

Elastic gel can imbibe water when placed in it and undergo swelling, non-elastic gels are incapable of doing so. This phenomenon is known as imbibition or swelling.

6.10 APPLICATIONS OF COLLOIDS

Most of the substances, we come across in our daily life, are colloids. The meal we eat, the clothes we wear, the wooden furniture we use, the houses we live in, the newspapers we read, are largely composed of colloids.

The applications of colloid chemistry are limitless. These can be divided mainly into two classes:

1. Natural applications
2. Technical applications

1. Natural Applications

(i) **Blue colour of the sky:** Colloidal particles scatter blue light. Dust particles along with water suspended in air scatter blue light which reaches our eyes and the sky looks blue to us.

(ii) **Fog, mist and rain:** When a large mass of air, containing dust particles, is cooled below its dewpoint, the moisture from the air condenses on the surfaces of these particles forming fine droplets. These droplets being colloidal in nature continue to float in the air in the form of mist or fog.

Clouds are aerosols having small droplets of water suspended in air. On account of condensation in the upper atmosphere, the colloidal droplets of water grow bigger and bigger in size, till they come down in the form of rain. Sometimes, the rainfall occurs when two oppositely charged clouds meet.

It is possible to cause artificial rain by throwing electrified sand or spraying a sol carrying charge opposite to the one on clouds from an aeroplane.

(iii) **Food articles:** Milk, butter, halwa, ice creams, fruit juices, etc., are all colloids in one form or the other.

(iv) **Blood:** Blood is a colloidal solution of an albuminoid substance. The styptic action of alum and ferric chloride solution is due to coagulation of blood forming a clot which stops further bleeding.

(v) **Soils:** Fertile soils are colloidal in nature in which humus acts as a protective colloid. On account of colloidal nature, soils absorb moisture and nourishing materials.

(vi) **Formation of delta:** River water is colloidal solution of clay. Seawater contains a number of electrolytes. When river water meets the seawater, the electrolytes present in seawater coagulate the colloidal solution of clay which gets deposited with the formation of delta.

2. Technical Applications

(i) **Electrical precipitation of smoke:** Smoke is a colloidal solution of solid particles such as carbon, arsenic compounds, dust, etc., in air. The smoke, before it comes out from the chimney, is led through a chamber containing plates having a charge opposite to that carried by smoke particles. The particles on coming in contact with these plates lose their charge and get

precipitated. The particles thus, settle down on the floor of the chamber. The precipitator is called **Cottrell precipitator**.

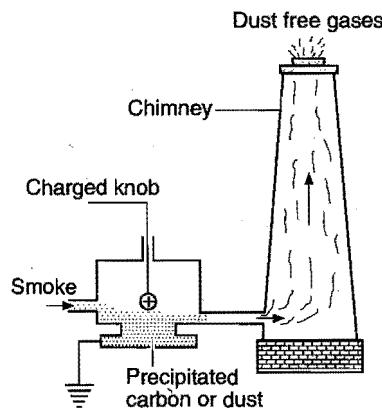


Fig. 6.14

(ii) **Purification of drinking water:** The water obtained from natural sources often contains bacteria and suspended impurities. Alum is added to such water so as to destroy the bacteria as well as to coagulate the suspended impurities and make water fit for drinking purposes.

(iii) **Medicines:** Most of the medicines in use are colloidal in nature. For example, argyrol is a silver sol used as an eye lotion. Colloidal antimony is used in curing kala-azar. Colloidal gold is used for intramuscular injection. Milk of magnesia (an emulsion) is used for stomach disorders. Colloidal medicines are more effective because these are easily assimilated.

(iv) **Tanning:** Animal hides are colloidal in nature. When a hide, which has positively charged particles, is soaked in tannin, which contains negatively charged colloidal particles, mutual coagulation takes place, which results in the hardening of leather. The process is termed as **tanning**. Chromium salts have also been used in place of tannin.

(v) **Cleansing action of soaps and detergents:** Already described in section 6.8.

(vi) **Photographic plates and films:** The photographic plates or films are prepared by coating an emulsion of the light sensitive silver bromide in gelatin over glass plates or celluloid films.

(vii) **Rubber industry:** Latex is a colloidal solution of rubber particles which are negatively charged. Rubber is obtained by coagulation of latex.

(viii) **Industrial products:** Paints, inks, synthetic plastics, rubber, graphite lubricants, cement, etc., are all colloidal solutions. Asphalt emulsion is used in road construction.

(ix) **Disinfectants:** The disinfectants such as dettol and lysol give emulsion of oil in water type when mixed with water.

(x) **In metallurgy:** Sulphide ores are concentrated by froth-flotation process. In this process; pulverised ore is treated with emulsion of pine oil.

SUMMARY AND IMPORTANT POINTS TO REMEMBER

1. Crystalloids and colloids: Thomas Graham classified the soluble substances into two categories; crystalloids and colloids. Crystalloids are the substances which in solution diffuse readily through animal or vegetable membranes, e.g., urea, sugar, salt and other crystalline compounds. Colloids (Greek word, *Kolla*, meaning glue-like) are the substances which in solution diffuse very slowly or do not diffuse through animal or vegetable membranes, e.g., gelatin, glue, silicic acid, etc. It was soon realised that many of the crystalloids can be converted into colloidal form by suitable means. Thus, colloid is a state of matter like solid, liquid or gas in which any substance can be brought by suitable means.

2. Colloidal state: It depends upon the particle size. It is regarded as an intermediate state between true solution and suspension. Colloidal state is a heterogeneous system in which solute particles of size ranging between 10 \AA to 10^3 \AA (10^{-7} to 10^{-5} cm) are dispersed into a solvent (dispersion medium).

3. Types of colloidal solutions: A colloidal solution consists two types, viz, dispersed or internal or discontinuous phase and the dispersion or external or continuous phase. Depending on these phases eight types of colloidal solutions are possible. The important ones are:

- (i) Solid dispersed in liquid—It is called sol.
- (ii) Liquid dispersed in liquid—It is called emulsion.
- (iii) Solid dispersed in gas—It is called aerosol.
- (iv) Liquid dispersed in solid—It is called gel.

Lyophobic: Colloidal solutions in which dispersed phase has very little affinity for the dispersion medium. These are less stable and irreversible in nature. These are also called suspensoids.

Lyophilic: Colloidal solutions in which dispersed phase has great affinity for dispersion medium. These are stable and reversible in nature. These are also called emulsoids.

The colloidal solutions are also named according to the dispersion phase or medium used.

| Dispersion medium | Name of colloidal solution |
|-------------------|----------------------------|
| Water | Hydrosols |
| Alcohol | Alcosols |
| Benzene | Benzosols |
| Air | Aerosols |

4. Preparation of colloidal solutions: To get a substance in colloidal form either the substance is broken down into fine particles of colloidal dimension or increasing the size of molecular particles as to form large aggregates. Thus, there are two ways by which lyophobic sols can be prepared.

(i) Dispersion methods: By splitting coarse aggregates of a substance into colloidal size. The dispersion methods include (a) mechanical dispersion (b) electro-dispersion (c) ultrasonic dispersion and (d) peptization. Peptization is a process of converting precipitates into colloidal state by adding small amount of suitable electrolyte.

(ii) Condensation methods: By aggregating very small particles into colloidal particles. These include (a) exchange of solvents (b) change of physical state and (c) chemical methods such as double decomposition, oxidation, reduction, hydrolysis, etc.

5. Purification of colloidal solutions: The process of reducing the impurities (electrolytes or soluble substances) to a requisite minimum in a colloidal solution is known as purification of colloidal solution.

Dialysis: It is a process of removing a dissolved substance from a colloidal solution by means of diffusion through suitable membrane. Animal membranes, parchment paper or cellophane sheet can be used for this purpose. The electrolytes can be readily removed by electrodialysis.

6. Properties of colloidal solutions: Colloidal solutions possess the following properties:

- (i) **Heterogeneous character:** Consist of two phases.
- (ii) **Visibility:** Particles are not visible to naked eye or with the help of microscope.
- (iii) **Filtrability:** Particles pass through ordinary filter paper but not through parchment and other fine membranes.
- (iv) **Surface tension and viscosity:** These are not very different from those of dispersion medium in the case of lyophobic sols. Lyophilic sols show higher viscosity and lower surface tension.
- (v) **Colligative properties:** These properties are of small order as compared to true solutions at same concentrations.
- (vi) **Tyndall effect:** It is the scattering of light from the surface of colloidal particles. A beam of light passed through a colloidal solution becomes visible as a bright streak. The illuminated path is called Tyndall cone.
- (vii) **Brownian movement:** It is a ceaseless zig-zag motion of colloidal particles. Smaller the size and lesser the viscosity, faster is the motion. This is due to unbalanced bombardment of particles by the molecules of dispersion medium. It is somewhat responsible for stability of sols as the particles are not allowed to settle.
- (viii) **Charge on colloidal particles:** Colloidal particles are electrically charged either carrying positive or negative charge. The origin of charge in most cases is due to preferential adsorption of ions on the surface. When an electric current is passed through the colloidal solution, the particles move towards a particular electrode. This is termed electrophoresis or cataphoresis. When only the medium is allowed to migrate and not the particles, the phenomenon is known as electroosmosis.

(ix) Coagulation: The phenomenon of change of colloidal state to suspension state is known as coagulation or precipitation or flocculation of colloidal solution. The coagulation is affected either by boiling of colloidal solution or by mutual action of colloidal sols (by mixing oppositely charged colloidal solutions) or by electrophoresis or by the addition of electrolytes.

The positive ion is effective in coagulating negative sol and vice-versa. The effectiveness of anion is governed by Hardy-Schulze rule. The rule states that the precipitating power of an ion depends upon its valency, i.e., higher the valency of the ion greater is the precipitating power of the ion.

