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# Chemical Kinetics



Reaction Rate and Mechanism

- INTRODUCTION
- Two questions are of interest to a chemist when considering a chemical reaction
  - Is the reaction feasible or not? and
  - What is the timescale of occurrence of the reaction?
- The first concern is addressed by thermodynamics which
  - predicts the spontaneity or otherwise of the chemical process as well as
  - the equilibrium conditions of the reaction.
- The time scale and the possible pathways in the transformation of the reactants to products can only be determined through the knowledge of REACTION KINETICS.
- In summary, thermodynamics addresses the **why** of a chemical process while chemical kinetics addresses the **how** of the reaction.

- Rate of Reaction
- rate at which reactants are used up, or equivalently the rate at which products are formed.
  - units of concentration per unit time,  $\text{mol dm}^{-3} \text{s}^{-1}$ 
    - (alternative units of concentration are often used such as units of pressure – Torr, mbar or Pa, for gas phase reactions).
- Reaction rate is measured by monitoring the concentration of one of the reactant or products with time
- Consider the reaction:



- The stoichiometric coefficients of  $\text{N}_2$ ,  $\text{H}_2$  and  $\text{NH}_3$  are 1, 3, and 2 respectively.
- We could determine the rate of this reaction in any one of three ways, by monitoring the changing concentration of  $\text{N}_2$ ,  $\text{H}_2$  or  $\text{NH}_3$

.

- Assuming  $x$  moles of  $N_2$  are consumed within a given time, then  $3x$  moles of  $H_2$  will be consumed and  $2x$  moles of  $NH_3$  formed within the same given time – this then could mean that the following would be obtained

$$-\frac{d[N_2]}{dt} = x \text{ mol dm}^{-3} \text{ s}^{-1}$$

$$-\frac{d[H_2]}{dt} = 3x \text{ mol dm}^{-3} \text{ s}^{-1}$$

$$+\frac{d[NH_3]}{dt} = 2x \text{ mol dm}^{-3} \text{ s}^{-1}$$

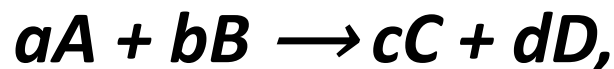


- Clearly, the same reaction cannot have three different rates, so there appear to be a problem.
- the reaction rate is actually defined as the rate of change of the concentration of a reactant or product divided by its stoichiometric coefficient.
- For the above reaction, the rate (usually given the symbol  $v$ ) is therefore

$$v = -\frac{d[N_2]}{dt} = -\frac{1}{3} \frac{d[H_2]}{dt} = +\frac{1}{2} \frac{d[NH_3]}{dt}$$

- Note that a negative sign appears when we define the rate using the concentration of one of the reactants.
- This is because the rate of change of a reactant is negative (since it is being used up in the reaction), but the reaction rate needs to be a positive quantity.

- In summary, for an hypothetical reaction:



- the rate in terms of all the species involved is

$$\text{Rate} = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$$

# Illustrations

- $4\text{NO}(g) + \text{O}_2(g) \rightarrow 2\text{N}_2\text{O}_3(g)$ 
  - For the reaction above, express the rate in terms of the change in concentration with time for each substance
  - How fast is  $[\text{O}_2]$  decreasing when  $[\text{NO}]$  is decreasing at a rate of  $1.60 \times 10^{-4} \text{ mol/L}\cdot\text{s}$ ?

- SOLUTION

$$v = -\frac{1}{4} \frac{d[\text{NO}]}{dt} = -\frac{d[\text{O}_2]}{dt} = +\frac{1}{2} \frac{d[\text{N}_2\text{O}_3]}{dt}$$
$$\Rightarrow -\frac{d[\text{O}_2]}{dt} = -\frac{1}{4} \frac{d[\text{NO}]}{dt} = \frac{1}{4} \times (1.6 \times 10^{-4})$$
$$= 4.0 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$$

$[\text{O}_2]$  is decreasing 0.25 times as fast as  $[\text{NO}]$

- For a particular reaction, the reaction rate in terms of the change in concentration with time for each substance is

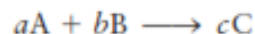
$$\text{Rate} = -\frac{1}{4} \frac{d[\text{NH}_3]}{dt} = -\frac{1}{5} \frac{d[\text{O}_2]}{dt} = \frac{1}{4} \frac{d[\text{NO}]}{dt} = \frac{1}{6} \frac{d[\text{H}_2\text{O}]}{dt}$$

- SOLUTION
- The balanced equation is



- Can you try this?

Consider the general reaction



and the following average rate data over a specific time period  $\Delta t$ :

$$-\frac{\Delta\text{A}}{\Delta t} = 0.0080 \text{ mol L}^{-1} \text{ s}^{-1}$$

$$-\frac{\Delta\text{B}}{\Delta t} = 0.0120 \text{ mol L}^{-1} \text{ s}^{-1}$$

$$\frac{\Delta\text{C}}{\Delta t} = 0.0160 \text{ mol L}^{-1} \text{ s}^{-1}$$

Determine a set of possible coefficients to balance this general reaction.



# Rate Law Expression

- The major theme of any kinetic study is what is known as the rate law or rate equation. It expresses the rate as a function of concentrations and temperature
- The rate law is based on experiment
- For a general reaction:  $aA + bB \longrightarrow cC + dD$ ,
- Experimentally, the rate is proportional to the concentrations of the reactants in the form

$$Rate \propto [A]^x [B]^y$$



- Expressing the expression above mathematically by introducing a constant of proportionality  $k$ , gives the rate law as

$$Rate = k [A]^x [B]^y$$

- $k$  is known as the rate constant that is specific to the particular reaction of interest at a given temperature and does not change as the reaction proceeds

- The exponents  $x$  and  $y$  are the order of the reaction with respect to the concentrations of A and B in the reaction.
  - The order with respect to a reactant is a measure of how the rate of the reaction depends on the concentration of the particular reactant.
  - The coefficients of A and B in the balanced equation do not necessarily related to the exponents  $x$  and  $y$  in the rate law expression
  - The terms in the rate law expression are all experimentally determined parameters
- The various parameters in the rate law expression can be obtained by measuring the concentrations of the reactants to determine the initial rate – (REMEMBER THAT YOU WERE TAUGHT INITIAL RATE METHOD IN PART ONE)

## Some Methods of Determining the Initial Rate

- ***Spectrometric methods measure the concentration of a component that absorbs (or emits) characteristic wavelengths of light.***
  - For example, in the reaction of NO and O<sub>3</sub>, only NO<sub>2</sub> has a color (an indication that NO<sub>2</sub> absorbs some wavelength of visible light):
  - ***NO(g, colorless) + O<sub>3</sub>(g, colorless) → O<sub>2</sub>(g, colorless) + NO<sub>2</sub>(g, brown)***  

  - Known amounts of reactants are injected into a tube of known volume within a spectrometer, which is set to measure the wavelength and intensity of the color.
  - The rate of NO<sub>2</sub> formation is proportional to the increase in that intensity over time.  


- **Conductometric methods rely on the change in electrical conductivity of the reaction solution** when nonionic reactants form ionic products, or vice versa.
  - Consider the substitution reaction between a haloalkane, such as 2-bromo-2-methylpropane, and water:
    - $(\text{CH}_3)_3\text{C-Br(l)} + \text{H}_2\text{O(l)} \rightarrow (\text{CH}_3)_3\text{C-OH(l)} + \text{H}^+(\text{aq}) + \text{Br}^-(\text{aq})$
    - The HBr that forms is a strong acid, so it dissociates completely in the water.
    - As time passes, more ions form, so the conductivity of the reaction mixture increases.
    - There are other examples in which the conductivity decreases



- ***Manometric methods employ a manometer attached to a reaction vessel of fixed*** volume and temperature. The manometer measures the pressure change in the vessel due to a reaction that involves a change in the number of moles of gas.
  - Consider the decomposition reaction of hydrogen peroxide:
  - $2\text{H}_2\text{O}_2(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$
  - The rate is directly proportional to the increase in pressure as  $\text{O}_2$  gas forms.

## Determination of the Order of a Reaction

- The rate as a function of reactants' concentration
  - Initial Rate Method: (Please read this up from CHM 101)
- The rate as a function of time - Integrated Rate Law Method
  - We will proceed by first looking at reactions involving a single reactant:  $aA \rightarrow \text{products}$

$$\text{Rate} = -\frac{d[A]}{dt} = k[A]^x$$

- Consider the integrated rate laws individually for the cases  $x = 1$  (first order),  $x = 2$  (second order), and  $x = 0$  (zero order).
- *First order Rate Law: Consider the reaction*



- Experiment showed that the rate law is

$$\text{Rate} = -\frac{d[\text{N}_2\text{O}_5]}{dt} = k[\text{N}_2\text{O}_5]$$

- Integration of the above rate law with boundary conditions:

$$\text{At time } t = 0 : [\text{N}_2\text{O}_5] = [\text{N}_2\text{O}_5]_0$$

$$\text{At time } t = t : [\text{N}_2\text{O}_5] = [\text{N}_2\text{O}_5]_t$$

- The rate law yields



$$\ln[\text{N}_2\text{O}_5] = -kt + \ln[\text{N}_2\text{O}_5]_0$$

- OR

$$\log_{10} [\text{N}_2\text{O}_5]_t = -\frac{kt}{2.303} + \log_{10} [\text{N}_2\text{O}_5]_0$$

- Generally for the reaction:  $aA \rightarrow \text{products}$ , where the order of the reaction is 1 with respect to [A]

$$\text{Rate} = -\frac{d[A]}{dt} = k[A]$$

- The integrated rate law is

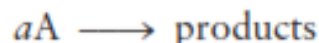
$$\ln [A]_t = -kt + \ln [A]_0$$

- Things to note about this equation

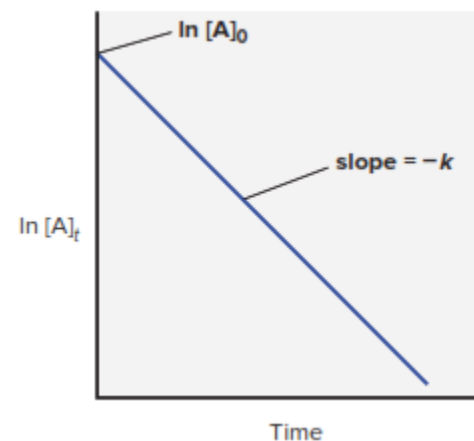
- The equation shows how the concentration of A depends on time. If the initial concentration of A and the value of the rate constant  $k$  are known, the concentration of A at any time can be calculated.
- Equation (15.2) is of the form  $y = mx + b$ , where a plot of  $y$  versus  $x$  is a straight line with slope  $m$  and intercept  $b$ . In this case

$$y = \ln[A] \quad x = t \quad m = -k \quad b = \ln[A]_0$$

Thus, for a first-order reaction, plotting the natural logarithm of concentration versus time always gives a straight line. This fact is often used to test whether a reaction is first order. For the reaction of the type



the reaction is first order in A if a plot of  $\ln[A]$  versus  $t$  is a straight line. ◀  
Conversely, if the plot is not a straight line, the reaction is not first order.



- The integrated rate law for a first-order reaction can also be expressed in terms of the *ratio* of  $[A]$  and  $[A]_0$  as follows:

$$\ln\left(\frac{[A]_0}{[A]}\right) = kt$$



- The unit of the rate constant for a first order reaction can be obtained from the last equation by making  $k$  the subject of the expression

$$k = \frac{1}{t} \ln \left( \frac{[A]_0}{[A]_t} \right)$$

*Unit of  $k$  is therefore the reciprocal of time such as  $s^{-1}$ ,  $\text{min}^{-1}$ ,  $\text{hr}^{-1}$  etc*

- **ILLUSTRATION**

- Problem At  $1000^\circ\text{C}$ , cyclobutane ( $\text{C}_4\text{H}_8$ ) decomposes in a first-order reaction, with the very high rate constant of  $87 \text{ s}^{-1}$ , to two molecules of ethylene ( $\text{C}_2\text{H}_4$ ).

- (a) The initial  $\text{C}_4\text{H}_8$  concentration is  $2.00 \text{ M}$ . What is the concentration after  $0.010 \text{ s}$ ?

- (b) How long will it take for 70.0% of the  $\text{C}_4\text{H}_8$  to decompose?

- **SOLUTION**

- From the unit of the rate constant, the reaction is first order with respect to [cyclobutane]

$$\ln [C_4H_8]_{t=0.010s} = -kt + \ln [C_4H_8]_0$$

$$\Rightarrow \ln [C_4H_8]_{t=0.010s} = -87s^{-1} \times 0.010s + \ln(2.00)$$

$$= -0.1769$$

$$\therefore [C_4H_8]_{t=0.010s} = \exp(-0.1769) = 0.84M$$



- For 70% decomposition, it means

$$[C_4H_8]_t = 0.30 [C_4H_8]_0$$

$$\therefore t = \frac{1}{k} \ln \left( \frac{[A]_0}{[A]_t} \right) = \frac{1}{87s^{-1}} \ln \left( \frac{[A]_0}{0.30[A]_0} \right)$$

$$= 0.0138s$$

# PRACTISE QUESTIONS

A certain reaction has the following general form:



At a particular temperature and  $[A]_0 = 2.00 \times 10^{-2} \text{ M}$ , concentration versus time data were collected for this reaction, and a plot of  $\ln[A]$  versus time resulted in a straight line with a slope value of  $-2.97 \times 10^{-2} \text{ min}^{-1}$ .

- Determine the rate law, the integrated rate law, and the value of the rate constant for this reaction.
- Calculate the half-life for this reaction.
- How much time is required for the concentration of A to decrease to  $2.50 \times 10^{-3} \text{ M}$ ?

The rate law for the decomposition of phosphine ( $\text{PH}_3$ ) is

$$\text{Rate} = -\frac{d[\text{PH}_3]}{dt} = k[\text{PH}_3]$$

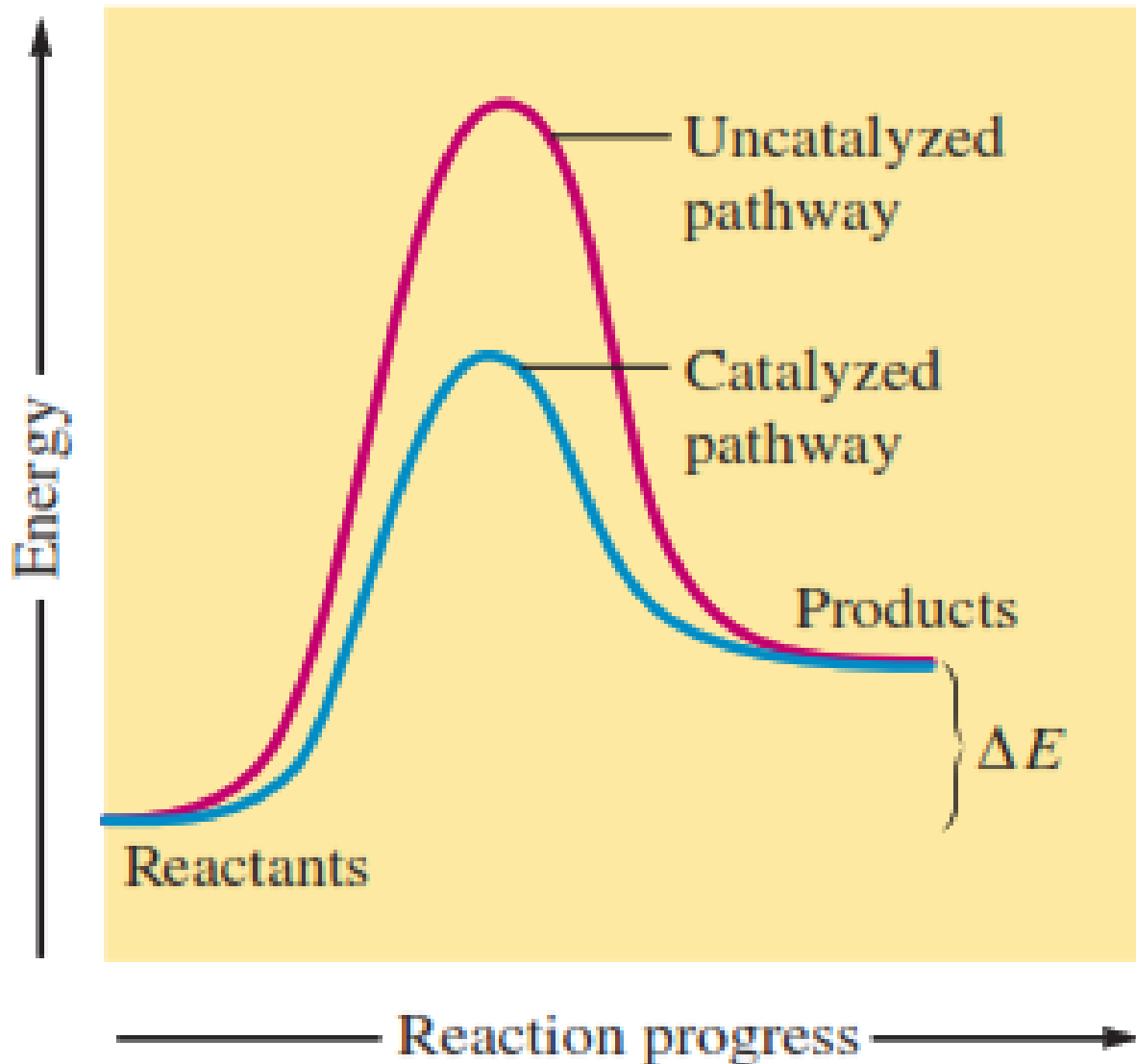
It takes 120. s for the concentration of 1.00 M  $\text{PH}_3$  to decrease to 0.250 M. How much time is required for 2.00 M  $\text{PH}_3$  to decrease to a concentration of 0.350 M?

# FACTORS AFFECTING RATE OF REACTION

- A number of factors influence the rate of reactions. Such factors include:
- Concentration of reactants
- Nature of reactants and products formed
- Presence of catalyst, and
- Temperature
- All of these factors were taught in detail during CHM 101 and so, be advised to revisit your CHM 101 note. However, we will be looking more into the effect of catalyst as well as, temperature on the rate of reaction

- Effect of Catalyst
  - A catalyst is a substance that speed up the rate of reaction by providing an alternative pathway of low activation energy for the reaction.
  - The catalyst is not used up in the course of the reaction, it can however, be transformed from one form of existence to another
  - Nature is the master designer and user of catalysts: every organism relies on protein catalysts, known as ***enzymes***, to speed up life-sustaining reactions, and even the simplest bacterium employs thousands of them.
- Basics of Catalytic Activity
- A catalyst provides a different reaction mechanism with a lower activation energy, which in turn makes the rate constant larger and, thus, the reaction rate higher:
- Catalyst  $\Rightarrow$  ***lower  $E_a$***   $\Rightarrow$  ***larger  $k$***   $\Rightarrow$  ***higher rate***

- For each reaction a certain energy barrier must be surmounted.



- Catalysts are classified as homogeneous or heterogeneous.
  - A homogeneous catalyst is one that is present in the same phase (physical state) as the reacting molecules.
  - A heterogeneous catalyst exists in a different phase, usually as a solid.



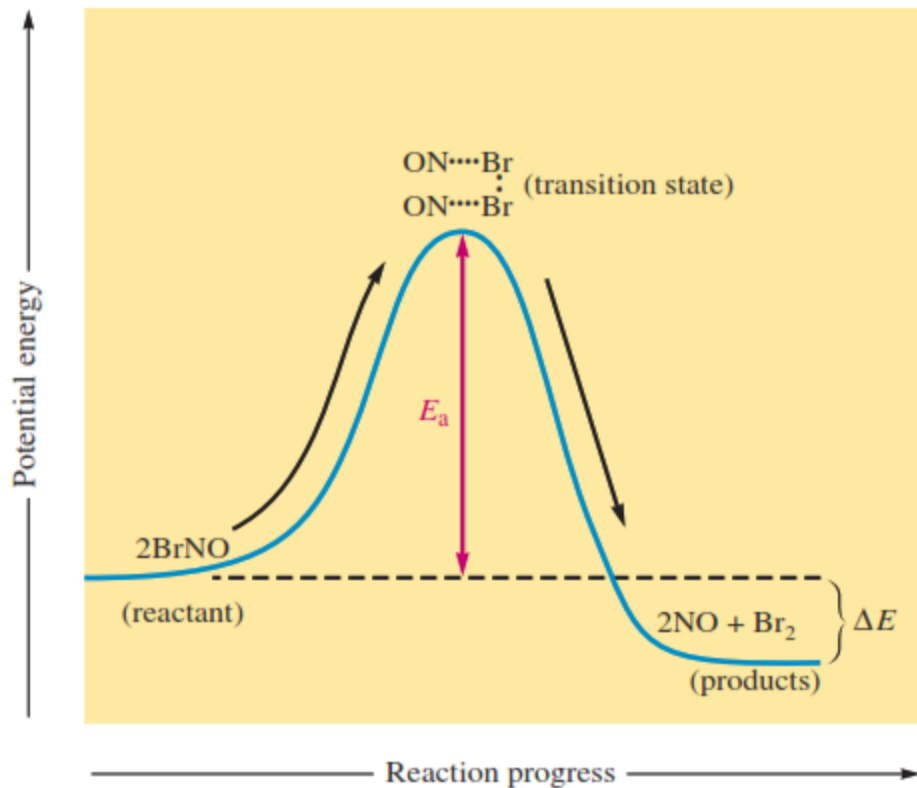
# EFFECT OF TEMPERATURE ON RATE OF REACTION AND THE COLLISION THEORY

- Atoms, molecules, or ions must collide with one another for a reaction to occur – this is the basis of the COLLISION THEORY
  - This assumption can explain the concentration dependence of reaction rates.
    - Increase in concentration increases the number of molecules colliding and the frequency of collision increases, thus, the rate of the reaction increases
- It is found that the rate of reaction is much smaller than the calculated collision frequency in a given collection of gas particles. This must mean that *only a small fraction of the collisions produces a reaction. Why?*
  - To answer this question, Svante Arrhenius proposed the existence of a *threshold energy, called the **activation energy**, **that*** must be overcome to produce a chemical reaction.

- Consider the gas phase reaction



- In this reaction two Br-N bonds must be broken and one Br-Br bond must be formed. Breaking a Br-N bond requires considerable energy (243 kJ/mol), which must come from somewhere.
- The collision model postulates that the energy required to break the bonds comes from the kinetic energies possessed by the reacting molecules before the collision.
- This kinetic energy is changed into potential energy as the molecules are distorted during a collision, breaking bonds and rearranging the atoms into the product molecules.



Only collisions with energy greater than the activation energy are able to react (get over the barrier).

- the fraction of collisions with the required activation energy increases dramatically.
- When the temperature is doubled, the fraction of effective collisions much more than doubles.
- The fraction of effective collisions increases *exponentially* with temperature.
- This agrees with the observation that rates of reactions increases exponentially with temperature.

