Chapter 10

THERMODYNAMICS AND THERMOCHEMISTRY

1. INTRODUCTION

It is the study of flow of energy. It encompasses the study of flow of heat as well as mass.

The law of thermodynamics deals energy changes of macroscopic systems involving a large number of molecules rather than microscopic systems containing a few molecules. Thermodynamics is not concerned about how and at what rate these energy transformations are carried out, but is based on initial and final states of a system undergoing the changes.

2. THERMODYNAMIC TERMS

2.1 System and The Surroundings

A system in the thermodynamics refers to that part of universe in which observations are made and remaining universe constitutes the surroundings. The surroundings include everything other than the system. System and the surroundings together constitute the universe.

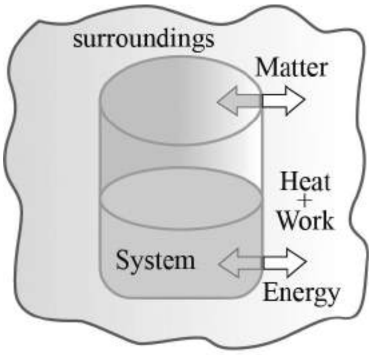
The Universe = The System + The Surrounding

2.2 Types of System

2.2.1 Open System

In an open system, there is exchange of energy and matter between system and surroundings. The presence of reactants in an open beaker is an example of an open system.

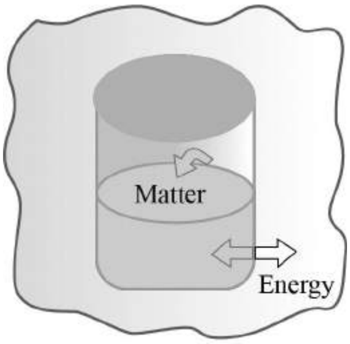
Here the boundary is an imaginary surface enclosing the beaker and reactants.



Open system

2.2.2 Closed System

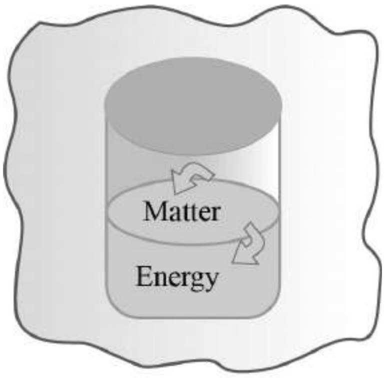
In a closed system, there is no exchange of matter, but exchange of energy is possible between system and the surroundings. The presence of reactants in a closed vessel made of conducting material. i.e., Copper or steel, is an example of a closed system.



Closed system

2.2.3 Isolated System

In an isolated system, there is no exchange of energy or matter between the system and the surroundings. The presence of reactants in a thermos flask or any other closed insulated vessel is an example of an isolated system.



Isolated system

2.3 State of a System

In thermodynamics, state of the system defined by state functions and state variables.

2.3.1 State Functions

These physical quantities whose value depend only upon the status of the the system and does not depend upon the path by which this state has been attained are said to be state function. In other words, if the physical quantity depends only upon the initial state and final state of the system independent of the path by which this change had been brought upon is known as a state function. Some common state functions are pressure (p), volume (V), temperature (T), internal energy (U), enthalpy (H), entropy (S), etc.

2.3.2 State Variables

If any of P, V or T is changed, it act as state variable and the other which depends on first one are state functions.

2.3.3 Path Functions

Functions, which are associated with the path they carried through, are called path functions. Values of path functions varies if the followed path is different. The common path funtions are heat and work.

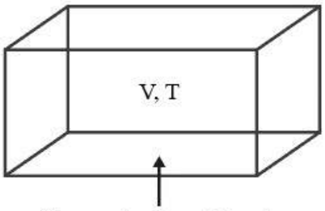
2.4 Extensive and Intensive Properties

In thermodynamics, a distinction is made between extensive properties and intensive properties. An extensive property is a property whose value depends on the quantity or size of matter present in the system. For example, mass, volume, internal energy, enthalpy, heat capacity, etc. are extensive properties.

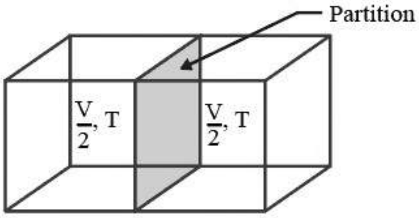
Those properties which do not depend on the quantity or size of matter present are known as intensive properties. For example temperature, density, pressure etc. are intensive properties.

Example

A container having the volume V, contains water at temperature 25ºC . If we put a partition exactly in the middle, each part will have a volume V/2, but the temperature will remain same, i.e, 25ºC.



(A gas at volume V and temperature T)



(Each part having half the volume of the gas)

Extensive and intensive properties

2.5 Thermodynamic Processes

Let us consider a system having P_1V_1 and T_1 state functions if T_1 is chaged to T_2 then the resulting system is characterized by state functions P_1V_1 and T_2 and the process of changing state is called thermodynamic process. A thermodynamic process can be defined as a process having change in state of system. These are of following types:

2.5.1 Isothermal Process

The thermodynamic process in which temperature remains constant throughout is called isothermal process.

2.5.2 Adiabatic Process

The thermodynamic process in which heat exchange between system and surrounding is not possible.

2.5.3 Isobaric Process

The thermodynamic process occurrring at constant pressure is called isobaric process.

2.5.4 Isochoric Process

The thermodynamic process occurring at constant volume is called isochoric process.

2.5.5 Cyclic Process

The therymodynamic process having same initial and final state is called cyclic process.

2.6 Thermodynamic Equilibrium

A system is said to be under thermodynamic equilibrium when none of the state variables are changing and it satisfies the three equilibriums.

2.6.1 Mechanical Equilibrium

There is no mechanical motion and the pressure and the volume of the system are not changing.

2.6.2 Thermal Equilibrium

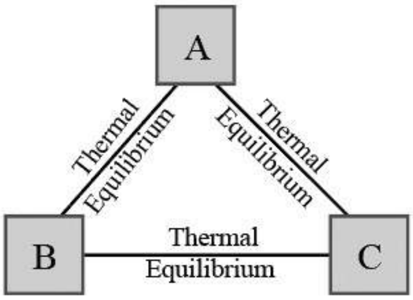
There is no flow of heat and the temperature and the system does not change with time.

2.6.3 Chemical Equilibrium

If any chemical reaction is taking place in the system then the rate of forward reaction is equal to the rate of backward reaction which means that the overall moles of the system is constant.

3. ZEROTH LAW OF THERMODYNAMICS

This statement just says that, if body 'A' is in thermal equilibrium with body 'B' and body 'B' is in thermal equilibrium with body 'C' then body 'A' will also be in thermal equilibrium with body 'C' and all three will be in thermal equilibrium with each other.



Zeroth law of thermodynamics

4. INTERNAL ENERGY

A thermodynamic system containing some quantitiy of matter is itself associated with a certain quantity of energy. It is the sum of all different types of energies associated with atoms and molecules such as electronic energy (E_e), nuclear energy (E_n), chemical bond energy (E_c), potential energy (E_p) and kinetic energy (E_k). This total energy of a system always implies internal energy represented by the symbol 'U'. Thus

$$U = E_e + E_n + E_c + E_p + E_k$$

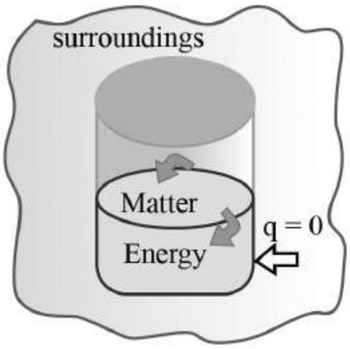
The change in internal energy can be brought about whenever heat is absorbed or realeased by the system, work is done on or by the system or matter enters or leaves the system.

5. CONCEPT OF HEAT AND WORK

5.1 Thermodynamic Work

Let us first examine a change in internal energy by doing work. We take a system containing some quantity of water in a thermo flask or in an insulated beaker.

Let us bring the change in the internal energy of the system by doing some work on it.



Adiabatic system

Let us call the initial state of the system as state A and its temperature as T_A. Let the internal energy of the system in state A be called U_A. We can change the state of the system in two different ways.

First way: We do some mechanical work, say 1 kJ, by rotating a set of small paddles and thereby churning water. Let the new state be called B state and its temperature, as T_B. It is found that $T_B > T_A$ and the change in temperature, $\Delta T = T_B - T_A$. Let the internal energy of the system in state B be U_B and the change in internal energy, $\Delta U = U_B - U_A$.

Second way: We now do an equal amount (i.e., 1 kJ) electrical work with the help of an immersion rod and note down the temperature change. We find that the change in temperature is same as in the earlier case, say, $T_B - T_A$.

In fact, the experiments in the above manner were done by J. P. Joule between 1840–50 and he was able to show that a given amount of work done on the system, no matter how it was done (irrespective of path) produced the same change of state, as measured by the change in the temperature of the system.

So, the adiabatic work, w_{ad} required to bring about a change of state is equal to the difference between the value of U in one state and that in another state, ΔU i.e.,

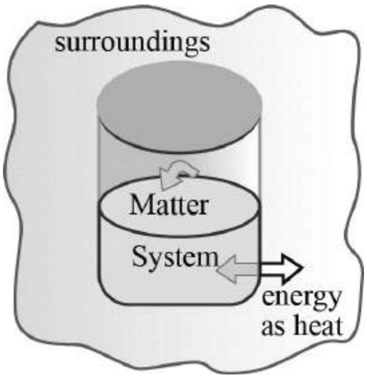
$$\Delta U = U_2 - U_1 = w_{ad}$$

Therefore, internal energy, U, of the system is a state function.

By conventions of IUPAC in chemical thermodynamics. The positive sign expresses that w_{ad} is positive when work is done on the system and the internal energy of system increases. Similarly, if the work is done by the system, w_{ad} will be negative because internal energy of the system decreases.

5.2 Heat

We can also change the internal energy of a system by transfer of heat from the surroundings to the system or vice-versa without expenditure of work. This exchange of energy, which is a result of temperature difference is called heat, q. Let us consider bringing about the same change in temperature by transfer of heat through thermally conducting walls instead of adiabatic walls.



Non-adiabatic system

We take water at temperature, T_A in a container having thermally conducting walls, it in a huge heat reservoir at temperature, T_B.The heat absorbed by the system (water), q can be measured in terms of temperature difference , $T_B - T_A$. In this case change in internal energy,

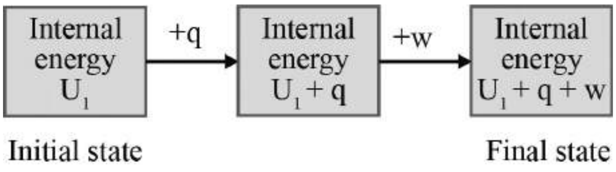
$\Delta U = q$, when no work is done at constant volume. By conventions of IUPAC in chemical thermodynamics. The q is positive, when heat is transferred from the surroundings to the system and the internal energy of the system increases and q is negative when heat is transferred from system to the surroundings resulting in decrease of the internal energy of the system.

6. FIRST LAW OF THERMODYNAMICS

Let us consider the general case in which a change of state is brought about both by doing work nad transfer of heat. The change in internal energy for this case can be written as

$$\Delta U = q + w$$

Lets simplify it through a diagrammatic representation of system undergoing changes.



First law of thermodynamics

Now the final internal energygy U_2 is given by

$$U_2 = U_1 + q + w$$

$$\text{or } U_2 - U_1 = q + w$$

$$\text{or } \Delta U = q + w$$

i.e., change in internal energy = Heat absorbed + Work done on the system

For a given change in state, q and w can vary depending on how the change is carried out. However $q + w = \Delta U$ will depend only on initial and final state. It will be independent of the way the change is carried out. If there is no transfer of energy as heat of energy as heat or as work (isolated system) i.e., if $w = 0$ and $q = 0$, then $\Delta U = 0$.

The equation, $\Delta U = q + w$ is a mathematical statement of the first law of thermodynamics which states that, **"Energy can neither be created nor be destroyed although it may be changed from one form to another".**

From this statement it follows that total energy of the universe, i.e., system and surroundings taken together is always constant during any physical or chemical process.

7. CONCEPT OF REVERSIBILITY

A process whose direction can be changed by an infinitesimal change to the system or surroundings and which can be reversed by retracing the original path and the system is restored to the initial state. The driving force of a reversible process is very-very small and such a process is extremely slow. For a process to be reversible there must not be any dissipative forces and also the system should be in a Quasi Static State.

7.1 Quasi Static State

A quasi static state means that the system seems to be static at all intervals of time but actually is not. The motion is so slow that it is almost impossible to detect the motion and the system seems to be in equilibrium with the surroundings at all instants of time.

7.2 Irrversible Process

Processes other than reversible processes are known as irreversible process as these processes do not meet the requirements of reversibilty. So it can be defined as "When a process goes from initial to final state in a single step and can not be carried out in the reverse order, it is said to be an irreversible process".

Difference between Reversible Process and Irreversible Process

S.NO.	Reversible Process	Irreversible process
1.	It takes place in infinite number of number of infinitesimally small steps and it would take infinite time to occur	It takes place in single step
2.	It is imaginary as it assumes the presence of, frictionless and weightless piston	It is real and can be performed actually
3.	It is in the state of equilibrium at all the stages of operation	It is an equilibrium state only at the initial and final stages of the operation
4.	All changes are reversed when the process is carried out in reversible direction	After the occurring of the process changes do not return to the initial state by themselves
5.	It is extremely slow.	It proceeds at measureable speed.
6.	Work done by a reversible process is greater than the corresponding irreversible process	Work done in irreversible process is smaller than the corresponding reversible process.

8. EXPANSION WORK

First of all, let us concentrate on the nature of work a system can do. We will consider only pressure-volume work.

For understanding pressure-volume work, let us consider a cylinder which contains one mole of an ideal gas fitted with a frictionless piston. Total volume of the gas is V_i and pressure of the gas inside is p. If external pressure is p_{ex} which is greater than p, piston is moved inward till the pressure inside becomes equal to p_{ex}. Let this change be achieved in a single step and the final volume be V_f. During this compression, suppose piston moves a distance, l and is cross-sectional area of the piston is A.

then, volume change $= \ell \times A = \Delta V = \left(V_f - V_i\right)$

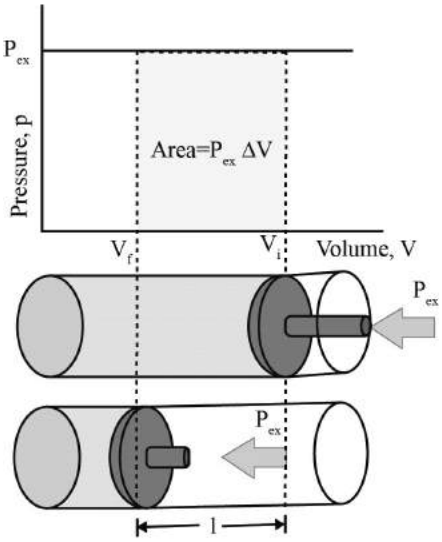
We also know, pressure $= \dfrac{\text{force}}{\text{area}}$

Therefore, force on the piston $= p_{ex} \cdot A$

If w is the work done on the system by movement of the piston then

$w = \text{force} \times \text{distance} = p_{ex}.A.\ell$

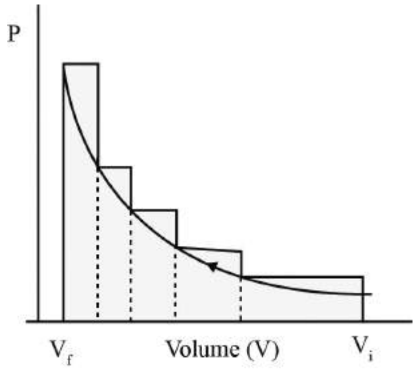
$= p_{ex} \cdot (-\Delta V) = -p_{ex}\,\Delta V = -p_{ex}\,(V_f - V_i)$



Work done on an ideal gas in a cylinder when it is compressed by a constant external pressure

The negative sign of this expression is required to obtain conventional sign for w, which will be positive. It indicates that in case of compression work is done on the system. Here $(V_f - V_i)$ will be negative and negative multiplied by negative will be positive. Hence the sign obtained for the work will be positive.

If the pressure is not constant at every stage of compression, but changes in number of finite steps, work done on the gas will be summed over all the steps and will be equal to - $\sum p\,\Delta V$

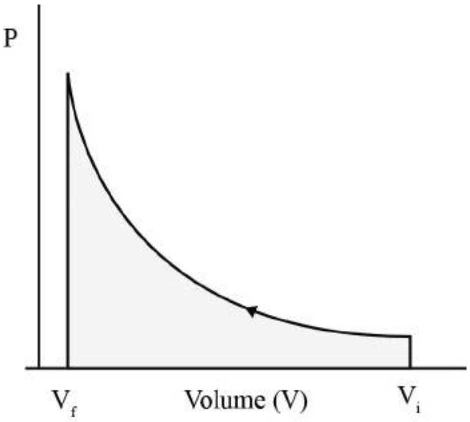


P-V plot when pressure is not constant and changes in finite steps

If the pressure is not constant but changes during the process such that it is always infinitesimally greater than the pressure of the gas, then, at each stage of compression, the volume decreases by an infinitesimal amount, dV. In such a case we can calculate the work done on the gas by the relation

$$w = -\int_{V_i}^{V_f} p_{ex} dV$$

Here, p_{ex} at each stage is equal to $(P_{in} + dp)$ in case of compression. In an expansion process under similar conditions, the external pressure is always less than the pressure of the system i.e., $p_{ex} = (p_{in} - dp)$. In general case we can write, $p_{ex} = (p_{in} + dp)$. Such processes are called **reversible processes.**



P-V plot when pressure is not constant and changes in infinite steps

$$w = -\int_{V_i}^{V_f} p_{ex} dV = -\int_{V_i}^{V_f} (p_{in} \pm dp) dV$$

Since dp × dV is very small we can write

$$w = -\int_{V_i}^{V_f} p_{in} dV$$

Now, the pressure of the gas (p_{in} which we can write as p now) can be expressed in terms of its volume through gas equation. For n mol of an ideal gas i.e., pV = nRT.

$$\Rightarrow p = \frac{nRT}{V}$$

Therefore, at constant temperature (isothermal process),

$$w_{rev} = -\int_{V_i}^{V_f} nRT \frac{dV}{V} = -nRT \ln \frac{V_f}{V_i}$$

$$w_{rev} = -2.303nRT \log \frac{V_f}{V_i}$$

Work in Cyclic Process

A cyclic process is one which comes back to its initial state. The graph of a cyclic process is always a closed graph. For a cyclic process, $\Delta U_{net} = 0$ and $q_{net} = -w_{net}$.

Isothermal Free Expansion of an Ideal Gas

For isothermal (T = constant) expansion of an ideal gas into vacuum ; w = 0 since $p_{ex} = 0$. Also, Joule determined experimentally that q = 0; therefore, $\Delta U = 0$

Equation, $\Delta U = q + w$ can be expressed for isothermal irreversible and reversible changes as follows:

1. For isothermal irreversible change
   $q = -w = p_{ex} (V_f - V_i)$
2. For isothermal reversible change

$$q = -w = nRT \ln \frac{V_f}{V_i}$$

$$= 2.303nRT \log \frac{V_f}{V_i}$$

3. For adiabatic change, q = 0, $\Delta U = w_{ad}$

8.1 Work Done in Various Types of Thermodynamic Processes

8.1.1 Isothermal Process

These processes are the ones in which the temperature is constant throughout the process.

$\Delta U = 0$; $\Delta H = 0$

$$w = -2.303nRT \log\left(\frac{V_2}{V_1}\right) = -2.303nRT \log\left(\frac{P_1}{P_2}\right)$$

8.1.2 Adiabatic Process

These processes are the ones in which the heat exchanged with the surroundings is zero. Such processes are generally defined by the equations:

$TV^{\gamma-1} = \text{constant}, \; T^{\gamma}P^{1-\gamma} = \text{constant}, \; PV^{\gamma} = \text{constant}.$

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

$$\Delta U = nC_V\Delta T = \left(\frac{P_2V_2 - P_1V_1}{\gamma - 1}\right) = \frac{nR\Delta T}{\gamma - 1}$$

$\Delta H = nC_p\Delta T$

8.1.3 Isochoric Process

These processes are the ones in which the volume remains constant. Since the change in volume is zero therefore we can say that

$w = 0$

$\Delta U = nC_V\Delta T = q_V$

8.1.4 Isobaric Process

These are the processes in which the pressure remains constant $(dp = 0)$

$w = -P\Delta V = -nR\Delta T$

$\Delta H = nC_p\Delta T$

NOTE

All these processes are happening on a system containing an ideal gas therefore we can apply $PV = nRT$ at any stage that we find suitable.

9. HEAT CAPACITY OF A SYSTEM

The heat capacity (C) of the system is the amount of heat needed to raise the temperature of the system by 1K.

$$C = \frac{q}{\Delta T}$$

9.1 Molar Heat Capacity

The molar heat capacity of a system (C_M) is the amount of heat needed to raise the temperature of one mole gas by 1K.

$$C_M = \frac{q}{n\Delta T}$$

9.1.1 Molar Heat Capacity at Constant Pressure

The molar heat capacity of a system at constant pressure (C_p) is the amount of heat needed to raise the temperature of one mole gas by 1K. at constant pressure.

$$C_p = \frac{q_p}{n\Delta T}$$

9.1.2 Molar Heat Capacity at Constant Volume

The molar heat capacity of a system at constant volume (C_V) is the amount of heat needed to raise the temperature of one mole gas by 1K. at constant volume.

$$C_v = \frac{q_v}{n\Delta T}$$

Heat Capacities of Different Types of Gases

Types of gas	C_v	C_p	$\gamma = C_p/C_v$
Monoatomic	3R/2	5R/2	5/3 = 1.67
Diatomic	5R/2	7R/2	7/5 = 1.4
Non-linear Polyatomic	3R	4R	4/3 = 1.34

9.1.3 Relation between C_p and C_V

We know that : $\Delta H = nC_p\Delta T$ and $\Delta U = nC_V\Delta T$

for 1 mole (n = 1) of an ideal gas

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

Putting $\Delta H = C_p\Delta T$ and $\Delta U = C_V\Delta T$

$C_p\Delta T = C_V\Delta T + R\Delta T$

$C_p = C_V + R$

9.2 Polytropic Process

It is a generalized form of any thermodynamic process which has a form $PV^n = \text{constant}$ where n is a real number. For an isothermal process n = 1 and for an adiabatic process $n = \gamma$. The heat capacity of a polytropic process can be calculated using the first law of thermodynamics and comes out to be :

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

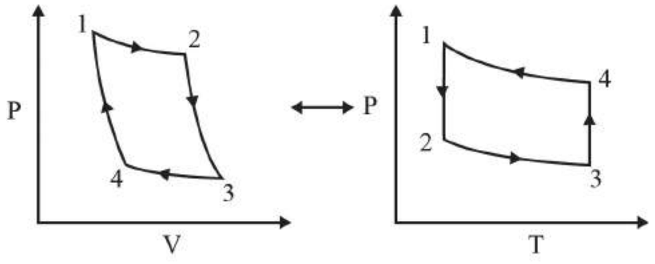
10. GRAPH TRANSFORMATION

When a thermodynamic process is plotted in terms of two state variable it can be transformed into a graph involving the other state variable by doing the following

1. Identify the type of curve given, whether it is P-V, V-T or P-T

graph.

2. Then, Identify every step of the process
3. Then one by one convert every step into the required graph bearing in mind critical points like, an expansion process will remain an expansion process and so on.
4. A cyclic process should remain cyclic whichever graph we make.



P-V and P-T graphs of cyclic process

NOTE

From the given P–V graph.

Process 1→2 is isothermal expansion; 2→3 adiabatic expansion; 3→4 isothermal compression & 4→1 adiabatic compression.

11. ENTHALPY (H)

According to the first law of thermodynamics

$\Delta U = q_p - p\Delta V$ at constant pressure, where q_p is heat absorbed by the system and $-p\Delta V$ represent expansion work done by the system.

Let us represent the initial state by subscript 1 and final state by subscript 2. We can rewrite the equation as:

$U_2 - U_1 = q_p - p(V_2 - V_1)$

On rearranging, we get

$q_p = (U_2 + pV_2) - (U_1 + pV_1)$

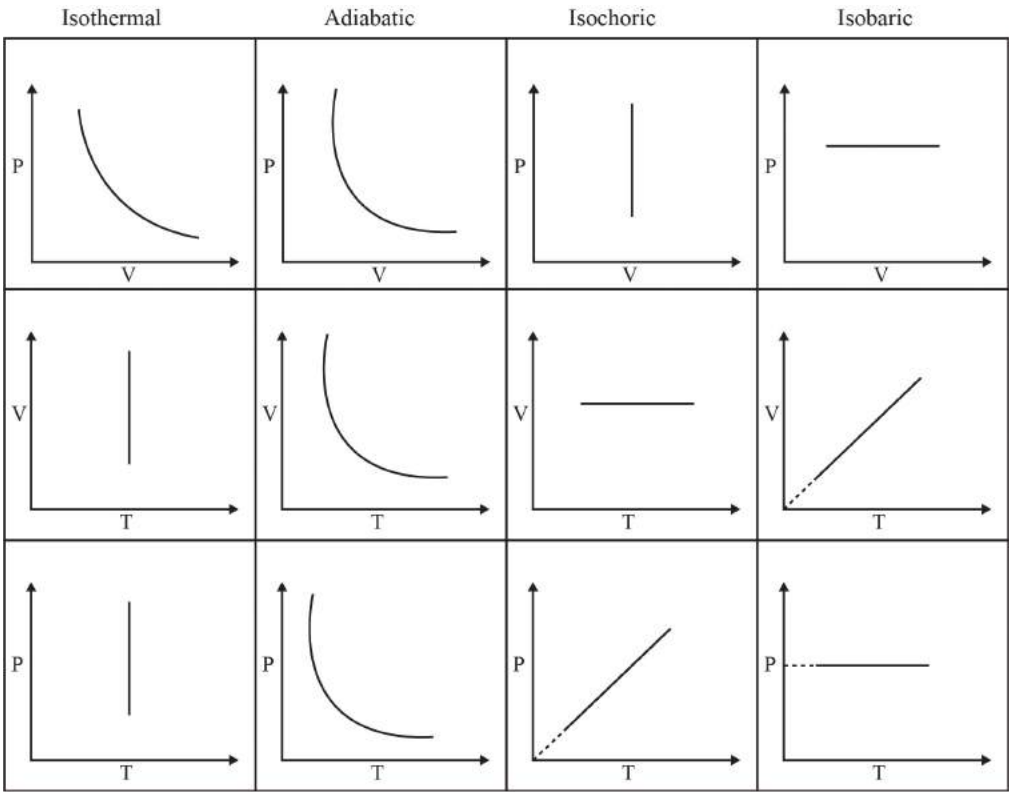
Now we can define another thermodynamic function, the enthalpy as: $H = U + pV$

so, equation becomes

$q_p = H_2 - H_1 = \Delta H$

Hence, $\Delta H = \Delta U + p\Delta V$

It is important to note that when heat is absorbed by the system at constant pressure, we are actually measuring changes in the enthalpy.



Graphical representation of various thermodynamic processes

Remember $\Delta H = q_p$, heat absorbed by the system at constant pressure.

ΔH is negative for exothermic reactions and ΔH is positive for endothermic reactions.

Let us consider a reaction involving gases. If V_A is the total volume of the gaseous reactants, V_B is the total volume of the gaseous products, n_A is the number of moles of gaseous reactants and n_B is the number of moles of gaseous products, all at constant pressure and temperature, then using the ideal gas law, we write,

$$pV_A = n_A RT$$

and $pV_B = n_B RT$

Thus, $pV_B - pV_A = n_B RT - n_A RT = (n_B - n_A)RT$

or $p(V_B - V_A) = (n_B - n_A)RT$

or $p\,\Delta V = \Delta n_g RT$

Here, Δn_g refers to the number of moles of gaseous products minus the number of moles of gaseous reactants.

This gives the relation, $\Delta H = \Delta U + \Delta n_g RT$

12. CALORIMETRY: MEASUREMENT OF ΔU AND ΔH

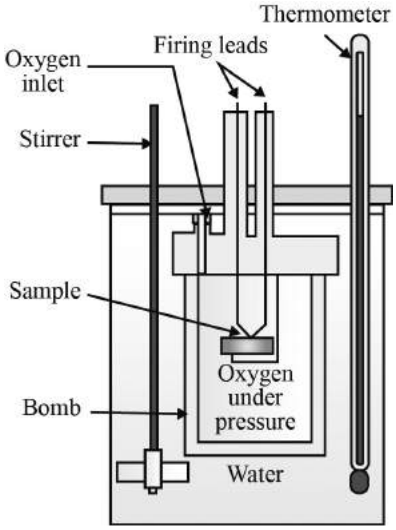
We can measure energy changes associated with chemical or physical processes by an experimental technique called calorimetry. In calorimetry, the process is carried out in a vessel called calorimeter, which is immersed in a known volume of a liquid. Knowing the heat capacity of the liquid in which calorimeter is immersed and the heat capacity of calorimeter, it is possible to determine the heat evolved in the process by measuring temperature changes. Measurements are made under two different conditions:

i) at constant volume, q_V

ii) at constant pressure, q_p

12.1 ΔU Measurements

For chemical reactions, heat absorbed at constant volume, is measured in a bomb calorimeter.

