a reaction has a positive value, how would you know the sign requirement of ΔS for it so that the reaction is spontaneous ?

Section (B) : Entropy Calculation

- B-1.** The entropy of vaporization of benzene is $85 \text{ JK}^{-1} \text{ mol}^{-1}$. When 117 g benzene vaporizes at its normal boiling point, calculate the entropy change of surrounding.
- B-2.** Calculate standard entropy change in the reaction

$$\text{Fe}_2\text{O}_3 (\text{s}) + 3\text{H}_2 (\text{g}) \longrightarrow 2\text{Fe} (\text{s}) + 3\text{H}_2\text{O} (\ell)$$

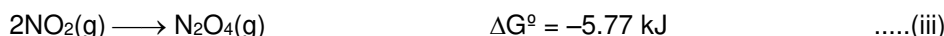
 Given : $S^\circ_m(\text{Fe}_2\text{O}_3, \text{S}) = 87.4$, $S^\circ_m(\text{Fe}, \text{S}) = 27.3$, $S^\circ_m(\text{H}_2, \text{g}) = 130.7$, $S^\circ_m(\text{H}_2\text{O}, \ell) = 69.9 \text{ JK}^{-1} \text{ mol}^{-1}$.
- B-3.** One mole of liquid iron at its boiling point was vaporized in an oven at 3500 K. If iron boils at 3133 K and enthalpy of vaporization is 349 KJ mol^{-1} , determine ΔS_{system} , $\Delta S_{\text{surrounding}}$ and $\Delta S_{\text{universe}}$. (Oven is considered as surroundings).
- B-4.** Calculate the entropy change in surroundings when 1.00 mol of $\text{H}_2\text{O}(\ell)$ is formed under standard conditions at 298 K. Given $\Delta_r H^\circ = -286 \text{ kJ mol}^{-1}$.
- B-5.** Order of increasing of entropy among given condition of substance is :
 (I) 1 mole of $\text{H}_2\text{O}(\ell)$ at 298 K and 0.101 M Pa (II) 1 mole of ice at 273 K and 0.101 M Pa
 (III) 1 mole of $\text{H}_2(\text{g})$ at 298 K and 1 atm (IV) 1 mole of $\text{C}_2\text{H}_6(\text{g})$ at 298 K and 1 atm
- B-6.** Oxygen & ozone are gases at standard temperature. Their molar entropies are in the sequence $\text{O}_2 < \text{O}_3$. Using molecular properties, explain why ozone is more disordered than oxygen.

Section (C) : Free energy

- C-1.** What will be the states of a chemical reaction occurring at constant pressure and temperature conditions when :
 (i) $\Delta G = 0$ (ii) $\Delta G > 0$ (iii) $\Delta G < 0$
- C-2.** A gaseous reactant A forms two different product, in parallel reaction, B and C as follows :
 $\text{A} \longrightarrow \text{B}; \Delta H^\circ = -3\text{kJ}, \Delta S^\circ = 20\text{JK}^{-1}$; $\text{A} \longrightarrow \text{C}; \Delta H^\circ = -3.6 \text{ kJ}, \Delta S^\circ = 10 \text{ JK}^{-1}$
 Discuss the relative stability of B and C on the basis of Gibb's free energy change at 27°C .



C-3. With the following informations, determine standard Gibb's free energy of formation of $\text{N}_2\text{O}_4(\text{g})$.



C-4. For the equilibrium : $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ at 298 K, equilibrium constant, $K = 1.8 \times 10^{-7}$. What is ΔG° for the reaction ?

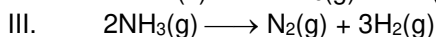
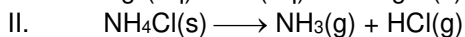
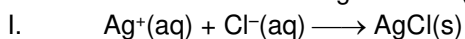
PART - II : ONLY ONE OPTION CORRECT TYPE

Section (A) : Introduction about entropy

A-1. In which state, matter have highest entropy

- (A) Solid (B) Liquid (C) Gas (D) Equal in all

A-2. Predict which of the following reaction (s) has a positive entropy change ?



- (A) I and II (B) III (C) II and III (D) II

A-3. Mixing of non-reacting ideal gases is generally accompanied by

- (A) Decrease in entropy (B) Increase in entropy
(C) Change in enthalpy (D) Increase in free energy

A-4. Which of the following reactions is associated with the most negative change in entropy ?

- (A) $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{SO}_3(\text{g})$ (B) $\text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) \longrightarrow \text{C}_2\text{H}_6(\text{g})$
(C) $\text{C}(\text{s, graphite}) + \text{O}_2 \longrightarrow \text{CO}_2(\text{g})$ (D) $3\text{C}_2\text{H}_2(\text{g}) \longrightarrow \text{C}_6\text{H}_6(\ell)$

A-5. For the gas - phase decomposition, $\text{PCl}_5(\text{g}) \xrightarrow{\Delta} \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$:

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

A-6. Which one of the following has ΔS° greater than zero.

- (A) $\text{CaO}(\text{s}) + \text{CO}_2(\text{g}) \rightleftharpoons \text{CaCO}_3(\text{s})$ (B) $\text{NaCl}(\text{aq}) \rightleftharpoons \text{NaCl}(\text{s})$
(C) $\text{NaNO}_3(\text{s}) \rightleftharpoons \text{Na}^+(\text{aq}) + \text{NO}_3^-(\text{aq})$ (D) $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$

A-7. For which reaction from the following, will be maximum entropy change :

- (A) $\text{Ca}(\text{s}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{CaO}(\text{s})$ (B) $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
(C) $\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$ (D) $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g})$

A-8. Which of the following statement is true. The entropy of the universe

- (A) Increases and tends towards maximum value
(B) Decreases and tends to be zero
(C) Remains constant
(D) Decreases and increases with a periodic rate

Section (B) : Entropy Calculation

B-1. An isolated system comprises the liquid in equilibrium with vapours. At this stage the molar entropy of the vapour is :

- (A) Less than that of liquid (B) more than that of liquid
(C) Equal to zero (D) Equal to that of liquid



- B-2.** When two mole of an ideal gas ($C_{p,m} = \frac{5}{2}R$) heated from 300 K to 600 K at constant pressure. The change in entropy of gas (ΔS) is :
- (A) $\frac{3}{2} R \ln 2$ (B) $-\frac{3}{2} R \ln 2$ (C) $5R \ln 2$ (D) $\frac{5}{2} R \ln 2$
- B-3.** The entropy change when two moles of ideal monoatomic gas is heated 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) $3R \ln \left(\frac{573}{273} \right)$ (D) $\frac{3}{2} R \ln \left(\frac{573}{473} \right)$
- B-4.** If one mole of an ideal gas ($C_{p,m} = \frac{5}{2}R$) is expanded isothermally at 300 K until its volume is tripled, then change in entropy of gas is :
- (A) zero (B) infinity (C) $\frac{5}{2} R \ln 3$ (D) $R \ln 3$
- B-5.** Calculate the total entropy change for the transition at 368 K of 1 mol of sulphur from the monoclinic to the rhombic solid state and $\Delta H = -401.7 \text{ J mol}^{-1}$ for the transition. Assume the surroundings to be an ice-water bath at 0°C :
- (A) -1.09 JK^{-1} (B) 1.47 JK^{-1} (C) 0.38 JK^{-1} (D) None of these

Section (C) : Free energy

- C-1.** Which of the following is incorrect regarding Gibbs free energy
- (A) it is a state function (B) it is extensive property
(C) it is macroscopic property (D) it is intensive property
- C-2.** Which of the following conditions regarding a chemical process ensures its spontaneity at all temperature ?
- (A) $\Delta H > 0, \Delta S < 0$ (B) $\Delta H < 0, \Delta S > 0$ (C) $\Delta H < 0, \Delta S < 0$ (D) $\Delta H > 0, \Delta S < 0$
- C-3.** When reaction in standard state is at equilibrium, then :
- (A) $\Delta H^\circ = 0$ (B) $\Delta S^\circ = 0$
(C) equilibrium constant $K = 0$ (D) equilibrium constant $K = 1$
- C-4.** 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
- C-5.** A reaction has $\Delta H = -33 \text{ kJ}$ and $\Delta S = -58 \text{ J/K}$. This reaction would be :
- (A) spontaneous at all temperatures (B) non-spontaneous at all temperatures
(C) spontaneous above a certain temperature (D) spontaneous below a certain temperature
- C-6.** For a reaction $A(g) \rightleftharpoons B(g)$ at equilibrium. The partial pressure of B is found to be one fourth of the partial pressure of A. The value of ΔG° of the reaction $A \rightarrow B$ is
- (A) $RT \ln 4$ (B) $-RT \ln 4$ (C) $RT \log 4$ (D) $-RT \log 4$
- C-7.** If $\Delta G^\circ = -177 \text{ K cal}$ for (1) $2 \text{ Fe(s)} + \frac{3}{2} \text{ O}_2(\text{g}) \longrightarrow \text{Fe}_2\text{O}_3(\text{s})$
and $\Delta G^\circ = -19 \text{ K cal}$ for (2) $4 \text{ Fe}_2\text{O}_3(\text{s}) + \text{Fe(s)} \longrightarrow 3 \text{ Fe}_3\text{O}_4(\text{s})$
What is the Gibbs free energy of formation of $\text{Fe}_3\text{O}_4(\text{s})$?
- (A) $+229.6 \text{ kcal/mol}$ (B) -242.3 kcal/mol (C) -727 kcal/mol (D) -229.6 kcal/mol
- C-8.** For a particular reaction $\Delta H^\circ = -76.6 \text{ KJ}$ and $\Delta S^\circ = 226 \text{ JK}^{-1}$. This reaction is :
- (A) Spontaneous at all temperatures (B) Non spontaneous at all temperatures
(C) Spontaneous at temperature below 66°C (D) Spontaneous at temperature above 66°C



PART - III : MATCH THE COLUMN

1. Match the column:

	Column-I		Column-II
(A)	$(\Delta G_{\text{system}})_{T,P} = 0$	(p)	Process is in equilibrium
(B)	$\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0$	(q)	Process is nonspontaneous
(C)	$\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} < 0$	(r)	Process is spontaneous
(D)	$(\Delta G_{\text{system}})_{T,P} > 0$	(s)	System is unable to do useful work

2. Match the column :

	Column-I		Column-II
(A)	Reversible adiabatic compression	(p)	$\Delta S_{\text{system}} > 0$
(B)	Reversible vaporisation of liquid	(q)	$\Delta S_{\text{system}} < 0$
(C)	$2\text{N(g)} \longrightarrow \text{N}_2\text{(g)}$	(r)	$\Delta S_{\text{surrounding}} < 0$
(D)	$\text{MgCO}_3\text{(s)} \xrightarrow{\Delta} \text{MgO(s)} + \text{CO}_2\text{(g)}$	(s)	$\Delta S_{\text{surrounding}} = 0$

Exercise-2

PART - I : ONLY ONE OPTION CORRECT TYPE

- Which of the following option the first compound has less entropy than second :
 (A) (i) aqueous solution of 1 M of MgCl_2 (ii) aqueous solution of 1 M of NaCl
 (B) (i) Br_2 liquid at 25°C (ii) Br_2 liquid at 20°C
 (C) (i) HgO solid (ii) HgS solid
 (D) (i) Br_2 liquid (ii) I_2 solid
- Isentropic process is
 (A) adiabatic and irreversible process (B) isothermal and reversible process
 (C) adiabatic and reversible process (D) isothermal and reversible for which $Q = 0$
- Third law of thermodynamics states that :
 (A) the entropy of a perfectly crystalline pure substance at zero K is zero.
 (B) absolute entropy of hydrogen ion is zero at zero K.
 (C) net change in entropy in conversion $\text{H}_{2\text{(g)}} (130\text{ K}) \rightarrow \text{H}_{2\text{(g)}} (200\text{ K})$ is zero.
 (D) entropy generally decrease in combustion reactions.
- Select correct statements :
 S_1 : For every chemical reaction at equilibrium, standard gibbs energy of reaction is zero
 S_2 : At constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing gibbs energy.
 S_3 : Spontaneity is related to change in entropy of universe.
 (A) S_1, S_2, S_3 (B) only S_1 (C) S_2, S_3 (D) S_1, S_3

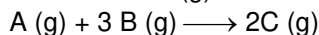
PART - II : SINGLE AND DOUBLE VALUE INTEGER TYPE

- The equilibrium constant for a reaction is 10. What will be the magnitude value of ΔG° ?
 $R = 8.31\text{ JK}^{-1}\text{ mol}^{-1}$, $T = 314\text{ K}$. (Approximate integer value in KJ mol^{-1})
- For the reaction at 298 K
 $\text{A(g)} + \text{B(g)} \rightleftharpoons \text{C(g)} + \text{D(g)}$
 If $\Delta H^\circ = -29.8\text{ Kcal}$ and $\Delta S^\circ = -0.1\text{ Kcal K}^{-1}$ then calculate equilibrium constant (K) :
- Calculate the magnitude of free energy in KJ mol^{-1} when 1 mole of an ionic salt MX(s) is dissolved in water at 27°C . Given
 Lattice energy of $\text{MX} = 780\text{ kJ mol}^{-1}$
 Hydration energy of $\text{MX} = -775.0\text{ kJ mol}^{-1}$
 Entropy change of dissolution at $27^\circ\text{C} = 40\text{ J mol}^{-1}\text{ K}^{-1}$





4. For the formation of C (g) at 300 K.



Calculate the magnitude of ΔG° (Kcal) if given data :

	A	B	C
ΔH_f° (Kcal mol ⁻¹)	0	0	-10
ΔS_f° (Cal K ⁻¹ mol ⁻¹)	40	30	45

5. The entropies of H₂(g) and H(g) are 60 and 50 J mole⁻¹ K⁻¹ respectively at 300 K. Using the data given below calculate the bond enthalpy of H₂ (g) in Kcal mole⁻¹.
 $H_2(g) \longrightarrow 2H(g)$; $\Delta G^\circ = 21.6 \text{ KJ mole}^{-1}$
6. The free energy change for a reaction is -213.3 kJ mol⁻¹ at 25°C. If the enthalpy change of the reaction is -217.77 kJ mole⁻¹. Calculate the magnitude of entropy change for the reaction in Joule mole⁻¹.
7. Calculate the magnitude of standard entropy change for reaction $X \rightleftharpoons Y$ if $\Delta H^\circ = 25 \text{ KJ}$ and K_{eq} is 10^{-7} at 300 K.
8. Calculate the magnitude of standard free energy of formation of ammonium chloride at 25°C (approximate integer in Kcal mol⁻¹), the equation showing the formation of NH₄Cl from its elements is $\frac{1}{2}N_2(g) + 2H_2(g) + \frac{1}{2}Cl_2(g) \longrightarrow NH_4Cl(s)$
 For NH₄Cl, ΔH_f° is -313 kJ mol⁻¹, Also given that
 $S_{N_2}^\circ = 191.5 \text{ JK}^{-1} \text{ mol}^{-1}$ $S_{H_2}^\circ = 130.6 \text{ JK}^{-1} \text{ mol}^{-1}$
 $S_{Cl_2}^\circ = 223.0 \text{ JK}^{-1} \text{ mol}^{-1}$ $S_{NH_4Cl}^\circ = 94.6 \text{ JK}^{-1} \text{ mol}^{-1}$
9. For the reaction $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g)$; $\Delta H = -30 \text{ kJ}$ to be at equilibrium at 477°C. If standard entropy of N₂ (g) and NH₃ (g) are 60 and 50 J mole⁻¹ K⁻¹ respectively then calculate the standard entropy of H₂(g) in Jmole⁻¹K⁻¹.

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

1. In which of the following entropy increases :
 (A) $Fe(s) + O_2(g) \longrightarrow Fe_2O_3(s)$. (B) Melting of ice
 (C) Crystallisation of sugar from solution (D) Vaporisation of camphor
2. When a liquid solidifies, generally, there is :
 (A) Decrease in enthalpy (B) Decrease in entropy
 (C) Increase in enthalpy (D) Increase in entropy
3. Which of the following is false about molar entropy ?
 (A) It is same for all type of gases
 (B) For the gas of comparable mass. It decreases with the increase in atomicity.
 (C) Under identical condition, it is greater for heavier gas.
 (D) For ideal gas of comparable molar mass it decreases with the increase in thermo molecular attractions.
4. Which of the following statements is/are correct.
 (A) Reversible adiabatic process is iso entropic process
 (B) ΔS_{system} for irreversible adiabatic compression is greater than zero
 (C) ΔS_{system} for free expansion is zero
 (D) $\Delta S_{surrounding}$ for irreversible isothermal compression is greater than zero
5. The normal boiling point of a liquid 'X' is 400 K. Which of the following statement is true about the process $X(l) \longrightarrow X(g)$?
 (A) at 400 K and 1 atm pressure $\Delta G = 0$ (B) at 400 K and 2 atm pressure $\Delta G = +ve$
 (C) at 400 K and 0.1 atm pressure $\Delta G = -ve$ (D) at 410 K and 1 atm pressure $\Delta G = +ve$



6. For isothermal expansion in case of an ideal gas :
 (A) $\Delta H = 0$ (B) $\Delta E = 0$ (C) $\Delta G = -T \cdot \Delta S$ (D) $T_{\text{final}} = T_{\text{initial}}$

PART - IV : COMPREHENSION

Read the following passage carefully and answer the questions.

Comprehension # 1

Entropy is a state function and its value depends on two or three variables temperature (T), Pressure (P) and volume (V). Entropy change for an ideal gas having number of moles (n) can be determined by the following equation.

$$\Delta S = 2.303 n C_V \log \left(\frac{T_2}{T_1} \right) + 2.303 n R \log \left(\frac{V_2}{V_1} \right)$$

$$\Delta S = 2.303 n C_P \log \left(\frac{T_2}{T_1} \right) + 2.303 n R \log \left(\frac{P_1}{P_2} \right)$$

Since free energy change for a process or a chemical equation is a deciding factor of spontaneity, which can be obtained by using entropy change (ΔS) according to the expression, $\Delta G = \Delta H - T\Delta S$ at a temperature T.

- What would be the entropy change involved in thermodynamic expansion of 2 moles of a gas from a volume of 5 L to a volume of 50 L at 25°C [Given $R = 8.3 \text{ J/mole} - \text{K}$]
 (A) 38.23 J/K (B) 26.76 J/K (C) 20 J/K (D) 28.23 J/K
- An isobaric process having one mole of ideal gas has entropy change 23.03 J/K for the temperature range 27°C to 327°C. What would be the molar specific heat capacity (C_V) ?
 (A) $\frac{10}{\log 2} \text{ J/K mol}$ (B) $\frac{10}{\log 2} - 8.3 \text{ J/K mol}$
 (C) $10 \times \log 2 \text{ J/K mol}$ (D) $10 \log 2 + 8.3 \text{ J/K mol}$
- For a reaction $M_2O(s) \longrightarrow 2M(s) + \frac{1}{2} O_2(g)$; $\Delta H = 30 \text{ kJ/mol}$ and $\Delta S = 0.07 \text{ kJ/K-mol}$ at 1 atm. Calculate upto which temperature the reaction would not be spontaneous.
 (A) $T > 428.6 \text{ K}$ (B) $T > 300.8 \text{ K}$ (C) $T < 300.8 \text{ K}$ (D) $T < 428.6 \text{ K}$

Comprehension # 2

Dependence of spontaneity on temperature :

For a process to be spontaneous, at constant temperature and pressure, there must be decrease in free energy of the system in the direction of the process, i.e. $\Delta G_{P,T} < 0$. $\Delta G_{P,T} = 0$ implies the equilibrium condition and $\Delta G_{P,T} > 0$ corresponds to non-spontaneity.

Gibbs-Helmholtz equation relates the free energy change to the enthalpy and entropy changes of the process as :

$$\Delta G_{P,T} = \Delta H - T\Delta S \quad \dots(1)$$

The magnitude of ΔH does not change much with the change in temperature but the entropy factor $T\Delta S$ changes appreciably. Thus, spontaneity of a process depends very much on temperature.

For endothermic process, both ΔH and ΔS are positive. The energy factor, the first factor of equation, opposes the spontaneity whereas entropy factor favours it. At low temperature the favourable factor $T\Delta S$ will be small and may be less than ΔH , ΔG will have positive value indicating the nonspontaneity of the process. On raising temperature, the factor $T\Delta S$ increases appreciably and when it exceeds ΔH , ΔG would become negative and the process would be spontaneous.

For an exothermic process, both ΔH and ΔS would be negative. In this case the first factor of eq. 1 favours the spontaneity whereas the second factor opposes it. At high temperature, when $T\Delta S > \Delta H$, ΔG will have positive value, showing thereby the non-spontaneity of the process. However, on decreasing temperature, the factor $T\Delta S$ decreases rapidly and when $T\Delta S < \Delta H$, ΔG becomes negative and the process occurs spontaneously. Thus, an exothermic process may be spontaneous at low temperature and non-spontaneous at high temperature.



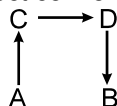
4. When CaCO_3 is heated to a high temperature, it undergoes decomposition into CaO and CO_2 whereas it is quite stable at room temperature. The most likely explanation of it, is
 (A) The enthalpy of reaction (ΔH) overweighs the term $T\Delta S$ at high temperature.
 (B) The term $T\Delta S$ overweighs the enthalpy of reaction at high temperature.
 (C) At high temperature, both enthalpy of reaction and entropy change become negative.
 (D) None of these.
5. For the reaction at 25°C , $\text{X}_2\text{O}_4(\ell) \longrightarrow 2\text{XO}_2(\text{g})$
 $\Delta H = 2.1 \text{ Kcal}$ and $\Delta S = 20 \text{ cal K}^{-1}$. The reaction would be
 (A) spontaneous (B) non-spontaneous (C) at equilibrium (D) unpredictable
6. For the reaction at 298 K , $2\text{A} + \text{B} \longrightarrow \text{C}$
 $\Delta H = 100 \text{ kcal}$ and $\Delta S = 0.050 \text{ kcal K}^{-1}$. If ΔH and ΔS are assumed to be constant over the temperature range, above what temperature will the reaction become spontaneous ?
 (A) 1000 K (B) 1500 K (C) 2000 K (D) 2500 K
7. A reaction has a value of $\Delta H = -40 \text{ kcal}$ at 400 K . Above 400 K , the reaction is spontaneous, below this temperature, it is not. The values of ΔG and ΔS at 400 K are respectively.
 (A) $0, -0.1 \text{ cal K}^{-1}$ (B) $0, 100 \text{ cal K}^{-1}$
 (C) $-10 \text{ kcal}, -100 \text{ cal K}^{-1}$ (D) $0, -100 \text{ cal K}^{-1}$
8. The enthalpy change for a certain reaction at 300 K is $-15.0 \text{ K cal mol}^{-1}$. The entropy change under these conditions is $-7.2 \text{ cal K}^{-1} \text{ mol}^{-1}$. The free energy change for the reaction and its spontaneous/non-spontaneous character will be
 (A) $-12.84 \text{ kcal mol}^{-1}$, spontaneous (B) $12.84 \text{ kcal mol}^{-1}$, non-spontaneous
 (C) $-17.16 \text{ kcal mol}^{-1}$, spontaneous (D) None of these

Exercise-3

* Marked Questions may have more than one correct option.

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

1. The direct conversion of A to B is difficult, hence it is carried out by the following shown path:



$$\Delta S(\text{A} \longrightarrow \text{C}) = 50; \quad \Delta S(\text{C} \longrightarrow \text{D}) = 30; \quad \Delta S(\text{B} \longrightarrow \text{D}) = +20$$

The entropy change for the process $\text{A} \longrightarrow \text{B}$ is

- (A) 100 (B) -60 (C) -100 (D) +60

[JEE 2006, 3/184]

2. $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ $K = 4 \times 10^6$ at 298
 $K = 41$ at 400 K

Which statements is correct ?

[JEE 2006, 3/184]

- (A) If N_2 is added at equilibrium condition, the equilibrium will shift to the forward direction because according to IInd law of thermodynamics the entropy must increases in the direction of spontaneous reaction.
 (B) The condition for equilibrium is $2G_{\text{NH}_3} = 3G_{\text{H}_2} + G_{\text{N}_2}$ where G is Gibbs free energy per mole of the gaseous species measured at that partial pressure.
 (C) Addition of catalyst does not change K_p but changes ΔH .
 (D) At 400 K addition of catalyst will increase forward reaction by 2 times while reverse reaction rate will be changed by 1.7 times.

3. The value of $\log_{10} K$ for a reaction $\text{A} \rightleftharpoons \text{B}$ is :

(Given : $\Delta_f H_{298 \text{ K}}^\circ = -54.07 \text{ kJ mol}^{-1}$, $\Delta_f S_{298 \text{ K}}^\circ = 10 \text{ JK}^{-1} \text{ mol}^{-1}$ and $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$; $2.303 \times 8.314 \times 298 = 5705$)

[JEE 2007, 3/162]

- (A) 5 (B) 10 (C) 95 (D) 100



4. For the process $\text{H}_2\text{O}(\ell)$ (1 bar, 373 K) \longrightarrow $\text{H}_2\text{O}(\text{g})$ (1 bar, 373 K), the correct set of thermodynamic parameters is :
[JEE 2007, 3/162]
 (A) $\Delta G = 0$, $\Delta S = +ve$ (B) $\Delta G = 0$, $\Delta S = -ve$ (C) $\Delta G = +ve$, $\Delta S = 0$ (D) $\Delta G = -ve$, $\Delta S = +ve$
5. **Statement-1** : For every chemical reaction at equilibrium, standard Gibbs energy of reaction is zero.
Statement-2 : At constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing Gibbs energy.
[JEE 2008, 3/163]
 (A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
 (B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1
 (C) Statement-1 is True, Statement-2 is False
 (D) Statement-1 is False, Statement-2 is True
6. **Statement-1** : There is a natural asymmetry between converting work to heat and converting heat to work.
Statement-2 : No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work.
[JEE 2008, 3/163]
 (A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
 (B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1
 (C) Statement-1 is True, Statement-2 is False
 (D) Statement-1 is False, Statement-2 is True
- 7.* For an ideal gas, consider only P-V work in going from an initial state X to the final state Z. The final state Z can be reached by either of the two paths shown in the figure. Which of the following choice(s) is (are) correct? [take ΔS as change in entropy and w as work done].
[JEE 2012, 4/136]
-
- (A) $\Delta S_{X \rightarrow Z} = \Delta S_{X \rightarrow Y} + \Delta S_{Y \rightarrow Z}$
 (B) $w_{X \rightarrow Z} = w_{X \rightarrow Y} + w_{Y \rightarrow Z}$
 (C) $w_{X \rightarrow Y \rightarrow Z} = w_{X \rightarrow Z}$
 (D) $\Delta S_{X \rightarrow Y \rightarrow Z} = \Delta S_{X \rightarrow Z}$
8. For the process, $\text{H}_2\text{O}(\ell) \longrightarrow \text{H}_2\text{O}(\text{g})$ at $T = 100^\circ\text{C}$ and 1 atmosphere pressure, the correct choice is :
[JEE(Advanced) 2014, 3/120]
 (A) $\Delta S_{\text{system}} > 0$ and $\Delta S_{\text{surroundings}} > 0$ (B) $\Delta S_{\text{system}} > 0$ and $\Delta S_{\text{surroundings}} < 0$
 (C) $\Delta S_{\text{system}} < 0$ and $\Delta S_{\text{surroundings}} > 0$ (D) $\Delta S_{\text{system}} < 0$ and $\Delta S_{\text{surroundings}} < 0$
9. Match the thermodynamic processes given under Column-I with the expressions given under Column-II.
[JEE(Advanced) 2015, 8/168]
- | | Column-I | | Column-II |
|-----|---|-----|-----------------------------|
| (A) | Freezing of water at 273 K and 1 atm | (P) | $q = 0$ |
| (B) | Expansion of 1 mol of an ideal gas into a vacuum under isolated conditions | (Q) | $w = 0$ |
| (C) | Mixing of equal volumes of two ideal gases at constant temperature and pressure in an isolated container | (R) | $\Delta S_{\text{sys}} < 0$ |
| (D) | Reversible heating of $\text{H}_2(\text{g})$ at 1 atm from 300 K to 600 K, followed by reversible cooling to 300 K at 1 atm | (S) | $\Delta U = 0$ |
| | | (T) | $\Delta G = 0$ |
10. One mole of an ideal gas at 300 K in thermal contact with surroundings expands isothermally from 1.0 L to 2.0 L against a constant pressure of 3.0 atm. In this process, the change in entropy of surroundings (ΔS_{surr}) in JK^{-1} is : (1 L atm = 101.3 J)
[JEE(Advanced) 2016, 3/124]
 (A) 5.763 (B) 1.013 (C) -1.013 (D) -5.763



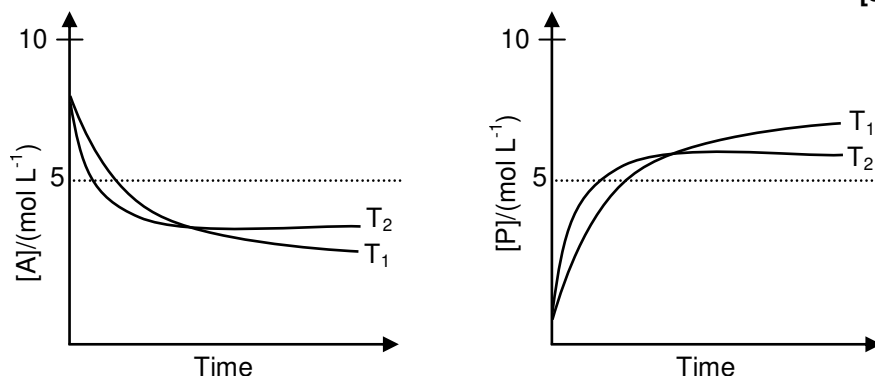
- 11.* For a reaction taking place in a container in equilibrium with its surroundings, the effect of temperature on its equilibrium constant K in terms of change in entropy is described by

[JEE(Advanced) 2017, 4/122]

- (A) With increase in temperature, the value of K for endothermic reaction increases because unfavourable change in entropy of the surroundings decreases
 (B) With increase in temperature, the value of K for exothermic reaction decreases because favourable change in entropy of the surroundings decreases
 (C) With increase in temperature, the value of K for endothermic reaction increases because the entropy change of the system is negative
 (D) With increase in temperature, the value of K for exothermic reaction decreases because the entropy change of the system is positive

- 12.* For a reaction, $A \rightleftharpoons P$, the plots of $[A]$ and $[P]$ with time at temperature T_1 and T_2 are given below.

[JEE(Advanced) 2018, 4/120]

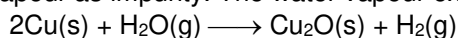


If $T_2 > T_1$, the correct statement(s) is (are)

(Assume ΔH^θ and ΔS^θ are independent of temperature and ratio of $\ln K$ at T_1 to $\ln K$ at T_2 is greater than T_2/T_1 . Here H , S , G and K are enthalpy, entropy, Gibbs energy and equilibrium constant, respectively.)

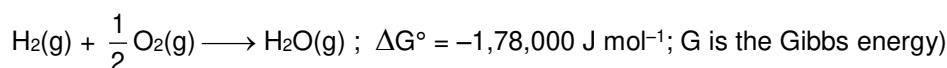
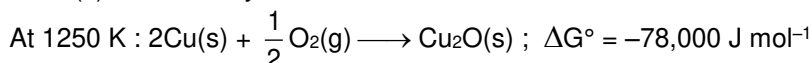
- (A) $\Delta H^\theta < 0$, $\Delta S^\theta < 0$ (B) $\Delta G^\theta < 0$, $\Delta H^\theta > 0$
 (C) $\Delta G^\theta < 0$, $\Delta S^\theta < 0$ (D) $\Delta G^\theta < 0$, $\Delta S^\theta > 0$

13. The surface of copper gets tarnished by the formation of copper oxide. N_2 gas was passed to prevent the oxide formation during heating of copper at 1250 K. However, the N_2 gas contains 1 mole % of water vapour as impurity. The water vapour oxidises copper as per the reaction given below :



p_{H_2} is the minimum partial pressure of H_2 (in bar) needed to prevent the oxidation at 1250 K. The value of $\ln(p_{H_2})$ is _____.

(Given: total pressure = 1 bar, R (universal gas constant) = $8 \text{ J K}^{-1} \text{ mol}^{-1}$, $\ln(10) = 2.3$, Cu(s) and $\text{Cu}_2\text{O(s)}$ are mutually immiscible.)



[JEE(Advanced) 2018, 3/120]

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

1. Identify the correct statement regarding a spontaneous process : [AIEEE 2007, 3/120]
 (1) Exothermic processes are always spontaneous.
 (2) Lowering of energy in the reaction process is the only criterion for spontaneity.
 (3) For a spontaneous process in an isolated system, the change in entropy is positive.
 (4) Endothermic processes are never spontaneous.



2. In conversion of lime-stone to lime, $\text{CaCO}_3(\text{s}) \longrightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ the values of ΔH° and ΔS° are + 179.1 kJ mol⁻¹ and 160.2 J/K respectively at 298 K and 1 bar. Assuming that ΔH° and ΔS° do not change with temperature, temperature above which conversion of limestone to lime will be spontaneous is : **[AIEEE 2007, 3/120]**
 (1) 845 K (2) 1118 K (3) 1008 (4) 1200 K
3. Standard entropy of X_2 , Y_2 and XY_3 are 60, 40 and 50 JK⁻¹ mol⁻¹, respectively. **[AIEEE 2008, 3/105]**
 For the reaction, $\frac{1}{2} \text{X}_2 + \frac{3}{2} \text{Y}_2 \longrightarrow \text{XY}_3$ $\Delta H = -30$ kJ. To be at equilibrium the temperature will be :
 (1) 500 K (2) 750 K (3) 1000 K (4) 1250 K
4. For a particular reversible reaction at temperature T, ΔH and ΔS were found to be both +ve. If T_e is the temperature at equilibrium, the reaction would be spontaneous when. **[AIEEE 2010, 4/144]**
 (1) $T_e > T$ (2) $T > T_e$ (3) T_e is 5 times T (4) $T = T_e$
5. The entropy change involved in the isothermal reversible expansion of 2 moles of an ideal gas from a volume of 10 dm³ to a volume of 100 dm³ at 27°C is : **[AIEEE 2011, 4/120]**
 (1) 38.3 J mol⁻¹ K⁻¹ (2) 35.8 J mol⁻¹ K⁻¹ (3) 32.3 J mol⁻¹ K⁻¹ (4) 42.3 J mol⁻¹ K⁻¹
6. In view of the signs of $\Delta_r G^\circ$ for the following reactions :
 $\text{PbO}_2 + \text{Pb} \longrightarrow 2\text{PbO}$, $\Delta_r G^\circ < 0$; $\text{SnO}_2 + \text{Sn} \longrightarrow 2\text{SnO}$, $\Delta_r G^\circ > 0$,
 which oxidation states are more characteristics for lead and tin ? **[AIEEE 2011, 4/120]**
 (1) For lead +2, for tin +2 (2) For lead +4, for tin +4
 (3) For lead +2, for tin +4 (4) For lead +4, for tin +2
7. The incorrect expression among the following is : **[AIEEE 2012, 4/120]**
 (1) $\frac{\Delta G_{\text{system}}}{\Delta S_{\text{total}}} = -T$ (2) In isothermal process, $w_{\text{reversible}} = -nRT \ln \frac{V_f}{V_i}$
 (3) $\ln K = \frac{\Delta H^\circ - T\Delta S^\circ}{RT}$ (4) $K = e^{-\Delta G^\circ/RT}$
8. The following reaction is performed at 298 K.
 $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$
 The standard free energy of formation of NO(g) is 86.6 kJ/mol at 298 K. What is the standard free energy of formation of NO₂(g) at 298 K ? ($K_P = 1.6 \times 10^{12}$) **[JEE(Main) 2015, 4/120]**
 (1) $R(298) \ln (1.6 \times 10^{12}) - 86600$ (2) $86600 + R(298) \ln (1.6 \times 10^{12})$
 (3) $86600 - \frac{\ln (1.6 \times 10^{12})}{R (298)}$ (4) $0.5 [2 \times 86,600 - R (298) \ln (1.6 \times 10^{12})]$
9. The combustion of benzene (l) gives CO₂(g) and H₂O(l). Given that heat of combustion of benzene at constant volume is -3263.9 kJ mol⁻¹ at 25°C; heat of combustion (in kJ mol⁻¹) of benzene at constant pressure will be : ($R = 8.314$ JK⁻¹ mol⁻¹) **[JEE(Main) 2018, 4/120]**
 (1) 3260 (2) -3267.6 (3) 4152.6 (4) -452.46

JEE-MAIN ONLINE PROBLEMS

1. The molar heat capacity (C_p) of CD₂O is 10 cal at 1000 K. The change in entropy associated with cooling of 32 g of CD₂O vapour from 1000 K to 100 K at constant pressure will be : (D = deuterium, at. mass = 2 u) **[JEE(Main) 2014 Online (11-04-14), 4/120]**
 (1) 23.03 cal deg⁻¹ (2) -23.03 cal deg⁻¹ (3) 2.303 cal deg⁻¹ (4) -2.303 cal deg⁻¹
2. Then entropy (S°) of the following substances are :
 $\text{CH}_4(\text{g})$ 186.2 JK⁻¹ mol⁻¹, $\text{O}_2(\text{g})$ 205.0 JK⁻¹ mol⁻¹
 $\text{CO}_2(\text{g})$ 213.6 JK⁻¹ mol⁻¹, $\text{H}_2\text{O}(\ell)$ 69.9 JK⁻¹ mol⁻¹
 The entropy change (ΔS°) for the reaction $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\ell)$ is : **[JEE(Main) 2014 Online (12-04-14), 4/120]**
 (1) -312.5 JK⁻¹ mol⁻¹ (2) -242.3 JK⁻¹ mol⁻¹ (3) -108.1 JK⁻¹ mol⁻¹ (4) -37.6 JK⁻¹ mol⁻¹