- There is, however, another complication.
  - Experiments show that the observed reaction rate is considerably smaller than the rate of collisions with enough energy to surmount the barrier.
  - This means that many collisions, even though they have the required energy, still do not produce a reaction. Why not?
- The answer lies in the molecular orientations during collisions.
- In summary, two requirements must be satisfied for reactants to collide successfully (to rearrange to form products):
  - The collision must involve enough energy to produce the reaction; that is, the collision energy must equal or exceed the activation energy.
  - The relative orientations of the reactants must allow formation of any new bonds necessary to produce products.

- Taking these factors into account, the rate constant can be represented as

$$k = zpe^{-E_a/RT}$$

- where  $z$  is the collision frequency (the total number of collisions per second).
- The factor  $p$  in this expression, called the steric factor, reflects the fraction of collisions with effective orientations.
- The factor  $e^{-E_a/RT}$  represents the fraction of collisions with sufficient energy to produce a reaction.

- The expression above can be written in the well-known form as – The Arrhenius Equation  $k = Ae^{-E_a/RT}$

- Taking logarithm of both sides of the equation:

$$\ln(k) = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln(A)$$

- One of the most important applications of this equation is in the determination of the activation energy  $E_a$  for a reaction.

- *This involves measuring the rate constant  $k$  at several temperatures and then plotting  $\ln(k)$  versus  $1/T$ ,*

- $E_a$  can also be calculated from the values of  $k$  at only two temperatures using a formula that can be derived as follows from the equation above.

At temperature  $T_1$ , the rate constant is  $k_1$ ; thus

$$\ln(k_1) = -\frac{E_a}{RT_1} + \ln(A)$$

- At temperature  $T_2$ , the rate constant is  $k_2$ ; thus

$$\ln(k_2) = -\frac{E_a}{RT_2} + \ln(A)$$

- Subtracting the last two equations from one another gives

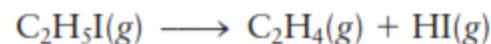
$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

- **Therefore, the values of  $k_1$  and  $k_2$  measured at temperatures  $T_1$  and  $T_2$  can be used to calculate  $E_a$ .**

# PRACTISE QUESTIONS

- 1 The activation energy for the decomposition of HI(g) to H<sub>2</sub>(g) and I<sub>2</sub>(g) is 186 kJ/mol. The rate constant at 555 K is  $3.52 \times 10^{-7} \text{ L mol}^{-1} \text{ s}^{-1}$ . What is the rate constant at 645 K?

- 2 The decomposition of iodoethane in the gas phase proceeds according to the following equation:



At 660. K,  $k = 7.2 \times 10^{-4} \text{ s}^{-1}$ ; at 720. K,  $k = 1.7 \times 10^{-2} \text{ s}^{-1}$ . What is the rate constant for this first-order decomposition at 325°C? If the initial pressure of iodoethane is 894 torr at 245°C, what is the pressure of iodoethane after three half-lives?

- 3 A certain reaction has an activation energy of 54.0 kJ/mol. As the temperature is increased from 22°C to a higher temperature, the rate constant increases by a factor of 7.00. Calculate the higher temperature.

# MECHANISM OF REACTIONS





- Mechanism
- a sequence of single reaction steps that sum to the overall equation.
- a series of **elementary steps** by which a chemical reaction occurs
  - An elementary step - a step involving a one-, two-, or three-entity collision that cannot be explained by simpler reactions
- To understand a chemical reaction completely, we must know its mechanism. One of the main purposes for studying reaction rates is to learn as much as possible about the steps involved in a chemical reaction. For example  $\text{NO}_2(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{CO}_2(\text{g})$ 
  - the rate law expression was determined experimentally as

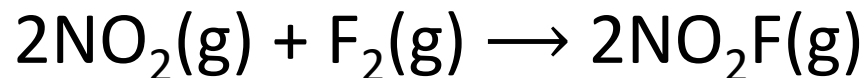
$$-\frac{d[\text{NO}_{(g)}]}{dt} = k[\text{NO}_{(g)}]^2$$

- The question, therefore, is what mechanism can explain this experimentally observed rate law equation?
- The following elementary steps were proposed



- Since the first step is the slowest step in the reaction mechanism, the overall reaction must proceed at the rate of the first step.
- That is, the products of the overall reaction, gaseous nitrogen dioxide and carbon dioxide, can be produced only as fast as the slowest step, Step 1.
- Step 1 is therefore called the rate-determining step, **which is the step in a reaction mechanism that determines the rate of the overall reaction.**
- A careful look at the proposed mechanism shows that  $\text{NO}_3$  is produced in the step 1 but consumed in step 2. Such a specie is called a **REACTION INTERMEDIATE**

- The sum of the two elementary steps above gives the overall balanced equation.
- For a plausible reaction mechanism, the following conditions must be obeyed:
  - Summing the elementary steps in the reaction mechanism must give the overall balanced equation for the reaction.
  - The elementary steps must be reasonable. They should generally involve one reactant particle (unimolecular) or two (bimolecular).
  - The reaction mechanism must agree with the experimentally determined rate law.
- For example, consider the reaction between nitrogen dioxide and fluorine is another example of such a reaction:



- The experimental rate law is first order in  $\text{NO}_2$  and in  $\text{F}_2$ ,  
Rate =  $k[\text{NO}_2][\text{F}_2]$

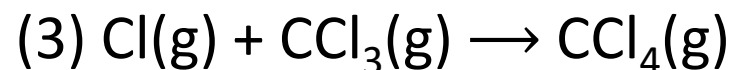
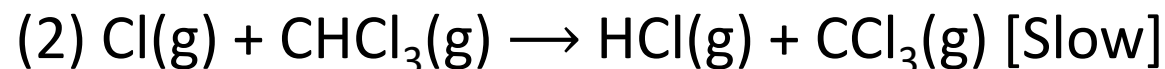
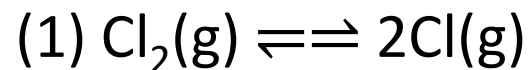
- The proposed mechanism is
- (1)  $\text{NO}_2(\text{g}) + \text{F}_2(\text{g}) \longrightarrow \text{NO}_2\text{F}(\text{g}) + \text{F}(\text{g})$  [slow]
- (2)  $\text{NO}_2(\text{g}) + \text{F}(\text{g}) \longrightarrow \text{NO}_2\text{F}(\text{g})$  [fast]
- Is the mechanism a plausible one or not?

## SOLUTION

- The slow step is rate determining, therefore,
- $\text{Rate} = k_1[\text{NO}_2][\text{F}_2] = k[\text{NO}_2][\text{F}_2]$ . This is in agreement with the experimentally determined rate law
- Summing the two elementary steps above also gives the overall reaction.
  - Note that elemental F is produced in the step 1 and consumed in step 2 – reaction intermediate – and did not feature in the rate law
- The two elementary steps involved 2 molecules in each step, so each step is bimolecular.
- Hence the three criteria for a plausible mechanism is obeyed by the proposed mechanism

- Example 2

- The following elementary steps are proposed for a reaction mechanism:



- If the observed rate law is

$$\text{Rate} = k[\text{Cl}_2]^{1/2}[\text{CHCl}_3]$$

- Show that the mechanism is consistent with this rate law

- SOLUTION

- The rate law from the slow step is

$$\text{Rate} = k_2[\text{Cl}][\text{CHCl}_3]$$

From the elementary steps in the mechanism, Cl and CCl<sub>3</sub> are INTERMEDIATES and so should not feature in the rate law

Step 1 is an equilibrium step such that:

$$K_{eq} = \frac{k_1}{k_{-1}} = \frac{[Cl]^2}{[Cl_2]}$$

$$\Rightarrow [Cl]^2 = \frac{k_1 [Cl_2]}{k_{-1}}$$

$$\Rightarrow [Cl] = \left( \frac{k_1 [Cl_2]}{k_{-1}} \right)^{1/2}$$

- Substitute for [Cl] in the rate law to obtain

- $Rate = k_2 [Cl] [CHCl_3]$

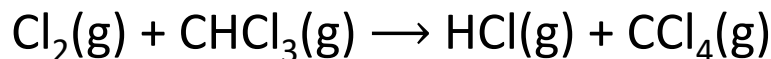
$$Rate = k_2 \left( \frac{k_1 [Cl_2]}{k_{-1}} \right)^{1/2} [CHCl_3] = k_2 \left( \frac{k_1}{k_{-1}} \right)^{1/2} [Cl_2]^{1/2} [CHCl_3]$$

$$= k [Cl_2]^{1/2} [CHCl_3]$$

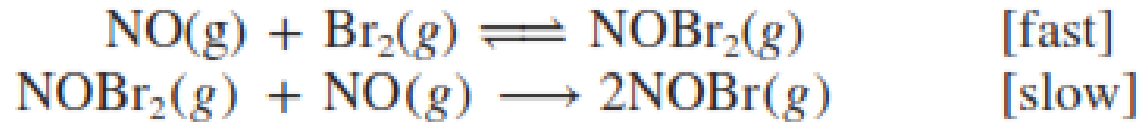
where  $k = k_2 \left( \frac{k_1}{k_{-1}} \right)^{1/2}$

and  $k_1$ ,  $k_{-1}$  are the rate constant for the forward and reverse reactions in step 1

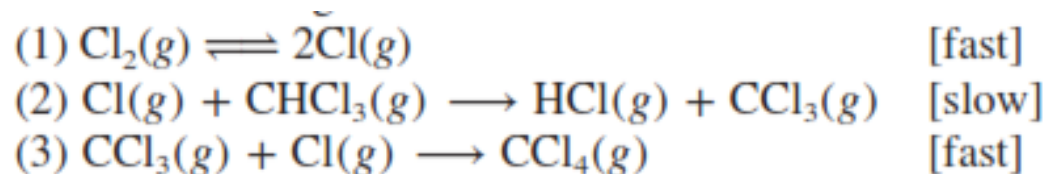
- The above is in agreement with the observed rate law. Also, the sum of the elementary steps is



- In a study of nitrosyl halides, a chemist proposes the following mechanism for the synthesis of nitrosyl bromide:



- If the rate law is  $\text{rate} = k[\text{NO}]^2[\text{Br}_2]$ , is the proposed mechanism valid? If so, show that it satisfies the three criteria for validity.
- Experiment shows that the rate of formation of carbon tetrachloride from chloroform,  $\text{CHCl}_3(g) + \text{Cl}_2(g) \rightarrow \text{CCl}_4(g) + \text{HCl}(g)$  is first order in  $\text{CHCl}_3$ ,  $1/2$  order in  $\text{Cl}_2$ , and  $3/2$  order overall. Show that the following mechanism is consistent with the rate law:



# 6. CHEMICAL THERMODYNAMICS AND ENERGETICS

## 1. THERMODYNAMICS

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

## 2. THERMODYNAMICS TERMINOLOGY

### 2.1 System

The part of the Universe under observation is called system.

### 2.2 Surrounding

The part of the Universe not under observation is called Surrounding.

**System + Surrounding = Universe**

### 2.3 Types of system

**2.3.1 Open System :** A system in which both flow of mass and heat is possible.

**2.3.2 Closed System :** A system in which flow of heat is possible but flow of mass is not possible.

**2.3.3 Isolated System :** A system in which neither heat nor mass can flow in or out.

## 3. STATE OF A SYSTEM

The state variables (P, V, T, n) describes the condition of a system. On changing any one or more of these variables the state of the system changes.

## 4. PROPERTIES OF SYSTEM

All the properties of a system can be categorized into one of the following two types :

### 4.1 Extensive Properties

Such properties of a system which depends on the mass or the total number of particles in the system are categorized as Extensive Properties. eg. Total Energy, volume.

### 4.2 Intensive Properties

Such properties of a system which depends on concentration and does not depend on the mass or the total number of particles in the system are categorized as Intensive properties. eg. Pressure, Density, Reractive Index.

## 5. STATE AND PATH FUNCTIONS

Such thermodynamic functions which depend only on the initial and final states of the system and not on the path followed are called **state functions** eg. Internal energy, Enthalpy and the functions which depend on the path followed while changing from one state to the other are called **path functions**. eg. work heat.

## 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.

### 6.1 Mechanical Equilibrium

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

### 6.2 Thermal Equilibrium

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

### 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.

## 7. INTERNAL ENERGY

It is the sum total of the components of energy of the system due to the internal factors. It is denoted by U (sometimes by E). Since the system under observation is an ideal gas thus the internal energy of the system is dependent only on the kinetic energy of the gas and therefore is only a function of temperature.  $U \propto T$ . Since internal energy depends only on temperature thus, it is a **state function**.



## 8. MODES OF ENERGY TRANSFER

There are two methods to alter the internal energy of a system viz.

**Heat and work.**

### 8.1 Heat

Heat is the energy transferred due to temperature difference between the system and the surrounding. On heating, the kinetic energy of the molecules increases and therefore the internal energy increases.

### 8.2 Work

Work is the energy spent to overcome an external force. When the system does work against an external pressure (expansion) it tends to reduce the internal energy and on the other hand when the system contracts due to the external pressure it tends to increase the internal energy.

## 9. FIRST LAW OF THERMODYNAMICS

The first law of Thermodynamics states that Energy can neither be created nor destroyed.

$$\Delta U = q + w$$

**Conventions :** In the above system if work is done by the system then  $w$  is negative and if work is done on the system then  $w$  is positive. Also, if heat flows into the system then  $q$  is positive and if heat flows out of the system then  $q$  is negative.

## 10. 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.

### 10.1 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.

## 11. EXPANSION WORK

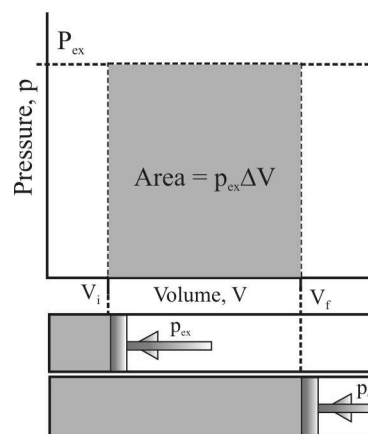
It is the work done due to the volume changes of the gas. The

mathematical expression for the expansion work is  $w = -\int P_{\text{ex}} dV$ .

Always remember, be it expansion or compression we always take the external pressure as the driving force. For a reversible process,

$$P_{\text{ex}} \approx P_{\text{GAS}} \text{ and } w = -\int P_{\text{GAS}} dV.$$

If we draw a process curve between  $P$  and  $V$  then the work done is represented by the area covered under the  $P$ - $V$  graph as shown in Fig.



### NOTE

**Sign of  $w$  :** If the volume of the system is increasing then the sign of  $w$  is **-ve** and if volume is decreasing  **$w$  is +ve**

**Sign of  $\Delta U$  :** If the temperature of the system is decreasing or the product pressure and volume ( $PV$ ) is reducing then the sign of  $\Delta U$  is **-ve** else, the sign of  **$\Delta U$  is +ve.**

**Sign of  $q$  :** The sign of  $q$  needs to be determined using the first law of thermodynamics.

## 12. 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,  $\Delta U_{\text{net}} = 0$  and  $q_{\text{net}} = -w_{\text{net}}$ .

### 13. ENTHALPY (H)

Enthalpy is another thermodynamic function (like internal energy, work and heat) which we study in various thermodynamic processes. It is also a state function like internal energy. It is defined as the sum of the energy stored in the system and the energy used in doing work. Mathematically,  $H = U + PV$ . At constant pressure  $\Delta H = q_p$  and at constant volume  $\Delta U = q_v$ .

### 14. HEAT CAPACITY (C)

The heat capacity of the system is the amount of heat needed to raise the temperature of the system by  $1^\circ\text{C}$  or  $1\text{K}$ .

$$C = q/\Delta T.$$

#### 14.1 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  $1^\circ\text{C}$  or  $\text{K}$ .

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

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 the system by  $1^\circ\text{C}$  at constant pressure.

$$C_p = q_p/n\Delta T.$$

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  $1^\circ\text{C}$  at constant volume.

$$C_v = q_v/n\Delta T.$$

Thus, we can say that :  $\Delta H = nC_p\Delta T$  and  $\Delta U = nC_v\Delta T$  and  $C_p = C_v + R$ .

Type of Gas	$C_v$	$C_p$	$\gamma = C_p/C_v$
monatomic	$3R/2$	$5R/2$	$5/3 = 1.67$
diatomic	$5R/2$	$7R/2$	$7/5 = 1.4$
Non-linear Polyatomic	$3R$	$4R$	$4/3 = 1.34$

### 15. TYPES OF THERMODYNAMIC PROCESSES

There are four important types of processes to be studied in this chapter. The basic meanings and difference of these four processes are :

#### 15.1 Isothermal Process

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

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

$$w = -2.303 nRT \log_{10}(V_2/V_1) = -2.303 nRT \log_{10}(P_1/P_2)$$

$$q = +2.303 nRT \log_{10}(V_2/V_1) = +2.303 nRT \log_{10}(P_1/P_2)$$

#### 15.2 Adiabatic Process

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

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

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

$$\Delta U = nC_v\Delta T = (P_2V_2 - P_1V_1)/(\gamma-1) = (nR\Delta T)/(\gamma-1)$$

$$\Delta H = nC_p\Delta T$$

#### 15.3 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

$$w = 0$$

$$\Delta U = nC_v\Delta T = q_v \quad \Delta H = nC_p\Delta T$$

#### 15.4 Isobaric Process

These are the processes in which the pressure remains constant.

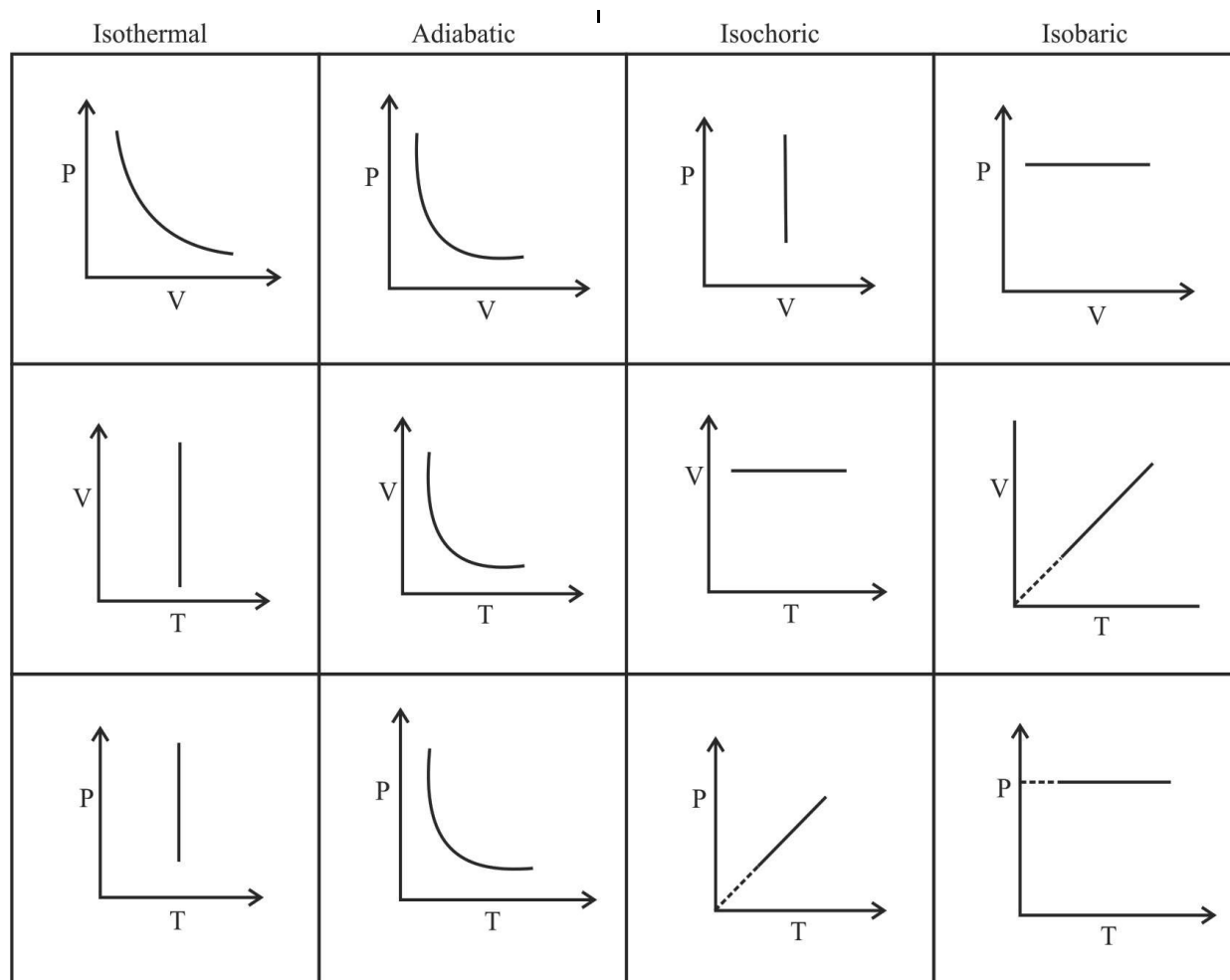
$$w = -P\Delta V = -nR\Delta T$$

$$\Delta U = nC_v\Delta T$$

$$\Delta H = nC_p\Delta T$$

#### 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.

**NOTE**

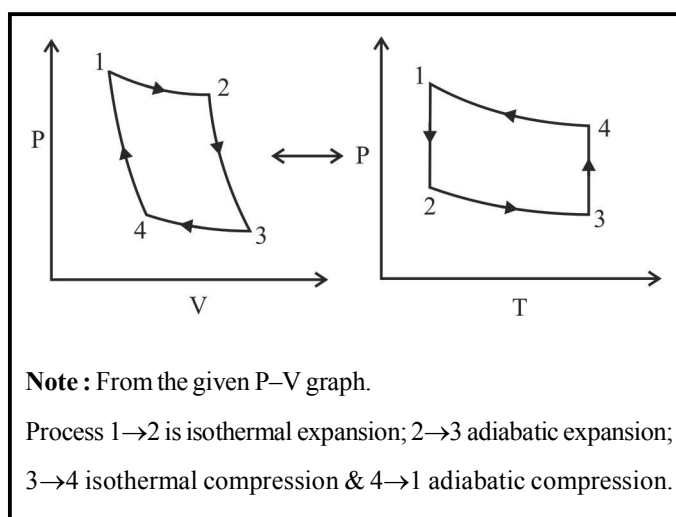
Although the graph of isothermal and adiabatic processes are similar in nature it should be noted that the P-V graph of an adiabatic process is steeper than that of an isothermal process.

**16. 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.



## 17. IRREVERSIBLE PROCESS

For an irreversible process the work done is given by

$W = - \int P_{\text{EXT}} dV$ . We cannot take the external pressure to be equal to the pressure of the gas in these processes.

## 18. FREE EXPANSION

If the external pressure of the gas is zero that is the gas is expanding against vacuum then the work done is always zero, this is called the case of free expansion. In this process the gas does no work as there is no effort put in expansion process. If no heat is supplied to the gas then there is no change in temperature too. That is why such a process is both Isothermal and Adiabatic.