For negative sol, the power varies as $M^{3+} > M^{2+} > M^+$ and for positive sol the power varies as $[Fe(CN)_6]^{4-} > SO_4^{2-} > Cl^-$.

Flocculating value: It is the minimum concentration in millimoles per litre of an electrolyte required to cause precipitation of a sol in 2 hours. The smaller is the flocculating power greater shall be the precipitating power of an ion.

(x) **Protective action:** Lyophilic sols are more stable than lyophobic sols. Thus, lyophilic colloids have the property of protecting lyophobic sols. When a lyophilic sol is added to lyophobic sol, the lyophilic particles form a layer around lyophobic particles and thus protect them from electrolytes. The protective power of lyophilic colloid is measured in terms of gold number. It is defined as the number of milligrams of a lyophilic colloid that will just prevent the precipitation of 10 mL of a gold sol on the addition of 1 mL of 10% NaCl solution. Lower the gold number, higher will be the protective power. Gelatin (Gold Number 0.005–0.01) and starch (Gold Number 25–50) have the maximum and minimum protective powers.

(xi) **Coacervation:** The loss of the stability of a lyophilic sol, quite often results in a separation of the system into two liquid phases. The separation of colloidal sol into two liquid phases is called coacervation.

7. **Emulsion:** It is a colloidal solution of a liquid in another immiscible liquid. Emulsions are usually of two types:

- (a) Oil in water—Examples: Milk, cream, face cream, etc.
- (b) Water in oil—Examples: Butter, cold cream, etc.

Emulsifying agent: It is added to an oil and water emulsion to increase its stability. It has polar and non-polar groups; the former attaches to water and the latter to oil and so binds them together in an emulsion. Soaps and detergents act as emulsifying agents.

8. **Gel:** It is a colloidal system in which liquid is dispersed in solid. Fruit-jellies, cheese, etc., are the examples of gels. Gels may be elastic or non-elastic according to their mechanical properties.

9. **Applications of colloids:** The applications can be divided mainly into two classes:

(i) Natural applications:

- (a) Blue colour of the sky
- (b) Fog, mist and rain
- (c) Food articles
- (d) Blood
- (e) Soils
- (f) Formation of delta

(ii) Technical applications:

- (a) Electrical precipitation of smoke
- (b) Purification of drinking water
- (c) Medicines
- (d) Tanning
- (e) Cleansing action of soaps and detergents
- (f) Photographic plates and films
- (g) Rubber industry
- (h) Paints, inks, plastics, lubricants, cement, etc.

Questions

1. Match the following:
[A]

- | | |
|-------------------------|--|
| (i) Gold number | (a) Coagulation |
| (ii) Lyophobic | (b) An emulsion |
| (iii) Butter | (c) Gold sol |
| (iv) Hardy-Schulze rule | (d) Gel |
| (v) Micelles | (e) Purification of colloidal solution |
| (vi) Purple of cassius | (f) Protective colloids |
| (vii) Cheese | (g) Solvent hating |
| (viii) Dialysis | (h) Associated colloids |

[B]

- | | |
|-------------------------------|------------------------|
| (i) Brownian movement | (a) Aerosol |
| (ii) Water loving colloids | (b) Ultramicroscope |
| (iii) Liquid dispersed in gas | (c) Irreversible |
| (iv) Tyndall effect | (d) Sewage disposal |
| (v) Hydrophobic | (e) Smoke precipitator |
| (vi) Coagulation | (f) Hydrophilic |
| (vii) Electrophoresis | (g) Emulsifying agent |
| (viii) Soap | (h) Robert Brown |

[C] Property**Statement****Application / discoverer**

- | | | |
|-------------------------|---|------------------------|
| (i) Tyndall effect | (a) Due to unequal bombardment by solvent molecules | 1. Sewage disposal |
| (ii) Coagulation | (b) Surface area is large | 2. Smoke precipitator |
| (iii) Brownian movement | (c) Movement of colloidal particles under the influence of electric field | 3. Ultramicroscope |
| (iv) Adsorption | (d) Due to neutralisation of charge | 4. Ice cream |
| (v) Electrophoresis | (e) Due to scattering of light | 5. Colloidal medicines |
| (vi) Stability | (f) Addition of protective colloid | 6. Robert Brown |

2. Matrix Matching Problems (For IIT Aspirants):

- [A]** Match the colloids in Column-I with the classifications in Column-II:

| Column-I | Column-II |
|-----------------|------------------|
| (a) Rain cloud | (p) Gel |
| (b) Smoke | (q) Foam |

- (c) Butter (r) Aerosol

- (d) Soap sud (s) Gas as dispersion medium

[B] Match the terms of List-I with those of List-II:

| List-I | List-II |
|---------------|----------------|
|---------------|----------------|

- | | |
|--------------------|---|
| (a) Coagulation | (p) Scattering of light |
| (b) Peptization | (q) Purification of colloidal solution |
| (c) Tyndall effect | (r) Addition of electrolyte |
| (d) Dialysis | (s) Precipitation of colloidal solution |

[C] Match the Column-I with Column-II and Column-III:

| Column-I (Colloidal solution) | Column-II (Dispersed phase) | Column-III (Dispersion medium) |
|--|--|---|
|--|--|---|

- | | | |
|----------------|---------------|-------------|
| (a) Colloidion | (p) Water | (u) Ethanol |
| (b) Fog | (q) Cellulose | (v) Oil |
| (c) Butter | (r) Fat | (w) Air |
| (d) Milk | (s) Water | (x) Water |

[D] Match the terms in Column-I with their explanations in Column-II:

| Column-I | Column-II |
|-----------------|------------------|
|-----------------|------------------|

- | | |
|----------------------------|--|
| (a) Cottrell precipitation | (p) Purification of blood |
| (b) Electrophoresis | (q) Precipitation of colloidal particles by addition of electrolytes |
| (c) Hemodialysis | (r) Removal of pollutants from industrial waste gases |
| (d) Coagulation | (s) Movement of charged colloidal particles towards oppositely charged electrode |

[E] Match the terms in Column-I with those of Column-II:

| Column-I | Column-II |
|-----------------|------------------|
|-----------------|------------------|

- | | |
|---------------------------|--------------------------------|
| (a) Emulsifier | (p) Colloidal sol. of graphite |
| (b) Colloidal electrolyte | (q) Detergent |
| (c) Oil dag | (r) Cellophane |
| (d) Xerogel | (s) Dextrin |

[F] Match the Column-I with Column-II:

| Column-I | Column-II |
|-----------------|------------------|
|-----------------|------------------|

- | | |
|------------|--------------|
| (a) Milk | (p) Aerosol |
| (b) Dust | (q) Emulsion |
| (c) Cheese | (r) Gel |
| (d) Froth | (s) Foam |

3. The coagulation of 100 mL of a colloidal solution of gold is completely prevented by adding 0.25 g of starch to it before adding 10 mL of 10% NaCl solution. Find out the gold number of starch.

[Hint: 10 mL of 10% NaCl solution is added to 100 mL of solution of gold.]

Thus, 1 mL of 10% NaCl solution has been added to 10 mL solution of gold.

Since, 100 mL gold solution required = 0.25 g starch

$$= 0.25 \times 10^3 \text{ mg starch}$$

$$\text{So, } 10 \text{ mL gold solution required} = \frac{0.25 \times 10^3}{100} \times 10$$

$$= 25 \text{ mg starch}$$

Thus, by definition, the gold number of starch is 25.]

4. For the coagulation of 100 mL of arsenious sulphide solution, 5 mL of 1 M NaCl is required. What is the coagulating power of NaCl?

[Hint: Total volume after addition of 5 mL of 1 M NaCl solution = 105 mL]

Thus, $105 \times \text{molarity of NaCl in colloidal solution} = 5 \times 1$

$$\text{Molarity of NaCl in colloidal solution} = \frac{5}{105}$$

$$\text{Concentration in millimole} = \frac{5}{105} \times 1000$$

$$= 47.6$$

Answers

- [A] (i—g); (ii—g); (iii—b); (iv—a); (v—h); (vi—c); (vii—d); (viii—e)
 [B] (i—h); (ii—f); (iii—a); (iv—b); (v—c); (vi—d); (vii—e); (viii—g)
 [C] (i—e—3); (ii—d—1); (iii—a—6); (iv—b—5); (v—c—2); (vi—f—4).
- [A] (a—r, s) (b—r, s) (c—p) (d—q)
 [B] (a—r, s) (b—r) (c—p) (d—q)
 [C] (a—q—u) (b—p—w) (c—p—v) (d—r—x)
 [D] (a—r, s) (b—s) (c—p) (d—q)
 [E] (a—q, s) (b—q) (c—p) (d—r)
 [F] (a—q) (b—p) (c—r) (d—s)

OBJECTIVE QUESTIONS

Set-1: Questions with single correct answer

- Difference between crystalloid and colloid is of:
 (a) particle size (b) chemical composition
 (c) ionic character (d) solubility
- Substances whose solutions can readily diffuse through animal membranes are called:
 (a) colloids (b) crystalloids
 (c) electrolytes (d) non-electrolytes
- Suspensions are:
 (a) visible to naked eye
 (b) invisible through microscope
 (c) not visible by any means
 (d) invisible under electron microscope
- The size of the colloidal particles is in between: (CPMT 1990)
 (a) $10^{-7} - 10^{-9}$ cm (b) $10^{-9} - 10^{-11}$ cm
 (c) $10^{-5} - 10^{-7}$ cm (d) $10^{-2} - 10^{-3}$ cm
- The size of a colloidal particle is: [PMT (MP) 1990]
 (a) $> 0.1\mu$ (b) $1\mu\text{m}$ to $0.1\mu\text{m}$
 (c) $< 0.1\mu\text{m}$ (d) more than $3000\mu\text{m}$
- If liquid is dispersed in solid medium, then this is called: (DCE 2009)
 (a) sol (b) emulsion
 (c) liquid aerosol (d) gel