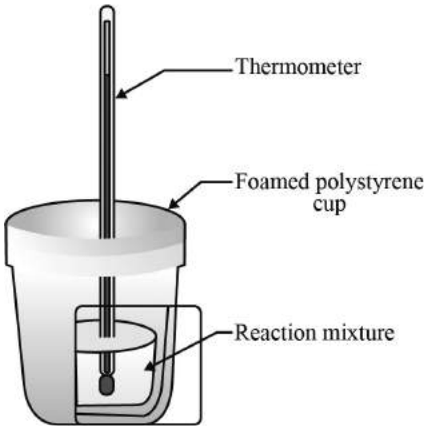


Bomb calorimeter

Here, a steel vessel (the bomb) is immersed in a water bath to ensure that no heat is lost to the surroundings. A combustible substance is burnt in pure dioxygen supplied in the steel bomb. Heat evolved during the reaction is transferred to the water around the bomb and its temperature is monitored. Since the bomb calorimeter is sealed, its volume does not change. Under these conditions, no work is done as the reaction is carried out at constant volume in the bomb calorimeter. Temperature change of the calorimeter produced by the completed reaction is then converted to q_V, by using the known heat capacity of the calorimeter.

12.2 ΔH Measurements

Measurement of heat change at constant pressure (generally under atmospheric pressure) can be done in a calorimeter shown in the figure below.



Coffee cup calorimeter

We know that $\Delta H = q_p$ (at constant p) and, therefore, heat absorbed or evolved, q_p at constant pressure is also called the heat of reaction or enthalpy of reaction, ΔH.

In an exothermic reaction, heat is evolved, and system loses heat to the surroundings. Therefore, q_p will be negative and ΔH will also be negative. Similarly in an endothermic reaction, heat is absorbed, q_p is positive and ΔH will be positive.

13. NEED FOR SECOND LAW

13.1 Spontaneous Process

A spontaneous process is one which happens on its own. Example, heat always flows spontaneously from higher temperature to lower temperature.

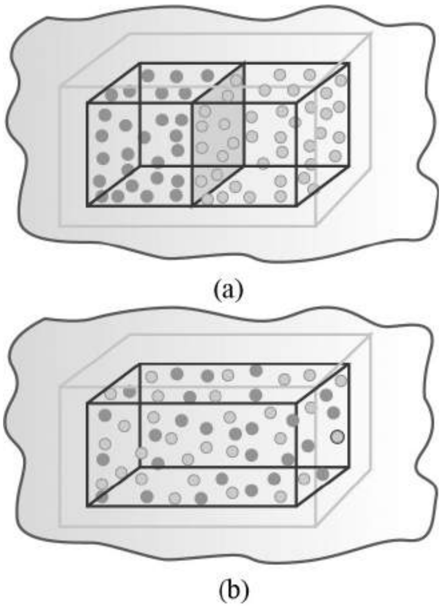
The first law talks about the conservation of energy in a process but does not speak of the feasibility of a process. It does not tell whether a process will happen on its own i.e. whether the process is spontaneous or not.

According to first law any process where energy remains conserved is feasible, but this is not true for all processes. Hence, we need some other basis for feasibility of a process.

13.2 Entropy and Spontaneity

Let us consider diffusion of two gases into each other in a closed container which is isolated from the surroundings as shown in fig. (a) and (b).

The two gases, say, gas A and gas B are represented by blue dots and pink dots respectively and separated by a movable partition fig. (a) When the partition is withdrawn the gases begin to diffuse into each other and after a period of time, diffusion will be complete fig (b).



Diffusion of two gases

With partition we can pick the molecules of gas with surety that it is from gas A or gas B. But, if we were to pick up molecules from container when partition is removed, we are not sure whether the molecules picked are of gas A or gas B. We say that the system has become less predictable or more chaotic.

At this point, we introduce another thermodynamic function, **entropy** denoted as **S.** The above mentioned disorder is the manifestation of entropy. ΔS is independent of path. For a given substance, the crystalline solid state is the state of lowest entropy (most ordered), The gaseous state is state of highest entropy.

Whenever heat is added to the system, it increases molecular motions causing increased randomness in the system. Thus heat (q) has randomising influence on the system. Therefore ΔS is related with q and T for a reversible reaction as :

$$\Delta S = \frac{q_{rev}}{T}$$

The total entropy change (ΔS_{total}) for the system and surroundings of a spontaneous process is given by

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surr} > 0$$

When a system is in equilibrium, the entropy is maximum, and the change in entropy, $\Delta S = 0$.

We can say that entropy for a spontaneous process increases till it reaches maximum and at equilibrium the change in entropy is zero. Since entropy is a state property, we can calculate the change in entropy of a reversible process by.

$$\Delta S = \frac{q_{sys,rev}}{T}$$

We find that both for reversible and irreversible expansion for an ideal gas, under isothermal conditions, $\Delta U = 0$, but ΔS_{total} i.e.,

$\Delta S_{sys} + \Delta S_{surr}$ is not zero for irreversible process. Thus, ΔU does not discriminate between reversible and irreversible process, whereas ΔS does.

13.3 Entropy change in Thermodynamic Processes

The entropy changes in a thermodynamic process can be mathematically calculated by the equation:

$$\Delta S = nC_V \ell n\left(\frac{T_2}{T_1}\right) + nR\ell n\left(\frac{V_2}{V_1}\right)$$

This expression can be simplified for the four processes studied earlier as :

For Isothermal Process: $\Delta S = nR\ell n\left(\frac{V_2}{V_1}\right)$

For Isochoric Process: $\Delta S = nC_V \ell n\left(\frac{T_2}{T_1}\right)$

For Isobaric Process: $\Delta S = nC_P \ell n\left(\frac{T_2}{T_1}\right)$

For Adiabatic Process: $\Delta S = 0\left(q_{rev} = 0\right)$

13.4 Entropy Change During Phase Transition

Entropy of Fusion

$$\Delta S_{fusion} = S_{liquid} - S_{solid} = \frac{\Delta H_{fusion}}{T_f}$$

Entropy of Vapourisation

$$\Delta S_{vapour} = S_{vapour} - S_{liquid} = \frac{\Delta H_{vapour}}{T_{bp}}$$

Entropy of Sublimation

$$\Delta S_{sub} = S_{vapour} - S_{solid} = \frac{\Delta H_{sub}}{T_{sub}}$$

Important points to Remember:

1. Entropy of a system remains constant in a reversible adiabatic process. Therefore, it is also known as **isoentropic process.**
2. Entropy of an ideal gas will always increase in isothermal expansion.
3. In a reversible adiabatic process the entropy of both system and surroundings remains the same and there is no overall change in entropy as well.

   $\Delta S_{System} = \Delta S_{Surroundings} = \Delta S_{Total} = 0$
4. In a reversible isothermal expansion the entropy of surroundings will always decrease to balance the increase in system's entropy to make the overall entropy constant.
5. In free expansion the entropy of the system always increases and that of surrounding remains constant. Free expansion is both isothermal and adiabatic and is irreversible.

14. SECOND LAW OF THEROMODYNAMICS

"The entropy of an isolated system/Universe tends to increase."

or

"In a spontaneous process the entropy of the universe increases."

$\Delta S_{Total} = \Delta S_{System} + \Delta S_{Surrounding} > 0$

(for a sponataneous change)

Thus, in a reversible process the entropy of the Universe remains constant i.e. $\Delta S_{Total} = 0$

15. GIBBS FREE ENERGY AND SPONTANEITY

We have seen that for a system, it is the total entropy change, ΔS_{total} which decides the spontaneity of the process. It is clear from the discussion in previous sections that neither decrease in enthalpy nor increase in entropy alone can determine the direction of spontaneous change.

For this purpose, we define a new thermodynamic function the Gibbs energy or Gibbs function, G, as

$G = H - TS$

Gibbs function, G is an extensive property and a state function. The change in Gibbs energy for the system, ΔG_{sys} can be written as

$$\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys} - S_{sys}\Delta T$$

At constant temperature, $\Delta T = 0$

$$\therefore \Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys}$$

Usually the subscript 'system' is dropped and we simply write this equation as

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

This equation is known as the Gibbs equation, one of the most important equations in chemistry. Here, we have considered both terms together for spontaneity: energy (in terms of ΔH) and entropy (ΔS, a measure of disorder) as indicated earlier. Dimensionally if we analyse, we find that ΔG has units of energy because, both ΔH and the TΔS are energy terms, since TΔS = (K)(J/K) = J.

Now let us consider how ΔG is related to reaction spontaneity.

We know,

$$\Delta S_{total} = \Delta S_{sys} - \Delta S_{surr}$$

If the system is in thermal equilibrium with the surrounding, then the temperature of the surrounding is same as that of the system. Also, increase in enthalpy of the surrounding is equal to decrease in the enthalpy of the system.

Therefore, entropy change of surroundings,

$$\Delta S_{surr} = \frac{\Delta H_{surr}}{T} = -\frac{\Delta H_{sys}}{T}$$

$$\Delta S_{total} = \Delta S_{sys} + \left(-\frac{\Delta H_{sys}}{T}\right)$$

Rearranging the above equation:

$$T\Delta S_{total} = T\Delta S_{sys} - \Delta H_{sys}$$

For spontaneous process, $\Delta S_{total} > 0$, so

$$T\Delta S_{sys} - \Delta H_{sys} > 0$$

$$\Rightarrow -\left(\Delta H_{sys} - T\Delta S_{sys}\right) > 0$$

Using equation , the above equation can be written as

$-\Delta G > 0$

$\Delta G = \Delta H - T\Delta S < 0$

ΔH_{sys} is the enthalpy change of a reaction, $T\Delta S_{sys}$ is the energy which is not available to do useful work. So ΔG is the net energy available to do useful work and is thus a measure of the 'free energy'. For this reason, it is also known as the free energy of the reaction.

ΔG gives a criteria for spontaneity at constant pressure and temperature.

(i) If ΔG is negative (< 0), the process is spontaneous.

(ii) If ΔG is positive (> 0), the process is non spontaneous.

Effect of Temperature on Spontaneity

$\Delta_f H^o$	$\Delta_f S^o$	$\Delta_f G^o$	Description
–	+	–	Spontaneous at all temperatures
+	–	+	Nonspontaneous at all tempertures
–	–	+ (at high T)	Nonspontaneous at high temeprature
–	–	– (at low T)	Spontaneous at low temperature
+	+	+ (at low T)	Non-spontaneous at low temperature
+	+	– (at high T)	Spontaneous at high temperature

16. THIRD LAW OF THERMODYNAMICS

Molecules of a substance may move in a straight line in any direction, they may spin like a top and the bonds in the molecules may stretch and compress. These motions of the molecule are called translational, rotational and vibrational motion respectively. When temperature of the system rises, these motions become more vigarous and entropy increases. On the other hand when temperature is lowered, the entropy decreases.

The absolute entropy of a perfectly crystalline substance at absolute zero temperature is zero.

This is called third law of thermodynamics. This is so because there is perfect order in a crystal at absolute zero. The statement is confined to pure crystalline solids because theoretical arguments and practical evidences have shown that entropy of solutions and super cooled liquids is not zero at 0 K. The importance of the third law lies in the fact that it permits the calculation of absolute values of entropy of pure substance from thermal data alone.

For a pure substance, this can be done by summing $\frac{q_{rev}}{T}$ increments from 0 K to 298 K.

17. THERMOCHEMICAL EQUATIONS

A chemical equation which gives us all the information like energy changes associated with a chemical reaction and phases of various reactants and products is called thermochemical equation.

For a chemical reaction, $\Delta H_{Reaction} = H_{Products} - H_{Reactants}$

The change in enthalpy during a chemical reaction occurs due to breaking and making of bonds.

Also, $\Delta H = \Delta U + \Delta n_g RT$.

All reactions can be categorized into one of the following two categories :

17.1 Endothermic Reactions

These are chemical reactions which absorb energy.

$(\Delta H = \text{positive})$

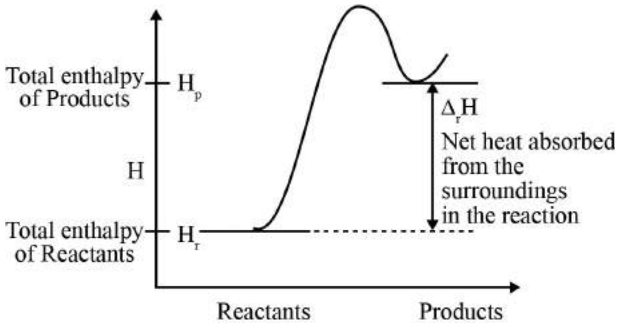


Fig. 10.17: Enthalpy diagram for endothermic reactions

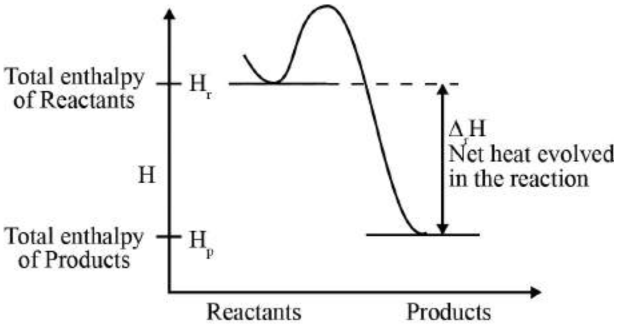
$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$

$\Delta H = -890$ kJ/mol

17.2 Exothermic Reactions

These are chemical reactions which release energy.

(ΔH = negative)



Enthalpy diagram for exothermic reaction

17.3 Enthalpy Change During Phase Transformation

17.3.1 Enthalpy of fusion (Symbol $\Delta_{fus}H^o$)

The heat change (or enthalpy change) that is accompanied when one mole of a solid substance undergoes melting in standard state is called standard enthalpy of fusion or molar enthalpy of fusion, $\Delta_{fus}H^{\ominus}$

For example, ice requires heat for melting. Normally this melting takes place at constant pressure, i.e., atmospheric pressure and during the phase transition, temperature remains constant (273K).

$$H_2O(s) \rightarrow H_2O(l); \Delta_{fus}H^{\ominus} = 6.00 kJmol^{-1}$$

If process is reversed, an equal amount of heat is given off to the surroundings.

17.3.2 Enthalpy of vaporization (Symbol $\Delta_{vap}H^o$)

The enthalpy change (or heat change) when one mole of liquid at constant temperature and under pressure (1 bar) undergoes vaporization is called standard enthalpy of vaporization or molar enthalpy of vaporization, $\Delta_{vap}H^{\ominus}$.

For example, water requires heat for evaporation, at constant temperature of its boiling point T_b and at constant pressure

$$H_2O(l) \rightarrow H_2O(g); \Delta_{vap}H^{\ominus} = +40.79 kJmol^{-1}$$

17.3.3 Enthalpy of sublimation (Symbol $\Delta_{sub}H^o$)

Sublimation is the process when a solid changes directly into gaseous state without changing into liquid state. The change in state occurs at a temperature below its melting point. In this case the enthalpy of sublimation is defined as the change in enthalpy when one mole of a solid substance is directly converted into the gaseous state at a constant temperature and standard pressure (1 bar).

For example: Solid CO_2 or 'dry ice' sublimes at 195 K

$$CO_2(s) \rightarrow CO_2(g); \Delta_{sub}H^{\ominus} = 25.2 kJmol^{-1}$$

Naphthalene sublimes slowly and for this $\Delta_{sub}H^{\ominus} = 73.0 kJmol^{-1}$

18. ENTHALPIES OF REACTIONS

Enthalpy change can be calculated for all reactions and is sometimes called the Heat of Reaction. Let's take a look at various types of reactions and enthalpy changes associated with them :

$$\Delta H^o_{Reaction} = \sum H^o_{Product} - \sum H^o_{Reactants}$$

18.1 Enthalpy of Formation

It is the heat absorbed or released when one mole of a compound is formed from its constituent elements under their standard elemental forms. The enthalpy for formation of the following substances is taken to be zero under 1 bar pressure and 298 K.

ΔH_f^o (O_2, g) = 0; ΔH_f^o (S, Rhombic) = 0

ΔH_f^o (C, graphite) = 0; ΔH_f^o (P, white) = 0

ΔH_f^o (Br_2, l) = 0; ΔH_f^o (H_2, g) = 0

18.2 Enthalpy of Combustion

It is the heat released when one mole of a substance undergoes combustion in presence of oxygen.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) \quad \Delta H = -890 \text{ kJ/mol}$$

18.3 Enthalpy of Neutralization

It is the heat released or absorbed when one equivalent of an acid undergoes neutralisation with one equivalent of a base. e.g.

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l) \qquad \Delta H = -57.3 \text{ kJ/mol}$$

18.4 Enthalpy of Solution

It is the heat released or absorbed when 1 mole of a compound is dissolved in excess of a solvent (water).

$$MgSO_4(s) + H_2O(\text{excess}) \rightarrow Mg^{2+}(aq) + SO_4^{2-}(aq)$$

$$\Delta H^o_{Sol} = -91.211 \text{ kJ/mol}$$

18.5 Enthalpy of Hydration

It is the energy released or absorbed when 1 mole of anhydrous or partially hydrated salt undergoes hydration by the addition of water of crystallisation. e.g.

$$CuSO_{4(s)} + 5H_2O_{(l)} \rightarrow CuSO_4.5H_2O(s) \quad \Delta H_{hyd} = -78.9 \text{ kJ/mol}$$

18.6 Lattice Enthalpy

The lattice enthalpy of an ionic compound is the enthalpy change which occurs when one mole of an ionic compound dissociates into its ions in gaseous state. It is denoted by $\Delta_{\text{lattice}}H^\circ$

For example:

$$NaCl(s) \rightarrow Na^+(g) + Cl^-(g); \qquad \Delta_{\text{lattice}}H^\circ = +788 \text{kJ mol}^{-1}$$

Relationship of $\Delta_{\text{sol}}H$, $\Delta_{\text{lattice}}H$ and $\Delta_{\text{hyd}}H$

$$\Delta_{\text{sol}}H = \Delta_{\text{lattice}}H + \Delta_{\text{hyd}}H$$

18.7 Bond Dissociation Enthalpy

The energy needed to break the bonds of one mole molecules is called the bond dissociation Enthalpy of the substance. It is defined per mol of molecule.

e.g. Bond dissociation enthalpy of H_2 is 436 kJ/mol

$$H_2(g) \rightarrow 2H(g) \quad \Delta H = 436 \text{ kJ / mole}$$

18.8 Heat of Atomization

It is defined as the energy required to convert any substance to gaseous atoms. This is defined per mol of the gaseous atoms. For example heat of atomisation of H will be 218 kJ/mol atoms.

$$H_2(g) \rightarrow 2H(g) \quad \Delta H = 436 \text{ kJ / mole}$$

For diatomic molecules bond dissociation energy and heat of atomization are same.

18.9 Resonance Energy

Generally there is a good agreement between the enthalpies of formation as calculated from bond energies and those determined experimentally. However, if a compound exhibits resonance, there is a considerable difference between the two values. This difference gives a measure of the resonance energy of the compound. As an example, we may consider the dissociation of benzene:

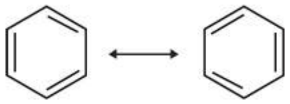
$$C_6H_6(g) \rightarrow 6C(g) + 6H(g)$$

Assuming that benzene ring consists of three single and three double bonds (Kekule's structure), the calcualted dissociation energy comes out to be 5384.1 kJ as illustrated below:

$$\Delta H_g = 3(\Delta H_{C-C}) + 3(\Delta H_{C-C}) + 6(\Delta H_{C-H})$$

$$= 3 \times 347.3 + 3 \times 615.0 + 6 \times 416.2 = 5384.1 \text{ kJ mol}^{-1}$$

The experimental value is known to be 5535.1 kJ mol^{-1}. Evidently, the actual energy required for the dissociation of benzene is 151 kJ more than the calcualted value. This clearly show that the acutal structure of benzene is more stable than the Kekule structure by 151 kJ. The actual structure of benzene is known to be the resonance hybrid of the two Kekule structures.

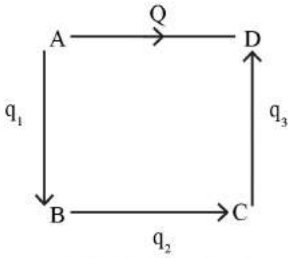


Resonating structures of benzene

The difference of 151 kJ gives the resonance energy of benzene.

19. HESS LAW

"If a reaction takes place in several steps then its standard reaction enthalpy is the sum of the standard enthalpies of the intermediate reactions into which the overall reaction may be divided at the same temperature". This is called the Hess law of constant heat summation

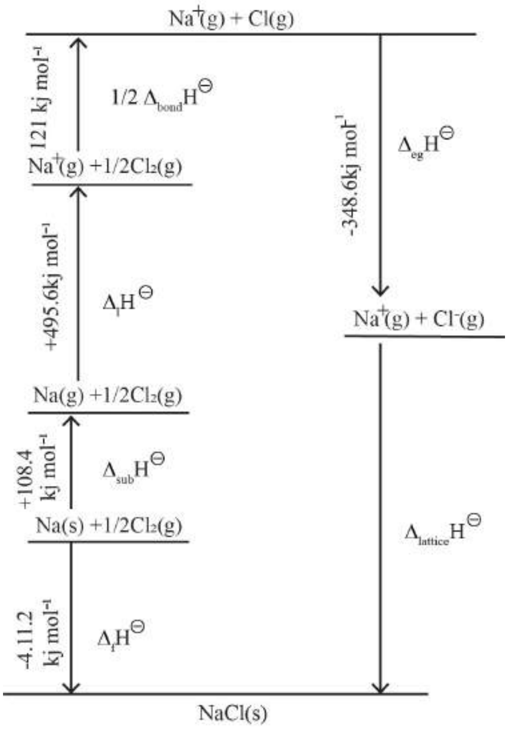


$[Q = q_1 + q_2 + q_3 \;]$

Representation of Hess law

19.1 Born Haber Cycle

The entire thermodynamics process of formation of an ionic crystal lattice is called Born Haber cycle. An ionic compound is formed from its constituents through a series of steps involving conversion of atoms/molecules into gaseous phase for ion formation, ionisation and electron gain to form ions and then the reaction of gaseous ions to form solid lattice



Born Haber Cycle of NaCl

20. KIRCHHOFF EQUATION

The enthalpy of any process, whether physical or chemical, varies with temperature. The influence of temperature can be worked out as follows:

$$\Delta H_{\text{reaction}} = \sum H_{\text{products}} - \sum H_{\text{reactants}}$$

Differentiating with respect to temperature, keeping pressure constant, we have

$$\left(\frac{d\Delta H}{dT}\right)_P = \left(\frac{dH_{\text{product}}}{dT}\right)_P - \left(\frac{dH_{\text{reactant}}}{dT}\right)_P = (C_P)_{\text{product}} - (C_P)_{\text{reactant}}$$

If ΔC_P = Sum of heat capacities of products – Sum of heat capacities of reactants, then

$$d(\Delta H) = \Delta C_P dT$$

This equation is called the Kirchhoff equation. It states that the variation of ΔH of a reaction as temperature at constant pressure is equal to ΔC_P of the system.

The temperature-dependence of enthalpy of reaction at constant volume is given by

$$d(\Delta U) = \Delta C_V dT$$

21. GIBBS ENERGY CHANGE AND EQUILIBRIUM

Gibbs energy for a reaction in which all reactants and products are in standard state, $\Delta_r G°$ is related to the equilibrium constant of the reaction as follows:

$$0 = \Delta_r G° + RT + \ln K$$

Or $\Delta_r G° = -RT \ln K$

Or $\Delta_r G° = -2.303 RT \log K$

We also know that

$$\Delta_r G° = \Delta_r H° - T\Delta_r S° = -RT \ln K$$

For strongly endothermic reactions, K is smaller while for exothermic reactions, K is much larger than 1.

SUMMARY

- **System:** A part of universe which is under investigation.
- **Surroundings:** The rest of the universe which is not a part of the system.
- **State of the system:** The conditions of existence of a system when its macroscopic properties have definite values.
- **State functions:** The thermodynamic quantities which depend only on the initial and final state of the system.
- Energy is exchanged between the system and the surroundings as heat if they are at different temperatures.
- The properties of the system whose value is independent of the amount of substance are called **intensive properties,** e.g., temperature, pressure, viscosity, surface tension, dielectric, specific heat capacity.
- The properties of the system whose value depends upon the amount of substance present in the system are called **extensive properties.** e.g., mass, volume, surface area, energy, enthalpy, entropy, free energy, heat capacity.
- **Work** is also a mode of transference of energy between system and the surroundings. Work done by the system on the surroundings is given by $P\Delta V$.
- **Internal energy (U):** The energy associated with the system at a particular conditions of temperature and pressure.
- **Internal energy change (ΔU):** It is a measure of heat change occurring during the process at constant temperature and constant volume.

  $q_v = \Delta U$
- **First law of thermodynamics:** It states that the energy of the universe always remains constant during chemical and physical changes. Mathematically.

  $\Delta U = q + w$
- Internal energy of an ideal gas depends only on temperature. Therefore, in an isothermal process involving ideal gas, $\Delta U = 0$.
- Work of expansion, $w = -P\Delta V$.
- Work of expansion in vacuum.

  $p_{ext} = 0, w = 0$
- **Enthalpy (H):** It is sum of internal energy and pressure-volume energy of the system at a particular temperature and pressure. It is also called **heat content** $(H = U + PV)$.
- **Enthalpy change (ΔH):** It is the measure of heat change taking place during the process at constant temperature and constant pressure.

  $q_p = \Delta H$

  Enthalpy ΔH and internal energy change (ΔU) are related as

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

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

  Where Δn_g = Gaseous moles of products – Gaseous moles of reactants
- **Enthalpy of reaction $\left(\Delta_r H^\ominus\right)$:** The enthalpy change accompanying a chemical reaction when the number of moles of reactants react to give the products as given by the balanced chemical equation.
- **Standard enthalpy of formation $\left(\Delta_f H^\ominus\right)$:** The enthalpy change accompanying the formation of one mole of the compound from its element at standard conditions and all the substances being in their standard states.

  As a convention, the $\Delta_f H^\ominus$ of every element is assumed to be zero.
- **Enthalpy of combustion $\left(\Delta_c H^\ominus\right)$:** The amount of heat change when 1 mole of the substance is completely burnt in excess of oxygen or air. $\Delta_c H^\ominus$ is always negative.
- **Enthalpy of solution $\left(\Delta_{sol} H^\ominus\right)$:** The enthalpy change when one mole of a substance is dissolved in large excess of solvent so that further dilution does not give any further enthalpy change.
- **Enthalpy of hydration:** It is the enthalpy change during the hydration of 1 mole of anhydrous salt to a specific hydrate.

- **Hess law:** The enthalpy change in a particular reaction is the same whether the reaction takes place in one step or in a number of steps.
- **Bond enthalpy:** The average amount of energy required to break one mole of the bonds of a particular type in gaseous molecules.
- **Entropy:** $\Delta S = \frac{q_{rev}}{T}$
- $\Delta_r S^o = \Sigma \Delta S^o$ (products) $-$ $\Sigma \Delta S^o$ (reactants)

  i.e., $\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$ must be positive
- **Gibbs energy:** Gibbs energy is the energy in a system that can be converted into useful work

  $\Delta G = -w_{useful}$

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

  For a spontaneous process $\Delta G < 0$

  For a non - spontaneous process $\Delta G > 0$

  For a process at equilibrium $\Delta G = 0$
- **Relation of Gibbs energy and equilibrium constant:**

  $\Delta_r G^\circ = -2.303RT \log K$

SOLVED EXAMPLES

Example - 1

Calculate the internal energy change in each of the following cases :

(i) A system absorbs 15 kJ of heat and does 5 kJ of work.

(ii) 5 kJ of work is done on the system and 15 kJ of heat is given out by the system.

Sol. (i) Here, $q = +15$ kJ

$w = -5$ kJ

$\therefore$ According to first law of thermodynamics, $\Delta U = q + w = 15 + (-5) = 10$ kJ

Thus, internal energy of the system increases by 10 kJ.

(ii) Here, $w = +5$ kJ

$q = -5$ kJ

$\therefore$ According to first law of thermodynamics, $\Delta U = q + w = -15 + (+5) = -10$ kJ

Thus, the internal energy of the system decreases by 10 kJ.

Example - 2

Calculate w, q and ΔU when 0.75 mol of an ideal gas expands isothermally and reversibly at 27°C from a volume of 15 L to 25 L.

Sol. For isothermal reversible expansion of an ideal gas, $w = -2.303\ nRT \log \frac{V_2}{V_1}$ Putting $n = 0.75$ mol, $V_1 = 15$ L, $V_2 = 25$ L, $T = 27 + 273 = 300$ K and $R = 8.314\ J\ K^{-1}\ mol^{-1}$, we get $w = -2.303 \times 0.75 \times 8.314 \times 300 \log \frac{25}{15} = -955.5$ J

(–ve sign represents work of expansion)

For isothermal expansion of an ideal gas, $\Delta U = 0$

$\therefore \Delta U = q + w$ gives $q = -w = +955.5$ J.

Example - 3

Carbon monoxide is allowed to expand isothermally and reversibly from 10 m^3 to 20 m^3 at 300 K and work obtained is 4.754 kJ. Calculate the number of moles of carbon monoxide.