3. For the reaction, $A(g) + B(g) \rightarrow C(g) + D(g)$, ΔH° and ΔS° are, respectively, $-29.8 \text{ kJ mol}^{-1}$ and $-0.100 \text{ kJ K}^{-1} \text{ mol}^{-1}$ at 298 K. The equilibrium constant for the reaction at 298 K is:
[JEE(Main) 2016 Online (09-04-16), 4/120]
 (1) 1 (2) 10 (3) 1.0×10^{-10} (4) 1.0×10^{10}
4. A reaction at 1 bar is non-spontaneous at low temperature but becomes spontaneous at high temperature. Identify the correct statement about the reaction among the following:
[JEE(Main) 2016 Online (09-04-16), 4/120]
 (1) Both ΔH and ΔS are positive. (2) ΔH is negative while ΔS is positive.
 (3) ΔH is positive while ΔS is negative. (4) Both ΔH and ΔS are negative.
5. $\Delta_f G^\circ$ at 500 K for substance 'S' in liquid state and gaseous state are $+100.7 \text{ kcal mol}^{-1}$ and $+103 \text{ kcal mol}^{-1}$, respectively. Vapour pressure of liquid 'S' at 500 K is approximately equal to :
 (R = $2 \text{ cal K}^{-1} \text{ mol}^{-1}$)
[JEE(Main) 2018 Online (15-04-18), 4/120]
 (1) 0.1 atm (2) 1 atm (3) 10 (4) 100 atm
6. Given
 (i) $2\text{Fe}_2\text{O}_3(s) \rightarrow 4\text{Fe}(s) + 3\text{O}_2(g)$; $\Delta_r G^\circ = +1487.0 \text{ kJ mol}^{-1}$
 (ii) $2\text{CO}(g) + \text{O}_2(g) \rightarrow 2\text{CO}_2(g)$; $\Delta_r G^\circ = -514.4 \text{ kJ mol}^{-1}$
 Free energy change, $\Delta_r G^\circ$ for the reaction $2\text{Fe}_2\text{O}_3(s) + 6\text{CO}(g) \rightarrow 4\text{Fe}(s) + 6\text{CO}_2(g)$ will be
[JEE(Main) 2018 Online (15-04-18), 4/120]
 (1) $-112.4 \text{ kJ mol}^{-1}$ (2) $-56.2 \text{ kJ mol}^{-1}$ (3) $-168.2 \text{ kJ mol}^{-1}$ (4) $-208.0 \text{ kJ mol}^{-1}$
7. For which of the following processes, ΔS is negative ? **[JEE(Main) 2018 Online (16-04-18), 4/120]**
 (1) $\text{C}(\text{diamond}) \rightarrow \text{C}(\text{graphite})$ (2) $\text{N}_2(g, 1 \text{ atm}) \rightarrow \text{N}_2(g, 5 \text{ atm})$
 (3) $\text{N}_2(g, 273 \text{ K}) \rightarrow \text{N}_2(g, 300 \text{ K})$ (4) $\text{H}_2(g) \rightarrow 2\text{H}(g)$
8. The entropy change associated with the conversion of 1 kg of ice at 273 K to water vapours at 383 K is: (Specific heat of water liquid and water vapour are $4.2 \text{ kJ K}^{-1} \text{ kg}^{-1}$ and $2.0 \text{ kJ K}^{-1} \text{ kg}^{-1}$; heat of liquid fusion and vapourisation of water are 334 kJ kg^{-1} and 2491 kJ kg^{-1} , respectively). ($\log 273 = 2.436$, $\log 373 = 2.572$, $\log 383 = 2.583$)
[JEE(Main) 2019 Online (09-01-19), 4/120]
 (1) $8.49 \text{ kJ kg}^{-1} \text{ K}^{-1}$ (2) $9.26 \text{ kJ kg}^{-1} \text{ K}^{-1}$ (3) $2.64 \text{ kJ kg}^{-1} \text{ K}^{-1}$ (4) $7.90 \text{ kJ kg}^{-1} \text{ K}^{-1}$
9. A process has $\Delta H = 200 \text{ J mol}^{-1}$ and $\Delta S = 40 \text{ JK}^{-1} \text{ mol}^{-1}$. Out of the values given below, choose the minimum temperature above which the process will be spontaneous :
[JEE(Main) 2019 Online (10-01-19), 4/120]
 (1) 5 K (2) 12 K (3) 4 K (4) 20 K
10. The process with negative entropy change is: **[JEE(Main) 2019 Online (10-01-19), 4/120]**
 (1) Sublimation of dry ice
 (2) Dissolution of iodine in water
 (3) Dissociation of $\text{CaSO}_4(s)$ to $\text{CaO}(s)$ and $\text{SO}_3(g)$
 (4) Synthesis of ammonia from N_2 and H_2
11. Two blocks of the same metal having same mass and at temperature T_1 and T_2 , respectively, are brought in contact with each other and allowed to attain thermal equilibrium at constant pressure. The change in entropy, ΔS , for this process is: **[JEE(Main) 2019 Online (11-01-19), 4/120]**

- (1) $2C_P \ln \left(\frac{T_1 + T_2}{4T_1 T_2} \right)$ (2) $2C_P \ln \left[\frac{(T_1 + T_2)^{\frac{1}{2}}}{T_1 T_2} \right]$
 (3) $C_P \ln \left[\frac{(T_1 + T_2)^2}{4T_1 T_2} \right]$ (4) $2C_P \ln \left[\frac{T_1 + T_2}{2T_1 T_2} \right]$



12. For the chemical reaction $X \rightleftharpoons Y$, the standard reaction Gibbs energy depends on temperature T (in K) as $\Delta_r G^\circ (\text{in kJ mol}^{-1}) = 120 - \frac{3}{8}T$. The major component of the reaction mixture at T is :
[JEE(Main) 2019 Online (11-01-19), 4/120]
 (1) Y is $T = 280$ K (2) Y is $T = 300$ K (3) X if $T = 315$ K (4) X if $T = 350$ K
13. The standard reaction Gibbs energy for a chemical reaction at an absolute temperature T is given by $\Delta G^\circ = A - BT$, where A and B are non-zero constants. Which of the following is TRUE about this reaction ?
[JEE(Main) 2019 Online (11-01-19), 4/120]
 (1) Endothermic if $A > 0$ (2) Exothermic if $B < 0$
 (3) Exothermic if $A > 0$ and $B < 0$ (4) Endothermic if $A < 0$ and $B > 0$
14. For the equilibrium $2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$, the value of ΔG° at 298 K is approximately :
[JEE(Main) 2019 Online (11-01-19), 4/120]
 (1) 80 kJ mol⁻¹ (2) -100 kJ mol⁻¹ (3) -80 kJ mol⁻¹ (4) 100 kJ mol⁻¹
15. The reaction, $\text{MgO(s)} + \text{C(s)} \rightarrow \text{Mg(s)} + \text{CO(g)}$, for which $\Delta_r H^\circ = +491.1 \text{ kJ mol}^{-1}$ and $\Delta_r S^\circ = 198.0 \text{ JK}^{-1} \text{ mol}^{-1}$, is not feasible at 298 K. Temperature above which reaction will be feasible is:
[JEE(Main) 2019 Online (11-01-19), 4/120]
 (1) 2380.5 K (2) 1890.0 K (3) 2040.5 K (4) 2480.3 K



Answers

EXERCISE - 1

PART - I

- A-1.** Because larger space creates more disorder.
- A-2.** Dissolution of solute makes the motion of solute particles free. Also the increased number of particles in mixed state increases disorderness.
- A-3.** (a) ΔS_{sys} is positive; ΔS_{surr} is negative, (b) ΔS_{sys} is positive; ΔS_{surr} is negative;
(c) ΔS_{sys} is positive; ΔS_{surr} is negative.
- A-4.** Entropy of the universe is constantly increasing. $\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0$ for a spontaneous process.
- A-5.** At 0 K, entropy of a perfect crystalline pure substance is taken to be zero.
- A-6.** $\Delta G_{T,P} = (-)$ ve or $\Delta S_{\text{total}} > 0$
- A-7.** $\Delta G = \Delta H - T\Delta S$
For spontaneous reaction $\Delta G = (-)$ ve
 $\therefore \Delta S$ Should be positive
- B-1.** $-1.5 \times 85 \text{ J/K}$
- B-2.** $-215.2 \text{ JK}^{-1} \text{ mol}^{-1}$
- B-3.** $\Delta S_{\text{system}} = 111.4 \text{ JK}^{-1}$, $\Delta S_{\text{surr}} = -99.71 \text{ JK}^{-1}$, $\Delta S_{\text{univ}} = +11.69 \text{ JK}^{-1}$
- B-4.** Entropy change in surroundings = 959.73 JK^{-1} .
- B-5.** $\text{II} < \text{I} < \text{III} < \text{IV}$
- B-6.** Ozone has three atoms per molecule, whereas O_2 has only two.
- C-1.** (i) Chemical reaction in equilibrium state (ii) non-spontaneous (iii) Spontaneous.
- C-2.** ΔG° indicates that B is more stable than C.
- C-3.** 97.79 kJ
- C-4.** ΔG° of reaction is 38477 J/mol .

PART - II

- | | | | | |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| A-1. (C) | A-2. (C) | A-3. (B) | A-4. (D) | A-5. (B) |
| A-6. (C) | A-7. (B) | A-8. (A) | B-1. (B) | B-2. (C) |
| B-3. (C) | B-4. (D) | B-5. (C) | C-1. (D) | C-2. (B) |
| C-3. (D) | C-4. (D) | C-5. (D) | C-6. (A) | C-7. (B) |
| C-8. (A) | | | | |

PART - III

1. (A) \rightarrow (p, s); (B) \rightarrow (r); (C) \rightarrow (q, s); (D) \rightarrow (q, s).
2. (A) \rightarrow (s); (B) \rightarrow (p, r); (C) \rightarrow (q); (D) \rightarrow (p, r)



EXERCISE – 2

PART - I

1. (C) 2. (C) 3. (A) 4. (C)

PART - II

1. 6 2. 1 3. 7 kJ mol^{-1} 4. 8 5. 8
6. 15 7. 51 8. 48 9. 40

PART - III

1. (BD) 2. (AB) 3. (ABD) 4. (ABD) 5. (ABC)
6. (ABCD)

PART - IV

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

EXERCISE – 3

PART - I

1. (D) 2. (B) 3. (B) 4. (A) 5. (D)
6. (A) 7. (AC) 8. (B)
9. (A-R,T); (B-P,Q,S); (C-P,Q,S); (D-P,Q,S,T) 10. (C) 11. (AB)
12. (AC) 13. -14.6

PART - II

JEE-MAIN OFFLINE PROBLEMS

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

JEE-MAIN ONLINE PROBLEMS

1. (2) 2. (2) 3. (1) 4. (1) 5. (1)
6. (2) 7. (2) 8. (2) 9. (1) 10. (4)
11. (3) 12. (3) 13. (1) 14. (1) 15. (4)



THERMOCHEMISTRY

Exercise-1

PART - I : SUBJECTIVE QUESTIONS

Section (A) : Calculation ΔU , ΔH & W for chemical reaction

- A-1.** For the reaction : $C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(g)$
if $\Delta U^\circ = -1373 \text{ kJ mol}^{-1}$ at 298 K. Calculate ΔH°
- A-2.** 2 mole of zinc is dissolved in HCl at 25°C. Calculate the work done in open vessel.

Section (B) : Basics & Kirchoff's law

- B-1.** Diborane is a potential rocket fuel which undergoes combustion according to the reaction
 $B_2H_6(g) + 3O_2(g) \longrightarrow B_2O_3(s) + 3H_2O(g)$
 From the following data, calculate the enthalpy change for the combustion of diborane
 $2B(s) + (3/2) O_2(g) \longrightarrow B_2O_3(s) \Delta H = -1273 \text{ kJ mol}^{-1}$
 $H_2(g) + (1/2)O_2(g) \longrightarrow H_2O(l) \Delta H = -286 \text{ kJ mol}^{-1}$
 $H_2O(l) \longrightarrow H_2O(g) \Delta H = 44 \text{ kJ mol}^{-1}$
 $2B(s) + 3H_2(g) \longrightarrow B_2H_6(g) \Delta H = 36 \text{ kJ mol}^{-1}$
- B-2.** Predict the standard reaction enthalpy of $2 NO_2(g) \rightarrow N_2O_4(g)$ at 100°C. ΔH° at 25°C is $-57.2 \text{ kJ mol}^{-1}$
 $C_p(NO_2) = 37.2 \text{ J mol}^{-1} K^{-1}$ $C_p(N_2O_4) = 77.28 \text{ J mol}^{-1} K^{-1}$.

Section (C) : Enthalpy of formation & combustion

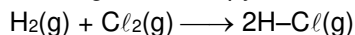
- C-1.** The heat of combustion of ethyl alcohol is -300 kcal . If the heats of formation of $CO_2(g)$ and $H_2O(l)$ are -94.3 and -68.5 kcal respectively, calculate the heat of formation of ethyl alcohol.
- C-2.** If $H_2 + 1/2 O_2 \longrightarrow H_2O$, $\Delta H = -68 \text{ kcal}$
 $K + H_2O + \text{water} \longrightarrow KOH(aq) + 1/2 H_2$, $\Delta H = -48 \text{ kcal}$
 $KOH + \text{water} \longrightarrow KOH(aq)$, $\Delta H = -14 \text{ kcal}$
 Find the heat of formation of KOH.
- C-3.** The standard enthalpy of decomposition of the yellow complex H_3NSO_2 into NH_3 and SO_2 is $+40 \text{ kJ mol}^{-1}$. Calculate the standard enthalpy of formation of H_3NSO_2 . $\Delta H_f^\circ(NH_3) = -46.17 \text{ kJ mol}^{-1}$, $\Delta H_f^\circ(SO_2) = -296.83$.
- C-4.** When 12.0 g of carbon (graphite) reacted with oxygen to form CO and CO_2 at 25°C and constant pressure, 252 kJ of heat was released and no carbon remained. If $\Delta H_f^\circ(CO, g) = -110.5 \text{ kJ mol}^{-1}$ and $\Delta H_f^\circ(CO_2, g) = -393.5 \text{ kJ mol}^{-1}$, calculate the mass of oxygen consumed.

Section (D) : Bond enthalpy method & Resonance energy

- D-1.** Calculate the bond energy of Cl-Cl bond from the following data :
 $CH_4(g) + Cl_2(g) \longrightarrow CH_3Cl(g) + HCl(g)$; $\Delta H = -100.3 \text{ kJ}$. Also the bond enthalpies of C-H, C-Cl, H-Cl bonds are 413, 326 and 431 kJ mol^{-1} respectively.
- D-2.** Calculate ΔH_f° for the reaction $CH_2Cl_2(g) \longrightarrow C(g) + 2H(g) + 2Cl(g)$. The average bond enthalpies of C-H and C-Cl bonds are 414 kJ mol^{-1} and 330 kJ mol^{-1} .
- D-3.** Calculate the enthalpy change (ΔH) of the following reaction $2C_2H_2(g) + 5O_2(g) \longrightarrow 4CO_2(g) + 2H_2O(g)$ given average bond enthalpies of various bonds, i.e., C-H, C≡C, O=O, C=O, O-H as 414, 814, 499, 724 and 640 kJ mol^{-1} respectively.



D-4. Calculate change in enthalpy for the reaction at 27°C



by using the bond energy and energy data

Bond energies of H-H, Cl-Cl and H-Cl bonds are 435 kJ mol⁻¹, 240 kJ mol⁻¹ and 430 kJ mol⁻¹ respectively.

D-5. Estimate the average S-F bond enthalpy in SF₆. The values of standard enthalpy of formation of SF₆(g), S(g) and F(g) are : -1100, 274 and 80 kJ mol⁻¹ respectively.

Section (E) : Enthalpy of solution & Born Haber's cycle

E-1. Calculate the standard enthalpy of solution of AgCl(s) in water $\Delta H^\circ_f(\text{AgCl}, \text{s}) = -127.07 \text{ kJ mol}^{-1}$, $\Delta H^\circ_f(\text{Ag}^+, \text{aq}) = 105.58 \text{ kJ mol}^{-1}$, $\Delta H^\circ_f(\text{Cl}^-, \text{aq}) = -167.35 \text{ kJ mol}^{-1}$.

E-2. Enthalpies of solution of BaCl₂(s) and BaCl₂·2H₂O(s) are -20 kJ/mole and 8.0 kJ/mole respectively. Calculate heat of hydration of BaCl₂(s).

E-3. Setup of Born-Haber cycle; calculate lattice energy of MgO(s). The given that - enthalpy of formation of MgO(s) = -602, sublimation of Mg(s) = 148 ; 1st & 2nd ionization energy of Mg = 738 & 1450 respectively. For Oxygen bond dissociation energy = 498; 1st & 2nd electron gain enthalpy = -141 & 844 respectively (all unit in kJmol⁻¹).

Section (F) : Enthalpy of neutralization

F-1. 10 mL of each 1 M HCl and 1M H₂SO₄ are neutralized by 1 M NaOH solution that liberate the heat of a & b kJ/mol respectively. What is relation between a and b ?

F-2. The enthalpy of neutralization of 1M HCl by 1M NaOH is -57 kJ/mole. The enthalpy of formation of water is -285 kJ/mole. The enthalpy of formation of OH⁻ ion is :

F-3. The standard enthalpy of neutralization of KOH with HCN and HCl in dilute solution is -2480 cal.mol⁻¹ and -13.68 kcalmol⁻¹ respectively. Find the enthalpy of dissociation of HCN at the same temperature.

PART - II : ONLY ONE OPTION CORRECT TYPE

Section (A) : Calculation ΔU , ΔH & W for chemical reaction

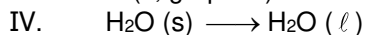
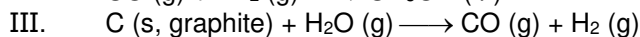
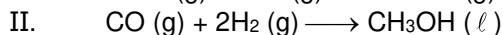
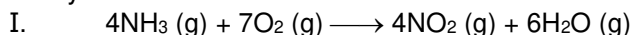
A-1. The free energy change for a reversible reaction at equilibrium is :

- (A) Positive (B) Negative (C) Zero (D) Cannot say

A-2. ΔH° for the reaction $\text{X}_{(\text{g})} + \text{Y}_{(\text{g})} \rightleftharpoons \text{Z}_{(\text{g})}$ is -4.6 Kcal, the value of ΔU° of the reaction at 227°C is (R = 2 cal.mol⁻¹ K⁻¹) :

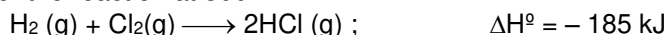
- (A) -3.6 kcal (B) -5.6 kcal (C) -4.6 kcal (D) -2.6 kcal

A-3. Determine which of the following reactions at constant pressure represent surrounding that do work on the system :



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

A-4. Consider the reaction at 300 K



If 2 mole of H₂ completely react with 2 mole of Cl₂ to form HCl. What is ΔU° for this reaction ?

- (A) 0 (B) -185 kJ (C) 370 kJ (D) -370 kJ

A-5. A mixture of 2 mole of CO and 1 mole of O₂, in a closed vessel is ignited to convert the CO to CO₂. If ΔH is the enthalpy change and ΔU is the change in internal energy then :

- (A) $\Delta H < \Delta U$ (B) $\Delta H > \Delta U$ (C) $\Delta H = \Delta U$ (D) $\Delta H = 2\Delta U$



Section (B) : Basics & Kirchoff's law

- B-1.** For which of the following change $\Delta H \neq \Delta E$?
 (A) $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \longrightarrow 2\text{HI}(\text{g})$ (B) $\text{HCl}(\text{aq}) + \text{NaOH}(\text{aq}) \longrightarrow \text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l})$
 (C) $\text{C}(\text{s}) + \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g})$ (D) $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g})$
- B-2.** Calculate the Standard internal energy of formation of liquid methyl acetate ($\text{CH}_3\text{COOCH}_3$) from its standard enthalpy of formation, which is $-442.91 \text{ kJ mole}^{-1}$ at 25°C .
 (A) -433 (B) $+433$ (C) -452.82 (D) 452.82
- B-3.** $2\text{C} + \text{O}_2 \longrightarrow 2\text{CO}$; $\Delta H = -220 \text{ kJ}$
 Which of the following statement is correct for this reaction
 (A) Heat of combustion of carbon is 110 kJ (B) Reaction is exothermic
 (C) Reaction needs no initiation (D) All of these are correct
- B-4.** $\text{C}(\text{s}) + \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g})$; $\Delta H = -94.3 \text{ kcal/mol}$
 $\text{CO}(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g})$; $\Delta H = -67.4 \text{ kcal/mol}$
 $\text{O}_2(\text{g}) \longrightarrow 2\text{O}(\text{g})$; $\Delta H = 117.4 \text{ kcal/mol}$
 $\text{CO}(\text{g}) \longrightarrow \text{C}(\text{g}) + \text{O}(\text{g})$; $\Delta H = 230.6 \text{ kcal/mol}$
 Calculate ΔH for $\text{C}(\text{s}) \longrightarrow \text{C}(\text{g})$ in kcal/mol .
 (A) 171 (B) 154 (C) 117 (D) 145

Section (C) : Enthalpy of formation & combustion

- C-1.** In the reaction, $\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \longrightarrow \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g})$; $\Delta H = 2.8 \text{ kJ}$, ΔH represents
 (A) heat of reaction (B) heat of combustion (C) heat of formation (D) heat of solution
- C-2.** Given, $\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \longrightarrow 2\text{HBr}(\text{g})$, ΔH°_1 and standard enthalpy of condensation of bromine is ΔH°_2 , standard enthalpy of formation of HBr at 25°C is
 (A) $\Delta H^\circ_1 / 2$ (B) $\Delta H^\circ_1 / 2 + \Delta H^\circ_2$ (C) $\Delta H^\circ_1 / 2 - \Delta H^\circ_2$ (D) $(\Delta H^\circ_1 - \Delta H^\circ_2) / 2$
- C-3.** For the following reaction, $\text{C}(\text{diamond}) + \text{O}_2 \longrightarrow \text{CO}_2(\text{g})$; $\Delta H = -94.3 \text{ kcal/mol}$
 $\text{C}(\text{graphite}) + \text{O}_2 \longrightarrow \text{CO}_2(\text{g})$; $\Delta H = -97.6 \text{ kcal/mol}$
 The heat required to change 1 g of $\text{C}(\text{graphite}) \longrightarrow \text{C}(\text{diamond})$ is
 (A) 1.59 kcal (B) 0.1375 kcal (C) 0.55 kcal (D) 0.275 kcal
- C-4.** The standard heat of combustion of solid boron is equal to :
 (A) $\Delta H^\circ_f(\text{B}_2\text{O}_3)$ (B) $1/2 \Delta H^\circ_f(\text{B}_2\text{O}_3)$ (C) $2\Delta H^\circ_f(\text{B}_2\text{O}_3)$ (D) $4\Delta H^\circ_f(\text{B}_2\text{O}_3)$
- C-5.** The heat of combustion of sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) is 1350 kcal/mol . How much of heat will be liberated when 17.1 g of sucrose is burnt ?
 (A) 67.5 kcal (B) 13.5 kcal (C) 40.5 kcal (D) 25.5 kcal
- C-6.** If $\text{S} + \text{O}_2 \longrightarrow \text{SO}_2$, $\Delta H = -298.2 \text{ kJ mole}^{-1}$
 $\text{SO}_2 + 1/2 \text{O}_2 \longrightarrow \text{SO}_3$, $\Delta H = -98.7 \text{ kJ mole}^{-1}$
 $\text{SO}_3 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_4$, $\Delta H = -130.2 \text{ kJ mole}^{-1}$
 $\text{H}_2 + 1/2 \text{O}_2 \longrightarrow \text{H}_2\text{O}$, $\Delta H = -287.3 \text{ kJ mole}^{-1}$
 the enthalpy of formation of H_2SO_4 at 298 K will be :
 (A) $-814.4 \text{ kJ mol}^{-1}$ (B) $+814.4 \text{ kJ mole}^{-1}$ (C) $-650.3 \text{ kJ mole}^{-1}$ (D) $-433.7 \text{ kJ mole}^{-1}$
- C-7.** When a certain amount of ethylene was combusted, 5644 kJ heat was evolved. If heat of combustion of ethylene is 1411 kJ , the volume of O_2 (at NTP) that entered into the reaction is :
 (A) 268.8 ml (B) 268.8 L (C) $6226 \times 22.4 \text{ L}$ (D) 22.4 L
- C-8.** The values of heat of combustion of ethane (C_2H_6) and ethyne (C_2H_2) are -341 and -310 Kcal respectively. Then which of the following is better fuel on mass basis :
 (A) C_2H_2 (B) C_2H_6 (C) Both (A) & (B) (D) None of these



Section (D) : Bond enthalpy method & Resonance energy

- D-1.** If enthalpy of dissociation of CH_4 and C_2H_6 are 320 and 600 calories respectively then bond energy of C–C bond is :
 (A) 80 cal (B) 40 cal (C) 60 cal (D) 120 cal
- D-2.** The bond dissociation energy of gaseous H_2 , Cl_2 and HCl are 104, 58 and 103 kcal mol^{-1} respectively. The enthalpy of formation for HCl gas will be
 (A) – 44.0 kcal (B) – 22.0 kcal (C) 22.0 kcal (D) 44.0 kcal
- D-3.** AB , A_2 and B_2 are diatomic molecules. If the bond enthalpies of A_2 , AB & B_2 are in the ratio 1 : 1 : 0.5 and enthalpy of formation of AB from A_2 and B_2 is – 100 kJ mol^{-1} . What is the bond enthalpy of A_2 .
 (A) 400 kJ mol^{-1} (B) 200 kJ mol^{-1} (C) 100 kJ mol^{-1} (D) 300 kJ mol^{-1}

Section (E) : Enthalpy of Solution & Born Haber's cycle

- E-1.** One mole of anhydrous MgCl_2 dissolves in water and liberates 25 cal/mol of heat. $\Delta H_{\text{hydration}}$ of $\text{MgCl}_2 = -30$ cal/mol. Heat of dissolution of $\text{MgCl}_2 \cdot \text{H}_2\text{O}$ is
 (A) +5 cal/mol (B) –5 cal/mol (C) 55 cal/mol (D) –55 cal/mol
- E-2.** The enthalpy of solution of NaOH (s) in water is – 41.6 kJ mole^{-1} . When NaOH is dissolved in water then the temperature of water :
 (A) Increase (B) Decrease (C) Does not change (D) Fluctuates
- E-3.** The enthalpy change for the reaction of 5 liter of ethylene with 5 liter of H_2 gas at 1.5 atm pressure is $\Delta H = -0.5$ kJ. The value of ΔU will be : (1 atm Lt = 100 J)
 (A) – 1.25 kJ (B) + 1.25 kJ (C) 0.25 kJ (D) – 0.25 kJ
- E-4.** For which one of the following reaction does the molar enthalpy change of a reaction corresponds to Lattice energy of KBr ?
 (A) $\text{KBr(s)} \longrightarrow \text{K(s)} + \frac{1}{2}\text{Br}_2(\text{g})$ (B) $\text{KBr(g)} \longrightarrow \text{K(g)} + \text{Br(g)}$
 (C) $\text{KBr(s)} \longrightarrow \text{K}^+(\text{g}) + \text{Br}^-(\text{g})$ (D) $\text{KBr(g)} \longrightarrow \text{K}^+(\text{g}) + \text{Br}^-(\text{g})$
- E-5.** Calculate the lattice energy for the reaction
 $\text{Li}^+(\text{g}) + \text{Cl}^-(\text{g}) \longrightarrow \text{LiCl(s)}$
 Given that :
 $\Delta H_{\text{sub}}(\text{Li}) = 160$; $\Delta H_{\text{diss}}(\text{Cl}_2) = 244$; $\text{IP}(\text{Li}) = 520$;
 $E_{\text{A}}(\text{Cl}) = -365$ and $\Delta H_{\text{f}}(\text{LiCl}) = -400$ (all in kJ mole^{-1})
 (A) –837 (B) –959 (C) –1567 (D) –37

Section (F) : Enthalpy of neutralization

- F-1.** The enthalpy of neutralization of which of the following acid & base is nearly – 13.6 kcal.
 (A) HCN and NaOH (B) CH_3COOH and NH_4OH
 (C) HCl and KOH (D) HCl and NH_4OH
- F-2.** If heat of dissociation of CHCl_2COOH is 0.7 kcal/mole then ΔH for the reaction :
 $\text{CHCl}_2\text{COOH} + \text{KOH} \longrightarrow \text{CHCl}_2\text{COOK} + \text{H}_2\text{O}$
 (A) – 13 kcal (B) + 13 kcal (C) – 14.4 kcal (D) – 13.7 kcal

PART - III : MATCH THE COLUMN

- 1.** Match the column :

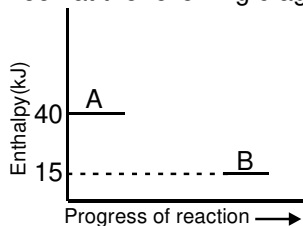
	Column-I		Column-II
(A)	$\text{C (s, graphite)} + \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g})$	(p)	$\Delta H_{\text{combustion}}^\circ$
(B)	$\text{C(s, graphite)} \longrightarrow \text{C(g)}$	(q)	$\Delta H_{\text{formation}}^\circ$
(C)	$\text{CO(g)} + \frac{1}{2} \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g})$	(r)	$\Delta H_{\text{atomization}}^\circ$
(D)	$\text{CH}_4(\text{g}) \longrightarrow \text{C(g)} + 4\text{H(g)}$	(s)	$\Delta H_{\text{sublimation}}^\circ$



Exercise-2

PART - I : ONLY ONE OPTION CORRECT TYPE

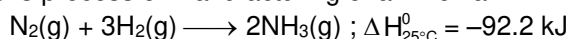
1. Look at the following diagram :



The enthalpy change for the reaction $A \rightarrow B$ will be

- (A) -25 kJ (B) -40 kJ (C) $+25 \text{ kJ}$ (D) -65 kJ

2. In Haber's process of manufacturing of ammonia :



Molecule	$\text{N}_2(\text{g})$	$\text{H}_2(\text{g})$	$\text{NH}_3(\text{g})$
$C_P \text{ JK}^{-1} \text{ mol}^{-1}$	29.1	28.8	35.1

If C_P is independent of temperature, then reaction at 100°C as compared to that of 25°C will be :

- (A) More endothermic (B) Less endothermic (C) More exothermic (D) Less exothermic

3. In the reaction $\text{AB}_2(\ell) + 3\text{X}_2(\text{g}) \rightleftharpoons \text{AX}_2(\text{g}) + 2\text{BX}_2(\text{g})$ $\Delta H = -270 \text{ kcal per mol. of AB}_2(\ell)$, the enthalpies of formation of $\text{AX}_2(\text{g})$ & $\text{BX}_2(\text{g})$ are in the ratio of 4 : 3 and have opposite sign. The value of $\Delta H_f^\circ(\text{AB}_2(\ell)) = +30 \text{ kcal/mol}$. Then

- (A) $\Delta H_f^\circ(\text{AX}_2) = -96 \text{ kcal/mol}$
 (B) $\Delta H_f^\circ(\text{BX}_2) = +480 \text{ kcal/mol}$
 (C) $K_p = K_c$ & $\Delta H_f^\circ(\text{AX}_2) = +480 \text{ kcal/mol}$
 (D) $K_p = K_c RT$ & $\Delta H_f^\circ(\text{AX}_2) + \Delta H_f^\circ(\text{BX}_2) = -240 \text{ kcal/mol}$

4. The heat of formation of $\text{C}_2\text{H}_5\text{OH}(\ell)$ is -66 kcal/mole . The heat of combustion of $\text{CH}_3\text{OCH}_3(\text{g})$ is -348 kcal/mole . ΔH_f for H_2O and CO_2 are -68 kcal/mole and -94 kcal/mole respectively. Then, the ΔH for the isomerisation reaction $\text{C}_2\text{H}_5\text{OH}(\ell) \longrightarrow \text{CH}_3\text{OCH}_3(\text{g})$ and ΔE for the same are at $T = 25^\circ\text{C}$

- (A) $\Delta H = 18 \text{ kcal/mole}$, $\Delta E = 17.301 \text{ kcal/mole}$ (B) $\Delta H = 22 \text{ kcal/mole}$, $\Delta E = 21.408 \text{ kcal/mole}$
 (C) $\Delta H = 26 \text{ kcal/mole}$, $\Delta E = 25.709 \text{ kcal/mole}$ (D) $\Delta H = 30 \text{ kcal/mole}$, $\Delta E = 28.522 \text{ kcal/mole}$

5. Cesium chlorides is formed according to the following equation $\text{Cs}(\text{s}) + 0.5 \text{Cl}_2(\text{g}) \rightarrow \text{CsCl}(\text{s})$. The enthalpy of sublimation of Cs, enthalpy of dissociation of chlorine, ionization energy of Cs and electron affinity of chlorine are 81.2, 243.0, 375.7 and $-348.3 \text{ kJ mol}^{-1}$. The energy change involved in the formation of CsCl is $-388.6 \text{ kJ mol}^{-1}$. Calculate the lattice energy of CsCl.

- (A) $618.7 \text{ kJ mol}^{-1}$ (B) $1237.4 \text{ kJ mol}^{-1}$ (C) $-1237.4 \text{ kJ mol}^{-1}$ (D) $-618.7 \text{ kJ mol}^{-1}$

6. The enthalpies of neutralization of a weak base AOH and a strong base BOH by HCl are -12250 cal/mol and -13000 cal/mol respectively. When one mole of HCl is added to a solution containing 1 mole of AOH and 1 mole of BOH, the enthalpy change was -12500 cal/mol . In what ratio the acid is distributed between AOH and BOH ?

- (A) 2 : 1 (B) 2 : 3 (C) 1 : 2 (D) None of these

7. The enthalpy of neutralization of 40.0 g of NaOH by 60.0 g of CH_3COOH will be :

- (A) $57.1 \text{ kJ equiv}^{-1}$ (B) less than $57.1 \text{ kJ equiv}^{-1}$
 (C) more than $57.1 \text{ kJ equiv}^{-1}$ (D) $13.7 \text{ kJ equiv}^{-1}$

8. Given $\Delta_{\text{ioniz}} H^\circ(\text{HCN}) = 45.2 \text{ kJ mol}^{-1}$ and $\Delta_{\text{ioniz}} H^\circ(\text{CH}_3\text{COOH}) = 2.1 \text{ kJ mol}^{-1}$. Which one of the following facts is true ?

- (A) $\text{pK}_a(\text{HCN}) = \text{pK}_a(\text{CH}_3\text{COOH})$ (B) $\text{pK}_a(\text{HCN}) > \text{pK}_a(\text{CH}_3\text{COOH})$
 (C) $\text{pK}_a(\text{HCN}) < \text{pK}_a(\text{CH}_3\text{COOH})$ (D) $\text{pK}_a(\text{HCN}) = (45.17/2.07) \text{pK}_a(\text{CH}_3\text{COOH})$





9. The average O–H bond energy in H_2O with the help of following data.
 (1) $\text{H}_2\text{O}(\ell) \longrightarrow \text{H}_2\text{O}(\text{g})$; $\Delta H = + 40.6 \text{ KJ mol}^{-1}$
 (2) $2\text{H}(\text{g}) \longrightarrow \text{H}_2(\text{g})$; $\Delta H = - 435.0 \text{ KJ mol}^{-1}$
 (3) $\text{O}_2(\text{g}) \longrightarrow 2\text{O}(\text{g})$; $\Delta H = + 489.6 \text{ KJ mol}^{-1}$
 (4) $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{H}_2\text{O}(\ell)$; $\Delta H = - 571.6 \text{ KJ mol}^{-1}$
 (A) $584.9 \text{ KJ mol}^{-1}$ (B) $279.8 \text{ KJ mol}^{-1}$ (C) $462.5 \text{ KJ mol}^{-1}$ (D) 925 KJ mol^{-1}
10. Enthalpy of polymerisation of ethylene, as represented by the reaction, $n\text{CH}_2=\text{CH}_2 \longrightarrow (-\text{CH}_2-\text{CH}_2-)_n$ is -100 kJ per mole of ethylene. Given bond enthalpy of $\text{C}=\text{C}$ bond is 600 kJ mol^{-1} , enthalpy of $\text{C}-\text{C}$ bond (in kJ mol^{-1}) will be :
 (A) 116.7 (B) 350 (C) 700 (D) indeterminate
11. The average energy required to break a $\text{P}-\text{P}$ bond in $\text{P}_4(\text{s})$ into gaseous atoms is $53.2 \text{ kcal mol}^{-1}$. The bond dissociation energy of $\text{H}_2(\text{g})$ is $104.2 \text{ kcal mol}^{-1}$; ΔH_f° of $\text{PH}_3(\text{g})$ from $\text{P}_4(\text{s})$ is $5.5 \text{ kcal mol}^{-1}$. The $\text{P}-\text{H}$ bond energy in kcal mol^{-1} is [Neglect presence of Van der Waals forces in $\text{P}_4(\text{s})$]
 (A) 85.2 (B) 57.6 (C) 76.9 (D) 63.3

PART - II : SINGLE AND DOUBLE VALUE INTEGER TYPE

1. If heat of reaction for the given acid-base reaction :
 $\text{HA} + \text{NaOH} \longrightarrow \text{NaA} + \text{H}_2\text{O}$; $\Delta H = - 4.7 \text{ kcal}$
 The heat of dissociation of HA is _____ .
2. The enthalpy of combustion at 25°C of $\text{H}_2(\text{g})$, cyclohexane and cyclohexene are -241 , -3920 and $-3717 \text{ kJ mol}^{-1}$ respectively. The heat of hydrogenation of cyclohexene is (Kcal/mole) approximate integer :
3. When 0.36 g of glucose was burned in a bomb calorimeter (Heat capacity 600 JK^{-1}) the temperature rise by 10 K . Calculate the standard molar enthalpy of combustion (MJ/mole).
4. Calculate the enthalpy change when infinitely dilute solution of CaCl_2 and Na_2CO_3 are mixed. ΔH_f° for $\text{Ca}^{+2}(\text{aq})$, $\text{CO}_3^{2-}(\text{aq})$ and $\text{CaCO}_3(\text{s})$ are -129.80 , -161.7 , $-288.50 \text{ kcal mol}^{-1}$ respectively.
5. How many of the following have standard heat of formation is zero.
 (i) $\text{Br}_{2(\ell)}$ (ii) $\text{CO}_{2(\text{g})}$ (iii) $\text{C}_{(\text{graphite})}$ (iv) $\text{Cl}_{2(\ell)}$ (v) $\text{Cl}_{2(\text{g})}$
 (vi) $\text{F}_{2(\text{g})}$ (vii) $\text{F}_{(\text{g})}$ (viii) $\text{I}_{2(\text{g})}$ (ix) $\text{S}_{(\text{monoclinic})}$ (x) $\text{N}_{2(\text{g})}$
 (xi) $\text{P}_{(\text{Black})}$ (xii) $\text{P}_{(\text{red})}$ (xiii) CH_4
6. Standard enthalpy of combustion of cyclopropane is -2091 kJ/mole at 25°C then calculate the enthalpy of formation of cyclopropane. If $\Delta H_f^\circ(\text{CO}_2) = -393.5 \text{ kJ/mole}$ and $\Delta H_f^\circ(\text{H}_2\text{O}) = -285.8 \text{ kJ/mole}$.
7. Bond energies of $\text{N}\equiv\text{N}$; $\text{H}-\text{H}$ and $\text{N}-\text{H}$ bonds are 945 , 463 & 391 kJ mol^{-1} respectively, the enthalpy of the following reactions is :
 $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g})$
8. The reaction of nitrogen with hydrogen to make ammonia has $\Delta H = -92 \text{ kJ}$
 $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g})$
 What is the value of ΔU (in kJ) if the reaction is carried out at a constant pressure of 40 bar and the volume change is -1.25 litre .
9. Calculate ΔU of reaction for the hydrogenation of acetylene at constant volume and at 77°C .
 Given that $\Delta H_f(\text{H}_2\text{O}) = -67.8 \text{ kcal mole}$; $\Delta H_{\text{comb}}(\text{C}_2\text{H}_2) = -310.1 \text{ kcal/mole}$, $\Delta H_{\text{comb}}(\text{C}_2\text{H}_4) = -337.2 \text{ kcal/Mole}$
10. Calculate the $\text{C}-\text{C}$ bond enthalpy from the following data :
 (a) $\text{C}(\text{s}) \longrightarrow \text{C}(\text{g})$; $\Delta H = 170 \text{ Kcal}$ (b) $\frac{1}{2} \text{H}_2(\text{g}) \longrightarrow \text{H}(\text{g})$; $\Delta H = 52 \text{ Kcal}$
 (c) Heat of formation of ethane = -20 Kcal (d) $\text{C}-\text{H}$ bond enthalpy = 99 Kcal .