- Which of the following forms a colloidal solution in water?
 (CPMT 1990)
 (a) NaCl (b) Glucose (c) $\text{Ba}(\text{NO}_3)_2$ (d) Starch
- The number of phases present in colloidal solution is:
 (a) 2 (b) 4 (c) 3 (d) 1
- The colloidal system of a solid dispersed in liquid medium is called: [CET (J&K) 2007]
 (a) aerosol (b) sol (c) gel (d) foam
- When dispersed phase is liquid and dispersion medium is gas, the colloidal system is called:
 (a) smoke (b) emulsion (c) cloud (d) gel
- Water loving colloids are called as:
 (a) hydrophilic (b) hydrophobic
 (c) lyophobic (d) irreversible
- An emulsion is a colloidal solution consisting of:
 (a) two solids (b) two liquids
 (c) two gases (d) one solid and one liquid
- The colloidal solution of gelatin is known as:
 (a) solvent loving (b) reversible
 (c) hydrophilic (d) all of these
- Sol is a type of colloid in which: [PET (Raj.) 2008]
 (a) solid is dispersed in liquid
 (b) liquid is dispersed in solid
 (c) gas is dispersed in liquid
 (d) solid is dispersed in solid

15. Butter is a colloid formed when:
 (a) fat is dispersed in fat
 (b) fat is dispersed in water
 (c) water is dispersed in fat
 (d) suspension of casein in water
16. Milk is: [PMT (MP) 2007; C.G. PET 2008]
 (a) fat dispersed in water (b) water dispersed in fat
 (c) water dispersed in oil (d) fat dispersed in fat
17. Smoke is an example of: (CPMT 1991)
 (a) solid dispersed in solid (b) solid dispersed in gas
 (c) solid dispersed in liquid (d) gas dispersed in solid
18. Fog is a colloidal solution of: [PMT (MP) 1991; CET (J&K) 2005; DUMET 2009]
 (a) gaseous particles dispersed in gas
 (b) gaseous particles dispersed in liquids
 (c) liquid dispersed in gas
 (d) solid dispersed in liquid
19. Lyophobic colloids are:
 (a) reversible (b) irreversible
 (c) water loving (d) solvent loving
20. Sulphur sol contains:
 (a) discrete sulphur atoms
 (b) discrete sulphur molecules
 (c) water dispersed in solid sulphur
 (d) large aggregates of sulphur molecules
21. Which of the following is not a colloidal system?
 (a) Bread (b) Muddy water
 (c) Concrete (d) Sugar in water
22. Peptization denotes: (MHT-CET 2007)
 (a) digestion of food
 (b) hydrolysis of proteins
 (c) breaking and dispersion into colloidal state
 (d) precipitation of solid from colloidal dimension
23. Colloids are purified by: (CPMT 1990)
 (a) Brownian motion (b) precipitation
 (c) dialysis (d) filtration
24. The separation of colloidal particles from those of molecular dimension is known as:
 (a) dialysis (b) electrophoresis
 (c) peptization (d) pyrolysis
25. Bredig's arc method is used for the preparation of colloidal solution of:
 (a) metals like silver, gold, etc.
 (b) organic compounds
 (c) two liquids
 (d) inorganic compounds
26. Which of the following reactions is not used for the preparation of a colloidal solution?
 (a) $2\text{AuCl}_3 + 3\text{SnCl}_2 \longrightarrow 3\text{SnCl}_4 + 2\text{Au}$
 (b) $\text{FeCl}_3 + 3\text{H}_2\text{O} \longrightarrow \text{Fe(OH)}_3 + 3\text{HCl}$
 (c) $2\text{Mg} + \text{CO}_2 \longrightarrow 2\text{MgO} + \text{C}$
 (d) $2\text{H}_2\text{S} + \text{SO}_2 \longrightarrow 2\text{H}_2\text{O} + 3\text{S}$
27. When freshly precipitated Fe(OH)_3 is boiled with water in the presence of few drops of dil. HCl, a hydrated ferric oxide sol is obtained. This method is termed:
28. Which of the following substances gives a positively charged sol? [PMT (MP) 1990]
 (a) Gold (b) Arsenious sulphide
 (c) Starch (d) Ferric hydroxide
29. The kinetic activity of colloidal particles in dispersion medium is known as:
 (a) electro-osmosis (b) cataphoresis
 (c) Brownian movement (d) electrophoresis
30. Brownian movement was discovered by:
 (a) Robert Brown (b) Zsigmondy
 (c) Hardy-Schulze (d) Graham
31. The Brownian movement is due to:
 (a) temperature fluctuations within the liquid phase
 (b) attraction and repulsion between charges on colloidal particles
 (c) impact of molecules of the dispersion medium on colloidal particles
 (d) convection currents
32. Tyndall phenomenon is shown by:
 (a) dilute solution (b) colloidal solution
 (c) suspension (d) true solution
33. The sky looks blue due to:
 (a) dispersion effect (b) reflection
 (c) transmission (d) scattering
34. Tyndall effect in colloidal solution is due to: (MHT-CET 2007)
 (a) absorption of light
 (b) scattering of light
 (c) reflection of light
 (d) presence of electrically charged particles
35. The migration of colloidal particles under the influence of an electric field is known as:
 (a) electro-osmosis (b) Brownian movement
 (c) cataphoresis (d) dialysis
36. The stability of lyophilic colloids is due to: [PMT (MP) 1990]
 (a) charge on their particles
 (b) large size of their particles
 (c) smaller size of their particles
 (d) a layer of medium of dispersion on their particles
37. 'Greater the valency, the higher is the coagulating power of ion.' This rule was introduced by:
 (a) Hardy-Schulze (b) Graham
 (c) Kossel and Lewis (d) Faraday
38. Bleeding is stopped by the application of ferric chloride. This is because:
 (a) the blood starts flowing in opposite direction
 (b) the ferric chloride seals the blood vessel
 (c) the blood reacts and forms a solid which seals the blood vessel
 (d) the blood is coagulated and thus, the blood vessel is sealed
39. Which property of colloidal solution is used to determine the nature of charge on the particles?
 (a) Sedimentation (b) Electrophoresis
 (c) Dialysis (d) Ultrafiltration

40. When excess of electrolyte is added to a colloid it:
 (CBSE 1990)
 (a) coagulates (b) gets diluted
 (c) precipitates (d) does not change
41. The colloidal solutions of gold prepared by different methods have different colours. This is due to:
 (MLNR 1993)
 (a) difference in size of colloidal particles
 (b) different concentration of gold
 (c) presence of different types of foreign particles
 (d) the variable valency of gold
42. The capacity of an ion to coagulate a colloidal solution depends on:
 (a) its shape
 (b) the amount of its charge
 (c) the sign of the charge
 (d) both, the amount and the sign of the charge
43. Lyophilic sols are more stable than lyophobic sols because:
 (AFMC 1998)
 (a) the colloidal particles have positive charge
 (b) the colloidal particles have negative charge
 (c) the colloidal particles are solvated
 (d) there are strong electrostatic repulsions
44. Which of the following will have the highest coagulating power for As_2S_3 colloid?
 (a) PO_4^{3-} (b) Al^{3+} (c) SO_4^{2-} (d) Na^+
45. A negatively charged suspension of clay in water will need for precipitation the minimum amount of:
 (a) aluminium chloride (b) potassium sulphate
 (c) sodium hydroxide (d) hydrochloric acid
46. Which of the following electrolytes is least effective in causing flocculation of ferric hydroxide sol? (MLNR 1991)
 (a) $\text{K}_3\text{Fe}(\text{CN})_6$ (b) K_2CrO_4
 (c) KBr (d) K_2SO_4
47. Fe^{3+} ions coagulate blood. This shows blood contains colloidal particles bearing:
 (a) negative charge
 (b) positive charge
 (c) no charge
 (d) either positive or negative charge
48. Gold number is a measure of:
 (CPMT 1991)
 (a) stability of colloidal system
 (b) coagulating power of a colloid
 (c) size of colloidal particles
 (d) efficiency of the protective colloid
49. Gold number is a measure of:
 [PET (MP) 2004]
 (a) the amount of gold present in the colloidal solution
 (b) the amount of gold required to break the colloid
 (c) the amount of gold required to protect the colloid
 (d) none of the above
50. Which of the following methods is used for destruction of a colloidal solution?
 (a) Condensation
 (b) Dialysis
 (c) Diffusion through animal membrane
 (d) Addition of an electrolyte
51. Which of the following is not a property of hydrophilic sols?
 (a) High concentration of dispersed phase can be easily attained
 (b) Coagulation is reversible
 (c) Viscosity and surface tension are nearly as that of water
 (d) The charge on the particles depends on the pH value of the medium; it may be positive, negative or even zero
52. Gelatin is added in manufacture of ice cream in order to:
 (a) prevent formation of a colloid
 (b) stabilise the colloid and prevent crystallisation
 (c) cause the mixture to solidify easily
 (d) improve flavour
53. Which one of the following will act as best protective colloid?
 (a) Gelatin (Gold No. 0.005)
 (b) Starch (Gold No. 25)
 (c) Gum arabic (Gold No. 0.15)
 (d) Egg albumin (Gold No. 0.08)
54. Gold number is a measure of the:
 (a) protective action by a lyophilic colloid on lyophobic colloid
 (b) protective action by a lyophobic colloid on lyophilic colloid
 (c) number of mg of gold in a standard red gold sol
 (d) none of the above
55. On addition of one mL solution of 10% NaCl to 10 mL gold sol in presence of 0.025 g of starch, the coagulation is just prevented. The gold number of starch is:
 (a) 25.0 (b) 2.5 (c) 0.25 (d) 0.025
56. The stability of lyophobic sols is due to:
 (a) Brownian motion only
 (b) electric charge only
 (c) both Brownian motion and electric charge
 (d) particle size
57. Which one of the following colloidal solutions is positive sol?
 (CPMT 1992)
 (a) Blood
 (b) Clay soil
 (c) Smoke
 (d) Gelatin in strongly acidic solution
58. All colloidal solutions show:
 (a) very high osmotic pressure
 (b) high osmotic pressure
 (c) low osmotic pressure
 (d) no osmotic pressure
59. Which of the following is associated colloid?
 (a) Soap (b) Detergent
 (c) Both (d) None of these
60. Which of the following is an emulsifier?
 (a) Oil (b) Soap (c) Solvent (d) KCl
61. An emulsifier is a substance which:
 (a) helps in the dispersion of liquid in liquid
 (b) stabilises the emulsion
 (c) coagulates the emulsion
 (d) purifies the emulsion