## 19. 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 :

$$C = C_v - R/(n - 1).$$

## 20. NEED FOR SECOND LAW

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. A spontaneous process is one which happens on its own. Example, heat always flows spontaneously from higher temperature to lower temperature : Nothing in the first law mentions that the opposite process cannot happen. According to first law any process where energy remains conserved is feasible. But we need some other basis for feasibility of a process. This is where the second law is important.

## 21. TYPES OF PROCESSES

### 21.1 Spontaneous processes

Spontaneous processes have a natural tendency to take place and no external work is needed to carry out these processes. All natural processes are spontaneous.

### 21.2 Non-Spontaneous processes

They are driven by external work and cannot take place naturally.

## 22. CONCEPT OF ENTROPY

- ☀ Matter has a natural tendency to get disordered or randomised
- ☀ Energy has a tendency to become disordered or dispersed.

It was concluded that any such process in which the total randomness of the universe (system + surrounding) increases is a spontaneous process. **Entropy is a measure of randomness or disorder.** It is a state function represented by  $S$ . We can safely say that in a spontaneous process there is a tendency for increase in entropy. Hence the statement of second law :

**The entropy of an isolated system/Universe tends to increase OR In a spontaneous process the entropy of the Universe increases.**

$$\Delta S = q_{\text{rev}}/T.$$

$$\Delta S_{\text{TOTAL}} = \Delta S_{\text{SYSTEM}} + \Delta S_{\text{SURROUNDING}} > 0$$

(for a spontaneous change)

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

### 22.1 Entropy changes in a Thermodynamic Process

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

$\Rightarrow \Delta S = nC_v \ln (T_2/T_1) + nR \ln (V_2/V_1)$ . This expression can be simplified for the four processes studied earlier as :

**Isothermal process :  $\Delta S = nR \ln (V_2/V_1)$**

**Isochoric process :  $\Delta S = nC_v \ln (T_2/T_1)$**

**For isobaric process :  $\Delta S = nC_p \ln (T_2/T_1)$**

**Adiabatic process :  $\Delta S = 0$  ( $q_{\text{rev}} = 0$ )**

### 22.2 Important points to Remember

1. Entropy of a system remains constant in a reversible adiabatic process. Therefore, it is also known as “**isentropic 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.

$$\Delta S_{\text{SYSTEM}} = \Delta S_{\text{SURROUNDINGS}} = \Delta S_{\text{TOTAL}} = 0$$

- 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.
- 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.

### 23. GIBB'S FREE ENERGY

Gibb's Free energy function gives us a very convenient parameter to judge the spontaneity of a process from system's perspective. At a constant temperature and pressure,  $\Delta G = -T\Delta S_{\text{TOTAL}}$  and for a process to be spontaneous,  $\Delta G < 0$ . The change in Gibb's free energy can also be represented in terms of the system parameters as :

$$\Delta G_{\text{SYS}} = \Delta H - T\Delta S_{\text{SYS}} \text{ at a constant temperature.}$$

### 24. THERMOCHEMICAL EQUATION

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.

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

#### 24.1 Endothermic Reactions

Are those chemical reactions which absorb energy.

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

#### 24.2 Exothermic Reactions

Are those chemical reactions which release energy.

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

For a chemical reaction,  $\Delta H_{\text{REACTION}} = H_{\text{PRODUCTS}} - H_{\text{REACTANTS}}$

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

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

### 25. ENTHALPY 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 :

#### 25.1 Enthalpy of Formation $\Delta H_f^0$

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.

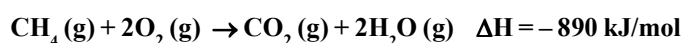
$$\Delta H_f^0 (\text{O}_2, \text{g}) = 0 \quad \Delta H_f^0 (\text{S, Rhombic}) = 0$$

$$\Delta H_f^0 (\text{C, graphite}) = 0 \quad \Delta H_f^0 (\text{P, white}) = 0$$

$$\Delta H_f^0 (\text{Br}_2, \text{l}) = 0 \quad \Delta H_f^0 (\text{H}^+, \text{aq}) = 0$$

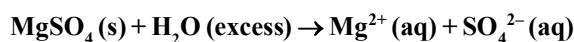
#### 25.2 Enthalpy of Combustion

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



#### 25.3 Enthalpy of Solution

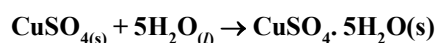
It is the heat released or absorbed when 1 mole of a compound is dissolved in excess of a solvent (water).



$$\Delta H_{\text{Sol}}^0 = -91.211 \text{ kJ/mol}$$

#### 25.4 Enthalpy of Hydration

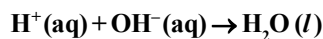
It is the energy released or absorbed when 1 mole of anhydrous or partially hydrated salt undergoes hydration by the addition of water of crystallisation. e.g.



$$\Delta H_{\text{HYD}} = -78.9 \text{ kJ/mol}$$

#### 25.5 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.



$$\Delta H_{\text{R}} = -57.3 \text{ kJ/mol}$$

### 26. HESS LAW OF CONSTANT HEAT SUMMATION

Since enthalpy is a state function thus for a reaction which takes place in steps the net change in enthalpy can be calculated by adding the enthalpy changes of each step. This is called the **Hess Law**.

### 27. 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.

### 28. 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. eg. Bond dissociation enthalpy of  $H_2$  is 436 kJ/mol

### 29. 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.

### 30. RESONANCE ENERGY

Many compounds exhibit resonance. Due to resonance they exist in a structure which is different from the expected one and more stable.

$$\text{Resonance energy} = \Delta H_f^0(\text{actual}) - \Delta H_f^0(\text{calculated})$$

## 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,  $q = +15 \text{ kJ}$   
 $w = -5 \text{ kJ}$

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

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

(ii) Here,  $w = +5 \text{ kJ}$   
 $q = -5 \text{ kJ}$

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

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

### Example : 2

Calculate  $w$ ,  $q$  and  $\Delta U$  when 0.75 mol of an ideal gas expands isothermally and reversibly at  $27^\circ\text{C}$  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  $n = 0.75 \text{ mol}$ ,  $V_1 = 15 \text{ L}$ ,  
 $V_2 = 25 \text{ L}$ ,  $T = 27 + 273 = 300 \text{ K}$  and  $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  
 we get

$$w = -2.303 \times 0.75 \times 8.314 \times 300 \log \frac{25}{15} = -955.5 \text{ J}$$

(–ve sign represents work of expansion)

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

$\therefore \Delta U = q + w$  gives  $q = -w = +\mathbf{955.5 \text{ J}}$ .

### Example : 3

Carbon monoxide is allowed to expand isothermally and reversibly from  $10 \text{ m}^3$  to  $20 \text{ m}^3$  at  $300 \text{ K}$  and work obtained is  $4.754 \text{ kJ}$ . 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  $n = \mathbf{2.75 \text{ moles}}$ .

### Example : 4

A 5-litre cylinder contained 10 moles of oxygen gas at  $27^\circ\text{C}$ . 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.**  $V_{\text{initial}} = 5 \text{ L}$ ,  $T = 27^\circ\text{C} = 27 + 273 \text{ K} = 300 \text{ K}$

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

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

$$w_{\text{exp}} = -P\Delta V = -1 \times 241.3 \text{ L atm} = -241.3 \times 101.3 \text{ J}$$

$$= \mathbf{-24443.7 \text{ J}}$$

### Example : 5

Two moles of an ideal gas initially at  $27^\circ\text{C}$  and one atmospheric pressure are compressed isothermally and reversibly till the final pressure of the gas is 10 atm. Calculate  $q$ ,  $w$  and  $\Delta U$  for the process.

**Sol.** Here,  $n = 2 \text{ moles}$ ,  $T = 27^\circ\text{C} = 300 \text{ K}$ ,  $P_1 = 1 \text{ atm}$ ,  $P_2 = 10 \text{ atm}$

$$w = -2.303 nRT \log \frac{P_1}{P_2} = -2.303 \times 2 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times$$

$$300 \text{ K} \times \log \frac{1}{10} = \mathbf{11488 \text{ J}}$$

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

Further,  $\Delta U = q + w \therefore q = -w = \mathbf{-11488 \text{ J}}$ .

### Example : 6

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

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

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

$$W = 103.991 \text{ cal}$$

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

$$\therefore q = \Delta U - W \quad \therefore q = -W = -103.991 \text{ cal}$$

**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.

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

$$\therefore W = -1 \times 4 \text{ litre-atm} = -4 \times 1.01325 \times 10^2 \text{ J} \\ = 405.3 \text{ J}$$

Now from first law of thermodynamics

$$q = \Delta U - W$$

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

**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  $w$ ,  $q$ ,  $\Delta U$  and  $\Delta H$  for the process. What will be the difference if the same process is carried out irreversibly? What are the values of  $w$ ,  $q$ ,  $\Delta U$ ,  $\Delta H$  for the irreversible process?

**Sol.** For an isothermal irreversible expansion :

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

$$w = -P_{\text{EXT}}(V_2 - V_1)$$

$V_2$  and  $V_1$  can be calculated from ideal gas equation.

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

$$V_2 = nRT/P_2 = 124.7 \text{ m}^3$$

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

$$= -9980 \text{ J}$$

$$q = +9980 \text{ J}$$

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

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

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

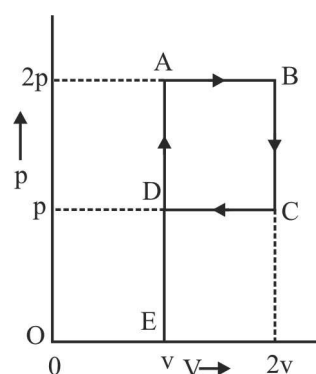
$$= -5 \times 8.314 \times 300 \times \ln 5$$

$$= -20071.3 \text{ J}$$

$$q = +20071.3 \text{ J}$$

**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  $\Delta E = 0$

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

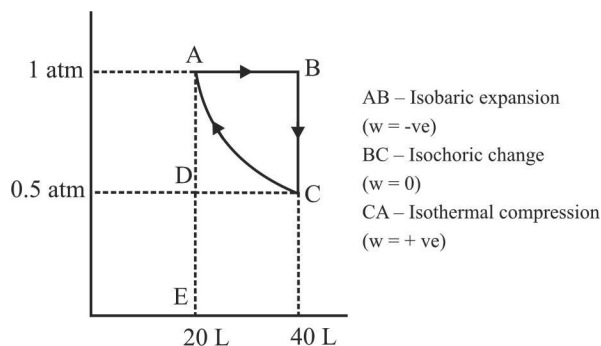
where  $q$  is the heat absorbed in the cyclic process.

### Example : 10

Two mole of a perfect gas undergo the following processes:

- a reversible isobaric expansion from (1.0 atm, 20.0L) to (1.0 atm, 40.0L).
  - a reversible isochoric change of state from (1.0 atm, 40.0L) to (0.5 atm, 40.0L)
  - a reversible isothermal compression from (0.5 atm, 40.0L) to (1.0 atm, 20.0L).
- sketch with labels each of the processes on the same P-V diagram.
  - Calculate the total work ( $w$ ) and the total heat change ( $q$ ) involved in the above processes.
  - What will be the value of  $\Delta U$ ,  $\Delta H$  and  $\Delta S$  for the overall process ?

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



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

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

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

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

$$= -2026.5 \text{ J}$$

$$W_{BC} = 0 \text{ (Isochoric)}$$

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

$n = 2 \text{ mol.}$

At point C :  $P = 0.5 \text{ atm, } V = 40 \text{ L}$

$$PV = nRT$$

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

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

$$= 1404.07 \text{ J}$$

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

$$= -622.43 \text{ J}$$

For cyclic process :  $\Delta U = 0$

$$\Rightarrow q = -w$$

$$q = +622.43 \text{ J}$$

### Example : 11

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

- 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.
- 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 ( $\Delta U$ ) in each case if the process were carried out adiabatically.

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

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

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

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

$$P = 1 \text{ atm} \therefore w = -P\Delta V$$

$$= -1 \times 4 \text{ litre atm} = -4 \text{ litres atm}$$

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

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<sup>3</sup> of an unknown gas at S.T.P. required 52.25 J of heat to raise its temperature by 10°C at constant volume. Calculate  $C_v$ ,  $C_p$  and  $\gamma$  of the gas

**Sol.** The 22.4 dm<sup>3</sup> 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 10° rise, 0.25 mol of the gas at constant volume require heat = 52.25 J

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

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

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

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

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

**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

- the entropy change of the system (copper block)
- the entropy change in the surroundings
- the total entropy change in the universe due to this process

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

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

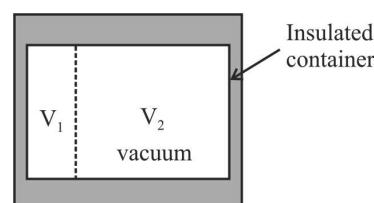
$$(i) \Delta S_{\text{system}} = \frac{q_{\text{system}}}{T_{\text{system}}} = \frac{-340 \text{ J}}{403 \text{ K}} = -0.84 \text{ J K}^{-1}$$

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

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

**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 partition 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  $T$ .

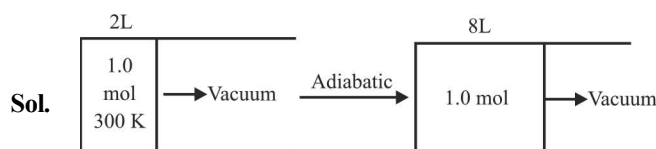
$$\Delta S_{\text{system}} = nR \ln \frac{V_1 + V_2}{V_1} > 0 \quad \because V_1 + V_2 > V_1$$

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

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

**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  $W$ ,  $\Delta E$ ,  $\Delta H$ ,  $\Delta S_{\text{univ}}$  and  $\Delta G$ .



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

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

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

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

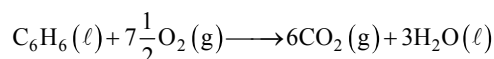
$$\Rightarrow \Delta S_{\text{univ}} = 11.52 \text{ J K}^{-1}$$

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

**Example : 16**

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

**Sol.** The reaction is:



In this reaction,  $\text{O}_2$  is the only gaseous reactant and  $\text{CO}_2$  is the only gaseous product.

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

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

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

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

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

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

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

**Example : 17**

Calculate the amount of heat evolved when

- (i)  $500 \text{ cm}^3$  of  $0.1 \text{ M}$  hydrochloric acid is mixed with  $200 \text{ cm}^3$  of  $0.2 \text{ M}$  sodium hydroxide solution  
 (ii)  $200 \text{ cm}^3$  of  $0.2 \text{ M}$  sulphuric acid is mixed with  $400 \text{ cm}^3$  of  $0.5 \text{ M}$  potassium hydroxide solution.

Assuming that the specific heat of water is  $4.18 \text{ J K}^{-1} \text{ g}^{-1}$  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  $\text{HCl} = \frac{0.1}{1000} \times 500 = 0.05 = 0.05 \text{ mole of H}^+$  ions

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

mole of  $\text{NaOH} = 0.04 \text{ mole} = 0.04 \text{ mole of OH}^-$  ions

Thus,  $0.04 \text{ mole of H}^+$  ions will combine with  $0.04 \text{ mole of OH}^-$  ions to form  $0.04 \text{ mole of H}_2\text{O}$  and  $0.01 \text{ mole of H}^+$  ions will remain unreacted.

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

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

(ii)  $200 \text{ cm}^3$  of  $0.2 \text{ M H}_2\text{SO}_4 = \frac{0.2}{1000} \times 200 \text{ mole of H}_2\text{SO}_4$   
 $= 0.04 \text{ mole of H}_2\text{SO}_4 = 0.08 \text{ mole of H}^+$  ions

$$400 \text{ cm}^3 \text{ of } 0.5 \text{ M KOH} = \frac{0.5}{1000} \times 400 \text{ mole of KOH} =$$

$0.2 \text{ mole of KOH} = 0.2 \text{ mole of OH}^-$  ions

Thus,  $0.08 \text{ mole of H}^+$  ions will neutralize  $0.08 \text{ mole of OH}^-$  ions. (out of  $0.2 \text{ mole of OH}^-$  ions) to form  $0.08 \text{ mole of H}_2\text{O}$ .

Hence, heat evolved =  $57.1 \times 0.08 = 4.568 \text{ kJ}$

In case (i), heat produced =  $2.284 \text{ kJ} = 2284 \text{ J}$

Total volume of the solution =  $500 + 200 = 700 \text{ mL}$

Assuming density of solution =  $1 \text{ g/mL}$

So mass of solution =  $700 \text{ g}$

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

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

In case (ii), heat produced =  $4.568 \text{ kJ} = 4568 \text{ J}$

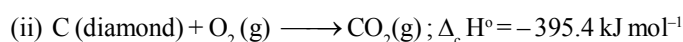
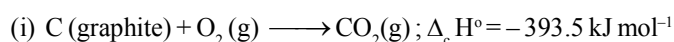
Total mass of the solution =  $200 + 400 = 600 \text{ g}$

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

**Example : 18**

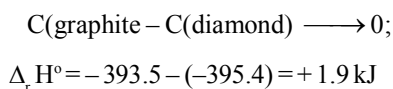
Calculate the enthalpy change accompanying the transformation of  $\text{C}$  (graphite) to  $\text{C}$  (diamond). Given that the enthalpies of combustion of graphite and diamond are  $393.5$  and  $395.4 \text{ kJ mol}^{-1}$  respectively.

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



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

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

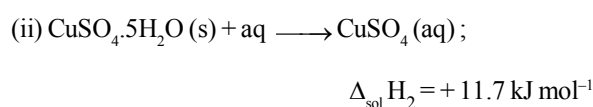
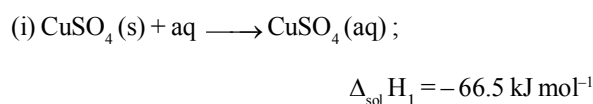


or  $\text{C}(\text{graphite}) \longrightarrow (\text{diamond}); \Delta_{\text{trans}} H = +1.9 \text{ kJ}$

**Example : 19**

Calculate the enthalpy of hydration of anhydrous copper sulphate ( $\text{CuSO}_4$ ) into hydrated copper sulphate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ). Given that the enthalpies of solutions of anhydrous copper sulphate and hydrated copper sulphate are  $-66.5$  and  $+11.7 \text{ kJ mol}^{-1}$  respectively

**Sol.** We are given



We aim at  $\text{CuSO}_4(\text{s}) + 5\text{H}_2\text{O}(\text{l}) \longrightarrow \text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{s});$   
 $\Delta_{\text{hyd}} H = ?$

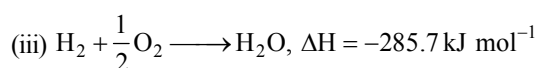
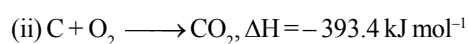
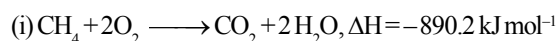
$$\Delta H = \Delta H_1 - \Delta H_2 = -66.5 - (+11.7) = -78.2 \text{ kJ/mol}$$

**Example : 20**

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

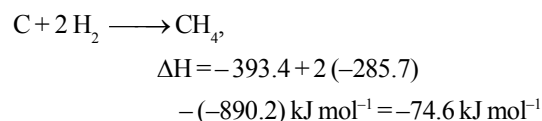
**Sol.** Remember : Enthalpy of combustion is always negative.

We are given :



We aim at :  $\text{C} + 2\text{H}_2 \longrightarrow \text{CH}_4, \Delta H = ?$

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 :

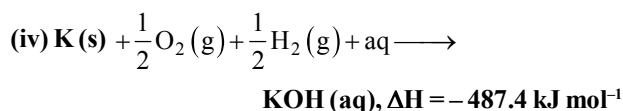
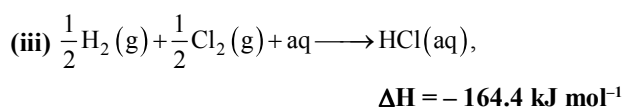
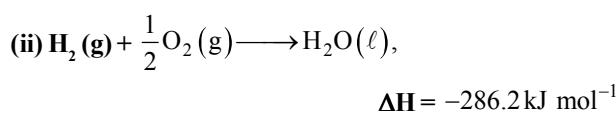
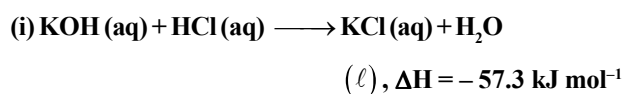


Hence, the heat of formation of methane is :

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

**Example : 21**

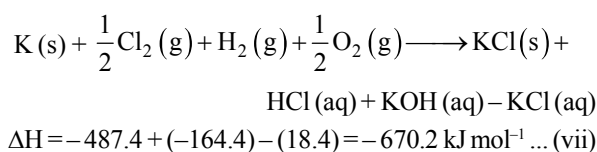
Calculate the heat of formation of KCl from the following data :



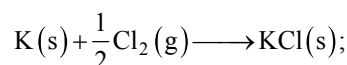
**Sol.** We aim at :  $\text{K}(\text{s}) + \frac{1}{2}\text{Cl}_2(\text{g}) \longrightarrow \text{KCl}(\text{s}), \Delta_f H = ?$

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

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



**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



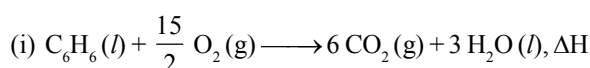
$$\Delta_f H = -670.2 + 57.3 - (-286.2) = -441.3 \text{ kJ}$$

**Example : 22**

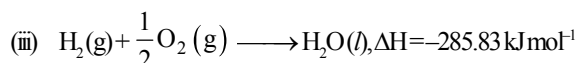
The combustion of 1 mole of benzene takes place at 298 K and 1 atm. After combustion,  $\text{CO}_2(\text{g})$  and  $\text{H}_2\text{O}(\text{l})$  are produced and 3267.0 kJ of heat is liberated. Calculate the standard enthalpy of formation,  $\Delta_f H^\circ$  of benzene. Standard enthalpies of formation of  $\text{CO}_2(\text{g})$  and  $\text{H}_2\text{O}(\text{l})$  are  $-393.5 \text{ kJ mol}^{-1}$  and  $-285.83 \text{ kJ mol}^{-1}$  respectively.

**Sol.** Aim :  $6 \text{ C}(\text{s}) + 3 \text{ H}_2(\text{g}) \longrightarrow \text{C}_6\text{H}_6(\ell), \Delta H = ?$

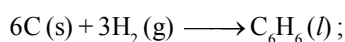
Given :



$$= -3267.0 \text{ kJ mol}^{-1}$$



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  $6 \times \text{Eqn. (ii)} + 3 \times \text{Eqn. (iii)} - \text{Eqn. (i)}$ , we get



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

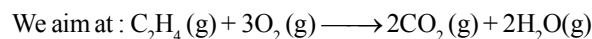
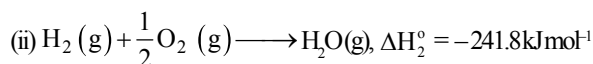
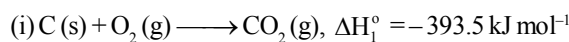
$$= -2361 - 857.49 + 3267.0 = 48.51 \text{ kJ mol}^{-1}$$

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  $\text{CO}_2(\text{gas})$  and  $\text{H}_2\text{O}(\text{gas})$  at 298 K and 1 atmospheric pressure. The enthalpies of formation of  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and  $\text{C}_2\text{H}_4$  are  $-393.5$ ,  $-241.8$ ,  $+52.3 \text{ kJ per mole}$  respectively.