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

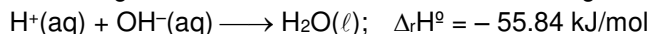
- Which of the following is(are) endothermic reaction :
 (A) Combustion of methane (B) Decomposition of water
 (C) Dehydrogenation of ethane to ethylene (D) Conversion of graphite to diamond
- Heat of reaction depend upon :
 (A) Physical state of reactants and products
 (B) Whether the reaction is carried out at constant pressure or at constant volume
 (C) Method by which the final products are obtained from the reactants
 (D) Temperature of the reaction
- Which of the following reaction cannot be used to define the heat of formation of CO_2 (g).
 (A) $\text{CO (g)} + \frac{1}{2} \text{O}_2 \longrightarrow \text{CO}_2 \text{ (g)}$ (B) $\text{C}_6\text{H}_6 (\ell) + \frac{7}{2} \text{O}_2 \text{ (g)} \longrightarrow 6\text{CO}_2 \text{ (g)} + 3\text{H}_2\text{O} (\ell)$
 (C) $\text{C (diamond)} + \text{O}_2 \text{ (g)} \longrightarrow \text{CO}_2 \text{ (g)}$ (D) $\text{C (graphite)} + \text{O}_2 \text{ (g)} \longrightarrow \text{CO}_2 \text{ (g)}$
- Heat of formation of CH_4 are :
 If given :
 $\text{C (s)} + \text{O}_2 \text{ (g)} \longrightarrow \text{CO}_2 \text{ (g)} \quad \Delta H = -394 \text{ kJ}$
 $\text{H}_2 \text{ (g)} + \frac{1}{2} \text{O}_2 \text{ (g)} \longrightarrow \text{H}_2\text{O} (\ell) \quad \Delta H = -284 \text{ kJ}$
 $\text{CH}_4 \text{ (g)} + 2\text{O}_2 \text{ (g)} \longrightarrow \text{CO}_2 \text{ (g)} + 2\text{H}_2\text{O} (\ell) \quad \Delta H = -892 \text{ kJ}$
 (A) -70 kJ (B) -16.7 kcal (C) -244 kJ (D) -50 kcal
- Heat of neutralization of the acid-base reaction is 57.32 kJ for :
 (A) $\text{HCOOH} + \text{KOH}$ (B) $\text{CH}_3\text{COOH} + \text{NaOH}$
 (C) $\text{HNO}_3 + \text{LiOH}$ (D) $\text{HCl} + \text{NaOH}$
- For which of the following reaction $\Delta H^\circ_{\text{reaction}}$ is not equal to ΔH°_f of product.
 (A) $2\text{CO(g)} + \text{O}_2\text{(g)} \longrightarrow 2\text{CO}_2\text{(g)}$ (B) $\text{N}_2\text{(g)} + \text{O}_3\text{(g)} \longrightarrow \text{N}_2\text{O}_3\text{(g)}$
 (C) $\text{CH}_4\text{(g)} + 2\text{Cl}_2\text{(g)} \longrightarrow \text{CH}_2\text{Cl}_2\text{(l)} + 2\text{HCl(g)}$ (D) $\text{Xe(g)} + 2\text{F}_2\text{(g)} \longrightarrow \text{XeF}_4\text{(g)}$
- The following is (are) endothermic reaction(s) :
 (A) Combustion of methane. (B) Decomposition of water
 (C) Dehydrogenation of ethane to ethylene. (D) Conversion of graphite to diamond.
- Which of the reaction defines molar ΔH_f° ?
 (A) $\text{CaO(s)} + \text{CO}_2\text{(g)} \longrightarrow \text{CaCO}_3 \text{ (s)}$ (B) $\frac{1}{2} \text{Br}_2(\ell) + \frac{1}{2} \text{H}_2\text{(g)} \longrightarrow \text{HBr(g)}$
 (C) $\text{N}_2\text{(g)} + 2\text{H}_2\text{(g)} + \frac{3}{2} \text{O}_2\text{(g)} \longrightarrow \text{NH}_4 \text{NO}_3\text{(s)}$ (D) $\frac{1}{2} \text{I}_2\text{(s)} + \frac{1}{2} \text{H}_2\text{(g)} \longrightarrow \text{HI(g)}$

PART - IV : COMPREHENSION

Comprehension # 1

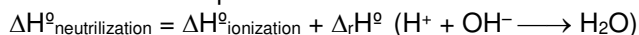
Enthalpy of neutralization is defined as the enthalpy change when 1 mole of acid/base is completely neutralized by base/acid in dilute solution.

For strong acid and strong base neutralization net chemical change is



$\Delta H^\circ_{\text{ionization}}$ of aqueous solution of strong acid and strong base is zero.

When a dilute solution of a weak acid or base is neutralized, the enthalpy of neutralization is some what less because of the absorption of heat in the ionization of the weak acid or base, for weak acid/base



- If enthalpy of neutralization of CH_3COOH by NaOH is -49.86 kJ/mol then enthalpy of ionization of CH_3COOH is:
 (A) 5.98 kJ/mol (B) -5.98 kJ/mol (C) 105.7 kJ/mol (D) None of these



2. What is ΔH° for complete neutralization of strong diacidic base $A(OH)_2$ by HNO_3 ?
 (A) -55.84 kJ (B) -111.68 kJ (C) 55.84 kJ/mol (D) None of these
3. Under the same condition how many mL of 0.1 M NaOH and 0.05 M H_2A (strong diprotic acid) solution should be mixed for a total volume of 100 mL produce the highest rise in temperature :
 (A) $25 : 75$ (B) $50 : 50$ (C) $75 : 25$ (D) $66.66 : 33.33$

Comprehension # 2

Answer Q.4, Q.5 and Q.6 by appropriately matching the information given in the three columns of the following table.

Column-1		Column-2		Column-3	
(I)	$2Ag_2O(s) \longrightarrow 4Ag(s) + O_2(g)$	(i)	$w_{rxn} > 0$	(P)	Reaction is spontaneous at high temperature.
(II)	$2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$	(ii)	$w_{rxn} < 0$	(Q)	Reaction is spontaneous at all temperatures.
(III)	$2C(s) + O_2(g) \longrightarrow 2CO(g)$	(iii)	$\Delta_{rxn}H > 0$	(R)	Reactant mixture is diamagnetic.
(IV)	$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$	(iv)	$\Delta_{rxn}S > 0$	(S)	One of the reactant is used to reduce metallic oxide in to metal.

4. The only incorrect combination is –
 (A) (I) (ii) (P) (B) (II) (iii) (P) (C) (IV) (ii) (R) (D) (III) (ii) (Q)
5. The only correct combination is –
 (A) (I) (iv) (Q) (B) (II) (ii) (S) (C) (II) (iii) (R) (D) (IV) (ii) (S)
6. The only correct combination is –
 (A) (III) (iv) (S) (B) (IV) (i) (Q) (C) (II) (iii) (S) (D) (I) (i) (P)

Exercise-3

* Marked Questions may have more than one correct option.

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

1. The species which by definition has **ZERO** standard molar enthalpy of formation at 298 K is :
 [JEE 2010, 3/163]
 (A) $Br_2(g)$ (B) $Cl_2(g)$ (C) $H_2O(g)$ (D) $CH_4(g)$
2. The bond energy (in kcal mol^{-1}) of a C–C single bond is approximately :
 [JEE 2010, 3/163]
 (A) 1 (B) 10 (C) 100 (D) 1000
3. Match the transformation in **column-I** with appropriate options in **column-II**.
 [JEE 2011, 8/180]
- | Column-I | Column-II |
|---|----------------------------|
| (A) $CO_2(s) \longrightarrow CO_2(g)$ | (p) phase transition |
| (B) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$ | (q) allotropic change |
| (C) $2H \longrightarrow H_2(g)$ | (r) ΔH is positive |
| (D) $P_{(white, solid)} \longrightarrow P_{(red, solid)}$ | (s) ΔS is positive |
| | (t) ΔS is negative |
4. Using the data provided, calculate the multiple bond energy (kJ mol^{-1}) of a $C \equiv C$ bond C_2H_2 . That energy is (take the bond energy of a C–H bond as 350 kJ mol^{-1})
 [JEE 2012, 3/136]
 $2C(s) + H_2(g) \longrightarrow C_2H_2(g)$ $\Delta H = 225 \text{ kJ mol}^{-1}$
 $2C(s) \longrightarrow 2C(g)$ $\Delta H = 1410 \text{ kJ mol}^{-1}$
 $H_2(g) \longrightarrow 2H(g)$ $\Delta H = 330 \text{ kJ mol}^{-1}$
 (A) 1165 (B) 837 (C) 865 (D) 815



5. The standard enthalpies of formation of $\text{CO}_2(\text{g})$, $\text{H}_2\text{O}(\text{l})$ and glucose(s) at 25°C are -400 kJ/mol , -300 kJ/mol and -1300 kJ/mol , respectively. The standard enthalpy of combustion per gram of glucose at 25°C is
 (A) $+2900 \text{ kJ}$ (B) -2900 kJ (C) -16.11 kJ (D) $+16.11 \text{ kJ}$ [JEE (Advance) 2013, 2/120]
6. The standard state Gibbs free energies of formation of C(graphite) and C(diamond) at $T = 298 \text{ K}$ are
 $\Delta_f G^\circ[\text{C}(\text{graphite})] = 0 \text{ kJ mol}^{-1}$
 $\Delta_f G^\circ[\text{C}(\text{diamond})] = 2.9 \text{ kJ mol}^{-1}$
 The standard state means that the pressure should be 1 bar, and substance should be pure at a given temperature. The conversion of graphite [C(graphite)] to diamond [C(diamond)] reduces its volume by $2 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$. If C(graphite) is converted to C(diamond) isothermally at $T = 298 \text{ K}$, the pressure at which C(graphite) is in equilibrium with C(diamond), is :
 [Useful information: $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$, $1 \text{ Pa} = 1 \text{ kg m}^{-1} \text{ s}^{-2}$; $1 \text{ bar} = 10^5 \text{ Pa}$]
 (A) 58001 bar (B) 1450 bar (C) 14501 bar (D) 29001 bar [JEE(Advanced) 2017, 3/122]

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

JEE-MAIN OFFLINE PROBLEMS

1. $(\Delta H - \Delta U)$ for the formation of carbon monoxide (CO) from its elements at 298 K is
 ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)
 (1) $1238.78 \text{ J mol}^{-1}$ (2) $-2477.57 \text{ J mol}^{-1}$ (3) $2477.57 \text{ J mol}^{-1}$ (4) $-1238.78 \text{ J mol}^{-1}$ [AIEEE 2006]
2. The standard enthalpy of formation ($\Delta_f H^\circ$) at 398 K for methane, $\text{CH}_4(\text{g})$ is 74.8 kJ mol^{-1} . The additional information required to determine the average energy for C–H bond formation would be :
 (1) the dissociation energy of H_2 and enthalpy of sublimation of carbon
 (2) latent heat of vapourisation of methane
 (3) the first four ionization energies of carbon and electron gain enthalpy of hydrogen
 (4) the dissociation energy of hydrogen molecule, H_2 [AIEEE 2007, 3/120]
3. On the basis of the following thermochemical data : ($\Delta_f G^\circ \text{H}^+(\text{aq}) = 0$)
 $\text{H}_2\text{O}(\ell) \longrightarrow \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq.}) ; \Delta H = 57.32 \text{ kJ}$
 $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{O}(\ell) ; \Delta H = -286.20 \text{ kJ}$
 The value of enthalpy of formation of OH^- ion at 25°C is :
 (1) -228.88 kJ (2) $+228.88 \text{ kJ}$ (3) -343.52 kJ (4) -22.88 kJ [AIEEE 2009, 8/144]
4. In a fuel cell methanol is used as fuel and oxygen gas is used as an oxidizer. The reaction is

$$\text{CH}_3\text{OH}(\ell) + \frac{3}{2} \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\ell)$$

 At 298 K , standard Gibb's energies of formation for $\text{CH}_3\text{OH}(\ell)$, $\text{H}_2\text{O}(\ell)$ and $\text{CO}_2(\text{g})$ are -166.2 , -237.2 and $-394.4 \text{ kJ mol}^{-1}$ respectively. If standard enthalpy of combustion of methanol is -726 kJ mol^{-1} , efficiency of the fuel cell will be :
 (1) 87% (2) 90% (3) 97% (4) 80% [AIEEE 2009, 8/144]
5. The standard enthalpy of formation of NH_3 is $-46.0 \text{ kJ mol}^{-1}$. If the enthalpy of formation of H_2 from its atoms is -436 kJ mol^{-1} and that of N_2 is -712 kJ mol^{-1} , the average bond enthalpy of N–H bond in NH_3 is
 (1) -964 kJ mol^{-1} (2) $+352 \text{ kJ mol}^{-1}$ (3) $+1056 \text{ kJ mol}^{-1}$ (4) $-1102 \text{ kJ mol}^{-1}$ [AIEEE 2010, 4/144]
6. The value of enthalpy change (ΔH) for the reaction, $\text{C}_2\text{H}_5\text{OH}(\text{l}) + 3\text{O}_2(\text{g}) \longrightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l})$ at 27°C is $-1366.5 \text{ kJ mol}^{-1}$. The value of internal energy change for the above reaction at this temperature will be:
 (1) -1369.0 kJ (2) -1364.0 kJ (3) -1361.5 kJ (4) -1371.5 kJ [AIEEE 2011, 4/120]
7. Consider the reaction : $4\text{NO}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{N}_2\text{O}_5(\text{g})$, $\Delta_r H = -111 \text{ kJ}$.
 If $\text{N}_2\text{O}_5(\text{s})$ is formed instead of $\text{N}_2\text{O}_5(\text{g})$ in the above reaction, the $\Delta_r H$ value will be:
 (given, ΔH of sublimation for N_2O_5 is 54 kJ mol^{-1})
 (1) $+54 \text{ kJ}$ (2) $+219 \text{ kJ}$ (3) -219 kJ (4) -165 kJ [AIEEE 2011, 4/120]



8. For complete combustion of ethanol, $\text{C}_2\text{H}_5\text{OH}(l) + 3\text{O}_2(g) \longrightarrow 2\text{CO}_2(g) + 3\text{H}_2\text{O}(l)$, the amount of heat produced as measured in bomb calorimeter, is $1364.47 \text{ kJ mol}^{-1}$ at 25°C . Assuming ideality the Enthalpy of combustion, $\Delta_c H$, for the reaction will be : ($R = 8.314 \text{ J mol}^{-1}$) **[JEE(Main) 2014, 4/120]**
 (1) $-1366.95 \text{ kJ mol}^{-1}$ (2) $-1361.95 \text{ kJ mol}^{-1}$ (3) $-1460.50 \text{ kJ mol}^{-1}$ (4) $-1350.50 \text{ kJ mol}^{-1}$
9. The heats of combustion of carbon and carbon monoxide are -393.5 and $-283.5 \text{ kJ mol}^{-1}$, respectively. The heat of formation (in kJ) of carbon monoxide per mole is : **[JEE(Main) 2016, 4/120]**
 (1) 676.5 (2) -676.5 (3) -110.5 (4) 110.5
10. Given : $\text{C}_{(\text{graphite})} + \text{O}_2(g) \longrightarrow \text{CO}_2(g)$; $\Delta_r H^\circ = -393.5 \text{ kJ mol}^{-1}$;
 $\text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \longrightarrow \text{H}_2\text{O}(l)$; $\Delta_r H^\circ = -285.8 \text{ kJ mol}^{-1}$;
 $\text{CO}_2(g) + 2\text{H}_2\text{O}(l) \longrightarrow \text{CH}_4(g) + 2\text{O}_2(g)$; $\Delta_r H^\circ = +890.3 \text{ kJ mol}^{-1}$
 Based on the above thermochemical equations, the value of $\Delta_r H^\circ$ at 298 K for the reaction :
 $\text{C}_{(\text{graphite})} + 2\text{H}_2(g) \longrightarrow \text{CH}_4(g)$ will be : **[JEE(Main) 2017, 4/120]**
 (1) $+144.0 \text{ kJ mol}^{-1}$ (2) $-74.8 \text{ kJ mol}^{-1}$ (3) $-144.0 \text{ kJ mol}^{-1}$ (4) $+74.8 \text{ kJ mol}^{-1}$

JEE-MAIN ONLINE PROBLEMS

1. The standard enthalpy of formation of NH_3 is -46.0 kJ/mol . If the enthalpy of formation of H_2 from its atoms is -436 kJ/mol and that of N_2 is -712 kJ/mol , the average bond thalpy of N-H bond in NH_3 is : **[JEE(Main) 2014 Online (09-04-14), 4/120]**
 (1) -1102 kJ/mol (2) -964 kJ/mol (3) $+352 \text{ kJ/mol}$ (4) $+1056 \text{ kJ/mol}$
2. The standard enthalpy of formation ($\Delta_f H^\circ_{298}$) for methane, CH_4 is $-74.9 \text{ kJ mol}^{-1}$. In order to calculate the average energy given out in the formation of a C-H bond from this it is necessary to know which one of the following ? **[JEE(Main) 2014 Online (12-04-14), 4/120]**
 (1) the dissociation energy of the hydrogen molecule, H_2 .
 (2) the first four ionisation energies of carbon.
 (3) the dissociation energy of H_2 and enthalpy of sublimation of carbon (graphite).
 (4) the first four ionisation energies of carbon and electron affinity of hydrogen.
3. The heat of atomisation of methane and ethane are 360 kJ/mol and 620 kJ/mol , respectively. The longest wavelength of light capable of breaking the C-C bond is : **[JEE(Main) 2015 Online (10-04-15), 4/120]**
 (A vogadro number = 6.02×10^{23} , $h = 6.62 \times 10^{-34} \text{ J s}$):
 (1) $2.48 \times 10^3 \text{ nm}$ (2) $1.49 \times 10^3 \text{ nm}$ (3) $2.49 \times 10^4 \text{ nm}$ (4) $2.48 \times 10^4 \text{ nm}$
4. For a reaction, $\text{A}(g) \rightarrow \text{A}(l)$; $\Delta H = -3RT$. The correct statement for the reaction is : **[JEE(Main) 2017 Online (08-04-17), 4/120]**
 (1) $\Delta H = \Delta U \neq 0$ (2) $|\Delta H| > |\Delta U|$ (3) $|\Delta H| < |\Delta U|$ (4) $\Delta H = |\Delta U| = 0$
5. For which of the following reactions, ΔH is equal to ΔU ? **[JEE(Main) 2018 Online (15-04-18), 4/120]**
 (1) $\text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g)$ (2) $2\text{HI}(g) \rightarrow \text{H}_2(g) + \text{I}_2(g)$
 (3) $2\text{SO}_2(g) + \text{O}_2(g) \rightarrow 2\text{SO}_3(g)$ (4) $2\text{NO}_2(g) \rightarrow \text{N}_2\text{O}_4(g)$
6. Given : (i) $\text{C}(\text{graphite}) + \text{O}_2(g) \rightarrow \text{CO}_2(g)$; $\Delta_r H^\circ = x \text{ kJ mol}^{-1}$
 (ii) $\text{C}(\text{graphite}) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{CO}(g)$; $\Delta_r H^\circ = y \text{ kJ mol}^{-1}$
 (iii) $\text{CO}(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{CO}_2(g)$; $\Delta_r H^\circ = z \text{ kJ mol}^{-1}$
 Based on the above thermochemical equations, find out which one of the following algebraic relationship is correct? **[JEE(Main) 2019 Online (12-01-19), 4/120]**
 (1) $x = y - z$ (2) $y = 2z - x$ (3) $x = y + z$ (4) $z = x + y$



Answers

EXERCISE – 1

PART – I

A-1.	$-1368 \text{ kJ mol}^{-1}$	A-2.	-4.955 kJ	B-1.	$-2035 \text{ kJ mol}^{-1}$
B-2.	$-56.98 \text{ kJ mol}^{-1}$	C-1.	(-94.1 kcal)	C-2.	-102 kcal
C-3.	-383 kJ mol^{-1}	C-4.	24 g	D-1.	$243.7 \text{ kJ mol}^{-1}$
D-2.	1488 kJ mol^{-1}	D-3.	-2573 kJ/mole	D-4.	-185 kJ
D-5.	309 kJ mol^{-1}	E-1.	$-65.3 \text{ kJ mol}^{-1}$	E-2.	-28 kJ/mole
E-3.	3890 kJmole^{-1}	F-1.	$2a = b$	F-2.	-228 kJ/mole.
F-3.	11.2 Kcal				

PART – II

A-1.	(C)	A-2.	(A)	A-3.	(D)	A-4.	(D)	A-5.	(A)
B-1.	(D)	B-2.	(A)	B-3.	(B)	B-4.	(D)	C-1.	(A)
C-2.	(D)	C-3.	(D)	C-4.	(B)	C-5.	(A)	C-6.	(A)
C-7.	(B)	C-8.	(A)	D-1.	(D)	D-2.	(B)	D-3.	(A)
E-1.	(A)	E-2.	(A)	E-3.	(C)	E-4.	(C)	E-5.	(A)
F-1.	(C)	F-2.	(A)						

PART – III

1. (A) \rightarrow (p, q) ; (B) \rightarrow (q, r, s) ; (C) \rightarrow (p) ; (D) \rightarrow (r)

EXERCISE – 2

PART – I

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

PART – II

1.	9	2.	9 Kcal/mole	3.	3	4.	3	5.	5
6.	53	7.	-12 kJ	8.	-87	9.	40	10.	78 Kcal

PART – III

1.	(BCD)	2.	(ABCD)	3.	(ABC)	4.	(AB)	5.	(CD)
6.	(ABC)	7.	(BCD)	8.	(BCD)				

**PART – IV**

- | | | | | |
|--------|--------|--------|--------|---------|
| 1. (A) | 2. (B) | 3. (B) | 4. (B) | 5. (AD) |
| 6. (A) | | | | |

EXERCISE – 3**PART – I**

- | | | |
|--------|--------|---|
| 1. (B) | 2. (C) | 3. (A – p, r, s) ; (B – r, s) ; (C – t) ; (D – p, q, t) |
| 4. (D) | 5. (C) | 6. (C) |

PART – II**JEE-MAIN OFFLINE PROBLEMS**

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

JEE-MAIN ONLINE PROBLEMS

- | | | | | |
|--------|--------|--------|--------|--------|
| 1. (3) | 2. (3) | 3. (2) | 4. (2) | 5. (2) |
| 6. (3) | | | | |



Additional Problems for Self Practice (APSP)

This Section is not meant for classroom discussion. It is being given to promote self-study and self testing amongst the Resonance students.

PART - I : PRACTICE TEST-1 (IIT-JEE (MAIN Pattern))

Max. Time : 1 Hr.

Max. Marks : 120

Important Instructions

- The test is of **1 hour** duration.
- The Test Booklet consists of **30** questions. The maximum marks are **120**.
- Each question is allotted **4 (four)** marks for correct response.
- Candidates will be awarded marks as stated above in Instructions No. 3 for correct response of each question.
 $\frac{1}{4}$ (**one fourth**) marks will be deducted for indicating incorrect response of each question. No deduction from the total score will be made if no response is indicated for an item in the answer sheet.
- There is only one correct response for each question. Filling up more than one response in any question will be treated as wrong response and marks for wrong response will be deducted accordingly as per instructions 4 above.

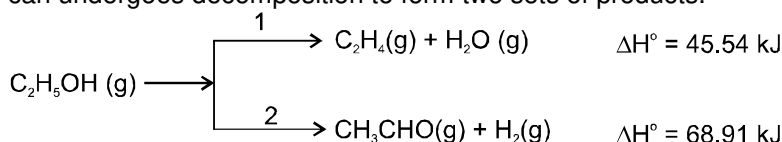
- Among them intensive property is :
 (1) Mass (2) Volume (3) Surface tension (4) Enthalpy
- Which of the following is true for an adiabatic process :
 (1) $\Delta H = 0$ (2) $\Delta W = 0$ (3) $\Delta Q = 0$ (4) $\Delta V = 0$
- Which of the following is not a state function :
 (1) S (2) G (3) H (4) Q
- The relation between ΔU and ΔH at constant pressure is :
 (1) $\Delta H = \Delta U - P\Delta V$ (2) $\Delta H = \Delta U + P\Delta V$ (3) $\Delta U = \Delta V + \Delta H$ (4) $\Delta U = \Delta H + P\Delta V$
- The work done in ergs for the reversible expansion of one mole of an ideal gas from a volume of 10 litres to 20 litres at 25°C is :
 (1) $-2.303 \times 298 \times 0.082 \log 2$ (2) $-298 \times 10^7 \times 8.31 \times 2.303 \log 2$
 (3) $-2.303 \times 298 \times 0.082 \log 0.5$ (4) $-8.31 \times 10^7 \times 298 - 2.303 \log 0.5$
- A coffee cup calorimeter initially contains 125 g of water, at a temperature of 24.2°C . 8 g of ammonium nitrate (NH_4NO_3), also at 24.2°C , is added to the water, and the final temperature is 18.2°C . What is the heat of solution of ammonium nitrate in kJ/mol ? The specific heat capacity of the solution is $4.2 \text{ J/}^\circ\text{C g}$.
 (1) 33.51 kJ/mol (2) 39.5 kJ/mol (3) 32.2 kJ/mol (4) 37.3 kJ/mol
- The molar heat capacities at constant pressure (assumed constant with respect to temperature) at A, B and C are in ratio of 3 : 1.5 : 2.0 The enthalpy change for the exothermic reaction $\text{A} + 2\text{B} \longrightarrow 3\text{C}$ at 300 K and 310 K is ΔH_{300} and ΔH_{310} respectively then :
 (1) $\Delta H_{300} > \Delta H_{310}$ (2) $\Delta H_{300} < \Delta H_{310}$ (3) $\Delta H_{300} = \Delta H_{310}$
 (4) if $T_2 > T_1$ then $\Delta H_{310} > \Delta H_{300}$ and if $T_2 < T_1$ then $\Delta H_{310} < \Delta H_{300}$
- Heat of combustion of ethanol at constant pressure and at temperature T K ($= 298 \text{ K}$) is found to be $-q \text{ J mol}^{-1}$. Hence, heat of combustion (in J mol^{-1}) of ethanol at the same temperature at constant volume will be :
 (1) $RT - q$ (2) $-(q + RT)$ (3) $q - RT$ (4) $q + RT$
- When 1.0 g of oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) is burned in a bomb calorimeter whose heat capacity is 8.75 kJ/K , the temperature increases by 0.312 K . The enthalpy of combustion of oxalic acid at 27°C is :
 (1) -245.7 kJ/mol (2) -244.452 kJ/mol (3) -246.947 kJ/mol (4) None of these



10. Benzene burns according to the following equation at 300 K ($R = 25/3 \text{ J mole}^{-1}\text{K}^{-1}$)
 $2\text{C}_6\text{H}_6(\ell) + 15 \text{O}_2(\text{g}) \longrightarrow 12 \text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\ell) \quad \Delta H^\circ = -6547.5 \text{ KJ}$
 What is the ΔE° for the combustion of 1.5 mol of benzene
 (1) -3271 kJ (2) -9813 kJ (3) -4905 kJ (4) -9810 kJ
11. Ethyl chloride ($\text{C}_2\text{H}_5\text{Cl}$), is prepared by reaction of ethylene with hydrogen chloride :
 $\text{C}_2\text{H}_4(\text{g}) + \text{HCl}(\text{g}) \longrightarrow \text{C}_2\text{H}_5\text{Cl}(\text{g}) \quad \Delta H = -72.3 \text{ kJ/mol.}$
 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.
 (1) -64.81 (2) -190.71 (3) -209.41 (4) -224.38
12. Which statement regarding entropy is correct ?
 (1) A completely ordered deck of cards has more entropy than a shuffled deck in which cards are arranged randomly.
 (2) A perfect ordered crystal of solid nitrous oxide has more entropy than a disordered crystal in which the molecules are oriented randomly.
 (3) 1 mole N_2 gas at STP has more entropy than 1 mole N_2 gas at 273 K in a volume of 11.2 litre.
 (4) 1 mole N_2 gas at STP has more entropy than 1 mole N_2 gas at 273 K and 0.25 atm.
13. 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 work done 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.
 $\text{Zn}(\text{s}) + 2\text{H}^+(\text{aq}) \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + \text{H}_2(\text{g})$
 (1) -1.53 KJ (2) -2.53 KJ (3) Zero (4) 2.53 KJ
14. The enthalpy change for the reaction of 50 mL of ethylene with 50.0 mL of H_2 at 1.5 atm pressure is $\Delta H = -0.31 \text{ KJ}$. What is the ΔE ?
 (1) -0.3024 (2) -0.6048 (3) -0.12 (4) None
15. When 0.1 mole of ice melt at 0°C and at constant pressure of 1 atm 144 calories of heat are absorbed by the system. Calculate ΔH for the reaction.
 (1) $\Delta H = 720 \text{ J}\cdot\text{mol}^{-1}$ (2) $\Delta H = 1440 \text{ Cal}\cdot\text{mol}^{-1}$ (3) $\Delta H = 1.4 \text{ kCal}\cdot\text{mol}^{-1}$ (4) $\Delta H = 0$
16. One mole of ideal monoatomic gas is carried through the reversible cyclic process as shown in figure. Calculate net heat absorbed by the gas in the path BC.
 (1) $\frac{1}{2} P^\circ V^\circ$ (2) $\frac{7}{2} P^\circ V^\circ$
 (3) $2 P^\circ V^\circ$ (4) $\frac{5}{2} P^\circ V^\circ$
-
17. 130 g of Zn is dissolved in dilute sulphuric acid in an open beaker at 27°C . Find the work done in the process assuming isothermal operation.
 (1) -1200 cal (2) -1800 cal (3) $+1800 \text{ cal}$ (4) $+1200 \text{ cal}$
18. The enthalpy of combustion of propane (C_3H_8) gas in terms of given data is :
 Bond energy (kJ/mol)
 $\begin{array}{ccccc} \epsilon_{\text{C}-\text{H}} & \epsilon_{\text{O}=\text{O}} & \epsilon_{\text{C}=\text{O}} & \epsilon_{\text{O}-\text{H}} & \epsilon_{\text{C}-\text{C}} \\ +X_1 & +X_2 & +X_3 & +X_4 & +X_5 \end{array}$
 Resonance energy of CO_2 is $-z \text{ kJ/mol}$ and $\Delta H_{\text{vaporization}} [\text{H}_2\text{O}(\ell)]$ is $y \text{ kJ/mol}$.
 (1) $8x_1 + 2x_5 + 5x_2 - 6x_3 - 8x_4 - 4y - 3z$ (2) $6x_1 + x_5 + 5x_2 - 3x_3 - 4x_4 - 4y - 3z$
 (3) $8x_1 + 2x_5 + 5x_2 - 6x_3 - 8x_4 - y - z$ (4) $8x_1 + x_5 + 5x_2 - 6x_3 - 8x_4 - 4y + 3z$
19. If x_1 , x_2 and x_3 are enthalpies of H-H, O=O and O-H bonds respectively, and x_4 is the enthalpy of vaporisation of water, estimate the standard enthalpy of combustion of hydrogen.
 (1) $x_1 + \frac{x_2}{2} - 2x_3 + x_4$ (2) $x_1 + \frac{x_2}{2} - 2x_3 - x_4$ (3) $x_1 + \frac{x_2}{2} - x_3 + x_4$ (4) $2x_3 - x_1 - \frac{x_2}{2} - x_4$



20. $\text{NH}_3(\text{g}) + 3\text{Cl}_2(\text{g}) \longrightarrow \text{NCl}_3(\text{g}) + 3\text{HCl}(\text{g})$; ΔH_1
 $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g})$; ΔH_2
 $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \longrightarrow 2\text{HCl}(\text{g})$; ΔH_3
 The heat of formation of $\text{NCl}_3(\text{g})$ in the terms of ΔH_1 , ΔH_2 and ΔH_3 is
 (1) $\Delta H_f = -\Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$ (2) $\Delta H_f = \Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$
 (3) $\Delta H_f = \Delta H_1 - \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$ (4) None
21. ΔH°_f of water is $-285.5 \text{ kJ mol}^{-1}$. if enthalpy of neutralisation of monoacidic strong base with strong acid is $-57.3 \text{ kJ mol}^{-1}$, ΔH°_f of OH^- ion will be
 (1) $-228.5 \text{ kJ mol}^{-1}$ (2) $228.5 \text{ kJ mol}^{-1}$ (3) $114.5 \text{ kJ mol}^{-1}$ (4) $-114.5 \text{ kJ mol}^{-1}$
22. Ethanol can undergoes decomposition to form two sets of products.



If the molar ratio of C_2H_4 to CH_3CHO is 8 : 1 in a set of product gases, then the energy involved in the decomposition of 1 mole of ethanol is

- (1) 65.98 kJ (2) 48.137 kJ (3) 48.46 kJ (4) 57.22 kJ
23. Find the enthalpy of S-S bond from the following data.
 (i) $\text{C}_2\text{H}_5\text{S}-\text{C}_2\text{H}_5(\text{g})$ $\Delta H^\circ_f = -147.2 \text{ kJ/mol}$
 (ii) $\text{C}_2\text{H}_5\text{S}-\text{S}-\text{C}_2\text{H}_5(\text{g})$ $\Delta H^\circ_f = -201.9 \text{ kJ/mol}$
 (iii) $\text{S}(\text{g})$ $\Delta H^\circ_f = 222.8 \text{ kJ/mol}$
 (1) -168.1 kJ/mol (2) $+168.1 \text{ kJ/mol}$ (3) -277.5 kJ/mol (4) $+277.5 \text{ kJ/mol}$
24. Given the following equations and ΔH° values, determine the enthalpy of reaction at 298 K for the reaction :
- $$\begin{aligned} \text{C}_2\text{H}_4(\text{g}) + 6\text{F}_2(\text{g}) &\longrightarrow 2\text{CF}_4(\text{g}) + 4\text{HF}(\text{g}) \\ \text{H}_2(\text{g}) + \text{F}_2(\text{g}) &\longrightarrow 2\text{HF}(\text{g}) ; & \Delta H^\circ_1 &= -537 \text{ kJ} \\ \text{C}(\text{s}) + 2\text{F}_2(\text{g}) &\longrightarrow \text{CF}_4(\text{g}) ; & \Delta H^\circ_2 &= -680 \text{ kJ} \\ 2\text{C}(\text{s}) + 2\text{H}_2(\text{g}) &\longrightarrow \text{C}_2\text{H}_4(\text{g}) ; & \Delta H^\circ_3 &= 52 \text{ kJ} \end{aligned}$$
- (1) -1165 (2) -2486 (3) +1165 (4) +2486
25. Animals operate under conditions of constant pressure and most of the process that maintain life are isothermal (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 $+182.4 \text{ JK}^{-1}$ for the reaction stated above.
 $\Delta H_{\text{combustion}}[\text{glucose}] = -2808 \text{ kJ}$
 (1) -2754.4 kJ (2) -2864.5 kJ (3) -56.5 kJ (4) -2808 kJ

26. From the given table answer the following question :

	CO (g)	CO ₂ (g)	H ₂ O(g)	H ₂ (g)
$\Delta H^\circ_{298}(\text{Kcal/ mole})$	-26.42	-94.05	-57.8	0
$\Delta G^\circ_{298}(\text{Kcal/ mole})$	-32.79	-94.24	-54.64	0
$S^\circ_{298}(\text{Cal/ K mol})$	47.3	51.1	?	31.2

Reaction : $\text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{CO}_2(\text{g})$

Calculate $S^\circ_{298}[\text{H}_2\text{O}(\text{g})]$

- (1) $-119.47 \text{ Cal/ K mole}$ (2) $+119.47 \text{ Cal/ K mole}$
 (3) $-45.13 \text{ Cal/ K mole}$ (4) $+45.13 \text{ Cal/ K mole}$
27. Calculate the free energy change at 298 K for the reaction; $\text{Br}_2(\ell) + \text{Cl}_2(\text{g}) \longrightarrow 2\text{BrCl}(\text{g})$. For the reaction $\Delta H^\circ = 29.3 \text{ kJ}$ & the entropies of $\text{Br}_2(\ell)$, $\text{Cl}_2(\text{g})$ & $\text{BrCl}(\text{g})$ at the 298K are 152.3, 223.0, 239.7 $\text{J mol}^{-1}\text{K}^{-1}$ respectively.
 (1) -1721.8 J (2) -60321.8 J (3) $+60321.8 \text{ J}$ (4) $+1721.8 \text{ J}$



28. One gram sample of oxygen undergoes free expansion in insulated container from 0.75 L to 3.0 L at 298 K. Calculate ΔS , q , w , ΔH and ΔE .
 (1) $\Delta S = 0.36 \text{ JK}^{-1}$, $\Delta E = 0$ (2) $W = 227.97 \text{ J}$, $\Delta E = 0$
 (3) $q = -227.97 \text{ J}$, $\Delta E = 0$ (4) $W = 227.97 \text{ J}$, $\Delta H = 0$
29. Given that : $\Delta G_f^\circ (\text{CuO}) = -30.4 \text{ kcal/mole}$
 $\Delta G_f^\circ (\text{Cu}_2\text{O}) = -34.98 \text{ kcal/mole}$ $T = 298 \text{ K}$
 Now on the basis of above data which of the following predictions will be most appropriate under the standard conditions and reversible reaction.
 (1) Finely divided form of CuO kept in excess O_2 would be completely converted to Cu_2O
 (2) Finely divided form of Cu_2O kept in excess O_2 would be completely converted to CuO
 (3) Finely divided form of CuO kept in excess O_2 would be converted to a mixture of CuO and Cu_2O (having more of CuO)
 (4) Finely divided form of CuO kept in excess O_2 would be converted to a mixture of CuO and Cu_2O (having more of Cu_2O)
30. Calculate $\Delta_r G^\circ$ for $(\text{NH}_4\text{Cl}, \text{s})$ at 310 K.
 Given : $\Delta_r H^\circ (\text{NH}_4\text{Cl}, \text{s}) = -314.5 \text{ kJ/mol}$; $\Delta_r C_p = 0$
 $S^\circ_{\text{N}_2(\text{g})} = 192 \text{ JK}^{-1} \text{ mol}^{-1}$; $S^\circ_{\text{H}_2(\text{g})} = 130.5 \text{ JK}^{-1} \text{ mol}^{-1}$;
 $S^\circ_{\text{Cl}_2(\text{g})} = 233 \text{ JK}^{-1} \text{ mol}^{-1}$; $S^\circ_{\text{NH}_4\text{Cl}(\text{s})} = 99.5 \text{ JK}^{-1} \text{ mol}^{-1}$
 All given data are at 300 K.
 (1) -198.56 kJ/mol (2) -426.7 kJ/mol (3) -202.3 kJ/mol (4) None of these

Practice Test-1 (IIT-JEE (Main Pattern))

OBJECTIVE RESPONSE SHEET (ORS)

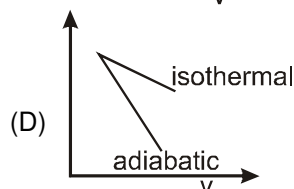
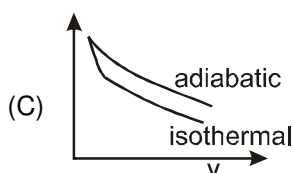
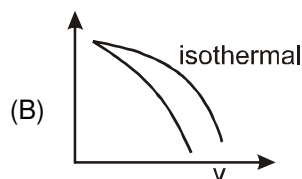
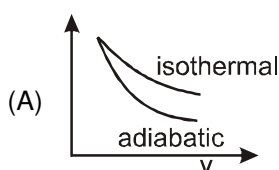
Que.	1	2	3	4	5	6	7	8	9	10
Ans.										
Que.	11	12	13	14	15	16	17	18	19	20
Ans.										
Que.	21	22	23	24	25	26	27	28	29	30
Ans.										