Sol. $w = -2.303\ nRT \log \frac{V_2}{V_1}$

$$-4754 = -2.303 \times n \times 8.314 \times 300 \log \frac{20}{10}.$$

This given $n = 2.75$ moles.

Example - 4

A 5-litre cylinder contained 10 moles of oxygen gas at 27°C. Due to sudden leakage through the hole, all the gas escaped into the atmosphere and the cylinder got empty. If the atmospheric pressure is 1.0 atmosphere, calculate the work done by the gas. (1 L atm = 101.3 J)

Sol. $V_{initial} = 5L, T = 27°C = 27 + 273\ K = 300\ K$

$$V_{final} = \frac{nRT}{P} = \frac{10 \times 0.0821 \times 300}{1.0} = 246.3\ L$$

$\Delta V = V_{final} - V_{initial} = 246.3 - 5 = 241.3$ L

$w_{exp} = -P\Delta V = -1 \times 241.3$ L atm

$= -241.3 \times 101.3\ J = -24443.7$ J.

Example - 5

Two moles of an ideal gas initially at 27°C and one atmospheric pressure are compressed isothermally and reversibly till the final pressure of the gas is 10 atm. Calculate q, w and ΔU for the process.

Sol. Here, $n = 2$ moles, $T = 27°C = 300$ K, $P_1 = 1$ atm, $P_2 = 10$ atm

$$w = -2.303\ n RT \log \frac{P_1}{P_2}$$

$$= -2.303 \times 2 \times 8.314\ JK^{-1}\ mol^{-1} \times 300\ K \times \log \frac{1}{10} = 11488\ J$$

For isothermal compression of ideal gas, $\Delta U = 0$

Further, $\Delta U = q + w \therefore q = -w = -11488$ J.

Example - 6

10g of argon gas is compressed isothermally and reversibly at a temperature of 27°C from 10L to 5L. Calculate q, W, ΔU and ΔH for this process. $R = 2.0$ cal K^{-1} mol^{-1}. $\log_{10} 2 = 0.30$ Atomic wt. of Ar = 40

Sol. $w = -2.303\ nRT \log_{10} \frac{V_2}{V_1}$

$$= -2.303 \times \frac{10}{40} \times 2 \times 300 \log_{10} \frac{5}{10}$$

$w = 103.991$ cal

$\Delta U = 0$; $\Delta H = 0$ (Constant temperature)

$\because q = \Delta U - w \quad \therefore q = -w = -103.991$ cal

Example - 7

A gas present in a cylinder fitted with a frictionless piston expands against a constant pressure of 1 atm from a volume of 2 litre to a volume of 6 litre. In doing so, it absorbs 800 J heat from surroundings. Determine increase in internal energy of process.

Sol. Since, work is done against constant pressure and thus, irreversible.

Given, $\Delta V = (6 - 2) = 4$ litre; $P = 1$ atm

$\therefore\ w = -1 \times 4$ litre-atm $= -4 \times 1.01325 \times 10^2$ J

$= 405.3$ J

Now from first law of thermodynamics

$q = \Delta U - w$

$800 = \Delta U + 405.3 \quad \therefore\ \Delta U = 394.7$ Joule

Example - 8

5 moles of an ideal gas at 300 K are expanded isothermally from an initial pressure of 500 Pa to a final pressure of 100 Pa against a constant external pressure of 100 Pa. Calculate w, q, ΔU and ΔH for the process. What will be the difference if the same process is carried out irreversibly ? What are the values of w, q, ΔU, ΔH for the irreversible process ?

Sol. For an isothermal irreversible expansion :

$\Delta U = \Delta H = 0$

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

V_2 and V_1 can be calculated from ideal gas equation.

$V_1 = nRT/P_1 = 5 \times 8.314 \times 300/500 = 24.9\ m^3$

$V_2 = nRT/P_2 = 124.7\ m^3$

Therefore, $w = -100 \times (124.5 - 24.9)$

$= -9980$ J

$q = +9980$ J

If this process is done reversibly then the internal and external pressure should be same throughout.

$\Delta U = \Delta H = 0$ (temperature is constant)

$w = -nRT\ ln\,(V_2/V_1)$

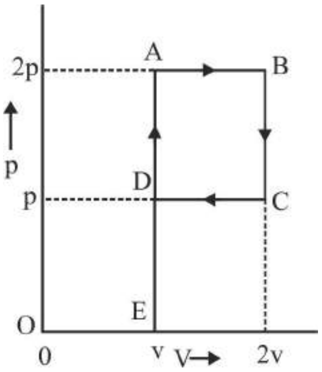
$= -5 \times 8.314 \times 300 \times ln\,5$

$= -20071.3$ J

$q = +20071.3$ J

Example - 9

The state of a mole of an ideal gas changed from state A (2p, v) through four different processes and finally returns to initial State A reversibly as shown below.



Calculate the total work done by the system and heat absorbed by the system in the cyclic process.

Sol. State A to State B (Isobaric expansion)

Pressure is held constant at 2p and the gas is heated until the volume v becomes 2v.

$\therefore\ W_1 = -p\Delta V = -2p\,(2v - v) = -2pv$

State B to State C (Isochoric process)

Volume is held constant at 2v and the gas is cooled until the pressure 2p reaches p.

$\therefore\ W_2 = 0\ (\because \Delta V = 0)$

State C to State D (Isobaric compression)

Pressure is held constant at p and the gas is further cooled until the volume 2v becomes v.

$\therefore\ W_3 = -p\,(v - 2v) = pv$

State D to State A (Isochoric process)

Volume is held constant at v and the gas is heated until the pressure p reaches 2p.

$\therefore\ W_4 = 0\ (\because \Delta V = 0)$

Total work done by the gas = $W = W_1 + W_2 + W_3 + W_4$

or $W = -2pv + 0 + pv + 0 = -pv$ (= area ABCD)

As the process is cyclic $\Delta E = 0$

$\therefore\ q = -w \Rightarrow q = +pv$

where q is the heat absorbed in the cylic process.

Example - 10

Two mole of a perfect gas undergo the following processes:

(a) a reversible isobaric expansion from (1.0 atm, 20.0L) to (1.0 atm, 40.0L).

(b) a reversible isochoric change of state from (1.0 atm, 40.0L) to (0.5 atm, 40.0L)

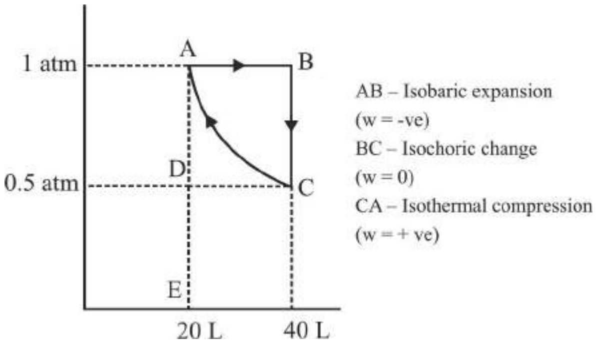
(c) a reversible isothermal compression from (0.5 atm, 40.0L) to (1.0 atm, 20.0L).

(i) sketch with labels each of the processes on the same P-V diagram.

(ii) Calculate the total work (w) and the total heat change (q) involved in the above processes.

(iii) What will be the value of ΔU, ΔH and ΔS for the overall process ?

Sol. The overall process is cyclic one, i.e., initial state is regained, thus $\Delta U = 0$; $\Delta H = 0$ and $\Delta S = 0$.



Now, total work $W = W_{A\to B} + W_{B\to C} + W_{C\to A}$

$W_{AB} = -P(V_B - V_A)$

$= -1\,(40-20) = -20\text{L atm}$

$= -20 \times 1.01325 \times 10^2\ \text{J}$

$= -2026.5\ \text{J}$

$W_{BC} = 0$ (Isochoric)

$$W_{CA} = -2.303\ nRT \log_{10}\frac{V_A}{V_C}$$

n = 2 mol.

At point C : P = 0.5 atm, V = 40L

PV = nRT

$$T = \frac{0.5 \times 40}{(0.0821)\,(2)} = 121.8\ \text{K}.$$

$$W_{CA} = -2.303\,(2)\,(8.314)\,(121.8) \log_{10}\left(\frac{20}{40}\right)$$

$= 1404.07$ J

Total work, $W = -2026.5 + 0 + 1404.07$

$= -622.43$ J

For cyclic process : $\Delta U = 0$

$\Rightarrow q = -w$

$q = +622.43$ J

Example - 11

Calculate the amount of work done in each of the following cases :

(i) One mole of an ideal gas contained in a bulb of 10 litre capacity at 1 bar is allowed to enter into an evacuated bulb of 100 litre capacity.

(ii) One mole of a gas is allowed to expand from a volume of 1 litre to a volume of 5 litres against the constant external pressure of 1 atm (1 litres atm = 101.3 J) Calculate the internal energy change (ΔU) in each case if the process were carried out adiabatically.

Sol. (i) $w = -P_{ext} \times \Delta V$

As expansion takes place into the evacuated bulb, i.e., against vacuum, $P_{ext} = 0$. Hence, w = 0.

For adiabatic process, q = 0 $\therefore \Delta U = q + w = 0 + 0 = 0$.

(ii) $\Delta V = V_2 - V_1 = 5 - 1 = 4$ litres

P = 1 atm $\therefore w = -P\Delta V$

$= -1 \times 4$ litre atm $= -4$ litres atm

$= -4 \times 101.3\ \text{J} = -405.2\ \text{J}$ (1 L – atm = 101.3J)

The negative sign implies that the work is done by the system.

For adiabatic process, $\Delta U = q + w = 0 - 405.2\ \text{J} = -405.2\ \text{J}$.

Example - 12

5.6 dm^3 of an unknown gas at S.T.P. required 52.25 J of heat to raise its temperature by 10ºC at constant volume. Calculate C_v, C_p and γ of the gas

Sol. The 22.4 dm^3 of a gas at S.T.P. = 1 mol

$$\therefore\ 5.6\ \text{dm}^3 \text{ of the gas at S.T.P.} = \frac{1}{22.4} \times 5.6 = 0.25\ \text{mol}$$

Thus, for 10º rise, 0.25 mol of the gas at constant volume require heat = 52.25 J

$\therefore$ For 1º rise, 1 mol of the gas at constant volume will require

$$\text{heat} = \frac{52.25}{10 \times 0.25} = 20.9$$

$\therefore C_v = 20.9\ \text{J K}^{-1}\ \text{mol}^{-1}$

Now, $C_p = C_v + R = 20.9\ \text{J K}^{-1}\ \text{mol}^{-1} + 8.314\ \text{J K}^{-1}\ \text{mol}^{-1} = 29.214\ \text{J K}^{-1}\ \text{mol}^{-1}$

$$\therefore \qquad \gamma = \frac{C_p}{C_v} = \frac{29.214}{20.9} = 1.4$$

Example - 13

A heated copper block at 130°C loses 340 J of heat to the surroundings which are at room temperature of 32°C. Calculate

(i) the entropy change of the system (copper block)

(ii) the entropy change in the surroundings

(iii) the total entropy change in the universe due to this process

Assume that the temperature of the block and the surroundings remains constant.

Sol. $T_{\text{system}} = 130^\circ\text{C} = 130 + 273\ \text{K} = 403\ \text{K}$, $T_{\text{surr}} = 32^\circ\text{C} = 32 + 273\ \text{K} = 305\ \text{K}$ $q_{\text{system}} = -340\ \text{J}$, $q_{\text{surr}} = +340\ \text{J}$

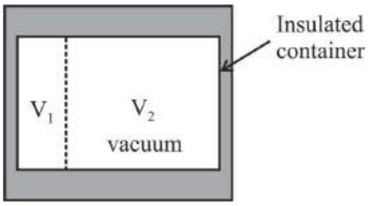
(i) $\Delta S_{\text{system}} = \dfrac{q_{\text{system}}}{T_{\text{system}}} = \dfrac{-340\ \text{J}}{403\ \text{K}} = -0.84\ \text{JK}^{-1}$

(ii) $\Delta S_{\text{surr}} = \dfrac{q_{\text{surr}}}{T_{\text{surr}}} = \dfrac{+340\ \text{J}}{305\ \text{K}} = +1.11\ \text{J K}^{-1}$

(iii) ΔS_{total} or $\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surr}} = -0.84 + (+1.11)\ \text{J K}^{-1} = 0.27\ \text{J K}^{-1}$

Example - 14

An ideal gas is originally confined to a volume V_1 in an insulated container of volume $V_1 + V_2$. The remainder of the container is evacuated. The portion is then removed and the gas expands to fill the entire container. If the initial temperature of the gas was T, what is the final temperature. Also predict qualitatively, the entropy change of system, surroundings and the universe.



Sol. This is a process of adiabatic free expansion of an ideal gas. The internal energy does not change thus the temperature also stays the same, i.e., the final temperature is still T.

$$\Delta S_{\text{system}} = nR\ln\frac{V_1 + V_2}{V_1} > 0 \quad \because V_1 + V_2 > V_1$$

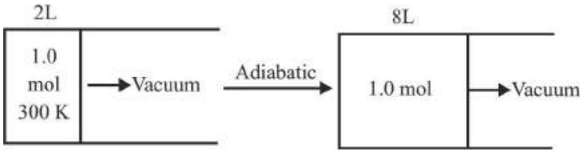
$$\Delta S_{\text{surr}} = 0 \quad \because q_{\text{surr.}} = 0$$

$$\Rightarrow \Delta S_{\text{univ}} > 0$$

Example - 15

1.0 mol of an ideal gas, initially present in a 2.00 L insulated cylinder at 300 K is allowed to expand against vacuum to 8.00 L. Determine W, ΔE, ΔH, ΔS_{univ} and ΔG.

Sol.



$W = -p_{\text{ext}}\Delta V = 0,\ q = 0, \quad \Rightarrow \Delta E = 0 = \Delta H$

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

$$\Delta S_{\text{sys}} = R\ln\frac{V_2}{V_1} = R\ln 4 = 11.52\ \text{JK}^{-1}$$

$\Delta S_{\text{surr}} = 0 \qquad \because q_{\text{sys}} = q_{\text{surr}} = 0$

$\Rightarrow \Delta S_{\text{univ}} = 11.52\ \text{JK}^{-1}$

$\Rightarrow \Delta G = -T\Delta S_{\text{univ}} = -300 \times 11.52 = -3456\ \text{J/mol}.$

Example - 16

The heat of combustion of benzene in a bomb calorimeter (i.e., constant volume) was found to be 3263.9 kJ mol^{-1} at 25°C. Calculate the heat of combustion of benzene at constant pressure.

Sol. The reaction is:

$$C_6H_{6(\ell)} + 7\frac{1}{2}O_{2(g)} \longrightarrow 6CO_{2(g)} + 3H_2O_{(\ell)}$$

In this reaction, O_2 is the only gaseous reactant and CO_2 is the only gaseous product.

$$\therefore \qquad \Delta n_g = n_p - n_r = 6 - 7\frac{1}{2} = -1\frac{1}{2} = -\frac{3}{2}$$

Also, we are given ΔU (or q_v) $= -3263.9\ \text{kJ mol}^{-1}$

$T = 25^\circ\text{C} = 298\text{K}$

$$R = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1} = \frac{8.314}{1000}\ \text{kJ K}^{-1}\ \text{mol}^{-1}$$

ΔH (or q_p) $= \Delta U + \Delta n_g RT = -3263.9$ kJ mol^{-1} +

$$\left(-\frac{3}{2}\text{mol}\right)\left(\frac{8.314}{1000}\text{kJ K}^{-1}\ \text{mol}^{-1}\right)(298\,\text{K})$$

$= -3263.9 - 3.7$ kJ mol^{-1} $= -3267.6$ kJ mol^{-1}.

Example - 17

Calculate the amount of heat evolved when

(i) 500 cm^3 of 0.1 M hydrochloric acid is mixed with 200 cm^3 of 0.2 M sodium hydroxide solution

(ii) 200 cm^3 of 0.2 M sulphuric acid is mixed with 400 cm^3 of 0.5 M potassium hydroxide solution.

Assuming that the specific heat of water is 4.18 J K^{-1} g^{-1} and ignoring the heat absorbed by the container, thermometer, stirrer etc., what would be the rise in temperature in each of the above cases ?

Sol. (i) moles of HCl $= \frac{0.1}{1000} \times 500 = 0.05 = 0.05$ mole of H$^+$ ions

200 cm^3 of 0.2 M NaOH $= \frac{0.2}{1000} \times 200$

mole of NaOH = 0.04 mole = 0.04 mole of OH$^-$ ions

Thus, 0.04 mole of H$^+$ ions will combine with 0.04 mole of OH$^-$ ions to from 0.04 mole of H_2O and 0.01 mole of H$^+$ ions will remain unreacted.

$\therefore$ Heat evolved when 1 mole of H$^+$ ions combine with 1 mole of OH$^-$ ions = 57.1 kJ.

$\therefore$ Heat evolved when 0.04 mole of H$^+$ ions combine with 0.04 mole of OH$^-$ ions = 57.1 × 0.04 = 2.284 kJ

(ii) 200 cm^3 of 0.2 M H_2SO_4 $= \frac{0.2}{1000} \times 200$ mole of H_2SO_4 = 0.04 mole of H_2SO_4 = 0.08 mole of H$^+$ ions

400 cm^3 of 0.5 M KOH $= \frac{0.5}{1000} \times 400$ mole of KOH = 0.2 mole of KOH = 0.2 mole of OH$^-$ ions

Thus, 0.08 mole of H$^+$ ions will neutralize 0.08 mole of OH$^-$ ions. (out of 0.2 mole of OH$^-$ ions) to form 0.08 mole of H_2O.

Hence, heat evolved = 57.1 × 0.08 = 4.568 kJ

In case (i), heat produced = 2.284 kJ = 2284 J

Total volume of the solution = 500 + 200 = 700 mL

Assuming density of solution = 1g/mL

So mass of solution = 700g

Specific heat = 4.18 J K^{-1} g^{-1}

$$Q = m \times C \times \Delta T \quad \therefore\ \Delta T = \frac{Q}{m \times C} = \frac{2284}{700 \times 4.18} = 0.78^\circ\text{C}$$

In case (ii), heat produced = 4.568 kJ = 4568 J

Total mass of the solution = 200 + 400 = 600 g

$$\therefore \qquad \Delta T = \frac{Q}{m \times C} = \frac{4568}{600 \times 4.18} = 1.82^\circ\text{C}$$

Example - 18

Calculate the enthalpy change accompanying the transformation of C (graphite) to C(diamond). Given that the enthalpies of combustion of graphite and diamond are 393.5 and 395.4 kJ mol^{-1} respectively.

Sol. Remember, enthalpy of combustion is always negative we are given

(i) C (graphite) + O_2 (g) $\longrightarrow$ CO_2(g) ; $\Delta_c H^\circ = -393.5$ kJ mol^{-1}

(ii) C (diamond) + O_2 (g) $\longrightarrow$ CO_2(g) ; $\Delta_c H^\circ = -395.4$ kJ mol^{-1}

We aim at C(graphite) $\longrightarrow$ C(diamond), $\Delta_{trans} H^\circ = ?$

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

C(graphite) – C(diamond) $\longrightarrow$ 0;

$\Delta_r H^\circ = -393.5 - (-395.4) = +1.9$ kJ

or

C(graphite) $\longrightarrow$ (diamond) ; $\Delta_{trans} H = +1.9$ kJ

Example - 19

Calculate the enthalpy of hydration of anhydrous copper sulphate ($CuSO_4$) into hydrated copper sulphate ($CuSO_4.5H_2O$). Given that the enthalpies of solutions of anhydrous copper sulphate and hydrated copper sulphate are –66.5 and + 11.7 kJ mol^{-1} respectively

Sol. We are given

(i) $CuSO_4$ (s) + aq $\longrightarrow$ $CuSO_4$ (aq) ;

$\Delta_{sol} H_1 = -66.5$ kJ mol^{-1}

(ii) $CuSO_4.5H_2O$ (s) + aq $\longrightarrow$ $CuSO_4$ (aq) ;

$\Delta_{sol} H_2 = +11.7$ kJ mol^{-1}

We aim at $CuSO_4\,(s) + 5H_2O\,(l) \longrightarrow CuSO_4.5H_2O(s)$;

$\Delta_{hyd}H = ?$

$\Delta H = \Delta H_1 - \Delta H_2 = -66.5 - (+11.7) = -78.2$ kJ/mol

Example - 20

Calculate the enthalpy of formation of methane, given that the enthalpies of combustion of methane, graphite and hydrogen are 890.2 kJ, 393.4 kJ and 285.7 kJ mol^{-1} respectively.

Sol. Remember : Enthalpy of combustion is always negative.

We are given :

(i) $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O, \Delta H = -890.2\text{ kJ mol}^{-1}$

(ii) $C + O_2 \longrightarrow CO_2, \Delta H = -393.4\text{ kJ mol}^{-1}$

(iii) $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O,\ \Delta H = -285.7\text{ kJ mol}^{-1}$

We aim at : $C + 2H_2 \longrightarrow CH_4, \Delta H = ?$

In order to get this thermochemical equation, multiply eqn. (iii) by 2 and add it to eqn. (ii) and then subtract eqn. (i) from their sum. We get :

$$C + 2H_2 \longrightarrow CH_4,$$
$$\Delta H = -393.4 + 2(-285.7) - (-890.2)\text{ kJ mol}^{-1} = -74.6\text{ kJ mol}^{-1}$$

Hence, the heat of formation of methane is :

$\Delta_f H = -74.6\text{ kJ mol}^{-1}$

Example - 21

Calculate the heat of formation of KCl from the following data :

(i) $KOH\,(aq) + HCl\,(aq) \longrightarrow KCl\,(aq) + H_2O(\ell), \Delta H = -57.3\text{ kJ mol}^{-1}$

(ii) $H_2\,(g) + \frac{1}{2}O_2\,(g) \longrightarrow H_2O(\ell),\ \Delta H = -286.2\text{ kJ mol}^{-1}$

(iii) $\frac{1}{2}H_2\,(g) + \frac{1}{2}Cl_2\,(g) + aq \longrightarrow HCl(aq),\ \Delta H = -164.4\text{ kJ mol}^{-1}$

(iv) $K\,(s) + \frac{1}{2}O_2\,(g) + \frac{1}{2}H_2\,(g) + aq \longrightarrow KOH\,(aq), \Delta H = -487.4\text{ kJ mol}^{-1}$

(v) $KCl\,(s) + aq \longrightarrow KCl\,(aq), \Delta H = +18.4\text{ kJ mol}^{-1}$

Sol. We aim at : $K(s) + \frac{1}{2}Cl_2\,(g) \longrightarrow KCl(s),\ \Delta_f H = ?$

In order to get this thermochemical equation, we follow the following two steps :

Step 1. Adding Eqns. (iii) and (iv) and subtacting Eq. (v). we have

$$K_{(s)} + \frac{1}{2}Cl_{2(g)} + H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow KCl_{(s)} + HCl_{(aq)} + KOH_{(aq)} - KCl_{(aq)}$$

$\Delta H = -487.4 + (-164.4) - (18.4) = -670.2\text{ kJ mol}^{-1}$ ... (vii)

Step 2. To cancel out the terms of this equation which do not appear in the required equation (vi), add eqn. (i) to eqn. (vii) and subtract eqn. (ii) from their sum. This gives

$$K(s) + \frac{1}{2}Cl_2\,(g) \longrightarrow KCl(s);$$

$\Delta_f H = -670.2 + 57.3 - (-286.2) = -441.3$ kJ

Example - 22

The combustion of 1 mole of benzene takes place at 298 K and 1 atm. After combustion, $CO_{2(g)}$ and $H_2O_{(l)}$ are produced and 3267.0 kJ of heat is liberated. Calculate the standard enthalpy of formation, $\Delta_f H^\circ$ of benzene. Standard enthalpies of formation of CO_2 (g) and H_2O (l) are – 393.5 kJ mol^{-1} and –285.83 kJ mol^{-1} respectively.

Sol. Aim : $6C_{(s)} + 3H_{2(g)} \longrightarrow C_6H_6(\ell), \Delta H = ?$

Given :

(i) $C_6H_{6\,(l)} + \frac{15}{2}O_{2(g)} \longrightarrow 6CO_{2(g)} + 3H_2O_{(l)}, \Delta H = -3267.0\text{ kJ mol}^{-1}$

(ii) $C_{(s)} + O_{2\,(g)} \longrightarrow CO_{2\,(g)}, \Delta H = -393.5\text{ kJ mol}^{-1}$

(iii) $H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(l)}, \Delta H = -285.83\text{ kJ mol}^{-1}$

In order to get the required thermochemical equation, multiply Eq. (ii) by 6 and Eq. (iii) by 3 and subtract Eq. (i) from their sum, i.e. operating 6 × Eqn. (ii) + 3 × Eqn. (iii) – Eqn. (i), we get

$$6C\,(s) + 3H_2\,(g) \longrightarrow C_6H_6\,(l)\,;$$

$$\Delta H = 6(-393.5) + 3(-285.83) - (-3267.0)$$

$$= -2361 - 857.49 + 3267.0 = 48.51 \text{ kJ mol}^{-1}$$

Thus, the enthalpy of formation of benzene is $\Delta_f H = -48.51 \text{ kJ mol}^{-1}$

Example - 23

Calculate the enthalpy of combustion of ethylene (gas) to form CO_2 (gas) and H_2O (gas) at 298 K and 1 atmospheric pressure. The enthalpies of formation of CO_2, H_2O and C_2H_4 are –393.5, –241.8, + 52.3 kJ per mole respectively.

Sol. We are given :

(i) $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)},\ \Delta H_1^\circ = -393.5 \text{ kJ mol}^{-1}$

(ii) $H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(g)},\ \Delta H_2^\circ = -241.8 \text{kJ mol}^{-1}$

(iii) $2C_{(s)} + 2H_{2(g)} \longrightarrow C_2H_{4(g)},\ \Delta H_3^\circ = +52.3 \text{ kJ mol}^{-1}$

We aim at : $C_2H_{4(g)} + 3O_{2(g)} \longrightarrow 2CO_{2(g)} + 2H_2O_{(g)}$

$\Delta H = -\Delta H_3 + 2\Delta H_1 + 2\Delta H_2$

$= -1322.9 \text{ kJ mol}^{-1}$

Example - 24

Given the following thermochemical equations:

(i) $S\,(\text{rhombic}) + O_2\,(g) \longrightarrow SO_2\,(g),\ \Delta H = -297.5 \text{ kJ mol}^{-1}$

(ii) $S(\text{monoclinic}) + O_2 \longrightarrow SO_2\,(g), \Delta H = -300.0 \text{ kJ mol}^{-1}$

Calculate ΔH for the transformation of one gram atom of rhombic sulphur into monoclinic sulphur.

Sol. We aim at

$S\,(\text{rhombic}) \rightarrow S\,(\text{monoclinic}),\ \Delta H = ?$

Equation (i) → Equation (ii) gives

$S(\text{rhombic}) - S(\text{monoclinic}) \longrightarrow 0,$

$\Delta H = -297.5 - (-300.0) = 2.5 \text{ kJ mol}^{-1}$

or

$S(\text{rhombic}) \longrightarrow S(\text{monoclinic}), \Delta H = +2.5 \text{ kJ mol}^{-1}$

Thus, for the transformation of one gram atom of rhombic sulphur into monoclinic sulphur, 2.5 kJ mol^{-1} of heat is absorbed.

Example - 25

Enthalpy of solution (ΔH) for $BaCl_2.2H_2O$ and $BaCl_2$ are 8.8 and –20.6 kJ mol^{-1} respectively. Calculate the heat of hydration of $BaCl_2$ to $BaCl_2.2H_2O$.

Sol. We are given

(i) $BaCl_2.2H_2O(s) + aq \longrightarrow BaCl_2(aq), \Delta_{sol}\ \Delta H_1^\circ = 8.8 \text{kJ mol}^{-1}$

(ii) $BaCl_2\,(s) + aq \longrightarrow BaCl_2(aq), \Delta_{sol}\ \Delta H_2^\circ = -20.6 \text{kJ mol}^{-1}$

We aim at

$BaCl_2\,(s) + 2H_2O \longrightarrow BaCl_2.2H_2O\,(s),\ \Delta_{hyd} H^\circ = ?$

$\Delta H = \Delta H_2 - \Delta H_1 = -29.4 \text{ kJ mol}^{-1}$

Example - 26

Calculate the enthalpy of hydrogenation of ethylene, given that the enthalpy of combustion of enthylene, hydrogen and ethane are – 1410.0, – 286.2 and – 1560.6 kJ mol^{-1} respectively at 298 K.

Sol. We are given (i) $C_2H_4\,(g) + 3O_2\,(g) \longrightarrow 2CO_2(g) + 2H_2O\,(l),$ $\Delta H = -1410 \text{ kJ mol}^{-1}$

(ii) $H_2\,(g) + \frac{1}{2}O_2\,(g) \longrightarrow H_2O\,(l), \Delta H = -286.2 \text{ kJ mol}^{-1}$

(iii) $C_2H_6\ (g) + 3\frac{1}{2}O_2\,(g) \longrightarrow 2CO_2\,(g) + 3H_2O\ (l),$ $\Delta H = -1560.6 \text{ kJ mol}^{-1}$

We aim at: $C_2H_4 + H_2(g) \longrightarrow C_2H_6\,(g), \Delta H = ?$

Equation (i) + Equation (ii) – Equation (iii) gives

$C_2H_4\,(g) + H_2\,(g) \longrightarrow C_2H_6\,(g),$

$\Delta H = -1410.0 + (-286.2) - (1560.6) = -135.6 \text{ kJ mol}^{-1}$

Example - 27

The thermite reaction used for welding of metals involves the reaction

$2\,Al\,(s) + Fe_2O_3\,(s) \longrightarrow Al_2O_3\,(s) + 2Fe\,(s)$

What is ΔH° at 25°C for this reaction ? Given that the standard heats of formation of Al_2O_3 and Fe_2O_3 are – 1675.7 kJ and –828.4 kJ mol^{-1} respectively.