**Sol.** We are given :

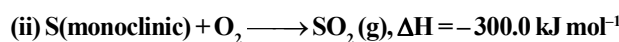
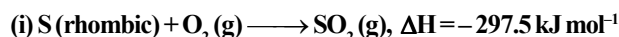


$$\Delta H = -\Delta H_3 + 2\Delta H_1 + 2\Delta H_2$$

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

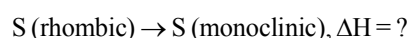
**Example : 24**

Given the following thermochemical equations:

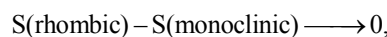


Calculate  $\Delta H$  for the transformation of one gram atom of rhombic sulphur into monoclinic sulphur.

**Sol.** We aim at



Equation (i)  $\rightarrow$  Equation (ii) gives



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

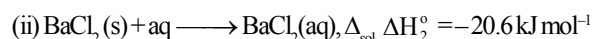


Thus, for the transformation of one gram atom of rhombic sulphur into monoclinic sulphur,  $2.5 \text{ kJ mol}^{-1}$  of heat is absorbed.

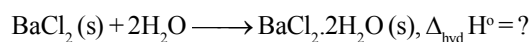
**Example : 25**

Enthalpy of solution ( $\Delta H$ ) for  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{BaCl}_2$  are 8.8 and  $-20.6 \text{ kJ mol}^{-1}$  respectively. Calculate the heat of hydration of  $\text{BaCl}_2$  to  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ .

**Sol.** We are given



We aim at

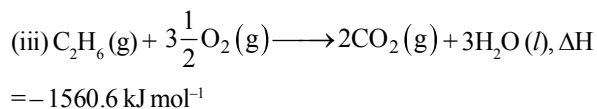
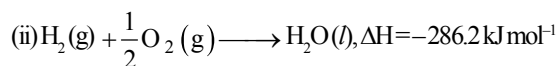


$$\Delta H = \Delta H_2 - \Delta H_1 = -29.4 \text{ kJ mol}^{-1}$$

**Example : 26**

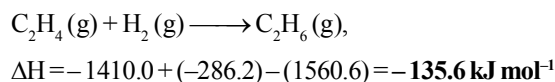
Calculate the enthalpy of hydrogenation of ethylene, given that the enthalpy of combustion of ethylene, hydrogen and ethane are  $-1410.0$ ,  $-286.2$  and  $-1560.6 \text{ kJ mol}^{-1}$  respectively at 298 K.

**Sol.** We are given (i)  $\text{C}_2\text{H}_4(\text{g}) + 3 \text{ O}_2(\text{g}) \longrightarrow 2 \text{ CO}_2(\text{g}) + 2 \text{ H}_2\text{O}(\text{l}), \Delta H = -1410 \text{ kJ mol}^{-1}$

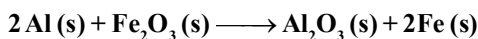


We aim at:  $\text{C}_2\text{H}_4 + \text{H}_2(\text{g}) \longrightarrow \text{C}_2\text{H}_6(\text{g}), \Delta H = ?$

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

**Example : 27**

The thermite reaction used for welding of metals involves the reaction



What is  $\Delta H^\circ$  at  $25^\circ\text{C}$  for this reaction? Given that the standard heats of formation of  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  are  $-1675.7 \text{ kJ}$  and  $-828.4 \text{ kJ mol}^{-1}$  respectively.

**Sol.** We aim at  $2 \text{Al}(\text{s}) + \text{Fe}_2\text{O}_3(\text{s}) \longrightarrow \text{Al}_2\text{O}_3(\text{s}) + 2\text{Fe}(\text{s})$   
(s),  $\Delta_r H^\circ = ?$

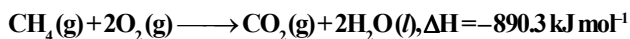
$$\Delta_r H = \text{Sum of } \Delta_f H^\circ \text{ of products} - \text{Sum of } \Delta_f H^\circ \text{ of reactants}$$

$$= [\Delta_f H^\circ(\text{Al}_2\text{O}_3) + 2 \times \Delta_f H^\circ(\text{Fe})] - [2 \times \Delta_f H^\circ(\text{Al}) + \Delta_f H^\circ(\text{Fe}_2\text{O}_3)]$$

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

**Example : 28**

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



- (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  $\text{CH}_4$ , i.e.,  $12 + 4 = 16 \text{ g}$  of  $\text{CH}_4$

$\therefore$  445.15 kJ of heat is produced from **8 g of  $\text{CH}_4$**

(b) From the given equation, when 890.3 kJ of heat is evolved,  $\text{CO}_2$  formed = 1 mole = 44 g

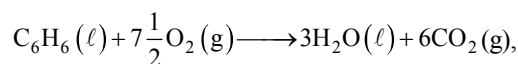
$\therefore$  When 445.15 kJ of heat is evolved,  $\text{CO}_2$  formed = **22 g**

(c) From the equation,  $\text{O}_2$  used in the production of 890.3 kJ of heat = 2 moles =  $2 \times 22.4$  litres at STP  
= 44.8 litres at STP

Hence,  $\text{O}_2$  used in the production of 445.15 kJ of heat = **22.4 litres at STP.**

**Example : 29**

From the thermochemical equation,



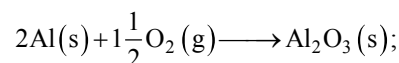
$$\Delta_c H = -3264.64 \text{ kJ mol}^{-1},$$

calculate the energy evolved when 39 g of  $\text{C}_6\text{H}_6$  are burnt in an open container.

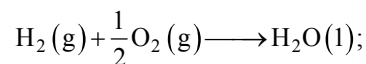
**Sol.** From the given equation,  
When 1 mole of  $\text{C}_6\text{H}_6$  (78 g of  $\text{C}_6\text{H}_6$ ) is burnt, heat evolved = 3264.64 kJ  
 $\therefore$  When 39 g of  $\text{C}_6\text{H}_6$  is burnt, heat evolved =  $\frac{3264.64}{78} \times 39 = 1632.32 \text{ kJ}$

**Example : 30**

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

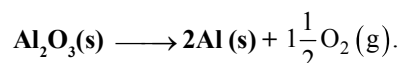


$$\Delta H = -1667.8 \text{ kJ mol}^{-1}$$



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

- (a) If equal masses of aluminium and hydrogen are used, which is a better rocket fuel?
- (b) Determine  $\Delta H$  for the reaction :



**Sol.** (a) From the first given equation,

2 moles of Al (i.e.,  $2 \times 27 \text{ g} = 54 \text{ g}$ ) on combustion give heat = 1667.8 kJ

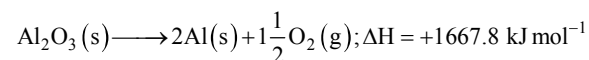
$$\therefore 1 \text{ g of Al on combustion gives heat} = \frac{1667.8}{54} = 30.9 \text{ kJ}$$

From the second given equation, 1 mole of  $\text{H}_2$  (= 2 g) on combustion gives heat = 285.9 kJ

$$\therefore 1 \text{ g of } \text{H}_2 \text{ on combustion gives heat} = \frac{285.9}{2} = 142.95 \text{ kJ}$$

Thus,  **$\text{H}_2$  is a better rocket fuel.**

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



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

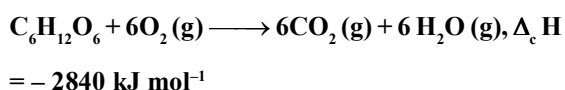
### Example : 31

**When 1 g liquid naphthalene ( $\text{C}_{10}\text{H}_8$ ) solidifies, 149 joules of heat is evolved. Calculate the enthalpy of fusion of naphthalene.**

**Sol.** Molar mass of naphthalene ( $\text{C}_{10}\text{H}_8$ ) =  $128 \text{ g mol}^{-1}$   
 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 =  $149 \times 128 \text{ joules} = 19072 \text{ joules}$   
 Since fusion is reverse of solidification, therefore, heat absorbed for fusion of one mole of naphthalene = 19072 joules.  
 i.e., Enthalpy of fusion ( $\Delta_{\text{fus}} H$ ) = + 19072 joules/mole

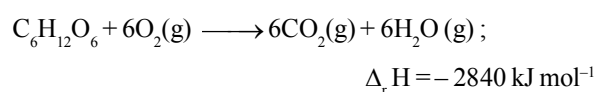
### Example : 32

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

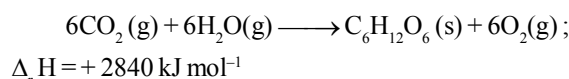


**What is the energy requirement for production of 0.36 g of glucose by the reverse reaction ?**

**Sol.** The given equation is :



Writing the reverse reaction, we have



Thus, for production of 1 mole of  $\text{C}_6\text{H}_{12}\text{O}_6$  (= 72 + 12 + 96 = 180 g), heat required (absorbed) = 2840 kJ.

$$\therefore \text{For production of 0.36 g of glucose, heat absorbed} = \frac{2840}{180} \times 0.36 = 5.68 \text{ kJ}$$

### Example : 33

**Calculate the bond energy of C–H bond, given that the heat of formation of  $\text{CH}_4$ , heat of sublimation of carbon and heat of dissociation of  $\text{H}_2$  are  $-74.8$ ,  $+719.6$  and  $435.4 \text{ kJ mol}^{-1}$  respectively.**

**Sol.** Here, we are given



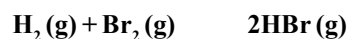
$$\Delta H = e_{\text{sub}(\text{C})} + 2e_{\text{H-H}} - 4e_{\text{C-H}}$$

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

$$e_{\text{C-H}} = 416.3 \text{ kJ/mol}$$

### Example : 34

**Calculate the enthalpy change for the reaction**



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

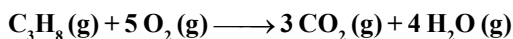
**Sol.**  $\Delta_r H = \Sigma \text{B.E. (Reactants)} - \Sigma \text{B.E. (Products)}$

$$= [\text{B.E. (H}_2) + \text{B.E. (Br}_2)] - 2 \text{B.E. (HBr)} =$$

$$435 + 192 - 2 \times 364 = -101 \text{ kJ}$$

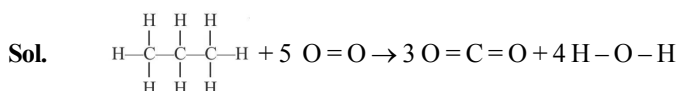
**Example : 35**

Propane has the structure  $\text{H}_3\text{C}-\text{CH}_2-\text{CH}_3$ . Calculate the change in enthalpy for the reaction:



Given that average bond enthalpies are:

C-C	C-H	C=O	O=O	O-H
347	414	741	498	464 kJ mol <sup>-1</sup>



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

**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<sup>-1</sup>).

Sol. Entropy change for ice  $\rightarrow$  water is given by  $\Delta_f S = \frac{\Delta_f H}{T_f}$

Here,  $\Delta_f H = 6025 \text{ J mol}^{-1}$ ,  $T_f = 273 \text{ K}$   $\therefore$

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

**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  $\Delta_{\text{vap}} H = 2.257 \text{ kJ/g}$ )

Sol. For the conversion of water  $\rightarrow$  vapour, the entropy

$$\text{change is given by } \Delta_{\text{vap}} S = \frac{\Delta_{\text{vap}} H}{T_b}$$

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

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

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

**Example : 38**

At 0°C, ice and water are in equilibrium and  $\Delta H = 6.00 \text{ kJ mol}^{-1}$  for the process  $\text{H}_2\text{O}(\text{s}) \rightarrow \text{H}_2\text{O}(\text{l})$ . What will be  $\Delta S$  and  $\Delta G$  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  $\Delta H = 6.0 \text{ kJ mol}^{-1} = 6000 \text{ J mol}^{-1}$  and  $T = 0^\circ\text{C} = 273 \text{ K}$

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

**Example : 39**

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

(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

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

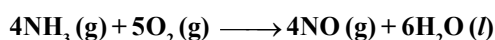
(i) For spontaneity from left to right,  $\Delta G$  should be -ve for the given reaction. This will be so if  $T < 300.3 \text{ K}$

(ii) For reverse reaction to occur,  $\Delta G$  should be +ve forward reaction. This will be so if  $T > 300.3 \text{ K}$ .



**Example : 40**

Calculate the standard free energy change for the reaction,



Given that the standard free energies of formation ( $\Delta_f G^\circ$ ) for  $\text{NH}_3(\text{g})$ ,  $\text{NO}(\text{g})$  and  $\text{H}_2\text{O}(\text{l})$  are  $-16.8$ ,  $+86.7$  and  $-237.2 \text{ kJ mol}^{-1}$  respectively. Predict the feasibility of the above reaction at the standard state.

**Sol.** Here, we are given

$$\Delta_f G^\circ(\text{NH}_3) = -16.8 \text{ kJ mol}^{-1}$$

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

$$\Delta_f G^\circ(\text{H}_2\text{O}) = -237.2 \text{ kJ mol}^{-1}$$

$$\therefore \Delta_r G^\circ = \sum \Delta_f G^\circ(\text{Products}) - \sum \Delta_f G^\circ(\text{Reactants}) =$$

$$[14 \times \Delta_f G^\circ(\text{NO}) + 6 \times \Delta_f G^\circ(\text{H}_2\text{O})] - [4 \times \Delta_f G^\circ(\text{NH}_3)$$

$$+ 5 \times \Delta_f G^\circ(\text{O}_2)]$$

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

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

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 :



Given that the standard entropies of  $\text{Fe}$ ,  $\text{O}_2$  and  $\text{Fe}_2\text{O}_3$  are  $27.3$ ,  $205.0$  and  $87.4 \text{ J K}^{-1} \text{ mol}^{-1}$  respectively. Will the reaction be spontaneous at room temperature ( $25^\circ\text{C}$ )? Justify your answer with appropriate calculations.

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

$$2 S^\circ(\text{Fe}_2\text{O}_3) - [4 S^\circ(\text{Fe}) + 3 S^\circ(\text{O}_2)]$$

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

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

This is the entropy change of the reaction, i.e., system ( $\Delta S_{\text{system}}$ )

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

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

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

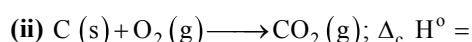
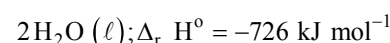
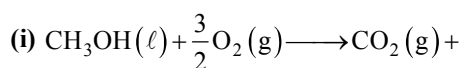
$$= -1648000 + 163721 \text{ J K}^{-1} \text{ mol}^{-1} =$$

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

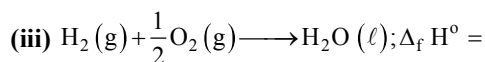
As  $\Delta_r G^\circ$  is  $-ve$ , the reaction is spontaneous.

**Example : 42**

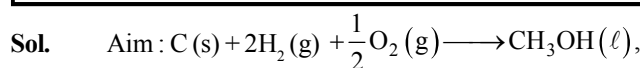
Calculate the standard enthalpy of formation of  $\text{CH}_3\text{OH}(\text{l})$  from the following data :



$$-393 \text{ kJ mol}^{-1}$$



$$-286 \text{ kJ mol}^{-1}.$$



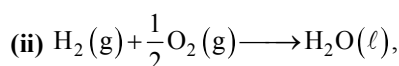
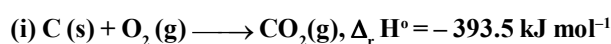
$$\Delta_f H^\circ = ?$$

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

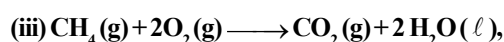
$$-239 \text{ kJ mol}^{-1}.$$

**Example : 43**

Calculate enthalpy of formation of methane ( $\text{CH}_4$ ) from the following data :



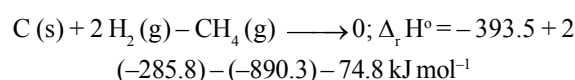
$$\Delta_r H^\circ = -285.8 \text{ kJ mol}^{-1}$$



$$\Delta_r H^\circ = -890.3 \text{ kJ mol}^{-1}$$



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



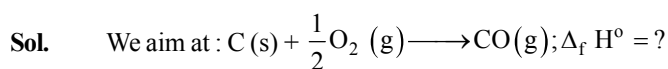
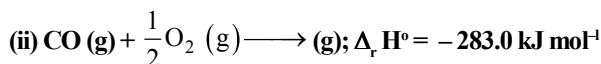
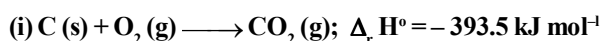


Hence, enthalpy of formation of methane is :

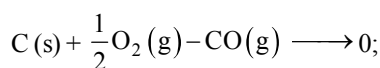
$$\Delta_f H^\circ = -74.8 \text{ kJ mol}^{-1}$$

**Example : 44**

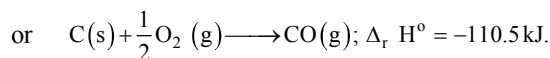
Calculate the enthalpy of formation of carbon monoxide (CO) from the following data :



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



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

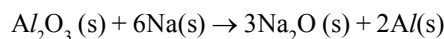


$\therefore$  Heat of formation of CO is :  $\Delta_f H^\circ = -110.5 \text{ kJ mol}^{-1}$

**Example : 45**

Determine whether or not, it is possible for sodium to reduce aluminium oxide to aluminium at 298 K. Given that  $G_f^\circ$  of  $\text{Al}_2\text{O}_3$  at 298 K = -1582 kJ mol<sup>-1</sup>;  $G_f^\circ$  of  $\text{Na}_2\text{O(s)}$  at 298 K = -377 kJ mol<sup>-1</sup>.

**Sol.** The given reaction is :



$$\text{Hence, } \Delta G^\circ = 3 \times G_f^\circ(\text{Na}_2\text{O}) - G_f^\circ(\text{Al}_2\text{O}_3)$$

$$(G^\circ \text{ for Na and Al} = 0)$$

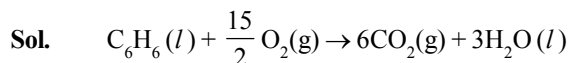
$$= 3 \times (-377) - (-1582) = 451 \text{ kJ mol}^{-1}$$

The reaction cannot occur since  $\Delta G^\circ$  (298 K) is positive.

**Example : 46**

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

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



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

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

$$\text{Now, } \Delta H = \Delta U + \Delta nRT$$

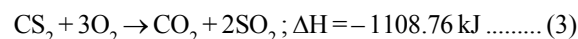
$$= -3270 + \left(-\frac{3}{2}\right) \times 8.3 \times 300 \times 10^{-3}$$

$$\Delta H = -3273.735 \text{ kJ}$$

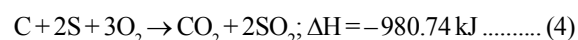
**Example : 47**

Calculate standard heat of formation of  $\text{CS}_2$ . Given that standard heat of combustion of C, S and  $\text{CS}_2$  are -393.3, -293.72 and -1108.76 kJ mol<sup>-1</sup>.

**Sol.** We have to find  $\Delta H$  for



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



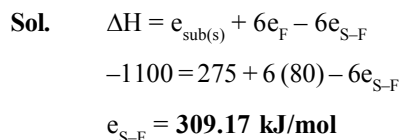
Subtract Eq. (3) from Eq. (4)



$$\Delta H_f \text{ of } \text{CS}_2 = +128.02 \text{ kJ}$$

**Example : 48**

Estimate the average S-F bond energy in  $\text{SF}_6$ . The standard heat of formation value of  $\text{SF}_6(\text{g})$ , S(g) and F(g) are : -1100, 275 and 80 kJ mol<sup>-1</sup> respectively.



**Example : 49**

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

- (i)  $C_{12}H_{22}O_{11}(s) + 12 O_2(g) \rightarrow 12 CO_2(g) + 11 H_2O(l)$   
 $\Delta_r H_1 = -5644 \text{ kJ mol}^{-1}$
- (ii)  $C(s) + O_2(g) \rightarrow CO_2(g)$   $\Delta_r H_2 = -393 \text{ kJ mol}^{-1}$
- (iii)  $H_2(g) + 1/2 O_2(g) \rightarrow H_2O(l)$   $\Delta_r H_3 = -286 \text{ kJ mol}^{-1}$

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

$$\begin{aligned} \Delta H &= 12\Delta H_2 + 11 \Delta H_3 - \Delta H_1 \\ &= 12(-393) + 11(-286) - (-5644) \\ &= -2218 \text{ kJ/mol} \end{aligned}$$

**Example : 50**

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

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

$$\begin{aligned} \Delta H_f(\text{cyclohexane}) - \Delta H_f(\text{benzene}) \\ &= -156 - (+49) \text{ kJ} \\ &= -205 \text{ kJ} \end{aligned}$$

Given, that,



Theoretical enthalpy of formation of 3 double bonds in benzene ring

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

$$\begin{aligned} \therefore \text{resonance energy of benzene} &= -357 - (-205) \text{ kJ} \\ &= -152 \text{ kJ mol}^{-1} \end{aligned}$$

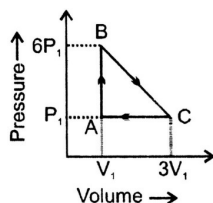
## EXERCISE- 1 : BASIC OBJECTIVE QUESTIONS

## State Functions &amp; Path Functions, Intensive &amp; Extensive Properties

- Which of the following is not a state function ?  
(a) Heat (b) Internal energy  
(c) Enthalpy (d) Entropy
- Which of the following quantities is not a state function ?  
(a) Temperature (b) Entropy  
(c) Enthalpy (d) Work
- Which of the following is not an intensive property ?  
(a) Entropy (b) Pressure  
(c) Temperature (d) Molar volume
- Which of the following is a state function and also an extensive property?  
(a) Internal energy (b) Pressure  
(c) Molar heat capacity (d) Temperature

## First Law of Thermodynamics &amp; Cyclic Process

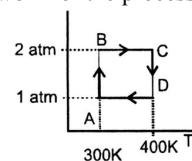
- A system absorb 10 kJ of heat at constant volume and its temperature rises from 27°C to 37°C. The value of  $\Delta U$  is  
(a) 100 kJ (b) 10 kJ  
(c) 0 (d) 1 kJ
- A sample of liquid in a thermally insulated container (a calorimeter) is stirred by a motor. Taking liquid as a system for this process choose the appropriate option :  
(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)  $w > 0$ ;  $q = 0$ ;  $\Delta U > 0$
- 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 :



- $12 P_1 V_1$
  - $6 P_1 V_1$
  - $5 P_1 V_1$
  - $P_1 V_1$
- 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

## Types of processes

- 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 ?