PART - II : NATIONAL STANDARD EXAMINATION IN CHEMISTRY (NSEC) STAGE-I

1. The enthalpy of hydrogenation for 1-pentene is +126 KJ/mol. The enthalpy of hydrogenation for 1 : 3-pentadiene is + 230 KJ/mol. Hence estimate the resonance (delocalization) energy of 1 : 3-pentadiene? [NSEC-2000]
 (A) 22 KJ (B) 104 KJ (C) 252 KJ
 (D) Cannot be calculated from this information.
2. The entropy change during an isothermal expansion of an ideal gas from V_1 to V_2 at temperature T is given by [NSEC-2000]
 (A) $\Delta S = 0$ (B) $\Delta S = 2.303 R \log_{10} V_2 / V_1$
 (C) $\Delta S = 2.303 RT \log_{10} V_2 / V_1$ (D) $\Delta S = 2.303 R \log_{10} V_1 / V_2$
3. An isothermal process is associated with [NSEC-2000]
 (A) constant entropy (B) constant temperature
 (C) constant enthalpy (D) large change in heat content
4. The heat change for the reaction, $\text{C}_{(\text{s})} + 2\text{S}_{(\text{s})} \rightarrow \text{CS}_{2(\text{l})}$ is known as [NSEC-2000]
 (A) heat of transition (B) heat of fusion
 (C) heat of vapourisation (D) heat of formation



5. When a solid melts, there is : [NSEC-2001]
 (A) decreases in enthalpy (B) increase in enthalpy
 (C) no increase in enthalpy (D) decrease in entropy
6. The entropy change for the vapourisation of water at 100°C (molar latent heat of vapourisation of water = 40.8 kJ mol⁻¹) is : [NSEC-2001]
 (A) 109.4 JK⁻¹mol⁻¹ (B) 0.1094 JK⁻¹mol⁻¹ (C) 0.408 JK⁻¹mol⁻¹ (D) 40.8 JK⁻¹mol⁻¹
7. The free energy change for an irreversible process is : [NSEC-2001]
 (A) zero (B) negative (C) positive (D) very large positive
8. An isobaric process is associated with : [NSEC-2001]
 (A) constant temperature (B) constant volume (C) constant pressure (D) small change in enthalpy
9. Lattice energy of ionic compound is calculated by using : [NSEC-2002]
 (A) Hess's law (B) Kirchoff's equation (C) Born-Haber cycle (D) Carnot cycle.
10. According to second law of thermodynamics [NSEC-2002]
 (A) total energy in the Universe remains constant
 (B) total enthalpy in the Universe remains constant
 (C) total entropy of the Universe always increases
 (D) total entropy of the Universe always decreases.
11. For a spontaneous reaction, ΔG and ΔS should be [NSEC-2002]
 (A) $\Delta G = +ve$ and $\Delta S = -ve$ (B) $\Delta G = -ve$ and $\Delta S = +ve$
 (C) $\Delta G = 0$ and $\Delta S = +ve$ (D) $\Delta G = +ve$ and $\Delta S = 0$
12. Which of the following expression is correct ? [NSEC-2002]
 (A) $E = H + PV$ (B) $H = E + PV$ (C) $H = E - PV$ (D) $P = E + HV$
13. The enthalpy change for the fusion of ice at 0°C (molar latent heat of fusion of ice = 6.025 kJ mol⁻¹) is : [NSEC-2002]
 (A) 22.07 JK⁻¹ mol⁻¹ (B) 1.226 JK⁻¹ mol⁻¹ (C) 2.207 JK⁻¹ mol⁻¹ (D) 25.0 JK⁻¹ mol⁻¹
14. The correct figure representing isothermal and adiabatic expansions of an ideal gas from a particular initial state is [NSEC-2003]

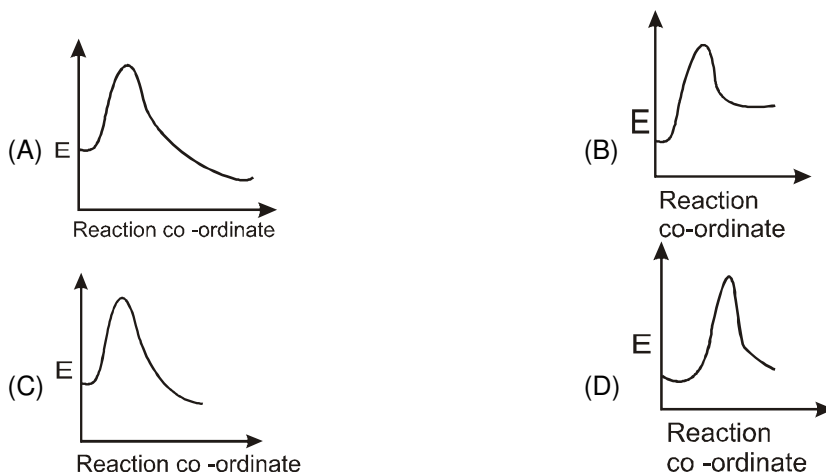


15. An ideal gas, on adiabatic expansion, gets cooled because [NSEC-2003]
 (A) the average distance between the gas molecules increases and hence the intermolecular interaction decreases
 (B) the internal energy of the gas is used in doing the work of expansion
 (C) the temperature of the gas is lower than the inversion temperature corresponding to Joule-Thomson effect
 (D) the pressure decreases and temperature is proportional to the pressure.

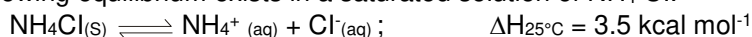


16. Which energy diagram corresponds to exothermic reaction and highest value of the rate constant ?

[NSEC-2003]



17. The following equilibrium exists in a saturated solution of NH_4Cl .



A change that will shift the equilibrium to the right is

[NSEC-2003]

- (A) decrease in temperature
(B) increase in temperature
(C) addition of NH_4Cl crystals to the reaction mixture
(D) addition of NH_4OH solution to the reaction mixture.

18. $\text{CCl}_4(\text{g}) + 2\text{H}_2\text{O}(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + 4\text{HCl}(\text{g})$. The standard enthalpies of formation at 298 K for $\text{CCl}_4(\text{g})$, $\text{H}_2\text{O}(\text{g})$, $\text{CO}_2(\text{g})$ and $\text{HCl}(\text{g})$ are -106.7 , -241.8 , -393.7 and $-92.5 \text{ kJ mol}^{-1}$ respectively. The value of ΔH_{298}° for the above reaction is

[NSEC-2004]

- (A) -137.7 kJ (B) 173.4 kJ (C) -173.4 kJ (D) 137.7 kJ .

19. The temperature of an ideal gas increases in an

[NSEC-2004]

- (A) adiabatic expansion (B) isothermal expansion
(C) adiabatic compression (D) isothermal compression.

20. The value of Δn for the combustion reaction of one mole of benzene in gaseous state when both the reactants and products are at 298 K is

[NSEC-2004]

- (A) 1 (B) 0 (C) $1/2$ (D) $-1/2$.

21. For two moles of an ideal gas

[NSEC-2004]

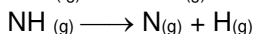
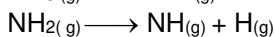
- (A) $C_V - C_P = R$ (B) $C_P - C_V = 2R$ (C) $C_P - C_V = R$ (D) $C_V - C_P = 2R$.

22. Heat of combustion of ethanol at constant pressure and at 298 K is found to be $-Q \text{ kJ mol}^{-1}$. Hence, heat of combustion of ethanol at the same temperature at constant volume will be

[NSEC-2004]

- (A) $(-Q + RT) \text{ kJ mol}^{-1}$ (B) $(-Q - RT) \text{ kJ mol}^{-1}$ (C) $(+Q - RT) \text{ kJ mol}^{-1}$ (D) $(Q + RT) \text{ kJ mol}^{-1}$.

23. $\text{NH}_3(\text{g}) \longrightarrow \text{NH}_2(\text{g}) + \text{H}(\text{g})$



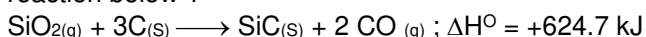
The enthalpy changes for the above reactions

[NSEC-2004]

- (A) are the same (B) are in increasing order
(C) are in decreasing order (D) cannot be correlated.

24. How much heat is absorbed in the complete reaction of 3.00 grams of SiO_2 with excess carbon in the reaction below ?

[NSEC-2005]



- (A) $1.33 \times 10^4 \text{ kJ}$ (B) $1.13 \times 10^5 \text{ kJ}$ (C) 5.06 kJ (D) 31.2 kJ





25. Estimate the temperature at which $\Delta G = 0$ for the following reaction:
(Given : $\Delta H = -176$ kJ and $\Delta S = -284.5$ J/K). Caution : Beware of units. [NSEC-2005]

$$\text{NH}_{3(g)} + \text{HCl}_{(g)} \longrightarrow \text{NH}_4\text{Cl}_{(s)}$$
 (A) 582 K (B) 467 K (C) 634 K (D) 619 K
26. A particular chemical reaction is characterised by $\Delta H_{\text{rxn}} = +250$ kJ/mol. Which of the following statements is/are true concerning this reaction ? [NSEC-2005]
 I. Heat is liberated to the surroundings.
 II. The reaction is endothermic.
 III. The total heat content of the products is lower than that of the reactants.
 (A) all are true (B) only II and III are true
 (C) only I and II are true (D) only II is true.
27. Of the following composition for the mixture of $\text{H}_{2(g)}$ and $\text{N}_{2(g)}$ which gives rise to maximum entropy of mixing? [NSEC-2006]
 (A) 2 mols of H_2 and 1 mol of N_2 (B) 1 mol of H_2 and 2 mols of N_2
 (C) 1.5 mols of H_2 and 1.5 mols of N_2 (D) 0.5 mol of H_2 and 2.5 mols of N_2 .
28. The enthalpy change, ΔH due to reversible adiabatic expansion of an ideal gas from P_1, V_1, T_1 , to P_2, V_2, T_2 is [NSEC-2006]
 (A) $C_V \ln \frac{T_2}{T_1}$ (B) $C_P \ln \frac{T_2}{T_1}$ (C) $R \ln \frac{V_2}{V_1}$ (D) $R \ln \frac{P_2}{P_1}$.
29. Which of the following processes is/are accompanied by an increase in the entropy of the system?
 (i) Water freezes
 (ii) Iodine sublimates at room temperature
 (iii) A building is constructed from bricks and mortar
 (iv) A partition is removed to allow two gases to mix [NSEC-2006]
 (A) (i) and (iv) (B) (i), (ii) and (iv) (C) (ii) and (iv) (D) only (iv).
30. A reference book lists the heat of formation of $\text{NH}_{3(g)}$ to be -46 kJ mol $^{-1}$. The ΔH (in kJ mol $^{-1}$) of the reaction: $2\text{NH}_{3(g)} \longrightarrow \text{N}_{2(g)} + 3\text{H}_{2(g)}$ is [NSEC-2006]
 (A) 46 (B) -46 (C) 92 (D) -92
31. Both the lattice energy (ΔU_o) and hydration enthalpy (ΔH_h) of a binary salt are negative quantities. However, if ΔU_o is more negative than ΔH_h then [NSEC-2006]
 (A) the salt will not dissolve in water (B) salt will dissolve in water
 (C) dissolution of salt in water is exothermic (D) dissolution of salt in water is endothermic
32. Preferred conditions for spontaneity in nature are [NSEC-2006]
 (A) low enthalpy and low entropy (B) high enthalpy and high entropy
 (C) high enthalpy and low entropy (D) low enthalpy and high entropy.
33. The change in free energy accompanied by the isothermal reversible expansion of 1 mol of an ideal gas when it doubles its volume is ΔG_1 . The change in free energy accompanied by sudden isothermal irreversible doubling of volume of 1 mol of the same gas is ΔG_2 . Ratio of ΔG_1 to ΔG_2 is : [NSEC-2007]
 (A) 1 (B) 1/2 (C) -1 (D) -1/2
34. The degree of freedom for $\text{NH}_4\text{Cl}_{(s)} \rightleftharpoons \text{NH}_4\text{Cl}_{(g)} \rightleftharpoons \text{NH}_{3(g)} + \text{HCl}_{(g)}$ will be [NSEC-2008]
 (A) 4 (B) 3 (C) 2 (D) 1
35. A reversible adiabatic expansion is an [NSEC-2008]
 (A) isothermal process (B) isobaric process (C) isentropic process (D) isochoric process
36. If the bond energies are as follows [NSEC-2008]
 (i) C-H = 413.8 kJ (ii) Cl-Cl = 238.0 kJ (iii) C-Cl = 327.2 kJ (iv) H-Cl = 429.8 kJ
 the enthalpy of the reaction: $\text{CH}_4 + 2\text{Cl}_2 \longrightarrow \text{CH}_2\text{Cl}_2 + 2\text{HCl}$ will be
 (A) +202.6 kJ (B) -202.6 kJ (C) +220.1 kJ (D) +870 kJ



37. For the isobaric gaseous reaction, the enthalpy change given by – [NSEC–2009]
 (A) $\Delta H = \Delta E + \Delta nRT$ (B) $\Delta H = \Delta E + P\Delta V$ (C) $\Delta H = \Delta E + \Delta nP\Delta V$ (D) $\Delta H = \Delta E + V\Delta P$
38. A reaction will never be spontaneous at any temperature and pressure if [NSEC–2010]
 (A) $\Delta S = +ve, \Delta H = +ve$ (B) $\Delta S = +ve, \Delta H = -ve$ (C) $\Delta S = -ve, \Delta H = +ve$ (D) $\Delta S = -ve, \Delta H = -ve$
39. The internal energy change involved when a system goes from state A to state B is 40 kJ. If the system goes from A to B by a reversible path and returns to A by an irreversible path, the net change in internal energy is [NSEC–2010]
 (A) 40 kJ (B) > 40 kJ (C) < 40 kJ (D) zero
40. The enthalpy of formation of carbon dioxide and water are –395 kJ and –285 kJ, respectively, and the enthalpy of combustion of acetic acid is –869 kJ. Hence the enthalpy of formation of acetic acid is [NSEC–2010]
 (A) 235 kJ (B) –235 kJ (C) 420 kJ (D) 491 kJ
41. For the reaction $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$ Which of the following is correct ? [NSEC–2010]
 (A) $\Delta H = \Delta E$ (B) $\Delta H > \Delta E$ (C) $\Delta H < \Delta E$ (D) $\Delta H = 2\Delta E$
42. The enthalpies of decomposition of methane (CH_4)(g) and ethane (C_2H_6)(g) are 400 and 670 kJ. mol⁻¹, respectively. The ΔH_{C-C} in kJ mol⁻¹ is [NSEC–2011]
 (A) 270 (B) 70 (C) 200 (D) 240
43. The degrees of freedom for the system $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ are [NSEC–2011]
 (A) 1 (B) 2 (C) 3 (D) 4
44. Which of the following has a positive entropy change ? [NSEC–2012]
 (A) $H_2O(g) \longrightarrow H_2O(l)$ (B) $BF_3(g) + NH_3(g) \longrightarrow F_3B.NH_3(s)$
 (C) $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$ (D) $2NH_4NO_3(s) \longrightarrow 2N_2(g) + 4H_2O(l) + O_2(g)$
45. The enthalpy changes for the following reactions are : [NSEC–2012]
 $C_{diamond} + O_2(g) \longrightarrow CO_2(g) \quad \Delta H = -395.3 \text{ kJ mol}^{-1}$
 $C_{graphite} + O_2(g) \longrightarrow CO_2(g) \quad \Delta H = -393.4 \text{ kJ mol}^{-1}$
 The enthalpy change for the transition $C_{diamond} \longrightarrow C_{graphite}$ will be :
 (A) – 3.8 kJ mol⁻¹ (B) + 3.8 kJ mol⁻¹ (C) – 1.9 kJ mol⁻¹ (D) + 1.9 kJ mol⁻¹
46. For a chemical reaction ΔH is negative and ΔS is positive. This reaction is [NSEC–2013]
 (A) spontaneous at all temperatures (B) nonspontaneous at all temperatures
 (C) spontaneous only at high temperatures (D) spontaneous only at low temperatures
47. 6.24 g of ethanol are vaporized by supplying 5.89 kJ of heat energy. What is the enthalpy of vapourisation of ethanol ? [NSEC–2013]
 (A) 43.42 kJ (B) 47.0 kJ (C) 21.75 kJ (D) 435.0 kJ
48. Two samples A and B of an ideal gas, initially at same temperature and pressure, are compressed from volume V to V/2, isothermally for A and adiabatically for B. The final pressure of A will be [NSEC–2014]
 (A) greater than that of B (B) less than that of B
 (C) twice that of B (D) equal to that at B
49. The **heat of formation** of ethanol, from the following data is [NSEC–2014]
 $C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l) \quad -1368 \text{ kJ}$
 $\Delta H_f CO_2(g) = -393.5 \text{ kJ/mol}; \quad \Delta H_f H_2O(l) = -286 \text{ kJ/mol}$
 (A) – 277 kJ/mol (B) – 1260.5 kJ/mol (C) – 688.5 kJ/mol (D) – 3013 kJ/mol
50. N_2 gas stored in a cylinder, fixed with a movable piston, undergoes adiabatic expansion. The statement that is true for the given situation is [NSEC–2014]
 (A) $q = W$ (B) $\Delta U = W$ (C) $\Delta U = 0$ (D) $\Delta U = q$
51. The enthalpy of vaporization of benzene is +35.3 kJ/mol at its boiling point of 80°C. The entropy change in the transition of vapour to liquid at its boiling point is [NSEC–2014]
 (A) –100 (B) +100 (C) +342 (D) –342



52. The process in which an ideal gas undergoes change from X to Y as shown in the following diagram is **[NSEC-2015]**
- (A) isothermal compression (B) adiabatic compression
(C) isothermal expansion (D) adiabatic expansion
-
53. Glucose when dissolved in water leads to cooling of the solution. Suppose you take 250 mL water at room temperature in an open container (such as a bowl) made of thermally insulated material and dissolve a spoonful of glucose in it. If you are able to accurately measure the heat absorbed by this solution in reaching back to room temperature (assuming negligible changes in the composition and the amount of solution during this process), you will be measuring **[NSEC-2015]**
- (A) The enthalpy of dissolution of the glucose in water
(B) The Gibbs free energy of dissolution of the glucose in Water
(C) The work done by the atmosphere on the system during the dissolution process
(D) The heat capacity of the solution
54. An ideal gas taken in an insulated chamber is released into interstellar space. The statement that is nearly true for this process is **[NSEC-2015]**
- (A) $Q = 0, W \neq 0$ (B) $W = 0, Q \neq 0$ (C) $\Delta U = 0, Q \neq 0$ (D) $Q = W = \Delta U = 0$
55. Standard molar enthalpy of formation of $\text{CO}_2(\text{g})$ is equal to **[NSEC-2016]**
- (A) Zero
(B) The standard molar enthalpy of combustion of carbon (graphite)
(C) The standard molar enthalpy of combustion of $\text{C}(\text{g})$
(D) The standard molar enthalpy of combustion of $\text{CO}(\text{g})$
56. For the conversion $\text{CCl}_4(\ell) \rightarrow \text{CCl}_4(\text{g})$ at 1 bar and 350 K, the correct set of thermodynamic parameters is (Boiling point of CCl_4 is 77°C) **[NSEC-2016]**
- (A) $\Delta G = 0, \Delta S = +ve$ (B) $\Delta G = 0, \Delta S = -ve$ (C) $\Delta G = -ve, \Delta S = 0$ (D) $\Delta G = -ve, \Delta S = +ve$
57. Which reaction is spontaneous at all temperatures at standard pressure and concentration? **[NSEC-2016]**
- (A) exothermic reaction with a decrease in entropy
(B) exothermic reaction with an increase in entropy
(C) endothermic reaction with a decrease in entropy
(D) endothermic reaction with an increase in entropy
58. Given $\Delta_r H^\circ = -54.08 \text{ kJ mol}^{-1}$ and $\Delta_r S^\circ = 10.0 \text{ J mol}^{-1}$ at 25°C , the value of $\log_{10} K$ for the reaction $\text{A} \rightleftharpoons \text{B}$ is **[NSEC-2016]**
- (A) 3.4 (B) 10 (C) 0.53 (D) 113
59. Three samples of 100 g of water (samples I, II and III), initially kept at 1 atm pressure and 298 K were given the following treatments.
Sample I was heated to 320 K and cooled to 298 K
Sample II was heated to 300 K, cooled to 273 K and heated to 298 K
Sample III was heated to 373 K and cooled to 298 K
At the end of these processes, the internal energy of **[NSEC-2017]**
- (A) III is the highest (B) II is the highest
(C) I and III are the same, II is lower than that of I and III (D) I, II and III are the same
60. For the following spontaneous process $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{s})$ at 268 K, which of the following is true?
- (A) $\Delta S_{\text{sys}} < 0$ (B) $\Delta S_{\text{sys}} > 0$ (C) $\Delta S_{\text{surr}} < 0$ (D) $\Delta S_{\text{sys}} = -\Delta S_{\text{surr}}$
61. At constant volume, 6.0 mol of H_2 gas at 0°C and 100 kPa was heated to 250 kPa. The molar heat of H_2 at constant pressure (C_P) = 28.9 J mol^{-1} . (Assume that the heat capacity values do not change with temperature). The final temperature of the H_2 gas and the change in entropy of the process are **[NSEC-2017]**
- (A) 273°C and $113 \text{ kJ mol}^{-1} \text{ K}^{-1}$ (B) 410°C and $158.8 \text{ J mol}^{-1} \text{ K}^{-1}$
(C) 682.5°C and $113 \text{ J mol}^{-1} \text{ K}^{-1}$ (D) 682.5 K and $113 \text{ J mol}^{-1} \text{ K}^{-1}$





62. Hydrazine used in rocket fuels can be obtained by the reaction of ammonia and hydrogen peroxide according to the following equations
 $2\text{NH}_3(\text{g}) + \text{H}_2\text{O}_2(\text{l}) \longrightarrow \text{N}_2\text{H}_4(\text{l}) + 2\text{H}_2\text{O}(\text{l})$ ($\Delta H^\circ_{\text{reaction}} = -241 \text{ kJ/mol}$)
 If ΔH° (formation) of NH_3 , H_2O_2 and H_2O are -46.1 , -187.8 and -285.8 kJ/mol respectively, ΔH° for the decomposition of hydrazine into N_2 and H_2 is [NSEC-2017]
 (A) 50.6 kJ/mol (B) 241 kJ/mol (C) -50.6 kJ/mol (D) 120.5 kJ/mol
63. At 298 K , change in internal energy for the complete combustion of fullerene, $\text{C}_{60}(\text{s})$, an allotrope of carbon, and the enthalpy of formation of $\text{CO}_2(\text{g})$ are $-25970 \text{ kJ mol}^{-1}$ and -393 kJ mol^{-1} respectively. The enthalpy of formation of $\text{C}_{60}(\text{s})$ at 298 K is [NSEC-2018]
 (A) -2390 kJ (B) $4.95 \times 10^4 \text{ kJ}$ (C) $2.60 \times 10^4 \text{ kJ}$ (D) 2390 kJ
64. The lattice enthalpy and enthalpy of solution in water for solid NaCl are 753 kJ mol^{-1} and 5 kJ mol^{-1} respectively (Fig. above). If the solution enthalpies of Na^+ and Cl^- are in the ratio $6 : 5$, the enthalpy of hydration of Na^+ ion is [NSEC-2018]
 (A) 408 kJ mol^{-1} (B) -412 kJ mol^{-1} (C) -408 kJ mol^{-1} (D) -412 kJ mol^{-1}
65. For the reaction $4\text{NO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{N}_2\text{O}_5(\text{g})$, $\Delta H_{\text{reaction}} = -112 \text{ kJ}$. If the N_2O_5 is assumed to be formed in the reaction as a solid, $\Delta H_{\text{reaction}}$ will be ($\Delta H_{\text{sublimation}}$ of N_2O_5 is 54 kJ mol^{-1}) [NSEC-2018]
 (A) -220 kJ (B) -4 kJ (C) -166 kJ (D) -332 kJ
66. 2.0 L of N_2 gas kept at 25°C and 5 atm pressure were expanded isothermally against a constant pressure of 1 atm until the pressure of the gas reaches 1 atm . Assuming ideal behavior, reversible work of expansion in this process (in J) is close to [NSEC-2018]
 (A) 810 J (B) -194 kJ (C) -810 kJ (D) 3390 kJ
67. The daily energy requirement of a teenager is 7800 kJ . As calculated from the data given in the table below, the amount of glucose he has to consume (g) per day assuming that the entire energy he requires comes from the combustion of glucose is [NSEC-2018]

Molecule	ΔH_f (kJ mol^{-1})
$\text{C}_6\text{H}_{12}\text{O}_6$	-1273
$\text{CO}_2(\text{g})$	-394
H_2O	-286

- (A) 262 (B) 500 (C) 131 (D) 250

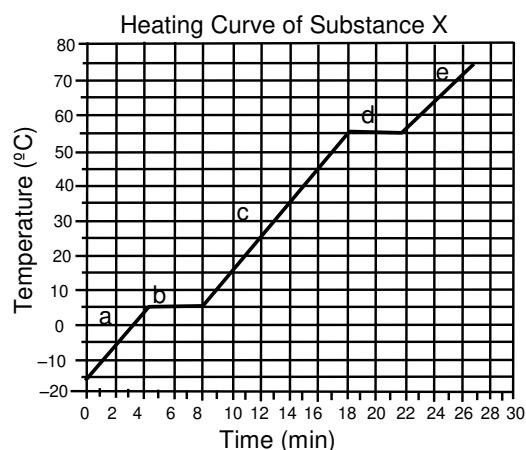
68. The standard molar entropies of $\text{H}_2(\text{g})$, $\text{N}_2(\text{g})$ and $\text{NH}_3(\text{g})$ are 130 , 190 and $193 \text{ J mol}^{-1}\text{K}^{-1}$ respectively. For the reaction $\frac{1}{2}\text{N}_2(\text{g}) + \frac{3}{2}\text{H}_2(\text{g}) \rightleftharpoons \text{NH}_3(\text{g})$ ($\Delta H_{\text{reaction}} = -45 \text{ kJ}$) to be in equilibrium, the temperature must be equal to [NSEC-2018]
 (A) 464 K (B) 928 K (C) 737 K (D) 354 K

69. A substance X was heated at constant pressure and the temperature observed at various times of heating was plotted as given below [NSEC-2018]

Which of the following is/are correct ?

- I. Melting point of X is -5°C
 II. Solid and liquid forms of X coexist in the region b
 III. Boiling point of X is 55°C
 IV. Solid and liquid forms of X coexist in the region d

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





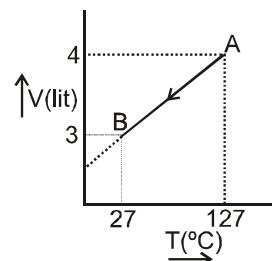
PART - III : HIGH LEVEL PROBLEMS (HLP)

SUBJECTIVE QUESTIONS

- 6 moles of an ideal gas expand isothermally and reversibly from a volume of 1 litre to a volume of 10 litres at 27°C. What is the maximum work done.
- Calculate work done by 1 mole of Ideal gas expand isothermally and irreversibly from pressure of 5 atm to 2 atm against a constant external pressure of 1 atm at 300 K temperature.
- One mole of Ideal gas ($C_{P,m} = 15 \text{ JK}^{-1} \text{ mole}^{-1}$) follow the process as shown in figure.

Predict the following :

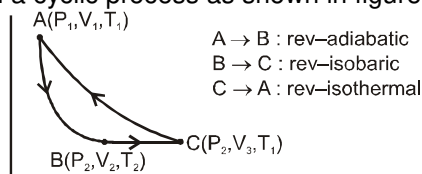
- Nature of process
- Calculate work done, Heat of process.



- 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 $C_V = 25.08 \text{ Jmol}^{-1}\text{K}^{-1}$ for CO_2 .
- (a) A certain mass of a gas initially at (1 L, 5 atm, 300 K) is expanded reversibly and isothermally to a final volume of 5L, calculate work done by the gas and heat supplied in this process to the gas.
(b) Now, if the gas is restored to initial position by compressing it using an external constant pressure of 5 atm. Find work done on the gas in this process and heat rejected by gas
(c) In the above two processes, what is the net heat gained by surroundings?
[Note : From above question see that surroundings has done extra work on the system but system has returned that work in the form of heat to surroundings and work is considered on organized form of energy while heat as an unorganised form hence in the above process, there must be net increment in randomness of universe which will be called **Entropy**, soon.]
- The molar heat capacity, C_V of helium gas is $\frac{3}{2} R$ and is independent of temperature. For hydrogen gas, C_V approaches $\frac{3}{2} R$ at very low temperatures, equal $\frac{5}{2} R$ at moderate temperatures and is higher than $\frac{5}{2} R$ at high temperatures. Give a reason for the temperature dependence of C_V in case of hydrogen, in not more than two or three sentences. [JEE 2003, 2/60]
- There is 1 mol liquid (molar volume 100 ml) in an adiabatic container initial, pressure being 1 bar Now the pressure is steeply increased to 100 bar, and the volume decreased by 1 ml under constant pressure of 100 bar. Calculate ΔH and ΔE . [Given 1 bar = 10^5 N/m^2] [JEE 2004, 2/60]
- One mole of monoatomic gas was taken through a cyclic process as shown in figure.

Calculate .

$$\sum_{ABCA} \frac{dq_{\text{rev}}}{T}$$



- One mole of ideal monoatomic gas was taken through 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)
- Comment on the following statements :
(a) An exothermic reaction is always thermodynamically spontaneous.
(b) Reaction with $\Delta G^\circ < 0$ always have an equilibrium constant greater than 1.





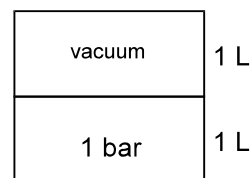
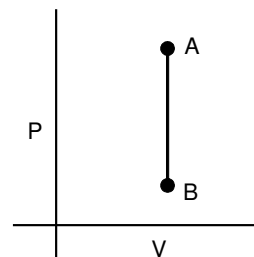
11. Following reaction occurs at 25°C :
 $2\text{NO}(\text{g}, 1 \times 10^{-5} \text{ atm}) + \text{Cl}_2(\text{g}, 1 \times 10^{-2} \text{ atm}) \rightleftharpoons 2\text{NOCl}(\text{g}, 1 \times 10^{-2} \text{ atm})$
 Calculate ΔG° [R = 8 J/mole K]
12. For the reaction : $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$
 (i) In a mixture of 5 mol NO_2 and 5 mol N_2O_4 and pressure of 20 bar. Calculate the value of ΔG for the reaction. Given $\Delta G_f^\circ(\text{NO}_2) = 50 \text{ kJ/mol}$, $\Delta G_f^\circ(\text{N}_2\text{O}_4) = 100 \text{ kJ/mol}$ and $T = 298 \text{ K}$.
 (ii) Predict the direction in which the reaction will shift, in order to attain equilibrium
 [Given at $T = 298 \text{ K}$, $2.303 RT = 5.7 \text{ kJ/mol}$.] [JEE 2004, 2/60]
13. The difference between heats of reaction at constant pressure and at constant volume for the reaction :
 $2\text{C}_6\text{H}_6(\ell) + 15\text{O}_2(\text{g}) \longrightarrow 12\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\ell)$ at 25°C in kJ is :
14. Classify the following processes as exothermic or endothermic :
 (A) Burning of a match stick (B) Melting of ice
 (C) Molten metal solidifies (D) Reaction between Na and H_2O
 (E) Rubbing alcohol evaporates.
15. Why is the enthalpy of sublimation equal to the sum of enthalpy of fusion and enthalpy of vaporisation ?
16. For a chemical reaction, ΔC_P is negative ($\Delta C_P < 0$).
 The heat required to increase temperature of reactants of this reaction by a certain amount = q_1 and heat required to increase temperature of products of the same reaction by same amount = q_2 , Relate q_1 and q_2
17. The specific heats of iodine vapour and solid are $0.031 \text{ cal g}^{-1} \text{ } ^\circ\text{C}^{-1}$ and $0.055 \text{ cal g}^{-1} \text{ } ^\circ\text{C}^{-1}$ respectively. If heat of sublimation of iodine is 24 cal/g at 200°C , what is its value at 250°C ?
18. Find out the heat evolved in combustion if 112 litres (at STP) of water gas (mixture of equal volume of $\text{H}_2(\text{g})$ and $\text{CO}(\text{g})$).
 $\text{H}_2(\text{g}) + 1/2 \text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{O}(\text{g}) \quad \Delta H = -241.8 \text{ kJ}$
 $\text{CO}(\text{g}) + 1/2 \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) \quad \Delta H = -283 \text{ kJ}$
19. Substance $\text{A}_2\text{B}(\text{g})$ can undergoes decomposition to form two set of products :
 $\text{A}_2\text{B}(\text{g}) \longrightarrow \text{A}_2(\text{g}) + \text{B}(\text{g}) ; \Delta H^\circ = 40 \text{ kJ/mole}$
 $\text{A}_2\text{B}(\text{g}) \longrightarrow \text{A}(\text{g}) + \text{AB}(\text{g}) ; \Delta H^\circ = 50 \text{ kJ/mole}$
 If the molar ratio of $\text{A}_2(\text{g})$ to $\text{A}(\text{g})$ is 5 : 3 in a set of product gases, calculate the energy involved in the decomposition of 1 mole of A_2B .
20. The $\Delta H_f^\circ(\text{KF}, \text{s})$ is -563 kJ mol^{-1} . The ionization enthalpy of $\text{K}(\text{g})$ is 419 kJ mol^{-1} . and the enthalpy of sublimation of potassium is 88 kJ mol^{-1} . The electron affinity of $\text{F}(\text{g})$ is 322 kJ mol^{-1} and F-F bond enthalpy is 158 kJ mol^{-1} . Calculate the lattice enthalpy of $\text{KF}(\text{s})$.
 The given data are as follows :
 (i) $\text{K}(\text{s}) + 1/2 \text{F}_2(\text{g}) \rightarrow \text{KF}(\text{s}) \quad \Delta H_f^\circ = -563 \text{ kJ mol}^{-1}$
 (ii) $\text{K}(\text{g}) \rightarrow \text{K}^+(\text{g}) + \text{e}^- \quad \Delta H_{\text{ioniz}}^\circ = 419 \text{ kJ mol}^{-1}$
 (iii) $\text{K}(\text{s}) \rightarrow \text{K}(\text{g}) \quad \Delta H_{\text{sub}}^\circ = 88 \text{ kJ mol}^{-1}$
 (iv) $\text{F}(\text{g}) + \text{e}^- \rightarrow \text{F}^-(\text{g}) \quad \Delta H_{\text{eg}}^\circ = -322 \text{ kJ mol}^{-1}$
 (v) $\text{F}_2(\text{g}) \rightarrow 2\text{F}(\text{g}) \quad \Delta H_{\text{diss}}^\circ = 158 \text{ kJ mol}^{-1}$
 (vi) $\text{K}^+(\text{g}) + \text{F}^-(\text{g}) \rightarrow \text{KF}(\text{s}) \quad \Delta H_{\text{L}}^\circ = ?$

ONLY ONE OPTION CORRECT TYPE

21. In thermodynamics, a process is called reversible when -
 (A) surroundings and system change into each other
 (B) there is no boundary between system and surroundings
 (C) the surroundings are always in equilibrium with the system
 (D) the system changes into the surroundings spontaneously

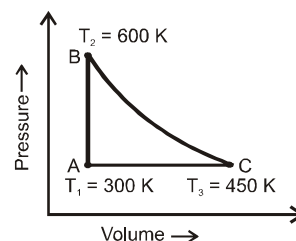
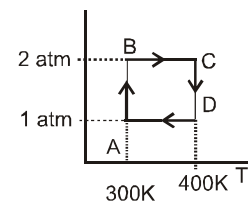


22. Two moles of an ideal gas expand spontaneously in vacuum. The work done is :
 (A) 2 Joule (B) 4 Joule (C) Zero (D) Infinite
23. Temperature of 1 mole of a gas is increased by 2°C at constant pressure, then work done is :
 (A) R (B) $2R$ (C) $R/2$ (D) Data insufficient
24. Mechanical work is specially important in system that contain
 (A) Solid-liquid (B) Liquid-Liquid (C) Solid-Solid (D) Gases
25. Which of the following statements is/are correct regarding the following process :
 (A) $dW = -P_{\text{ext.}}dv = 0$; Only if the system is undergoing only P-V work.
 (B) $dW = -P_{\text{ext.}}dv = 0$; Irrespective of any type of work done by the system.
 (C) $dU \neq dq_v$
 (D) $dW \neq 0$
26. A piece of zinc at a temperature of 20°C weighing 65.38 g is dropped into 180 g of boiling water ($T = 100^{\circ}\text{C}$). The specific heat of zinc is $0.4 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1}$ and that of water is $4.2 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1}$. What is the final common temperature reached by both the zinc and water ?
 (A) 97.3°C (B) 33.4°C (C) 80.1°C (D) 60.0°C
27. Which has maximum internal energy at 290 K ?
 (A) Neon gas (B) Nitrogen gas (C) Ozone gas (D) All have equal value
28. A sample of liquid in a thermally insulated container (a calorimeter) is stirred for 2 hr. by a mechanical linkage to a motor in the surrounding, for this process :
 (A) $w < 0$; $q = 0$; $\Delta U = 0$ (B) $w > 0$; $q > 0$; $\Delta U > 0$ (C) $w < 0$; $q > 0$; $\Delta U = 0$ (D) $w > 0$; $q = 0$; $\Delta U > 0$
29. A balloon of 1 L volume is filled with O_2 gas, kept in a spaceship at STP. Now this spaceship is sent in space & the balloon is released out of the spaceship. Then balloon expands upto bursting then calculate work done by balloon.
 (A) 0 (B) 1 (C) 2 (D) 3
30. 1 mole of an ideal diatomic gas undergoes a reversible polytropic process ($PV^2 = \text{constant}$). The gas expands from initial volume of 1 litre and temp 300 K to final volume 3 lit. Calculate change in internal energy (approx.)
 (A) -4.0 kJ (B) -4.2 kJ (C) -4.4 kJ (D) -4.6 kJ
31. A system containing real gas changes its state from state-1 to state-2.
 State-1 (2 atm, 3L, 300 K)
 State-2 (5 atm, 4L, 500 K)
 If change in internal energy = 30 L atm then calculate change in enthalpy.
 (A) 44 L atm (B) 35 L atm (C) 40 L atm (D) None of these
32. A container of volume 2L is separated into equal compartments. In one compartment one mole of an ideal monoatomic gas is filled at 1 bar pressure and the other compartment is completely evacuated. A pinhole is made in the separator so gas expands to occupy full 2L and heat is supplied to gas so that finally pressure of gas equals 1 bar. Then :
 (A) $\Delta U = \Delta H = 150 \text{ J}$ (B) $\Delta H = 250 \text{ J}$ (C) $\Delta U = 100 \text{ J}$ (D) $\Delta U = \Delta H = 0$
33. Which one of the following statement is false :
 (A) work is a state function
 (B) temperature is a state function
 (C) change in the state is completely defined when the initial and final states are specified
 (D) work appears at the boundary of the system.