Sol. We aim at $2Al\,(s) + Fe_2O_3(s) \longrightarrow Al_2O_3\,(s) + 2Fe\,(s),\ \Delta_r H^\circ = ?$

$\Delta_r H$ = Sum of $\Delta_f H^\circ$ of products – Sum of

$\Delta_f H^\circ$ of reactants

$= [\Delta_f H^\circ (Al_2O_3) + 2 \times \Delta_f H^\circ (Fe)] -$

$[2 \times \Delta_f H^\circ (Al) + \Delta_f H^\circ (Fe_2O_3)]$

$= [-1675.7 + 0] - [0 + (-828.4)] = -847.3 \text{ kJ mol}^{-1}$

Example - 28

The heat evolved in the combustion of methane is given by the equation :

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l), \Delta H = -890.3 \text{ kJ mol}^{-1}$$

(a) How many grams of methane would be required to produce 445.15 kJ of heat of combustion ?

(b) How many grams of carbon dioxide would be formed when 445.15 kJ of heat is evolved ?

(c) What volume of oxygen at STP would be used in the combustion process (a) or (b) ?

Sol. (a) From the given equation.

890.3 kJ of heat is produced from 1 mole of CH_4, i.e., 12 + 4 = 16 g of CH_4

$\therefore$ 445.15 kJ of heat is produced from 8 g of CH_4

(b) From the given equation, when 890.3 kJ of heat is evolved, CO_2 formed = 1 mole = 44 g

$\therefore$ When 445.15 kJ of heat is evolved, CO_2 formed = 22 g

(c) From the equation, O_2 used in the production of 890.3 kJ of heat = 2 moles = 2 × 22.4 litres at STP

= 44.8 litres at STP

Hence, O_2 used in the production of 445.15 kJ of heat = 22.4 litres at STP.

Example - 29

From the thermochemical equation,

$$C_6H_6(\ell) + 7\frac{1}{2}O_2(g) \longrightarrow 3H_2O(\ell) + 6CO_2(g),$$

$$\Delta_c H = -3264.64 \text{ kJ mol}^{-1},$$

calculate the energy evolved when 39 g of C_6H_6 are burnt in an open container.

Sol. From the given equation,

When 1 mole of C_6H_6 (78 g of C_6H_6) is burnt, heat evolved = 3264.64 kJ

$$\therefore \text{ When 39 g of } C_6H_6 \text{ is burnt, heat evolved} = \frac{3264.64}{78} \times 39$$

= 1632.32 kJ

Example - 30

The thermochemical equation for solid and liquid rocket fuel are given below :

$$2Al(s) + 1\frac{1}{2}O_2(g) \longrightarrow Al_2O_3(s);$$

$$\Delta H = -1667.8 \text{ kJ mol}^{-1}$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(1);$$

$$\Delta H = -285.9 \text{ kJ mol}^{-1}$$

(a) If equal masses of aluminium and hydrogen are used, which is a better rocket fuel ?

(b) Determine ΔH for the reaction :

$$Al_2O_3(s) \longrightarrow 2Al(s) + 1\frac{1}{2}O_2(g).$$

Sol. (a) From the first given equation,

2 moles of Al (i.e., 2 × 27 g = 54 g) on combustion give heat = 1667.8 kJ

$$\therefore \text{ 1 g of Al on combustion gives heat } = \frac{1667.8}{54} = 30.9 \text{ kJ}$$

From the second given equation, 1 mole of H_2 (= 2 g) on combsution gives heat = 285.9 kJ

$$\therefore \text{ 1 g of } H_2 \text{ on combustion gives heat } = \frac{285.9}{2} = 142.95 \text{ kJ}$$

Thus, H_2 is a better rocket fuel.

(b) Writing the reverse of the first reaction, we have

$$Al_2O_3(s) \longrightarrow 2Al(s) + 1\frac{1}{2}O_2(g); \Delta H = +1667.8 \text{ kJ mol}^{-1}$$

Thus, for the reaction given in part (b) of the problem, $\Delta H = +1667.8 \text{ kJ mol}^{-1}$

Example - 31

When 1 g liquid naphthalene ($C_{10}H_8$) solidifies. 149 joules of heat is evolved. Calculate the enthalpy of fusion of naphthalene.

Sol. Molar mass of naphthalene ($C_{10}H_8$) = 128 g mol^{-1}

When 1 g of liquid naphthalene solidified, heat evolved = 149 joules.

When 1 mole, i.e., 128 g of naphthalene solidifies, heat evolved = 149 joules.

When 1 mole, i.e., 128 g of naphthalene solidifies, heat evolved = 149 × 128 joules = 19072 joules

Since fusion is reverse of solidification, therefore, heat absorbed for fusion of one mole of naphthalene = 19072 joules.

i.e., Enthalpy of fusion (Δ_{fus} H) = + 19072 joules/mole

Example - 32

The heat evolved in the combustion of glucose is shown in the equation :

$$C_6H_{12}O_6 + 6O_2\,(g) \longrightarrow 6CO_2\,(g) + 6\,H_2O\,(g),\ \Delta_c H = -\,2840\ \text{kJ mol}^{-1}$$

What is the energy requirement for production of 0.36 g of glucose by the reverse reaction ?

Sol. The given equation is :

$$C_6H_{12}O_6 + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O\,(g)\,;\quad \Delta_r H = -\,2840\ \text{kJ mol}^{-1}$$

Writing the reverse reaction, we have

$$6CO_2\,(g) + 6H_2O(g) \longrightarrow C_6H_{12}O_6\,(s) + 6O_2(g)\,;$$
$$\Delta_r H = +\,2840\ \text{kJ mol}^{-1}$$

Thus, for production of 1 mole of $C_6H_{12}O_6$ (= 72 + 12 + 96 = 180 g), heat required (absorbed) = 2840 kJ.

∴ For production of 0.36 g of glucose, heat absorbed =

$$\frac{2840}{180} \times 0.36 = 5.68\text{kJ}$$

Example - 33

Calculate the bond energy of C–H bond, given that the heat of formation of CH_4, heat of sublimation of carbon and heat of dissociation of H_2 are – 74.8, + 719.6 and 435.4 kJ mol^{-1} respectively.

Sol. Here, we are given

$$C\,(s) + 2H_2\,(g) \longrightarrow CH_4(g),\ \Delta_r H^o = -\,74.8\ \text{kJ}$$

$$\Delta H = e_{sub(C)} + 2e_{H–H} - 4e_{C–H}$$

$$-\,74.8 = 719.6 + 2\,(435.4) - 4e_{C–H}$$

$$e_{C–H} = 416.3\ \text{kJ/mol}$$

Example - 34

Calculate the enthalpy change for the reaction

$$H_2\,(g) + Br_2\,(g) \longrightarrow 2HBr\,(g)$$

Given that the bond enthalpies of H–H, Br–Br, H–Br are 435, 192 and 364 kJ mol^{-1} respectively.

Sol. $\Delta_r H = \Sigma$ B.E. (Reactants) – Σ B.E. (Products)

$$= [\text{B.E.}\,(H_2) + \text{B.E.}\,(Br_2)] - 2\,\text{B.E.}\,(HBr) =$$
$$435 + 192 - 2 \times 364 = -\,101\ \text{kJ}$$

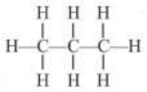
Example - 35

Propane has the structure $H_3C–CH_2–CH_3$. Calculate the change in enthalpy for the reaction:

$$C_3H_8\,(g) + 5\,O_2\,(g) \longrightarrow 3\,CO_2\,(g) + 4\,H_2O\,(g)$$

Given that average bond enthalpies are:

C–C	C–H	C=O	O=O	O–H
347	414	741	498	464 kJ mol^{-1}

Sol.  $+ 5\ O=O \rightarrow 3\ O=C=O + 4\ H-O-H$

$$\Delta H = (2e_{C–C} + 8e_{C–H} + 5e_{O=O}) - (6e_{C=O} + 8e_{O–H})$$
$$= 2\,(347) + 8\,(414) + 5\,(498) - 6\,(741) - 8\,(464)$$
$$= -\,1662\ \text{kJ mol}^{-1}$$

Example - 36

Calculate the entropy change involved in conversion of one mole (18 g) of solid ice at 273 K to liquid water at the same temperature (latent heat of fusion = 6025 J mol^{-1}).

Sol. Entropy change for ice → water is given by $\Delta_f\,S = \dfrac{\Delta_f H}{T_f}$

Here, $\Delta_f H = 6025$ J mol^{-}, $T_f = 273$ K ∴

$$\Delta_f\,S = \frac{6025\ \text{J K}^{-1}\,\text{mol}^{-1}}{273\,\text{K}} = 22.1\ \text{JK}^{-1}\text{mol}^{-1}.$$

Example - 37

Calculate the entropy change involved in the conversion of one mole of liquid water at 373 K to vapour at the same temperature (latent heat of vaporization of water $\Delta_{vap}H = 2.257$ kJ/g)

Sol. For the conversion of water → vapour, the entropy change is given by $\Delta_{vap}\,S = \dfrac{\Delta_{vap}H}{T_b}$

Here, $\Delta_{vap}H = 2.257$ kJ/g = 2.257 × 18 kJ/mol = 40.626 kJ/mol, $T_b = 373$ K

$$\therefore \quad \Delta_{vap} S = \frac{40.626 \text{ kJ mol}^{-1}}{373 \text{ K}} = 0.1089 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$= 108.9 \text{ J K}^{-1} \text{ mol}^{-1}.$$

Example - 38

At 0°C, ice and water are in equilibrium and $\Delta H = 6.00$ kJ mol^{-1} for the process H_2O (s) → H_2O (*l*). What will be ΔS and ΔG for the conversion of ice to liquid water ?

Sol. Since the given process is in equilibrium, $\Delta G = 0$

Putting this value in the relationship, $\Delta G = \Delta H - T\Delta S$, we get

$$0 = \Delta H - T\Delta S \text{ or } T\Delta S = \Delta H \text{ or } \Delta S = \frac{\Delta H}{T}$$

We are given $\Delta H = 6.0$ kj mol^{-1} = 6000 J mol^{-1} and T = 0°C = 273 K

$$\therefore \quad = \frac{6000 \text{ J mol}^{-1}}{273 \text{ K}} = 21.98 \text{ J K}^{-1} \text{ mol}^{-1}$$

Example - 39

$$A + B \longrightarrow C + D \,;\, \Delta H = -10{,}000 \text{ J mol}^{-1},$$

$$\Delta S = -33.3 \text{ J mol}^{-1} \text{ K}^{-1}$$

(i) At what temperature the reaction will occur spontaneously from left to right ?

(ii) At what temperature, the reaction will reverse?

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

At equilibrium, $\Delta G = 0$ so that $\Delta H = T\Delta S$ or

$$T = \frac{\Delta H}{\Delta S} = \frac{-10000 \text{ J mol}^{-1}}{-33.3 \text{ JK}^{-1} \text{ mol}^{-1}} = 300.03\text{K}$$

(i) For spontaneity from left to right. ΔG should be –ve for the given reaction. This will be so if $T < 300.3$ K

(ii) For reverse reaction to occur, ΔG should be +ve forward reaction. This will be so if $T > 300.3$ K.

Example - 40

Calculate the standard free energy change for the reaction,

$$4NH_3 (g) + 5O_2 (g) \longrightarrow 4NO (g) + 6H_2O (l)$$

Given that the standard free energies of formation ($\Delta_f G^\circ$) for NH_3 (g), NO (g) and H_2O (*l*) are – 16.8, + 86.7 and – 237.2 kJ mol^{-1} respectively. Predict the feasibility of the above reaction at the standard state.

Sol. Here, we are given

$\Delta_f G^\circ (NH_3) = -16.8 \text{ kJ mol}^{-1}$

$\Delta_f G^\circ (NO) = +86.7 \text{ kJ mol}^{-1}$

$\Delta_f G^\circ (H_2O) = -237.2 \text{ kJ mol}^{-1}$

$\therefore\ \Delta_r G^\circ = \Sigma \Delta_f G^\circ (\text{Products}) - \Sigma \Delta_f G^\circ (\text{Reactants}) = [14 \times \Delta_f G^\circ (NO) + 6 \times \Delta_f G^\circ (H_2O)] - [4 \times \Delta_f G^\circ (NH_3)$

$$+ 5 \times \Delta_f G^\circ (O_2)]$$

$$= [4 \times (86.7) + 6 \times (-237.2)] - [4 \times (-16.8) + 5 \times 0]$$

$$= -1009.2 \text{ kJ}$$

Since $\Delta_r G^\circ$ is negative, the process is feasible.

Example - 41

Calculate the entropy change for the rusting of iron according to the reaction :

$$4 \text{ Fe (s)} + 3 \text{ O}_2 \text{ (g)} \longrightarrow 2 \text{ Fe}_2\text{O}_3 \text{ (s)}, \Delta H^\circ = -1648 \text{ kJ mol}^{-1}$$

Given that the standard entropies of Fe, O_2 and Fe_2O_3 are 27.3, 205.0 and 87.4 J K^{-1} mol^{-1} respectively. Will the reaction be spontaneous at room temperature (25°C) ? Justify your answer with appropriate calculations.

Sol. $\Delta_r S^\circ = \Sigma S^\circ (\text{Products}) - \Sigma S^\circ (\text{Reactants}) =$

$$2 S^\circ (Fe_2O_3) - [4 S^\circ (Fe) + 3 S^\circ (O_2)]$$

$$= 2 \times 87.4 - [4 \times 27.3 + 3 \times 205.0] \text{ J K}^{-1} \text{ mol}^{-1} =$$

$$-549.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

This is the entropy change of the reaction, i.e., system (ΔS_{system})

Now, $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$

$$= -1648000 \text{ J mol}^{-1} - 298 \text{ K} \times (-549.4 \text{ J K}^{-1} \text{ mol}^{-1})$$

$$= -1648000 + 163721 \text{ J K}^{-1} \text{ mol}^{-1} =$$

$$-1484279 \text{ J K}^{-1} \text{ mol}^{-1}$$

As ΔG° is –ve, the reaction is spontaneous.

Example - 42

Calculate the standard enthalpy of formation of CH_3OH (*l*) from the following data :

$$\text{(i) } CH_3OH(\ell) + \frac{3}{2} O_2 (g) \longrightarrow CO_2 (g) +$$

$$2 H_2O (\ell); \Delta_r H^\circ = -726 \text{ kJ mol}^{-1}$$

(ii) $C(s) + O_2(g) \longrightarrow CO_2(g); \Delta_c H^\circ =$ -393 kJ mol^{-1}

(iii) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(\ell); \Delta_f H^\circ =$ -286 kJ mol^{-1}.

Sol. Aim : $C(s) + 2H_2(g) + \frac{1}{2}O_2(g) \longrightarrow CH_3OH(\ell)$, $\Delta_f H^\circ = ?$

Eqn. (ii) + 2 × Eqn. (iii) – Eqn. (i) gives the required eqn. with $\Delta H = -393 + 2(-286) - (-726)$ kJ mol^{-1} = -239 kJ mol^{-1}.

Example - 43

Calculate enthalpy of formation of methane (CH_4) from the following data :

(i) $C(s) + O_2(g) \longrightarrow CO_2(g), \Delta_r H^\circ = -393.5$ kJ mol^{-1}

(ii) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(\ell)$, $\Delta_r H^\circ = -285.8$ kJ mol^{-1}

(iii) $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(\ell)$, $\Delta_r H^\circ = -890.3$ kJ mol^{-1}

Sol. We aim at : $C(s) + 2H_2(g) \longrightarrow CH_4(g); \Delta_f H^\circ = ?$

Multiplying eqn. (ii) with 2, adding to eqn. (i) and then subtracting eqn. (iii) from the sum, i.e., operating eqn. (i) + 2 × eqn. (ii) – eqn. (iii), we get

$$C(s) + 2H_2(g) \rightarrow CH_4(g) \longrightarrow 0; \Delta_r H^\circ = -393.5 + 2(-285.8) - (-890.3) = 74.8 \text{ kJ mol}^{-1}$$

or $C(s) + 2H_2(g) \longrightarrow CH_4(g); \Delta_f H^\circ = -74.8$ kJ mol^{-1}

Hence, enthalpy of formation of methane is :

$\Delta_f H^\circ = -74.8$ kJ mol^{-1}

Example - 44

Calculate the enthalpy of formation of carbon monoxide (CO) from the following data :

(i) $C(s) + O_2(g) \longrightarrow CO_2(g); \Delta_r H^\circ = -393.5$ kJ mol^{-1}

(ii) $CO(g) + \frac{1}{2}O_2(g) \longrightarrow (g); \Delta_r H^\circ = -283.0$ kJ mol^{-1}

Sol. We aim at : $C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g); \Delta_f H^\circ = ?$

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

$$C(s) + \frac{1}{2}O_2(g) - CO(g) \longrightarrow 0;$$

$$\Delta_r H^\circ = -393.5 - (-283.0) = -110.5 \text{ kJ mol}^{-1}$$

or $C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g); \Delta_r H^\circ = -110.5$ kJ.

∴ Heat of formation of CO is : $\Delta_f H^\circ = -110.5$ kJ mol^{-1}

Example - 45

Determine whether or not, it is possible for sodium to reduce aluminium oxide to aluminium at 298 K. Given that G_f^0 of Al_2O_3 at 298 K = – 1582 kJ mol^{-1}; G_f^0 of $Na_2O(s)$ at 298 K = –377 kJ mol^{-1}.

Sol. The given reaction is :

$Al_2O_3(s) + 6Na(s) \rightarrow 3Na_2O(s) + 2Al(s)$

Hence, $\Delta G^\circ = 3 \times G_f^0(Na_2O) - G_f^0(Al_2O_3)$

(G° for Na and Al = 0)

$= 3 \times (-377) - (-1582) = 451$ kJ mol^{-1}

The reaction cannot occur since ΔG° (298 K) is positive.

Example - 46

The heat librerated on complete combustion of 7.8g benzene is 327 kJ. This heat has been measured at constant volume at 27°C. Calculate heat of combustion of benzene at constant pressure at 27°C.

($R = 8.3$ J mol^{-1} K^{-1}).

Sol. $C_6H_6(l) + \frac{15}{2}O_2(g) \rightarrow 6CO_2(g) + 3H_2O(l)$

$$\Delta n = 6 - \frac{15}{2} = -\frac{3}{2}$$

Also, ΔU per mol $= -\frac{327 \times 78}{7.8} = -3270$ kJ

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

$$= -3270 + \left(-\frac{3}{2}\right) \times 8.3 \times 300 \times 10^{-3}$$

$\Delta H = -3273.735$ kJ

Example - 47

Calculate standard heat of formation of CS_2. Given that standard heat of combustion of C, S and CS_2 are – 393.3, – 293.72 and – 1108.76 kJ mol^{-1}.

Sol. We have to find ΔH for

$C + 2S \rightarrow CS_2$; $\quad \Delta H = ?$

Given, $C + O_2 \rightarrow CO_2$; $\quad \Delta H = -393.3$ kJ .... (1)

$S + O_2 \rightarrow SO_2$; $\quad \Delta H = -293.72$ kJ .... (2)

$CS_2 + 3O_2 \rightarrow CO_2 + 2SO_2$; $\Delta H = -1108.76$ kJ .... (3)

Multiply Eq. (2) by 2 and add in Eq. (1)

$C + 2S + 3O_2 \rightarrow CO_2 + 2SO_2$; $\Delta H = -980.74$ kJ .... (4)

Subtract Eq. (3) from Eq. (4)

$C + 2S \rightarrow CS_2$; $\quad \Delta H = +128.02$ kJ

ΔH_f of $CS_2 = +128.02$ kJ

Example - 48

Estimate the average S–F bond energy in SF_6. The standard heat of formation value of $SF_6(g)$, S (g) and F (g) are : – 1100, 275 and 80 kJ mol^{-1} respectively.

Sol. $\Delta H = \Delta H_{sub(s)} + 6\Delta H_F - 6\Delta H_{S-F}$

$-1100 = 275 + 6\,(80) - 6\Delta H_{S-F}$

$\Delta H_{S-F} = 309.17$ kJ/mol

Example - 49

From the following themochemical equations, calculate the enthalpy of formation of cane sugar $(C_{12}H_{22}O_{11})$:

(i) $C_{12}H_{22}O_{11}\,(s) + 12\,O_2(g) \rightarrow 12\,CO_2(g) + 11\,H_2O\,(l)$ $\quad \Delta_rH_1 = -5644$ kJ mol^{-1}

(ii) $C\,(s) + O_2\,(g) \rightarrow CO_2(g)$ $\quad \Delta_rH_2 = -393$ kJ mol^{-1}

(iii) $H_2(g) + 1/2\,O_2(g) \rightarrow H_2O\,(l)$ $\quad \Delta_rH_3 = -286$ kJ mol^{-1}

Sol. Aim equation : $12C\,(s) + 11\,H_2\,(g) \rightarrow C_{12}\,H_{22}\,O_{11}\,(s)$ $\quad \Delta H = ?$

$\Delta H = 12\Delta H_2 + 11\,\Delta H_3 - \Delta H_1$

$= 12\,(-393) + 11\,(-286) - (-5644)$

$= -2218$ kJ/mol

Example - 50

The standard molar enthalpies of formation of cyclohexane (*l*) and benzene (*l*) at 25ºC are – 156 and + 49 kJ mol^{-1} respectively. The standard enthalpy of hydrogenation of cyclohexene (*l*) at 25ºC 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

$= \Delta H_f$ (Cyclohexane) – ΔH_f (Benzene)

$= -156 - (+49)$ kJ

$= -205$ kJ.

Given, that,

Cyclohexene + $H_2 \rightarrow$ Cyclohexane ; $\Delta H = -119$ kJ

Theoretical enthalpy of formation of 3 double bonds in benzene ring

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

∴ resonance energy of benzene $= -357 - (-205)$ kJ

$= -152$ kJ mol^{-1}.

EXERCISE - 1 : BASIC OBJECTIVE QUESTIONS

Introduction of Thermodynamics

1. Which of the following is not a state function ?

(a) Heat (b) Internal energy

(c) Enthalpy (d) Entropy

2. Which of the following quantities is not a state function ?

(a) Temperature (b) Entropy

(c) Enthalpy (d) Work

3. Which of the following is not an intensive property ?

(a) Entropy (b) Pressure

(c) Temperature (d) Molar volume

4. Which of the following is a state function and also an extensive property?

(a) Internal energy (b) Pressure

(c) Molar heat capacity (d) Temperature

5. 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

6. A tightly closed thermoflask contains some ice cubes. This constitutes

(a) closed system (b) open system

(c) isolated system

(d) Non-thermodynamic system

Internal Energy, Concept of Heat and Work

7. A sample of gas changes from P_1, V_1 and T_1 to P_2, V_2 and T_2 by one path and then back to P_1, V_1 and T_1, ΔU for the process is :

(a) Infinite (b) > 0

(c) < 0 (d) equal to 0

8. Which of the following changes would definitely increase the internal energy of a system?

(a) The system gains heat and performs work.

(b) The system gains heat and has work performed on it.

(c) The system loses heat and performs work.

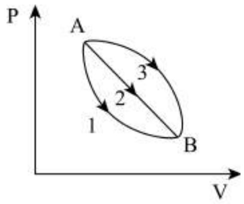
(d) The system loses heat and has work performed on it.

9. What is the change in internal energy when a gas contracts from 377 mL to 177 mL under a constant pressure of 1520 torr, while at the same time being cooled by removing 124 J heat?

(a) 40.52 J (b) –83.48 J

(c) –248 J (d) None of these

10. A given mass of gas expands from the state A to the state B by three paths 1, 2 and 3 as shown in the figure. If w_1, w_2 and w_3 respectively be the magnitudes work done by the gas along three paths then :

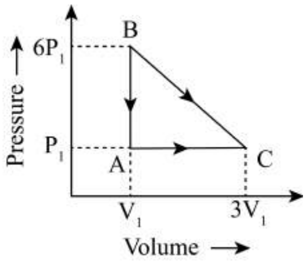


(a) $w_1 > w_2 > w_3$ (b) $w_1 < w_2 < w_3$

(c) $w_1 = w_2 = w_3$ (d) $w_2 < w_3 < w_1$

11. An ideal gas is taken around the cycle ABCA as shown in P-V diagram

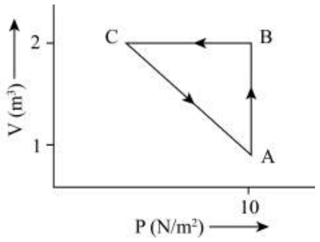
The net work done by the gas during the cycle is equal to :



(a) $12 P_1V_1$ (b) $6P_1V_1$

(c) $5P_1V_1$ (d) P_1V_1

12. An ideal gas is taken through the cycle $A \rightarrow B \rightarrow C \rightarrow A$ as shown in fig. If the net heat supplied to the gas in cycle is 5 J, the work done by the gas in the process $C \rightarrow A$.



(a) –5 J (b) –10 J

(c) –15 J (d) –20 J

13. In a system where $\Delta E = -51.0$ kJ, a piston expanded against a p_{ext} of 1.2 atm giving a change in volume of 32.0 L. What was the change in heat of this system?

(a) –36 kJ (b) –13 kJ

(c) –47 kJ (d) 24 kJ

First Law of Thermodynamics

14. A system absorb 10 kJ of heat at constant volume and its temperature rises from 27°C to 37°C. The value of ΔU is

(a) 100 kJ (b) 10 kJ

(c) 0 (d) 1 kJ

15. As per the First Law of thermodynamics, which of the following statement would be appropriate :

(a) Energy of the system remains constant

(b) Energy of the surroundings remains constant

(c) Entropy of the universe remains constant

(d) Energy of the universe remains constant

16. 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) $w > 0; q = 0; \Delta U > 0$

17. For a particular process $q = -10$ kJ and w=25 kJ. Which of the following statements is true?

(a) Heat flows from the surroundings to the system.

(b) The system does work on the surroundings.

(c) $\Delta E = -35$ kJ

(d) None of the above is true

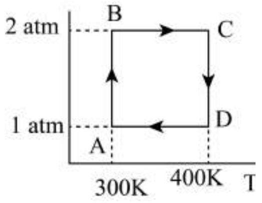
Reversible and Irreversible Work

18. In an isothermal expansion of an ideal gas

(a) $q = 0$ (b) $\Delta V = 0$

(c) $\Delta U = 0$ (d) $w = 0$

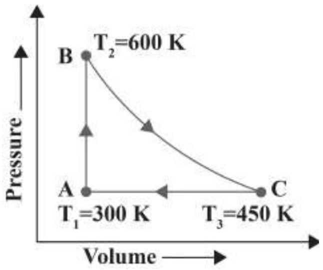
19. Two moles of Helium gas undergo a reversible cyclic process as shown in figure. Assuming gas to be ideal. What is the work for the process C to D ?



(a) $-800 R\ell n2$ (b) zero

(c) $+200 R\ell n2$ (d) $-600 R\ell n2$

20. A heat engine carries one mole of an ideal mono-atomic gas around the cycle as shown in 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

21. An ideal gas receives 10 J of heat in a reversible isothermal expansion. Then the work done by the gas :

(a) would be more than 10 J

(b) 10 J

(c) would be less than 10 J

(d) cannot be determined

22. The maximum work obtained by an isothermal reversible expansion of 1 mole of an ideal gas at 27°C from 2.24 to 22.4 L is (R = 2 cal)

(a) – 1381.8 cal (b) – 600 cal

(c) –138.18 cal (d) – 690.9 cal

23. 2 mole of an ideal gas at 27°C expands isothermally and reversibly from a volume of 4 litres to 40 litre. The work done (in kJ) is:

(a) $w = -28.72$ kJ (b) $w = -11.488$ kJ

(c) $w = -5.736$ kJ (d) $w = -4.988$ kJ

24. 5 mole of an ideal gas expand isothermally and irreversibly from a pressure of 10 atm to 1 atm against a constant external pressure of 1 atm. w_{irr} at 300 K is:

(a) –15.921kJ (b) –11.224 kJ

(c) –110.83 kJ (d) None of these

25. 10 mole of ideal gas expand isothermally and reversibly from a pressure of 10 atm to 1 atm at 300 K. What is the largest mass which can lifted through a height of 100 meter?

(a) 31842 kg (b) 58.55 kg

(c) 342.58 kg (d) None of these

26. Which of the following statement is true?

(a) A thermodynamic process is defined by initial and final states.

(b) $\Delta E=0$ for a reversible phase change at constant T and P.

(c) q must be zero for an isothermal process.

(d) A reversible adiabatic process is also isoentropic.

27. In the thermodynamic sense of the word, an irreversible process

(a) does the same work (but of opposite sign) as a reversible process

(b) violates the 1st law of thermodynamics, unlike a reversible process

(c) involves non-ideal gases (as opposed to ideal gases in a reversible process)

(d) exchanges the same amount of heat (but of opposite sign) as a reversible process.