62. The gold numbers of some colloidal solutions are given below:

| Colloidal solution | Gold number |
|--------------------|-------------|
| A | 0.01 |
| B | 2.5 |
| C | 20 |

The projective powers of these colloidal solutions follow the order:

[CET (J&K) 2006; AIEEE 2008]

- (a) $C > B > A$ (b) $A > B > C$
 (c) $A = B = C$ (d) $B > A > C$
63. Dialyser is a name given to:
- (a) lyophilic colloids
 (b) lyophobic colloids
 (c) to a membrane which can separate colloids from the solution
 (d) none of the above
64. Flocculation value is expressed in terms of:
- (a) millimole per litre (b) mol per litre
 (c) gram per litre (d) mol per millilitre

65. Which of the following has minimum flocculation value?
- [PET (MP) 1990]

- (a) Pb^{2+} (b) Pb^{4+} (c) Sr^{2+} (d) Na^+

66. The charge of As_2S_3 sol is due to the absorbed:
- (a) H^+ (b) OH^- (c) O^{2-} (d) S^{2-}

67. Which of the following has maximum flocculation value?

- (a) $[Fe(CN)_6]^{4-}$ (b) Cl^-
 (c) SO_4^{2-} (d) PO_4^{3-}

68. Above critical micelle concentration, particles get:
- [AMU (Medical) 2006]

- (a) associated (b) dissociated
 (c) both (a) and (b) (d) none of these

69. Continuous phase contains dispersed phase throughout. Example is:
- (VITEEE 2008)

- (a) water in milk (b) fat in milk
 (c) water droplets in mist (d) oil in water

70. The movement of dispersion medium in an electric field when the dispersed particles are prevented from moving is called:
- (a) cataphoresis (b) electrophoresis
 (c) electro-osmosis (d) Brownian movement

71. To coagulate gelatin sol, which of the following is most effective?
- (a) $NaCl$ (b) Na_3PO_4 (c) $AlCl_3$ (d) Alcohol

72. The emulsifying agent in milk is:
- [EAMCET (Med.) 2010]
- (a) lactic acid (b) fat
 (c) lactose (d) casein

73. Colloidal solutions of metals like Cu, Ag, Au and Pt are generally prepared by using:
- (a) peptization (b) Bredig's arc method
 (c) exchange of solvent (d) oxidation method

74. Silver iodide is used for producing artificial rain because AgI :
- (a) has crystal structure similar to ice
 (b) is easy to spray at high altitudes
 (c) is easy to synthesise
 (d) is soluble in water

75. The minimum concentration of an electrolyte required to cause coagulation of a sol. is called:

- (a) flocculation value (b) gold number
 (c) protective value (d) coagulation number

76. Purple of cassius is:
- (a) colloidal solution of silver
 (b) colloidal solution of gold
 (c) colloidal solution of platinum
 (d) oxy acids of gold

77. Which type of molecules form micelles?
- (a) Polar molecules (b) Non-polar molecules
 (c) Surfactant molecules (d) Any of these

78. The name aquadag is given to the colloidal solution of:
- (a) copper in water (b) platinum in water
 (c) gold in water (d) graphite in water

79. A liquid is found to scatter a beam of light but leaves no residue when passed through the filter paper. The liquid can be described as:
- (AIIMS 1993)

- (a) a suspension (b) oil
 (c) a colloidal sol. (d) true solution

80. Point out the false statement:
- [CET (Punjab) 1991]

- (a) colloidal sols. are homogeneous
 (b) colloidal sols. carry +ve or -ve charge
 (c) colloidal sols. show Tyndall effect
 (d) the size of colloidal particles ranges between 10–2000 Å

81. The potential difference between the fixed charged layer and the diffused layer having opposite charge is called:

- (a) colloidal potential (b) zeta potential
 (c) electrostatic potential (d) none of these

82. An example of micelle is:

- (a) As_2O_3 sol.
 (b) ruby glass
 (c) Na_2CO_3 solution
 (d) sodium stearate concentrated solution

83. Surface tension of lyophilic sols. is:
- [PMT (MP) 1992]

- (a) lower than H_2O (b) more than H_2O
 (c) equal to H_2O (d) none of these

84. Which is not shown by sols.?
- [PMT (MP) 1992]

- (a) Adsorption (b) Tyndall effect
 (c) Flocculation (d) Paramagnetism

85. An example of solid-solid system is:

- (a) smoke (b) coke
 (c) synthetic gems (d) pumice stone

86. Detergent action of synthetic detergents is due to their:

- (a) interfacial area (b) high molecular weight
 (c) ionisation (d) emulsifying properties

87. Blood contains:

- (a) positively charged particles
 (b) negatively charged particles
 (c) neutral particles
 (d) negatively as well as positively charged colloids

88. A colloidal solution always has at least:
- (CPMT 1993)

- (a) one-phase (b) more than two-phases
 (c) a true solution (d) two phases

89. Silica gel is commonly used as:

- (a) wetting agent (b) drying agent
 (c) solvent (d) catalyst

90. Which is not a colloidal solution of gas in liquid?
 (a) Froth (b) Foams with tiny bubbles
 (c) Mist (d) Whipped cream
91. Fog is a colloidal solution of:
 [MLNR 1995; PMT (MP) 1991]
 (a) liquid particles dispersed in gas
 (b) gaseous particles dispersed in liquid
 (c) solid particles dispersed in liquid
 (d) solid particles dispersed in gas
92. Emulsions of polyvinyl acetate are used in:
 (a) polishes (b) latex paints
 (c) fireworks (d) rayons
93. When white light is passed through a colloidal solution containing fine suspended particles of gold, then the scattering light seen in a direction different from that of incident light is:
 (a) yellow coloured (b) blue coloured
 (c) green coloured (d) red coloured
94. When a sulphur sol is evaporated, solid sulphur is left. On mixing with water no colloidal sol is formed. The sulphur sol is:
 (a) hydrophilic (b) hydrophobic
 (c) reversible (d) lyophilic
95. Tails of comets are visible due to:
 (a) Tyndall effect (b) reflection
 (c) Brownian movement (d) none of these
96. Milk is an example of:
 [CPMT 1995; PET (MP) 2004; CET (J&K) 2004]
 (a) fat dispersed in water
 (b) water dispersed in fat
 (c) water dispersed in oil
 (d) fat dispersed in fat
97. Smog is an example of:
 (a) ice dispersed in air
 (b) water dispersed in air
 (c) smoke dispersed in air
 (d) smoke and water dispersed in air
98. Peptization denotes: [ISM (Dhanbad) 1994]
 (a) digestion of food
 (b) hydrolysis of proteins
 (c) breaking of dispersion into colloidal state
 (d) precipitation of a solid from colloidal state
99. Whipped cream is an example of:

| Dispersion Medium | Dispersed Phase |
|-------------------|-----------------|
| (a) Liquid | Gas |
| (b) Liquid | Liquid |
| (c) Liquid | Solid |
| (d) Gas | Liquid |
100. Cottrell precipitator acts on which of the following principle?
 (a) Hardy-Schulze rule
 (b) Distribution law
 (c) Le Chatelier's principle
 (d) Neutralization of charge on the colloidal particles
101. CMC (critical micelle concentration) is:
 (a) concentration at which micelles are destroyed
 (b) concentration at which micelle formation starts
- (c) concentration of electrolyte added to destroy the micelles
 (d) concentration of micelles at room temperature
102. Cod liver oil is: (CPMT 1997)
 (a) fat dispersed in water (b) water dispersed in fat
 (c) water dispersed in oil (d) fat dispersed in fat
103. Which is not lyophilic colloid? [PMT (MP) 1998]
 (a) Milk (b) Gum (c) Fog (d) Blood
104. At the critical micelle concentration, the surfactant molecules:
 (a) decompose (b) dissociate
 (c) associate (d) become completely soluble
105. Which of the following ions can cause coagulation of proteins?
 (a) Ag^+ (b) Na^+ (c) Mg^{2+} (d) Ca^{2+}
106. In Brownian movement or motion the paths of the particles are:
 (a) linear (b) zig-zag
 (c) uncertain (d) curved
107. Which is used for ending charge on colloidal solutions?
 (a) Electrons (b) Electrolysis
 (c) Positively charged ions (d) Compounds
108. Cloud or fog is a colloidal system in which the dispersed phase and the dispersion medium are: (KCET 2000)
 (a) gas, liquid (b) liquid, gas
 (c) liquid, liquid (d) solid, solid
109. The electrolyte which has the least effect in the coagulation of Fe(OH)_3 sol is: [KCET 2008]
 (a) potassium carbonate (b) sodium sulphate
 (c) potassium ferrocyanide (d) potassium iodide
110. Blood may be purified by: [PMT (MP) 2000]
 (a) dialysis (b) electro-osmosis
 (c) coagulation (d) filtration
111. Gold number was given by:
 (a) Ostwald (b) Zsigmondy
 (c) William and Chang (d) Langmuir
112. The diameter of colloidal particle ranges from: (KCET 2004)
 (a) 10^{-9} m to 10^{-6} m (b) 10^{-9} m to 10^{-12} m
 (c) 10^3 m to 10^{-3} m (d) 10^{-3} m to 10^{-6} m
113. The Tyndall effect is not observed in:
 (a) suspensions (b) emulsions
 (c) colloidal solutions (d) true solutions
114. Which one is example of Micelle's system?
 (a) Soap + water (b) Rubber + benzene
 (c) Protein + water (d) None of these
115. Sedimentation potential is the reverse of:
 (a) electro-osmosis (b) electrophoresis
 (c) electrokinetic potential (d) Dorn potential
116. Smoke has generally blue tinge. It is due to:
 (a) scattering (b) coagulation
 (c) Brownian motion (d) electrophoresis
117. On adding AgNO_3 solution to KI solution, a negatively charged colloidal sol will be formed in which of the following conditions?