- $-800 R \ln 2$
  - zero
  - $+200 R \ln 2$
  - $-600 R \ln 2$
- In an isothermal expansion of an ideal gas  
(a)  $q = 0$  (b)  $\Delta V = 0$   
(c)  $\Delta U = 0$  (d)  $w = 0$
  - 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
  - 1 mole of  $\text{NH}_3$  gas at 27°C is expanded in reversible adiabatic condition to make volume 8 times ( $\gamma = 1.33$ ). 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
  - 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: ( $C_V = 20 \text{ J/K}$ )  
(a) 100 K (b) 150 K  
(c) 195 K (d) 255 K
  - Molar heat capacity of water in equilibrium with ice at constant pressure is  
(a) zero (b)  $\infty$   
(c) 40.45 kJ K<sup>-1</sup> mol<sup>-1</sup> (d) 75.48 J K<sup>-1</sup> mol<sup>-1</sup>
  - The pressure of a gas is 100 kPa. If it is compressed from 1 m<sup>3</sup> to 10 dm<sup>3</sup>, find the work done.  
(a) 990 J (b) 9990 J  
(c) 9900 J (d) 99000 J
  - An ideal gas expands in volume from  $1 \times 10^{-3}$  to  $1 \times 10^{-2}$  m<sup>3</sup> at 300 K against a constant pressure  $1 \times 10^5 \text{ Nm}^{-2}$ . The work done is  
(a) -900 J (b) -900 kJ  
(c) 270 kJ (d) 900 kJ

17. Calculate the work done when 1 mol of an ideal gas is compressed reversibly from 1 bar to 4 bar at a constant temperature of 300 K  
 (a) 4.01 kJ (b) - 8.02 kJ  
 (c) 18.02 kJ (d) None of these
18. 16g of oxygen gas expands isothermally and reversibly at 300 K from 10 dm<sup>3</sup> to 100 dm<sup>3</sup>. The work done is (in J)  
 (a) zero (b) - 2875 J  
 (c) + 2875 J (d) infinite
19. The work done during the expansion of a gas from a volume of 4dm<sup>3</sup> to 6 dm<sup>3</sup> against a constant external pressure of 3 atm is  
 (a) - 6J (b) - 608 J  
 (c) + 304 J (d) - 304 J

**Entropy & Gibb's Free Energy**

20. Entropy is a measure of  
 (a) disorder (b) internal energy  
 (c) efficiency (d) useful work done by the system
21. The enthalpy of vaporisation of a substance is 8400 J mol<sup>-1</sup> and its boiling point is -173°C. The entropy change for vaporisation is :  
 (a) 84 J mol<sup>-1</sup> K<sup>-1</sup> (b) 21 J mol<sup>-1</sup> K<sup>-1</sup>  
 (c) 49 J mol<sup>-1</sup> K<sup>-1</sup> (d) 12 J mol<sup>-1</sup> K<sup>-1</sup>
22. The enthalpy of vaporisation of a compound AB at its boiling point (127°C) is 6.4 kJ mol<sup>-1</sup>. Its entropy of vaporisation is :  
 (a) 2.56 kJ mol<sup>-1</sup> (b) 16 J mol<sup>-1</sup>  
 (c) 16 × 10<sup>-3</sup> J mol<sup>-1</sup> (d) 1.6 × 10<sup>3</sup> kJ mol<sup>-1</sup>
23. 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<sup>-1</sup> is :  
 (a) 7.32 J mol<sup>-1</sup> K<sup>-1</sup> (b) 14.62 J K<sup>-1</sup> mol<sup>-1</sup>  
 (c) 56.3 J mol<sup>-1</sup> K<sup>-1</sup> (d) 0
24. The following data is known about the melting of a compound AB. ΔH = 9.2 kJ mol<sup>-1</sup>. ΔS = 0.008 kJ K<sup>-1</sup> mol<sup>-1</sup>. Its melting point is :  
 (a) 736 K (b) 1050 K  
 (c) 1150 K (d) 1150°C
25. The entropy change when two moles of ideal monoatomic gas is heated from 200°C to 300°C reversibly and isochorically ?  
 (a)  $\frac{3}{2}R \ln\left(\frac{300}{200}\right)$  (b)  $\frac{5}{2}R \ln\left(\frac{573}{273}\right)$

$$(c) 3R \ln\left(\frac{573}{473}\right) \quad (d) \frac{3}{2}R \ln\left(\frac{573}{473}\right)$$

26. 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<sub>p,m</sub> ln2 (b) C<sub>v,m</sub> ln2  
 (c) R ln2 (d) (C<sub>v,m</sub> - R) ln2
27. One mole of an ideal diatomic gas (C<sub>v</sub> = 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)  $3 \ln \frac{298}{373} + 2 \ln 10$  (b)  $5 \ln \frac{373}{298} + 2 \ln 10$   
 (c)  $7 \ln \frac{373}{298} + 2 \ln \frac{1}{10}$  (d)  $5 \ln \frac{373}{298} + 2 \ln \frac{1}{10}$
28. Which of the following conditions is not favourable for the feasibility of a process ?  
 (a) ΔH = -ve, TΔS = -ve and TΔS < ΔH  
 (b) ΔH = +ve, TΔS = +ve and TΔS > ΔH  
 (c) ΔH = -ve, TΔS = +ve and ΔH > TΔS  
 (d) ΔH = +ve, TΔS = +ve and ΔH > TΔS
29. In which of the following cases, the reaction is spontaneous at all temperatures ?  
 (a) ΔH > 0, ΔS > 0 (b) ΔH < 0, ΔS > 0  
 (c) ΔH < 0, ΔS < 0 (d) ΔH > 0, ΔS < 0
30. Which of the following is true for the reaction ?  
 $\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{O}(g)$  at 100°C and 1 atm pressure  
 (a) ΔS = 0 (b) ΔH = TΔS  
 (c) ΔH = ΔU (d) ΔH = 0
31. A reaction has ΔH = - 33 kJ and ΔS = +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

**Thermochemistry**

32. For the reaction :  
 $\text{C}(s) + \text{O}_2(g) \longrightarrow \text{CO}_2(g)$   
 (a) ΔH < ΔU (b) ΔH > ΔU  
 (c) ΔH = ΔU (d) ΔH = 0
33. For which of the following reactions, ΔH is greater than ΔU ?  
 (a)  $\text{N}_2(g) + 3\text{H}_2(g) \longrightarrow 2\text{NH}_3(g)$   
 (b)  $\text{CH}_2(g) + 2\text{O}_2(g) \longrightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l)$

- (c)  $\text{PCl}_5(\text{g}) \longrightarrow \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$   
 (d)  $\text{HCl}(\text{aq}) + \text{NaOH}(\text{aq}) \longrightarrow \text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{aq})$
34.  $(\Delta U - \Delta H)$  for the formation of  $\text{NH}_3$  from  $\text{N}_2$  and  $\text{H}_2$  is :  
 (a)  $-2 RT$  (b)  $2 RT$   
 (c)  $RT$  (d)  $\frac{1}{2} RT$
35. The difference between heats of reaction at constant pressure and constant volume for the reaction.  
 $2\text{C}_2\text{H}_6(\text{l}) + 15\text{O}_2(\text{g}) \longrightarrow 12\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l})$  at  $25^\circ\text{C}$  is  
 (a)  $-7.43 \text{ kJ}$  (b)  $+3.72 \text{ kJ}$   
 (c)  $-3.72 \text{ kJ}$  (d)  $7.43 \text{ kJ}$
36. Consider the reaction at  $300 \text{ K}$   
 $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \longrightarrow 2\text{HCl}(\text{g}); \quad \Delta H^\circ = -185 \text{ kJ}$   
 If 2 mole of  $\text{H}_2$  completely react with 2 mole of  $\text{Cl}_2$  to form  $\text{HCl}$ . What is  $\Delta U^\circ$  for this reaction ?  
 (a) 0 (b)  $-185 \text{ kJ}$   
 (c)  $370 \text{ kJ}$  (d)  $-370 \text{ kJ}$
37. The enthalpies of formation of  $\text{N}_2\text{O}$  and  $\text{NO}$  at  $298 \text{ K}$  are  $82$  and  $90 \text{ kJ mol}^{-1}$ . The enthalpy of the reaction :  
 $\text{N}_2\text{O}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow 2\text{NO}(\text{g})$   
 (a)  $-8 \text{ kJ}$  (b)  $98 \text{ kJ}$   
 (c)  $-74 \text{ kJ}$  (d)  $8 \text{ kJ}$
38. The enthalpies of solution of anhydrous  $\text{CuSO}_4$  and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  are  $-15.89$  and  $2.80 \text{ kcal mol}^{-1}$  respectively. The enthalpy of hydration of  $\text{CuSO}_4$  to  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  is :  
 (a)  $-18.69 \text{ kcal}$  (b)  $13.09 \text{ kcal}$   
 (c)  $-13.09 \text{ kcal}$  (d)  $18.69 \text{ kcal}$
39. If  $\text{CH}_3\text{COOH} + \text{OH}^- \longrightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O} + x \text{ kJ}$   
 $\text{H}^+ + \text{OH}^- \longrightarrow \text{H}_2\text{O} + y \text{ kJ}$   
 The enthalpy change for the reaction :  
 $\text{CH}_3\text{COOH} \longrightarrow \text{CH}_3\text{COO}^- + \text{H}^+$  is  
 (a)  $x + y$  (b)  $x - y$   
 (c)  $y - x$  (d)  $x - y/2$
40. For the reaction,  
 $2\text{H}_2\text{O}(\text{g}) \longrightarrow 2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \Delta H = 571.6 \text{ kJ}$   
 $\Delta_f H^\circ$  of water is :  
 (a)  $285.8 \text{ kJ}$  (b)  $-285.8 \text{ kJ}$   
 (c)  $1143.2 \text{ kJ}$  (d)  $-1143.2 \text{ kJ}$
41.  $\Delta H$  for the reaction,  
 $\text{SO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightleftharpoons \text{SO}_3(\text{g}) \Delta H = -98.3 \text{ kJ}$   
 If the enthalpy of formation of  $\text{SO}_3(\text{g})$  is  $-395.4 \text{ kJ}$  then the enthalpy of formation of  $\text{SO}_2(\text{g})$  is :  
 (a)  $-297.1 \text{ kJ}$  (b)  $493.7 \text{ kJ}$   
 (c)  $-493.7 \text{ kJ}$  (d)  $297.1 \text{ kJ}$
42. When  $0.5 \text{ g}$  of sulphur is burnt to  $\text{SO}_2$   $4.6 \text{ kJ}$  of heat is liberated. What is the enthalpy of formation of sulphur dioxide ?  
 (a)  $-147.2 \text{ kJ}$  (b)  $+147.2 \text{ kJ}$   
 (c)  $+294.4 \text{ kJ}$  (d)  $-294.4 \text{ kJ}$
43. The heat of formation of  $\text{Fe}_2\text{O}_3(\text{s})$  is  $-824.2 \text{ kJ mol}^{-1}$ .  $\Delta H$  for the reaction.  
 $2\text{Fe}_2\text{O}_3(\text{s}) \longrightarrow 4\text{Fe}(\text{s}) + 3\text{O}_2(\text{g})$  is :  
 (a)  $-412.1 \text{ kJ}$  (b)  $-1648.4 \text{ kJ}$   
 (c)  $-3296.8 \text{ kJ}$  (d)  $1648.4 \text{ kJ}$
44. The  $\Delta H^\circ$  for the reaction,  
 $4\text{S}(\text{s}) + 6\text{O}_2(\text{g}) \longrightarrow 4\text{SO}_3(\text{g})$   
 is  $-1583.2 \text{ kJ}$ . Standard enthalpy of formation of sulphur trioxide is :  
 (a)  $-3166.4 \text{ kJ}$  (b)  $3166.4 \text{ kJ}$   
 (c)  $-395.8 \text{ kJ}$  (d)  $395.8 \text{ kJ}$
45. Calculate the heat of formation of  $\text{PCl}_5(\text{s})$  from the following data :  
 $2\text{P}(\text{s}) + 3\text{Cl}_2(\text{g}) \longrightarrow 2\text{PCl}_3(\text{l}) \quad \Delta H = -151.8 \text{ kcal}$   
 $\text{PCl}_3(\text{l}) + \text{Cl}_2(\text{g}) \longrightarrow \text{PCl}_5(\text{s}) \quad \Delta H = -32.8 \text{ kcal}$   
 (a)  $-108.7 \text{ kcal}$  (b)  $108.7 \text{ kcal}$   
 (c)  $-184.6 \text{ kcal}$  (d)  $184.6 \text{ kcal}$
46. If  $\text{S} + \text{O}_2 \longrightarrow \text{SO}_2 \quad \Delta H = -298.2 \text{ kJ}$   
 $\text{SO}_2 + \frac{1}{2}\text{O}_2 \longrightarrow \text{SO}_3 \quad \Delta H = -98.2 \text{ kJ}$   
 $\text{SO}_3 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_4 \quad \Delta H = -130.2 \text{ kJ}$   
 $\text{H}_2 + \frac{1}{2}\text{O}_2 \longrightarrow \text{H}_2\text{O} \quad \Delta H = -287.3 \text{ kJ}$   
 the enthalpy of formation of  $\text{H}_2\text{SO}_4$  at  $298 \text{ K}$  will be  
 (a)  $-433.7 \text{ kJ}$  (b)  $-650.3 \text{ kJ}$   
 (c)  $+320.5 \text{ kJ}$  (d)  $-813.9 \text{ kJ}$
47. The enthalpies of combustion of carbon and carbon monoxide are  $-393.5$  and  $-283.0 \text{ kJ mol}^{-1}$  respectively. The enthalpy of formation of carbon monoxide is :  
 (a)  $-676.5 \text{ kJ}$  (b)  $110.5 \text{ kJ}$   
 (c)  $-110.5 \text{ kJ}$  (d)  $676.5 \text{ kJ}$
48. Which of the following pairs has heat of neutralisation equal to  $-57.1 \text{ kJ}$  ?  
 (a)  $\text{HNO}_3, \text{KOH}$  (b)  $\text{HCl}, \text{NH}_4\text{OH}$   
 (c)  $\text{H}_2\text{SO}_4, \text{NH}_4\text{OH}$  (d)  $\text{CH}_3\text{COOH}, \text{NaOH}$
49. Which of the following neutralisation reactions is most exothermic ?  
 (a)  $\text{HCl}$  and  $\text{NaOH}$  (b)  $\text{HCN}$  and  $\text{NaOH}$   
 (c)  $\text{HCl}$  and  $\text{NH}_4\text{OH}$  (d)  $\text{CH}_3\text{COOH}$  and  $\text{NH}_4\text{OH}$
50. The enthalpy of neutralisation of  $\text{HCl}$  by  $\text{NaOH}$  is  $-57.1 \text{ kJ}$  and that of  $\text{HCN}$  by  $\text{NaOH}$  is  $-12.1 \text{ kJ mol}^{-1}$ . The enthalpy of ionization of  $\text{HCN}$  is :  
 (a)  $-69.2 \text{ kJ}$  (b)  $-45.0 \text{ kJ}$

- (c) 69.2 kJ (d) 45.0 kJ
51. For the reaction at 300 K  
 $A(g) + B(g) \longrightarrow C(g)$   
 $\Delta U = -3.0 \text{ kcal}$   $\Delta S = -10.0 \text{ cal/K}$   
 $(R \approx 2 \text{ cal mol}^{-1} \text{ K}^{-1})$   
 $\Delta G$  is :  
 (a) -600 cal (b) -3600 cal  
 (c) 2400 cal (d) 3000 cal
52. The standard enthalpies of formation of  $HCl(g)$ ,  $H(g)$  and  $Cl(g)$  are -92.2, 217.7 and 121.4  $\text{kJ mol}^{-1}$  respectively. The bond dissociation energy of  $HCl$  is:  
 (a) +431.3 kJ (b) 236.9 kJ  
 (c) -431.3 kJ (d) 339.1 kJ
53. The enthalpy changes at  $25^\circ\text{C}$  in successive breaking of O-H bonds of water are :  
 $H_2O(g) \longrightarrow H(g) + OH(g) \quad \Delta H = 498 \text{ kJ mol}^{-1}$   
 $OH(g) \longrightarrow H(g) + O(g) \Delta H = 428 \text{ kJ mol}^{-1}$   
 the bond enthalpy of the O-H bond is :  
 (a) 498  $\text{kJ mol}^{-1}$  (b) 463  $\text{kJ mol}^{-1}$   
 (c) 428  $\text{kJ mol}^{-1}$  (d) 70  $\text{kJ mol}^{-1}$
54. 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  $\text{kcal mol}^{-1}$  (b) -5.6  $\text{kcal mol}^{-1}$   
 (c) -2.8  $\text{kcal mol}^{-1}$  (d) -56  $\text{kcal mol}^{-1}$
55. 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
56. 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
57. Based on the values of B.E. given,  $\Delta_f H^\circ$  of  $N_2H_4(g)$  is:  
 Given: N-N = 159  $\text{kJ mol}^{-1}$ ; H-H = 436  $\text{kJ mol}^{-1}$   
 $N \equiv N = 941 \text{ kJ mol}^{-1}$ , N-H = 398  $\text{kJ mol}^{-1}$   
 (a) 711  $\text{kJ mol}^{-1}$  (b) 62  $\text{kJ mol}^{-1}$   
 (c) -98  $\text{kJ mol}^{-1}$  (d) -711  $\text{kJ mol}^{-1}$
58. 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 kcal/mole (b) 180 kcal/mole  
 (c) 130 kcal/mole (d) 80 kcal/mole
59. For the reaction of one mole of zinc dust with one mole of sulphuric acid in a bomb calorimeter,  $\Delta E$  and  $W$  corresponds to  
 (a)  $\Delta E < 0, W = 0$  (b)  $\Delta E = 0, W < 0$   
 (c)  $\Delta E > 0, W = 0$  (d)  $\Delta E = 0, W > 0$
60. The bond energies C - C, C = C, H - H and C - H linkages are 350, 600, 400 and 410  $\text{kJ/mol}$  respectively. The heat of hydrogenation of ethylene is  
 (a) -170  $\text{kJ mol}^{-1}$  (b) -260  $\text{kJ mol}^{-1}$   
 (c) -400  $\text{kJ mol}^{-1}$  (d) -450  $\text{kJ mol}^{-1}$
61. The standard heats of formation of  $CH_4$ ,  $H_2O$  and  $CH_3OH$  are -76, -242 and -266  $\text{kJ/mol}$  respectively. The enthalpy change for the following reaction is  
 $CH_3OH(l) + H_2(g) \longrightarrow CH_4(g) + H_2O(l)$   
 (a) -4  $\text{kJ/mol}$  (b) -556  $\text{kJ/mol}$   
 (c) -318  $\text{kJ/mol}$  (d) -52  $\text{kJ/mol}$
62. Which of the following reaction defines  $\Delta_f H^\circ$  ?  
 (a)  $C(\text{diamond}) + O_2(g) \longrightarrow CO_2(g)$   
 (b)  $\frac{1}{2} H_2(g) + \frac{1}{2} F_2(g) \longrightarrow HF(g)$   
 (c)  $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$   
 (d)  $CO(g) + \frac{1}{2} O_2(g) \longrightarrow CO_2(g)$
63. The heat of combustion of solid benzoic acid at constant volume is -321.30 kJ at  $27^\circ\text{C}$ . The heat of combustion at constant pressure is  
 (a) -321.30 - 300 R (b) -321.30 + 300 R  
 (c) -321.30 - 150 R (d) -321.30 + 900 R
64.  $\Delta H$  for the reaction,  
 $C(\text{graphite}) + 2H_2(g) \longrightarrow CH_4(g)$  at 298 K and 1 atm is -17900 cal. The  $\Delta E$  for the above conversion would be  
 (a) -17900 cal (b) 17900 cal  
 (c) 17308 cal (d) -17308 cal
65. If 150 kJ of energy is needed for muscular work to walk a distance of one km, then how much of glucose one has to consume to walk a distance of 5 km, provided only 30% of energy is available for muscular work. (The enthalpy of combustion of glucose is 3000  $\text{kJ mol}^{-1}$  is)  
 (a) 75 g (b) 30 g  
 (c) 180 g (d) 150 g
66. For the reaction,  
 $2H_2(g) + O_2(g) \longrightarrow 2H_2O(g); \Delta H^\circ = -573.2 \text{ kJ}$   
 The heat of decomposition of water per mole is

- (a) 286.6 kJ                      (b) 573.2 kJ  
(c) - 28.66 kJ                    (d) zero



## EXERCISE– 2 : PREVIOUS YEAR COMPETITION QUESTIONS

### First Law & Reversible and Irreversible Processes

- Which of the following units represents largest amount of energy ? **(CPMT 1980)**  
 (a) Calorie (b) Joule  
 (c) Erg (d) Electron volt.
- During isothermal expansion of an ideal gas, its **(PMT 1991,94)**  
 (a) internal energy increases  
 (b) enthalpy decreases  
 (c) enthalpy remains unaffected  
 (d) enthalpy reduces to zero.
- A well stoppered thermos flask contains some ice cubes. This is an example of a **(AIIMS 1992,94)**  
 (a) closed system  
 (b) open system  
 (c) isolated system  
 (d) non-thermodynamic system.
- In a closed insulated container a liquid is stirred with a paddle to increase the temperature. Which of the following is true ? **(PMT 2002)**  
 (a)  $\Delta E = W \neq 0, q = 0$  (b)  $\Delta E = W = q \neq 0$   
 (c)  $\Delta E = 0, W = q \neq 0$  (d)  $W = 0, \Delta E = q \neq 0$
- An adiabatic expansion of an ideal gas always has **(PMT 2002)**  
 (a) increase in temperature (b)  $q = 0$   
 (c)  $w = 0$  (d)  $\Delta H = 0$
- For an adiabatic process, which of the following is correct ? **(CPMT 1990)**  
 (a)  $P\Delta V = 0$  (b)  $q = +w$   
 (c)  $\Delta E = q$  (d)  $q = 0$ .
- In a reversible isothermal process, the change in internal energy is **(PMT 1993)**  
 (a) zero (b) positive  
 (c) negative (d) none of the above.
- Heat capacity is **(PMT 1996)**  
 (a)  $\frac{dQ}{dT}$  (b)  $dQ \times dT$   
 (c)  $\Sigma Q \cdot \frac{1}{dT}$  (d) None of these.
- The relation between enthalpy (H), pressure (P), volume (V) and internal energy (E) is given by **(PMT 1998)**  
 (a)  $E = H + PV$  (b)  $H = E + PV$

$$(c) H = E - PV \quad (d) H = E + P + V.$$

- One mole of an ideal gas at 300 K is expanded isothermally from an initial volume of 1 litre to 10 litres. The  $\Delta E$  for this process is **(PMT 1998)**  
 $(R = 2 \text{ cal mol}^{-1} \text{ K}^{-1})$   
 (a) 163.7 cal (b) zero  
 (c) 1381.1 cal (d) 9 lit atom.
- If 1 mole of an ideal gas expands isothermally at 37°C from 15 L to 25 L, the maximum work obtained is **(AFMC 2010)**  
 (a) -13 L-atm (b) -6.43 L-atm  
 (c) -8.57 L-atm (d) -2.92 L-atm