Heat Capacity of a System, Adiabatic Process and Poisson's Ratio

28. Molar heat capacity of water in equilibrium with ice at constant pressure is

(a) zero
(b) ∞
(c) $40.45\ \text{kJ K}^{-1}\ \text{mol}^{-1}$
(d) $75.48\ \text{J K}^{-1}\ \text{mol}^{-1}$

29. 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 (ice) = C_P (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) $75.48\ \text{JK}^{-1}\ \text{mol}^{-1}$

30. In an adiabatic expansion of an ideal gas

(a) $\Delta T = 0$
(b) $w = 0$
(c) $q = 0$
(d) $\Delta U = 0$

31. The temperature of the system decreases in an

(a) Isothermal compression
(b) Isothermal expansion
(c) Adiabatic compression
(d) Adiabtic expansion

32. 1 mole of NH_3 gas at 27°C is expanded in reversible adiabatic condition to make volume 8 times (γ = 1.33). Final temperature and work done by the gas respectively are :

(a) 150 K, 900 cal
(b) 150 K, 400 cal
(c) 250 K, 1000 cal
(d) 200 K, 800 cal

33. During the adiabatic expansion of an ideal gas against atmospheric pressure, the internal energy will

(a) Increase
(b) decrease
(c) stay the same
(d) Impossible to say

34. One mole of an ideal gas expands reversibly and adiabatically from a temperature of 27°C. If the work done during the process is 3 kJ, then final temperature of the gas is:($C_V = 20$ J/K)

(a) 100 K
(b) 150 K
(c) 195 K
(d) 255 K

Enthalpy of a System

35. For a chemical reaction at constant P and V, ΔH is equal to

(a) ΔU
(b) zero
(c) $\Delta U + P\Delta V$
(d) p/T

36. For an endothermic reaction, ΔS is positive. The reaction is :

(a) feasible when $T\Delta S > \Delta H$

(b) feasible when $\Delta H > T\Delta S$

(c) feasible at all temperatures

(d) not feasible at all

37. Which of the following conditions is not favourable for the feasibility of a process ?

(a) $\Delta H = -\text{ve}$, $T\Delta S = -\text{ve}$ and $T\Delta S < \Delta H$

(b) $\Delta H = +\text{ve}$, $T\Delta S = +\text{ve}$ and $T\Delta S > \Delta H$

(c) $\Delta H = -\text{ve}$, $T\Delta S = +\text{ve}$ and $\Delta H > T\Delta S$

(d) $\Delta H = +\text{ve}$, $T\Delta S = +\text{ve}$ and $\Delta H > T\Delta S$

38. In which of the following cases, the reaction is spontaneous at all temperatures ?

(a) $\Delta H > 0, \Delta S > 0$
(b) $\Delta H < 0, \Delta S > 0$
(c) $\Delta H < 0, \Delta S < 0$
(d) $\Delta H > 0, \Delta S < 0$

39. Which of the following is true for the reaction ?

$H_2O(\ell) \rightleftharpoons H_2O(g)$ at 100°C and 1 atm pressure

(a) $\Delta S = 0$
(b) $\Delta H = T\Delta S$
(c) $\Delta H = \Delta U$
(d) $\Delta H = 0$

40. For the reaction :

$$C(s) + O_2(g) \longrightarrow CO_2(g)$$

(a) $\Delta H < \Delta U$
(b) $\Delta H > \Delta U$
(c) $\Delta H = \Delta U$
(d) $\Delta H = 0$

41. For which of the following reactions, ΔH is greater than ΔU ?

(a) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

(b) $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$

(c) $PCl_5(g) \longrightarrow PCl_3(g) + Cl_2(g)$

(d) $HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(aq)$

42. For the reaction,

$$PCl_5(g) \longrightarrow PCl_3(g) + Cl_2(g)$$

(a) $\Delta H = \Delta U$ (b) $\Delta H > \Delta U$

(c) $\Delta H < \Delta U$ (d) None of these

43. $(\Delta U - \Delta H)$ for the formation of NH_3 from N_2 and H_2 is :

(a) RT (b) 2 RT

(c) -2 RT (d) $\frac{1}{2}$ RT

44. The difference between heats of reaction at constant pressure and constant volume for the reaction.

$2C_2H_6(l) + 15O_2(g) \longrightarrow 12CO_2(g) + 6H_2O(l)$ at 25°C is

(a) –7.43 kJ (b) +3.72 kJ

(c) –3.72 kJ (d) 7.43 kJ

45. For the reaction :

$$C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(\ell)$$

at 298 K, $\Delta U = -1415$ kJ.

If $R = 0.0084$ kJ K^{-1}, then ΔH is equal to

(a) –1400 kJ (b) –1410 kJ

(c) –1420 kJ (d) –1430 kJ

46. The difference between ΔH and ΔE on a molar basis for the combustion of methane gas at 300K (kelvin) would be :

(a) zero (b) –RT

(c) –2RT (d) –3RT

47. Consider the reaction at 300 K

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g); \qquad \Delta H^\circ = -185 \text{ kJ}$$

If 2 mole of H_2 completely react with 2 mole of Cl_2 to form HCl. What is ΔU° for this reaction ?

(a) 0 (b) –185 kJ

(c) 370 kJ (d) –370 kJ

48. In an endothermic reaction

(a) ΔH is negative

(b) Heat is given to the surroundings

(c) Enthalpy of the reactants is less than that of the products

(d) ΔE is negative

49 For the process : $CO_2(s) \longrightarrow CO_2(g)$

(a) Both ΔH and ΔS are +ve

(b) ΔH is –ve, ΔS is +ve

(c) ΔH is +ve, ΔS is –ve

(d) Both ΔH and ΔS are –ve.

Second Law of Thermodynamics

50. The statement "A heat engine always loses some of its heat energy to the surroundings." is an example of which of the following laws?

(a) The Law of Corresponding States

(b) The Zeroth Law of Thermodynamics

(c) The First Law of Thermodynamics

(d) The Second Law of Thermodynamics

51. The entropy of the universe

(a) tends towards a maximum

(b) tends towards a minimum

(c) tends to be zero

(d) remains constant

52. Heat cannot by self flow from a body at lower temperature to a body at higher temperature a statement of consequence of:

(a) 1st law of thermodynamics

(b) 2nd law of thermodynamics

(c) conservation of momentum

(d) conservation of mass

53. When steam condenses to water at 90°C, the entropy of the system decreases. What must be true if the second law of thermodynamics is to be satisfied?

(a) Entropy of the universe also decreases.

(b) Entropy of the surroundings also decreases.

(c) Entropy of the surroundings increases to same extent to which entropy of the system decreases.

(d) Increase in entropy in the surroundings is greater than decrease in entropy of the system.

Entropy and Spontaneity

54. Which of the following has highest entropy ?

(a) Mercury (b) Hydrogen

(c) Water (d) Graphite

55. For a reversible process at equilibrium, the change in entropy may be expressed as :

(a) $\Delta S = Tq_{rev}$ (b) $\Delta S = \frac{q_{rev}}{T}$

(c) $\Delta S = -\frac{\Delta H}{T}$ (d) $\Delta S = \Delta G$

56. Entropy is a measure of

(a) disorder

(b) internal energy

(c) efficiency

(d) useful work done by the system

57. When a solid is converted directly into gaseous state, the process is called sublimation. The entropy change during the process is :

(a) zero (b) negative

(c) positive (d) may be negative or zero

58. The enthalpy of vaporisation of a substance is 8400 J mol^{-1} and its boiling point is –173ºC. The entropy change for vaporisation is :

(a) 84 J mol^{-1} K^{-1} (b) 21 J mol^{-1} K^{-1}

(c) 49 J mol^{-1} K^{-1} (d) 12 J mol^{-1} K^{-1}

59. The enthalpy of vaporisation of a compound AB at its boiling point (127°C) is 6.4 kJ mol^{-1}. Its entropy of vaporisation is :

(a) 2.56 kJ mol^{-1} (b) 16 J mol^{-1}

(c) 16×10^{-3} J mol^{-1} (d) 1.6×10^{3} kJ mol^{-1}

60. The entropy change for the conversion of 1 mol of α–tin (at 13°C, 1 atm) to 1 mol of β–tin (13°C, 1 atm), if enthalpy of transition is 2.095 kJ mol^{-1} is :

(a) 7.32 J mol^{-1} K^{-1} (b) 14.62 J K^{-1} mol^{-1}

(c) 56.3 J mol^{-1} K^{-1} (d) 0

61. The following data is known about the melting of a compound AB. $\Delta H = 9.2$ kJ mol^{-1}. $\Delta S = 0.008$ kJ K^{-1} mol^{-1}. Its melting point is :

(a) 736 K (b) 1050 K

(c) 1150 K (d) 1150°C

62. When potassium chloride is dissolved in water

(a) Entropy increases

(b) Entropy decreases

(c) Entropy increases and then decreases

(d) Free energy increases

63. Which of the following processes is not accompanied by increase of entropy ?

(a) dissolution of NH_4Cl in water

(b) burning of rocket fuel

(c) sublimation of dry ice

(d) condensing steam

64. When two mole of an ideal gas $\left(C_{p,m.} = \frac{5}{2}R\right)$ heated from 300 K to 600 K constant pressure. The change in entropy of gas (ΔS) is :

(a) $\frac{3}{2}R\,\ell n\,2$ (b) $-\frac{3}{2}R\,\ell n\,2$

(c) $5\,R\,\ell n\,2$ (d) $\frac{5}{2}R\,\ell n\,2$

65. In the above question calculate ΔS_{gas} if process is carried out at constant volume :

(a) $5\,R\,\ell n\,2$ (b) $\frac{3}{2}R\,\ell n\,2$

(c) $3\,R\,\ell n\,2$ (d) $-3\,R\,\ell n\,2$

66. The entropy change when two moles of ideal monoatomic gas is heated from 200°C to 300°C reversibly and isochorically ?

(a) $\frac{3}{2}R\,\ell n\left(\frac{300}{200}\right)$ (b) $\frac{5}{2}R\,\ell n\left(\frac{573}{273}\right)$

(c) $3R\,\ell n\left(\frac{573}{473}\right)$ (d) $\frac{3}{2}R\,\ell n\left(\frac{573}{473}\right)$

67. If one mole of an ideal gas $\left(C_{p.m.} = \frac{5}{2}R\right)$ is expanded isothermally at 300 K until it's volume is tripled, then change in entropy of gas is :

(a) zero (b) infinity

(c) $\frac{5}{2}R\,\ell n\,3$ (d) $R\,\ell n\,3$

68. 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) $C_{p,m}$ ln2 (b) $C_{v,m}$ ln2

(c) R ln2 (d) ($C_{v,m}$ –R) ln2

69. Two mole of a monoatomic ideal gas is expanded irreversibly and isothermally at T Kelvin until its volume is doubled and q joules of heat is absorbed from surrounding. ΔS_{total} (J/K) (system + surrounding) is :

(a) zero (b) 2 Rln2–q/T

(c) 3Rln2–q/T (d) –2 Rln2 + q/T

70. One mole of an ideal diatomic gas (C_v = 5 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 calories/mol/K)

(a) $3\ell n\frac{298}{373} + 2\,\ell n 10$ (b) $5\ell n\frac{373}{298} + 2\,\ell n 10$

(c) $7\ell n\frac{373}{298} + 2\,\ell n\frac{1}{10}$ (d) $5\ell n\frac{373}{298} + 2\,\ell n\frac{1}{10}$

71. A reaction has $\Delta H = -33$ kJ and $\Delta S = +58$ J/K. This reaction would be :

(a) spontaneous below a certain temperature

(b) non-spontaneous at all temperature

(c) spontaneous above a certain temperature

(d) spontaneous at all temperature

72. Calculate the entropy change (J/mol K) of the given reaction. The molar entropies [J/K–mol] are given in brackets after each substance.

$$2\,PbS(s)\,[91.2] + 3O_2(g)[205.1] \longrightarrow$$

$$2PbO(s)\,[66.5] + 2SO_2(g)[248.2]$$

(a) –113.5 (b) –168.3

(c) +72.5 (d) –149.2

73. Given $\Delta_r S^\circ = -266$ and listed [S°_m values] calculate S° for $Fe_3O_4(s)$:

$$4Fe_3O_4(s)[.......] + O_2(g)[205] \rightarrow 6Fe_2O_3(S)[87]$$

(a) +111.1 (b) +122.4

(c) +145.75 (d) 248.25

Gibb's Energy, Enthalpy of reactions/processes

74. For a reaction to be spontaneous at all temperatures

(a) ΔG and ΔH should be negative

(b) $\Delta H = \Delta G = 0$

(c) ΔG and ΔH should be positive

(d) $\Delta H < \Delta G$

75. For isothermal expansion in case of an ideal gas :

(a) $\Delta G = \Delta S$ (b) $\Delta G = \Delta H$

(c) $\Delta G = -T.\Delta S$ (d) None of these

76. For the reaction at 300 K

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

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

($R \approx 2$ cal mol^{-1} K^{-1})

ΔG is :

(a) –600 cal (b) –3600 cal

(c) 2400 cal (d) 3000 cal

77. The enthalpies of elements in their standard states are taken as zero. Hence the enthalpy of formation of a compound

(a) should always be negative

(b) should always be positive

(c) will be equal to twice the energy of combination

(d) may be positive or negative

78. Which of the following pairs has heat of neutralisation equal to –57.1 kJ ?

(a) HNO_3,KOH (b) HCl, NH_4OH

(c) H_2SO_4,NH_4OH (d) CH_3COOH,NaOH

79. Which of the following neutralisation reactions is most exothermic ?

(a) HCl and NaOH

(b) HCN and NaOH

(c) HCl and NH_4OH

(d) CH_3COOH and NH_4OH

80. The enthalpy change for the reaction,

$H_2O(s) \longrightarrow H_2O(\ell)$ is called

(a) Enthalpy of formation

(b) Enthalpy of fusion

(c) Enthalpy of vaporisation

(d) Enthalpy of transition

81. The enthalpies of formation of N_2O and NO at 298 K are 82 and 90 kJ mol^{-1}. The enthalpy of the reaction :

$$N_2O(g) + \tfrac{1}{2}O_2(g) \longrightarrow 2NO(g)$$

(a) –8 kJ (b) 98 kJ

(c) –74 kJ (d) 8 kJ

82. The enthalpies of solution of anhydrous $CuSO_4$ and $CuSO_4.5H_2O$ are –15.89 and 2.80 k cal mol^{-1} respectively. The enthalpy of hydration of $CuSO_4$ to $CuSO_4.5H_2O$ is :

(a) –18.69 kcal (b) 13.09 kcal

(c) –13.09 kcal (d) 18.69 kcal

83. Calculate the heat required to make 6.4 Kg CaC_2 from CaO(s) and C(s) from the reaction :

$CaO(s) + 3\,C(s) \longrightarrow CaC_2(s) + CO(g)$ given that

$\Delta_f H^\circ(CaO) = -151.6$ kcal, $\Delta_f H^\circ(CaC_2) = -14.2$kcal.

$\Delta_f H^\circ(CO) = -26.4$ kcal.

(a) 5624 kcal (b) 1.11×10^4 kcal

(c) 86.24×10^3 (d) 1100 kcal

84. Given :

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g) + q_1$

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O\,(l) + q_2$

The enthalpy of vaporisation of water is equal to

(a) $q_1 + q_2$
(b) $q_1 - q_2$
(c) $q_2 - q_1$
(d) q_1q_2

85. If $CH_3COOH + OH^- \longrightarrow CH_3COO^- + H_2O + x\,kJ$

$H^+ + OH^- \longrightarrow H_2O + y\,kJ$

The enthalpy change for the reaction :

$CH_3COOH \longrightarrow CH_3COO^- + H^+$ is

(a) x + y
(b) x – y
(c) y – x
(d) x – y/2

86. Which of the following reactions represents enthalpy of formation of AgCl ?

(a) $Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$
(b) $AgCl(s) \longrightarrow Ag(s) + \frac{1}{2}Cl_2(g)$
(c) $Ag(s) + AuCl(s) \longrightarrow AgCl(s) + Au(s)$
(d) $Ag(s) + \frac{1}{2}Cl_2(g) \longrightarrow AgCl(s).$

87. Which of the following equations represents standard heat of formation of methane ?

(a) C (diamond) + $2H_2(g) \longrightarrow CH_4(g)$
(b) C (graphite) + $2H_2(g) \longrightarrow CH_4(g)$
(c) C (diamond) + $4H(g) \longrightarrow CH_4(g)$
(d) C (graphite) + $4H(g) \longrightarrow CH_4(g)$

88. For the reaction,

$$2H_2O(g) \longrightarrow 2H_2(g) + O_2(g) \quad \Delta H = 571.6\,KJ$$

$\Delta_f H^0$ of water is :

(a) 285.8 kJ
(b) –285.8 kJ
(c) 1143.2 kJ
(d) –1143.2 kJ

89. ΔH for the reaction,

$$SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g) \qquad \Delta H = -98.3\,kJ$$

If the enthalpy of formation of $SO_3(g)$ is –395.4 kJ then the enthalpy of formation of $SO_2(g)$ is :

(a) –297.1 kJ
(b) 493.7 kJ
(c) –493.7 kJ
(d) 297.1 kJ

90. The standard heat of formation at 101.3 kNm^{-2} and 298 K is arbitrarily taken to be zero for :

(a) gaseous bromine atoms
(b) gaseous bromine molecules
(c) liquid bromine
(d) solid bromine.

91. The enthalpy of formation of two compounds A and B are –84 kJ and –156 kJ respectively. Which one of the following statements is correct ?

(a) A and B are endothermic compounds
(b) A is more stable than B
(c) A is less stable than B
(d) Both A and B are unstable

92. When 0.5 g of sulphur is burnt to SO_2 4.6 kJ of heat is liberated. What is the enthalpy of formation of sulphur dioxide ?

(a) –147.2 kJ
(b) +147.2 kJ
(c) +294.4 kJ
(d) –294.4 kJ

93. The heat of formation of $Fe_2O_3(s)$ is –824.2 kJ mol^{-1}. ΔH for the reaction.

$2Fe_2O_3(s) \longrightarrow 4Fe(s) + 3O_2(g)$ is :

(a) –412.1 kJ
(b) –1648.4 kJ
(c) –3296.8 kJ
(d) 1648.4 kJ

94. The ΔH^0 for the reaction,

$4S(s) + 6O_2(g) \longrightarrow 4\,SO_3(g)$

is –1583.2 kJ. Standard enthalpy of formation of sulphur trioxide is :

(a) –3166.4 kJ
(b) 3166.4 kJ
(c) –395.8 kJ
(d) 395.8 kJ

95. Calculate the heat of formation of $PCl_5(s)$ from the following data :

$2P(s) + 3Cl_2(g) \longrightarrow 2PCl_3(l)$ $\Delta H = -151.8$ kcal

$PCl_3(l) + Cl_2(g) \longrightarrow PCl_5(s)$ $\Delta H = -32.8$ kcal

(a) –108.7 kcal
(b) 108.7 kcal
(c) –184.6 kcal
(d) 184.6 kcal

96. If $S + O_2 \longrightarrow SO_2 \quad \Delta H = -298.2 \text{ kJ}$

$$SO_2 + \frac{1}{2}O_2 \longrightarrow SO_3 \quad \Delta H = -98.2 \text{ kJ}$$

$$SO_3 + H_2O \longrightarrow H_2SO_4 \quad \Delta H = -130.2 \text{ kJ}$$

$$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O \quad \Delta H = -287.3 \text{ kJ}$$

the enthalpy of formation of H_2SO_4 at 298 K will be

(a) –433.7 kJ (b) –650.3 kJ

(c) +320.5 kJ (d) –813.9 kJ

97. The enthalpies of combustion of carbon and carbon monoxide are –393.5 and –283.0 kJ mol^{-1} respectively. The enthalpy of formation of carbon monoxide is :

(a) –676.5 kJ (b) 110.5 kJ

(c) –110.5 kJ (d) 676.5 kJ

98. On combustion, carbon forms two oxides CO and CO_2. Heat of formation of CO_2 is –393.5 kJ and that of CO is –110.5 kJ. Heat of combustion of CO is :

(a) –393.5 kJ (b) –504.0 kJ

(c) –283.0 kJ (d) 2830.0 kJ

99. Which of the following compounds will absorb maximum quantity of heat when dissolved in the same amount of water. The enthalpies of solution of these compounds at 25°C in kJ/mole are given in brackets ?

(a) P ($\Delta H = -32.6$ kJ mol^{-1}) (b) Q ($\Delta H = -17.3$ kJ mol^{-1})

(c) R ($\Delta H = +2.56$ kJ mol^{-1}) (d) S ($\Delta H = +25.6$ kJ mol^{-1})

100. Which of the following salts will have maximum cooling effect when 0.5 mole of the salt is dissolved in same amount of water. Integral heat of solution at 298 K is given for each salt ?

(a) KNO_3 ($\Delta H = 35.4$ kJ mol^{-1})

(b) NaCl ($\Delta H = 5.35$ kJ mol^{-1})

(c) HBr ($\Delta H = -83.3$ kJ mol^{-1})

(d) KOH ($\Delta H = -55.6$ kJ mol^{-1})

101. The enthalpy of neutralisation of HCl by NaOH is –57.1 kJ and that of HCN by NaOH is –12.1 kJ mol^{-1}. The enthalpy of ionization of HCN is :

(a) –69.2 kJ (b) –45.0 kJ

(c) 69.2 kJ (d) 45.0 kJ

102. The enthalpy of neutralisation of NH_4OH and HCl is :

(a) 57.1 kJ mol^{-1} (b) < 57.1 kJ mol^{-1}

(c) > 57.1 kJ mol^{-1} (d) zero

103. The heat of neutralisation of NaOH and HCl is 57.3 kJ mol^{-1}. The amount of heat liberated when 0.25 mol of H_2SO_4 reacts with 1 mole of NaOH is

(a) 57.3 kJ (b) 14.325 kJ

(c) 28.65 kJ (d) 114.6 kJ

104. The heat of neutralisation of strong base and strong acid is 57.0 kJ. The heat released when 0.5 mol of HNO_3 is added to 0.2 mol of NaOH solution is :

(a) 57.0 kJ (b) 11.40 kJ

(c) 28.5 kJ (d) 34.9 kJ

105. In which of the following neutralisation reaction, the heat of neutralisation will be highest ?

(a) NH_4OH and H_2SO_4 (b) HCl and NaOH

(c) CH_3COOH and KOH (d) CH_3COOH and NH_4OH

106. 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 is the acid distribution between AOH and BOH?

(a) 2:1 (b) 2:3

(c) 1:2 (d) None of these

107. In what proportion 1 M NaOH and 0.5M H_2SO_4 are mixed so as to release maximum amount of energy and to form 100 mL solution ?

(a) 33 and 67 (b) 67 and 33

(c) 40 and 60 (d) 50 and 50

108. The enthalpies of combustion of rhombic sulphur and monoclinic sulphur are –295.1 and –296.4 kJ mol^{-1} respectively. The enthalpy of allotropic transformation of monoclinic to rhombic sulphur is :

(a) 1.3 kJ (b) –1.3 kJ

(c) –591.5 kJ (d) 0

109. Which of the following enthalpies is always negative ?

(a) Enthalpy of solution

(b) Enthalpy of combustion

(c) Enthalpy of sublimation

(d) Enthalpy of formation

110. In the reaction :

$$CO_2(g) + H_2(g) \longrightarrow CO(g) + H_2O(g) \quad \Delta H = 2.8\ kJ$$

then ΔH represents

(a) heat of formation (b) heat of reaction

(c) heat of solution (c) heat of combustion

111. Using the following energy values, determine the lattice energy of KF(s):

Property	**Energy (kJ mol^{-1})**
$\Delta H_{atomization}$ of K(s)	90
$\Delta H_{atomization}$ of F_2(s)	158
ΔH_f of KF(s)	–567
IE of K(s)	419
EA of F(g)	328

(a) 51 kJ (b) + 827 kJ

(c) + 1145 kJ (d) + 1483 kJ

112. The lattice enthalpy and hydration enthalpy of four compounds are given below:

Compound	**Lattice enthalpy (kJ/mol)**	**Hydration enthalpy (kJ/mol)**
P	+780	–920
Q	+1012	–812
R	+828	–878
S	+632	–600

The pair of compounds which is soluble in water is

(a) P and Q (b) Q and R

(c) R and S (d) P and R

Bond Dissociation Enthalpy

113. The standard enthalpies of formation of HCl(g), H(g) and Cl(g) are –92.2, 217.7 and 121.4 kJ mol^{-1} respectively. The bond dissociation energy of HCl is :

(a) +431.3 kJ (b) 236.9 kJ

(c) –431.3 kJ (d) 339.1 kJ

114. The enthalpy changes at 25°C in successive breaking of O–H bonds of water are :

$$H_2O(g) \longrightarrow H(g) + OH(g) \ \Delta H = 498\ kJ\ mol^{-1}$$

$$OH(g) \longrightarrow H(g) + O(g) \quad \Delta H = 428\ kJ\ mol^{-1}$$

the bond enthalpy of the O–H bond is :

(a) 498 kJ mol^{-1} (b) 463 kJ mol^{-1}

(c) 428 kJ mol^{-1} (d) 70 kJ mol^{-1}

115. Calculate the heat of the reaction

$$CH_2 = CH_2(g) + H_2(g) \longrightarrow CH_3CH_3(g)$$

given that bond energy of C – C, C = C, C – H and H – H is 80, 145, 98 and 103 kcal.