- (a) 100 mL of 0.1 M AgNO_3 + 100 mL of 0.1 M KI
 (b) 100 mL of 0.1 M AgNO_3 + 50 mL of 0.2 M KI
 (c) 100 mL of 0.2 M AgNO_3 + 100 mL of 0.1 M KI
 (d) 100 mL of 0.1 M AgNO_3 + 100 mL of 0.15 M KI
118. Peptization of SnO_2 by NaOH gives:
 (a) $[\text{SnO}_2]\text{SnO}_3^{2-} : 2\text{Na}^+$ (b) $[\text{SnO}_2]\text{Sn}^{4+} : \text{O}^{2-}$
 (c) $[\text{SnO}_2]\text{Na}^+ : \text{OH}^-$ (d) $[\text{SnO}_2]\text{Sn}^{4+} : \text{OH}^-$
119. Alum helps in purifying water by: [AIEEE 2002]
 (a) forming Si complex with clay particles
 (b) sulphate part which combines with the dirt and remove it
 (c) aluminium which coagulates the mud particles
 (d) making the mud water soluble
120. Surface tension of lyophilic sols is: [PMT (MP) 2002]
 (a) lower than that of H_2O (b) equal to that of H_2O
 (c) more than that of H_2O (d) none of these
121. Arsenic sulphide is negative sol. The reagent with least precipitating power is: [PMT (Manipal) 2002]
 (a) AlCl_3 (b) NaCl (c) CaF_2 (d) glucose
122. Which one of the following is correctly matched? [CEE (Tamil Nadu) 2002]
 (a) Emulsion-curd (b) Foam-mist
 (c) Aerosol-smoke (d) Solid sol-cake
123. When H_2S gas is passed through nitric acid, the product is: [CEE (Kerala) 2002]
 (a) rhombic sulphur (b) prismatic sulphur
 (c) amorphous sulphur (d) monoclinic sulphur
 (e) plastic sulphur
124. Tyndall effect is shown by: [CECE (Bihar) Pre 2004]
 (a) precipitate (b) sol
 (c) plasma (d) solution
125. On addition of one mL of 10% NaCl solution to 10 mL gold sol in presence of 0.25 gm of starch, the coagulation is just prevented, starch has gold number: [PMT (MP) 2004]
 (a) 0.25 (b) 0.025 (c) 2.5 (d) none of these
126. Which of the following forms cationic micelles above certain concentration? [CBSE (PMT) 2004]
 (a) Sodium dodecyl sulphate
 (b) Sodium acetate
 (c) Urea
 (d) Cetyltrimethyl ammonium bromide
127. The smog is essentially caused by the presence of: [AIEEE 2004]
 (a) O_2 and O_3
 (b) O_2 and N_2
 (c) oxides of sulphur and nitrogen
 (d) O_3 and N_2
128. Which one of the following is most effective in causing the coagulation of an As_2S_3 sol? [EAMCET 2009]
 (a) KCl (b) AlCl_3
 (c) MgSO_4 (d) $\text{K}_3[\text{Fe}(\text{CN})_6]$
129. The fresh precipitate can be transformed in colloidal solution by: [CET (J&K) 2004]
 (a) peptization (b) coagulation
 (c) diffusion (d) none of these
130. Potassium stearate is obtained by the saponification of an oil or a fat. It has formula $\text{CH}_3 - (\text{CH}_2)_{16} - \text{COO}^- \text{K}^+$. The molecule has a lyophobic end ($\text{CH}_3 -$) and a lyophilic end $\text{COO}^- \text{K}^+$. Potassium stearate is an example for: [PET (Kerala) 2005]
 (a) lyophobic colloid
 (b) lyophilic colloid
 (c) multimolecular colloid
 (d) macromolecular colloid
 (e) associated colloid or micelle
131. Which one of the following forms micelles in aqueous solution above certain concentration? [CBSE (PMT) 2005]
 (a) Dodecyl trimethyl ammonium chloride
 (b) Glucose
 (c) Urea
 (d) Pyridinium chloride
132. Muddy water can be purified through coagulation using: [CET (J&K) 2005]
 (a) common salt (b) alums
 (c) sand (d) lime
133. The disperse phase in colloidal iron(III) hydroxide and colloidal gold is positively and negatively charged respectively. Which of the following is not correct? [AIEEE 2005]
 (a) Magnesium chloride solution coagulates the gold sol more readily than iron(III) hydroxide sol
 (b) Sodium sulphate solution causes coagulation in both sols
 (c) Mixing of the sols has no effect
 (d) Coagulation in both sols can be brought about by electrophoresis
134. An emulsifier is a substance which: [AIEEE 2005]
 (a) stabilises the emulsion
 (b) homogenises the emulsion
 (c) coagulates the emulsion
 (d) accelerates the dispersion of liquid in liquid
135. Gold number is associated with: [BHU (Mains) 2007; AMU (Engg.) 2010]
 (a) electrophoresis
 (b) purple of cassius
 (c) protective colloid
 (d) amount of pure gold
136. Which one of the following is a false statement? [PMT (Kerala) 2007]
 (a) Cell fluid is an example of sol
 (b) Butter is an example of gel
 (c) Hair cream is an example of emulsion
 (d) Whipped cream is an example of foam
 (e) Cheese is an example of emulsion
137. The presence of electric charge on colloidal particles is indicated by the property, called: [CET (J&K) 2007]
 (a) dialysis (b) solubility
 (c) electrophoresis (d) osmosis
138. Which of the following properties are characteristic of lyophobic sols? [SCRA 2007]
 1. Low viscosity, 2. High viscosity, 3. Reversibility and
 4. Coagulation by electrolytes at low concentration

Select the correct answer using the codes given below:

- | | |
|------------------|------------------|
| (a) 2, 3 and 4 | (b) 2 and 3 only |
| (c) 1 and 4 only | (d) 1 and 3 only |

139. In an electrical field, the particles of a colloidal system move towards cathode. The coagulation of the same sol is studied using K_2SO_4 (I), Na_3PO_4 (II), $K_4[Fe(CN)_6]$ (III) and $NaCl$ (IV). Their coagulating power should be :

[PMT (Kerala) 2008]

- | | |
|-------------------------------|-------------------------------|
| (a) (I) > (II) > (III) > (IV) | (b) (III) > (II) > (I) > (IV) |
| (c) (III) > (I) > (II) > (IV) | (d) (IV) > (III) > (I) > (II) |
| (e) (IV) > (I) > (II) > (III) | |

140. Cetyl trimethyl ammonium chloride is which type of detergent ? [CET (Gujarat) 2008]

- (a) Cationic (b) Anionic (c) Biosoft (d) Non-ionic

141. The effective ion used in clarification of water is: [KCET 2008]

- | | | | |
|---------------|---------------|-----------------|-----------------|
| (a) Al^{3+} | (b) Ca^{2+} | (c) SO_4^{2-} | (d) PO_4^{3-} |
|---------------|---------------|-----------------|-----------------|

142. The number of moles of lead nitrate needed to coagulate 2 mole of colloidal $[Ag I]^-$ is : [PET (Kerala) 2008]

- | | | | | |
|-------|-------|-------------------|-------------------|-------------------|
| (a) 2 | (b) 1 | (c) $\frac{1}{2}$ | (d) $\frac{2}{3}$ | (e) $\frac{5}{2}$ |
|-------|-------|-------------------|-------------------|-------------------|

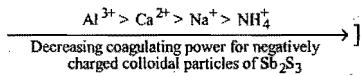
[Hint : $2[Ag I]^- + Pb^{2+} \rightarrow PbI_2 + 2AgI$

Thus, one mole of $Pb(NO_3)_2$ is required to coagulate 2 mole of $[AgI]^-$]

143. Among the electrolytes Na_2SO_4 , $CaCl_2$, $Al_2(SO_4)_3$ and NH_4Cl , the most effective coagulating agent for Sb_2S_3 sol is: [IIT 2009]

- | | |
|--------------------|--------------|
| (a) Na_2SO_4 | (b) $CaCl_2$ |
| (c) $Al_2(SO_4)_3$ | (d) NH_4Cl |

[Hint : Sb_2S_3 sol is negative colloid, therefore, $Al_2(SO_4)_3$ will be most effective coagulating agent.