34. Identify the state function among the following
 (A) q (B) $q - w$ (C) q/w (D) $q + w$
35. 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) $-100 R \ln 4$ (B) $+100 R \ln 4$
 (C) $+200 R \ln 4$ (D) $-200 R \ln 4$
36. Ice-Water mass ratio is maintained as 1 : 1 in a given system containing water in equilibrium with ice at constant pressure. If $C_P(\text{ice}) = C_P(\text{water}) = 4.18 \text{ J mol}^{-1} \text{ K}^{-1}$ molar heat capacity of such a system is
 (A) Zero (B) Infinity (C) $4.182 \text{ JK}^{-1} \text{ mol}^{-1}$ (D) $75.48 \text{ JK}^{-1} \text{ mol}^{-1}$
37. Two mole of an ideal gas is heated at constant pressure of one atmosphere from 27°C to 127°C . If $C_{V,m} = 20 + 10^{-2} T \text{ JK}^{-1} \text{ mol}^{-1}$, then q and ΔU for the process are respectively :
 (A) 6362.8 J, 4700 J (B) 3037.2 J, 4700 J (C) 7062.8, 5400 J (D) 3181.4 J, 2350 J
38. The increase in internal energy of 1 kg of water at 100°C when it is converted into steam at the same temperature and at 1 atm (100 k Pa) will be [The density of water and steam are 1000 kg/m^3 & 0.6 kg/m^3 respectively. The latent heat of vapourisation of water is $2.25 \times 10^6 \text{ J/kg}$.]
 (A) $2.08 \times 10^6 \text{ J}$ (B) $4 \times 10^7 \text{ J}$ (C) $3.27 \times 10^8 \text{ J}$ (D) $5 \times 10^9 \text{ J}$
39. Consider a classroom that is roughly $5 \text{ m} \times 10 \text{ m} \times 3 \text{ m}$. Initially $t = 27^\circ\text{C}$ and $P = 1 \text{ atm}$. There are 50 people in an insulated class losing energy to the room at the average rate of 150 watt per person. How long can they remain in class if the body temperature is 42°C and person feels uncomfortable above this temperature. Heat capacity of air = $(7/2) R$.
 (A) 4.34 minutes (B) 5.91 minutes (C) 6.86 minutes (D) 7.79 minutes
40. A heat engine carries one mole of an ideal mono-atomic gas around the cycle as shown in the figure, the amount of heat added in the process AB and heat removed in the process CA are :
 (A) $q_{AB} = 450 R$ and $q_{CA} = -450 R$
 (B) $q_{AB} = 450 R$ and $q_{CA} = -225 R$
 (C) $q_{AB} = 450 R$ and $q_{CA} = -375 R$
 (D) $q_{AB} = 375 R$ and $q_{CA} = -450 R$
41. There are two samples of same gas initially under similar initial state. Gases of both the samples are expanded. Ist sample using reversible isothermal process and IInd sample using reversible adiabatic process till final pressures of both the samples becomes half of initial pressure. Then :
 (A) Final volume of Ist sample < final volume of IInd sample
 (B) Final volume of IInd sample < final volume of Ist sample
 (C) Final volumes will be equal
 (D) Information is insufficient
42. In the above problem :
 (A) work done by gas in Ist sample > work done by gas in IInd sample
 (B) work done by gas in IInd sample > work done by gas in Ist sample
 (C) work done by gas in Ist sample = work done by gas in IInd sample
 (D) none of these
43. A new fluoro-carbon of molar mass 102 g mol^{-1} was placed in an electrically heated vessel. When the pressure was 650 torr, the liquid boiled at 77°C . After the boiling point had been reached, it was found that a current of 0.25 A from a 12.0 volt supply passed for 600 sec vaporises 1.8g of the sample. The molar enthalpy & internal energy of vaporisation of new fluoro-carbon will be :
 (A) $\Delta H = 102 \text{ kJ/mol}$, $\Delta E = 99.1 \text{ kJ/mol}$ (B) $\Delta H = 95 \text{ kJ/mol}$, $\Delta E = 100.3 \text{ kJ/mol}$
 (C) $\Delta H = 107 \text{ kJ/mol}$, $\Delta E = 105.1 \text{ kJ/mol}$ (D) $\Delta H = 92.7 \text{ kJ/mol}$, $\Delta E = 97.4 \text{ kJ/mol}$





44. Internal pressure of a perfect gas (ideal gas) is :
 (A) Zero (B) infinite
 (C) Calculated by $PV = nRT$ (D) Can not say directly
45. In a laboratory, liquid in a thermally insulated container is stirred for one hr, by a mechanical linkage to a in surrounding, for this process :
 (A) $W < 0$; $q = 0$ (B) $W < 0$; $q > 0$ (C) $W < 0$; $q > 0$ (D) $W > 0$; $q = 0$
46. If W_1 ; W_2 & W_3 are magnitude of work done of an ideal gas in isothermal, adiabatic & isobaric reversible expansion process from same initial stage to same final volume. Then correct order will be :
 (A) $W_3 > W_1 > W_2$ (B) $W_3 > W_2 > W_1$ (C) $W_2 > W_1 > W_3$ (D) $W_1 > W_2 > W_3$
47. A certain mass of gas is expanded from (1L, 10 atm) to (4L, 5 atm) against a constant external pressure of 1 atm. If initial temperature of gas is 300 K and the heat capacity of process is 50 J/°C. Then the enthalpy change during the process is (1L atm \simeq 100 J)
 (A) $\Delta H = 15$ kJ (B) $\Delta H = 15.7$ kJ (C) $\Delta H = 14.4$ kJ (D) $\Delta H = 14.7$ kJ
48. 2 moles of ideal gas is expanded isothermally & reversibly from 1 litre to 10 litre. Find the enthalpy change in kJ mol⁻¹. [JEE 2004, 3/84]
 (A) 0 (B) 11.7 (C) - 11.7 (D) 25
49. One mole of an ideal monoatomic gas at temperature T and volume 1L expands to 2L against a constant external pressure of one atm under adiabatic conditions, then final temperature of gas will be : [JEE 2005, 3/84]
 (A) $T + \frac{2}{3 \times 0.0821}$ (B) $T - \frac{2}{3 \times 0.0821}$ (C) $\frac{T}{2^{5/3-1}}$ (D) $\frac{T}{2^{5/3+1}}$
50. The ratio of P to V at any instant is constant and is equal to 1, for a monoatomic ideal gas under going a process. What is the molar heat capacity of the gas. [JEE 2006, 3/184]
 (A) $\frac{3R}{2}$ (B) $\frac{4R}{2}$ (C) $\frac{5R}{2}$ (D) 0
51. An ideal gas expands in volume from $1 \times 10^{-3} \text{ m}^3$ to $1 \times 10^{-2} \text{ m}^3$ at 300 K against a constant pressure of $1 \times 10^5 \text{ Nm}^{-2}$. The work is : [AIEEE 2004]
 (A) - 900 J (B) - 900 kJ (C) 270 kJ (D) + 900 kJ
52. Consider the reaction, $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g})$; carried out at constant temperature and pressure. If ΔH and ΔU are enthalpy change and internal energy change respectively, which of the following expressions is true ? [AIEEE 2005]
 (A) $\Delta H = 0$ (B) $\Delta H = \Delta U$ (C) $\Delta H < \Delta U$ (D) $\Delta H > \Delta U$
53. An ideal gas is allowed to expand both reversibly and irreversibly in an isolated system. If T_i is the initial temperature and T_f is the final temperature, which of the following statements is correct ? [AIEEE 2006]
 (A) $T_f > T_i$ for reversible process but $T_f = T_i$ for irreversible process (B) $(T_f)_{\text{rev}} = (T_f)_{\text{irrev}}$
 (C) $T_f = T_i$ for both reversible and irreversible processes (D) $(T_f)_{\text{irrev}} > (T_f)_{\text{rev}}$
54. When one mole of an ideal gas is compressed to half of its initial volume and simultaneously heated to twice its initial temperature, the change in entropy of gas (ΔS) is :
 (A) $C_{p,m} \ln 2$ (B) $C_{v,m} \ln 2$ (C) $R \ln 2$ (D) $(C_{v,m} - R) \ln 2$
55. Two mole of an ideal gas is expanded irreversibly and isothermally at 37°C until its volume is doubled and 3.41 kJ heat is absorbed from surrounding. ΔS_{total} (system + surrounding) is :
 (A) -0.52 J/K (B) 0.52 J/K (C) 22.52 J/K (D) 0
56. 1 mole of an ideal gas at 25°C is subjected to expand reversibly and adiabatically to ten times of its initial volume. Calculate the change in entropy during expansion (in J K⁻¹ mol⁻¹)
 (A) 19.15 (B) - 19.15 (C) 4.7 (D) zero
57. What is the change in entropy when 2.5 mole of water is heated from 27°C to 87°C ? Assume that the heat capacity is constant. ($C_{p,m}(\text{H}_2\text{O}) = 4.2 \text{ J/g-K} \ln(1.2) = 0.18$)
 (A) 16.6 J/K (B) 9 J/K (C) 34.02 J/K (D) 1.89 J/K



58. $\text{C}_2\text{H}_6(\text{g}) + 3.5 \text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{g})$
 $\Delta S_{\text{vap}}(\text{H}_2\text{O}, \ell) = x_1 \text{ cal K}^{-1}$ (boiling point = T_1)
 $\Delta H_f(\text{H}_2\text{O}, \ell) = x_2$
 $\Delta H_f(\text{CO}_2) = x_3$
 $\Delta H_f(\text{C}_2\text{H}_6) = x_4$
Hence, ΔH for the reaction is -
(A) $2x_3 + 3x_2 - x_4$ (B) $2x_3 + 3x_2 - x_4 + 3x_1T_1$
(C) $2x_3 + 3x_2 - x_4 - 3x_1T_1$ (D) $x_1T_1 + x_2 + x_3 - x_4$
59. Consider the ΔG°_f and ΔH°_f (kJ/mol) for the following oxides. Which oxide can be most easily decomposed to form the metal and oxygen gas?
(A) ZnO ($\Delta G^\circ = -318.4$, $\Delta H^\circ = -348.3$) (B) Cu_2O ($\Delta G^\circ = -146.0$, $\Delta H^\circ = -168.8$)
(C) HgO ($\Delta G^\circ = -58.5$, $\Delta H^\circ = -90.8$) (D) PbO ($\Delta G^\circ = -187.9$, $\Delta H^\circ = -217.3$)
60. If a refrigerator's door is opened, then we get
(A) Room heated (B) Room cooled
(C) More amount of heat is passed out (D) No effect on room
61. Which of the following statement (s) is/are correct?
Statement (i) : The entropy of isolated system with P-V work only, is always maximized at equilibrium.
Statement (ii) : It is possible for the entropy of close system to decrease substantially in an irreversible process.
Statement (iii) : Total entropy can be created but not destroyed.
Statement (iv) : ΔS_{system} is zero for reversible process in an isolated system.
(A) Statement i, ii, iii, (B) Statement ii, iv (C) Statement i, ii, iv (D) All of these
62. During winters, moisture condenses in the form of dew and can be seen on plant leaves and grass. The entropy of the system in such cases decreases as liquids possess lesser disorder as compared to gases. With reference to the second law, which statement is correct, for the above process?
(A) The randomness of the universe decreases
(B) The randomness of the surroundings decreases
(C) Increase in randomness of surroundings equals to the decrease in randomness of system
(D) The increase in randomness of the surroundings is greater as compared to the decrease in randomness of the system.
63. When $\text{CH}_3\text{OH}(\ell)$ is mixed in water :
(A) Degree of Randomness (entropy) decreases due to formation of Hydrogen bond.
(B) Entropy of surrounding decreases
(C) Mixing is spontaneous and reversible process
(D) All of the above are correct
64. Although graphite is thermodynamically most stable allotrope of Carbon but it has more entropy than diamond. Because :
(A) It has layer structure which slides on each other.
(B) In diamond Carbon is bonded with covalent bond.
(C) In graphite covalent bond only present within sheet and weak vanderwaal force present between sheets which allow sliding easily.
(D) Two types of bond lengths are present in graphite.
65. By how much does the entropy of universe change if 3 mole of an ideal gas is going from a pressure of 2 bar to a pressure of 1 bar without any change in temperature. If the surrounding is at 1 bar and 300 K. (Expansion is against the constant external pressure of surrounding).
(A) $+ 7.29 \text{ J-K}^{-1}$ (B) $+ 4.82 \text{ J-K}^{-1}$ (C) $- 5.29 \text{ J-K}^{-1}$ (D) $- 8.35 \text{ J-K}^{-1}$
66. For a perfectly crystalline solid $C_{p,m} = aT^3 + bT$, where a and b constant. If $C_{p,m}$ is 0.40 J/K mol at 10 K and 0.92 J/K mol at 20 K , then molar entropy at 20 K is :
(A) 0.92 J/K mol (B) 8.66 J/K mol (C) 0.813 J/K mol (D) None of these





67. For the hypothetical reaction $A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$
If $\Delta_r G^\circ$ and $\Delta_r S^\circ$ are 20 kJ/mol and $-20 \text{ JK}^{-1} \text{ mol}^{-1}$ respectively at 200 K.
 $\Delta_r C_p$ is $20 \text{ JK}^{-1} \text{ mol}^{-1}$ then $\Delta_r H^\circ$ at 400 K is :
(A) 20 kJ/mol (B) 7.98 kJ/mol (C) 28 kJ/mol (D) None of these
68. Given $\Delta_r S^\circ = -266$ and the listed $[S^\circ_m \text{ values}]$.
Calculate S° for $\text{Fe}_3\text{O}_4(\text{s})$:
 $4\text{Fe}_3\text{O}_4(\text{s}) [\dots\dots\dots] + \text{O}_2(\text{g}) [205] \longrightarrow 6\text{Fe}_2\text{O}_3(\text{s}) [87]$
(A) +111.1 (B) +122.4 (C) 145.75 (D) 248.25
69. The enthalpy change for a given reaction at 298 K is $-x \text{ J mol}^{-1}$ (x being positive). If the reaction occurs spontaneously at 298 K, the entropy change at that temperature
(A) can be negative but numerically larger than $x/298$
(B) can be negative but numerically smaller than $x/298$
(C) cannot be negative
(D) cannot be positive
70. Select the correct statement(s) :
 S_1 : AlCl_3 when dissolve in H_2O its entropy decreases therefore it is a non-spontaneous process.
 S_2 : When H_2 gas adsorbed at the surface of Pd, some amount of heat is released.
 S_3 : Entropy of D_2 gas is greater than H_2 gas.
(A) S_1, S_2 & S_3 (B) S_1 & S_3 (C) S_2 & S_3 (D) S_1 & S_2
71. One mole of an ideal diatomic gas ($C_v = 5 \text{ cal}$) was transformed from initial 25°C and 1 L to the state when temperature is 100°C and volume 10 L. The entropy change of the process can be expressed as ($R = 2 \text{ calories/mol/K}$)
(A) $3 \ln \frac{298}{373} + 2 \ln 10$ (B) $5 \ln \frac{373}{298} + 2 \ln 10$
(C) $7 \ln \frac{373}{298} + 2 \ln \frac{1}{10}$ (D) $5 \ln \frac{373}{298} + 2 \ln \frac{1}{10}$
72. Combustion of sucrose is used by aerobic organisms for providing energy for the life sustaining processes. If all the capturing of energy from the reaction is done through electrical process (non P-V work) then calculate maximum available energy which can be captured by combustion of 34.2 g of sucrose.
Given : $\Delta H_{\text{combustion}}(\text{sucrose}) = -6000 \text{ kJ mol}^{-1}$
 $\Delta S_{\text{combustion}} = 180 \text{ J/K-mol}$ and body temperature is 300 K
(A) 600 kJ (B) 594.6 kJ (C) 5.4 kJ (D) 605.4 kJ
73. Given the following data :
- | Substance | $\Delta H^\circ (\text{kJ/mol})$ | $S^\circ (\text{J/mol K})$ | $\Delta G^\circ (\text{kJ/mol})$ |
|-----------------------------|----------------------------------|----------------------------|----------------------------------|
| $\text{FeO}(\text{s})$ | -266.3 | 57.49 | -245.12 |
| $\text{C}(\text{Graphite})$ | 0 | 5.74 | 0 |
| $\text{Fe}(\text{s})$ | 0 | 27.28 | 0 |
| $\text{CO}(\text{g})$ | -110.5 | 197.6 | -137.15 |
- Determine at what temperature the following reaction is spontaneous ?
 $\text{FeO}(\text{s}) + \text{C}(\text{Graphite}) \longrightarrow \text{Fe}(\text{s}) + \text{CO}(\text{g})$
(A) 298 K (B) 668 K (C) 964 K
(D) ΔG° is +ve, hence the reaction will never be spontaneous
74. $\Delta H = 30 \text{ kJ mol}^{-1}$, $\Delta S = 75 \text{ J / k / mol}$. Find boiling temperature at 1 atm. [JEE 2004, 3/84]
(A) 400 K (B) 300 K (C) 150 K (D) 425 K
75. Spontaneous adsorption of a gas on a solid surface is exothermic process because [JEE 2004, 3/84]
(A) enthalpy of the system increases. (B) entropy increases.
(C) entropy decreases. (D) free energy change increases.



76. For a spontaneous reaction the ΔG , equilibrium constant (K) and E°_{cell} will be respectively [AIEEE 2005]
 (A) – ve, > 1, + ve (B) + ve, > 1, – ve (C) – ve, < 1, – ve (D) – ve, > 1, – ve
77. If ΔH is the change in enthalpy and ΔU the change in internal energy accompanying a gaseous reaction
 (A) ΔH is always greater than ΔU
 (B) $\Delta H < \Delta U$ only if the number of moles of the products is greater than the number of the reactants
 (C) ΔH is always less than ΔU
 (D) $\Delta H < \Delta U$ only if the number of moles of the products is less than the number of moles of the reactants
78. In the reaction $\text{CS}_2(\ell) + 3\text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + 2\text{SO}_2(\text{g})$, $\Delta H = -265 \text{ kcal}$
 The enthalpies of formation of CO_2 and SO_2 are both negative and are in the ratio 4 : 3. The enthalpy of formation of CS_2 is +26 kcal/mol. Calculate the enthalpy of formation of SO_2 .
 (A) – 90 kcal/mol (B) – 52 kcal/mol (C) – 78 kcal/mol (D) – 71.7 kcal/mol
79. Heat of hydrogenation of ethene is x_1 and that of benzene is x_2 . Hence, resonance energy is :
 (A) $x_1 - x_2$ (B) $x_1 + x_2$ (C) $3x_1 - x_2$ (D) $x_1 - 3x_2$
80. Calculate the resonance energy of gaseous benzene from the given data
 $\Delta H_{\text{C-H}} = 416$; $\Delta H_{\text{C-C}} = 331$; $\Delta H_{\text{C=C}} = 591$; $\Delta H_{\text{sub}}(\text{C, graphite}) = 718$
 $\Delta H_{\text{diss}}(\text{H}_2, \text{g}) = 436$ and $\Delta H_f(\text{benzene, g}) = 83$ (all unit in kJ mole^{-1})
 (A) 354 (B) 271 (C) 437 (D) 83
81. Born-Haber cycle is used to determine :
 (A) Lattice energy (B) Electron affinity (C) Crystal energy (D) All of these
82. Heat of neutralization of strong acid by a strong base is a constant value due to :
 (A) salt formed does not hydrolysis
 (B) only H^+ and OH^- ions react
 (C) The strong base and strong acid react completely
 (D) The strong base and strong acid react in aqueous solution
 Heat of neutralization of strong acid by a strong base is a constant value due to :
83. If $\text{CH}_3\text{COOH} + \text{OH}^- \longrightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O} + q_1$
 $\text{H}^+ + \text{OH}^- \longrightarrow \text{H}_2\text{O} + q_2$
 then the enthalpy change for the reaction $\text{CH}_3\text{COOH} \longrightarrow \text{CH}_3\text{COO}^- + \text{H}^+$ is equal to:
 (A) $(q_1 + q_2)$ (B) $(q_1 - q_2)$ (C) $(q_2 - q_1)$ (D) $-(q_1 + q_2)$
84. Enthalpy of neutralization of H_3PO_3 acid is -106.68 kJ/mol using NaOH . If enthalpy of neutralization of HCl by NaOH is -55.84 kJ/mol . Calculate $\Delta H_{\text{ionization}}$ of H_3PO_3 into its ions :
 (A) 50.84 kJ/mol (B) 5 kJ/mol (C) 2.5 kJ/mol (D) None of these
85. The difference between ΔH and ΔE (on a molar basis) for the combustion of n-octane (ℓ) at 25°C would be :
 (A) -13.6 kJ (B) -1.14 kJ (C) -11.15 kJ (D) $+11.15 \text{ kJ}$
86. The heat of formation of HCl at 348 K from the following data, will be
 $0.5 \text{ H}_2(\text{g}) + 0.5 \text{ Cl}_2(\text{g}) \longrightarrow \text{HCl}$ $\Delta H^\circ_{298} = -22060 \text{ cal}$
 The mean heat capacities over this temperature range are,
 $\text{H}_2(\text{g})$, $C_P = 6.82 \text{ cal mol}^{-1} \text{ K}^{-1}$; $\text{Cl}_2(\text{g})$, $C_P = 7.71 \text{ cal mol}^{-1} \text{ K}^{-1}$; $\text{HCl}(\text{g})$, $C_P = 6.81 \text{ cal mol}^{-1} \text{ K}^{-1}$
 (A) -20095 cal (B) -32758 cal (C) -37725 cal (D) -22083 cal
87. From the following data of ΔH , of the following reactions,
 $\text{C}(\text{s}) + \frac{1}{2} \text{O}_2(\text{g}) \longrightarrow \text{CO}(\text{g})$ $\Delta H = -110 \text{ kJ}$
 $\text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) \longrightarrow \text{CO}(\text{g}) + \text{H}_2(\text{g})$ $\Delta H = 132 \text{ kJ}$
 What is the mole composition of the mixture of steam and oxygen on being passed over coke at 1273 K , to maintain constant temperature :
 (A) $0.5 : 1$ (B) $1 : 0.6$ (C) $0.8 : 1$ (D) $1 : 1$



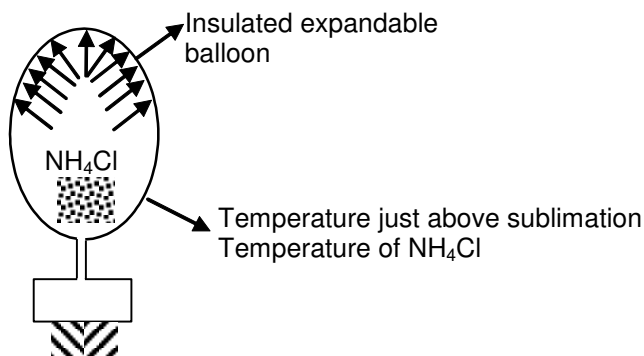
88. When 12.0 g of carbon reacted with limited quantity of oxygen, 57.5 kcal of heat was produced. Calculate the number of moles of CO produced ($\Delta_f H(\text{CO}_2) = -94.05 \text{ kcal}$, $\Delta_f H(\text{CO}) = -21.41 \text{ kcal}$).
(A) 0.5 mol (B) 0.46 mol (C) 0.64 mol (D) 0.74 mol
89. The standard enthalpy of formation of FeO & Fe_2O_3 is $-65 \text{ kcal mol}^{-1}$ and $-197 \text{ kcal mol}^{-1}$ respectively. A mixture of two oxides contains FeO & Fe_2O_3 in the mole ratio 2 : 1. If by oxidation, it is changed into a 1 : 2 mole ratio mixture, how much of thermal energy will be released per mole of the initial mixture ?
(A) 13.4 kcal/mole (B) 14.6 kcal/mole (C) 15.7 kcal/mole (D) 16.8 kcal/mole
90. Reactions involving gold have been of particular interest to alchemists. Consider the following reactions,

$$\text{Au}(\text{OH})_3 + 4 \text{HCl} \longrightarrow \text{HAuCl}_4 + 3 \text{H}_2\text{O}, \quad \Delta H = -28 \text{ kcal}$$

$$\text{Au}(\text{OH})_3 + 4 \text{HBr} \longrightarrow \text{HAuBr}_4 + 3 \text{H}_2\text{O}, \quad \Delta H = -36.8 \text{ kcal}$$
 In an experiment, there was an absorption of 0.44 kcal when one mole of HAuBr_4 was mixed with 4 moles of HCl. Then, the fraction of HAuBr_4 converted into HAuCl_4 (percentage conversion)
(A) 5% (B) 6% (C) 7% (D) 8%
91. The average Xe-F bond energy is 34 kcal/mol, first I.E. of Xe is 279 kcal/mol, electron affinity of F is 85 kcal/mol & bond dissociation energy of F_2 is 38 kcal/mol. Then, the enthalpy change for the reaction

$$\text{XeF}_4 \longrightarrow \text{Xe}^+ + \text{F}^- + \text{F}_2 + \text{F}$$
 will be
(A) 367 kcal/mole (B) 425 kcal/mole (C) 292 kcal/mole (D) 392 kcal/mole
92. Equal volumes of molar hydrochloric acid and sulphuric acid are neutralized by dil. NaOH solution and x kcal and y kcal of heat are liberated respectively. Which of the following is true ?
(A) $x = y$ (B) $x = \frac{1}{2} y$ (C) $x = 2y$ (D) None of these
93. A solution is 500 ml of 2 M KOH is added to 500 ml of 2 M HCl and the mixture is well shaken. The rise in temperature T_1 is noted. The experiment is then repeated using 250 ml of each solution and rise in temperature T_2 is again noted. Assume all heat is taken by the solution
(A) $T_1 = T_2$ (B) T_1 is 2 times as large as T_2
(C) T_2 is twice of T_1 (D) T_1 is 4 times as large as T_2
94. 50.0 mL of 0.10 M HCl is mixed with 50.0 mL of 0.10 M NaOH. The solution's temperature rises by 3.0°C . Calculate the enthalpy of neutralization per mole of HCl. (Assuming density of sol. = 1 g/ml & specific heat of water is $4.2 \text{ J/g}\cdot\text{K}$) is
(A) $-2.5 \times 10^2 \text{ kJ/mole}$ (B) $-1.3 \times 10^2 \text{ kJ/mole}$ (C) $-8.4 \times 10^1 \text{ kJ/mole}$ (D) $-6.3 \times 10^1 \text{ kJ/mole}$
95. A piece of NH_4Cl is kept inside a balloon filled with some air, having thermally insulated walls. The temperature is kept just above sublimation temperature of NH_4Cl .

$$\text{NH}_4\text{Cl}(\text{s}) \xrightarrow{\text{sublime}} \text{NH}_3(\text{g}) + \text{HCl}(\text{g}).$$
 Which of the following is correct regarding this :
(A) $q_{\text{system}} = \text{positive}$
(B) $\Delta U = \text{negative}$
(C) $w = \text{zero}$
(D) $\Delta U = \text{positive}$



96. Equal volume of HCOOH and NaOH are mixed. If x is the heat of formation of water from strong acid & strong base, then heat evolved of neutralization is :
(A) more than x (B) equal to x (C) twice of x (D) less than x
97. Which of the following equation gives the values of heat of formation ($\Delta_f H^\circ$) [JEE 2003, 3/84]
(A) $\text{C}(\text{diamond}) + \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g})$ (B) $\frac{1}{2} \text{H}_2(\text{g}) + \frac{1}{2} \text{F}_2(\text{g}) \longrightarrow \text{HF}(\text{g})$
(C) $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g})$ (D) $\text{H}_2(\text{g}) + \text{F}_2(\text{g}) \longrightarrow 2\text{HF}(\text{g})$



98. The enthalpies of combustion of carbon and carbon monoxide are -393.5 and -283 kJ mol^{-1} respectively. The enthalpy of formation of carbon monoxide per mole is [AIEEE 2004]
(A) 110.5 kJ (B) 676.5 kJ (C) -676.5 kJ (D) -110.5 kJ
99. If the bond dissociation energies of XY , X_2 and Y_2 (all diatomic molecules) are in the ratio of $1 : 1 : 0.5$ and ΔH_f for the formation of XY is -200 kJ mol^{-1} . The bond dissociation energy of X_2 will be [AIEEE 2005]
(A) 100 kJ mol^{-1} (B) 200 kJ mol^{-1} (C) 300 kJ mol^{-1} (D) 800 kJ mol^{-1}
100. The enthalpy changes for the following processes are listed below: [AIEEE 2006]
 $\text{Cl}_2(\text{g}) \longrightarrow 2\text{Cl}(\text{g}); 242.3 \text{ kJ mol}^{-1}$; $\text{I}_2(\text{g}) \longrightarrow 2\text{I}(\text{g}); 151.0 \text{ kJ mol}^{-1}$
 $\text{ICl}(\text{g}) \longrightarrow \text{I}(\text{g}) + \text{Cl}(\text{g}); 211.3 \text{ kJ mol}^{-1}$; $\text{I}_2(\text{s}) \longrightarrow \text{I}_2(\text{g}); 62.76 \text{ kJ mol}^{-1}$
 Given that the standard state for iodine and chlorine are $\text{I}_2(\text{s})$ and $\text{Cl}_2(\text{g})$, the standard enthalpy of formation for $\text{ICl}(\text{g})$ is
 (A) $-16.8 \text{ kJ mol}^{-1}$ (B) $+16.8 \text{ kJ mol}^{-1}$ (C) $+244.8 \text{ kJ mol}^{-1}$ (D) $-14.6 \text{ kJ mol}^{-1}$

MATCH THE COLUMN

101. Match column-I to column-II standard entropy in J/K-molar at 298 K

	Column-I		Column-II
(A)	C (s, diamond)	(p)	5.7
(B)	C (s, graphite)	(q)	2.37
(C)	$\text{H}_2(\text{g})$	(r)	117.6
(D)	H (g)	(s)	130.6

SINGLE AND DOUBLE VALUE INTEGER TYPE

102. A gas expands against a variable pressure given by $P = \frac{20}{V}$ bar-lit. During expansion from volume of 1 litre to 10 litre, the gas undergoes a change in internal energy of 400 J. Heat absorbed by the gas during expansion (in kJ) :
103. A sample of 4 mole He is originally confined in 20 L at 270 K and then undergoes adiabatic expansion against a constant pressure of 125 mbar until the volume has increased by a factor of 3. Calculate ΔT during process:
104. The molar enthalpy of vaporization of benzene at its boiling point (353K) is 29.7 KJ/mole. For how long (minute) would a 11.4 Volt source need to supply a 0.5 A current in order to vaporise 7.8 g of the sample at its boiling point ? (Round off to nearest integer)
105. At 5×10^5 bar pressure, density of diamond and graphite are 3 g/cc and 2 g/cc respectively, at certain temperature T. Find the value of $\left(\frac{\Delta U - \Delta H}{20}\right)$ for the conversion of 1 mole of graphite to 1 mole of diamond (in KJ) at temperature T. (1L.atm = 100 J)
106. 1 mole of an ideal gas A ($C_{v,m} = 3R$) and 2 mole of an ideal gas B are $\left(C_{v,m} = \frac{3}{2}R\right)$ taken in a container and expanded reversibly and adiabatically from 1 litre to 4 litre starting from initial temperature of 320 K. Find the magnitude value of $\Delta U/10R$ for the process is :
107. 10 litres of a monoatomic ideal gas at 0°C and 10 atm pressure is suddenly released to 1 atm pressure and the gas expands adiabatically against this constant pressure. The final volume (L) of the gas.
108. A system is provided 50 joule of heat and the change in internal energy during the process is 60 J. Magnitude of work done on the system is :
109. A system works in a cyclic process. It absorbs 20 calories of heat and rejects 60 J of heat during the process. The magnitude of work done (J) is [1 calorie = 4.2 J] :



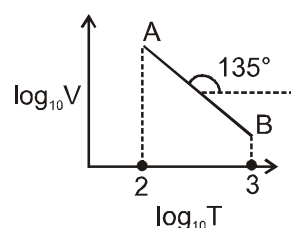
110. Two moles of an ideal gas is expanded isothermally and irreversibly at 27°C from volume V_1 to $7.5 V_1$ and 4.17 kJ heat is absorbed from surroundings. Determine ΔS_{sys} ? (Approximate integer in Cal)
111. The vapour pressure of liquid Hg at 433 K is 5 mm Hg. Calculate the free energy change accompanying the expansion of one mole of Hg vapour in equilibrium with liquid at 433 K to a pressure of 750 mm Hg at the same temperature assuming the vapour behaves like an ideal monoatomic gas in kJ mole^{-1} . (Approximate integer and $e^5 = 150$)
112. Two mole of an ideal gas originally at a volume of 8 L. at 1000 K, is allowed to expand adiabatically until final volume is 24 L. For the gas $C_V = 1.5 R$. Calculate values of ΔS for the process when :
 (i) The expansion takes place reversibly.
 (ii) The change in volume involves a free expansion.
 Sum of ΔS of these two case is _____. (Used : $e^{1.09} = 3$ and $1.09 \times 8.314 = 9$)
113. One litre sample of a mixture of CH_4 and O_2 measured at 32°C and 760 torr, was allowed to react at constant pressure in a calorimeter. The complete combustion of CH_4 to CO_2 and water caused a temperature rise in calorimeter of 1 K. Calculate mole % of CH_4 in original mixture.
 [Given : Heat of combustion of CH_4 is -210.8 Kcal/mol . Total heat capacity of the calorimeter = 2108 cal/K]
114. 150 mL of 0.5 N HCl solution at 25°C was mixed with 150 mL of 0.5 N NaOH solution at same temperature. Calculate heat of neutralization of HCl with NaOH, if final temperature was recorded to be 29°C. ($\rho_{\text{H}_2\text{O}} = 1 \text{ g/mL}$) (Give your answer magnitude wise).
115. Calculate the resonance energy of isoprene (C_5H_8) from the data given.
 Given that $\Delta H_{\text{C}=\text{C}} = 615 \text{ kJmole}^{-1}$; $\Delta H_{\text{C}-\text{C}} = 348 \text{ kJ mole}^{-1}$; $\Delta H_{\text{C}-\text{H}} = 413 \text{ kJmole}^{-1}$; $\Delta H_{\text{H}-\text{H}} = 435 \text{ kJmole}^{-1}$
 The standard heat of sublimation of graphite is 718 kJmole^{-1} and heat of formation of $\text{C}_5\text{H}_8(\text{g})$ is 79 kJmole^{-1}
 (Give your answer in kcal mole^{-1} ; approximate integer).
116. Calculate the amount of heat evolved during the complete combustion of 100 ml of liquid benzene from the following data. Predict your answer as $\frac{\Delta H}{100}$ (in KJ/mole).
 (i) 18 g of graphite on complete combustion evolve 585 KJ heat
 (ii) 15540 KJ heat is required to dissociate all the molecules of 1 litre water into H_2 and O_2 .
 (iii) The heat of formation of liquid benzene is 48 kJ/mol
 (iv) Density of C_6H_6 (ℓ) = 0.87 g/mL
117. The enthalpy of neutralisation of a weak acid in 1 M solution with a strong base is $-56.1 \text{ kJ mol}^{-1}$. If the enthalpy of ionization of the acid is 1.5 kJ mol^{-1} and enthalpy of neutralization of the strong acid with a strong base is $-57.3 \text{ kJ equiv}^{-1}$, what is the % ionization of the weak acid in molar solution (assume the acid to be monobasic)?
118. For reduction of ferric oxide by hydrogen, $\text{Fe}_2\text{O}_3(\text{s}) + 3 \text{H}_2(\text{g}) \longrightarrow 2 \text{Fe}(\text{s}) + 3 \text{H}_2\text{O}(\ell)$;
 $\Delta H_{300}^\circ = -26.72 \text{ kJ}$. The reaction was found to be too exothermic. To be convenient, it is desirable that ΔH° should be at the most -26 kJ . At what temperature difference it is possible ?
 $C_P[\text{Fe}_2\text{O}_3] = 105$, $C_P[\text{Fe}(\text{s})] = 25$, $C_P[\text{H}_2\text{O}(\ell)] = 75$, $C_P[\text{H}_2(\text{g})] = 30$ (all are in J/mol)
119. Calculate the enthalpy change of 1 mole of NaBr
 $\text{Na}(\text{s}) + \frac{1}{2} \text{Br}_2(\text{g}) \longrightarrow \text{NaBr}(\text{s})$ in kcal
 Given : $\Delta H_{\text{sub}}(\text{Na}) = 137 \text{ kJ mole}^{-1}$; $\Delta H_{\text{bond dissociation}}(\text{Br}_2(\text{g})) = 144 \text{ kJ mole}^{-1}$
 $\Delta H_{1\text{st ionisation}}(\text{Na}(\text{g})) = 496 \text{ kJ mole}^{-1}$; $\Delta H_{1\text{st electron affinity}}(\text{Br}(\text{g})) = -325 \text{ kJ mole}^{-1}$
 $\Delta H_{\text{Lattice energy}}(\text{NaBr}) = +742 \text{ kJ mole}^{-1}$

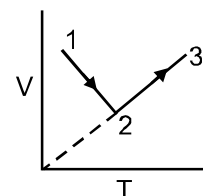


120. In a constant volume calorimeter, 3.5 g of a gas with molecular weight 28 was burnt in excess oxygen at 298.0 K. The temperature of the calorimeter was found to increase from 298.0 K to 298.45 K due to the combustion process. Given that the heat capacity of the calorimeter is 2.5 kJ K^{-1} , the numerical value for the enthalpy of combustion of the gas in kJ mol^{-1} is : **[JEE 2009, 4/160]**
121. One mole of an ideal gas is expanded isothermally at 300 K until its volume is tripled. Find the values of ΔS_{total} under the condition.
Expansion is carried out irreversibly where 900 J of heat is less absorbed than expansion is carried out reversibly. (Approximate integer value, Used $e^{1.09} = 3$ & $8.314 \times 1.09 = 9$)

ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

122. Which of the following are incorrect :
(A) Work done by the surrounding in case of infinite stage expansion is more than single stage expansion
(B) Irreversible work is always greater than reversible work. (with sign)
(C) On an ideal gas in case of single stage expansion and compression system as well as surrounding are restored back to their original states
(D) If a gas in thermodynamic equilibrium is taken from state A to state B, by four successive single stage expansions. Then we can plot 4 points on the P-V indicator diagram.
123. Identify the following processes in which non P-V work is involved :
(A) Transfer of electron through a resistor.
(B) Stirring of liquid through mechanical agitator.
(C) Falling of an apple on Newton's head.
(D) Attraction of iron filings towards a magnet.
124. 0.5 mole each of two ideal gases A and B $\left(C_{v,m} = \frac{5}{2}R\right)$ ($C_{v,m} = 3R$) are taken in a container and expanded reversibly and adiabatically, during this process temperature of gaseous mixture decreased from 350 K and 250 K. Then for the process :
(A) $\Delta U = -100 R$ (B) $\Delta U = -275 R$ (C) $\Delta H = -375 R$ (D) $\Delta H = -300 R$
125. 4 KJ of heat is absorbed when 1 mol of ice melts at 0°C and at constant pressure 1 atm. If molar volume of ice and water are 19 ml and 18 ml respectively, then [Take 1 atm = 10^5 Pa]
(A) $\Delta H > \Delta U$ (B) $\Delta U > \Delta H$ (C) $\Delta U = 4.1 \text{ KJ}$ (D) $\Delta U = 4.0001 \text{ KJ}$
126. 5 moles of a liquid L are converted into its vapour at its boiling point (273°C) and at a pressure of 1 atm. If the value of latent heat of vapourisation of liquid L is 273 L atm/mole, then which of the following statements is/are correct: Assume volume of liquid to be negligible and vapour of the liquid to behave ideally.
(A) Work done by the system in the above process is 224 L atm.
(B) The enthalpy change (ΔH) for the above process is 1365 L atm (with respect to magnitude only)
(C) The internal energy of the system increases in the above process.
(D) The value of ΔU for the above process is 1589 L atm.
127. Three moles of an ideal diatomic gas undergoes a change in state from A to B reversibly as follows :
Which of the following statements is/are correct regarding the above process :
(A) Work done on the gas is 2700 R
(B) In the above process, pressure varies inversely with square of volume.
(C) Heat supplied to the gas is 4050 R
(D) Data insufficient for the calculation of work and heat supplied.