(a) –28 kcal mol^{-1} (b) –5.6 kcal mol^{-1}

(c) –2.8 kcal mol^{-1} (d) –56 kcal mol^{-1}

116. The enthalpy change for the following reaction is 368 kJ. Calculate the average O–F bond energy.

$$OF_2(g) \rightarrow O(g) + 2F(g)$$

(a) 184 kJ/mol (b) 368 kJ/mol

(c) 536 kJ/mol (d) 736 kJ/mol

117. The enthalpy change for the reaction, $C_2H_6(g) \rightarrow 2C(g) + 6H(g)$ is X kJ. The bond energy of C–H bond is:

(a) $\frac{X}{2}$ (b) $\frac{X}{3}$

(c) $\frac{X}{6}$ (d) data insufficient

118. Based on the values of B.E. given, $\Delta_f H^\circ$ of N_2H_4(g) is:

Given: N–N = 159 kJ mol^{-1}; H–H = 436 kJ mol^{-1}

N ≡ N = 941 kJ mol^{-1}, N–H = 398 kJ mol^{-1}

(a) 711 kJ mol^{-1} (b) 62 kJ mol^{-1}

(c) –98 kJ mol^{-1} (d) –711 kJ mol^{-1}

119. The dissociation energy of CH_4 and C_2H_6 are respectively 360 and 620 kcal/mole. The bond energy of C–C is

(a) 260 k cal/mole (b) 180 k cal/mole

(c) 130 k cal/mole (d) 80 k cal/mole

120. An imaginary reaction X → Y takes place in three steps

$X \rightarrow A, \Delta H = -q_1; B \rightarrow A, \Delta H = -q_2, B \rightarrow Y, \Delta H = -q_3$

If Hess' law is applicable, then the heat of the reaction (X → Y) is:

(a) $q_1 - q_2 + q_3$ (b) $q_2 - q_3 - q_1$

(c) $q_1 - q_2 - q_3$ (d) $q_3 - q_2 - q_1$

EXERCISE - 2 : PREVIOUS YEAR JEE MAINS QUESTIONS

1. A reaction is non-spontaneous at the freezing point of water but is spontaneous at the boiling point of water, then **(2002)**

	ΔH	ΔS
(a)	+ ve	+ ve
(b)	– ve	– ve
(c)	– ve	+ ve
(d)	+ ve	– ve

2. A heat engine absorbs heat q_1 from a source at temperature T_1 and heat q_2 from a source at temperature T_2. Work done is found to be J $(q_1 + q_2)$. This is in accordance with **(2002)**

(a) First law of thermodynamics

(b) Second law of thermodynamics

(c) Joules equivalent law

(d) None of the above

3. Heat required to raise the temperature of 1 mole of a substance by 1° is called **(2002)**

(a) specific heat

(b) molar heat capacity

(c) water equivalent

(d) specific gravity

4. The correct relationship between free energy change in a reaction and the corresponding equilibrium constant K_c is **(2003)**

(a) $\Delta G = RT \ln K_c$

(b) $-\Delta G = RT \ln K_c$

(c) $\Delta G^o = RT \ln K_c$

(d) $-\Delta G^o = RT \ln K_c$

5. If at 298 K the bond energies of C—H, C—C, C═C and H—H bonds are respectively, 414, 347, 615 and 435 kJ mol^{-1}, the value of enthalpy change for the reaction,

$H_2C=CH_2(g) + H_2(g) \longrightarrow H_3C—CH_3(g)$ at 298 K will be **(2003)**

(a) + 250 kJ

(b) – 250 kJ

(c) + 125 kJ

(d) – 125 kJ

6. The internal energy change when a system goes from state A to B is 40 kJ/mol. If the system goes from A to B by a reversible path and returns to state A by an irreversible path, what would be the net change in internal energy ? **(2003)**

(a) 40 kJ

(b) > 40 kJ

(c) < 40 kJ

(d) zero

7. The enthalpy change for a reaction does not depend upon the **(2003)**

(a) physical state of reactants and products

(b) use of different reactants for the same product

(c) nature of intermediate reaction steps

(d) difference in initial or final temperatures of involved substances

8. 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 **(2004)**

(a) 110.5 kJ

(b) 676.5 kJ

(c) – 676.5 kJ

(d) – 110.5 kJ

9. An ideal gas expands in volume from 1×10^{-3} m^3 to 1×10^{-2} m^3 at 300 K against a constant pressure of 1×10^5 Nm^{-2}. The work done is **(2004)**

(a) – 900 J

(b) – 900 kJ

(c) 270 kJ

(d) 900 kJ

10. For a spontaneous reaction the ΔG, equilibrium constant (K) and E^o_{cell} will be respectively **(2005)**

(a) –ve, >1, –ve

(b) –ve, <1, –ve

(c) +ve, >1, –ve

(d) –ve, >1, + ve

11. 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 **(2005)**

(a) 400 kJ mol^{-1}

(b) 300 kJ mol^{-1}

(c) 800 kJ mol^{-1}

(d) None of these

12. Consider the reaction : $N_2 + 3H_2 \rightarrow 2NH_3$ carried out at constant temperature and pressure. If ΔH and ΔE are the enthalpy and internal energy changes for the reaction, which of the following expressions is true ? **(2005)**

(a) $\Delta H > \Delta E$

(b) $\Delta H < \Delta E$

(c) $\Delta H = \Delta E$

(d) $\Delta H = 0$

13. The standard enthalpy of formation (ΔH^o_f) at 298 K for methane, $CH_4(g)$ is – 74.8 kJ mol^{-1}.

The additional information required to determine the average energy for C—H bond formation would be **(2006)**

(a) the dissociation energy of H_2 and enthalpy of sublimation of carbon

(b) latent heat of vaporisation of methane

(c) the first four ionisation energies of carbon and electron gain enthalpy of hydrogen

(d) the dissociation energy of hydrogen molecule, H_2

14. The enthalpy changes for the following processes are listed below :

$Cl_2\,(g) \rightarrow 2Cl(g)$, 242.3 kJ mol^{-1}

$I_2(g) \rightarrow 2I(g)$, 151.0 kJ mol^{-1}

$ICl\,(g) \rightarrow I(g) + Cl\,(g)$, 211.3 kJ mol^{-1}

$I_2(s) \rightarrow I_2(g)$, 62.76 kJ mol^{-1}

Given that the standard states for iodine and chlorine are $I_2(s)$ and $Cl_2(g)$, the standard enthalpy of formation of $ICl\,(g)$ is **(2006)**

(a) – 14.6 kJ mol^{-1} (b) – 16.8 kJ mol^{-1}

(c) + 16.8 kJ mol^{-1} (d) + 244.8 kJ mol^{-1}

15. ($\Delta H - \Delta E$) for the formation of carbon monoxide (CO) from its elements at 298 K is (R=8.314 JK^{-1} mol^{-1}) **(2006)**

(a) – 1238.78 J mol^{-1}

(b) 1238.78 J mol^{-1}

(c) – 2477.57 J mol^{-1}

(d) 2477.57 J mol^{-1}

16. 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 ? **(2006)**

(a) $(T_f)_{irrev} > (T_f)_{rev}$

(b) $T_f > T_i$ for reversible process but $T_f = T_i$ for irreversible process

(c) $(T_f)_{rev} = (T_f)_{irrev}$

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

17. In conversion of limestone to lime,

$CaCO_3(s) \rightarrow CaO\,(s) + CO_2\,(g)$

the values of ΔH^o and ΔS^o are + 179.1 kJ mol^{-1} and 160.2 J/K respectively at 298 K and 1 bar. Assuming that ΔH^o and ΔS^o do not change with temperature, temperature above which conversion of limestone to lime will be spontaneous is **(2007)**

(a) 1008 K (b) 1200 K

(c) 845 K (d) 1118 K

18. Identify the correct statement regarding a spontaneous process. **(2007)**

(a) For a spontaneous process in an isolated system, the change in entropy is positive

(b) Endothermic processes are never spontaneous

(c) Exothermic processes are always spontaneous

(d) Lowering of energy in the reaction process is the only criterion for spontaneity

19. Assuming that water vapour is an ideal gas, the internal energy change (ΔE) when 1 mole of water is vaporised at 1 bar pressure and 100°C, (Given : molar enthalpy of vaporisation of water at 1 bar and 373 K = 41 KJ mol^{-1} and R = 8.3 J mol^{-1} K^{-1}) will be **(2007)**

(a) 4.100 kJ mol^{-1} (b) 3.7904 kJ mol^{-1}

(c) 37.904 kJ mol^{-1} (d) 41.00 kJ mol^{-1}

20. Standard entropy of X_2, Y_2 and XY_3 are 60, 40 and 50 JK^{-1} mol^{-1}, respectively. For the reaction,

$\frac{1}{2}X_2 + \frac{3}{2}Y_2 \rightarrow XY_3, \Delta H = -30\text{ kJ}$, to be at equilibrium, the temperature will be **(2008)**

(a) 1250 (b) 500 K

(c) 750 K (d) 1000 K

21. Oxidising power of chlorine in aqueous solution can be determined by the parameters indicated below :

$$\frac{1}{2}Cl_2(g) \xrightarrow{\frac{1}{2}\Delta_{diss}H^o} Cl(g) \xrightarrow{\Delta_{EA}H^o}$$

$$Cl^-(g) \xrightarrow{\Delta_{hyd}H^o} Cl^-(aq)$$

The energy involved in the conversion of $\frac{1}{2}Cl_2(g)$ to Cl^- (aq) will be (using the data, $\Delta_{diss}H^o_{Cl_2} = 240\text{ kJ mol}^{-1}$ $\Delta_{EA}H^o_{Cl} = -349\text{kJ mol}^{-1}$, $\Delta_{hyd}H^o_{Cl} = -381\text{ kJ mol}^{-1}$) **(2008)**

(a) + 152 kJ mol^{-1} (b) – 610 kJ mol^{-1}

(c) – 850 kJ mol^{-1} (d) + 120 kJ mol^{-1}

22. On the basis of the following thermochemical data $[\Delta G^\circ H^+(aq) = 0]$

$$H_2O(l) \longrightarrow H^+(aq) + OH^-(aq);\ \Delta H = 57.32\ kJ$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l);\ \Delta H = -286.02\ kJ$$

The value of enthalpy of formation of OH^- ion at 25°C is **(2009)**

(a) – 22.88 kJ (b) – 228.88 kJ

(c) + 228.88 kJ (c) – 343.52 kJ

23. In a fuel cell methanol is used as fuel and oxygen gas is used as an oxidiser. The reaction is $CH_3OH(l) + \frac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$. At 298 K standard Gibb's energies of formation for $CH_3OH(l)$, $H_2O(l)$ and $CO_2(g)$ are – 166.2, –237.2 and –394.4 kJ mol^{-1} respectively. If standard enthalpy of combustion of methanol is – 726 kJ mol^{-1}, efficiency of the fuel cell will be **(2009)**

(a) 80% (b) 87%

(c) 90% (d) 97%

24. 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 **(2010)**

(a) $T_e > T$ (b) $T > T_e$

(c) T_e is 5 times T (d) $T = T_e$

25. The standard enthalpy of formation of NH_3 is – 46.0 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 **(2010)**

(a) – 964 kJ mol^{-1} (b) + 352 kJ mol^{-1}

(c) + 1056 kJ mol^{-1} (d) – 1102 kJ mol^{-1}

26. Consider the reaction

$4NO_2(g) + O_2(g) \rightarrow 2N_2O_5(g)$, $\Delta_r H = -111$ kJ. If $N_2O_5(s)$ is formed instead of $N_2O_5(g)$ in the above reaction, the $\Delta_r H$ value will be

(Given, ΔH of sublimation for N_2O_5 is 54 kJ mol^{-1}) **(2011)**

(a) – 165 kJ (b) + 54 kJ

(c) +219 kJ (d) – 219 kJ

27. The value of enthalpy change (ΔH) for the reaction

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l),$$

at 27°C is – 1366.5 kJ mol^{-1}. The value of internal energy change for the above reaction at this temperature will be **(2011)**

(a) – 1371.5 kJ (b) – 1369.0 kJ

(c) – 1364.0 kJ (d) – 1361.5 kJ

28. The entropy change involved in the isothermal reversible expansion of 2 moles of an ideal gas from a volume of 10 dm^3 to a volume of 100 dm^3 at 27° C is **(2011)**

(a) 38.3 J mol^{-1}K^{-1} (b) 35.8 J mol^{-1}K^{-1}

(c) 32.3 J mol^{-1}K^{-1} (d) 42.3J mol^{-1}K^{-1}

29. For complete combustion of ethanol,

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l),$$

the amount of heat produced as measured in bomb calorimeter, is 1364.47 kJ mol^{-1} at 25°C. Assuming ideality the Enthalpy of combustion, $\Delta_C H$, for the reaction will be:

(R = 8.314 kJ mol^{-1}) **(2014)**

(a) –1361.95 kJ mol^{-1} (b) –1460.50 kJ mol^{-1}

(c) – 1350.50 kJ mol^{-1} (d) – 1366.95 kJ mol^{-1}

30. The standard enthalpy of formation of NH_3 is –46.0 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:

(Online 2014 Set - 1)

(a) – 1102 kJ mol^{-1} (b) – 964 kJ mol^{-1}

(c) + 352 kJ mol^{-1} (d) + 1056 kJ mol^{-1}

31. The molar heat capacity (C_p) of CD_2O is 10 cals at 1000K. The change in entropy associated with cooling of 32g of CD_2O vapour from 1000 K to 100 K at constant pressure will be: **(Online 2014 Set - 2)**

(D = deuterium, at. Mass = 2 u)

(a) 2.303 cal deg^{-1} (b) 23.03 cal deg^{-1}

(c) –23.03 cal deg^{-1} (d) –2.303 cal deg^{-1}

32. The entropy (S°) of the following substances are:

CH_4 (g) 186.2 J K^{-1} mol^{-1}

O_2 (g) 205.0 J K^{-1} mol^{-1}

CO_2 (g) 213.6 J K^{-1} mol^{-1}

H_2O (*l*) 69.9 J K^{-1} mol^{-1}

The entropy change (ΔS°) for the reaction

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O\ (l)$ is:

(Online 2014 Set - 2)

(a) –37.6 J K^{-1} mol^{-1} (b) –312.5 J K^{-1} mol^{-1}

(c) –242.8 J K^{-1} mol^{-1} (d) –108.1 J K^{-1} mol^{-1}

33. The ΔH and ΔS for a reaction at one atmospheric pressure are +30.558 kJ and 0.066 kJk^{-1} respectively. The temperature at which the free energy change will be zero and below of this temperature the nature of reaction would be

(Online 2015 Set - 1)

(a) 483 K, spontaneous (b) 443 K, spontaneous

(c) 463 K, spontaneous (d) 463 K, non-spontaneous

34. 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 : **(Online 2016 Set - 1)**

(a) Both “H and “S are negative.

(b) Both “H and “S are positive.

(c) “H is positive while “S is negative.

(d) “H is negative while “S is positive

35. For the reaction, $A(g) + B(g) \rightarrow C(g) + D(g)$, ΔH° and ΔS° are respectively, –29.8 kJ mol^{-1} and –0.100 kJ K^{-1} mol^{-1} at 298 K. The equilibrium constant for the reaction at 298 K is : **(Online 2016 Set - 1)**

(a) 1.0×10^{-10} (b) 1.0×10^{10}

(c) 10 (d) 1

36. If 100 mole of H_2O_2 decompose at 1 bar and 300 K, the work done (kJ) by one mole of $O_2(g)$ as it expands against 1 bar pressure is :

$$2H_2O_2(l) \rightleftharpoons 2H_2O(l) + O_2(g) \quad (R = 8.3\ JK^{-1}mol^{-1})$$

(Online 2016 Set- 2)

(a) 62.25 (b) 124.50

(c) 249.00 (d) 498.00

37. For a reaction, $A(g) \rightarrow A(l)$; H = –3RT. The correct statement for the reaction is : **(Online 2017 Set - 1)**

(a) $\Delta H = \Delta U \neq 0$ (b) $\Delta H = \Delta U = 0$

(c) $\Delta H < \Delta U$ (d) $\Delta H > \Delta U$

38. What is the value of change in internal energy at 1 atm in the process?

$$H_2O(\ell, 323K) \rightarrow H_2O(g, 423K)$$

Given :

$$C_{v,m}(H_2O, \ell) \rightarrow 75.0\ JK^{-1}mol^{-1};$$

$$C_{p,m}(H_2O, g) = 33.314\ JK^{-1}mol^{-1};$$

ΔH_{vap} at 373 K = 40.7 kJ/mol **(Online 2017 Set - 1)**

(a) 42.91 kJ/mol (b) 43086 kJ/mol

(c) 42.6 kJ/mol (d) 49.6 kJ/mol

39. An ideal gas undergoes isothermal expansion at constant pressure. During the process :

(Online 2017 Set - 2)

(a) enthalpy increases but entropy decreases.

(b) enthalpy remains constant but entropy increases.

(c) enthalpy decreases but entropy increases.

(d) Both enthalpy and entropy remain constant.

40. A gas undergoes change from state A to state B. In this process, the heat absorbed and work done by the gas is 5J and 8J, respectively. Now gas is brought back to A by another process during which 3J of heat is evolved. In this reverse process of B to A : **(Online 2017 Set - 2)**

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

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

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

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

41. ΔU is equal to : **(2017)**

(a) Isobaric work (b) Adiabatic work

(c) Isothermal work (d) Isochoric work

42. Given

$C_{(graphite)} + O_2(g) \rightarrow CO_2(g)$; $\Delta_rH° = -393.5$ kJ mol^{-1}

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$; $\Delta_rH° = -285.8$ kJ mol^{-1}

$CO_2(g) + 2H_2O(l) \rightarrow CH_4(g) + 2O_2(g)$;

$\Delta_rH° = +890.3$ kJ mol^{-1}

Based on the above thermochemical equations, the value of $\Delta_rH°$ at 298 K for the reaction

$C_{(graphite)} + 2H_2(g) \rightarrow CH_4(g)$ will be : **(2017)**

(a) + 144.0 kJ mol^{-1} (b) –74.8 kJ mol^{-1}

(c) –144.0 kJ mol^{-1} (d) +74.8 kJ mol^{-1}

43. The combustion of benzene (I) gives $CO_2(g)$ and $H_2O(l)$. 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}) **(2018)**

(a) – 3267.6 (b) 4152.6

(c) –452.46 (d) 3260

44. For which of the following reactions, ΔH is equal to ΔU? **(Online 2018 Set - 1)**

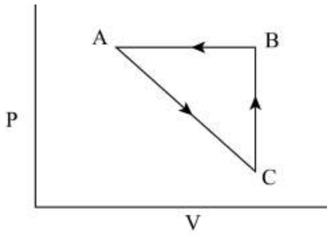
(a) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

(b) $2HI(g) \rightarrow H_2(g) + I_2(g)$

(c) $2NO_2(g) \rightarrow N_2O_4(g)$

(d) $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$

45. An ideal gas undergoes a cyclic process as shown in Figure.



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

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

Heat absorbed by the system during process CA is :

(Online 2018 Set - 1)

(a) -5 kJ mol^{-1} (b) +5 kJ mol^{-1}

(c) 18 kJ mol^{-1} (d) -18 kJ mol^{-1}

46. Δ_fG^0 at 500 K for substance 'S' in liquid state and gaseous state are +100.7 kcal mol^{-1} and +103 kcal mol^{-1}, respectively. Vapour pressure of liquid 'S' at 500 K is approximately equal to : (R = 2 cal K^{-1} mol^{-1})

(Online 2018 Set - 2)

(a) 0.1 atm (b) 1 atm

(c) 10 atm (d) 100 atm

47. Given

(i) $2Fe_2O_3(s) \rightarrow 4Fe(s) + 3O_2(g)$; $\Delta_rG^0 = +1487.0$ kJ mol^{-1}

(ii) $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$; $= -514.4$ kJ mo l^{-1}

Free energy change, for the reaction

$2Fe_2O_3(s) + 6CO(g) \rightarrow 4Fe(s) + 6CO_2(g)$ will be :

(Online 2018 Set - 2)

(a) -112.4 kJ mol^{-1} (b) -56.2 kJ mol^{-1}

(c) -168.2 kJ mol^{-1} (d) -208.0 kJ mol^{-1}

48. For which of the following processes, ΔS is negative ?

(Online 2018 Set - 3)

(a) $H_2(g) \rightarrow 2H(g)$

(b) N_2(g, 1 atm) $\rightarrow$ N_2(g, 5 atm)

(c) C(diamond) $\rightarrow$ C(graphite)

(d) N_2(g, 273 K) $\rightarrow$ N_2(g, 300 K)

49. At 320 K, a gas A_2 is 20 percent dissociated to A(g). The standard free energy change at 320 K and 1 atm in J mol^{-1} is approximately :

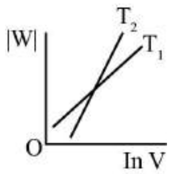
(R=8.314 JK^{-1} mol^{-1}; ln 2=0.693; ln 3=1.098)

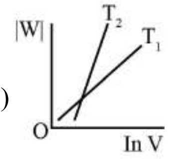
(Online 2018 Set - 3)

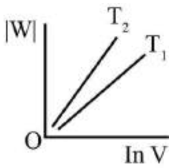
(a) 4763 (b) 2068

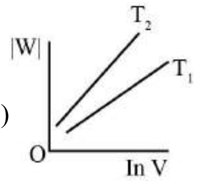
(c) 1844 (d) 4281

50. 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: **(2019)**

(a)


(b)


(c)


(d)


51. 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 kJ K^{-1} kg^{-1} and 2.0 kJ K^{-1} kg^{-1}: heat of fusion and vaporisation of water are 334 kJ kg^{-1} and 2491 kJ kg^{-1}. respectively). **(2019)**

$(\log 273 = 2.436, \log 373 = 2.572, \log 383 = 2.583)$

(a) $790 kJ\ kg^{-1}\ K^{-1}$ (b) $2.64 kJ\ kg^{-1}\ K^{-1}$

(c) $8.49 kJ\ kg^{-1}\ K^{-1}$ (d) $9.26 kJ\ kg^{-1}\ K^{-1}$

52. A process has $\Delta H = 200 J\,mol^{-1}$ and $\Delta S = 40 J\,K^{-1}\,mol^{-1}$. Out of the values given below, choose the minimum temperature above which the process will be spontaneous: **(2019)**

(a) 20 K (b) 12 K

(c) 5 K (d) 4 K

53. The process with negative entropy change is: **(2019)**

(a) Dissociation of $CaSO_4(s)$ to $CaO(s)$ and $SO_3(g)$

(b) Sublimation of dry ice

(c) Dissolution of iodine in water

(d) Synthesis of ammonia from N_2 and H_2

54. 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 24J mol^{-1} K^{-1} the temperature of Al increases by: **(2019)**

(a) $\frac{3}{2}K$ (b) 2 K

(c) $\frac{2}{3}K$ (d) 1 K

55. 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: **(2019)**

(a) $C_p \ln\left[\frac{(T_1+T_2)^2}{4T_1T_2}\right]$ (b) $C_p \ln\left[\frac{(T_1+T_2)^{\frac{1}{2}}}{4T_1T_2}\right]$

(c) $2C_p \ln\left[\frac{(T_1+T_2)}{4T_1T_2}\right]$ (d) $2C_p \ln\left[\frac{(T_1+T_2)}{2T_1T_2}\right]$

56. For the chemical reaction $X \rightleftharpoons Y$ the standard reaction Gibbs energy depends on temperature T(in K) as $\Delta_r G^\circ(\ln kJmol^{-1}) = 120 - \frac{3}{8}T$.

The major component of the reaction mixture at T is: **(2019)**

(a) Y if T = 300 K (b) Y if T = 280 K

(c) X if T = 350 K (d) X if T = 315 K

57. The reaction $MgO(s) + C(s) \rightarrow Mg(s) + CO(g)$, for which $\Delta H^\circ = +491.1 kJ\,mol^{-1}$ and $\Delta S^\circ = 198.0 K^{-1}\,mol^{-1}$, is not feasible at 298 K. Temperature above which reaction will be feasible is **(2019)**

(a) 2040.5 K (b) 1890.0 K

(c) 2480.3 K (d) 2380.5 K

58. The standard reaction Gibbs energy for a chemical reaction at an absolute temperature T is given by $\Delta_r G^\circ = A - BT$ Where A and B are non-zone constants. Which of the following is TRUE about this reaction? **(2019)**

(a) Exothermic if $B < 0$

(b) Endothermic if $A > 0$

(c) Endothermic if $A < 0$ and $B < 0$

(d) Exothermic if $A > 0$ and $B < 0$

59. Which one of the following equations does not correctly represent the first law of thermodynamics for the given processes involving an ideal gas? (Assume non-expansion work is zero) **(2019)**

(a) Cyclic process: $q = -w$

(b) Adiabatic process: $\Delta U = -w$

(c) Isochoric process: $\Delta U = q$

(d) Isothermal process: $q = -w$

60. 5 moles of an ideal gas at 100 K are allowed to undergo reversible compression till its temperature becomes 200 K. If $C_v = 28 J K^{-1} mol^{-1}$, calculate and for this process. $(R = 8.0 Jk^{-1} mol^{-1})$ **(2019)**

(a) $\Delta U = 14kJ; \Delta(pV) = 18kJ$

(b) $\Delta U = 14kJ; \Delta(pV) = 0.8kJ$

(c) $\Delta U = 14kJ; \Delta(pV) = 4kJ$

(d) $\Delta U = 14kJ; \Delta(pV) = 8.0kJ$

61. Among the following, the set of parameters that represents path functions, is: **(2019)**

I. $q + w$	II. q
III. w	IV. $H - TS$
(a) II and III	(b) II, III and IV
(c) I and IV	(d) I, II and III

62. During compression of a spring the work done is 10 kJ and 2 kJ escaped to the surroundings as heat. The change in internal energy, ΔU (in kJ) is: **(2019)**

(a) –12	(b) –8
(c) 8	(d) 12

63. A process will be spontaneous at all temperature if: **(2019)**

(a) $\Delta H < 0$ and $\Delta S < 0$

(b) $\Delta H > 0$ and $\Delta S < 0$

(c) $\Delta H < 0$ and $\Delta S > 0$

(d) $\Delta H > 0$ and $\Delta S > 0$

64. The difference between ΔH and $\Delta U (\Delta H - \Delta U)$, when the combustion of one mole of heptane(l) is carried out at a temperature T, is equal to: **(2019)**

(a) –4 RT	(b) –3 RT
(c) 4 RT	(d) 3 RT

65. Enthalpy of sublimation of iodine is 24 cal g^{-1} at 200°C. If specific heat of $I_2(s)$ and $I_2(vap)$ are 0.055 and 0.031 cal $g^{-1} K^{-1}$ respectively, then enthalpy of sublimation of iodine at 250°C in cal g^{-1} is: **(2019)**

(a) 2.85	(b) 5.7
(c) 22.8	(d) 11.4

66. If enthalpy of atomisation for $Br_2(l)$ is x kJ /mol and bond enthalpy for Br_2 is y kJ/mol, the relation between them : **(2020)**

(a) is $x > y$	(b) is $x < y$
(c) is $x = y$	(d) does not exist

67. The true satement amongst the following **(2020)**

(a) S is a function of temeprature but ΔS is not a function of temperature

(b) Both ΔS and S are functions of temperature

(c) Both S and ΔS are not functions of temperature

(d) S is not a function of temperature but ΔS is a function of temperature

68. For one mole of an ideal gas, which of these statements must be true? **(2020)**

(i) U and H each depends only on temeprature.

(ii) Compressiblity factor z is not equal to 1

(iii) $C_{p.m} - C_{v,m} = R$

(iv) du $= C_v dT$ for any process

(a) (i), (iii) and (iv)	(b) (i) and (iii)
(c) (iii) and (iv)	(d) (ii), (iii) and (iv)

69. The process that is not endothermic in nature is: **(2020)**

(a) $H_{(g)} + e^- \rightarrow H^-_{(g)}$

(b) $Na_{(g)} \rightarrow Na^+_{(g)} + e^-$

(c) $Ar_{(g)} + e^- \rightarrow Ar^-_{(g)}$

(d) $O^-_{(g)} + e^- \rightarrow O^{2-}_{(g)}$

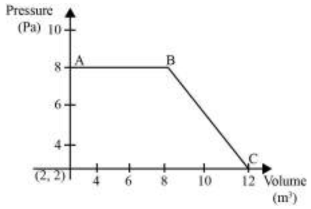
Numerical Value Type Questions

70. For the reaction $A(l) \rightarrow 2B(g)$

$\Delta U = 2.1 kcal, \Delta S = 20\ Cal\ K^{-1}$ at 300 K, Hence ΔG in kcal (numeric value) is **(2020)**

71. The standard heat of formation $(\Delta_f H_{298^o})$ of ethane (in kJ/mol), if the heat of combustion of ehtane, hydrogen and graphite are -1560, -393.5 and -286 kJ/mol, respectively, is ___________. **(2020)**

72. The magnitude of work done by gas that undergoes a reversible expansion along the path ABC shown in figure is ________. **(2020)**



73. At constant volume, 4 mol of an ideal gas when heated from 300 to 500 K changes its internal energy by 5000 J. The molar heat capacity at constant volume is _____ .

(2020)

74. The internal energy change (in J) when 90 g of water unergoes complete evaporation at 100°C is

(Given : ΔH_{vap} for water at 373 K = 41 kJ / mol, R = 8.314 JK^{-1} mol^{-1}) **(2020)**

75. The heat of combution of ethanol into carbon dioxide and water is -327 kcal at constant pressure. The heat evolved (in cal) at constant volume and 27°C (if all gases behave ideally) is (R = 2 cal mol^{-1} K^{-1}) .... **(2020)**

76. For a dimerization reaction, $2A(g) \rightarrow A_2(g)$ at 298 K, $\Delta U^{\circ} = -20\ kJ\ mol^{-1}, \Delta S^{\circ} = -30\ kJ\ mol^{-1}$, then the ΔG° will be .... j. **(2020)**

77. During which of the following processes, does entropy decrease?

(A) Freezing of water to ice at 0°C

(B) Freezing of water to ice at - 10°C

(C) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

(D) Adsorption of CO(g) on lead surface.

(E) $NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$

Choose the correct answer from the options given below : **(2021-03-17/Shift - 2)**

(a) (A), (C) and (E) only

(b) (A), (B), (C) and (D) only

(c) (A) and (E) only

(d) (B) and (C) only

78. The reaction of cyanamide, $NH_2CN_{(s)}$ with oxygen was run in a bomb calorimeter and ΔU was found to be -742.24 kJ mol^{-1}. The magnitude of ΔH_{298} for the reaction

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

is _____ kJ. (Rounded off to the nearest integer)

[Assume ideal gas and R = 8.314 J mol^{-1} K^{-1}]

(2021-02-25/Shift - 1)

79. Five moles of an ideal gas at 293 K is expanded isothermally from an initial pressure of 2.1 MPa to 1.3 Mpa against at constant external pressure 4.3 MPa. The heat transferred in this process is _______ kJ mol^{-1}. (Rounded-off to the nearest integer) [Use R = 8.314 J mol^{-1} K^{-1}]

(2021-02-25/Shift - 2)

80. For a chemical reaction $A + B \rightleftharpoons C + D$

($\Delta_r H^{\ominus} = 80\ kJ\ mol^{-1}$) the entropy change $\Delta_r S^{\ominus}$ depends on the temperature T (in K) as $\Delta_r S^{\ominus} = 2T(JK^{-1}mol^{-1})$.

Minimum temperature at which it will become sponatneous is _________ K. (Integer)

(2021-02-26/Shift - 1)

81. The average S-F bond energy in kJ mol^{-1} of SF_6 is ______. (Rounded off to the nearest integer)

[Given : The values of standard enthalpy of formation of SF_6(g), S(g) and F(g) are -1100, 275 and 80 kJ mol^{-1} respectively.] **(2021-02-26/Shift - 2)**

82. At 25°C, 50 g of iron reacts with HCl to form $FeCl_2$, The evolved hydrogen gas expands against a constant pressure of 1 bar. The work done by the gas during this expansion is (Round off to the Nearest Integer).

[Given : R = 8.314 J mol^{-1} K^{-1}. Assume, hydrogen is an ideal gas] **(2021-03-16/Shift - 2)**

[Atomic mass of Fe is 55.85 u]

83. The standard enthalpies of formation of Al_2O_3 and CaO are -1675 kJ mol^{-1} and -635 kJ mol^{-1} resepectively

For the reaction

$3CaO + 2Al \rightarrow 3Ca + Al_2O_3$ the standard reaction enthalpy

$\Delta_r H^{\circ}$ = ...kJ **(2021-03-17/Shift - 1)**

(Round off to the Nearest Integer).