144. A micelle formed during the cleansing action of soap is : [EAMCET (Engg.) 2010]

- | | |
|--|--|
| (a) a discrete particle of soap | |
| (b) aggregated particles of soap and dirt | |
| (c) a discrete particle of dust | |
| (d) an aggregated particle of dust and water | |

145. The dispersed phase and dispersion medium in soap lather are respectively : [PET (Kerala) 2010]

- | | |
|--------------------|----------------------|
| (a) gas and liquid | (b) liquid and gas |
| (c) solid and gas | (d) solid and liquid |

Set-2: The questions given below may have more than one correct answers

- Lysine is not used as:

| | |
|--------------------------|----------------------|
| (a) disinfectant | (b) germ killer |
| (c) treating eye disease | (d) anti-cancer drug |
- Which of the following are macromolecular colloids?

| | | | |
|------------|----------|---------------|---------------|
| (a) Starch | (b) Soap | (c) Detergent | (d) Cellulose |
|------------|----------|---------------|---------------|
- Multimolecular colloids are present in:

| | |
|--------------------|---------------------|
| (a) sol of sulphur | (b) sol of proteins |
| (c) sol of gold | (d) soap solution |
- Methods used for the preparation of colloidal solutions are:

| | |
|---------------------------|-----------------|
| (a) peptization | (b) hydrolysis |
| (c) ultrasonic dispersion | (d) coagulation |
- Isoelectric point is the pH at which colloidal particles:

| | |
|--------------------------------------|--|
| (a) coagulate | |
| (b) become electrically neutral | |
| (c) can move toward either electrode | |
| (d) none of the above | |
- Consider the following statements for micelles, which is/are correct?

| | |
|--|--|
| (a) At critical micelle concentration, several properties of solution of surfactants such as molar conductivity, surface tension and osmotic pressure change | |
| (b) Micelles from ionic surfactants can be formed only above a certain temperature called the Kraft temperature | |
| (c) Micelle formation is exothermic | |
| (d) Micelles are associated colloids | |
- Which of the following are negative colloids?

| | |
|--------------------|-------------------|
| (a) $Fe(OH)_3$ sol | (b) As_2S_3 sol |
| (c) Blood | (d) Gold sol |
- Which of the following are examples of aerosols?

| | |
|-------------------|-----------------|
| (a) Whipped cream | (b) Cloud |
| (c) Fog | (d) Soap lather |
- Tyndall effect is applicable when:

| | |
|--|--|
| (a) the diameter of the dispersed particles is not much smaller than the wavelength of the light used | |
| (b) the diameter of the dispersed particles is much smaller than the wavelength of the light used | |
| (c) the refractive indices of the dispersed phase and the dispersion medium must be same | |
| (d) the refractive indices of the dispersed phase and the dispersion medium must differ greatly in magnitude | |

Assertion-Reason TYPE QUESTIONS

The questions given below consist of two statements each printed as 'Assertion' (A) and 'Reason' (R). While answering these questions you are required to choose any one of the following four options:

- (a) If both (A) and (R) are correct and (R) is the correct explanation for (A).
 - (b) If both (A) and (R) are correct but (R) is not the correct explanation for (A).
 - (c) If (A) is correct but (R) is incorrect.
 - (d) If (A) is incorrect but (R) is correct.
1. (A) Colloidal silver iodide is prepared by adding silver nitrate in slight excess to potassium iodide solution. When subjected to an electric field, the colloidal particles migrate to the anode.
(R) Colloidal particles absorb ions and thus become electrically charged.
2. (A) Lyophilic colloids such as starch, gelatin, etc., act as protective colloids.
(R) Protective power of lyophilic colloids is expressed in terms of gold number.
3. (A) True solutions do not exhibit Tyndall effect.
(R) In true solutions, size of solute particles is much smaller than the wavelength of light used.
4. (A) The micelle formed by sodium stearate in water has $-\text{COO}^-$ groups at the surface.
(R) Surface tension of water is reduced by the addition of stearate. (AIIMS 2003)
5. (A) Lyophilic sols. are more stable than lyophobic sols.
(R) Lyophilic sols. are highly hydrated in the solution.
- 6. (A) Colloidal sol. of Fe(OH)_3 formed by peptization carries positive charge.
(R) During the formation of positively charged colloidal particles of Fe(OH)_3 , the electrons are lost by the colloidal particles of Fe(OH)_3 .
 - 7. (A) Colloidal solutions are purified by dialysis.
(R) In the process of dialysis, colloidal particles pass through parchment paper.
 - 8. (A) Fe^{3+} can be used for coagulation of As_2S_3 sol.
(R) Fe^{3+} reacts with As_2S_3 to give Fe_2S_3 . (AIIMS 2006)
 - 9. (A) Fat is digested in the intestine by emulsification.
(R) Bile salts stabilize the emulsion so formed.
 - 10. (A) NH_3Cl and RCOONa are colloidal electrolyte.
(R) The substances which behave as electrolyte below a certain concentration limit, beyond this limit colloidal sol. is formed, are called colloidal electrolyte.
 - 11. (A) Sulphide ores are concentrated by froth flotation process.
(R) Pine oil forms emulsion in water.
 - 12. (A) The conversion of fresh precipitate to colloidal state is called peptization.
(R) It is caused by addition of common ions. (AIIMS 2007)
 - 13. (A) Surfactant molecules form micelles above the critical micelle concentration (CMC).
(R) The conductance of solution of surfactant molecules decreases sharply at the (CMC).
 - 14. (A) Soap and detergent are macro-molecular colloids.
(R) Soap and detergent are molecular of large size.
 - 15. (A) Gold sol is hydrophobic and multimolecular.
(R) Gold sol is prepared by Bredig's arc method.

Answers : OBJECTIVE QUESTIONS

● Set-1

- | | | | | | | | |
|----------|----------|----------|----------|----------|----------|----------|----------|
| 1. (a) | 2. (b) | 3. (a) | 4. (c) | 5. (b) | 6. (d) | 7. (d) | 8. (a) |
| 9. (b) | 10. (c) | 11. (a) | 12. (b) | 13. (d) | 14. (a) | 15. (c) | 16. (a) |
| 17. (b) | 18. (c) | 19. (b) | 20. (d) | 21. (d) | 22. (c) | 23. (c) | 24. (a) |
| 25. (a) | 26. (c) | 27. (b) | 28. (d) | 29. (c) | 30. (a) | 31. (c) | 32. (b) |
| 33. (d) | 34. (b) | 35. (c) | 36. (d) | 37. (a) | 38. (d) | 39. (b) | 40. (a) |
| 41. (a) | 42. (d) | 43. (c) | 44. (b) | 45. (a) | 46. (c) | 47. (a) | 48. (d) |
| 49. (d) | 50. (d) | 51. (c) | 52. (b) | 53. (a) | 54. (a) | 55. (a) | 56. (c) |
| 57. (d) | 58. (c) | 59. (c) | 60. (b) | 61. (b) | 62. (b) | 63. (c) | 64. (a) |
| 65. (b) | 66. (d) | 67. (b) | 68. (a) | 69. (a) | 70. (c) | 71. (d) | 72. (d) |
| 73. (b) | 74. (a) | 75. (a) | 76. (b) | 77. (c) | 78. (d) | 79. (c) | 80. (a) |
| 81. (b) | 82. (d) | 83. (a) | 84. (d) | 85. (c) | 86. (d) | 87. (b) | 88. (d) |
| 89. (b) | 90. (c) | 91. (a) | 92. (b) | 93. (b) | 94. (b) | 95. (a) | 96. (a) |
| 97. (d) | 98. (c) | 99. (a) | 100. (c) | 101. (b) | 102. (c) | 103. (c) | 104. (c) |
| 105. (a) | 106. (b) | 107. (b) | 108. (b) | 109. (c) | 110. (a) | 111. (b) | 112. (a) |
| 113. (d) | 114. (a) | 115. (b) | 116. (a) | 117. (d) | 118. (a) | 119. (c) | 120. (a) |
| 121. (d) | 122. (c) | 123. (c) | 124. (b) | 125. (d) | 126. (d) | 127. (c) | 128. (b) |
| 129. (a) | 130. (e) | 131. (a) | 132. (b) | 133. (c) | 134. (a) | 135. (c) | 136. (e) |
| 137. (c) | 138. (c) | 139. (b) | 140. (a) | 141. (a) | 142. (b) | 143. (c) | 144. (b) |
| 145. (a) | | | | | | | |

● Set-2

- | | | | | | | | |
|--------------|-----------|-----------|--------------|--------------|--------------|--------------|-----------|
| 1. (b, c, d) | 2. (a, d) | 3. (a, c) | 4. (a, b, c) | 5. (a, b, c) | 6. (a, b, d) | 7. (b, c, d) | 8. (b, c) |
| 9. (a, d) | | | | | | | |

Answers : ASSERTION-REASON TYPE QUESTIONS

- | | | | | | | | |
|--------|---------|---------|---------|---------|---------|---------|--------|
| 1. (d) | 2. (b) | 3. (a) | 4. (a) | 5. (a) | 6. (c) | 7. (c) | 8. (c) |
| 9. (a) | 10. (a) | 11. (a) | 12. (b) | 13. (b) | 14. (d) | 15. (b) | |

BRAIN STORMING PROBLEMS

OBJECTIVE QUESTIONS for IIT ASPIRANTS

The following questions contain single correct option:

1. Which of the following statements are correct?
 1. On the application of an electric field, the particles of lyophobic sol may move in either direction or not move at all.
 2. Surface tension of lyophobic sols is similar to that of the dispersion medium.
 3. Electro-osmosis is the movement of the particles of dispersion medium under the influence of an electric field.