128. Following graph is constructed for the fixed amount of the gas.
 (A) From 1 - 2 pressure will increase
 (B) From 2 - 3 pressure remains constant
 (C) Gas pressure at (3) is greater at state (1)
 (D) From 1 - 2 pressure will decrease
129. Which of the following option show more entropy of first compound than second :
 (A) (i) 1-hexene at 273 K and 1 atm (ii) Cyclohexane at 273 K and 1 atm
 (B) (i) at NTP (ii) at NTP
 (C) (i) SO_2 (g) at 300 K and 0.1 atm (ii) SO_2 (g) at 300°C and 0.1 atm
 (D) (i) $\text{C}_2\text{H}_5\text{OH}$ (l) at 46°C and 1 atm (ii) CH_3OH (l) at 46°C and 1 atm
130. Choose the correct statement (s) :
 (A) Temperature, enthalpy and entropy are state functions
 (B) For reversible and irreversible both isothermal expansion of an ideal gas, change in internal energy and enthalpy is zero
 (C) for a reaction in which $\Delta n_{\text{gas}} = 0$, entropy change is not always zero
 (D) The entropy change associated with reversible isothermal expansion of an ideal gas is equal to $2.303 R \log_{10} \frac{P_1}{P_2}$
131. One mole of an ideal diatomic gas ($C_v = 5 \text{ cal}$) was transformed from initial 25°C and 1 L to the state when temperature is 100°C and volume 10 L. Then for this process ($R = 2 \text{ calories/mol/K}$) (take calories as unit of energy and kelvin for temp)
 (A) $\Delta H = 525$
 (B) $\Delta S = 5 \ln \frac{373}{298} + 2 \ln 10$
 (C) $\Delta E = 525$
 (D) ΔG of the process can not be calculated using given information.
132. Select the correct statements :
 (A) All combustion reactions are exothermic (B) Heat of combustion are always exothermic
 (C) $\text{N}_2 + \text{O}_2 \longrightarrow 2\text{NO}$; $\Delta H = +ve$ (D) $\text{F}_2 + \frac{1}{2} \text{O}_2 \longrightarrow \text{F}_2\text{O}$; $\Delta H = +ve$
133. Consider the reactions
 (i) $\text{S (rhombic)} + 3/2 \text{O}_2(\text{g}) \longrightarrow \text{SO}_3(\text{g})$, ΔH_1 (ii) $\text{S (monoclinic)} + 3/2 \text{O}_2(\text{g}) \longrightarrow \text{SO}_3(\text{g})$, ΔH_2
 (iii) $\text{S (rhombic)} + \text{O}_3(\text{g}) \longrightarrow \text{SO}_3(\text{g})$, ΔH_3 (iv) $\text{S (monoclinic)} + \text{O}_3(\text{g}) \longrightarrow \text{SO}_3(\text{g})$, ΔH_4
 (A) $\Delta H_1 < \Delta H_2 < \Delta H_4$ (magnitude only) (B) $\Delta H_1 < \Delta H_3 < \Delta H_4$ (magnitude only)
 (C) $\Delta H_1 < \Delta H_2 = \Delta H_3 < \Delta H_4$ (magnitude only) (D) $\Delta H_1 + \Delta H_4 = \Delta H_2 + \Delta H_3$
134. In an insulated rigid chamber some CO_2 , CO and carbon is placed and O_2 is passed in the chamber. The mixture is ignited and combustion takes place. Which of the following is/are correct :
 (A) ΔT for system > 0 (B) ΔT for system < 0 (C) $q_{\text{system}} = \text{zero}$ (D) $\Delta U = \text{zero}$
135. Which of the following is/are correct. (Consider all gases are ideal & reaction occurs at const. temperature & pressure).
 (A) $\text{CaCO}_3(\text{s}) \longrightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ (–ve P-V work)
 (B) $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \longrightarrow 2\text{HCl}(\text{g})$ (–ve P-V work)
 (C) $\text{Zn}(\text{s}) + \text{Cu}^{2+}(\text{aq}) \longrightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu}(\text{s})$ (Non zero non P-V work)
 (D) $\text{NaCl}(\text{s}) \longrightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$ (Non zero non P-V work)
136. If $\Delta H_f^\circ(\text{C}_2\text{H}_6)(\text{g}) = -85 \text{ kJ mol}^{-1}$, $\Delta H_f^\circ(\text{C}_3\text{H}_8)(\text{g}) = -104 \text{ kJ mol}^{-1}$, ΔH° for $\text{C}(\text{s}) \rightarrow \text{C}(\text{g})$ is 718 kJ mol^{-1} and heat of formation of H-atom is 218 kJ mol^{-1} then :
 (A) $\Delta H_{\text{C-C}} = 345 \text{ kJ}$ (B) $\Delta H_{\text{C-H}} = 414 \text{ kJ}$ (C) $\Delta H_{\text{H-H}} = 436 \text{ kJ}$ (D) $\Delta H_{\text{H-H}} = 218 \text{ kJ}$





COMPREHENSION

Comprehension # 1

A gaseous sample is generally allowed to do only expansion/compression type of work against its surroundings. The work done in case of an irreversible expansion (in the intermediate stages of expansion/compression the states of gases are not defined). The work done can be calculated using

$$dw = -P_{\text{ext}} dV$$

while in case of reversible process the work done can be calculated using

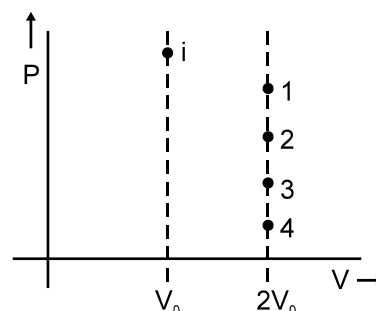
$dw = -PdV$ where P is pressure of gas at some intermediate stages. Like for an

isothermal reversible process. Since $P = \frac{nRT}{V}$, so

$$w = \int dw = - \int_{V_i}^{V_f} \frac{nRT}{V} \cdot dV = -nRT \ln \left(\frac{V_f}{V_i} \right)$$

Since $dw = -PdV$ so magnitude of work done can also be calculated by calculating the area under the PV curve of the reversible process in PV diagram.

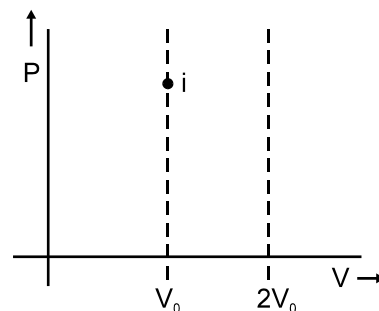
137. An ideal gaseous sample at initial state i (P_0, V_0, T_0) is allowed to expand to volume $2V_0$ using two different process; in the first process the equation of process is $PV^2 = K_1$ and in second process the equation of the process is $PV = K_2$. Then,
 (A) work done in first process will be greater than work in second process (magnitude wise)
 (B) The order of values of work done can not be compared unless we know the value of K_1 and K_2 .
 (C) value of work done (magnitude) in second process is greater in above expansion irrespective of the value of K_1 and K_2 .
 (D) Ist process is not possible
138. There are two samples of same gas initially under similar initial state. Gases of both the samples are expanded. Ist sample using reversible isothermal process and IInd sample using reversible adiabatic process till final pressures of both the samples becomes half of initial pressure, then
 (A) Final volume of Ist sample < final volume of IInd sample
 (B) Final volume of IInd sample < final volume of Ist sample
 (C) final volumes will be equal
 (D) Information is insufficient
139. In the above problem
 (A) work done by gas in Ist sample > work done by gas in IInd sample
 (B) work done by gas in IInd sample > work done by gas in Ist sample
 (C) work done by gas in Ist sample = work done by gas in IInd sample
 (D) none of these
140. If four identical samples of an ideal gas initially at similar state (P_0, V_0, T_0) are allowed to expand to double their volumes by four different process.
 I : by isothermal irreversible process
 II : by reversible process having equation $P^2 V = \text{constant}$
 III : by reversible adiabatic process
 IV : by irreversible adiabatic expansion against constant external pressure.
 Then, in the graph shown the final state is represented by four different points then, the correct match can be



- (A) 1 - I, 2 - II, 3 - III, 4 - IV
 (B) 1 - II, 2 - I, 3 - IV, 4 - III
 (C) 2 - III, 3 - II, 4 - I, 1 - IV
 (D) 3 - II, 1 - I, 3 - IV, 4 - III



141. Two samples (initially under same states) of an ideal gas are first allowed to expand to double their volume using irreversible isothermal expansion against constant external pressure, then samples are returned back to their original volume first by reversible adiabatic process and second by reversible process having equation $PV^2 = \text{constant}$ then
- (A) final temperature of both samples will be equal
 (B) final temperature of first sample will be greater than of second sample
 (C) final temperature of second sample will be greater than of first sample
 (D) none of these.



Comprehension # 2

Phase transitions are ubiquitous in nature. We are all familiar with the different phase of water (vapour, liquid and ice) and with the change from one to another, the change of phase are called phase transitions. There are six ways a substance can change between these three phase ; melting, freezing, evaporating, condensing ; sublimation and decomposition.

At 1 atm pressure vaporisation of 1 mole of water from liquid (75°C) to vapour (120°C).

$$C_V(\text{H}_2\text{O}, \ell) = 75 \text{ J mole}^{-1} \text{ K}^{-1} ; C_P(\text{H}_2\text{O}, \text{g}) = 33.3 \text{ J mole}^{-1} \text{ K}^{-1}$$

$$\Delta H_{\text{vap}} \text{ at } 100^\circ\text{C} = 40.7 \text{ kJ/mole.}$$

Calculate change in internal energy when

142. Liquid water is heated from 75°C to 100°C ?
 (A) 1875 J (B) 13125 J (C) – 1875 J (D) – 13125 J
143. Liquid water at 100°C is converted to vapour at 100°C ?
 (A) 40700 J (B) 37598.878 J (C) 43801.1 J (D) 3101.2 J
144. Water vapour at heated from 100°C to 120°C ?
 (A) 666 J (B) 2998 J (C) 499.72 J (D) 166.28 J

Comprehension # 3

A gaseous mixture of propane, acetylene and CO_2 is burnt in excess of air. Total 4800 kJ heat is evolved. The total volume of CO_2 (g) after combustion is 224 liters at NTP.

The total evolved heat is used to perform two separate process :

- (i) Vapourising 87.5% of water (liquid) obtained in the process of burning the original mixture.
 (ii) Forming 3808 liters ethylene measured at STP from its elements.

$$\begin{aligned} \Delta H_{\text{H-H}} &= 435 \text{ kJ/mol} & \Delta H_{\text{C-H}} &= 416 \text{ kJ/mol} & \Delta H_{\text{C-C}} &= 347 \text{ kJ/mol} \\ \Delta H_{\text{C=C}} &= 615 \text{ kJ/mol}, & \Delta H_{\text{C}\equiv\text{C}} &= 812 \text{ kJ/mol} & \Delta H_{\text{sublimation of (C,s)}} &= 718 \text{ kJ/mol} \\ \Delta H_f^\circ(\text{CO}_2, \text{g}) &= -394 \text{ kJ/mol} & \Delta H_f^\circ(\text{H}_2\text{O}, \ell) &= -286 \text{ kJ/mol.} & \Delta H_f^\circ(\text{H}_2\text{O}, \text{g}) &= -246 \text{ kJ/mol.} \end{aligned}$$

145. $\Delta H_{\text{rxn}}^\circ$ for $\text{C}_2\text{H}_2(\text{g}) + \text{H}_2(\text{g}) \longrightarrow \text{C}_2\text{H}_4(\text{g})$
 (A) –220 kJ/mol (B) –180 kJ/mol (C) –250 kJ/mol (D) –200 kJ/mol
146. Sum of enthalpies of combustion of $\text{C}_3\text{H}_8(\text{g})$ and $\text{C}_2\text{H}_2(\text{g})$ is :
 (A) –2198 kJ/mol (B) –3499 kJ/mol (C) –2798 kJ/mol (D) –3099 kJ/mol
147. Total moles of hydrocarbon gases taken in the initial mixture
 (A) 3 (B) 4 (C) 2 (D) 5





PART - IV : PRACTICE TEST-2 (IIT-JEE (ADVANCED Pattern))

Max. Time : 1 Hr.

Max. Marks : 81

Important Instructions

A. General :

- The test is of 1 hour duration.
- The Test Booklet consists of 27 questions. The maximum marks are 81.

B. Question Paper Format

- Each part consists of five sections.
- Section-1 contains 8 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE is correct.
- Section-2 contains 6 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE OR MORE THAN ONE are correct.
- Section 3 contains 6 questions. The answer to each of the questions is a single-digit integer, ranging from 0 to 9 (both inclusive).
- Section 4 contains 2 paragraphs each describing theory, experiment and data etc. 6 questions relate to paragraph. Each question pertaining to a particular passage should have only one correct answer among the four given choices (A), (B), (C) and (D).
- Section 5 contains 1 multiple choice questions. Question has two lists (list-1 : P, Q, R and S; List-2 : 1, 2, 3 and 4). The options for the correct match are provided as (A), (B), (C) and (D) out of which ONLY ONE is correct.

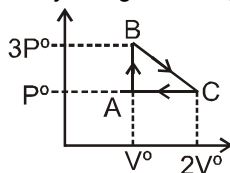
C. Marking Scheme

- For each question in Section 1, 4 and 5 you will be awarded 3 marks if you darken the bubble corresponding to the correct answer and zero mark if no bubble is darkened. In all other cases, minus one (– 1) mark will be awarded.
- For each question in Section 2, you will be awarded 3 marks. If you darken all the bubble(s) corresponding to the correct answer(s) and zero mark. If no bubbles are darkened. No negative marks will be answered for incorrect answer in this section.
- For each question in Section 3, you will be awarded 3 marks if you darken only the bubble corresponding to the correct answer and zero mark if no bubble is darkened. No negative marks will be awarded for incorrect answer in this section.

SECTION-1 : (Only One option correct Type)

This section contains 8 multiple choice questions. Each questions has four choices (A), (B), (C) and (D) out of which Only ONE option is correct.

- One mole of ideal monoatomic gas is carried through the reversible cyclic process as shown in figure. Calculate the max. temperature attained by the gas during the cycle.



(A) $\frac{25}{8} \left(\frac{P^\circ V^\circ}{R} \right)$

(B) $-\frac{25}{8} \left(\frac{P^\circ V^\circ}{R} \right)$

(C) $\frac{35}{8} \left(\frac{P^\circ V^\circ}{R} \right)$

(D) $-\frac{35}{8} \left(\frac{P^\circ V^\circ}{R} \right)$



2. Determine ΔU° at 300 K for the following reaction using the listed enthalpies of reaction :
- $$4\text{CO(g)} + 8\text{H}_2\text{(g)} \longrightarrow 3\text{CH}_4\text{(g)} + \text{CO}_2\text{(g)} + 2\text{H}_2\text{O(l)}$$
- $$\text{C(graphite)} + 1/2\text{O}_2\text{(g)} \longrightarrow \text{CO(g)}; \Delta H_1^\circ = -110.5 \text{ kJ}$$
- $$\text{CO(g)} + 1/2\text{O}_2\text{(g)} \longrightarrow \text{CO}_2\text{(g)}; \Delta H_2^\circ = -282.9 \text{ kJ}$$
- $$\text{H}_2\text{(g)} + 1/2\text{O}_2\text{(g)} \longrightarrow \text{H}_2\text{O(l)}; \Delta H_3^\circ = -285.8 \text{ kJ}$$
- $$\text{C(graphite)} + 2\text{H}_2\text{(g)} \longrightarrow \text{CH}_4\text{(g)}; \Delta H_4^\circ = -74.8 \text{ kJ}$$
- (A) -653.5 kJ (B) -686.2 kJ (C) -747.4 kJ (D) None of these
3. Determine enthalpy of formation for $\text{H}_2\text{O}_2(\ell)$, using the listed enthalpies of reactions :
- $$\text{N}_2\text{H}_4(\ell) + 2\text{H}_2\text{O}_2(\ell) \longrightarrow \text{N}_2\text{(g)} + 4\text{H}_2\text{O}(\ell); \Delta_r H^\circ_1 = -818 \text{ kJ/mol}$$
- $$\text{N}_2\text{H}_4(\ell) + \text{O}_2\text{(g)} \longrightarrow \text{N}_2\text{(g)} + 2\text{H}_2\text{O}(\ell); \Delta_r H^\circ_2 = -622 \text{ kJ/mol}$$
- $$\text{H}_2\text{(g)} + \frac{1}{2}\text{O}_2\text{(g)} \longrightarrow \text{H}_2\text{O}(\ell); \Delta_r H^\circ_3 = -285 \text{ kJ/mol}$$
- (A) -383 kJ/mol (B) -187 kJ/mol (C) -498 kJ/mol (D) None of these
4. The enthalpy of neutralization of a weak monoprotic acid (HA) in 1M solution with a strong base is -55.95 kJ/mol. If acid HA requires 1.4 kJ/mol heat for its complete ionization and enthalpy of neutralization of the strong monobasic acid with a strong monoacidic base is -57.3 kJ/mol. What is the % ionization of the weak acid in molar solution ?
- (A) 1% (B) 3.57% (C) 35.7% (D) 10%
5. Calculate $\Delta_r G^\circ$ for $(\text{NH}_4\text{Cl, s})$ at 310 K.
 Given : $\Delta_f H^\circ(\text{NH}_4\text{Cl, s}) = -314.5 \text{ kJ/mol}$; $\Delta_r C_p = 0$
 $S^\circ_{\text{N}_2(\text{g})} = 192 \text{ JK}^{-1} \text{ mol}^{-1}$; $S^\circ_{\text{H}_2(\text{g})} = 130.5 \text{ JK}^{-1} \text{ mol}^{-1}$;
 $S^\circ_{\text{Cl}_2(\text{g})} = 233 \text{ JK}^{-1} \text{ mol}^{-1}$; $S^\circ_{\text{NH}_4\text{Cl}(\text{s})} = 99.5 \text{ JK}^{-1} \text{ mol}^{-1}$
 All given data are at 300 K.
- (A) -198.56 kJ/mol (B) -426.7 kJ/mol (C) -202.3 kJ/mol (D) None of these
6. For a perfectly crystalline solid $C_{p,m} = aT^3$, where a is constant. If $C_{p,m}$ is 0.42 J/K-mol at 10 K, molar entropy at 10 K is
- (A) 0.42 J/K-mol (B) 0.14 J/K-mol (C) 4.2 J/K-mol (D) zero
7. The molar entropy content of 1 mole of oxygen (O_2) gas at 300 K and 1 atm is 250 J mole $^{-1}$ K $^{-1}$. Calculate ΔG when 1 mole of oxygen is expanded reversibly and isothermally from 300 K, 1 atm to double its volume (Take $R = 8.314 \text{ J mole}^{-1} \text{ K}^{-1}$, $\log e = 2.303$)
- (A) 1.728 KJ mole $^{-1}$ K $^{-1}$ (B) 0
 (C) -1.728 KJ mole $^{-1}$ K $^{-1}$ (D) 0.75 KJ mole $^{-1}$ K $^{-1}$
8. Fixed amount of an ideal mono atomic gas contained in a sealed rigid vessel ($V = 24.6$ litre) at 1.0 bar is heated reversibly from 27°C to 127°C. Determine change in Gibb's energy (in Joule) if entropy of gas $S = 10 + 10^{-2} T$ (J/K)
- (A) 530 J (B) -530 J (C) 1778.5 J (D) 3778.5 J

Section-2 : (One or More than one options correct Type)

This section contains 6 multipole choice questions. Each questions has four choices (A), (B), (C) and (D) out of which ONE or MORE THAN ONE are correct.

9. Which of the following statement(s) is/are true?
- (A) $\Delta E = 0$ for combustion of $\text{C}_2\text{H}_6(\text{g})$ in a sealed rigid adiabatic container
 (B) $\Delta_f H^\circ$ (S, monoclinic) $\neq 0$
 (C) If dissociation energy of $\text{CH}_4(\text{g})$ is 1656 kJ/mol and $\text{C}_2\text{H}_6(\text{g})$ is 2812 kJ/mol, then value of C—C bond energy will be 328 kJ/mol
 (D) If $\Delta_f H^\circ(\text{H}_2\text{O, g}) = -242 \text{ kJ/mol}$; $\Delta H_{\text{vap}}(\text{H}_2\text{O, l}) = 44 \text{ kJ/mol}$ then $\Delta_f H^\circ(\text{OH}^-, \text{aq.})$ will be -142 kJ/mol



10. From the following data, mark the option(s) where ΔH is correctly written for the given reaction.
 Given : $H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$; $\Delta H = -57.3 \text{ kJ}$
 $\Delta H_{\text{solution}}$ of $HA(g) = -70.7 \text{ kJ/mol}$
 $\Delta H_{\text{solution}}$ of $BOH(g) = 20 \text{ kJ/mol}$
 $\Delta H_{\text{ionization}}$ of $HA = 15 \text{ kJ/mol}$ and BOH is a strong base.
- | Reaction | $\Delta H_r \text{ (kJ/mol)}$ |
|--|-------------------------------|
| (A) $HA(aq) + BOH(aq) \longrightarrow BA(aq) + H_2O$ | -42.3 |
| (B) $HA(g) + BOH(g) \longrightarrow BA(aq) + H_2O$ | -93 |
| (C) $HA(g) \longrightarrow H^+(aq) + A^-(aq)$ | -55.7 |
| (D) $B^+(aq) + OH^-(aq) \longrightarrow BOH(aq)$ | -20 |
11. The value of $\Delta H_{\text{transition}}$ of $C(\text{graphite}) \longrightarrow C(\text{diamond})$ is 1.9 kJ/mol at 25°C entropy of graphite is higher than entropy of diamond. This implies that :
 (A) $C(\text{diamond})$ is more thermodynamically stable than $C(\text{graphite})$ at 25°C
 (B) $C(\text{graphite})$ is more thermodynamically stable than $C(\text{diamond})$ at 25°C
 (C) diamond will provide more heat on complete combustion at 25°C
 (D) $\Delta G_{\text{transition}}$ of $C(\text{diamond}) \longrightarrow C(\text{graphite})$ is -ve
12. Which of the following statement(s) is/are false ?
 (A) All adiabatic processes are isentropic (or isentropic) processes
 (B) When $(\Delta G_{\text{system}})_{T,P} < 0$; the reaction must be exothermic
 (C) $dG = VdP - SdT$ is applicable for closed system, both PV and non-PV work
 (D) the heat of vaporisation of water at 100°C is 40.6 kJ/mol . When 9 g of water vapour condenses to liquid at 100°C of 1 atm, then $\Delta S_{\text{system}} = 54.42 \text{ J/K}$
13. For the reaction $2Ag_2O(s) \longrightarrow 4Ag(s) + O_2(g)$, ΔH is $61.17 \text{ kJ mol}^{-1}$ and ΔS is $132 \text{ J K}^{-1} \text{ mol}^{-1}$. Compute the temperature above which the given reaction will be spontaneous.
 (A) $T > 463.4 \text{ K}$ (B) $T > 190.25^\circ\text{C}$ (C) $T < 190.25^\circ\text{C}$ (D) $T < 463.4 \text{ K}$
14. Select the correct enthalpy at corresponding temperature using following datas
 (i) Heat capacity of solid from 0 K to normal melting point 200 K
 $C_{P,m}(s) = 0.035 T \text{ JK}^{-1} \text{ mol}^{-1}$.
 (ii) Enthalpy of fusion = 7.5 KJ mol^{-1} ,
 (iii) Enthalpy of vaporisation = 30 KJ mol^{-1} .
 (iv) Heat capacity of liquid form 200 K to normal boiling point 300 K
 $C_{P,m}(l) = 60 + 0.016 T \text{ JK}^{-1} \text{ mol}^{-1}$.
 (v) Heat capacity of gas from 300 K to 600 K at 1 atm
 $C_{P,m}(g) = 50.0 \text{ JK}^{-1} \text{ mol}^{-1}$.
 (A) $S_{200}(s) = 7$ (B) $S_{300}(l) = 70.43$ (C) $S_{300}(g) = 170.43$ (D) $S_{600}(g) = 205.09$

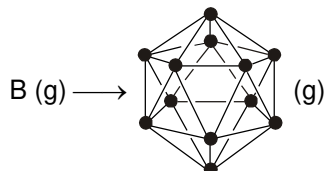
Section-3 : (One Integer Value Correct Type.)

This section contains 6 questions. Each question, when worked out will result in one integer from 0 to 9 (both inclusive)

15. Two moles of a perfect gas undergo the following processes :
 (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)
 Calculate the magnitude of work (W) done in L.atm [JEE 2002, 5/60]
16. The enthalpy of combustion of mol. wt. 180 glucose is -2808 KJmol^{-1} at 25°C . X and Y grams of glucose do you need to consume respectively cases [Assume wt = 62.5 Kg].
 (a) to climb a flight of stairs rising through 3M. (b) to climb a mountain of altitude 6000 M ?
 Assume that 25% of enthalpy can be converted to useful work.
 X and Y are related as $Y = mX$; then find $m/1000$.



17. A sample of certain mass of an ideal polyatomic gas is expanded against constant pressure of 1 atm adiabatically from volume 2 L, pressure 6 atm and temperature 300 K to state where its final volume is 8L. Then calculate entropy change (in J / K) in the process. (Neglect vibrational degrees of freedom) [1L atm = 100 J, $\log 2 = 0.3$, $\log 3 = 0.48$, $\log e = 2.3$] (approximate integer)
18. The heat of combustion of acetylene is 312 kcal. If heat of formation of CO_2 & H_2O are -94 & -68 kcal respectively. Given that heat of atomisation of C(s) & $\text{H}_2\text{(g)}$ are 150 & 100 kcal respectively and C–H bond energy is 95 kcal. Calculate $\frac{\Delta H_{\text{C}\equiv\text{C}}}{22}$.
19. Boron exist in different allotropic forms. All allotropic form contains icosahedral units (icosahedral is a regular shape with 12 corners & 20 faces) with boron atoms at all 12 corners and all bonds are equivalent. [M]



Calculate heat evolved at constant pressure (in kJ) per mole of boron atoms undergoing above change if $\Delta H_{\text{BE}}(\text{B}-\text{B}) = 200$ kJ/mol. Report your Answer after dividing by 100

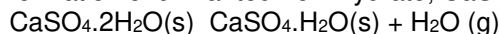
20. 1 mole of an ideal gas is allowed to expand isothermally at 27°C till its volume is tripled. If the expansion is carried out reversibly then the $\Delta S_{\text{universe}}$ will be ?

SECTION-4 : Comprehension Type (Only One options correct)

This section contains 1 paragraphs, each describing theory, experiments, data etc. 3 questions relate to the paragraph. Each question has only one correct answer among the four given options (A), (B), (C) and (D)

Paragraph for Questions 21 to 23

Concrete is produced from a mixture of cement, water, sand and small stones. It consists primarily of calcium silicates and calcium aluminates formed by heating and grinding of clay and limestone. In later steps of cement production a small amount of gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is added to improve subsequent hardening of concrete. The use of elevated temperatures during the final production may lead to formation of unwanted hemihydrate, $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$. Consider the following reaction :



The following thermodynamic data apply at 27°C , standard pressure : 1 bar

Compound	$\Delta H_f^\circ (\text{kJ/mol})$	$S^\circ (\text{JK}^{-1}\text{mol}^{-1})$
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O (s)}$	-2021.0	194.0
$\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O(s)}$	-1575.0	119.5
$\text{H}_2\text{O(g)}$	-242.8	188

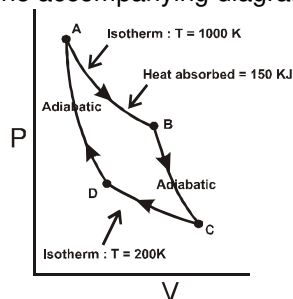
$$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$$

21. ΔH° for the formation of 1.45 kg of $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O(s)}$ from $\text{CaSO}_4 \cdot 2\text{H}_2\text{O(s)}$ is
 (A) +446 kJ (B) -830 kJ (C) -446 kJ (D) +818 kJ
22. Equilibrium pressure (in bar) of water vapour in closed vessel containing $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O(s)}$, $\text{CaSO}_4 \cdot \text{H}_2\text{O(s)}$, $\text{H}_2\text{O(g)}$ at 27°C : ($2.303R \times 300 \times 1.5 = 8645.83$, $\log 5.5 = 0.74$)
 (A) 15×10^{-4} bar (B) 2×10^{-4} bar (C) 5.5×10^{-3} bar (D) 7.00×10^{-4} bar
23. Approximate temperature at which the equilibrium water vapour pressure is 1.00 bar
 (A) 121°C (B) 400°C (C) 200°C (D) 240°C



Paragraph for Questions 24 to 26

The accompanying diagram represents a reversible Carnot cycle for an ideal gas :



24. How much heat is rejected at the lower temperature, 200 K, during the isothermal compression ?
 (A) 150 kJ (B) 30 kJ (C) 120 kJ
 (D) data are not sufficient to calculate exact value
25. What is the entropy increase during isothermal expansion at 1000 K ?
 (A) 0.15 JK^{-1} (B) 150 kJ K^{-1} (C) 150 JK^{-1} (D) 750 JK^{-1}
26. What is the Gibbs free energy change during the process $A \rightarrow B$?
 (A) 150 kJ (B) -150 kJ (C) 30 kJ (D) Data are not sufficient

SECTION-5 : Matching List Type (Only One options correct)

This section contains 1 questions, each having two matching lists. Choices for the correct combination of elements from List-I and List-II are given as options (A), (B), (C) and (D) out of which one is correct

27. Match column-I to column-II standard entropy in kJ/K-molar at 25°C

	Column-I		Column-II
1.	$\Delta H_{\text{C-C}}$	(p)	733.48
2.	$\Delta H_{\text{C-H}}$	(q)	97.81
3.	$\Delta H_{\text{C=C}}$	(r)	434.3
4.	$\Delta H_{\text{C}\equiv\text{C}}$	(s)	454.64
5.	$\Delta H_{\text{C=O}}$	(t)	804.22

Using the data (all values are in kJ/mol at 25°C) given below :

$\Delta H^\circ_{\text{combustion}}$ (ethane) = -1559.8	;	$\Delta H^\circ_{\text{combustion}}$ (ethene) = -1410.9
$\Delta H^\circ_{\text{combustion}}$ (acetylene) = -1299.7	;	$\Delta H^\circ_{\text{combustion}}$ (acetaldehyde) = -1192.3
$\Delta H^\circ_f \text{CO}_2(\text{g}) = -393.5$;	ΔH°_f of $\text{H}_2\text{O}(\ell) = -285.8$
ΔH° for $\text{C}(\text{s})$ (graphite) $\rightarrow \text{C}(\text{g}) = 716.68$;	Bond energy of $\text{H-H} = 435.94$
Bond energy of $\text{O=O} = 498.94$		

	1	2	3	4	5		1	2	3	4	5
(A)	q	s	r	p	t	(B)	r	p	t	q	s
(C)	q	p	s	r	t	(D)	p	s	q	r	t

Practice Test-2 (IIT-JEE (ADVANCED Pattern))

OBJECTIVE RESPONSE SHEET (ORS)

Que.	1	2	3	4	5	6	7	8	9	10
Ans.										
Que.	11	12	13	14	15	16	17	18	19	20
Ans.										
Que.	21	22	23	24	25	26	27			
Ans.										



APSP Answers

PART – I

- | | | | | |
|---------|---------|---------|---------|---------|
| 1. (3) | 2. (3) | 3. (4) | 4. (2) | 5. (2) |
| 6. (1) | 7. (3) | 8. (1) | 9. (3) | 10. (3) |
| 11. (3) | 12. (3) | 13. (2) | 14. (1) | 15. (2) |
| 16. (1) | 17. (1) | 18. (1) | 19. (2) | 20. (2) |
| 21. (1) | 22. (2) | 23. (4) | 24. (2) | 25. (2) |
| 26. (4) | 27. (1) | 28. (1) | 29. (2) | 30. (1) |

PART – II

- | | | | | |
|---------------------------------|---------|---------|---------|---------|
| 1. (A) | 2. (B) | 3. (B) | 4. (D) | 5. (B) |
| 6. (A) | 7. (B) | 8. (C) | 9. (C) | 10. (B) |
| 11. (B) | 12. (B) | 13. (A) | 14. (A) | 15. (B) |
| 16. (A) | 17. (B) | 18. (C) | 19. (C) | 20. (C) |
| 21. (C) | 22. (B) | 23. (D) | 24. (D) | 25. (D) |
| 26. (D) | 27. (C) | 28. (B) | 29. (C) | 30. (C) |
| 31. (D) | 32. (D) | 33. (A) | 34. (D) | 35. (C) |
| 36. (B) | 37. (B) | 38. (C) | 39. (D) | 40. (D) |
| 41. (C) | 42. (B) | 43. (A) | 44. (D) | 45. (C) |
| 46. (A) | 47. (A) | 48. (B) | 49. (A) | 50. (B) |
| 51. (A) | 52. (B) | 53. (A) | 54. (D) | 55. (B) |
| 56. (A) | 57. (B) | 58. (B) | 59. (D) | 60. (A) |
| 61. (D) | 62. (C) | 63. (D) | 64. (C) | 65. (A) |
| 66. (All options are incorrect) | | 67. (B) | 68. (A) | 69. (B) |

PART – III

- | | |
|---|---|
| 1. -34.465 kJ | 2. -0.7478 kJ |
| 3. (i) Isobaric | (ii) $w = 830.865 \text{ J}$, $q = -150 \text{ J}$ |
| 4. $T_2 = 100 \text{ K}$, $w = -5.016 \text{ KJ}$ | 5. (a) -816 J (b) +2026 J (c) 1210 J |
| 6. Hydrogen is diatomic so at high temperature rotational and vibrational motion also counts. | |
| 7. $\Delta H = 990 \text{ J}$, $\Delta E = 10 \text{ J}$ | 8. Zero |
| 9. (i) Rev. Process $\Delta S_{\text{system}} = \frac{3}{2} R \ln 10$; $\Delta S_{\text{surr}} = -\frac{3}{2} R \ln 10$; $\Delta S_{\text{Total}} = 0$ | |
| (ii) Irr. Process $\Delta S_{\text{system}} = \frac{3}{2} R \ln 10$; $\Delta S_{\text{surr}} = -\frac{3}{2} R (0.9)$; $\Delta S_{\text{Total}} = \frac{3}{2} R (1.403)$ | |
| 10. (a) When $\Delta H = -ve$ and $T\Delta S = -ve$, also $T\Delta S > \Delta H$ then $\Delta G = +ve$ in such case, the reaction will not be spontaneous. | |



(b) $-\Delta G^\circ = 2.303 RT \log K_c$.

If ΔG° is negative (not to say that $\Delta G < 0$) then K_c will be +ve and will have value greater than one.

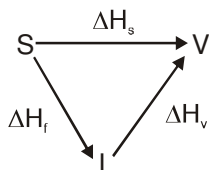
11. -43.92 KJ

12. (i) $\Delta G = 5.7 \text{ kJ/mol}$ (ii) backward shifting

13. -7.432 kJ

14. Exothermic A, C, D; endothermic : B, E

15. Since, sublimation involves



According to Hess's law, $\Delta H_{(f)} + \Delta H_{(v)} = \Delta H_{(s)}$

- | | | | |
|--------------------------------|---|-----------------------|---|
| 16. $q_1 > q_2$ | 17. 22.8 cal/g. | 18. 1312 kJ | 19. 43.73 kJ/mol |
| 20. -827 kJ mol^{-1} | 21. (C) | 22. (C) | 23. (B) |
| 25. (A) | 26. (A) | 27. (C) | 28. (D) |
| 30. (B) | 31. (A) | 32. (B) | 33. (A) |
| 35. (A) | 36. (B) | 37. (A) | 38. (A) |
| 40. (C) | 41. (B) | 42. (A) | 43. (A) |
| 45. (D) | 46. (A) | 47. (B) | 48. (A) |
| 50. (B) | 51. (A) | 52. (C) | 53. (D) |
| 55. (B) | 56. (D) | 57. (C) | 58. (B) |
| 60. (A) | 61. (D) | 62. (D) | 63. (B) |
| 65. (B) | 66. (D) | 67. (A) | 68. (C) |
| 70. (C) | 71. (B) | 72. (D) | 73. (C) |
| 75. (C) | 76. (A) | 77. (D) | 78. (D) |
| 80. (B) | 81. (D) | 82. (B) | 83. (C) |
| 85. (C) | 86. (D) | 87. (B) | 88. (A) |
| 90. (A) | 91. (C) | 92. (B) | 93. (A) |
| 95. (B) | 96. (D) | 97. (B) | 98. (D) |
| 100. (B) | 101. (A - q), (B - p), (C - s), (D - r) | 102. 5 | 103. 6 |
| 104. 9 | 105. 5 | 106. 96 | 107. 64 L |
| 109. 24 | 110. $\Delta S_{\text{system}} = 8 \text{ Cal}$ | 111. 18 | 112. 18 |
| 113. 25%. | 114. -16 Kcal. | 115. 5 | 116. 36 kJ |
| 118. 9 | 119. $-362 \text{ kJ mole}^{-1}$ | 120. 9 | 121. $\Delta S_{\text{total}} = 3 \text{ J K}^{-1}$ |
| 22. (ACD) | 123. (ABCD) | 124. (BC) | 125. (BD) |
| 127. (ABC) | 128. (ABC) | 129. (AD) | 130. (ABCD) |
| 132. (ABCD) | 133. (ABD) | 134. (ACD) | 135. (ACD) |
| 137. (C) | 138. (B) | 139. (A) | 140. (B) |
| | | | 141. (C) |





142. (A) 143. (B) 144. (C) 145. (A) 146. (B)
147. (A)

PART – IV

1. (A) 2. (D) 3. (B) 4. (B) 5. (A)
6. (B) 7. (C) 8. (B) 9. (ABC) 10. (ABC)
11. (BCD) 12. (ABCD) 13. (AB) 14. (ABCD)
15. $(-20 + 0 + 14) = -6 \text{ L atm}$ 16. 2 17. 3 18. 7
19. 5 20. 0 21. (D) 22. (C) 23. (A)
24. (B) 25. (C) 26. (B) 27. (A)

APSP Solutions

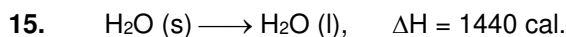
PART – I

6. $\Delta H_{\text{solution}} = \frac{(125+8) \times 4.2 \times 6}{8} \times 80 = 33516 \text{ J/mol or } 33.51 \text{ kJ/mol.}$
7. $\Delta_r C_p = 0, \therefore \Delta H_{300} = \Delta H_{310}$
8. $\text{C}_2\text{H}_5\text{OH}(\ell) + 3\text{O}_2(\text{g}) \longrightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\ell)$
 $\Delta n_g = 2 - 3 = -1$
 so $\Delta U = \Delta H - \Delta n_g RT$
 $= -q + RT$
9. $\text{H}_2\text{C}_2\text{O}_4(\ell) + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{O}(\ell) + 2\text{CO}_2(\text{g});$
 $\Delta n_g = 3/2$
 $\Delta U_c = -\frac{0.312 \times 8.75}{1} \times 90 = -245.7 \text{ kJ/mol}$
 $\Delta H = \Delta U + \Delta n_g RT$
 $= -245.7 + \frac{3}{2} \times \frac{8.314 \times 300}{1000} = -241.947 \text{ kJ/mol.}$
10. From given reaction $\Delta n_g = 12 - 15 = -3$
 so $\Delta E^\circ = \Delta H^\circ - \Delta n_g RT = -6542 + 3RT$
 for 1.5 mole, $\Delta E^\circ = \frac{1.5}{2} \{-6542 + 3RT\} = 4900.9 \text{ kJ}$
11. $\Delta n_g = 1 - 2 = -1$
 $\Delta E = \Delta H - \Delta n_g RT = \Delta H - RT = -72.3 + 8.314 \times 300 \times 10^{-3} = -69.806 \text{ kJ/mole}$
 so for 3 mole we will get $\Delta E = -69.806 \times 3 \text{ kJ/mole} = 209.42 \text{ kJ/mole}$
12. For same amount of gas at constant temperature, lesser is the volume, lower will be the entropy.
13. $W = -P_{\text{ext}}(\Delta V) = -(1 \text{ atm}) \times 500 \times 50 \times 10^{-3} \text{ L}$
 $= -25 \text{ L atm} = -25 \times 101.3 \times 10^{-3} \text{ kJ} = -2.53 \text{ kJ}$
14. $\text{C}_2\text{H}_4 + \text{H}_2 \longrightarrow \text{C}_2\text{H}_6$
 50 ml 50 ml 0
 X X 50 ml
 $\Delta H = \Delta U + P(\Delta V)$
 $-0.31 = \Delta U + 1.5 \times 1.01 \times 10^5 (-50 \times 10^{-6}).$





$$\Delta U = -0.3024 \text{ kJ.}$$



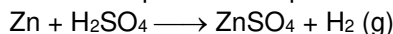
16. $\Delta E = q + w$

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

$$\Delta E = nC_V\Delta T = 1 \times \frac{3}{2} R \left(\frac{P^0 2V^0}{R} - \frac{3P^0 V^0}{R} \right) = -\frac{3}{2} P^0 V^0$$

$$q_{BC} = \Delta E - W = -\frac{3}{2} P^0 V^0 + 2P^0 V^0 = \frac{1}{2} P^0 V^0$$

17. Beaker is open and in open beaker external pressure remains constant.

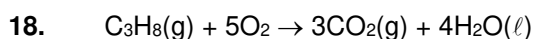


$$\frac{130}{65} = 2 \text{ mole}$$

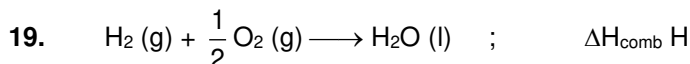
$$PV = nRT$$

$$P\Delta V = n_g RT$$

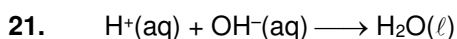
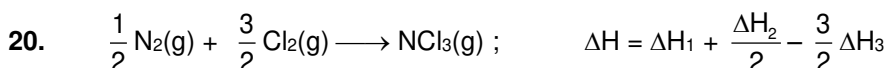
$$W = -n_g RT = 2 \times 2 \times 300 = -1200 \text{ cal.}$$



$$\Delta_c H = \left[\begin{array}{l} 8 \times \text{B.E. (C-H)} \\ +2 \times \text{B.E. (C-C)} \\ +5 \times \text{B.E. (O=O)} \end{array} \right] - \left[\begin{array}{l} 6 \times \text{B.E. (C=O)} \\ +8 \times \text{B.E. (O-H)} \\ +3 \times |\text{R.E.}| \text{ of } \text{CO}_2 \\ +4 \times \Delta_{\text{vap}} \text{H(H}_2\text{O)} \end{array} \right]$$



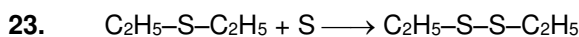
$$\Delta H_{\text{comb}} = \Delta H_{\text{H-H}} + \frac{1}{2} \Delta H_{\text{O=O}} - 2\Delta H_{\text{O-H}} - \Delta H_{\text{vap}} = x_1 + \frac{x_2}{2} - 2x_3 - x_4$$



$$\text{so } \Delta H^\circ = -57.3 = -285.5 - \Delta H_f^\circ (\text{H}^+, \text{aq}) - \Delta H_f^\circ (\text{OH}^-, \text{aq})$$

$$\text{so } \Delta H_f^\circ (\text{OH}^-, \text{aq}) = -228.5 \text{ kJ/mole (as } \Delta H_f^\circ (\text{H}^+, \text{aq}) = 0)$$

22. $\Delta_r H = \frac{8}{9} \times 45.54 + \frac{1}{9} \times 68.91 = 48.137 \text{ kJ.}$



$$\Delta H_f^\circ (\text{C}_2\text{H}_5\text{-S-C}_2\text{H}_5) = \Delta H_f^\circ (\text{C}_2\text{H}_5\text{-S-S-C}_2\text{H}_5) - \Delta H_{\text{S-S}} + \Delta H_{\text{sub S}}$$

$$-201.9 = -147.2 - \Delta H_{\text{S-S}} + 222.8$$

$$\Delta H_{\text{S-S}} = 277.5 \text{ kJ/mol}$$

24. $\Delta H^\circ = 2 \times \Delta H_1^\circ + 2 \times \Delta H_2^\circ - \Delta H_3^\circ$

25. $\Delta G = \Delta H - T\Delta S = -2808 - 310 \times 182.4 \times 10^{-3} = -2864.5 \text{ kJ}$

26. $\Delta S = 10.13 = 31.2 + 51.1 - 47.3 - S_{\text{H}_2\text{O}}$

$$S_{\text{H}_2\text{O}} = 45.13 \text{ cal/k mole.}$$

27. $\Delta G = 29.3 \times 10^3 - (2 \times 239.7 - 152.3 - 223) \times 298 = -1721.8 \text{ Joule.}$





28. Since, expansion occurred at constant temperature,

$$\Delta S = nR \ln \frac{V_2}{V_1} = \frac{1}{32} \times 8.314 \ln \frac{3.0}{0.75} = 0.36 \text{ JK}^{-1}$$

Since, this is case of free expansion, $P_{\text{ext}} = 0$. $\Rightarrow -W = P_{\text{ext}} \Delta V = 0$, $q = 0$
Also, since, $\Delta T = 0 \Rightarrow \Delta H = \Delta E = 0$.