84. For the reaction $C_2H_6 \rightarrow C_2H_4 + H_2$ the reaction enthalpy $\Delta_r H$ = ...kJ mol^{-1}. (Round off to the Nearest Integer) . [Given : Bond enthalpies in kJ mol^{-1} : C - C = 347, C = C = 611; C - H = 414, H - H = 436]

(2021-03-18/Shift - 1)

85. An average person needs about 10000 kJ energy per day. The amount of glucose (molar mass = 180.0 g mol^{-1}) needed to meet this energy requirement is _____ g. (nearest integer) (Use : $\Delta_C H(\text{glucose}) = -2700 \text{ kJ mol}^{-1}$)

(2021-07-20/Shift - 1)

86. For a given chemical reaction $A \to B$ at 300 K the free energy change is -49.4 kJ mol^{-1} and the enthalpy of reaction is 51.4 kJ mol^{-1}. The entropy change of the reaction is _____ J K^{-1} mol^{-1}. **(2021-07-20/Shift - 2)**

87. If the standard molar enthalpy change for combustion of graphite powder is 2.48×10^2 kJ mol^{-1}, the amount of heat generated on combustion of 1 g of graphite powder is _____kJ. (Nearest Integer) **(2021-07-22/Shift - 2)**

88. At 298 K, the enthalpy of fusion of a solid (X) is 2.8 kJ mol^{-1} and the enthalpy of vaporization of the liquid (X) in kJ mol^{-1} is _______ . (in nearest integer)

(2021-07-25/Shift - 1)

89. A system does 200 J of work and at the same time absorbs 150 J of heat. The magnitude of the change in interval energy is ________ J. **(2021-07-25/Shift - 2)**

90. When 400 mL of 0.2 M H_2SO_4 solution is mixed with 600 mL of 0.1 M NaOH solution, the increase in temperature of the final solution is ______ × 10^{-2} K. (Round off to the nearest integer). **(2021-07-27/Shift - 2)**

[Use : $H^+(aq) + OH^-(aq) \rightarrow H_2O : \Delta_r H = -57.1 \text{ kJ mol}^{-1}$]

Specific heat of H_2O = 4.18 J K^{-1} g^{-1}

Density of H_2O = 1.0 g cm^{-3}

Assume no change in volume of solution on mixing.

91. For water at 100°C and 1 bar,

$\Delta_{vap}H - \Delta_{vap}U = \_\_\_\_\_\_\_\_\_\_\_ \times 10^2 \text{ Jmol}^{-1}$

(Round off to the Nearest Integer. Use:R = 8.31J mol^{-1} K^{-1} Assume volume of $H_2O(l)$ is much smaller than volume of H_2O (g). Assume $H_2O(g)$ treated as an ideal gas).

(2021-07-27/Shift - 1)

92. For water $\Delta_{vap}H = 41 \text{kJmol}^{-1}$ at 373 K and 1 bar pressure.

Assuming that water vapour is an ideal gas that occupies a much larger volume than liquid water, the internal energy change during evaporation of water is ____ kJ mol^{-1}

[Use : R = 8.3 J mol^{-1} K^{-1}] **(2021-08-26/Shift - 2)**

93. 200 mL of 0.2 M HCl is mixed with 300 mL of 0.1 M NaOH. The molar heat of neturalization of this reaction is -57.1 kJ. The increase in temperature in °C of the system on mixing is x × 10^{-2}. The value of x is ______. (Nearest integer) [Given : Specific heat of water = 4.18 J g^{-1} K^{-1} Density of water = 1.00 g cm^{-3}] Assume no volume change on mixing) : **(2021-08-27/Shift - 1)**

94. Data given for the following reaction is as follows :

$FeO_{(s)} + C_{(graphite)} \rightarrow Fe_{(s)} + CO_{(g)}$

Substance	$\Delta H^\circ (\text{kJ mol}^{-1})$	$\Delta S^\circ (\text{J mol}^{-1}\text{K}^{-1})$
$FeO_{(s)}$	-266.3	57.49
$C_{(graphite)}$	0	5.74
$Fe_{(s)}$	0	27.28
$CO_{(g)}$	-110.5	197.6

The minimum temperature in K at which the reaction becomes spontaneous is _______. (Integer answer)

(2021-08-27/Shift - 2)

95. For the reaction $2NO_2(g) \rightleftharpoons N_2O_4(g)$, when

$\Delta S = -176.0 \text{JK}^{-1}$ and $\Delta H = -57.8 \text{ kJ mol}^{-1}$, the

magnitude of ΔG at 298 K for the reaction is ____ kJ mol^{-1}. (Nearest integer) **(2021-09-01/Shift - 2)**

EXERCISE - 3 : ADVANCED OBJECTIVE QUESTIONS

Objective Questions I [Only One Correct Option]

1. An ideal gas at constant temperature and pressure expands, then its

(a) Internal energy remains same

(b) Internal energy decreases

(c) Internal energy increases

(d) Entropy first increases and then decreases

2. The internal energy of a substance

(a) Increases with increase in temperature

(b) Decreases with increase in temperature

(c) Can be calculated by the relation $E = mc^2$

(d) Remains unaffected with change in temperature

3. Which of the following is correct ?

(a) $C_P - C_V = R$ (b) $\frac{C_P}{C_V} = \gamma$

(c) $C_P > C_V$ (d) All of these

4. C_P for monoatomic gas is

(a) 5/2 R (b) 3/2 R

(c) 7/2 R (d) R

5. Standard molar enthalpy of formation of CO_2 is equal to

(a) zero

(b) the standard molar enthalpy of combustion of gaseous carbon

(c) the sum of standard enthalpies of formation of CO and O_2

(d) the standard molar enthalpy of combustion of carbon (graphite)

6. The mathematical expression for the standard enthalpy of sublimation is given by

(a) ΔH° (sublimation) = ΔH° (fusion) – $2\Delta H^\circ$ (vaporization)

(b) ΔH° (sublimation) = ΔH° (fusion) – ΔH° (vaporization)

(c) ΔH° (sublimation) = ΔH° (fusion) + ΔH° (vaporization)

(d) ΔH° (sublimation) = ΔH° (combustion) + ΔH° (dissociation)

7. Energy required to dissociate 4g of gaseous hydrogen into free gaseous atoms is 208 kcal at 25°C. The bond energy of H — H bond will be

(a) 104 kcal (b) 10.4 kcal

(c) 1040 kcal (d) 1.04 kcal

8. Consider an ideal gas. When $dw = 0$ and $dq < 0$,

(a) the temperature will decrease

(b) the volume will increase

(c) the pressure will remain constant

(d) the temperature will increase

9. When heat is supplied to an ideal gas in an isothermal process, the

(a) gas will do positive work

(b) gas will do negative work

(c) kinetic energy of the gas will increase

(d) gas will not obey the law of conservation of energy

10. 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

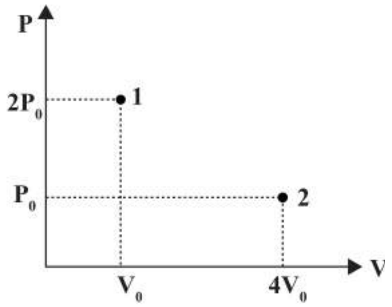
(a) $\Delta H_1 > \Delta H_2$

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

(c) $\Delta H_1 = \Delta H_2$, enthalpy being a state function

(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.

11. A liquid which is confined inside an adiabatic piston is suddenly taken from state 1 to state 2 by a single stage process. If the piston comes to rest at point 2 as shown. Then the enthalpy change for the process will be :



(a) $\Delta H = \frac{2\gamma P_0 V_0}{\gamma - 1}$ (b) $\Delta H = \frac{3\gamma P_0 V_0}{\gamma - 1}$

(c) $\Delta H = -P_0 V_0$ (d) None of these

12. A gas expands adiabatically at constant pressure such that $T \propto V^{-1/2}$. The value of γ ($C_{p,m}/C_{v,m}$) of the gas will be :

(a) 1.30 (b) 1.50

(c) 1.70 (d) 2

13. 1 mole of an ideal gas A ($C_{v,m} = 3$ R) and 2 mole of an ideal gas B $\left(C_{v,m} = \frac{3}{2}R\right)$ are taken in a container and expanded reversibly and adiabatically from 1 litre to 4 litre starting from initial temperature of 320 K. ΔE or ΔU for the process is :

(a) –240 R (b) 240 R

(c) 480 R (d) –960 R

14. 2 mole of an ideal monoatomic gas undergoes a reversible process for which $PV^2 = C$. The gas is expnaded from initial volume of 1 L to final volume of 3L starting from initial temperature of 300 K. Find ΔH for the process:

(a) –600R (b) –1000R

(c) –3000R (d) None of these

15. A certain gas in expanded from (lL, 10 atm) to (4L, 5 atm) against a constant external pressure of 1 atm. If the initial temperature of gas is 300 K and heat capacity for the process is 50 J/°C, the enthalpy change during the process is : (Use : $1L\ atm \approx 100\ J$)

(a) 15 kJ (b) 15.7 kJ

(c) 14.3 kJ (d) 14.7 kJ

16. The molar heat capacities at constant pressure (assumed constant with respect to temperature) for A, B and C are in ratio of 3 : 1.5 : 2.0. The enthalpy change for the exothermic $A + 2B \rightarrow 3C$ at 300 K and 310 K is ΔH_{300} and ΔH_{310} (magnitudes) respectively then :

(a) $\Delta H_{300} > \Delta H_{310}$

(b) $\Delta H_{300} < \Delta H_{310}$

(c) $\Delta H_{300} = \Delta H_{310}$

(d) if $T_2 > T_1$ then $\Delta H_{310} > \Delta H_{300}$ and if $T_2 < T_1$ then $\Delta H_{310} < \Delta H_{300}$

17. The specific heat of a gas at constant volume is 0.075 cal/g. Predict the atomicity of the gas. Molar mass of gas is 40 g mol^{-1}.

(a) 1 (b) 2

(c) 3 (d) None of these

18. 10 mole of an ideal gas is heated at constant pressure of one atmosphere from 27°C to 127°C. If $C_{v,m} = 21.686 + 10^{-3}T$, then ΔH for the process is :

(a) 3000 J (b) 3350 J

(c) 3700 J (d) 30350 J

19. For an ideal gas undergoing adiabatic expansion in vaccum,

(a) $\Delta U = 0$ (b) $q = 0$

(c) $W = 0$ (d) all the above are true

20. What is the change in molar entropy of helium in the following process ?

1 He (298 K, 1 bar) → 1 He (100 K, 10 bar)

(a) 41.8 J K^{-1} mol^{-1} (b) 4.18 J K^{-1} mol^{-1}

(c) – 41.8 J K^{-1} mol^{-1} (d) – 4.18 J K^{-1} mol^{-1}

21. $\Delta S = \frac{\Delta H}{T}$ holds good for

(a) an adiabatic process

(b) an isothermal reversible-phase change

(c) a process at constant pressure

(d) a process under any condition

22. $\Delta_r H^0$ for solid-to-liquid transition for proteins A and B are 2.73 kcal mol^{-1} and 3.03 kcal mol^{-1}. The two melting points are 0°C and 30°C respectively. The entropy changes ΔS_A and ΔS_B at two transition temperatures are related as :

(a) $\Delta S_A = \Delta S_B$ (b) $\Delta S_A < \Delta S_B$

(c) $\Delta S_B > \Delta S_A$ (d) $\Delta S_B = \frac{303\Delta S_A}{273}$

23. For the real gases reaction

$2CO(g) + O_2(g) \longrightarrow 2CO_2(g)\ \Delta H = -560$ kJ.

In 10 litre rigid vessel at 500 K the initial pressure is 70 bar and after the reaction it becomes 40 bar. The change in internal energy is :

(a) –557 kJ (b) –530 kJ

(c) –563 kJ (d) None of these

24. 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 $\Delta U - \Delta H$ for the conversion of 1 mole of graphite to 1 mole of diamond at temperature 'T':

(a) 100 kJ/mol (b) 50 kJ/mol

(c) – 100 kJ/mol (d) None of these

25. The enthalpy of formation of $NH_3(g)$ at constant pressure and 350^0C temperature is $-50.0\ kJ\ mol^{-1}$. What will be the enthalpy of formation of $NH_3(g)$ at constant volume at the same temperature ?

(a) $-50.0\ kJ\ mol^{-1}$ (b) $-45\ kJ\ mol^{-1}$

(c) $-60.4 kJ\ mol^{-1}$ (d) $-54\ kJ\ mol^{-1}$

26. $Mg(s) + 2HCl(aq.) \rightarrow MgCl_2(aq) + H_2(g);$

$\Delta_r H^0 = -467\ kJ/mol$

$MgO\ (s) + 2HCl\ (aq) \rightarrow MgCl_2\ (aq) + H_2O\ (l)\ ;$

$\Delta_r H^0 = -151\ kJ/mol$

According to the information, and given the fact that for water, $\Delta_f H^0 = -286\ kJ/mol$, what is the $\Delta_f H^0$ for MgO(s) ?

(a) -904 kJ/mol (b) -602 kJ/mol

(c) -334 kJ/mol (d) -30 kJ/mol

27. The enthalpy of reaction $CH_4(g) + \frac{1}{2}O_2(g) \rightarrow CH_3OH(L)$ is negative. If enthalpy of combustion of CH_4 and CH_3OH are x and y respectively then which of the following relations is correct?

(a) $x > y$ (b) $x < y$

(c) $x = y$ (d) $x \geq y$

28. For the allotropic change represented by the equation C (diamond) → (graphite) the enthalpy change is $\Delta H = -1.89\ kJ$

If 6g of diamond and 6 g of graphite are separately burnt to yield carbon dioxide, the heat, liberated in the first case is

(a) less than in the second case by 1.89 kJ

(b) more than in the second case by 1.89 kJ

(c) less than in the second case by 11.34 kJ

(d) more than in the second case by 0.945 kJ

29. The enthalpy of combustion for octane (a major component of gasoline) is – 47.8 kJ/g. How much energy is released by burning 1.0 L of octane (density 0.740 g/mL) ?

(a) -35400 kJ (b) -64600 kJ

(c) -47800 kJ (d) -57200 kJ

30. Given that,

$\Delta H_f^0\ (CO_2, g) = -393.509\ kJ\ mol^{-1},$

$\Delta H_f^0\ (H_2O, l) = -285.830\ kJ\ mol^{-1},$

$\Delta H_f^0\ (C_2H_5OH, l) = -277.800\ kJ\ mol^{-1}.$

Calculate the $\Delta H°$ (combustion) of liquid ethanol. The following is the required reaction.

$C_2H_5OH\ (l) + 3O_2\ (g) \rightarrow 2CO_2\ (g) + 3H_2O\ (l)$

(a) $-1366.82\ kJ\ mol^{-1}$ (b) $-278.82\ kJ\ mol^{-1}$

(c) $-2264.66\ kJ\ mol^{-1}$ (d) $-1155.78\ kJ\ mol^{-1}$

31. The enthalpy of neutralization of a strong acid by a strong base is $-57.32\ kJ\ mol^{-1}$. The enthalpy of formation of water is $-285.84\ kJ\ mol^{-1}$. The enthalpy of formation of the hydroxyl ion is

(a) $+228.52\ kJ\ mol^{-1}$ (b) $-114.26\ kJ\ mol^{-1}$

(c) $-228.52\ kJ\ mol^{-1}$ (d) $+114.26\ kJ\ mol^{-1}$

32. Heat of neutralisation of NaOH and HCl is –57.46 kJ/equivalent. The heat of ionisation of water will be :

(a) -57.46 kJ/mol (b) 57.46 kJ/mol

(c) -114.92 kJ/mol (d) 114.92 kJ/mol

33. In which case of mixing of a strong acid and strong base, each of 1N concentration, temperature increase is the highest ?

(a) 20 ml acid and 30 ml alkali

(b) 10 ml acid and 40 ml alkali

(c) 25 ml acid and 25 ml alkali

(d) 35 ml acid and 15 ml alkali

34. Heat of neutralization of a strong dibasic acid in dilute solution by NaOH is nearly

(a) -27.4 kcal/eq (b) 13.7 kcal/mol

(c) -13.7 kcal/eq (d) -13.7 kcal/mol

35. Heat released in neutralization of strong acid and strong base is 13.4 kcal/mol. The heat released on neutralization of NaOH with HCN is 2.9 kcal/mol, then $\Delta H°$ of ionization of HCN in water is

(a) 10.5 kcal (b) 16.3 kcal

(c) 9.5 kcal (d) 11.5 kcal

36. Calculate the enthalpy change when 1.0 g of water is frozen at 0^0C ($\Delta H_f^0 = 1.435$ kcal mol^{-1})

(a) – 1.435 cal g^{-1} (b) – 80.0 cal g^{-1}

(c) 80.0 cal g^{-1} (d) – 55.6 cal g^{-1}

37. Given are the following entropy values at 298 K and 1 atm:

H_2 (g) = 130.6 J K^{-1} mol^{-1}; Cl_2 (g) = 223.0 J K^{-1} mol^{-1};

HCl (g) = 186.7 J K^{-1} mol^{-1}

The entropy change for the reaction

H_2 (g) + Cl_2 (g) $\rightarrow$ 2HCl (g) would be

(a) +540.3 J K^{-1} mol^{-1} (b) +727 J K^{-1} mol^{-1}

(c) –166.9 J K^{-1} mol^{-1} (d) +19.8 J K^{-1} mol^{-1}

38. The free-energy change for the conversion of maleate into fumarate is 3.0 kJ. In metabolism, this reaction is coupled with the conversion fumarate to asparate, which is exergonic by 15.5 kJ. Calculate ΔG^0 for the overall reaction.

(a) – 18.5 kJ (b) + 18.5 KJ

(c) – 12.5 kJ (d) – 25.0 kJ

39. The ΔG for the following reactions at 800^0C are given as

S_2 (s) + $2O_2$ (g) $\rightarrow$ $2SO_2$ (g); ΔG = – 544 kJ

2Zn (s) + S_2 (s) $\rightarrow$ 2ZnS (s) ; ΔG = – 293 kJ

2Zn (s) + O_2 (g) $\rightarrow$ 2ZnO (s); ΔG = – 480 kJ

The ΔG for the reaction

2Zn S + $3O_2$ (g) $\rightarrow$ 2ZnO (s) + $2SO_2$ (g) will be

(a) – 357 kJ (b) – 731 kJ

(c) – 773 kJ (d) – 229 kJ

40. Consider the reaction below at 298 K :

C (graphite) + $2H_2$ (g) $\rightarrow$ CH_4 (g) $\Delta_f H^o$ (kJ/mol) = 74.9

$S^0{}_m$ (J/K/mol)

+ 5.6 + 130.7 + 186.3

Which statement below is correct ?

(a) $\Delta_r G^0$ is – 50.8 kJ and the reaction is driven by enthalpy only.

(b) $\Delta_r G^0$ is – 50.8 kJ and the reaction is driven by entropy only.

(c) $\Delta_r G^0$ is + 50.8 kJ and the reaction is driven by both enthalpy and entropy.

(d) $\Delta_r G^0$ is – 50.8 kJ and the reaction is driven by both enthalpy and entropy.

41.

Given	$\Delta_f H^0$ (kJ/mol)	S_m^0 (J/k/mol)
CCl_4 (*l*)	– 135.4	215.4
CCl_4 (g)	– 103.0	308.7

What is the boiling point of carbon tetrachloride ?

(a) 8.25ºC (b) 74.3ºC

(c) 92.3ºC (d) 45.8ºC

42. Calculate $\Delta_f G^\circ$ for (NH_4Cl, s) at 310 K.

Given : $\Delta_f H^\circ$ (NH_4Cl, s)=–314.5 kJ/mol; $\Delta_r C_p$ =0

$S^o_{N_2(g)}$ =192 JK^{-1} mol^{-1}; $S^o_{H_2(g)}$ =130.5JK^{-1} mol^{-1}

$S^o_{Cl_2(g)}$ =233 JK^{-1} mol^{-1} $S^o_{NH_4Cl(s)}$ = 99.5 JK^{-1} mol^{-1}

(All data given at 300K)

(a) – 198.56 kJ/mol (b) –426.7 KJ/mol

(c) –202.3 KJ/mol (d) None of these

43. The bond energy of H_2 is 104.3 kcal/mol. It means that

(a) 104.3 kcal heat is needed to break one bond to form two atoms

(b) 104.3 kcal is required to break 6.02 × 10^{23} molecules into 1.2406 × 10^{24} atoms of hydrogen

(c) 104.3 kcal is required to break 3.015 × 10^{23} hydrogen molecules to 6.02 × 10^{23} hydrogen atoms

(d) none of these

44. Determine C–C and C–H bond enthalpy (in kJ/mol)

Given: $\Delta_f H^\circ(C_2H_6, g)$ =–85 kJ/mol

$\Delta_f H^\circ(C_3H_8, g)$ =–104 kJ/mol

$\Delta_{sub} H^\circ(C, s)$ =718 kJ/mol B.E.(H – H) = 436 kJ/mol

(a) 414, 345 (b) 345, 414

(c) 287, 404.5 (d) None of these

45. What is the bond enthalpy of Xe–F bond?

$$XeF_4 \rightarrow Xe^+(g) + F^-(g) + F_2(g) + F(g); \quad \Delta_r H = 292\,\text{kcal/mol}$$

Given: Ionization energy of Xe = 279 kcal/mol

B.E. (F–F) = 38 kcal/mol,

Electron affinity of F = 85 kcal/mol

(a) 24 kcal/mol (b) 34 kcal/mol

(c) 8.5 kcal/mol (d) None of these

46. The lattice energy of solid NaCl is 180 kcal per mol. The dissolution of the solid in water in the form of ions is endothermic to the extent of 1 kcal per mol. If the solvation energies of Na^+ and Cl^- ions are in the ratio 6 : 5, what is the enthalpy of hydration of sodium ion ?

(a) – 85.6 kcal/mol (b) – 97.5 kcal/mol

(c) 82.6 kcal/mol (d) + 100 kcal/mol

47. 0.5 mole each of two ideal gases A $\left(C_{v,m} = \frac{5}{2}R\right)$ and B ($C_{v,m}$ = 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. Find ΔH (in cal/mol) for the process :

(a) –100 R (b) –137.5 R

(c) –375 R (d) None of these

Objective Questions II

[One or more than one correct option]

48. Among the following, the state function(s) is/are

(a) Internal energy

(b) Irreversible expansion work

(c) Reversible expansion work

(d) Molar enthalpy

49. If enthalpy of hydrogenation of $C_6H_6(l)$ into $C_6H_{12}(l)$ is –205 kJ and resonance energy of $C_6H_6(l)$ is –152 kJ/mol then enthalpy of hydrogenation of  is

Assume ΔH_{vap} of $C_6H_6(l)$, $C_6H_8(l)$, $C_6H_{12}(l)$ all are equal:

(a) – 535.5 kJ/mol (b) – 238 kJ/mol

(c) – 357 kJ/mol (d) – 119 kJ/mol

50. A sample containing 1.0 mol of an ideal gas is expanded isothermally and reversibly to ten time of its original volume, in two separate experiments. The expansion is carried out 200 K and at 400 K, respectively. Choose the correct option.

(a) Work done at 400 K is twice the work done at 200 K.

(b) Work done at 400 K is twice the work doen at 200 K.

(c) Work done at 400 K is 20 times the work done at 200 K.

(d) ΔE = 0 in both cases.

51. The normal boiling point of a liquid 'X' is 400 K. Which of the following statement is true about the process $X(l) \rightarrow X(g)$?

(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 $\Delta G = +ve$

Numerical Value Type Questions

52. Assume that the human body is a heat engine. For a food intake equivalent to 1.0×10^7 J day^{-1}, a human can work for 6 h day^{-1} at a rate equivalent to 0.0374 HP (1 HP = 746 W). What is the efficiency of the human body?

53. Heat of neutralisation of a polybasic acid by a strong base is -54.8 k cal mol^{-1}. What is basicity of the acid?

54. Find change in internal energy, when 0.5 mole of Ar having a specific heat at constant pressure of 20.814 J g^{-1} deg^{-1} is heated from 27°C to 31°C at constant volume. (Atomic mass of Ar = 40) (give your answer in kJ)

55. The enthalpy of neturalizaton of 0.4 M H_2SO_4 will be how many times the enthalpy of neutralization of 0.1 M HCl?

Assertion Reason

(A) If both Assertion and Reason are correct and Reason is the correct explanation of Assertion.

(B) If both Assertion and Reason are true but Reason is not the correct explanation of Assertion.

(C) If Assertion is true but Reason is false.

(D) If Assertion is false but Reason is true.

56. **Assertion (A) :** The extensive properties of a single pure substance will not only depend upon the number of moles of the substance present but also on any two of the three variables.

Reason (R) : Any extensive property if expressed as per mole or per gram becomes an intensive property.

(a) A (b) B
(c) C (d) D

57. **Assertion (A) :** There is no change in internal energy for an ideal gas at constant temperature.

Reason (R) : Internal energy of an ideal gas is a function of temperature only.

(a) A (b) B
(c) C (d) D

58. **Assertion (A) :** A reversible process produces more work than the same process if it is carried out irreversibly for the same increase in volume.

Reason (R) : A reversible process is exothermic while irreversible process is endothermic

(a) A (b) B
(c) C (d) D

59. **Assertion (A) :** Entropy change in reversible adiabatic expansion of an ideal gas is zero.

Reason (R) : The increase in entropy due to volume increase just componsate the decrease in entropy due to fall in temperature.

(a) A (b) B
(c) C (d) D

60. **Assertion (A) :** When internal energy of reactants becomes greater than that of products the energy is given out to the surrounding.

Reason (R) : All exothermic reactions take place at constant temperature, ΔE will be positive.

(a) A (b) B
(c) C (d) D

61. **Assertion (A) :** Heat of neutralization of HF is more than that of HC*l* by NaOH.

Reason (R) : HC*l* is stronger acid than HF.

(a) A (b) B
(c) C (d) D

62. **Assertion (A) :** Enthalpy of neutralization of CH_3COOH by NaOH is less than that of HCl by NaOH.

Reason (R) : Enthalpy of neutralization of CH_3COOH is less because of the absorption of heat in the ionization process.

(a) A (b) B
(c) C (d) D

63. **Assertion (A) :** When a salt dissolves in water, the temperature of solution decreases.

Reason (R) : Energy equal to lattice energy is required to ionize the salt in solution.

(a) A (b) B
(c) C (d) D

Match the following

Each questions has two columns. Four options are given representing matching elements from Column-I and Column-II. Only one of these four options corresponds to a correct matching for each questions.

64. Match the Column-I with Column-II

Column - I	Column - II
A. $H_2O(l) \rightleftharpoons H_2O(g)$	p. $\Delta G < 0$
B. $C(s) + O_2(g) \rightarrow CO_2(g)$	q. $\Delta H < 0$
C. $H_2O(s) \rightarrow H_2O(l)$	r. $\Delta S > 0$
D. $C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$	s. $\Delta H < 0$

65. Match the Column-I with Column-II

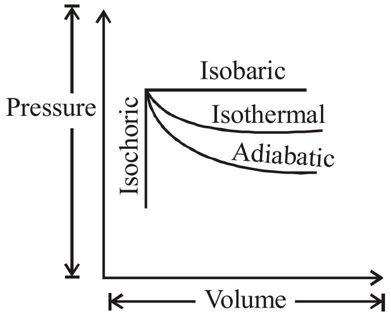
Column I	Column II
(A) O_2	(p) $\gamma = 1.4$
(B) N_2	(q) $C_P = \frac{7}{2}R$
(C) CO_2, CH_4	(r) $C_P = \frac{23}{6}R$
(D) 1 mol O_2 + 2 mol O_3	(s) $\gamma = 1.33$

Paragraph Type Questions

Use the following passage, to solve Q. 66 to Q. 68

Passage

Observe the following graphic representation of four basic thermodynamic processes.



66. Which of the following is true for isochoric process ?

(a) $\Delta V = 0$ (b) $\Delta U = q + P\Delta V$

(c) $\Delta U = q_v$ (d) All of these

67. Which of the following is not true for isothermal process ?

(a) $w_{exp} = -2.303 \text{ nRT} \log \frac{V_2}{V_1}$

(b) $w_{exp} = -2.303 \text{ nRT} \log \frac{P_1}{P_2}$

(c) $\Delta T = 0$

(d) $T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$

68. If the ratio $\frac{C_P}{C_V} = 1.30$, the atomicity of gas is

(a) 1 (b) 2

(c) 3 (d) 4

Use the following passage, to solve Q. 69 to Q. 70

Passage

Standard Gibb's energy of reaction ($\Delta_r G^o$) at a certain temperature can be computed as $\Delta_r G^o = \Delta_r H^o - T.\Delta_r S^o$ and the change in the value of $\Delta_r H^o$ and $\Delta_r S^o$ for a reaction with temperature can be computed as follow:

$$\Delta_r H^o_{T_2} - \Delta_r H^o_{T_1} = \Delta_r C^o_p (T_2 - T_1)$$

$$\Delta_r S^o_{T_2} - \Delta_r S^o_{T_1} = \Delta_r C^o_p \ln\left(\frac{T_2}{T_1}\right)$$

$$\Delta_r G^o = \Delta_r H^o - T.\Delta_r S^o$$

and by $\Delta_r G^o = -RT \ln K_{eq}$.