Select the correct answer using codes given below:
Codes:
 (a) 1, 2 and 3 (b) 1 and 3 (c) 2 and 3 (d) 1 and 2
2. Which of the following statements are correct?
 1. The smaller the gold number of lyophobic colloid, the larger will be its protective power.
 2. Lyophilic sols, in contrast to lyophobic sols are easily coagulated on addition of small amounts of electrolytes.
 3. Ferric chloride solution is used to stop bleeding from a fresh cut because it coagulates the blood.
 4. The flocculation value of arsenious sulphide sol is independent of the anion of the coagulating electrolyte.

Codes:
 (a) 1, 2 and 3 (b) 1, 3 and 4 (c) 2, 3 and 4 (d) 1, 2 and 4
3. Match the List-I with List-II and select the correct answer using the codes given below the lists:

| List-I | List-II |
|-------------------|-----------------------------|
| A. Coagulation | 1. Scattering |
| B. Lyophilization | 2. Washing of precipitates |
| C. Peptization | 3. Purification of colloids |
| D. Tyndall effect | 4. Electrolyte |

Codes:

| A | B | C | D |
|-------|---|---|---|
| (a) 4 | — | 2 | 1 |
| (b) 2 | — | 3 | 4 |
| (c) — | 1 | 2 | 4 |
| (d) 4 | 3 | 1 | — |
4. The flocculating power of the given ions for the specified colloidal sols will be such that:

| Arsenic sulphide sol | Ferric hydroxide sol |
|---|---|
| (a) $[\text{Fe}(\text{CN})_6]^{4-} > \text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{Cl}^-$ | $\text{Al}^{3+} > \text{Ba}^{2+} > \text{Na}^+$ |
| (b) $\text{Al}^{3+} > \text{Ba}^{2+} > \text{Na}^+$ | $[\text{Fe}(\text{CN})_6]^{4-} > \text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{Cl}^-$ |
| (c) $\text{Na}^+ > \text{Ba}^{2+} > \text{Al}^{3+}$ | $\text{Cl}^- > \text{SO}_4^{2-} > \text{PO}_4^{3-} > [\text{Fe}(\text{CN})_6]^{4-}$ |
| (d) $\text{Cl}^- > \text{SO}_4^{2-} > \text{PO}_4^{3-} > [\text{Fe}(\text{CN})_6]^{4-}$ | $\text{Na}^+ > \text{Ba}^{2+} > \text{Al}^{3+}$ |
5. The coagulation value in millimoles per litre of electrolytes used for the coagulation of As_2S_3 are as below:
 I. $\text{NaCl} = 52$ II. $\text{KCl} = 51$
 III. $\text{BaCl}_2 = 0.69$ IV. $\text{MgSO}_4 = 0.22$
 The correct order of their flocculating power is:
 (a) I > II > III > IV (b) I > II > III = IV
 (c) IV > III > II > I (d) IV = III > II > I
6. Cotrell precipitator works on the principle of:
 (a) distribution law
 (b) addition of electrolyte
 (c) neutralisation of charge on colloids
 (d) Le Chatelier's principle
7. The substances involved in micellization are:
 (a) polyphilic in nature (b) non-polar in nature
 (c) diphilic in nature (d) uniphilic in nature
8. The swelling of 'gel' when placed in water is called:
 (a) gelation (b) imbibition (c) thixotropy (d) syneresis
9. A lyophilic sol is at its isoelectric point then it is:
 (a) negatively charged (b) positively charged
 (c) not charged (d) none of these
10. Sedimentation potential is reverse of:
 (a) electro-osmosis (b) electrophoresis
 (c) electrokinetic potential (d) streaming potential
11. The potential difference between the fixed charged layer and the diffused layer having opposite charge is called:
 (a) zeta potential (b) colloidal potential
 (c) Dorn potential (d) streaming potential
12. Silver iodide is used for producing artificial rains because AgI :
 (a) is easy to spray at high altitude
 (b) is insoluble in water
 (c) is easy to synthesize
 (d) has crystals similar to ice
13. All colloidal solutions show:
 (a) very high osmotic pressure
 (b) high osmotic pressure
 (c) low osmotic pressure
 (d) no osmotic pressure
14. Colloidion is a colloidal solution of:
 (a) sucrose in water
 (b) cellulose in water
 (c) cellulose nitrate in water
 (d) cellulose nitrate in ethyl alcohol
15. During micelle formation:
 (a) $\Delta H = + \text{ve}$, $\Delta S = + \text{ve}$ (b) $\Delta H = - \text{ve}$, $\Delta S = - \text{ve}$
 (c) $\Delta H = - \text{ve}$, $\Delta S = + \text{ve}$ (d) $\Delta H = + \text{ve}$, $\Delta S = - \text{ve}$
16. Which of the following is not the property of hydrophilic solutions?
 (a) High concentration of dispersed phase can be easily obtained

- (b) Coagulation is reversible
 (c) Viscosity and surface tension are nearly same as that of water
 (d) The charge of the particles depends on the pH of the medium and it may be positive, negative or zero
17. The coagulation of 100 mL of colloidal solution of gold is completely prevented by addition of 0.25 g of a substance "X" to it before addition of 1 mL of 10% NaCl solution. The gold number of "X" is:
 (a) 0.25 (b) 25 (c) 250 (d) 2.5
[Hint: Number of milligrams of protective colloid added in 10 mL of colloidal gold to prevent its coagulation on addition of 1 mL of 10% NaCl solution is called its gold number.
 ∴ Gold number of present colloid = 25]
18. Select the non-elastic gel out of the following:
 (a) starch (b) agar-agar (c) silicic acid (d) gelatin
19. The colligative properties of a colloidal solution compared to the solution of non-electrolyte of same concentration will be:
 (a) same (b) higher
 (c) lower (d) higher or lower
20. 1 mole of AgI/Ag^+ sol. is coagulated by:
 (a) 1 mole of KI (b) 500 mL of 1 M K_2SO_4
 (c) 300 mL of 1 M Na_3PO_4 (d) 1 mole of AgI
21. Match the List-I (Colloidal dispersion) with List-II (Nature of dispersion) and select the correct answer using the codes given below the lists: (SCRA 2007)

List-I
(Colloidal dispersion)
 A. Milk
 B. Clouds

List-II
(Nature of dispersion)
 1. Solid in liquid
 2. Liquid in gas

- C. Paints 3. Solids in solid
 D. Jellies 4. Liquids in liquid
 5. Liquid in solid
 (a) A-4, B-2, C-1, D-5 (b) A-1, B-5, C-3, D-2
 (c) A-4, B-5, C-1, D-2 (d) A-1, B-2, C-3, D-5
22. At CMC, the surfactant molecules undergo:
 (a) association (b) aggregation
 (c) micelle formation (d) all of these
23. The blue colour of the water of the sea is due to:
 (a) reflection of blue light by salts present in water
 (b) scattering of blue light by sol. particles
 (c) refraction of blue coloured light by the impurities present in seawater
 (d) absorption of radiation of different colours except blue light
24. **Statement :** To stop bleeding from an injury ferric chloride can be applied.
 Which comment about the statement is justified?
[PMT (Kerala) 2008]
- (a) It is not true, ferric chloride is a poison
 (b) It is true, Fe^{3+} ions coagulate blood which is negatively charged sol
 (c) It is not true, Cl^- ions form positively charged sol, profuse bleeding takes place
 (d) It is true, coagulation takes place because of formation of negatively charged sol with Cl^- ions
 (e) It is not true, ferric chloride is ionic and gets into blood stream

Answers

- | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (c) | 2. (a) | 3. (a) | 4. (b) | 5. (c) | 6. (c) | 7. (c) | 8. (b) |
| 9. (c) | 10. (b) | 11. (a) | 12. (a) | 13. (c) | 14. (c) | 15. (a) | 16. (c) |
| 17. (b) | 18. (c) | 19. (c) | 20. (a) | 21. (a) | 22. (d) | 23. (b) | 24. (b) |

LINKED COMPREHENSION TYPE QUESTIONS

● Passage 1

There are certain substances which behave as normal, strong electrolytes at low concentration but at higher concentration they behave as colloidal solutions due to the formation of aggregated particles. Such colloids are called associated colloids and the aggregated particles are called micelles. Soaps and detergents are the examples of associated colloids. The formation of micelles takes place above certain concentration called critical micellization concentration (CMC) and a characteristic temperature.

Answer the following questions:

- Micelles are:
 (a) emulsions cum gels
 (b) associated colloids
 (c) adsorbed catalysts
 (d) ideal solutions

- What type of molecules form micelles?
 (a) Non-polar molecules
 (b) Polar molecules
 (c) Surfactant molecules
 (d) Salt of weak acid and weak base
- Micelles are formed only:
 (a) below the CMC and the Kraft temperature
 (b) above the CMC and below the Kraft temperature
 (c) above the CMC and above the Kraft temperature
 (d) below the CMC and above the Kraft temperature
- Above CMC, the surfactant molecules undergo:
 (a) dissociation (b) aggregation
 (c) micelle formation (d) all of these

5. Micelles are used in:

- (a) detergents
- (b) magnetic separation
- (c) petroleum recovery
- (d) all of these

● Passage 2

Emulsions are also the colloidal solutions in which disperse phase as well as dispersion medium are liquids. It may be oil in water or water in oil type. Bancroft proposed that the phase in which the emulsifier is more soluble becomes the outer phase of the emulsion. Emulsifiers can be used to stabilize the emulsion. Soaps, detergents, proteins and gum, etc., are used as emulsifiers.