### Entropy & Gibb's Free Energy

- For a spontaneous chemical process, the free energy change is **(BHU 1981)**  
 (a) positive  
 (b) negative  
 (c) either positive or negative  
 (d) zero.
- For which reaction from the following,  $\Delta S$  will be maximum ? **(AIIMS 1982,83)**  
 (a)  $\text{Ca (s)} + \frac{1}{2} \text{O}_2 \text{ (g)} \rightarrow \text{CaO (s)}$   
 (b)  $\text{CaCO}_3 \text{ (s)} \rightarrow \text{CaO (s)} + \text{CO}_2 \text{ (g)}$   
 (c)  $\text{C (s)} + \text{O}_2 \text{ (g)} \rightarrow \text{CO}_2 \text{ (g)}$   
 (d)  $\text{N}_2 \text{ (g)} + \text{O}_2 \text{ (g)} \rightarrow 2\text{NO (g)}$
- All the naturally occurring processes proceed spontaneously in a direction which leads to **(PMT 1985)**  
 (a) decrease of entropy  
 (b) increase of enthalpy  
 (c) increase of free energy  
 (d) decrease of free energy
- The occurrence of reaction is impossible if **(AIIMS 1994)**  
 (a)  $\Delta H$  is +ve ;  $\Delta S$  is also +ve  
 (b)  $\Delta H$  is -ve ;  $\Delta S$  is also -ve  
 (c)  $\Delta H$  is -ve ;  $\Delta S$  is +ve  
 (d)  $\Delta H$  is +ve ;  $\Delta S$  is -ve
- In which of the following, the entropy decreases ? **(CPMT 1988)**  
 (a) Crystallisation of sucrose from solution  
 (b) Rusting of iron  
 (c) Melting of ice

- (d) Vaporization of camphor.
17. Which of the following statements is true ? The entropy of the universe (PMT 1993)
- (a) increases and tends towards maximum value  
 (b) decreases and tends to zero  
 (c) remains constant  
 (d) decreases and increases with a periodic rate.
18. The total entropy change for a system and its surroundings increases, if the process is (PMT 1993)
- (a) reversible (b) irreversible  
 (c) exothermic (d) endothermic.
19. A chemical reaction will be spontaneous if it is accompanied by a decrease of (PMT 1994)
- (a) entropy of the system  
 (b) enthalpy of the system  
 (c) internal energy of the system  
 (d) free energy of the system.
20. Gibb's free energy  $G$ , enthalpy  $H$  and entropy  $S$  are related to one another by (BUU 1994)
- (a)  $G = H + TS$  (b)  $G = H - TS$   
 (c)  $G - TS = H$  (d)  $S = H - G$ .
21.  $\Delta S^\circ$  will be highest for the reaction (AIIMS 1994)
- (a)  $\text{Ca (s)} + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{CaO (s)}$   
 (b)  $\text{CaCO}_3(\text{g}) \rightarrow \text{CaO (s)} + \text{CO}_2(\text{g})$   
 (c)  $\text{C (g)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$   
 (d)  $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{NO (g)}$ .
22. For a reaction to occur spontaneously (PMT 1995)
- (a)  $\Delta S$  must be negative  
 (b)  $(\Delta H - T\Delta S)$  must be negative  
 (c)  $(\Delta H + T\Delta S)$  must be negative  
 (d)  $\Delta H$  must be negative.
23. According to third law of thermodynamics, which one of the following quantities for a perfectly crystalline solid is zero at absolute zero? (PMT 1996)
- (a) Entropy (b) Free energy  
 (c) Internal energy (d) Enthalpy.
24. The enthalpy and entropy change for a chemical reaction are  $-2.5 \times 10^3$  cal and  $7.4$  cal  $\text{deg}^{-1}$  respectively. The reaction at  $298$  K will be (AFMC 1998)
- (a) spontaneous (b) reversible  
 (c) irreversible (d) non-spontaneous.
25. Identify the correct statement regarding entropy. (BHU 1998)
- (a) At absolute zero of temperature, entropy of a perfectly crystalline substance is taken to be zero  
 (b) At absolute zero of temperature, the entropy of a perfectly crystalline substance is positive  
 (c) Absolute entropy of a substance cannot be determined  
 (d) At  $0^\circ\text{C}$ , the entropy of a perfectly crystalline substance is taken to be zero.
26. One mole of an ideal gas is allowed to expand freely and adiabatically into vacuum until its volume has doubled. The expression which is not true concerning statement is (PMT 1998)
- (a)  $\Delta H = 0$  (b)  $\Delta S = 0$   
 (c)  $\Delta E = 0$  (d)  $W = 0$
27. For which of the process,  $\Delta S$  is negative ? (PMT 1998)
- (a)  $\text{H}_2(\text{g}) \rightarrow 2 \text{H (g)}$   
 (b)  $\text{N}_2(\text{g } 1 \text{ atm}) \rightarrow \text{N}_2(\text{g } 8 \text{ atm})$   
 (c)  $2 \text{SO}_3(\text{g}) \rightarrow 2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g})$   
 (d)  $\text{C}_{(\text{diamond})} \rightarrow \text{C}_{(\text{graphite})}$ .
28. Heat exchanged in a chemical reaction at constant temperature and pressure is called (PMT 2001)
- (a) entropy  
 (b) enthalpy  
 (c) internal energy  
 (d) free energy
29. Which one of the following has  $\Delta S^\circ$  greater than zero? (AIIMS 2003)
- (a)  $\text{CaO (s)} + \text{CO}_2(\text{g}) \rightleftharpoons \text{CaCO}_3(\text{s})$   
 (b)  $\text{NaCl (aq)} \rightleftharpoons \text{NaCl (s)}$   
 (c)  $\text{NaNO}_3(\text{s}) \rightleftharpoons \text{Na}^+(\text{aq}) + \text{NO}_3^-(\text{aq})$   
 (d)  $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$
30. If the enthalpy of vaporisation of water is  $186.5 \text{ J mol}^{-1}$ , the entropy of its vaporisation will be (CPMT 1988)
- (a)  $0.5 \text{ JK}^{-1} \text{ mol}^{-1}$  (b)  $1.0 \text{ JK}^{-1} \text{ mol}^{-1}$   
 (c)  $1.5 \text{ JK}^{-1} \text{ mol}^{-1}$  (d)  $2.0 \text{ JK}^{-1} \text{ mol}^{-1}$ .
31. If  $900 \text{ J/g}$  of heat is exchanged at boiling point of water, then what is increase in entropy? (BHU 1998)
- (a)  $43.4 \text{ J/mole}$  (b)  $87.2 \text{ mole}$   
 (c)  $900 \text{ J/mole}$  (d) zero.

32. 1 mole of ice is converted to liquid at 273 K ;  $\text{H}_2\text{O} (s)$  and  $\text{H}_2\text{O} (l)$  have entropies 38.20 and 60.03  $\text{J mol}^{-1} \text{deg}^{-1}$ . Enthalpy change in the conversion will be  
(DPMT 1994)  
(a) 59.59 J/mol (b) 595.95 J/mol  
(c) 5959.5 J/mol (d) 595959.0 J/mol.
33. 2 mole of an ideal gas at 27°C temperature is expanded reversibly from 2 lit to 20 lit. Find entropy change ( $R = 2 \text{ cal/mol K}$ ) (PMT 2002)  
(a) 92.1 (b) 0  
(c) 4 (d) 9.2
34. What is the entropy change (in  $\text{JK}^{-1} \text{mol}^{-1}$ ) when one mole of ice is converted into water at 0°C ?  
(The enthalpy change for the conversion of ice to liquid water is 6.0  $\text{kJ mol}^{-1}$  at 0°C)  
(CBSE Med. 2003)  
(a) 20.13 (b) 2.013  
(c) 2.198 (d) 21.98
35. What is the free energy change,  $\Delta G$ , when 1.0 mole of water at 100°C and 1 atm pressure is converted into steam at 100°C and 1 atm pressure ?  
(PMT 1998)  
(a) 540 cal (b) -9800 cal  
(c) 9800 cal (d) 0 cal.
36. The densities of graphite and diamond at 298 K are 2.25 and 3.31  $\text{g cm}^{-3}$  respectively. If the standard free energy difference ( $\Delta G^\circ$ ) is equal to 1895  $\text{J mol}^{-1}$ , the pressure at which graphite will be transformed into diamond at 298 K is (CBSE 2003)  
(a)  $9.92 \times 10^8 \text{ Pa}$  (b)  $9.92 \times 10^7 \text{ Pa}$   
(c)  $9.92 \times 10^6 \text{ Pa}$  (d) None of these
- Thermochemistry**
37. The compound with negative heat of formation is known as (DPMT 1981)  
(a) endothermic compound  
(b) exothermic compound  
(c) endoergonic compound (d) none of the above.
38.  $\Delta H_{\text{combustion}}$  of a compound is (PMT 1985)  
(a) positive (b) negative  
(c) zero (d) positive or negative
39. Heat of neutralization of  $\text{NH}_4\text{OH}$  and  $\text{HCl}$  is (PMT 1985)  
(a) 13.7 kcal/mole (b) < 13.7 kcal/mole  
(c) > 13.7 kcal/mol (d) zero
40. Heat of neutralisation of a strong acid and a strong base is nearly equal to (AIIMS 1988)  
(a) 10 kJ/mole (b) 10 Cal/mole  
(c) -57 kJ/mole (d) -57 Cal/mole.
41. The mutual heat of neutralisation of 40 g  $\text{NaOH}$  and 60 g  $\text{CH}_3\text{COOH}$  will be (AIIMS 1988)  
(a) 57.1 kJ (b) less than 57.1 kJ  
(c) more than 57.1 kJ (d) 13.7 kJ.
42. For the transition (PMT 2002)  
 $\text{C} (\text{diamond}) \rightarrow \text{C} (\text{graphite}); \Delta H = -1.5 \text{ kJ}$ .  
It follows that  
(a) diamond is exothermic  
(b) graphite is endothermic  
(c) graphite is stabler than diamond  
(d) diamond is stabler than graphite.
43. Which of the following reaction can be used to define the heat of formation of  $\text{CO}_2(\text{g})$  ? (PMT 1989)  
(a)  $\text{C} (\text{graphite}) + \text{O}_2 (\text{g}) \rightarrow \text{CO}_2(\text{g})$   
(b)  $\text{CH}_4(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O} (l)$   
(c)  $\text{CO} (\text{g}) + \frac{1}{2} \text{O}_2 (\text{g}) \rightarrow \text{CO}_2 (\text{g})$   
(d)  $\text{C}_6\text{H}_6 (l) + 7 \frac{1}{2} \text{O}_2(\text{g}) \rightarrow 6 \text{CO}_2(\text{g}) + 3 \text{H}_2\text{O} (l)$
44. The molar neutralisation heat for  $\text{KOH}$  and  $\text{HNO}_3$  as compared to molar neutralisation heat of  $\text{NaOH}$  and  $\text{HCl}$  is (PMT 1989)  
(a) less (b) more  
(c) equal (d) depends on pressure
45. If  $\Delta H$  is the change in enthalpy and  $\Delta E$ , the change in internal energy accompanying a gaseous reaction, then (CBSE PMT 1990)  
(a)  $\Delta H$  is always greater than  $\Delta E$   
(b)  $\Delta H < \Delta E$  only if the number of moles of the products is greater than the number of moles of the reactants  
(c)  $\Delta H$  is always less than  $\Delta E$   
(d)  $\Delta H < \Delta E$  only if the number of moles of products is less than the number of moles of the reactants.
46. Heat of neutralisation is least when (PMT 1990)  
(a)  $\text{NaOH}$  is neutralised by  $\text{CH}_3\text{COOH}$   
(b)  $\text{NaOH}$  is neutralised by  $\text{HCl}$   
(c)  $\text{NH}_4\text{OH}$  is neutralised by  $\text{CH}_3\text{COOH}$   
(d)  $\text{NH}_4\text{OH}$  is neutralised by  $\text{HNO}_3$ .

47.  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2\text{HI}(\text{g})$ ;  $\Delta\text{H} = 12.40$  kcal. According to this reaction heat of formation of HI will be (PMT 1990)  
 (a) 12.4 kcal (b) -12.4 kcal  
 (c) -6.20 kcal (d) 6.20 kcal.
48. Equal volumes of molar hydrochloric acid and sulphuric acid are neutralized by dil. NaOH solution and x kcal and y kcal of heat are liberated respectively. Which of the following is true? (PMT 1994)  
 (a)  $x = y$  (b)  $x = \frac{1}{2}y$   
 (c)  $x = 2y$  (d) None of these.
49. Which of the following values of heat of formation indicates that the product is least stable? (PMT 1991)  
 (a) -94 kcal (b) -231.6 kcal  
 (c) +21.4 kcal (d) +64.8 kcal.
50. In which of the following neutralization reaction, the heat of neutralisation will be highest? (PMT 1989,91)  
 (a)  $\text{NH}_4\text{OH}$  and  $\text{H}_2\text{SO}_4$   
 (b)  $\text{HCl}$  and  $\text{NaOH}$   
 (c)  $\text{CH}_3\text{COOH}$  and  $\text{KOH}$   
 (d)  $\text{CH}_3\text{COOH}$  and  $\text{NH}_4\text{OH}$ .
51. For the reaction (PMT 1991)  
 $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ ,  $\Delta\text{H} = ?$   
 (a)  $\Delta\text{E} + 2\text{RT}$  (b)  $\Delta\text{E} - 2\text{RT}$   
 (c)  $\Delta\text{E} + \text{RT}$  (d)  $\Delta\text{E} - \text{RT}$ .
52. An exothermic reaction is one in which the reacting substances (CPMT 1974)  
 (a) Have more energy than the products  
 (b) Have less energy than the products  
 (c) Have the same energy as the products  
 (d) Are at a higher temperature than the products.
53. The enthalpy change ( $-\Delta\text{H}$ ) for the neutralisation of 1 M HCl by caustic potash in dilute solution at 298 K is (BHU 1993)  
 (a) 68 kJ (b) 65 kJ  
 (c) 57.3 kJ (d) 50 kJ.
54. Evaporation of water is (PMT 1993)  
 (a) An exothermic change  
 (b) An endothermic change  
 (c) A process where no heat changes occur  
 (d) A process accompanied by chemical reaction.
55. At constant T and P which one of the following statements is correct for the reaction?  
 $\text{S}_8(\text{s}) + 8\text{O}_2(\text{g}) \rightarrow 8\text{SO}_2(\text{g})$  (PMT 1993)  
 (a)  $\Delta\text{H} < \Delta\text{E}$  (b)  $\Delta\text{H} = \Delta\text{E}$   
 (c)  $\Delta\text{H} > \Delta\text{E}$  (d)  $\Delta\text{H}$  is independent of the physical state of the reactants.
56. Consider the following reaction occurring in an automobile  $2\text{C}_8\text{H}_{18}(\text{g}) + 25\text{O}_2(\text{g}) \rightarrow 16\text{CO}_2 + 18\text{H}_2\text{O}(\text{g})$  the sign of  $\Delta\text{H}$ ,  $\Delta\text{S}$  and  $\Delta\text{G}$  would be (PMT 1994)  
 (a) +, -, + (b) -, +, -  
 (c) -, +, + (d) +, +, -.
57. Heat of neutralisation of strong acid against strong base is constant and is equal to (PMT 1993)  
 (a) 13.7 kcal (b) 57 kJ  
 (c)  $5.7 \times 10^4$  J (d) All of the above.
58. When water is added to quick lime, the reaction is (PMT 1995)  
 (a) explosive (b) endothermic  
 (c) exothermic (d) photochemical
59. The heat of formation of the compound in the following reaction is  
 $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl}(\text{g}) + 44$  kcal (PMT 1995)  
 (a) -44 kcal mol<sup>-1</sup> (b) -22 kcal mol<sup>-1</sup>  
 (c) 11 kcal mol<sup>-1</sup> (d) -88 kcal mol<sup>-1</sup>.
60. For the reaction  $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$  (BHU 1995)  
 (a)  $\Delta\text{H} > \Delta\text{E}$  (b)  $\Delta\text{H} < \Delta\text{E}$   
 (c)  $\Delta\text{H} = \Delta\text{E}$  (d) None of these.
61. Enthalpy of a reaction  $\Delta\text{H}$  is expressed as (AIIMS 1996)  
 (a)  $\Delta\text{H} = \sum\Delta\text{H}_\text{p} - \sum\Delta\text{H}_\text{R}$  (b)  $\Delta\text{H} = \text{dH}_\text{p} + \text{dH}_\text{R}$   
 (c)  $\Delta\text{H} = \frac{\text{dH}_\text{p}}{\text{dH}_\text{R}}$  (d)  $\Delta\text{H} = \frac{\sum\text{H}_\text{p}}{\text{dH}_\text{R}}$ .
62. The enthalpy change of a reaction does not depend on (AIIMS 1997)  
 (a) the state of reactants and products  
 (b) nature of reactants and products  
 (c) different intermediate reactions  
 (d) initial and final enthalpy change of a reaction.

63. Given that  $C + O_2 \rightarrow CO_2, \Delta H^0 = -x$  kJ  
 $2 CO + O_2 \rightarrow 2 CO_2, \Delta H^0 = -y$  kJ  
 the enthalpy of formation of carbon monoxide will be  
**(PMT 1997)**  
 (a)  $\frac{2x-y}{2}$  (b)  $\frac{y-2x}{2}$   
 (c)  $2x-y$  (d)  $y=2x$ .
64. The neutralisation of a strong acid by a strong base liberates and amount of energy per mole of  $H^+$   
**(BHU 1998)**  
 (a) depends upon which acid and base are involved  
 (b) depends upon the temperature at which the reaction takes place  
 (c) depends upon which catalyst is used  
 (d) is always the same.
65. Equal volumes of methanoic acid and sodium hydroxide are mixed. If  $x$  is the heat of formation of water, then heat evolved on neutralisation is  
**(BHU 1998)**  
 (a) more than  $x$  (b) equal to  $x$   
 (c) less than  $x$  (d) twice  $x$ .
66.  $S + \frac{3}{2} O_2 \rightarrow SO_3 + 2x$  kcal  
 $SO_2 + \frac{1}{2} O_2 \rightarrow SO_3 + y$  kcal  
 Find out the heat of formation of  $SO_2$  **(PMT 1999)**  
 (a)  $(y-2x)$  (b)  $-(2x+y)$   
 (c)  $-(x+y)$  (d)  $-2x/y$ .
67. For the reaction  
 $C_3H_8(g) + 5 O_2(g) \rightarrow 3 CO_2(g) + 4 H_2O(l)$  at constant temperature,  $\Delta H - \Delta E$  is  
**(CBSE Med. 2003)**  
 (a)  $+RT$  (b)  $-3RT$   
 (c)  $+3RT$  (d)  $-RT$
68. For which one of the following equations is  $\Delta H^0_{\text{reaction}}$  equal to  $\Delta H^0_f$  for the product? **(CBSE Med. 2003)**  
 (a)  $N_2(g) + O_3(g) \rightarrow N_2O_3(g)$   
 (b)  $CH_4(g) + 2 Cl_2(g) \rightarrow CH_2Cl_2(l) + 2 HCl(g)$   
 (c)  $Xe(g) + 2 F_2(g) \rightarrow XeF_4(g)$   
 (d)  $2 CO(g) + O_2(g) \rightarrow 2 CO_2(g)$
69. In which of the following process of neutralisation magnitude of  $\Delta H_{\text{neutralisation}}$  is less than that of  $\Delta H_{\text{ionization}}$  of water? **(BHU 2003)**  
 (a)  $HCl + NaOH$  (b)  $H_2SO_4 + NaOH$   
 (c)  $CH_3COOH + NaOH$  (d)  $HClO_4 + KOH$
70. The enthalpy of formation for  $C_2H_4(g)$ ,  $CO_2(g)$  and  $H_2O(l)$  at  $25^\circ C$  and 1 atm pressure are 52, -394 and -286 kJ mol<sup>-1</sup> respectively. The enthalpy of combustion of  $C_2H_4(g)$  will be **(PMT 1995)**  
 (a) +1412 kJ mol<sup>-1</sup> (b) -1412 kJ mol<sup>-1</sup>  
 (c) +141.2 kJ mol<sup>-1</sup> (d) -141.2 kJ mol<sup>-1</sup>.
71. The heat of combustion of benzene at  $27^\circ C$  found by bomb calorimeter i.e. for the reaction  
 $C_6H_6(l) + 7 \frac{1}{2} O_2(g) \rightarrow 6 CO_2(g) + 3 H_2O(l)$  is 780 kcal mol<sup>-1</sup>. The heat evolved on burning 39 g of benzene in an open vessel will be **(PMT 2001)**  
 (a) 390 kcal (b) 780.9 kcal  
 (c) 390.45 kcal (d) 780 kcal.
72. If  $S + O_2 \rightarrow SO_2, \Delta H = -298.2$  kJ  
 $SO_2 + \frac{1}{2} O_2 \rightarrow SO_3, \Delta H = -98.7$  kJ  
 $SO_3 + H_2O \rightarrow H_2SO_4, \Delta H = -130.2$  kJ  
 $H_2 + \frac{1}{2} O_2 \rightarrow H_2O, \Delta H = -287.3$  kJ.  
 Then the enthalpy of formation of  $H_2SO_4$  at 298K will be **(DPMT 1994)**  
 (a) -814.4 kJ (b) +320.5 kJ  
 (c) -650.3 kJ (d) -933.7 kJ
73.  $H_2 + 1/2 O_2 \rightarrow H_2O; \Delta H^0 = -68$  kcal **(CPMT 1988)**  
 $K + H_2O + aq \rightarrow KOH(aq) + 1/2 H_2; \Delta H^0 = -48$  kcal  
 $KOH + aq \rightarrow KOH(aq); \Delta H^0 = -14$  kcal  
 From the above data, the standard heat of formation of KOH in kcal is :  
 (a)  $-68 + 48 - 14$  (b)  $-68 - 48 + 14$   
 (c)  $68 - 48 + 14$  (d)  $68 + 48 + 14$ .
74. The enthalpies of combustion of carbon and carbon monoxide are -390 kJ mol<sup>-1</sup> and -278 kJ mol<sup>-1</sup> respectively. The enthalpy of formation of carbon monoxide is **(BHU 1994)**  
 (a) 668 kJ mol<sup>-1</sup> (b) 112 kJ mol<sup>-1</sup>  
 (c) -112 kJ mol<sup>-1</sup> (d) -668 kJ mol<sup>-1</sup>
75.  $C + O_2 \rightarrow CO_2, \Delta H = -x$   
 $CO + \frac{1}{2} O_2 \rightarrow CO_2, \Delta H = -y$   
 then  $\Delta H_f$  for CO will be **(DPMT 2002)**  
 (a)  $2x + y$  (b)  $x - y$   
 (c)  $y - 2x$  (d)  $y - x$
76. The amount of energy released when 20 ml of 0.5 M NaOH are mixed with 100 mL of 0.1 M HCl is  $x$  kJ. The heat of neutralisation (in kJ mol<sup>-1</sup>) is **(PMT 2002)**  
 (a) -100  $x$  (b) -50  $x$   
 (c) +100  $x$  (d) +50  $x$