Consider the following reaction:

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

Given: $\Delta_f H^o(CH_3OH, g) = -201$ kJ/mol; $\Delta_f H^o(CO, g) = -144$ kJ/mol

$S^o(CH_3OH, g) = 240$ J/K-mol; $S^o(H_2, g) = 29$ $JK^{-1}mol^{-1}$

$S^o(CO, g) = 198$ J/mol-K; $C^o_{p,m}(H_2) = 28.8$ J/mol-K

$C^o_{p,m}(CO) = 29.4$ J/mol-K; $C^o_{p,m}(CH_3OH) = 44$ J/mol-K

and $\ln\left(\frac{320}{300}\right) = 0.06$, all data at 300 K

69. $\Delta_r S^o$ at 300 K for the reaction is :

(a) 152.6 J/K-mol (b) 181.6 J/K-mol

(c) –16 J/K-mol (d) None of these

70. $\Delta_r H^o$ at 300 K for the reaction is :

(a) –87 kJ/mol (b) 87 kJ/mol

(c) –315 kJ/mol (d) –288 kJ/mol

EXERCISE - 4 : PREVIOUS YEAR JEE ADVANCED QUESTIONS

Objective Questions I [Only One Correct Option]

1. The difference between heats of reaction at constant pressure and constant volume for the reaction

$2C_6H_6\,(l) + 15O_{2(g)} \rightarrow 12CO_2(g) + 6H_2O\,(l)$

at 25° C in kJ is **(1991)**

(a) – 7.43 (b) + 3.72

(c) – 3.72 (d) + 7.43

2. For an endothermic reaction, where ΔH represents the enthalpy of the reaction in kJ/mol, the minimum value for the energy of activation will be **(1992)**

(a) less than ΔH (b) zero

(c) more than ΔH (d) equal to ΔH

3. The ΔH^o_f for $CO_2(g)$, $CO(g)$ and $H_2O\,(g)$ are – 393.5, – 110.5 and – 241.8 kJ mol^{-1} respectively. The standard enthalpy change (in kJ mol^{-1}) for the reaction

$CO_2\,(g) + H_2(g) \rightarrow CO(g) + H_2O(g)$ is. **(2000)**

(a) 524.1 (b) + 41.2

(c) – 262.5 (d) – 41.2

4. In thermodynamics, a process is called reversible when **(2001)**

(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

5. Which of the following statements is false ? **(2001)**

(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

6. One mole of a non-ideal gas undergoes a change of state (2.0 atm, 3.0 L, 95 K) → (4.0 atm, 5.0 L, 245 K) with a change in internal energy, $\Delta E = 30.0$ L-atm. The change in enthalpy (ΔH) of the process in L-atm is **(2002)**

(a) 40.0 (b) 42.10

(c) 44.0

(d) not defined, because pressure is not constant

7. Which of the following reactions defines ΔH^o_f ? **(2003)**

(a) $C_{(diamond)} + O_2(g) \rightarrow CO_2\,(g)$

(b) $\frac{1}{2}H_2(g) + \frac{1}{2}F_2(g) \rightarrow HF(g)$

(c) $N_2\,(g) + 3H_2\,(g) \rightarrow 2NH_3(g)$

(d) $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$

8. Spontaneous adsorption of a gas on solid surface is an exothermic process because **(2004)**

(a) ΔH increases for system (b) ΔS increases for gas

(c) ΔS decreases for gas (d) ΔG increases for gas

9. ΔH_{vap} = 30 kJ/mol and ΔS_{vap} = 75 $Jmol^{-1}K^{-1}$. Find temperature of vapour, at one atmosphere. **(2004)**

(a) 400 K (b) 350 K

(c) 298 K (d) 250 K

10. 2 moles of an ideal gas expanded isothermally and reversibly from 1 L to 10 L at 300 K. What is the enthalpy change ? **(2004)**

(a) 4.98 kJ (b) 11.47 kJ

(c) – 11.47 kJ (d) 0 kJ

11. When one mole of monoatomic ideal gas at TK undergoes adiabatic change under a constant external pressure of 1 atm changes volume from 1 L to 2 L. The final temperature in kelvin would be **(2005)**

(a) $\frac{T}{2^{2/3}}$ (b) $T + \frac{2}{3 \times 0.0821}$

(c) T (d) $T - \frac{2}{3 \times 0.0821}$

12. A monoatomic ideal gas undergoes a process in which the ratio of p to V at any instant is constant and equals to 1. What is the molar heat capacity of the gas ? **(2006)**

(a) $\frac{4R}{2}$ (b) $\frac{3R}{2}$

(c) $\frac{5R}{2}$ (d) 0

13. The direct conversion of A to B is difficult, hence it is carried out by the following shown path

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

Given $\Delta S_{(A\to C)} = 50$ eu

$\Delta S_{(C\to D)} = 30$ eu

$\Delta S_{(D\to B)} = 20$ eu

where eu is entropy unit, then $\Delta S_{(A\to B)}$ is **(2006)**

(a) + 100 eu (b) + 60 eu

(c) – 100 eu (d) – 60 eu

14. For the process $H_2O(l)$ (1 bar, 273 K) → $H_2O(g)$ (1 bar, 373 K), the correct set of thermodynamic parameters is **(2007)**

(a) $\Delta G = 0, \Delta S = +ve$ (b) $\Delta G = 0, \Delta S = -ve$

(c) $\Delta G = +ve, \Delta S = 0$ (d) $\Delta G = -ve, \Delta S = +ve$

15. The value of $\log_{10} K$ for a reaction $A \rightleftharpoons B$ is

(Given : $\Delta_r H^o_{298K} = -54.07$ kJ mol^{-1},

$\Delta_r S^o_{298\,K} = 10$ JK^{-1} mol^{-1} and R = 8.314 JK–1 mol^{-1};

$2.303 \times 8.314 \times 298 = 5705$ **(2010)**

(a) 5 (b) 10

(c) 95 (d) 100

16. For the pocess

$$H_2O(\ell) \to H_2O(g)$$

at T = 100°C and 1 atmosphere pressure, the correct choice is **(2014)**

(a) $\Delta S_{system} > 0$ and $\Delta S_{surroundings} > 0$

(b) $\Delta S_{system} > 0$ and $\Delta S_{surroundings} < 0$

(c) $\Delta S_{system} < 0$ and $\Delta S_{surroundings} > 0$

(d) $\Delta S_{system} < 0$ and $\Delta S_{surroundings} < 0$

17. One mode 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 (1L atm = 101.3 J) **(2016)**

(a) 5.763 (b) 1.013

(c) –1.013 (d) –5.763

18. The standard state Gibbs free energies of formation of C(graphite) and C(diamond) at T = 298 K are

$\Delta_f G^o$ [C(graphite)] = 0 kJ mol^{-1}

$\Delta_f G^o$ [C(diamond)] = 2.9 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 2×10^{-6} m^3 mol^{-1}. If C(graphite) is converted to C(diamond) isothermally at T = 298 K, the pressure at which C(graphite) is in equilibrium with C(diamond), is

[Useful information : 1 J = 1 kg m^{2}s^{-2},

1 Pa = 1 kg m^{-1} s^{-2}; 1 bar = 10^5 Pa] **(2017)**

(a) 58001 bar (b) 1450 bar

(c) 14501 bar (d) 29001 bar

Objective Questions II

[One or more than one correct option]

19. Identify the intensive quantities from the following **(1993)**

(a) enthalpy (b) temperature

(c) volume (d) refractive index

20. The following is (are) endothermic reaction (s) **(1999)**

(a) combustion of methane

(b) decomposition of water

(c) dehydrogenation of ethane to ethylene

(d) conversion of graphite to diamond

21. Among the following, the state function(s) is (are) **(2009)**

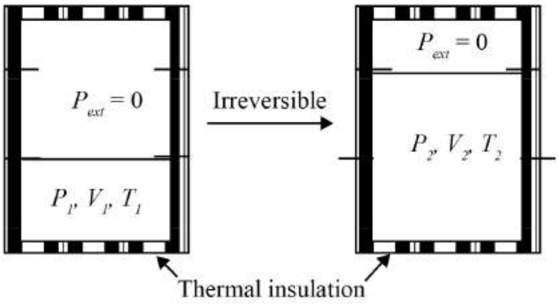
(a) internal energy

(b) irreversible expansion work

(c) reversible expansion work

(d) molar enthalpy

22. 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, **(2014)**



(a) $q = 0$ (b) $T_2 = T_1$

(c) $P_2V_2 = P_1V_1$ (d) $P_2V_2^{\gamma} = P_1V_1^{\gamma}$

23. 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) **(2017)**

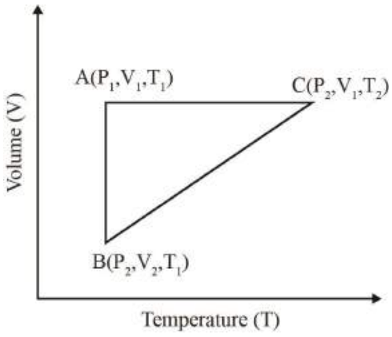
(a) The work done by the gas is less when it is expanded reversibly from V_1 to V_2 under adiabatic conditions as compared to that when expanded reversibly from V_1 to V_2 under isothermal conditions.

(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 irrversibly from (p_2, V_2) to (p_1, V_1) against constant pressure p_1.

24. 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) **(2018)**

(a) $q_{AC} = \Delta U_{BC}$ and $w_{AB} = P_2(V_2 - V_1)$

(b) $w_{BC} = P_2(V_2 - V_1)$ and $q_{BC} = \Delta H_{AC}$

(c) $\Delta H_{CA} < \Delta U_{CA}$ and $q_{BC} = \Delta H_{AC}$

(d) $q_{BC} = \Delta H_{AC}$ and $\Delta H_{CA} > \Delta U_{CA}$

25. Choose the reaction(s) from the following options, for which the standard enthalpy of reaction is equal to the standard enthalpy of formation **(2019)**

(a) $\frac{1}{8}S_8(s) + O_2(g)SO_2(g)$

(b) $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

(c) $\frac{3}{2}O_2(g) \rightarrow O_3(g)$

(d) $2C(g) + 3H_2(g) \rightarrow C_2H_6(g)$

26. In thermodynamics the P-V work done is given by

$$w = -\int dVP_{ext.}$$

For a system undergoing a particular process, the work done is,

$$w = -\int dV\left(\frac{RT}{V-b} - \frac{a}{V^2}\right).$$

The equation is applicable to a **(2020)**

(a) System that satisfies the van der Waals equation of state.

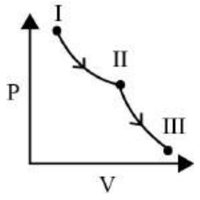
(b) Process that is reversible and isothermal

(c) Process that is reversible and adiabatic

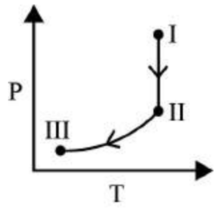
(d) Process that is irreverisble and at constant isothermal.

27. An ideal gas undergoes a reversible isothermal expansion from state I to stable II followed by a reversible adiabatic expansion from state II to state III. The correct plot(s) representing the changes from state I to state III is(are) (p : pressure, V : volume, T : tempeature, H : enthalpy, S : entropy) **(2021)**

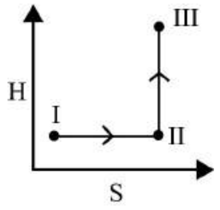
(a)



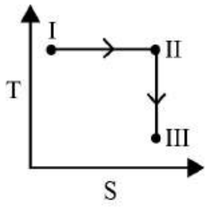
(b)



(c)



(d)



Numerical Value Type Questions

28. The enthalpy for the following reactions (ΔH^o) at 25°C are given below

(i) $\frac{1}{2}H_2(g) + \frac{1}{2}O_2(g) \rightarrow OH(g) \qquad \Delta H^o = -10.06$ kcal

(ii) $H_2(g) \rightarrow 2H(g) \qquad \Delta H^o = 104.18$ kcal

(iii) $O_2(g) \rightarrow 2O(g) \qquad \Delta H^o = 118.32$ kcal

Calculate the O — H bond energy in the hydroxyl radical. **(1981)**

29. The standard heats of formation of $CCl_4(g)$, $H_2O(g)$, $CO_2(g)$ and $HCl(g)$ at 298 K are –25.5, –57.8, – 94.1 and –22.1 kcal/mol respectively. Calculate ΔH^o (298 K) for the reaction

$CCl_4(g) + 2H_2O(g) \rightarrow CO_2(g) + 4HCl(g)$ **(1982)**

30. The molar heats of combustion of $C_2H_2(g)$, C (graphite) and $H_2(g)$ are 310.62 kcal, 94.05 kcal and 68.32 kcal respectively. Calculate the standard heat of formation of $C_2H_2(g)$. **(1983)**

31. Given the following standard heats of reactions

(i) heat of formation of water = – 68.3 kcal

(ii) heat of combustion of acetylene = – 310.6 kcal

(iii) heat of combustion of ethylene = – 337.2 kcal

Calculate the heat of reaction for the hydrogenation of acetylene at constant volume (25° C). **(1984)**

32. The bond dissociation energies of gaseous H_2, Cl_2 and HCl are 104, 58 and 103 kcal/mol respectively. Calculate the enthalpy of formation of HCl gas. **(1985)**

33. The standard molar heat of formation of ethane, carbon dioxide and liquid water are –21.1, –94.1, and –68.3 kcal respectively. Calculate the standard molar heat of combustion of ethane. **(1986)**

34. An intimate mixture of ferric oxide, Fe_2O_3, and aluminium, Al, is used in solid fuel rockets. Calculate the fuel value per gram and fuel value per cc of the mixture. Heats of formation and densities are as follows :

$$H_f(Al_2O_3) = -399 \text{ kcal/mol}$$

$$H_f(Fe_2O_3) = -199 \text{ kcal/mol}$$

Density of Fe_2O_3 = 5.2 g/cc,

Density of Al = 2.7 g/cc **(1989)**

35. An athlete is given 100g of glucose ($C_6H_{12}O_6$) of energy equivalent to 1560 kJ. He utilizes 50 percent of this gained energy in the event. In order to avoid storage of energy in the body, calculate the weight of water the would need to perspire. The enthalpy of evaporation of water is 44 kJ/mol. **(1989)**

36. The standard enthalpy of combustion at 25°C of hydrogen, cyclohexene (C_6H_{10}) and cyclohexane (C_6H_{12}) are –241, – 3800 and –3920 kJ/mol respectively. Calculate the heat of hydrogenation of cyclohexene. **(1989)**

37. Determine the enthalpy of the reaction,

$C_3H_8(g) + H_2(g) \rightarrow C_2H_6(g) + CH_4(g)$, at 25°C, using the given heat of combustion values under standard conditions.

Compound :	$H_2(g)$	$CH_4(g)$	$C_2H_6(g)$	C(graphite)
ΔH° (kJ/mol) :	–285.8	–890.0	–1560.0	–393.0

The standard heat of formation of $C_3H_8(g)$ is –103 kJ/mol. **(1992)**

38. The polymerization of ethylene to linear polyethylene is represented by the reaction,

$$n\,[CH_2 = CH_2] \longrightarrow [CH_2 - CH_2]_n$$

where, n has large integral value. Given that the average enthalpies of bond dissociation for C=C and C—C at 298 K are + 590 and +311 kJ/mol respectively, calculate the enthalpy of polymerization per mole of ethylene at 298 K. **(1994)**

39. From the following data, calculate the enthalpy change for the combustion of cyclopropane at 298 K. The enthalpy of formation of $CO_2(g)$, $H_2O\,(l)$ and propane (g) are –393.5, –285.8 and 20.42 kJ mol^{-1} respectively. The enthalpy of isomerization of cyclopropane to propene is –33.0 kJ mol^{-1}. **(1998)**

40. Estimate the average S–F bond energy in SF_6. The values of standard enthalpy of formation of $SF_6(g)$, S(g) and F(g) are :

– 1100, 275 and 80 kJ mol^{-1} respectively. **(1999)**

41. A sample of argon gas at 1 atm pressure and 27ºC expands reversibly and adiabatically from 1.25 dm^3 to 2.50 dm^3. Calculate the enthalpy change in this process C_{V_m} for argon is 12.49 JK^{-1} mol^{-1}. **(2000)**

42. 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. **(2000)**

$$2B(s) + \frac{3}{2}O_2(g) \rightarrow B_2O_3(s), \quad \Delta H = -1273 \text{ kJ mol}^{-1}$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l), \quad \Delta H = -286 \text{ kJ mol}^{-1}$$

$$H_2O(l) \longrightarrow H_2O(g), \quad \Delta H = 44 \text{ kJ mol}^{-1}$$

$$2B\,(s) + 3H_2\,(g) \longrightarrow B_2H_6\,(g), \quad \Delta H = 36 \text{ kJ mol}^{-1}$$

43. In a constant volume calorimeter, 3.5g of a gas with molecular weight 28 was burnt in excess oxygen at 298.0 K. The temperature of the calorimeter was found to increases 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 **(2009)**

44. 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 : **(2018)**

$$2Cu(s) + H_2O(g) \rightarrow Cu_2O(s) + H_2(g)$$

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) = 8J K^{-1} mol^{-1}, ln (10) = 2.3. Cu(s) and Cu_2O(s) are mutually immiscible.

45. Tin is obtained from cassiterite by reduction with coke. Use the data given below to determine the minimum tempeature (in K) at which the reduction of cassiterite by coke would take place. **(2020)**

At 298 K : $\Delta_f H^0(SnO_2(s)) = 581.0 kJmol^{-1}$,

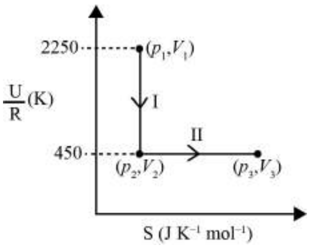
$$\Delta_f H^0(CO_2(g)) = -394.0 \text{ kJ mol}^{-1}$$

$$S^0(SnO_2(s)) = 56.0 JK^{-1}mol^{-1}, S^0(Sn(s)) = 52.0 \text{ JK}^{-1}mol^{-1}$$

$$S^0(C(s)) = 6.0 JK^{-1}mol^{-1}, S^0(CO_2(g)) = 210.0 \text{ J K}^{-1}mol^{-1}$$

Assume that the enthalpies and the entropies are temeprature independent.

46. One mole of an ideal gas at 900 K, undergoes two reversible processes, I followed by II, as shown below. If the work done by the gas in the two processes are same, the value of $\ln\frac{V_3}{V_2}$ is _________. **(2021)**



(U : Internal energy, S : entropy, p : pressure, V : volume, R : gas constant)

(Given : molar heat capacity at constant volume, $C_{V,m}$ of the gas is $\frac{5}{2}R$)

Assertion Reason

(A) If both Assertion and Reason are correct and Reason is the correct explanation of Assertion.

(B) If both Assertion and Reason are true but Reason is not the correct explanation of Assertion.

(C) If Assertion is true but Reason is false.

(D) If Assertion is false but Reason is true.

47. **Assertion (A) :** The heat absorbed during the isothermal expansion of an ideal gas against vacuum is zero.

Reason (R) : The volume occupied by the molecules of an ideal gas is zero. **(2000)**

(a) A
(b) B
(c) C
(d) D

48. **Assertion (A) :** For every chemical reaction at equilibrium standard Gibbs' energy of reaction is zero.

Reason (R) : At constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing Gibbs' energy. **(2008)**

(a) A
(b) B
(c) C
(d) D

49. **Assertion (A) :** There is a natural asymmetry between converting work to heat and converting heat to work.

Reason (R) : No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work. **(2008)**

(a) A
(b) B
(c) C
(d) D

Subjective Type Questions

50. Following statement is true only under some specific conditions. Write the conditions for that in not more than two sentences

"The heat energy q, absorbed by a gas is ΔH." **(1984)**

51. In order to get maximum calorific output, a burner should have an optimum fuel to oxygen ratio which corresponds to 3 times as much oxygen as is required theoretically for complete combustion of the fuel. A burner which has been adjusted for methane as fuel (with x litre/hour of CH_4 and 6x litre/hour of O_2) is to be readjusted for butane, C_4H_{10}. In order to get the same calorific output, what should be the rate of supply of butane and oxygen ? Assume that losses due to incomplete combustion etc., are the same for both fuels and that the gases behave ideally. Heats of combustions :

$CH_4 = -809$ kJ/mol, $C_4H_{10} = -2878$ kJ/mol **(1993)**

52. The standard enthalpies of formation of cyclohexane (*l*) and benzene (*l*) at 25°C are –156 and +49 kJ mol^{-1} respectively. The standard enthalpy of hydrogenation of cyclohexene (*l*) at 25°C is –119 kJ mol^{-1}. Use these data to estimate the magnitude of the resonance energy of benzene. **(1996)**

53. Show that the reaction,

$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$ at 300 K, is spontaneous and exothermic, when the standard entropy change is –0.094 kJ mol^{-1} K^{-1}. The standard Gibbs' free energies of formation for CO_2 and CO are –394.4 and –137.2 kJ mol^{-1}, respectively. **(2000)**

54. When 1-pentyne (A) is treated with 4 N alcoholic KOH at 175°C, it is converted slowly into an equilibrium mixture of 1.3% 1-pentyne (A), 95.2% 2-pentyne (B) and 3.5% of 1, 2-pentadiene (C). The equilibrium was maintained at 175°C. Calculate ΔG° for the following equilibria.

$B \rightleftharpoons A, \qquad \Delta G_1^{o} = ?$

$B \rightleftharpoons C, \qquad \Delta G_2^{o} = ?$

From the calculated value of ΔG_1^{o} and ΔG_2^{o} indicate the order of stability of (A), (B) and (C). Write a reasonable reaction mechanism showing all intermediates leading to (A), (B) and (C) **(2001)**

55. Two moles of a perfect gas undergo the following processes :

(a) a reversible isobaric expansion from (1.0 atm, 20.0L) 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, 40.0L) to (1.0 atm, 20.0 L)

(i) Sketch with labels each of the processes on the same p-V diagram.

(ii) Calculate the total work (W) and the total heat change (Q) involved in the above processes.

(iii) What will be the values of ΔU, ΔH and ΔS for the overall process ? **(2002)**

56. C_V value of He is always $\frac{3R}{2}$ but C_V value of H_2 is $\frac{3R}{2}$ at low temperature and $\frac{5R}{2}$ at moderate temperature and more than $\frac{5R}{2}$ at higher temperature. Explain in two or three lines. **(2003)**

57. 100 mL of a liquid contained in an isolated container at a pressure of 1 bar. The pressure is steeply increased to 100 bar. The volume of the liquid is decreased by 1 mL at this constant pressure. Find the ΔH and ΔU. **(2004)**

Fill in the Blanks

58. The total energy of one mole of an ideal monatomic gas at 27°C is .... cal. **(1984)**

59. $C_p - C_V$ for an ideal gas is .... **(1984)**

60. A system is said to be .... if it can neither exchange matter nor energy with the surroundings. **(1993)**

61. The heat content of the products is more than that of the reactants in an .... reaction. **(1993)**

62. When Fe(s) is dissolved in aqueous hydrochloric acid in a closed vessel, the work done is .... **(1997)**

63. Enthalpy is an .... property. **(1997)**

True / False

64. First law of thermodynamics is not adequate in predicting the direction of a process. **(1982)**

65. Heat capacity of a diatomic gas is higher than that of a monatomic gas. **(1985)**

Answer Key

CHAPTER -10 | THERMODYNAMICS AND THERMOCHEMISTRY

EXERCISE - 1 :
BASIC OBJECTIVE QUESTIONS

1. (a) **2.** (d) **3.** (a) **4.** (a) **5.** (c)

6. (c) **7.** (d) **8.** (b) **9.** (b) **10.** (b)

11. (c) **12.** (a) **13.** (c) **14.** (b) **15.** (d)

16. (d) **17.** (d) **18.** (c) **19.** (a) **20.** (c)

21. (b) **22.** (a) **23.** (b) **24.** (b) **25.** (b)

26. (d) **27.** (c) **28.** (b) **29.** (b) **30.** (c)

31. (d) **32.** (a) **33.** (b) **34.** (b) **35.** (a)

36. (a) **37.** (d) **38.** (b) **39.** (b) **40.** (c)

41. (c) **42.** (b) **43.** (b) **44.** (a) **45.** (c)

46. (c) **47.** (d) **48.** (c) **49.** (a) **50.** (d)

51. (a) **52.** (b) **53.** (d) **54.** (b) **55.** (b)

56. (a) **57.** (c) **58.** (a) **59.** (b) **60.** (a)

61. (c) **62.** (a) **63.** (d) **64.** (c) **65.** (c)

66. (c) **67.** (d) **68.** (d) **69.** (b) **70.** (b)

71. (d) **72.** (b) **73.** (c) **74.** (a) **75.** (c)

76. (a) **77.** (d) **78.** (a) **79.** (a) **80.** (b)

81. (b) **82.** (a) **83.** (b) **84.** (c) **85.** (c)

86. (d) **87.** (b) **88.** (b) **89.** (a) **90.** (c)

91. (c) **92.** (d) **93.** (d) **94.** (c) **95.** (a)

96. (d) **97.** (c) **98.** (c) **99.** (d) **100.** (a)

101. (d) **102.** (b) **103.** (c) **104.** (b) **105.** (b)

106. (a) **107.** (d) **108.** (b) **109.** (b) **110.** (b)

111. (b) **112.** (d) **113.** (a) **114.** (b) **115.** (a)

116. (a) **117.** (d) **118.** (b) **119.** (d) **120.** (b)

EXERCISE - 2 :
PREVIOUS YEAR JEE MAINS QUESTIONS

1. (a) **2.** (d) **3.** (b) **4.** (d) **5.** (d)

6. (d) **7.** (c) **8.** (d) **9.** (a) **10.** (d)

11. (c) **12.** (b) **13.** (a) **14.** (c) **15.** (a)

16. (a) **17.** (d) **18.** (a) **19.** (c) **20.** (c)

21. (b) **22.** (b) **23.** (d) **24.** (b) **25.** (b)

26. (d) **27.** (c) **28.** (a) **29.** (d) **30.** (c)

31. (c) **32.** (c) **33.** (d) **34.** (b) **35.** (d)

36. (b) **37.** (d) **38.** (c) **39.** (d) **40.** (d)

41. (b) **42.** (b) **43.** (a) **44.** (b) **45.** (b)

46. (a) **47.** (b) **48.** (b) **49.** (d) **50**. (b)

51. (d) **52.** (c) **53.** (d) **54.** (c) **55.** (a)

56. (d) **57.** (c) **58.** (b) **59.** (b) **60.** (c)

61. (a) **62.** (c) **63.** (c) **64.** (a) **65.** (c)

66. (a) **67**. (b) **68.** (a) **69**. (a) **70.** (2.70)

71. (-192.50) **72**. (48.00) **73.** (6.25)

74. (189494.39) **75.** (-326400.00)

76. (-13538.00) **77.** (b)

78. (741.00) **79**. (15.00)

80. (200.00) **81**. (309.00)

82. (2218.00) **83**. (230.00)

84. (128.00) **85**. (667.00)

86. (336.00) **87**. (21.00)

88. (101.00) **89**. (50.00)

90. (82.00) **91**. (31.00)

92. (38.00) **93**. (82.00)

94. 964.00) **95**. (5.00)

CHAPTER -10 | THERMODYNAMICS AND THERMOCHEMISTRY

EXERCISE - 3 : ADVANCED OBJECTIVE QUESTIONS

1. (a) **2.** (a) **3.** (d) **4.** (a) **5.** (d)
6. (c) **7.** (a) **8.** (a) **9.** (a) **10.** (b)
11. (c) **12.** (b) **13.** (d) **14.** (b) **15.** (b)
16. (c) **17.** (c) **18.** (d) **19.** (d) **20.** (c)
21. (b) **22.** (a) **23.** (b) **24.** (a) **25.** (b)
26. (b) **27.** (a) **28.** (d) **29.** (a) **30.** (a)
31. (c) **32.** (b) **23.** (c) **34.** (c) **35.** (a)
36. (b) **37.** (d) **38.** (c) **39.** (b) **40.** (a)
41. (b) **42.** (a) **43.** (b) **44.** (b) **45.** (b)
46. (b) **47.** (d) **48.** (a, d) **49.** (c,d) **50.** (b, d)
51. (a, b, c) **52.** (6.00) **53.** (4.00) **54.** (1.00)
55. (8.00) **56.** (b) **57.** (a) **58.** (d)
59. (a) **60.** (c) **61.** (b) **62.** (a) **63.** (d)
64. (A → p, q, r) ; (B → p, s); (C → p, q, r); D → (p, r, s)
65. (A → p,q) ; (B → p, q); (C → s); (D → r)
66. (d) **67.** (c) **68.** (c) **69.** (c) **70.** (a)

EXERCISE - 4 : PREVIOUS YEAR JEE ADVANCED QUESTIONS

1. (a) **2.** (c) **3.** (b) **4.** (c) **5.** (a)
6. (c) **7.** (b) **8.** **(c)** **9.** (a) **10.** (d)
11. (d) **12.** (a) **13.** (a) **14.** (a) **15.** (b)
16. (b) **17.** (c) **18.** (c) **19.** (b,d)
20. (b,c,d) **21.** (a,c,d)
22. (a,b,c) **23.** (a,c,d)
24. (b, c) **25.** (a, c)
26. (a, b, c) **27.** (a, b, d)
28. (121.31) **29.** (-41.4)
30. (-54.2) **31.** (41.104)
32. (22.0) **33.** (-372.0)
34. (3.94) **35.** (319.1)
36. (-121.0) **37.** (-55.7)
38. (72.0) **39.** (-2091.32)
40. (309.16) **41.** (-115.41)
42. (-2035.0) **43.** (9.00)
44. (-14.6) **45.** (935.00)
46. (10.00) **47.** (b)
48. (c) **49.** (b)
58. (900) **59.** (R)
60. (Isolated) **61.** (Exothermic rection)
62. (Zero) **63.** (Extensive)
64. True **65.** True