29. (2) $\text{Cu}_2\text{O(s)} + \frac{1}{2} \text{O}_2\text{(g)} \rightleftharpoons 2\text{CuO(s)}$

$$\Delta G^\circ_{\text{reaction}} = [2 \times (-30.4)] - [-34.98] = -25.82 \text{ kcal}$$

$$\text{and } -25.82 \times 10^3 = 2.303 \times 2 \times 298 \log K$$

$\therefore K 10^{19}$, a very high value, hence reaction will be almost complete with a trace of Cu_2O .

30. $\Delta_f S^\circ(\text{NH}_4\text{Cl, s})$ at 300 K

$$= S^\circ_{\text{NH}_4\text{Cl(s)}} - \left[\frac{1}{2} S^\circ_{\text{N}_2} + 2S^\circ_{\text{H}_2} + \frac{1}{2} S^\circ_{\text{Cl}_2} \right] = -374 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$\Delta_f C_P = 0$$

$$\therefore \Delta_f S^\circ_{310} = \Delta_f S^\circ_{300} = -374 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$\Delta_f H^\circ_{310} = \Delta_f H^\circ_{300} = -314.5$$

$$\Delta_f G^\circ_{310} = \Delta_f H^\circ - 310$$

$$\Delta S^\circ = -314.5 - \frac{310(-374)}{1000} = -198.56 \text{ kJ/mol.}$$

PART - III

1. $W = -2.303 nRT \log \frac{V_2}{V_1} = -2.303 \times 6 \times 8.314 \times 300 \log \frac{10}{1} = -34464.8 \text{ Joule} = 34.465 \text{ kJ}$

2. $\int dW = - \int P_{\text{ext}} dv$

$$W_{\text{irr}} = -P_{\text{ext}} [V_2 - V_1] = -P_{\text{ext}} \left(\frac{nRT}{P_2} - \frac{nRT}{P_1} \right) = -P_{\text{ext}} \times nRT \left(\frac{1}{P_2} - \frac{1}{P_1} \right)$$

$$= -1 \times 1 \times .082 \times 300 \left(\frac{1}{2} - \frac{1}{5} \right) = -1 \times .082 \times 300 \times \frac{3}{10} = -7.38 \text{ L.atm} = -747.8 \text{ J}$$

$$W_{\text{irr}} = -0.7478 \text{ KJ}$$

3. (i) $\left(\frac{Pv}{nRT} \right)_A = \left(\frac{Pv}{nRT} \right)_B$

$$\frac{P_A \times 4}{nR \times 400} = \frac{P_B \times 3}{nR \times 300} = \frac{P_A}{100} = \frac{P_B}{100} \Rightarrow P_A = P_B \text{ Hence process is isobaric.}$$

$$(ii) W = -P_{\text{ext}} (V_2 - V_1) = - \left(\frac{nRT_A}{V_A} \right) (V_B - V_A) = - \left(\frac{1 \times .082 \times 300}{3} \right) (3 - 4) \times 101.325 \text{ J} = 830.865 \text{ J}$$

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

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

$$300 \times V^{1/3} = T_2 \times (27 V)^{1/3} \Rightarrow T_2 = 100 \text{ K}$$

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

For reversible adiabatic process,

$$q = 0$$

$$\Delta U = W$$

$$\Rightarrow W = n C_V \Delta T$$



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

$$5. \quad PV = nRT \quad \Rightarrow \quad 5 \times 1 = n \times 0.082 \times 300 \quad \Rightarrow \quad n = 0.203.$$

	Initial	Final
(a)	$V = 1 \text{ L.}$	$V_2 = 5 \text{ L.}$
	$P = 5 \text{ atm}$	
	$T = 300 \text{ K}$	$T = 300 \text{ K}$

$$w = -2.303 nRT \log \frac{V_2}{V_1} = -2.303 \times 0.203 \times 8.314 \times 300 \log 5 = -816 \text{ J}$$

$$w = -816 \text{ J and } q = -w = 816 \text{ J}$$

So, work done by the gas = 816 J.

$$(b) \quad w = -P_{\text{ext}} (V_2 - V_1) = -5 [1-5] = +20 \times 101.325$$

$$w = 2026 \text{ J.}$$

$$(c) \quad q_1 = -w_1 = +816 \text{ J}$$

$$q_2 = -w_2 = -2026 \text{ J}$$

$$q_1 + q_2 = -1210 \text{ J}$$

So, Net heat released by the system = -1210

Net Heat gained by the surroundings = 1210

6. Helium (He) gas is monoatomic and it has three translational degree of freedom. Hence, the contribution of each translational degree of freedom towards C_v being $R/2$, so the **total contribution towards $C_v = 3 \times R / 2$** . Hydrogen molecule is diatomic. At low temperature, rotational and vibrational contribution for H_2 are zero. So, C_v for H_2 at low temperature continues to be $3R/2$. At moderate temperature, rotational contribution ($= 2 \times R / 2$) also becomes dominant and hence total contribution towards $C_v = \frac{3R}{2} + R = \frac{5R}{2}$. At even high temperature, vibrational contribution ($= 1 \times R$) also becomes

significant. Hence total contribution towards $C_v = \frac{3R}{2} + R + R = \frac{7R}{2}$

$$7. \quad \Delta U = q + W$$

for adiabatic process $q = 0$, hence $\Delta U = W$ and $W = -p(\Delta V) = -P(V_2 - V_1)$

$$\text{so, } \Delta U = -100(99 - 100) = -100(-1) = 100 \text{ bar mL} = 10 \text{ J}$$

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

Here ΔU already calculated above and

$$\Delta PV = (P_2V_2 - P_1V_1)$$

$$\text{So, } \Delta H = 100 + (100 \times 99 - 1 \times 100) = 9900 \text{ bar mL} = 990 \text{ J}$$

$$8. \quad dS = \frac{dq_{\text{rev.}}}{T} \quad \Rightarrow \quad \sum \frac{dq_{\text{rev.}}}{T} = \Delta S$$

As 'S' being a state function, $\Delta S = 0$ in a cyclic process.

$$\therefore \sum \frac{dq_{\text{rev.}}}{T} = 0.$$

$$9. \quad (i) \quad \Delta S_{\text{system}} = nC_v \ln \frac{T_2}{T_1} = \frac{3}{2} R \ln 10 \text{ and}$$

$$\Delta S_{\text{surr}} = \int -\frac{dq_{\text{sys}}}{T} = \int_{T_1}^{T_2} -\frac{nC_v dT}{T} = -nC_v \ln \frac{T_2}{T_1} = -\frac{3}{2} R \ln 10$$

(ii) Entropy is a state function.

$$\Delta S_{\text{system}} = \frac{3}{2} R \ln 10.$$

$$\Delta S_{\text{surr}} = \frac{q}{T} = -\frac{nC_v(T_2 - T_1)}{T_2} = -\frac{3}{2} R (0.9).$$

$$\Delta S_{\text{Total}} = \frac{3}{2} R \ln 10 - \frac{3}{2} R (0.9) = \frac{3}{2} R (1.403)$$



10. (a) When $\Delta H = -ve$ and $T\Delta S = -ve$, also $T\Delta S > \Delta H$ then $\Delta G = +ve$ in such case, the reaction will not be spontaneous.
 (b) $-\Delta G^\circ = 2.303 RT \log K_c$.
 If ΔG° is negative (not to say that $\Delta G < 0$) then K_c will be +ve and will have value greater than one.
11. $2NO (9, 1 \times 10^{-5} \text{ atm}) + Cl_2 (9, 1 \times 10^{-2}) \rightleftharpoons 2NOCl (9, 1 \times 10^{-2})$
 $\Delta G^\circ = -2.303 RT \left(\log \frac{(1 \times 10^{-2})^2}{(1 \times 10^{-5})^2 (1 \times 10^{-2})} \right) = -2.303 RT \left[\log \frac{1 \times 10^{-2}}{1 \times 10^{-10}} \right]$
 $= -2.303 RT [\log 1 \times 10^8] = -2.303 \times 8 \times 298 \times 8 = -43.92 \text{ KJ}.$
12. (a) (i) ΔG° for the reaction
 $\Delta G^\circ_{\text{reac.}} = 2\Delta G^\circ_f (NO_2) - \Delta G^\circ_f (N_2O_4)$
 $100 - 100 = 0$
 Now, $\Delta G = 2.303 RT \log Q_P + \Delta G^\circ$
 Here $Q_P = \frac{P_{NO_2}^2}{P_{N_2O_4}} = \frac{100}{10} = 10 \text{ atm}$
 So, $\Delta G = 2.303 RT \log Q_P + 0 = 2.303 RT \log Q_P = 2.303 RT \log_{10} 10 = 2.303 RT = 5.7 \text{ kJ/mole}$
 (ii) Since Q_P is more than K_P
 (Calculate K_P by putting the value of ΔG° in the equation $\Delta G^\circ = 2.303 RT \log K_P$ as $\Delta G^\circ = 0$ that's why K_P comes as 1.)
 Hence, the reaction will proceed in backward direction.
13. $\Delta H = \Delta U + \Delta nRT$
 $\Delta H - \Delta U = -3RT$
 $= -3 \times 8.314 \times 298 = -7432 \text{ J} = -7.432 \text{ kJ}$
16. $\Delta C_p = -ve$; $C_p (\text{products}) < C_p (\text{Reactants})$ so $q_2 < q_1$
17. $\Delta H_2 - 24 = -0.024 \times (523 - 473) \text{ cal/g.} \therefore \Delta H_2 = 22.8 \text{ cal/g.}$
18. Equal volume of $H_2(g)$ & $CO(g)$
 Total volume = 112 L
 So, volume of CO = volume of H_2 = 56 L
 Mole of CO = Mole of H_2 = 2.5 mole
- | | |
|---|---|
| $H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(g)$ | $\Delta H = -241.8 \text{ kJ}$ |
| For 1 mole | $\Delta H = -241.8 \text{ kJ}$ |
| For 2.5 mole | $\Delta H = -241.8 \times 2.5$ |
| Similarly, $CO(g) + \frac{1}{2} O_2(g) \longrightarrow CO_2(g)$ | $\Delta H = -283 \text{ kJ}$ |
| | $\Delta H = -283 \times 2.5 \text{ kJ}$ |
- Total Heat evolved = $[-241.8 + (-283) \times 2.5] = -1312 \text{ kJ}$
19. $\Delta_r H = \frac{5}{8} \times 40 + \frac{3}{8} \times 50 = 43.75 \text{ kJ/mol}$
20. Equation (vi) can be generated by the following manipulations.
 Eq. (i) – Eq. (ii) – Eq. (iii) – Eq. (iv) – $\frac{1}{2}$ Eq. (v)
 Carrying out the corresponding manipulations on ΔH°_L , we get
 $\Delta H^\circ_L = (-563 - 419 - 88 + 322 - 79) \text{ kJ mol}^{-1} = -827 \text{ kJ/mole}$
21. In a reversible process, the driving and the opposite forces are nearly equal, hence the system and the surroundings always remain in equilibrium with each other.
22. (C) An ideal gas under going expansion in vacuum shows, $\Delta E = 0$, $W = 0$ and $q = 0$.
23. $W_2 - P(V_2 - V_1) = nR\Delta T = 1 \times R \times 2 = 2R.$



24. Mechanical work is important only in gases as they undergo appreciable change in volume.

26. Let final common temperature is T_f .
Heat gained by Zinc piece = Heat lost by water
 $0.4 (T_f - 20) \times 65.38 = 4.2 (100 - T_f) \times 180 \Rightarrow T_f = 97.3^\circ\text{C}$

27. Internal energy of a gas = $\frac{f}{2} nRT$
Internal energy of a gas $\propto f$

28. Mechanical work is done on the system and internal energy increases.

29. \therefore The process is of free expansion then $W = 0$.

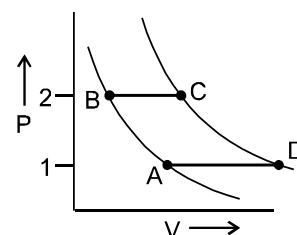
30. For polytropic process ($n = 2$)
 $PV^2 = C$
 $TV = C$
 $T_1V_1 = T_2V_2$
 $300 \times 1 = T_2 \times 3 \Rightarrow T_2 = 100\text{ K}$
 $\Delta U = nC_{v,m} \Delta T$
 $= 1 \times \frac{fR}{2} (T_2 - T_1) = 1 \times \frac{5 \times R}{2} \times (100 - 300) = \frac{1 \times 5 \times R}{2} \times 200 = -500 R = -4.2\text{ kJ}$

32. Final temperature of gas must be double of the initial temperature
 $\Delta H = \Delta U + \Delta(PV) = nC_v \Delta T + \Delta(PV) \quad (\Delta T = T_f - T_i = 2T_i)$
 $= \frac{nR}{(\gamma - 1)} T_i + \Delta(PV) = \frac{3}{2} \times 100 + 100 = 250\text{ J}.$

33. Work is not a state function because it depends upon the path followed.

34. $q + w = \Delta U$ is a state function.

35. $W_{\text{Total}} = \text{area enclosed}$
 $V = \frac{nRT}{P}$
 $V_A = \frac{2R \times 300}{1} = \frac{600 R}{1}$
 $V_B = \frac{2R \times 300}{2} = \frac{300 R}{1}; V_C = \frac{2 R \times 400}{2} = \frac{400 R}{1}$
 $V_D = \frac{800 R}{1}$
 $W_{AB} = -nRT_A \ln \frac{V_B}{V_A} = -2R (300) \ln \frac{1}{2} = 600 R \ln 2$
 $W_{BC} = -2(400 - 300) R = -200 R$
 $W_{CD} = -2 R (400) \ln \frac{V_D}{V_C} = -800 R \ln 2$
 $W_{AD} = -1(600 R - 800 R) = 200 R$
 $W_{\text{Total}} = W_{AB} + W_{BC} + W_{CD} + W_{AD} = -200 R \ln 2 = -100 R \ln 4$



36. Since ice-water ratio is maintained as 1 : 1. So, $\Delta T = 0$.

37. (A) $w = -nR \Delta T = -2 \times 8.314 \times 100 = -1662.8\text{ J}$
 $\Delta U = n \int_{300}^{400} C_{v,m} dT = 2 \times \int_{300}^{400} (20 + 10^{-2} T) dT = 2 \left[20 \times 100 + \frac{10^{-2}}{2} (400^2 - 300^2) \right] = 4700\text{ J}$
 $4700 = q - 1662.8$



- $\therefore q = 6362.8 \text{ J}$
38. latent heat of vaporisation of water = $2.25 \times 10^6 \text{ J/kg}$
 $\Delta H = 2.25 \times 10^6 \text{ J/kg}$
 work done = $-P_{\text{ext}}(V_2 - V_1)$
 $\Delta H = 2.25 \times 10^6 \text{ J/kg}$
 $\Delta H = \Delta U + P\Delta V$
 (a) Now, volume of water $V = \left(\frac{m}{d}\right) = \frac{1}{1000} \text{ M}^3 = 1 \text{ L}$
 (b) volume of steam = $\frac{1000}{0.6} = 1666.67 \text{ L}$
 $2.25 \times 10^6 = \Delta U + 1 [1666.67 - 1] 101.325$
 $\Delta U = 22.5 \times 10^5 - 1.68 \times 10^5 = 20.8 \times 10^5 = 2.08 \times 10^6 \text{ J}$
- 39.** Volume = $5 \times 10 \times 3 = 150 \text{ m}^3 = 150 \times 10^3 \text{ L}$; $T = 27^\circ\text{C} = 300 \text{ K}$; $P = 1 \text{ atm}$
 $PV = nRT \Rightarrow 1 \times 150 \times 10^3 = n \times 0.082 \times 300 \Rightarrow n = 6097.6$
 Total energy released per second = $150 \times 50 = 7500 \text{ J/sec}$.
 Amount of energy released by persons = energy gained by air $\Rightarrow [7500] t_{\text{sec}} = n C[dT]$
 $\Rightarrow 7500 t_{\text{sec}} = 6097.6 \times \frac{7}{2} \times 8.312 \times 15 \Rightarrow t_{\text{sec}} = 354.87 \text{ sec} = \frac{354.87}{60} = 5.91 \text{ minutes}$
- 40.** At constant volume $\Delta U = q_v = nC_{v,m} \Delta T = \frac{3}{2} R \times 300 = 450 R$
 At constant pressure $\Delta H = q_p = nC_{p,m} \Delta T = \frac{5}{2} R (-150) = -375 R$
- 41.** FACTUAL
42. FACTUAL
- 43.** Molar mass = 102 gram/mole
 $P = 650 \text{ torr}$; $T = 77 + 273 = 350 \text{ K}$
 $Q = i \times t = 0.25 \times 600 = 150$
 $E = Q \times V = 150 \times 12 = 1800 \text{ J}$
 This heat is supplied to the system at constant pressure that's why this is used for change in enthalpy
 \therefore For vaporisation of 1.8 gram, amount of heat required $q = 1800 \text{ J}$
 \therefore For vaporisation of 102 gram, amount of heat required $q = \frac{1800}{1.8} \times 102 \text{ J}$
 $= 102 \times 10^3 \text{ J} = 102 \text{ KJ/mole}$
 $\Delta H = \Delta U + P\Delta V$
 $\Delta H = \Delta U + \Delta n_g RT$
 For determination of ΔU per mol ($\Delta n_g = 1$)
 $102 \text{ (KJ/mol)} = \Delta U + (1 \times 8.3 \times 350) \times 10^{-3}$ $\Delta U = 102 - 2.9 = 99.1 \text{ KJ/mole}$
- 44.** In a perfect gas is no energy of interaction between the molecules of the gas, so change the distance between the molecular by changing the volume of the gas cannot affect the internal energy of the gas. U is independent of V . Hence internal pressure is zero.
- 45.** $W = +ve$ because work done on system.
 $W = 0$ because thermally insulated container.
- 47.** State 1 \longrightarrow State 2
 (1 L, 10 atm, 300 K) (4L, 5 atm, 600 K)
 Heat given, $q = 50 \times (600 - 300) = 15000 \text{ J}$
 $W = -P_{\text{ext}}(V_2 - V_1) = -1(4 - 1) = -3 \text{ L atm} = -300 \text{ J}$
 $\Delta E = q + W = 15000 - 300 = 14700 \text{ J}$
 $\Delta H = \Delta E + P_2V_2 - P_1V_1 = 14700 \text{ J} + (20 - 10) \times 100 \text{ J} = 15.7 \text{ KJ}$



48. $\therefore H = E + PV$ and $\Delta H = \Delta E + P\Delta V$
 $P\Delta V = nRT$.
 $\therefore \Delta H = \Delta E + nR\Delta T$
 For isothermal and reversible process
 $\Delta T = 0$.
 $\therefore \Delta H = \Delta E + 0$.
 $\therefore \Delta E = 0$. $\therefore \Delta H$ is also equal to zero.
49. $\Delta U = W$
 $nC_v (T_2 - T_1) = -P \times (V_2 - V_1)$
 $\frac{3}{2} R (T_2 - T_1) = -1 \Rightarrow \therefore T_2 = T - \frac{2}{3 \times 0.0821}$
50. From first law of Thermodynamics, $\Delta E = q + w \Rightarrow nC_v dT = nC_d T - PdV$ (1)
 Now according to process, $P = V$ and according to ideal gas equation, $PV = nRT$
 We have, $V^2 = nRT$
 On differentiating, $2VdV = nRdT$ and $PdV = VdV = \frac{nR}{2} dT$
 So, from first equation we have, $nC_v dT = nC_d T - \frac{nR}{2} dT$
 So, $C_v = C - \frac{R}{2}$ Hence, $C = \frac{4R}{2}$
51. $W = -P\Delta V = -1 \times 10^5 (1 \times 10^{-2} - 1 \times 10^{-3}) = -1 \times 10^5 \times 9 \times 10^{-3} = -900 \text{ J}$.
52. $N_2 + 3H_2 \rightarrow 2NH_3$ $\Delta n = 2 - 4 = -2$
 $\Delta H = \Delta U + \Delta nRT = \Delta U - 2RT$. $\therefore \Delta H < \Delta U$.
53. In isolated system, the expansion of gas is carried out adiabatically. Since heat exchange between system and surrounding is not possible i.e. $q = 0$ and secondary w_{rev} is always greater than w_{irr} therefore for reversible process there must be comparatively higher decreases in internal energy i.e. ΔU for reversible process will be more negative. Hence, final temperature in reversible process will be smaller than irreversible process.
 $\therefore (T_f)_{irr} > (T_f)_{rev}$
54. $\Delta S = nC_{v,m} \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} = C_{v,m} \ln 2 + R \ln \left(\frac{1}{2}\right) = (C_{v,m} - R) \ln 2$
55. $\Delta S_{system} = nR \ln \frac{V_2}{V_1} = 2 \times R \times \ln 2 = 11.52 \text{ J/K}$
 $\Delta S_{surrounding} = -\frac{3.41 \times 1000}{310} = -11 \text{ J/K}$
 $\Delta S_{total} = +11.52 - 11 = +0.52 \text{ J/K}$
56. $\Delta S = nC_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$
 For adiabatic process ($Q = 0$)
 $\Delta E = W \Rightarrow nC_v \ln \frac{T_2}{T_1} = -nR \ln \frac{V_2}{V_1} \therefore \Delta S = 0$.
57. $\Delta S = nC_{p,m} \ln \frac{T_2}{T_1} = 2.5 \times 18 \times 4.2 \ln \left(\frac{360}{300}\right) = 34.02 \text{ J/K}$

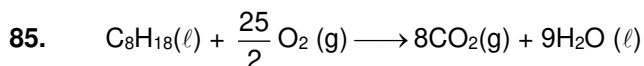


58. $\text{H}_2\text{O}(\text{l}) \longrightarrow \text{H}_2\text{O}(\text{g})$ $\Delta H_{\text{vap}} = \Delta S_{\text{vap}} T_{\text{B.P.}} = x_1 T_1$
 $\Delta H_f(\text{H}_2\text{O}, \text{g}) = \Delta H_f(\text{H}_2\text{O}, \text{l}) + \Delta H_{\text{vap}} = x_2 + x_1 T_1$
 $\Delta H_{\text{reaction}} = 2\Delta H_f(\text{CO}_2, \text{g}) + 3\Delta H_f(\text{H}_2\text{O}, \text{g}) - \Delta H_f(\text{C}_2\text{H}_6, \text{g})$
 $= 2x_3 + 3(x_2 + x_1 T_1) - x_4 = 2x_3 + 3x_2 + 3x_1 T_1 - x_4.$
59. Lesser the ΔG°_f , lesser its stability & easily it can decompose.
60. The compressor has to run for longer time releasing more heat to the surroundings.
61. All these are statements of second law of thermodynamics.
62. As dew formation is spontaneous process, therefore, entropy or randomness of the universe will increase. As randomness of the system has decreased but randomness of the surrounding will increase larger so that change is positive.
65. $\Delta S(\text{gas}) = nR \ln \frac{P_1}{P_2} = 3 \times 8.314 \times \ln 2 = 17.29 \text{ J/K}$
 Since $\Delta T = 0$, therefore $\Delta U = 0$,
 So, $q = -W$
 $= nRT \left[1 - \frac{P_2}{P_1} \right]$
 $q = T \times 12.47 \text{ J/K}$
 $\Delta S_{\text{surr}} = -\frac{q}{T} = -12.47 \text{ J/K}$
 Change in $\Delta S = +4.82 \text{ J/K}$
66. $0.40 = aT_1^3 + bT_1 \Rightarrow 0.40 = a \times (1000) + b \times 10 \Rightarrow 0.4 = 1000a + 10b \dots(1)$
 $0.92 = aT + bT_2 \Rightarrow 0.92 = a \times 8000 + 20b \dots(2)$
 from Eqs. (1) and (2)
 $a = 2 \times 10^{-5}, b = 0.038$
 $S_m = \int \frac{aT^3 + bT}{T} \cdot dT = \frac{a[T_2^3 - T_1^3]}{3} + b[T_2 - T_1] = 0.427 \text{ J/K-mol}$
67. (A) $\Delta G_{200}^\circ = \Delta H_{200}^\circ - T \Delta S_{200}^\circ$
 $\Delta H_{200}^\circ = 20 - 4 = 16 \text{ kJ/mol}$
 $\Delta H_{T_2}^\circ = \Delta H + \Delta C_p [T_2 - T_1]$
 $\Delta H_{400}^\circ = \Delta H_{200}^\circ + \frac{20 \times 200}{1000} \text{ kJ/mol} = 16 + 4 = 20 \text{ kJ/mol}.$
68. $\Delta S_{\text{reaction}} = 6(87) - 4X - 205 \Rightarrow x = 145.75 \text{ J/mole K}$
69. It is because of the fact that for spontaneity, the value of $\Delta G = (\Delta H - T\Delta S)$ should be < 0 . If ΔS is $-ve$, the value of $T\Delta S$ shall have to be less than ΔH or the value of ΔS has to be less than $\frac{\Delta H}{T}$ i.e., $\frac{x}{298}$.
71. $\Delta S = nC_v \ln \left(\frac{T_f}{T_i} \right) + nR \ln \left(\frac{V_f}{V_i} \right) = \frac{5}{2} \times 2 \ln \frac{373}{298} + 2 \ln 10$
72. (D) No. of moles of sucrose = $\frac{34.2}{342} = 0.1$
 $-(\Delta G)_{T,P} = \text{useful work done by the system}$
 $-\Delta G = -\Delta H + T \cdot \Delta S = + (6000 \times 0.1) + \frac{180 \times 0.1 \times 300}{1000} = 605.4 \text{ kJ}.$





73. $\Delta G = \Delta H - T\Delta S$
 $\Delta H = \sum \Delta H_p - \sum \Delta H_r$
 $\Delta H = -110.5 + 266.3 = 155.8 \text{ KJ}$
 $\Delta S = \sum S_p - \sum S_r$
 $\Delta S = 197.6 + 27.28 - (57.5 + 5.74) = 161.64 \text{ J/mole K}$
 For reaction to be spontaneous, $\Delta G < 0$
 $\Delta H - T\Delta S < 0 \Rightarrow T > \frac{\Delta H}{\Delta S} = \frac{155800}{161.64} = 964 \text{ K}$
74. Given that, $\Delta H_{\text{vaps}} = 30 \text{ kJ/mol} = 30 \times 10^3 \text{ J/mol}$.
 $\Delta S_{\text{vaps}} = 75 \text{ J/mol}$.
 We know that, $\Delta S = \frac{\Delta H_{\text{vap}}}{T_{\text{B.P}}}$
 $\therefore \Delta H = T\Delta S \Rightarrow 30 \times 10^3 = T \times 75$
 $T = 400 \text{ K}$
75. In adsorption there is bond formation between the gases and solid surface which decrease the entropy.
76. For spontaneous process, $\Delta G = -ve$, $K > 1$ and $E^\circ_{\text{cell}} = +ve$.
77. If $\Delta n = -ve$ then $\Delta H < \Delta U$.
78. $\text{CS}_2 (\ell) + 3\text{O}_2 (\text{g}) \longrightarrow \text{CO}_2 (\text{g}) + 2\text{SO}_2 (\text{g}) \quad \Delta H = -256 \text{ Kcal}$
 Let $\Delta H_f (\text{CO}_2, \text{g}) = -4x$ and $\Delta H_f (\text{SO}_2, \text{g}) = -3x$
 $\Delta H_{\text{reaction}} = \Delta H_f (\text{CO}_2, \text{g}) + 2 \Delta H_f (\text{SO}_2, \text{g}) - \Delta H_f (\text{CS}_2, \ell)$
 $-265 = -4x - 6x - 26$
 $x = +23.9$
 $\therefore \Delta H_f (\text{SO}_2, \text{g}) = 3x = -71.7 \text{ Kcal / mol}$
79. $\text{CH}_2 = \text{CH}_2 + \text{H}_2 \longrightarrow \text{CH}_3-\text{CH}_3 \quad \Delta H = X_1$
 So, Hydrogenation energy of benzene should be $3x_1$
 $\Delta H_{\text{calculated}} = 3x_1$
 So, Resonance energy = $[3x_1 - x_2]$
80. Required reaction $\Rightarrow 6\text{C}_{(\text{graphite})} + 3\text{H}_{2(\text{g})} \longrightarrow \text{C}_6\text{H}_{6(\text{g})}$
 1. $6\text{C}_{(\text{g})} + 6\text{H}_{(\text{g})} \longrightarrow \text{C}_6\text{H}_{6(\text{g})}$
 $\Delta H_1 = -(6 \times \Delta H_{\text{C-H}} + 3\Delta H_{\text{C=C}} + 3\Delta H_{\text{C-C}}) = -(6 \times 416 + 3 \times 591 + 3 \times 331) = -5262 \text{ kJ mole}^{-1}$
 2. $6\text{C}_{(\text{graphite})} \longrightarrow 6\text{C}_{(\text{g})} \quad \Delta H_2 = 6 \times 718 = 4308$
 3. $3\text{H}_{2(\text{g})} \longrightarrow 6\text{H}_{(\text{g})} \quad \Delta H_3 = 3 \times 436 = 1308$
 Adding (1) + (2) + (3)
 $6\text{C}_{(\text{graphite})} + 3\text{H}_{2(\text{g})} \longrightarrow \text{C}_6\text{H}_{6(\text{g})}$
 $\Delta H = \Delta H^\circ_f (\text{C}_6\text{H}_6, \text{g}) = \Delta H_1 + \Delta H_2 + \Delta H_3 = 354 \text{ kJ mole}^{-1}$
 Hence resonance energy = $\Delta H_f (\text{cal.}) - \Delta H^\circ_f (\text{theo}) = 354 - 83 = 271 \text{ kJ mole}^{-1}$
82. In neutralization of strong acid and base only H^+ and OH^- ions react in every case. So, heat of neutralization is remain constant and equal to -13.7 kcal (approximate).
83. Eqn. (ii) is for heat of neutralisation of strong acid with strong base. Eqn. (i) for weak acid with strong base. The difference $q_2 - q_1$ is heat of dissociation of weak acid.
84. $\text{H}_3\text{PO}_3 \longrightarrow 2\text{H}^+ + \text{HPO}_3^{2-}; \Delta_r H = ?$
 $2\text{H}^+ + 2\text{OH}^- \longrightarrow 2\text{H}_2\text{O};$
 $\Delta_r H = -55.84 \times 2 = -111.68$
 $-106.68 = \Delta_{\text{ion}} H - 55.84 \times 2$
 $\Delta_{\text{ion}} H = 5 \text{ kJ/mol}$



$$\Delta n_g = 8 - \frac{25}{2} = \frac{16 - 25}{2} = -\frac{9}{2} = -4.5$$

$$\Delta H - \Delta E = \Delta n_g RT = -\frac{4.5 \times 8.314 \times 298}{1000} = -11.15 \text{ kJ}$$

86. $\Delta C_P = C_P(\text{HCl}) - \frac{1}{2} C_P(\text{H}_2) - \frac{1}{2} C_P(\text{Cl}_2) = 6.81 - \frac{1}{2} \times 6.82 - \frac{1}{2} \times 7.71$
 $= 6.81 - 3.41 - 3.855 = -0.45$

$$\Delta H_{348} = \Delta H_{298} + (\Delta C_P)(\Delta T) = -22060 + (-0.45) \times 50 = -22082.5 \text{ cal}$$

87. Let mixture contain x mole of steam & y mole oxygen then,
 Here, temperature is constant. So, amount of heat released = amount of heat gain

$$x \times 132 = y(220) \quad \Rightarrow \quad \frac{x}{y} = \frac{220}{132} = \frac{1.66}{1} \quad \Rightarrow \quad y : x = 1 : 0.6$$

88. 12g C = 1 mole, suppose CO produced = x moles.

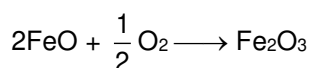
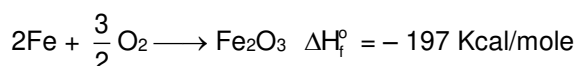
Then CO_2 produced = (1 - x) mole

$$\therefore x(-21.41) + (1-x)(-94.05) = -57.5$$

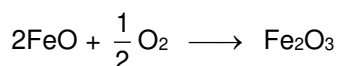
This on solving gives x = 0.54 mole.

89. $\text{FeO} + \text{Fe}_2\text{O}_3$

$$2x \quad x$$

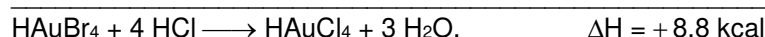
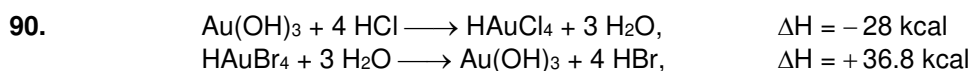


$$\Delta H = -197 + 65 \times 2 \Rightarrow \Delta H = -67 \text{ Kcal/mole}$$



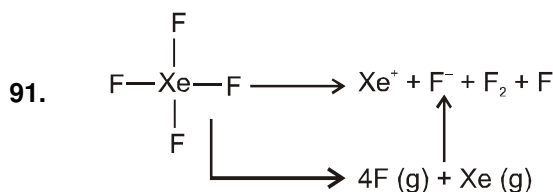
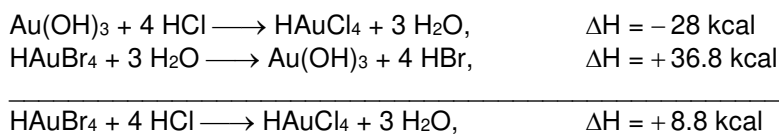
$$\frac{\frac{1}{3}}{\frac{2}{3} - 2x} = \frac{\frac{2}{3}}{\frac{1}{3} + x} \Rightarrow x = \frac{1}{5}$$

$$\text{So, energy released} = \frac{1}{5} \times 67 = 13.4 \text{ kcal/mole}$$



When 100% conversion, heat absorbed = 8.8 Kcal

$$\% \text{ conversion} = \frac{0.44}{8.8} \times 100 = 5\%$$



$$\Delta H = 4E_{\text{Xe-F}} + \Delta H_{\text{Ioni}} [\text{Xe} \longrightarrow \text{Xe}^+] - \Delta E_{\text{F-F}} - \Delta H_{\text{eg}} [\text{F} \longrightarrow \text{F}^-]$$

$$= 4 \times 34 + 279 - 85 - 38 = 136 + 279 - 123 = 415 - 213 = 292 \text{ kcal/mole.}$$

92. 1 M $\text{H}_2\text{SO}_4 = 2\text{g eq. of } \text{H}_2\text{SO}_4$

hence, $y = 2x$ or $x = \frac{1}{2}y$.

93. $Q = m S \Delta T_1 \Rightarrow \frac{Q_R}{2} = \frac{m}{2} S \Delta T_1 \Rightarrow \text{So, } \Delta T_1 = \Delta T_2$

94. Assuming density of solution is 1g/cc
and specific heat is 4.2 J/g-K

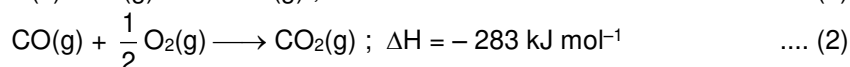
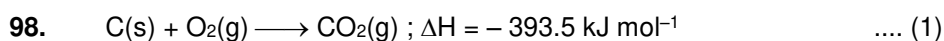
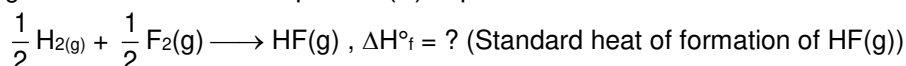
$$q = ms\Delta T = 100 \times 4.2 \times 3$$

millimoles of acid neutralized = 5

$$\Delta H = -100 \times 4.2 \times 3 \times \frac{1000}{5} = -2.52 \times 10^2 \text{ kJ/mole.}$$

96. HCOOH is a weak acid so heat of neutralization is less than x .

97. The amount of heat either evolved or absorbed when one gram mole of a substance is formed from its **constituent elements**, is known as the standard heat of formation (ΔH_f°).
Standard state temperature is 25°C or 298K and pressure of gaseous substance is one atmosphere.
Thus in given thermochemical equation '(B)' represents the standard heat of formation of HF .