77. Heat of neutralisation for the reaction  
 $\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O}$   
 is  $57.1 \text{ kJ mol}^{-1}$ . What will be the heat released when 0.25 mole of NaOH reacts with 0.25 mole of HCl?  
**(PMT 1990)**  
 (a)  $22.5 \text{ kJ mol}^{-1}$  (b)  $57.1 \text{ kJ mol}^{-1}$   
 (c)  $14.3 \text{ kJ mol}^{-1}$  (d)  $28.6 \text{ kJ mol}^{-1}$ .
78. Enthalpy of neutralisation of HCl with NaOH is  $x$ . The heat evolved when 500 mL of 2 N HCl are mixed with 250 ml of 4 N NaOH will be **(AFMC 2002)**  
 (a)  $500x$  (b)  $100x$   
 (c)  $x$  (d)  $10x$
79. The enthalpy of dissolution of  $\text{BaCl}_2$  (s) and  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  (s) are  $-20.6$  and  $8.8 \text{ kJ mol}^{-1}$  respectively. The enthalpy of hydration for  $\text{BaCl}_2(\text{s}) + 2 \text{H}_2\text{O} \rightarrow \text{BaCl}_2 \cdot 2\text{H}_2\text{O}(\text{s})$  is **(PMT 1994)**  
 (a)  $29.4 \text{ kJ}$  (b)  $-29.4 \text{ kJ}$   
 (c)  $-11.8 \text{ kJ}$  (d)  $38.2 \text{ kJ}$ .
80. The heats of combustion of rhombic and monoclinic sulphur are respectively 70960 and 71030 calories. What will be the heat of conversion of rhombic sulphur to monoclinic?  
**(PMT 1988)**  
 (a) 70960 calories (b) 71030 calories  
 (c)  $-70$  calories (d)  $+70$  calories.
81.  $\Delta H_f$  of graphite is  $0.23 \text{ kJ/mole}$  and  $\Delta H_f$  of diamond is  $1.896 \text{ kJ/mol}$ .  $\Delta H_{\text{transition}}$  from graphite to diamond is **(BHU 2003)**  
 (a)  $1.66 \text{ kJ/mol}$  (b)  $2.1 \text{ kJ/mole}$   
 (c)  $2.33 \text{ kJ/mole}$  (d)  $1.5 \text{ kJ/mole}$
82. The enthalpies of formation of  $\text{N}_2\text{O}$  and  $\text{NO}$  are 82 and 90  $\text{kJ/mole}$  respectively. The enthalpy of the reaction  
 $2 \text{N}_2\text{O}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 4 \text{NO}(\text{g})$  is equal to  
**(PMT 1991)**  
 (a) 8 kJ (b) 88 kJ  
 (c)  $-16 \text{ kJ}$  (d)  $196 \text{ kJ}$ .
83. Based on the following thermochemical equations  
 $\text{H}_2\text{O}(\text{g}) + \text{C}(\text{s}) \rightarrow \text{CO}(\text{g}) + \text{H}_2(\text{g}); \Delta H = 131 \text{ kJ}$   
 $\text{CO}(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}); \Delta H = -282 \text{ kJ}$   
 $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g}); \Delta H = -242 \text{ kJ}$   
 $\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}); \Delta H = X \text{ kJ}$ ,  
 the value of  $X$  will be **(PMT 1992)**  
 (a)  $-393 \text{ kJ}$  (b)  $-655 \text{ kJ}$   
 (c)  $+393 \text{ kJ}$  (d)  $+655 \text{ kJ}$ .
84. If  $\Delta H_f^\circ$  for  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{O}$  are  $-188 \text{ kJ/mole}$  and  $-286 \text{ kJ/mole}$ , what will be the enthalpy change of the reaction  $2 \text{H}_2\text{O}_2(\text{l}) \rightarrow 2 \text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$ ?  
**(PMT 1992)**  
 (a)  $-196 \text{ kJ/mole}$  (b)  $146 \text{ kJ/mole}$   
 (c)  $-494 \text{ kJ/mole}$  (d)  $-98 \text{ kJ/mole}$ .
85. Considering the following reactions,  
 $\text{C} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO} \Delta H = -26.4 \text{ K}$ .  
 $\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}(\text{l}) \Delta H = -57.8 \text{ kcal}$ ,  
 $\Delta H$  for the reaction  
 $\text{H}_2\text{O} + \text{C} \rightarrow \text{H}_2 + \text{CO}$  is **(PMT 1994)**  
 (a)  $62.8 \text{ kcal}$  (b)  $31.4 \text{ kcal}$   
 (c)  $-31.4 \text{ kcal}$  (d)  $-84.2 \text{ kcal}$ .
86. Given :  
 $\text{C}(\text{graphite}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{CO}(\text{g}); \Delta H = -110.5 \text{ kJ}$   
 $\text{CO}(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}); \Delta H = -283.2 \text{ kJ}$   
 The heat of reaction for  
 $\text{C}(\text{graphite}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$  will be  
**(PMT 1989)**  
 (a)  $-393.7 \text{ kJ}$  (b)  $+393.7 \text{ kJ}$   
 (c)  $-172.2 \text{ kJ}$  (d)  $+172.2 \text{ kJ}$
87. Heat of combustion  $\Delta H$  for  $\text{C}(\text{s})$ ,  $\text{H}_2(\text{g})$  and  $\text{CH}_4(\text{g})$  are  $-94$ ,  $-68$  and  $-213 \text{ kcal/mol}$ . Then  $\Delta H$  for  $\text{C}(\text{s}) + 2\text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g})$  is **(PMT 2002)**  
 (a)  $-17 \text{ kcal}$  (b)  $-111 \text{ kcal}$   
 (c)  $-170 \text{ kcal}$  (d)  $-85 \text{ kcal}$
88. The enthalpy changes at 298 K in successive breaking of O-H bonds of HOH are  
 $\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}(\text{g}) + \text{OH}(\text{g}), \Delta H = 498 \text{ kJ mol}^{-1}$   
 $\text{OH}(\text{g}) \rightarrow \text{H}(\text{g}) + \text{O}(\text{g}), \Delta H = 428 \text{ kJ mol}^{-1}$   
 The bond enthalpy of the O-H bond is **(PMT 1994)**  
 (a)  $498 \text{ kJ mol}^{-1}$  (b)  $463 \text{ kJ mol}^{-1}$   
 (c)  $428 \text{ kJ mol}^{-1}$  (d)  $70 \text{ kJ mol}^{-1}$
89. The bond energy of an O-H bond is  $109 \text{ kcal mol}^{-1}$ . When a mole of water is formed **(PMT 1994)**  
 (a)  $218 \text{ kcal}$  is released (b)  $109 \text{ kcal}$  is released  
 (c)  $218 \text{ kcal}$  is absorbed (d)  $109 \text{ kcal}$  is absorbed.
90. Energy required to dissociate 4 g of gaseous hydrogen into free gaseous atoms is  $208 \text{ kcal}$  at  $25^\circ\text{C}$ . The bond energy of H-H bond will be **(CPMT 1989)**  
 (a)  $104 \text{ kcal}$  (b)  $10.4 \text{ kcal}$   
 (c)  $1040 \text{ kcal}$  (d)  $104 \text{ kcal}$ .

91. Given the reaction at 1240 K and 1 atm.  $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$   
 $\Delta H = 176 \text{ kJ/mol}$ , the  $\Delta E$  equals (BHU 1993)  
 (a) 160.0 kJ (b) 165.6 kJ  
 (c) 186.4 kJ (d) 180.0 kJ
92. The latent heat of vaporisation of a liquid at 500 K and 1 atm. pressure is 10.0 kcal/mol. What will be the change in internal energy of 3 moles of the liquid at the same temperature and pressure? (PMT 1994)  
 (a) 27.0 kcal (b) 13.0 kcal  
 (c) -27.0 kcal (d) -13.0 kcal
93. Given the following entropy values (in  $\text{JK}^{-1} \text{mol}^{-1}$ ) at 298 K and 1 atm :  $\text{H}_2(\text{g})$  : 130.6,  $\text{Cl}_2(\text{g})$  : 223.0 and  $\text{HCl}(\text{g})$  : 186.7. The entropy change (in  $\text{JK}^{-1} \text{mol}^{-1}$ ) for the reaction  
 $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2 \text{HCl}(\text{g})$  is (PMT 1996)  
 (a) +540.3 (b) +727.0  
 (c) -166.9 (d) 19.8
94. One gram sample of  $\text{NH}_4\text{NO}_3$  is decomposed in a bomb calorimeter. The temperature of the calorimeter increases by 6.12 K. The heat capacity of the system is 1.23 kJ/g/deg. What is the molar heat of decomposition for  $\text{NH}_4\text{NO}_3$ ? (AIIMS 2003)  
 (a) -7.53 kJ/mol (b) -398.1 kJ/mol  
 (c) -16.1 kJ/mol (d) -602 kJ/mol
95. How much energy is released when 6 moles of octane is burnt in air? Given  $\Delta H_f^\circ$  for  $\text{CO}_2(\text{g})$ ,  $\text{H}_2\text{O}(\text{g})$  and  $\text{C}_8\text{H}_{18}(\ell)$  respectively are -490, -240 and +160 J/mol (AIIMS 2004)  
 (a) -6.2 kJ (b) -37.4 kJ  
 (c) -35.5 kJ (d) -20.0 kJ
96.  $\Delta H_f^\circ$  (298 K) of methanol is given by the chemical equation, (AIIMS 2005)  
 (a)  $\text{CH}_4(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{CH}_3\text{OH}(\text{g})$   
 (b)  $\text{C}(\text{graphite}) + \frac{1}{2} \text{O}_2(\text{g}) + 2\text{H}_2(\text{g}) \rightarrow \text{CH}_3\text{OH}(\ell)$   
 (c)  $\text{C}(\text{diamond}) + \frac{1}{2} \text{O}_2(\text{g}) + 2\text{H}_2(\text{g}) \rightarrow \text{CH}_3\text{OH}(\ell)$   
 (d)  $\text{CO}(\text{g}) + 2\text{H}_2(\text{g}) \rightarrow \text{CH}_3\text{OH}(\ell)$
97. Assume each reaction is carried out in an open container. For which reaction will  $\Delta H = \Delta E$ ? (CBSE AIPMT 2006)  
 (a)  $\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightarrow 2\text{HBr}(\text{g})$   
 (b)  $\text{C}(\text{s}) + 2\text{H}_2\text{O}(\text{g}) \rightarrow 2\text{H}_2(\text{g}) + \text{CO}_2(\text{g})$   
 (c)  $\text{PCl}_5(\text{g}) \rightarrow \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$   
 (d)  $2\text{CO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g})$
98. The enthalpy change ( $\Delta H$ ) for the reaction,  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$  is -92.38 kJ at 298 K. The internal energy change  $\Delta U$  at 298 K is (AIIMS 2007)  
 (a) -92.38 kJ (b) -87.42 kJ  
 (c) -97.34 kJ (d) -89.9 kJ
99. The enthalpy of hydrogenation of cyclohexene is -119.5 kJ  $\text{mol}^{-1}$ . If resonance energy of benzene is -150.4 kJ  $\text{mol}^{-1}$ , its enthalpy of hydrogenation would be (AIIMS 2007)  
 (a) -208.1 kJ  $\text{mol}^{-1}$  (b) -269.9 kJ  $\text{mol}^{-1}$   
 (c) -358.5 kJ  $\text{mol}^{-1}$  (d) -508.9 kJ  $\text{mol}^{-1}$
100. One mole of methanol when burnt in  $\text{O}_2$ , gives out 723 kJ  $\text{mol}^{-1}$  heat. If one mole of  $\text{O}_2$  is used, what will be the amount of heat evolved? (AIIMS 2007)  
 (a) 723 kJ (b) 924 kJ  
 (c) 482 kJ (d) 241 kJ
101. What will be the heat of formation of methane, if the heat of combustion of carbon is '-x' kJ, heat of formation of water is '-y' kJ and heat of combustion of methane is '-z' kJ? (AIIMS 2008)  
 (a)  $(-x-y+z)$  kJ (b)  $(-z-x+y)$  kJ  
 (c)  $(-x-2y-z)$  kJ (d)  $(-x-2y+z)$  kJ
102. Enthalpy of combustion of methane and ethane are -210 kcal/mol and -368 kcal/mol respectively. The enthalpy of combustion of decane is (AIIMS 2009)  
 (a) -158 kcal (b) -1632 kcal  
 (c) -1700 kcal (d) Data is incomplete
103. The heat liberated when 1.89 g of benzoic acid is burnt in a bomb calorimeter at 25°C increases the temperature of 18.94 kg of water by 0.632°C. If the specific heat of water at 25°C is 0.998 cal/g-deg, the value of the heat of combustion of benzoic acid is (AFMC 2010)  
 (a) 881.1 kcal (b) 771.4 kcal  
 (c) 981.1 kcal (d) 871.2 kcal
104. Enthalpy change for the reaction,  $4\text{H}(\text{g}) \rightarrow 2\text{H}_2(\text{g})$  is -869.5 kJ. The dissociation energy of H—H bond is (CBSE AIPMT 2011)  
 (a) +217.4 kJ (b) -434.8 kJ  
 (c) -869.6 kJ (d) +434.8 kJ

**ANSWER KEY****EXERCISE-1 : BASIC OBJECTIVE QUESTIONS**

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1. (a)	2. (d)	3. (a)	4. (a)	5. (b)	6. (d)	7. (c)	8. (b)	9. (a)	10. (c)
11. (a)	12. (a)	13. (b)	14. (b)	15. (d)	16. (a)	17. (d)	18. (b)	19. (b)	20. (a)
21. (a)	22. (b)	23. (a)	24. (c)	25. (c)	26. (d)	27. (b)	28. (d)	29. (b)	30. (b)
31. (d)	32. (c)	33. (c)	34. (c)	35. (a)	36. (d)	37. (b)	38. (a)	39. (c)	40. (b)
41. (a)	42. (d)	43. (d)	44. (c)	45. (a)	46. (d)	47. (c)	48. (a)	49. (a)	50. (d)
51. (a)	52. (a)	53. (b)	54. (a)	55. (a)	56. (d)	57. (b)	58. (d)	59. (a)	60. (a)
61. (d)	62. (b)	63. (c)	64. (d)	65. (d)	66. (a)				

**EXERCISE-2 : PREVIOUS YEARS COMPETITION QUESTIONS**

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1. (a)	2. (c)	3. (c)	4. (a)	5. (b)	6. (d)	7. (a)	8. (a)	9. (b)	10. (b)
11. (a)	12. (b)	13. (b)	14. (d)	15. (d)	16. (a)	17. (a)	18. (b)	19. (d)	20. (b)
21. (b)	22. (b)	23. (a)	24. (a)	25. (a)	26. (b)	27. (b)	28. (b)	29. (c)	30. (a)
31. (a)	32. (c)	33. (d)	34. (d)	35. (d)	36. (d)	37. (b)	38. (b)	39. (b)	40. (c)
41. (b)	42. (c)	43. (a)	44. (c)	45. (d)	46. (c)	47. (d)	48. (b)	49. (d)	50. (b)
51. (b)	52. (a)	53. (c)	54. (b)	55. (b)	56. (b)	57. (d)	58. (c)	59. (b)	60. (c)
61. (a)	62. (c)	63. (b)	64. (d)	65. (c)	66. (a)	67. (b)	68. (c)	69. (c)	70. (b)
71. (c)	72. (a)	73. (b)	74. (c)	75. (d)	76. (a)	77. (c)	78. (c)	79. (b)	80. (c)
81. (a)	82. (d)	83. (a)	84. (a)	85. (b)	86. (a)	87. (a)	88. (b)	89. (a)	90. (a)
91. (b)	92. (a)	93. (d)	94. (d)	95. (b)	96. (b)	97. (a)	98. (b)	99. (a)	100. (c)
101. (d)	102. (b)	103. (b)	104. (d)						

*Dream on !!*






# QUANTIZATION OF ENERGY



- Quantization is a familiar concept and encounter frequently, albeit, unconsciously.
  - The naira is an integral multiples of kobo.
  - Musical instruments like a piano or a trumpet can produce only certain musical notes, such as C or F sharp.
    - these instruments cannot produce a continuous range of frequencies, their frequencies are quantized.
  - The electrical charge is also quantized: an ion may have a charge of  $-1$  or  $-2$  but *not*  $-1.33$  electron charges.

- Origin of energy quantization
- Up to the end of the 19<sup>th</sup> century, Physics was complete except for a few decimal places !
- Newtonian mechanics explained macroscopic behavior of matter -- planetary motion, fluid flow, elasticity, etc.
- Thermodynamics  had its first two laws and most of their consequences
- Basic statistical mechanics had been applied to chemical systems
- Light was explained as an electromagnetic wave

- However there were several experiments that could not be explained by classical physics and the accepted dogma !
  - Blackbody radiation
  - Photoelectric effect
  - Discrete atomic spectra
  - The electron as a subatomic particle
- Inescapable conclusions would result from these problems
  - Atoms are not the most microscopic objects
  - Newton's laws do not apply to the microscopic world of the electron

OUTCOME

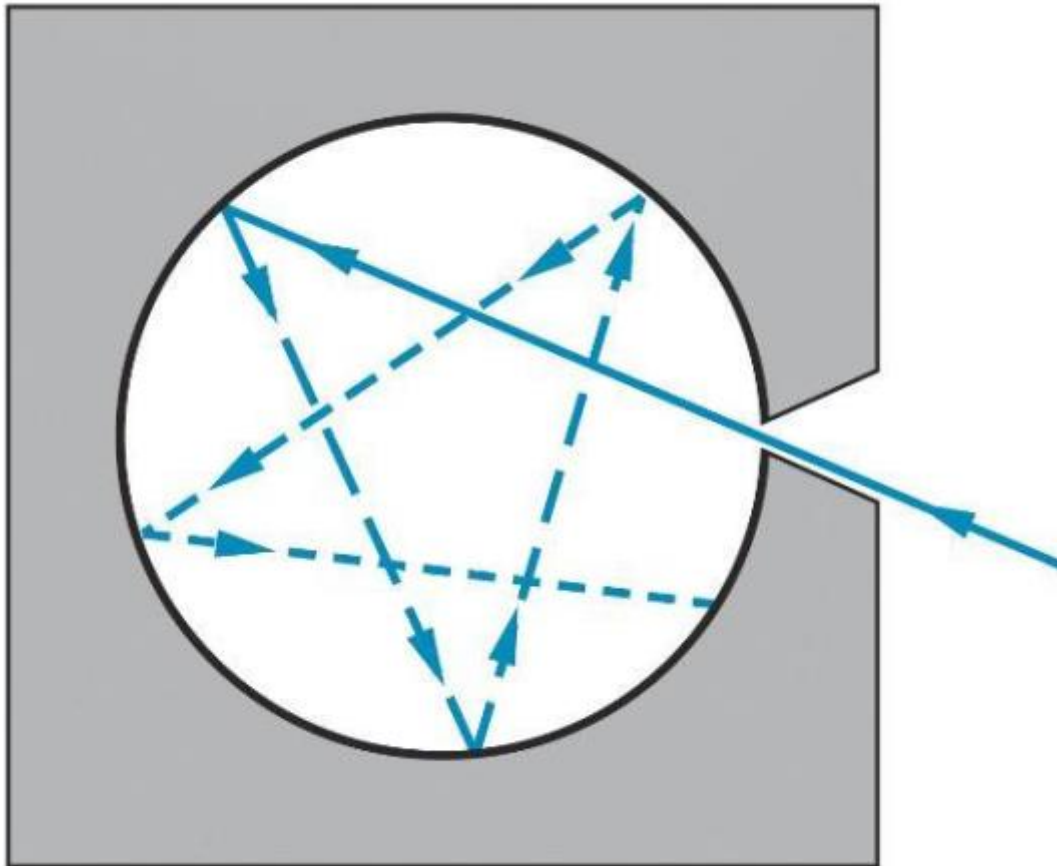


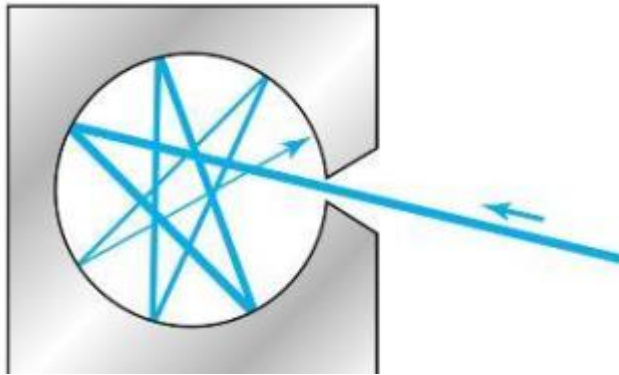
New Rules!!!

- Quantization of Energy!!!
- Describes rules that apply to electrons in atoms and molecules
- Explains unsolved problems of late 19th century physics
- Explains bonding, structure, and reactivity in chemistry



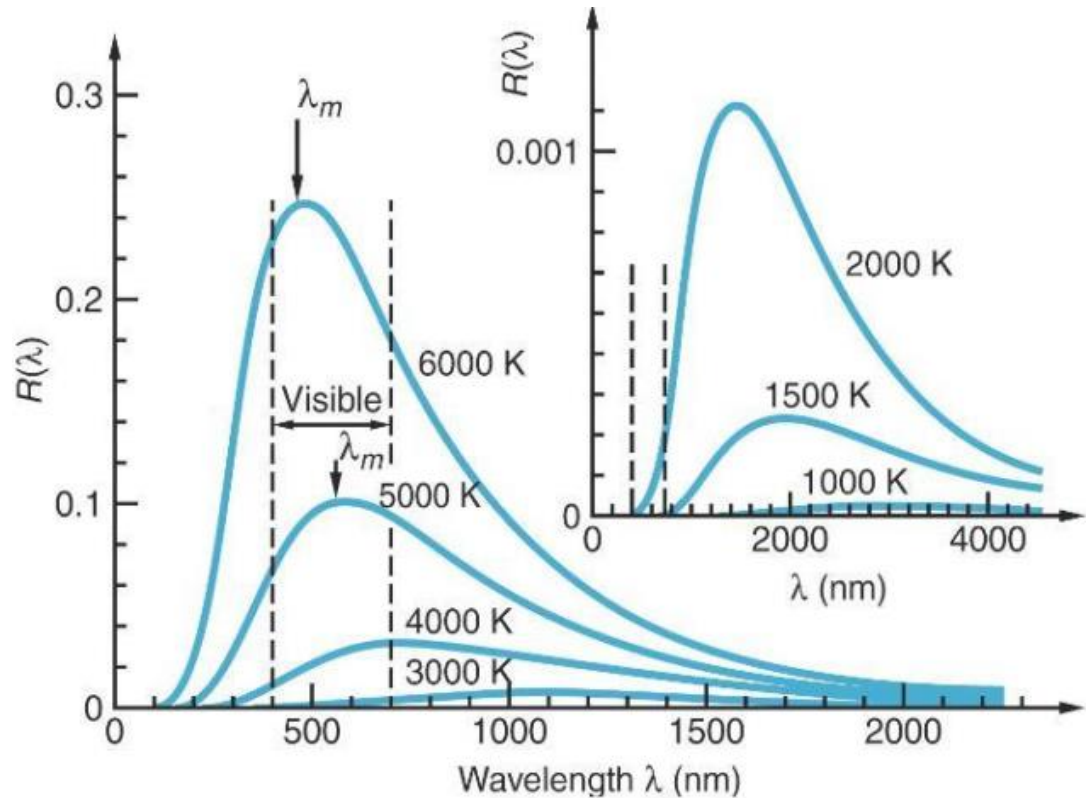
# BLACK BODY/CAVITY RADIATION





- A small hole in the wall of the cavity approximating an ideal blackbody. Electromagnetic radiation (for example, light) entering the hole has little chance of leaving before it is completely adsorbed within the cavity.
- As the walls of the cavity absorb this incoming radiation, their temperature rises and the body begin to irradiate.
- A blackbody is a cavity within a material that only emits thermal radiation. Incoming radiation is absorbed in the cavity.
- Blackbody radiation is theoretically interesting because the radiation properties of the blackbody **are independent of the particular material.**
- The properties of irradiated intensity can be studied as a function of wavelength at fixed temperatures.