On subtraction equation (2) from equation (1), we get $\text{C(s)} + \text{O}_{2(\text{g})} \rightarrow \text{CO(g)}; \Delta H = -110.5 \text{ kJ mol}^{-1}$.
The enthalpy of formation of carbon monoxide per mole = $-110.5 \text{ kJ mol}^{-1}$.

99. Let the bond dissociation energy of XY , X_2 and Y_2 be x , x and x , $\frac{x}{2}$ KJ/mol respectively,



$\Delta H_{\text{reaction}} = [(\text{sum of bond dissociation energy of all reactants}) - (\text{sum of bond dissociation energy of all product})]$

$$= \left[\frac{1}{2} \Delta H_{\text{X}_2} + \frac{1}{2} \Delta H_{\text{Y}_2} - \Delta H_{\text{XY}} \right] = \frac{x}{2} + \frac{0.5x}{2} - x = -200$$

$$\therefore x = \frac{200}{0.25} = 800 \text{ KJ mol}^{-1}.$$



100. $\frac{1}{2} \text{I}_2(\text{s}) + \frac{1}{2} \text{Cl}_2(\text{g}) \rightarrow \text{ICl}(\text{g})$ $\Delta H_f, \text{ICl}(\text{g}) = \left[\frac{1}{2} \Delta H_{\text{I}_2(\text{s}) \rightarrow \text{I}_2(\text{g})} + \frac{1}{2} \Delta H_{\text{I-I}} + \frac{1}{2} \Delta H_{\text{Cl-Cl}} \right] - [\Delta H_{\text{I-Cl}}]$
 $= \left[\frac{1}{2} \times 62.76 + \frac{1}{2} \times 151.0 + \frac{1}{2} \times 242.3 \right] - [211.3] = 16.73 \text{ kJ/mol.}$
102. $\Delta W = \int_1^{10} P dv = -20 \int_1^{10} \frac{dv}{V} = -20 [\ln(V)]_1^{10} = -20 \ln(10) = -4605 \text{ J}$
 $\Delta q = \Delta U - \Delta W$
 $= 400 - (-4605) = 5005 \text{ J} \approx 5 \text{ kJ.}$
103. $n = 4$
 $V_1 = 20 \text{ lit.} \quad V_2 = 60 \text{ lit}$
 $\Delta W = -P_{\text{ext}} (V_2 - V_1)$
 $= -\frac{125}{1000} \times (60 - 20) \times 100 = -500 \text{ J.}$
 In case of adiabatic process $\Delta q = 0$
 $\Delta U = 0 + \Delta W$
 $nC_p \Delta T = \Delta W$
 $4 \times \frac{5}{2} \times R \Delta T = -500$
 $\Delta T = -6 \text{ K}$
104. $\text{mole} = \frac{7.8}{78} = 0.1$
 $\Delta H = n \times \Delta H_{\text{vap}}$
 $= 0.1 \times 29.7 \text{ KJ} = 2.97 \text{ KJ} = 2970 \text{ J}$
 $\Delta H = \text{vaporization}$
 $t = \frac{\Delta H}{v.i} = \frac{2970}{11.4 \times .5}$
 $t = 540 \text{ second}$
 $t = 9 \text{ minute}$
105. $\text{C}_{(\text{graphite})} \longrightarrow \text{C}_{(\text{diamond})}$
 1 mole 1 mole
 $\rho = 2 \text{ g/cm}^3 \quad \rho = 3 \text{ g/cm}^3$
 $V = \frac{12}{2} \text{ ml} \quad V = \frac{12}{3} \text{ ml}$
 $\Delta H = \Delta U + P \Delta V$
 $\Delta U - \Delta H = -P \Delta V$
 $= -5 \times 10^5 \left(\frac{12}{3} - \frac{12}{2} \right) \times 10^{-3} \text{ L.atm} = -5 \times 10^5 \times \frac{12}{6} \times 10^{-1} \text{ J} = 100 \text{ KJ/mole} = 10 \times 10^4 \text{ J} = 100 \text{ KJ/mole}$
 $\frac{\Delta U - \Delta H}{20} = \frac{100}{20} = 5 \text{ Ans.}$
106. $\text{Avg. } C_{V, m} = \frac{n_1 C_{V, m_1} + n_2 C_{V, m_2}}{n_1 + n_2} = \frac{1 \times 3R + 2 \times \frac{3}{2}R}{3} = 2R$
 $T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1} \Rightarrow 320 \times 1^{\frac{3}{2}-1} = T_2 \times (4)^{\frac{3}{2}-1} \Rightarrow T_2 = 160 \text{ K}$
 $\Delta U = (n_1 + n_2) C_{V, \text{avg}} \Delta T = 3 \times 2R \times (160 - 320) = -960 R$
 $|(\Delta U/10R)| = |-960 R/10R| = 96$



107. This is adiabatic irreversible process so, for this process

$PV^\gamma = \text{Constant}$, is not applicable

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

But for adiabatic process

$$W = dU = \left(\frac{P_2 V_2 - P_1 V_1}{\gamma - 1} \right)$$

$$PV = nRT \Rightarrow 10 \times 10 = n \times 0.082 \times 273 \quad n = 4.47 \text{ moles}$$

$$-P_{\text{ext}}(V_2 - V_1) = \left(\frac{P_2 V_2 - P_1 V_1}{\gamma - 1} \right) \Rightarrow -1 \times (V_2 - 10) = \frac{1 \times V_2 - 10 \times 10}{1.67 - 1}$$

$$\Rightarrow (10 - V_2) = \frac{V_2 - 100}{0.67} \Rightarrow 6.7 - 0.67 V_2 = V_2 - 100 \Rightarrow 106.7 = 1.67 V_2 \Rightarrow V_2 = 64$$

108. $\Delta E = q + w \quad 60 = 50 + w \quad w = 10 \text{ J}$

109. $\Delta E = 0 \Rightarrow 20 \times 4.2 - 60 + W = 0$

$$W = -24 \text{ J.}$$

110. $\Delta S_{\text{sys}} = nR \ln \frac{V_2}{V_1} + nC_v \ln \frac{T_2}{T_1}$

$$\Delta S_{\text{system}} = nR \ln \frac{V_2}{V_1} = 2 \times 8.314 \ln 7.5 = \mathbf{33.6 \text{ J}} = 8 \text{ Cal.}$$

111. $\text{Hg}(\ell) \longrightarrow \text{Hg}(\text{g})$ at 433 K and 4.19 mm of Hg is reversible and $\Delta G = 0$ but ΔG for $\text{Hg}(\text{g})$ (4.19 mm of Hg) $\longrightarrow \text{Hg}(\text{g})$ (760 mm of Hg)

$$\text{with } \Delta G = nRT \ln \frac{P_2}{P_1} \quad \Delta G = 18 \text{ J/mol.}$$

112. (i) In case of adiabatic reversible expansion, $dq_{\text{rev}} = 0 \Rightarrow \Delta S = 0$.

(ii) In case of free expansion (Adiabatically)

$$W = 0, \quad q = 0, \quad \Delta U = 0 \Rightarrow nC_v(T_2 - T_1) = 0 \Rightarrow T_2 = T_1$$

$$\Delta S = nR \ln \left(\frac{V_2}{V_1} \right) = 2R \ln(3) = \mathbf{18 \text{ J/K.}}$$

113. Heat generated = $C_T \Delta T = 1260 \times 0.667 \text{ cal.}$

$$\therefore n_{\text{CH}_4} = \frac{2.108 \times 1}{210.8} = 0.01$$

$$n_{\text{total}} = \frac{PV}{RT} = 0.04 \quad \therefore \text{mol\%} = \frac{0.01}{0.04} \times 100 = 25\% \text{ Ans.}$$

114. Total mass of solution = $(150 + 150) = 300 \text{ g}$ $\{\rho_{\text{H}_2\text{O}} = 1 \text{ g/mL}\}$

$$Q_{\text{total}} = m\Delta T = 300 \times 1 \times (29 - 25) = 1200 \text{ Cal}$$

Since heat is liberated.

$$\text{Heat of neutralization} = \frac{Q}{150} \times 1000 \times \frac{1}{0.5} = \frac{1200}{150} \times 1000 \times \frac{1}{0.5} = 16 \text{ kcal}$$

Hence Heat of neutralization = -16 kcal

115. $2\text{C}_{(\text{s})} \longrightarrow 5\text{C}_{(\text{g})} \quad \Delta H_1 = 5 \times 718 = 3590$
 $4\text{H}_{2(\text{g})} \longrightarrow 8\text{H}_{(\text{g})} \quad \Delta H_2 = 4 \times 435 = 1740$
 $5\text{C}_{(\text{g})} + 8\text{H}_{(\text{g})} \longrightarrow \text{C}_5\text{H}_{8(\text{g})} \quad \Delta H_3 = -(8 \times 913 + 2 \times 348 + 2 \times 615) = -5230$
 (1) + (2) + (3)
 $5\text{C}_{(\text{s})} + 4\text{H}_{2(\text{g})} \longrightarrow \text{C}_5\text{H}_{8(\text{g})} \quad \Delta H_{\text{rxn}} = \Delta H_f(\text{C}_5\text{H}_8) = \Delta H_1 + \Delta H_2 + \Delta H_3 = 100$
 so resonance energy = $79 - 100 = -21 \text{ kJ mole}^{-1}$
 Hence resonance energy in $\text{Kcalmole}^{-1} = 5$





116. (i) $C(s) + O_2(g) \longrightarrow CO_2(g)$; $\Delta H_f^\circ = -390 \text{ KJ/mol}$; $\Delta H_f^\circ = \frac{585}{18} \times 12$
- (ii) $H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l)$; $\Delta H_f^\circ = -280 \text{ KJ/mol}$; $\Delta H_f^\circ = \frac{15540}{55.5}$
- (iii) $C_6H_6(l) + \frac{15}{2} O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(l)$; $\Delta H_f^\circ = -48$
- $\therefore \Delta H^\circ = [6(-390) + 3(-280)] - 48 = -3228 \text{ KJ/mol}$
- Mass of benzene is $= 0.87 \times 100 = 87 \text{ g}$
- \therefore Heat evolved from 87 g benzene $= 3600 \text{ KJ}$.
- Hence, $\frac{\Delta H}{100} = 36 \text{ kJ}$.

117. $\Delta H_{\text{ionization}} = \Delta H_{\text{neutralization of WA + SB}} - \Delta H_{\text{neutralization of SA + SB}}$
 $= -56.1 - (-57.3) = 1.2 \text{ KJ eq}^{-1}$
 Enthalpy of ionization for making 100% ionization when there is no ionization at all $= 1.5 \text{ KJ eq}^{-1}$
 \therefore % of ionization $= \frac{1.5-1.2}{1.5} \times 100 = 20\%$

118. $Fe_2O_3(s) + 3H_2(g) \longrightarrow 2Fe(s) + 3H_2O(l)$
 $\Delta H_{300 \text{ K}}^\circ = -35 \text{ kJ}$
 $\Delta H^\circ = -26 \text{ KJ}$
 $\Delta C_P = 2C_P(Fe, s) + 3C_P(H_2O, l) - C_P(Fe_2O_3, s) - 3C_P(H_2, g)$
 $\Delta C_P = 80$
 $-26 \times 10^3 = -80 \times 26720 + 80(\Delta T)$
 $\Delta T = 9$

119. $Na(s) + \frac{1}{2}Br_2(g) \longrightarrow NaBr(s)$
- $\downarrow \Delta H_{\text{sub}} = 137$ $\downarrow H_{\text{diss}} = 144$
 $Na(g)$ $Br(g)$
 $\downarrow \Delta H_{1st} = 496$ $\downarrow \Delta H_{1st} = -325$
 $Na^+(g) + Br^-(g)$
- $-\Delta H_{\text{Lattice energy}}$

so, $\Delta H_{rxn} = \Delta H_f(NaBr) = \Delta H_{\text{sub}} + \Delta H_{1st \text{ ionisation}}(Na) + \Delta H_{\text{diss.}}(Br_2(g)) + \Delta H_{1st \text{ e-affinity}} - \Delta H_{L.E.}$
 $= 137 + 496 + 144 - 325 - 742 = 294$

for .1 mole $\Rightarrow \Delta H_{rxn} = 29.4 \text{ kJ mole}^{-1}$

so, in kcal mole $^{-1}$ $\Delta H_{rxn} = \frac{29.4}{4.2} = 7 \text{ kcal mole}^{-1}$

120. $n = \frac{3.5}{28}$
 $\Delta T = T_2 - T_1 = 298.45 - 298 = 0.45$
 $C_V = 2.5 \text{ kJ K}^{-1} = 2500 \text{ JK}^{-1}$; $C_P = C_V + R = 2500 + 8.314 = 2508.314 \text{ JK}^{-1}$
 $Q_P = C_P \Delta T = 1128.74 \text{ J}$
 $\Delta H = \frac{Q_P}{n} = \frac{1128.74}{3.5/28} = 9030 \text{ J mol}^{-1} = 9.030 \text{ KJ mol}^{-1} = 9 \text{ KJ mol}^{-1}$.

121. $q = -w = nRT \ln \frac{V_2}{V_1} = 2700 \text{ J}$
 $\Delta S_{\text{gas}} = nR \ln \frac{V_2}{V_1} = 8.314 \times 2.303 \times \log 3 = 9 \text{ JK}^{-1}$
 $q = 2700 - 900 = 1800 \text{ J}$
 As entropy is a state function and ΔS of system will be same as above one.
 $\Delta S_{\text{gas}} = 9 \text{ J K}^{-1}$
 $\Delta S_{\text{surr}} = -\frac{1800}{300} = -6 \text{ J K}^{-1}$; $\Delta S_{\text{total}} = 3 \text{ J K}^{-1}$



122. I – Work done by the system in case of infinite stage expansion is more than single stage expansion.
 III – Single stage process is a irreversible process.
 IV – We have 5 points on PV diagram.

124. $\Delta H = (n_1 C_{p,m1} + n_2 C_{p,m2}) \Delta T = \left(0.5 \times \frac{7}{2} R + 0.5 \times 4 R \right) (-100) = -375 R$

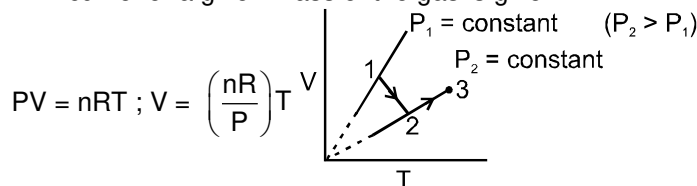
and $\Delta U = (0.5 \times \frac{5}{2} R + 0.5 \times 3R) (-100) = -275 R$.

125. $\Delta H = 4 \text{ KJ}$
 $\Delta H = \Delta U + \Delta(PV)$
 $\Delta U = 4 - P(V_2 - V_1)$
 $= 4 - \frac{10^5(18-19) \times 10^{-6}}{10^3} = 4 + 1 \times 10^{-4} = 4.0001 \text{ KJ}$

126. $1 \times V_f = 5 \times R \times 546 = 224 \text{ L}$
 $W = -P_{\text{ext}}(\Delta V) = -1 \text{ atm}(224 \text{ L}) = -224 \text{ L atm}$
 \therefore work done by system = 224 L atm
 Enthalpy change (ΔH) = $q = 273 \times 5 = 1365 \text{ L atm}$
 $\Delta U = q + W = 1365 - 224 = 1141 \text{ L atm}$.

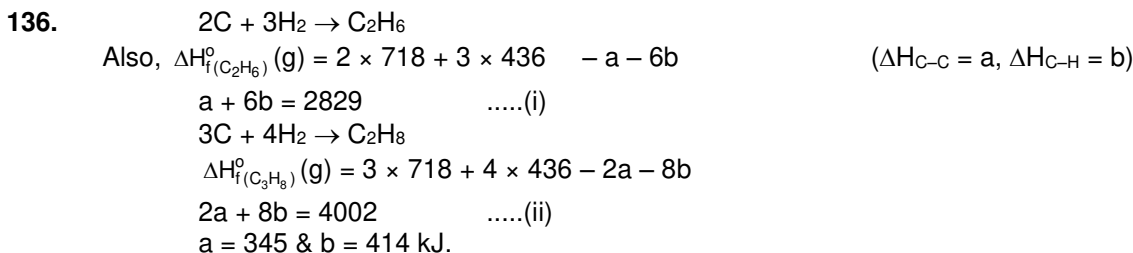
127. From graph, slope = -1
 $\therefore \log_{10} V + \log_{10} T = \text{constant}$
 $\therefore VT = \text{constant}$ or $PV^2 = \text{constant}$
 $C = C_v + \frac{R}{1-n} \therefore C = \frac{5R}{2} + \frac{R}{1-2} = \frac{3R}{2}$
 $\therefore q = nC\Delta T = 3 \times \frac{3R}{2} \times (1000-100) = 4050 R$
 $\Delta U = nC_v\Delta T = 3 \times \frac{5R}{2} \times (1000 - 100) = 6750 R$
 $\therefore W = \Delta U - q = 6750 R - 4050 R = 2700 R$

128. V-T curve for a given mass of the gas is given



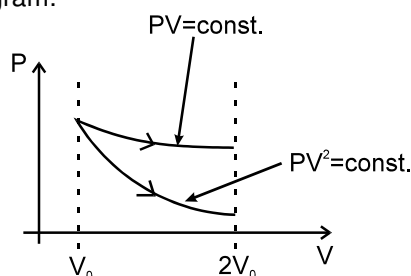
131. $\Delta S = nC_v \ln \left(\frac{T_f}{T_i} \right) + nR \ln \left(\frac{V_f}{V_i} \right) = 5 \ln \frac{373}{298} + 2 \ln 10$

$\Delta H = nC_p \Delta T = n(C_v + R) \Delta T = 1 \times 7 \times 75 = 525 \text{ cal}$

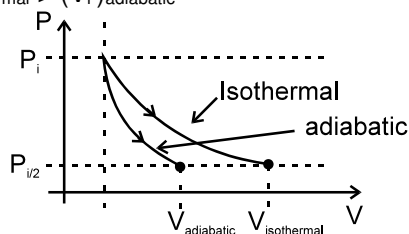




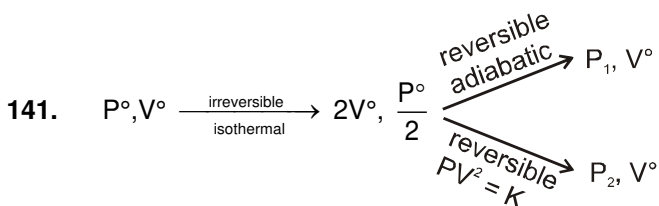
137. Work done in isothermal process will be more than $PV^2 = \text{const}$, process whatever be the value of K_1 and K_2 as is shown in the diagram.



138. Clearly $(V_f)_{\text{isothermal}} > (V_f)_{\text{adiabatic}}$



139. Work done in isothermal process is more than in adiabatic process as shown in the diagram above.



For reversible adiabatic,

$$\frac{P^\circ}{2} (2V^\circ)^\gamma = P_1 V_0^\gamma \Rightarrow P_1 = P^\circ 2^{\gamma-1}$$

For reversible $PV^2 = K$

$$\frac{P^\circ}{2} (2V^\circ)^2 = P_2 V_0^2 \Rightarrow P_2 = 2P^\circ$$

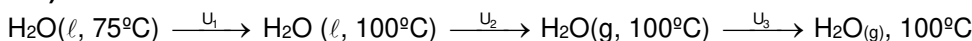
So, $P_2 > P_1$

Since final volume is same

$$P \propto T$$

So, $T_2 > T_1$

(142 to 144)



$$U_1 = nC_{V,m(\ell)} \Delta T = 1 \times 75 \times (100 - 75) = 1875 \text{ J}$$

$$U_2 = n \times \Delta H_{\text{vap}} - \Delta n_g RT = 1 \times 40700 - 1 \times 8.314 \times 373 = 37598.878 \text{ J}$$

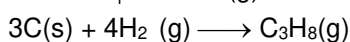
$$U_3 = nC_{V,m(\text{g})} \Delta T = n(C_{p,m(\text{g})} - R) \Delta T$$

$$= 1 \times (33.3 - 8.314) \times (120 - 100) = 24.986 \times 20 = 499.72 \text{ J}$$

(145 to 147)

Let moles of $\text{C}_3\text{H}_8 = x$, moles of $\text{C}_2\text{H}_2 = y$ & moles of $\text{CO}_2 = z$.

Calculation of ΔH_f° of $\text{C}_3\text{H}_8(\text{g})$



$$\Delta H_f^\circ \text{ of } \text{C}_3\text{H}_8(\text{g}) = [3(718) + 4(435)] - [2(347) + 8(416)]$$

$$= 3894 - 4022 = -128 \text{ kJ/mol.}$$





Calculations of ΔH_f° of $C_2H_2(g)$

$$\begin{aligned} 2C(s) + H_2(g) &\longrightarrow C_2H_2(g) \\ \Delta H_f^\circ \text{ of } C_2H_2(g) &= [2(718) + (435)] - [(812) + 2(416)] \\ &= (1436 + 435) - [1644] \\ &= 227 \text{ kJ/mol.} \end{aligned}$$

Calculations of ΔH_f° of $C_2H_4(g)$

$$\begin{aligned} 2C(s) + 2H_2(g) &\longrightarrow C_2H_4(g) \\ \Delta H_f^\circ \text{ of } C_2H_4(g) &= 2(718) + 2(435) - [615 + 4(416)] \\ &= 2306 - 2279 = 27 \text{ kJ/mol.} \end{aligned}$$

Calculation of $\Delta H_{\text{comb}}^\circ$ of $C_3H_8(g)$

$$\begin{aligned} C_3H_8(g) + 5O_2(g) &\longrightarrow 3CO_2(g) + 4H_2O(\ell) \\ \Delta H_{\text{comb}}^\circ \text{ of } C_3H_8 &= [3\Delta H_f^\circ(CO_2) + 4\Delta H_f^\circ(H_2O, \ell)] - \Delta H_f^\circ(C_3H_8, g) \\ &= [3(-394) + 4(-286)] - (-128) = -2198 \text{ kJ/mol.} \end{aligned}$$

Calculation of $\Delta H_{\text{comb}}^\circ$ of $C_2H_2(g)$

$$\begin{aligned} C_2H_2(g) + 2.5O_2(g) &\longrightarrow 2CO_2(g) + H_2O(\ell) \\ \Delta H_{\text{comb}}^\circ \text{ of } C_2H_2 &= [2\Delta H_f^\circ(CO_2) + \Delta H_f^\circ(H_2O, \ell)] - \Delta H_f^\circ(C_2H_2, g) \\ &= [2(-394) + (-286)] - 227 = -1301 \text{ kJ/mol.} \end{aligned}$$

Now total heat released during combustion

$$\begin{aligned} 2198x + 1301y &= 4800 \quad (i) \\ \text{Combustion} &= 3x + 2y + z = 10 \quad (ii) \end{aligned}$$

Total moles of $H_2O(\ell)$ formed = $4x + y$.

$$\text{moles of } C_2H_2(g) \text{ to be prepared} = \frac{3808}{22.4} = 170.$$

Total heat absorbed during evaporation of water formation of 170 moles C_2H_2 = 4800.

$$\begin{aligned} [(4x + y) \times 0.875 \times 40] + (170 \times 27) &= 4800 \\ 4x + y &= 6 \quad (iii) \end{aligned}$$

on solvent (i), (ii) and (iii)

$$\text{we get } x = 1, y = 2, \text{ and } z = 3$$

PART - IV

1. BC is a straight line & equation can be obtained by using

$$(y - y_1) = \frac{y_2 - y_1}{x_2 - x_1} (x - x_1)$$

$$(P - 3P^\circ) = \frac{P^\circ - 3P^\circ}{2V^\circ - V^\circ} (V - V^\circ) \Rightarrow (P - 3P^\circ) = -\frac{2P^\circ}{V^\circ} (V - V^\circ) \quad \dots (1)$$

Replacing P by T by using $P = \frac{RT}{V}$ in equation (1)

$$\left(\frac{RT}{V} - 3P^\circ \right) = -\frac{2P^\circ}{V^\circ} (V - V^\circ) \Rightarrow T = \frac{2P^\circ V(V - V^\circ)}{V^\circ R} + \frac{3P^\circ V}{R}$$

For T to be maximum

$$\frac{dT}{dV} = 0$$

$$\frac{dT}{dV} = -\frac{2P^\circ(2V - V^\circ)}{V^\circ R} + \frac{3P^\circ}{R} = 0 \Rightarrow V = \frac{5}{4} V^\circ$$

$$T_{\text{max}} = -\frac{2P^\circ \times \frac{5}{4} V^\circ \left(\frac{5}{4} V^\circ - V^\circ \right)}{V^\circ R} + \frac{3P^\circ \times \frac{5}{4} V^\circ}{R} = \frac{25}{8} \left(\frac{P^\circ V^\circ}{R} \right)$$





$$\begin{aligned} 2. \quad \Delta H^\circ &= -3\Delta H_1^\circ + \Delta H_2^\circ + 2\Delta H_3^\circ + 3\Delta H_4^\circ \\ &= -747.4 \text{ kJ} \end{aligned}$$

$$\begin{aligned} \Delta H^\circ &= \Delta U^\circ + \Delta n_g RT; \text{ where } \Delta n_g = -8 \\ -747.4 &= \Delta U^\circ - \frac{8 \times 8.314 \times 300}{1000} \end{aligned}$$

$$\Delta U^\circ = -727.44 \text{ kJ.}$$

$$3. \quad \text{For } H_2(g) + O_2(g) \longrightarrow H_2O_2(l)$$

$$\Delta_f H^\circ (H_2O_2, l) = \Delta_f H^\circ + \frac{\Delta_r H_2^\circ}{2} - \frac{\Delta_r H_1^\circ}{2}$$

$$4. \quad HA \longrightarrow H^+ + A^-; \Delta_r H = 1.4 \text{ kJ/mol}$$

$$\Delta H_{\text{neutralization}} = \Delta H_{\text{ionization}} + \Delta_r H \text{ of } (H^+ + OH^- \longrightarrow H_2O)$$

$$-55.95 = \Delta H_{\text{ionization}} - 57.3$$

$$\Delta H_{\text{ionization}} \text{ for 1 M HA} = 1.35 \text{ kJ/mol}$$

$$\% \text{ heat utilized by 1 M acid for ionization} = \frac{1.35}{1.4} \times 100 = 96.43\%$$

$$\text{So, acid is } 100 - 96.43 = 3.57\% \text{ ionized.}$$

$$5. \quad \Delta_f S^\circ (NH_4Cl, s) \text{ at } 300 \text{ K}$$

$$= S_{NH_4Cl(s)}^\circ - \left[\frac{1}{2} S_{N_2}^\circ + 2S_{H_2}^\circ + \frac{1}{2} S_{Cl_2}^\circ \right]$$

$$= -374 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$\Delta_f C_p = 0$$

$$\begin{aligned} \therefore \Delta_f S_{310}^\circ &= \Delta_f S_{300}^\circ \\ &= -374 \text{ JK}^{-1} \text{ mol}^{-1} \end{aligned}$$

$$\Delta_f H_{310}^\circ = \Delta_f H_{300}^\circ = -314.5$$

$$\Delta_f G_{310}^\circ = \Delta_f H^\circ - 310 \Delta S^\circ = -314.5 - \frac{310(-374)}{1000} = -198.56 \text{ kJ/mol.}$$

$$6. \quad 0.42 = a(10)^3 \Rightarrow a = 0.42 \times 10^{-3}$$

$$S_m = \int_0^{10} \frac{C_{p,m}}{T} dT = \int_0^{10} aT^2 = \frac{a}{3} [10^3 - 0] = \frac{0.42}{3} = 0.14 \text{ J/K-mol}$$

$$7. \quad \Delta G = \Delta H - \Delta(TS)$$

$$= \Delta H - T\Delta S \quad (\text{isothermal})$$

$$= 0 - T\Delta S = -T \left(\int \frac{dq_{\text{rev}}}{T} \right)$$

$$= - \int dq_{\text{rev}} = -q_{\text{rev}} = W_{\text{rev}}$$

$$\text{as process is isothermal so } \Delta E = 0 = q_{\text{rev}} + W_{\text{rev}}$$

$$\text{so } \Delta G = -nRT \ln \left(\frac{V_f}{V_i} \right)$$

$$\begin{aligned} &= -RT \ln 2 = -8.314 \times 300 \times 0.693 \times 10^{-3} \text{ KJ mol}^{-1} \text{ K}^{-1} \\ &= -1.728 \text{ KJ mol}^{-1} \text{ K}^{-1} \end{aligned}$$

$$8. \quad \Delta G = \int_{P_1}^{P_2} V dP - \int_{T_1}^{T_2} S dT = 24.6 \left(\frac{4}{3} - 1 \right) \times 100 - \int (10 + 10^{-2} T) dT$$

$$= 820 - \left[10 (T_2 - T_1) + \frac{10^{-2} (T_2^2 - T_1^2)}{2} \right] = 820 - \left[10 (400 - 300) + 10^{-2} \frac{[(400)^2 - (300)^2]}{2} \right]$$

$$= 820 - 1000 - 350 = -530 \text{ J}$$



9. (A) ΔE will be -ve for combustion reactions
 (B) ΔH_f° (S, rhombic) = 0
 (C) $\text{CH}_4(\text{g}) \longrightarrow \text{C}(\text{g}) + 4\text{H}(\text{g}) \quad \Delta H = 1656 \text{ kJ/mole} = 4 \Delta H_{\text{C-H}}$
 $\text{C}_2\text{H}_6(\text{g}) \longrightarrow 2\text{C}(\text{g}) + 6\text{H}(\text{g}) \quad \Delta H = 2812 \text{ kJ/mole} = 6 \Delta H_{\text{C-H}} + \Delta H_{\text{C-C}}$
 so $\Delta H_{\text{C-C}} = (2812 - \frac{6}{4} \times 1656) \text{ kJ/mole} = 328 \text{ kJ/mole}$
 (D) Can not be concluded from given data.
10. (D) $\text{BOH}(\text{g}) + \text{aqueous} \longrightarrow \text{B}^+(\text{aq}) + \text{OH}^-(\text{aq}) \quad \Delta H = -20 \text{ kJ/mole}$
11. More heat is evolved due to combustion of less stable form.
12. (A) Reversible adiabatic process is isoentropic
 (B) Reaction is spontaneous, need not be exothermic.
 (C) Only when PV work is involved
 (D) $\Delta S_{\text{system}} = \frac{\Delta H_{\text{system}}}{T_b} = -\frac{40600}{373 \times 2} = -54.42 \text{ J/K}$
13. The given reaction will be spontaneous when ΔG would be negative when $\Delta H - T\Delta S$ is negative. That is,
 or $\frac{\Delta H - T\Delta S < 0}{T >}$ or $\frac{T\Delta S > \Delta H}{T >}$ or $T > 463.4 \text{ K}$
14. $S_{200}(\text{B}) = \int_0^{200} \frac{C_p}{T} dT = 7 \text{ J mol}^{-1} \text{ K}^{-1}$
 $S_{200}(\text{f}) = 7 + \frac{7500}{200} = 44.5 \text{ J mol}^{-1} \text{ K}^{-1}$
 $S_{300}(\text{f}) = 44.5 + \int_{200}^{300} \frac{C_p}{T} dT = 44.5 + 60 \ln \frac{300}{200} + 1.6 = 70.43 \text{ J mol}^{-1} \text{ K}^{-1}$
 $S_{300}(\text{g}) = 70.43 + \frac{30000}{300} = 170.43 \text{ J mol}^{-1} \text{ K}^{-1}$
 $S_{600}(\text{g}) = 170.43 + 50 \ln \frac{600}{300} = 205.09 \text{ J K}^{-1} \text{ mol}^{-1}$
15. (a) State A to state B (Isobaric expansion)
 Work done by the gas = $W_1 = -p(V_B - V_A) = -1(40 - 20) = -20 \text{ L atm}$
 (b) State B to state C (isochoric process)
 Work done by the gas = $W_2 = 0$ ($\because \Delta V = 0$)
 (c) State C to state A (Isothermal compression)
 Work done on the gas = $W_3 = -2.303 nRT \log \frac{V_A}{V_C}$
 $= -2.303 pV \log \frac{V_A}{V_C}$ ($pV = p_A V_A = p_B V_B = nRT = 20$) $= -20 \ln(2) = 20 \times \ln(2) = 14$
 \therefore total work done by the gas = $W_1 + W_2 + W_3 = -20 + 0 + 14 = -6 \text{ L atm}$
16. (a) $0.25 \times 2808 \times \frac{x}{180} \times 10^3 = 62.5 \times 9.81 \times 3$
 $x = 0.47 \text{ g}$
 (b) $0.25 \times 2808 \times 10^3 \times \frac{y}{180} = 62.5 \times 9.81 \times 6000$
 $Y = 940 \text{ g}$
 $Y = mX \quad \Rightarrow \quad 940 = m \times 0.47 \quad \Rightarrow \quad m = 2000$



17. $W = -P_{\text{ext}} (V_f - V_i) = - (1 \text{ atm}) (8 - 2) \text{ L} = -6 \text{ L atm}$
as $q = 0$ so

$$\Delta E = W \Rightarrow 3 (8 P_f - 12) = -6$$

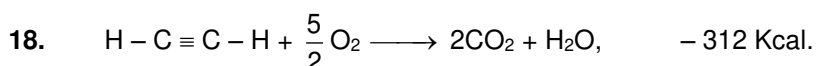
$$8 P_f = 12 - \frac{6}{3} = 10 \Rightarrow P_f = \frac{5}{4} \text{ atm}$$

so, $\frac{T_f}{T_i} = \frac{\frac{5}{4} \times 3}{6 \times 2} = \frac{10}{12}$

so $\Delta S = n C_{V,m} \ln \left(\frac{T_f}{T_i} \right) + n R \ln \left(\frac{V_f}{V_i} \right) = 3 \times \frac{12}{300} \ln \left(\frac{10}{12} \right) + \frac{12}{300} \ln 4$

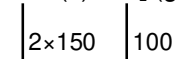
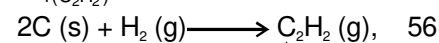
$$= 3.312 \text{ J/K}$$

Ans. 3 J/K



$$-312 = [2(-94) + (-68)] - \Delta H_f(\text{C}_2\text{H}_2) \cdot$$

$$\Delta H_f(\text{C}_2\text{H}_2) = 56 \text{ Kcal.}$$



$$56 = [(2 \times 150) + 100] - [(2 \times 95) + x].$$

$$x = 154 \text{ Kcal.}$$

$$\frac{\Delta H_{\text{C} \equiv \text{C}}}{22} = 7$$

19. Heat evolved per mol of 'B' atoms = $\frac{5}{2} \times 200 = 500 \text{ kJ}$

20. In isothermal reversible process.

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

$$q = -w = 2.303 RT \log \frac{V_2}{V_1}$$

$$= 2740.6 \text{ J/mole}$$

$$\Delta S_{\text{surr.}} = \frac{q_{\text{rev}}}{T} = \frac{2740.6}{300} = 9.135 \text{ J/K mole}$$

$$\Delta S_{\text{surr.}} = -\Delta S_{\text{system}} = -9.135 \text{ JK}^{-1} \text{ mole}^{-1}$$

$$\Delta S_{\text{universe}} = 0$$

21. $\Delta H^\circ = \Delta H_f^\circ \text{ of } \text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O (s)} + \Delta H_f^\circ \text{ of } \frac{3}{2} \text{H}_2\text{O (g)} - \Delta H_f^\circ \text{ of } \text{CaSO}_4 \cdot 2\text{H}_2\text{O (s)} = +83 \text{ kJ mol}^{-1}$

22. $\Delta S^\circ = 119.5 + (188 \times 1.5) - 194 = 207.5 \text{ J/K mol}$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ = 19550 \text{ J mol}^{-1}$$

$$\Delta G^\circ = -2.303 RT \log K_p = -2.303 R \times 300 \log (P_{\text{H}_2\text{O}})^{3/2}$$

$$\log P_{\text{H}_2\text{O}} = -\frac{19550}{8645.83} = -2.26; \quad P_{\text{H}_2\text{O}} = 4 \times 10^{-3} \text{ atm}$$





23. $P_{H_2O} = 1, K_p = 1$

$\Delta G^\circ = 0$ at eqm.

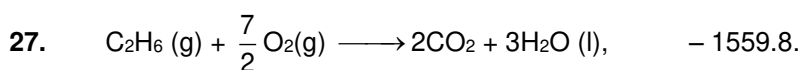
$$\Delta H^\circ - T\Delta S^\circ \Rightarrow T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{83000}{207.5} = 400 \text{ K} = 127^\circ\text{C}$$

(24 to 26)

1. $-q_c = q_h \left(\frac{T_c}{T_h} \right) = 150 \times \frac{200}{1000}$ Heat rejected = 30 kJ

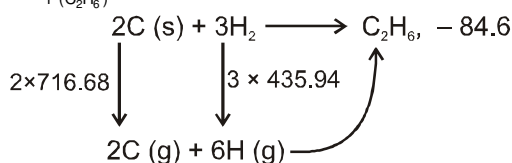
2. $\Delta S = \frac{q_{rev}}{T} = \frac{q_h}{T_h} = \frac{150 \times 10^3}{1000} = 150 \text{ JK}^{-1}$

3. $\Delta G = \Delta H - T\Delta S$; $\Delta H = 0$; $\Delta S = 150 \text{ JK}^{-1}$; $\Delta G = -150 \text{ kJ}$



$-1559.8 = 2 \times (-393.5) + 3 \times (-285.8) - \Delta H_f(C_2H_6)$

$\Rightarrow \Delta H_f(C_2H_6) = -84.6.$

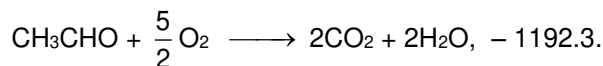


$\Delta H' = 0 - 6 \times BE_{C-H} - BE_{C-C}.$

$2 \times 716.68 + 3 \times 435.94 - 6BE_{C-H} - BE_{C-C} = -84.6.$

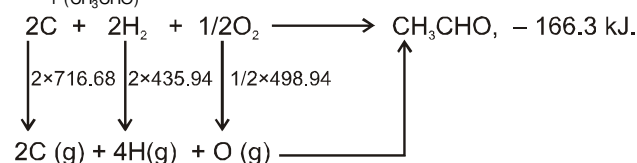
$6BE_{C-H} + BE_{C-C} = 2741.18 \text{ kJ.}$

.....(i)



$-1192.3 = 2 \times (-393.5) + 2 \times (-285.8) - \Delta H_f(CH_3CHO)$

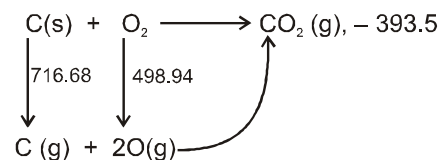
$\Delta H_f(CH_3CHO) = -116.3 \text{ kJ.}$



$\Delta H' = 0 - 4 \times BE_{C-H} - BE_{C=O}.$

$-166.3 = 2 \times 716.68 + 2 \times 435.94 + \frac{1}{2} \times 498.94 - 4BE_{C-H} - BE_{C=O}$

.....(ii)



$\Delta H' = 0 - 2 \times BE_{C=O}.$

$716.68 + 498.94 - 2 \times BE_{C=O} = -393.5.$

$BE_{C=O} = 804.56 \text{ kJ.}$

.....(iii)

Now we can find all bond energies.