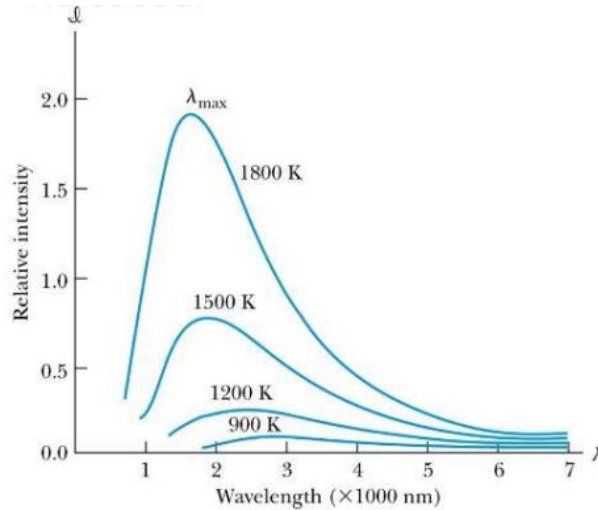
Spectral distribution function  $R(\lambda)$  measured at different temperatures. The  $R(\lambda)$  axis is in arbitrary units for comparison only. Notice the range in  $\lambda$  of the visible spectrum. The Sun emits radiation very close to that of a blackbody at **5800 K**.  $\lambda_m$  is indicated for the **5000-K** and **6000-K** curves.





# WIEN'S DISPLACEMENT LAW

- The spectral intensity  $R(\lambda, T)$  is the total power irradiated per unit area per unit wavelength at a given temperature.
- **Wien's displacement law:** The maximum of the spectrum shifts to smaller wavelengths as the temperature is increased.



$$\lambda_{\max} T = 2.898 \times 10^{-3} \text{ m} \cdot \text{K}$$

- The total radiated power  $R$ , the spectral distribution of the radiation emitted by a blackbody is found empirically to depend only on the absolute temperature  $T$ . The dependence of maximum wavelength as a function is given as:

$$\lambda_m \propto \frac{1}{T}$$

- Such that

$$\lambda_m T = \text{constant} = 2.898 \times 10^{-3} \text{ mK}$$

- The above is known as the Wien's displacement law
- For illustration:

➤ The wavelength at the peak of the spectral distribution for a blackbody at **4300 K** is **674 nm** (red). What would be the temperature of the blackbody that have the peak in intensity at **420 nm** (violet)?

➤ SOLUTION:

From Wien's law

$$\lambda_m(1)T(1) = \lambda_m(2)T(2)$$

$$\begin{aligned} \therefore T(2) &= \frac{\lambda_m(1)T(1)}{\lambda_m(2)} \\ &= \frac{674\text{nm} \times 4300\text{K}}{420\text{nm}} \\ &= 6900\text{K} \end{aligned}$$

# WIEN'S DISPLACEMENT LAW CONT'D

This law is used to determine:

- the surface temperatures of stars by analyzing their radiation.
- It can also be used to map out the variation in temperature over different regions of the surface of an object. Such a map is called *thermograph*.
  - ✓ For example *thermograph* can be used to detect cancer because cancerous tissue results in increased circulation which produce a slight increase in skin temperature.

The radiation emitted by the surface of the sun emits maximum power at wavelength of about **500 nm**. Assuming the sun to be a blackbody emitter, (a) what is its surface temperature?

(b) Calculate  $\lambda_{max}$  for a blackbody at room temperature,  $T=300\text{ K}$ .


# STEFAN-BOLTZMAN LAW

- Total amount of radiation emitted by blackbody at all wavelengths and found it varied with absolute temperature. - Stefan's experimental findings
- Theoretical calculation of the variation of the total amount of radiation with temperature - Boltzman.
- The total power radiated as a function of absolute temperature is given as:

$$P(T) = \int_0^{\infty} R(\lambda, T) d\lambda = \sigma T^4$$

- Where

$$\sigma = 5.67 \times 10^{-8} \text{ Wm}^{-2} \text{ K}^{-4}$$

- Blackbody radiation – Absorbed all radiation incident on it and when heated, emit light of all wavelength! 

- Classically –

- Radiation from a blackbody is the result of electrons oscillating with frequency  $\nu$
- The electrons can oscillate (& radiate) equally well at any frequency

⇒ Rayleigh-Jeans Law for spectral density  $\rho(\nu)$ , where intensity of emitted light in frequency range from  $\nu$  to  $\nu+d\nu$  is  $I(\nu) \sim \rho(\nu)d\nu$

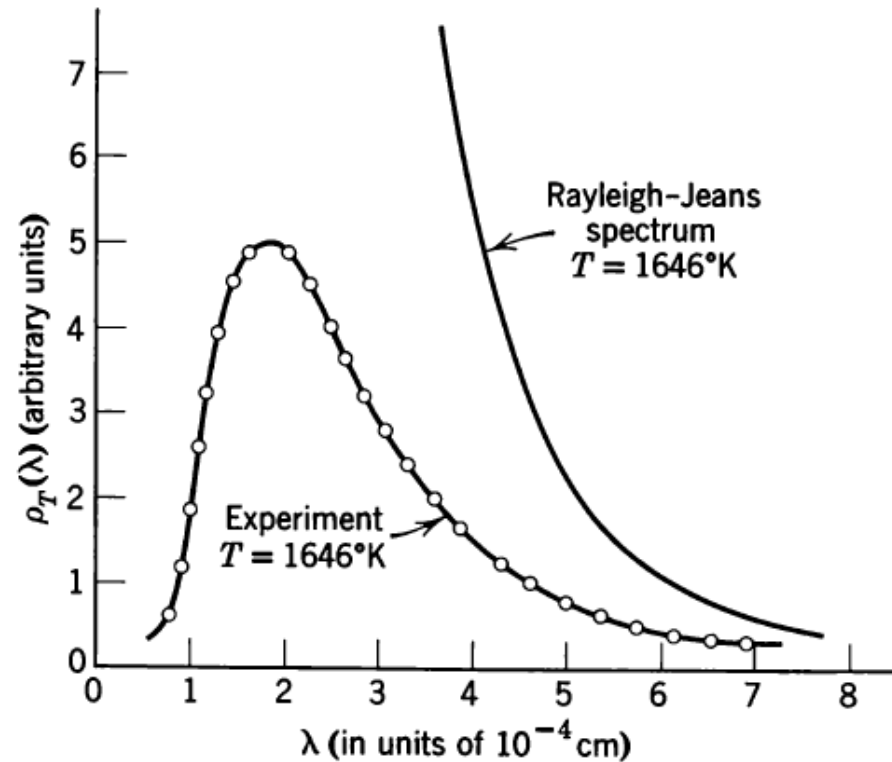
$$d\rho = \rho(\nu, T) d\nu = \frac{8\pi kT}{c^3} \nu^2 d\nu \quad \boxed{\propto \nu^2}$$

where  $d\rho(\nu, T)$  = density of radiative energy in frequency range from  $\nu$  to  $\nu+d\nu$  at temperature  $T$

$k$  = Boltzmann's constant [=  $R/N_A$  (gas constant per molecule)]

$c$  = speed of light

- A comparison of the Rayleigh-Jeans spectrum and experiment.



- Note that the Rayleigh-Jeans law reproduces the experimental data at low frequencies.
- At high frequencies, however, the Rayleigh-Jeans law predicts that the radiant energy density diverges as  $\nu^2$ .
- Because the frequency increases as the radiation enters the ultraviolet region, this divergence was termed the ultraviolet catastrophe, a phenomenon that classical physics could not reconcile theoretically.

# Planck's Theory

- Resolved the discrepancy between experiment and theory
- introduction of a postulate which was not only new, but also drastically at variance with certain concepts of classical physics
- Any physical entity whose single "coordinate" executes simple harmonic oscillations (i.e., is a sinusoidal function of time  $t$ ) can possess only total energies  $\varepsilon$  which satisfy the relation

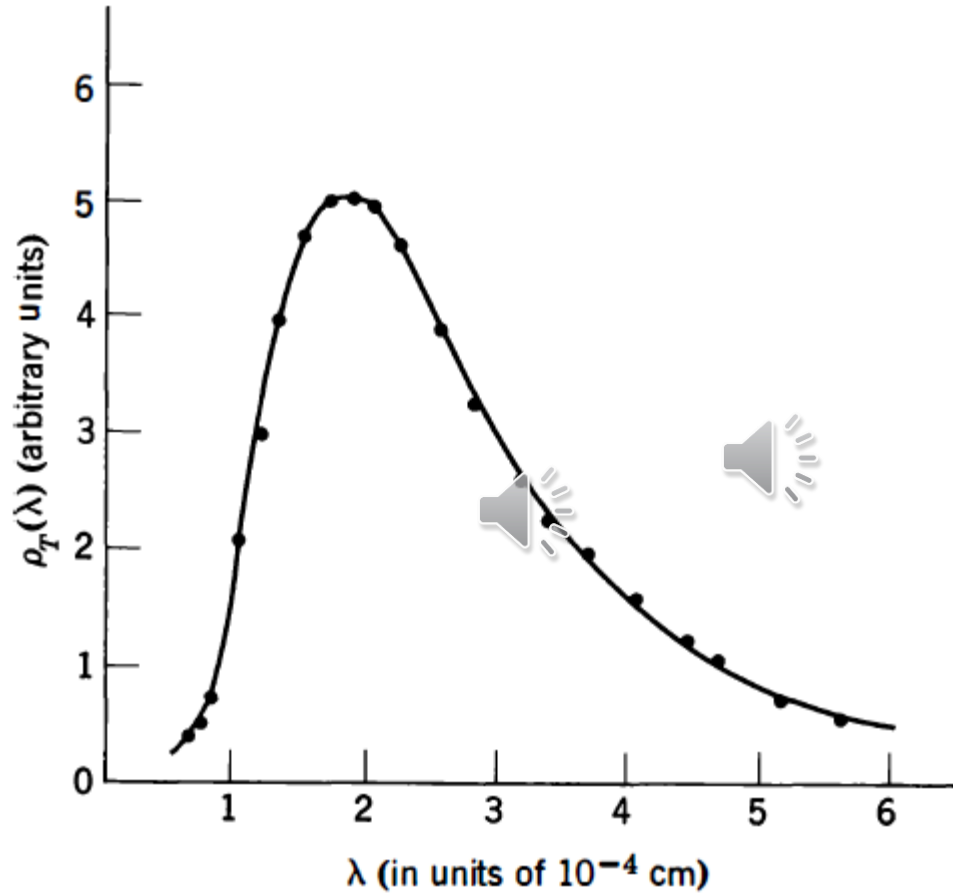
$$\varepsilon = nh\nu, \quad n = 0, 1, 2, 3, \dots$$

- where  $\nu$  is the frequency of the oscillation and  $h$  is a universal constant.
- Planck used statistical mechanics to derive the expression for black body radiation as:

$$d\rho(\lambda, T) = \rho_\lambda(T)d\lambda = \frac{8\pi hc}{\lambda^5} \frac{d\lambda}{e^{hc/\lambda k_B T} - 1}$$



- A comparison of Planck's spectrum and experiment. The dots are experimental and the curve is theoretical.  $T = 1646^\circ \text{ K}$ .



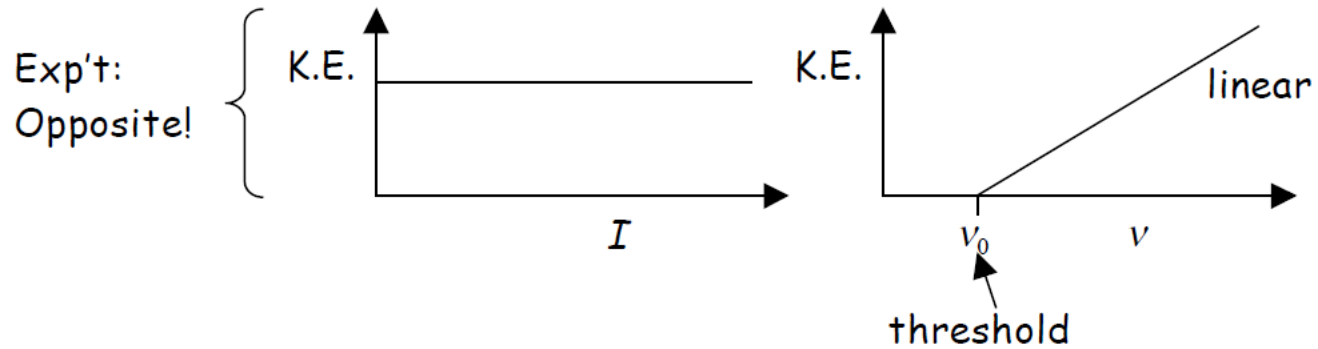
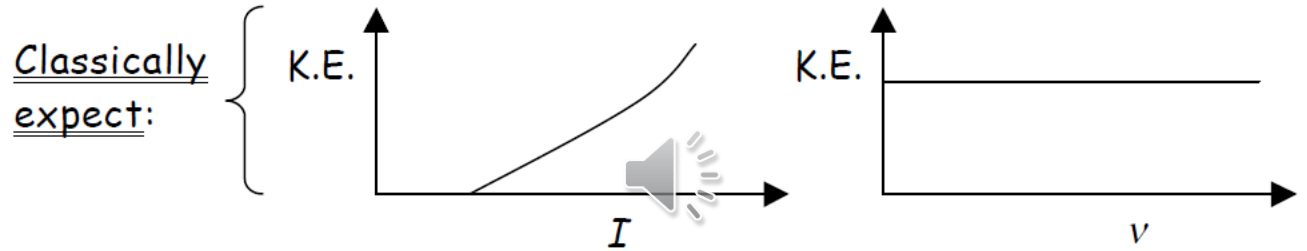
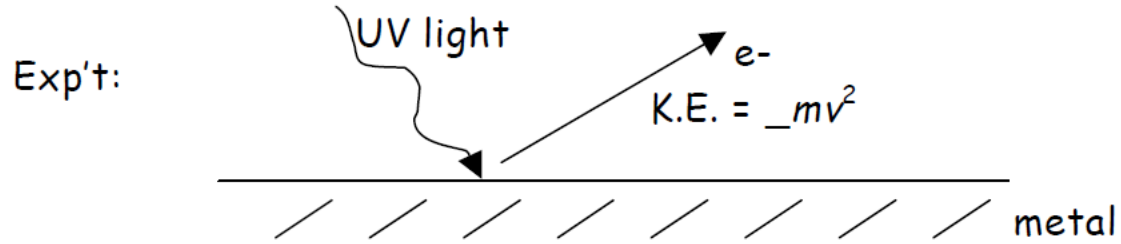
Fitting exp't to model  $\Rightarrow$

$$h = 6.626 \times 10^{-34} \text{ J-sec}$$

Planck's constant



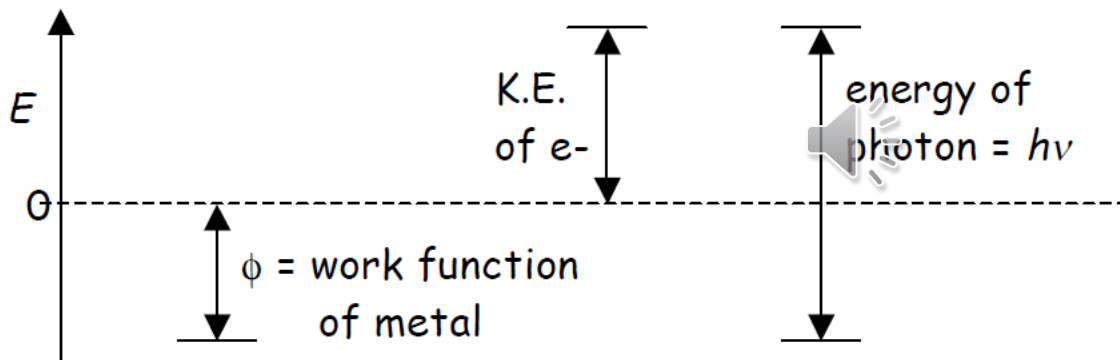
# • The Photoelectric Effect



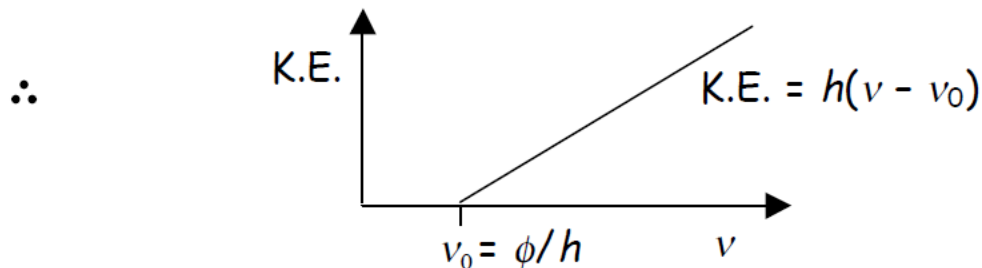
- Einstein (1905) proposed:
- Light is made up of energy “packets: “photons”
- The energy of a photon is proportional to the light frequency

$$E = h\nu \quad h \equiv \text{Planck's constant}$$

New model of photoelectric effect:



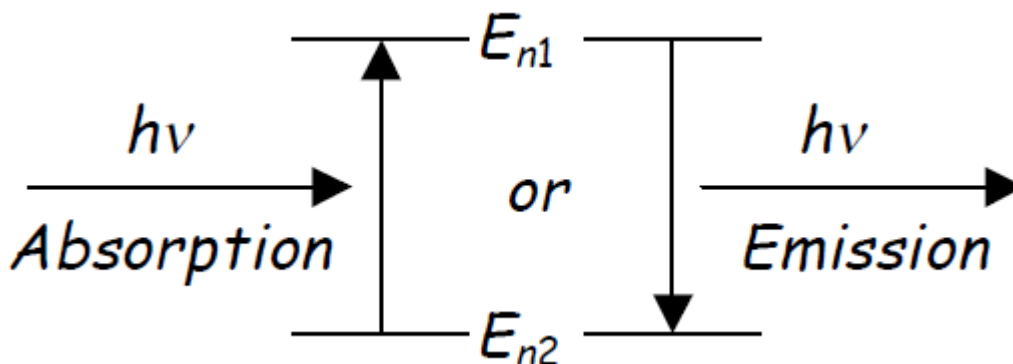
$$\therefore \text{K.E.} = h\nu - \phi = h\nu - h\nu_0 = h(\nu - \nu_0)$$



# Niel Bohr's Model of the Atom

- Atoms can exist in stable “states” without radiating.
- The states have discrete energies  $E_n$ ,  $n = 1, 2, 3, \dots$ , where  $n = 1$  is the lowest energy state (the most negative, relative to the dissociated atom at zero energy),  $n = 2$  is the next lowest energy state, etc.
- The number “ $n$ ” is an integer, a quantum number, that labels the state.
- Transitions between states can be made with the absorption or  $\Delta E$  emission of a photon of frequency  $\nu$  given as

$$\nu = \frac{\Delta E}{h}.$$



- These two assumptions “explain” the discrete spectrum of atomic vapor emission. Each line in the spectrum corresponds to a transition between two particular levels. This is the birth of modern spectroscopy.
- Angular momentum is quantized:

$$\ell = n\hbar \quad \text{where } \hbar = \frac{h}{2\pi}$$

$$r = \frac{Ze^2}{4\pi\epsilon_0 mv^2} \Rightarrow r = \frac{n^2}{Z} \left(4\pi\epsilon_0\right) \frac{\hbar^2}{me^2} \quad \text{The radius is quantized!!}$$

$$\left(4\pi\epsilon_0\right) \frac{\hbar^2}{me^2} \equiv a_0 \quad \text{the Bohr radius}$$

For H atom with  $n = 1$ ,  $r = a_0 = 5.29 \times 10^{-11} \text{ m} = 0.529 \text{ \AA}$  ( $1 \text{ \AA} = 10^{-10} \text{ m}$ )

$$E = T + V = -Ze^2/2r = -T$$

$$E = -\frac{1}{2} \frac{Ze^2}{4\pi\epsilon_0 r} \Rightarrow \boxed{E_n = -\frac{1}{n^2} \frac{Z^2 me^4}{8\epsilon_0^2 h^2}} \quad \text{Energies are quantized!!!}$$



For H atom, emission spectrum

$$\bar{\nu}(\text{cm}^{-1}) = \frac{E_{n_2}}{hc} - \frac{E_{n_1}}{hc} = \frac{me^4}{8\epsilon_0^2 h^3 c} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Rydberg formula! with  $R = \frac{me^4}{8\epsilon_0^2 h^3 c} = 109,737 \text{ cm}^{-1}$

Measured value is  $109,678 \text{ cm}^{-1}$  (Slight difference due to model that gives nucleus no motion at all, i.e. infinite mass.)

### Names, Wavelength Ranges, and Formulas for the Hydrogen Series

Lyman	Ultraviolet	$k = R_{\text{H}} \left( \frac{1}{1^2} - \frac{1}{n^2} \right), \quad n = 2, 3, 4, \dots$
Balmer	Near ultraviolet and visible	$k = R_{\text{H}} \left( \frac{1}{2^2} - \frac{1}{n^2} \right), \quad n = 3, 4, 5, \dots$
Paschen	Infrared	$k = R_{\text{H}} \left( \frac{1}{3^2} - \frac{1}{n^2} \right), \quad n = 4, 5, 6, \dots$
Brackett	Infrared	$k = R_{\text{H}} \left( \frac{1}{4^2} - \frac{1}{n^2} \right), \quad n = 5, 6, 7, \dots$
Pfund	Infrared	$k = R_{\text{H}} \left( \frac{1}{5^2} - \frac{1}{n^2} \right), \quad n = 6, 7, 8, \dots$

Comparing to exp't, value of "h" matches the one found by Planck!

*This was an extraordinary result !*

## Summary:

- (1) Structure of atom can't be explained classically
- (2) Discrete atomic spectra and Rydberg's formula can't be explained
- (3) Blackbody radiation can be "explained" by quantifying energy of oscillators  $E = h\nu$
- (4) Photoelectric effect can be "explained" by quantifying energy of light  $E = h\nu$