Answer the following questions:

1. Addition of lyophilic solution to the emulsion forms:
 - (a) a protective film around the dispersed phase
 - (b) a protective film around the dispersion medium
 - (c) an aerosol
 - (d) true solution
2. Which of the following examples is/are oil in water type emulsion?

| | |
|----------|---------------|
| (a) Ink | (b) Detergent |
| (c) Soap | (d) Milk |
3. Emulsions can be destroyed by:
 - (a) the addition of emulsifier which tends to form another emulsion
 - (b) electrophoresis with high potential
 - (c) freezing
 - (d) all of the above
4. Which of the following is homogeneous?

| | |
|-------------|-------------------|
| (a) Milk | (b) Paint |
| (c) Shampoo | (d) None of these |
5. Milk is an emulsion in which:
 - (a) milk fat is dispersed in water
 - (b) a solid is dispersed in water
 - (c) a gas is dispersed in water
 - (d) lactose is dispersed in water

● Passage 3

The process of dialysis finds application in the purification of blood by artificial kidney. In this method, impure blood is introduced in the artificial kidney apparatus, where the waste material (electrolyte) diffuses through the membrane. The membrane used in the dialyser is different from the membrane used in osmosis. These membranes allow the movement of ions through them.

Blood is a negatively charged sol. The haemoglobin particles carry a positive charge. Blood is slightly alkaline (pH 7.36–7.42). Acidic salts like alum and FeCl_3 decrease the pH of the blood and the denaturation of globular proteins present in blood takes place. Due to denaturation, these globular proteins become fibrous which are insoluble and stop bleeding. Blood is lyophobic in nature.

Answer the following questions:

1. To stop bleeding, FeCl_3 is applied locally because:
 - (a) FeCl_3 seals the blood vessels
 - (b) FeCl_3 changes the direction of blood flow
 - (c) FeCl_3 reacts with blood to form a solid substance which seals the blood vessel
 - (d) FeCl_3 causes denaturation of proteins present in blood
2. Which of the following colloidal solutions does not contain negatively charged particles?

| | | | |
|-----------------------|-----------------------------|-----------|--------------|
| (a) Fe(OH)_3 | (b) As_2S_3 | (c) Blood | (d) Gold sol |
|-----------------------|-----------------------------|-----------|--------------|
3. The coagulating power of an electrolyte for blood decreases in the order:

| | |
|---|---|
| Na^+ , Al^{3+} , Ba^{2+} | PO_4^{3-} , SO_4^{2-} , Cl^- |
| (c) Al^{3+} , Ba^{2+} , Na^+ | (d) Cl^- , SO_4^{2-} , PO_4^{3-} |
4. Which of the following statements is/are not true?
 - (a) Blood is positively charged sol
 - (b) Soap solution contains ionic micelles as the colloidal particles
 - (c) Blood is purified by the process of dialysis
 - (d) Ca^{2+} and K^+ cause coagulation of blood if added in excess
5. Which of the following is/are lyophobic colloids?

| | | | |
|-----------|------------|-------------|----------|
| (a) Blood | (b) Starch | (c) Gelatin | (d) Gold |
|-----------|------------|-------------|----------|

Answers

Passage 1.

1. (b)

2. (c)

3. (c)

4. (b, c)

5. (a, c)

Passage 2.

1. (a)

2. (d)

3. (b, c)

4. (d)

5. (a)

Passage 3.

1. (d)

2. (a)

3. (c)

4. (a)

5. (a, d)



ASSIGNMENT NO. 6

SECTION-I

Straight Objective Type Questions

This section contains 10 multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which only one is correct.

1. Dispersed phase and dispersion medium in butter are respectively: [EAMCET (Medical) 2007]
 - (a) solid and liquid
 - (b) liquid and liquid
 - (c) liquid and solid
 - (d) solid and solid
2. Which one of the following acts as the best coagulating agent for ferric hydroxide sol? [PMT (Kerala) 2007]
 - (a) Magnesium chloride
 - (b) Hydrochloric acid
 - (c) Aluminium chloride
 - (d) Potassium oxalate
 - (e) Potassium ferricyanide
3. The colloidal sol found effective in the treatment of eye disease is:
 - (a) colloidal sulphur
 - (b) colloidal antimony
 - (c) colloidal silver
 - (d) colloidal gold
4. When alcohol is added to the saturated solution of calcium acetate in water then we first of all get sol which changes to gelatinous mass called solid alcohol. Solid alcohol is.....
 - (a) aerosol
 - (b) gel
 - (c) solid foam
 - (d) solid sol
5. Colloidal solutions of gold prepared by different methods are of different colours because of:
 - (a) variable valency of gold
 - (b) impurities produced by different methods
 - (c) different diameters of colloidal gold particles
 - (d) different concentration of gold particles
6. Emulsions of polyvinyl acetate are used in:
 - (a) polishes
 - (b) latex paints
 - (c) fire works
 - (d) rayons
7. The outcome of internal liquid of gel on shaking is called:
 - (a) syneresis
 - (b) imbibition
 - (c) thixotropy
 - (d) precipitation
8. Which of the following shows the maximum hydrophobic behaviour?
 - (a) Adenine
 - (b) Glucose
 - (c) Stearic acid
 - (d) Glycine
9. The solution of natural rubber in benzene is an example of:
 - (a) lyophobic colloids
 - (b) macromolecular colloid
 - (c) multimolecular colloid
 - (d) associated colloid
10. When NaCl solution is added to Fe(OH)_3 sol then:
 - (a) $[\text{Fe(OH)}_3]\text{Fe}^{3+}$ is formed
 - (b) $[\text{Fe(OH)}_3]\text{Cl}^-$ is formed
 - (c) Fe(OH)_3 is coagulated
 - (d) $[\text{Fe(OH)}_3]\text{Na}^+$ is formed

SECTION-II

Multiple Answers Type Objective Questions

11. Which of the following are lyophilic in nature?
 - (a) Gum
 - (b) Sulphur
 - (c) Starch
 - (d) Protein
12. Surfactant molecules form micelles in aqueous solution, which:
 - (a) tend to congregate due to their hydrophobic tails
 - (b) are colloidal-sized cluster of molecules
 - (c) provide protection due to their hydrophobic head
 - (d) none of the above
13. Crystalloid and colloid differ with respect to:
 - (a) Tyndall effect
 - (b) particle size
 - (c) diffusion through animal or vegetable membrane
 - (d) number of particles per unit volume of solution
14. Select the correct statements among the following:
 - (a) Milk is emulsion of fat in water
 - (b) An emulsifier stabilizes the emulsion
 - (c) Emulsifier forms a thin film around the droplets of dispersed phase
 - (d) Milk is an emulsion of protein in water
15. Which of the following statements are true?
 - (a) Flocculation value is inversely proportional to the coagulating power
 - (b) Colloidal silica is a protective colloid
 - (c) Alum is used for cleaning muddy water
 - (d) Gelatin is added in ice cream, it acts as emulsifier

SECTION-III

Assertion-Reason Type Questions

This section contains 5 questions. Each question contains Statement-1 (Assertion) and Statement-2 (Reason). Each question has following 4 choices (a), (b), (c) and (d), out of which only one is correct.

- (a) Statement-1 is true; statement-2 is true; statement-2 is a correct explanation for statement-1.
- (b) Statement-1 is true; statement-2 is true; statement-2 is not a correct explanation for statement-1.
- (c) Statement-1 is true; statement-2 is false.
- (d) Statement-1 is false; statement-2 is true.

16. Statement-1: Micelles are formed by surfactant molecules above the critical micellar concentration (CMC).

Because

Statement-2: The conductivity of solution having surfactant molecules decreases sharply at the CMC. (IIT 2007)

[Hint: Micellisation takes place above certain minimum concentration called critical micellar concentration (CMC). Each micelle contains at least 100 molecules, therefore conductivity of solution decreases sharply at the CMC.]

17. **Statement-1:** Aqueous gold colloidal solution is red in colour.

Because

Statement-2: The colour arises due to scattering of light by colloidal gold particles.

18. **Statement-1:** An emulsion becomes stable if soap is added to it.

Because

Statement-2: Soap contains hydrophobic and hydrophilic parts.

19. **Statement-1:** Colloidal solutions are electrically neutral.

Because

Statement-2: Dispersed phase and dispersion medium are of same charge.

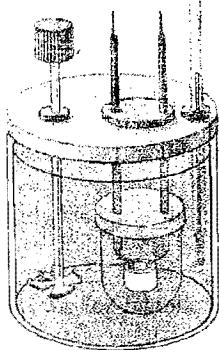
20. **Statement-1:** Colloidal sol scatter the beam of light while true solutions do not.

Because

Statement-2: The particles in colloidal sol are bigger than those of true solutions.

Answers

- | | | | | | | | |
|---------|---------|---------------|---------------|---------------|---------------|---------------|---------|
| 1. (b) | 2. (e) | 3. (c) | 4. (b) | 5. (c) | 6. (b) | 7. (c) | 8. (a) |
| 9. (b) | 10. (c) | 11. (a, c, d) | 12. (a, b, c) | 13. (a, b, c) | 14. (a, b, c) | 15. (a, c, d) | 16. (b) |
| 17. (b) | 18. (a) | 19. (c) | 20. (a) | | | | |



CHAPTER

7

CHEMICAL THERMODYNAMICS AND THERMOCHEMISTRY

7.1 INTRODUCTION

Thermodynamics is a Greek word. Its literal meaning is motion or flow (dynamics) of heat (thermos). However, the term is used in a more general way. **Thermodynamics is the branch of science which deals with all changes in energy or transfers of energy that accompany physical and chemical processes.** It is concerned with interconversion of various forms of energy.

Chemical thermodynamics is the branch of thermodynamics which deals with the study of processes in which chemical energy is involved.

Or

Chemical thermodynamics is one of the branches of physical chemistry which deals with transport of heat either as a result of physical change or as a result of chemical change.

Chemical thermodynamics is concerned with the following questions:

(i) When two or more substances are put together, will they react?

(ii) If they do react, what energy changes will be associated with the reaction?

(iii) If a reaction occurs, at what concentrations of the reactants and their products will equilibrium be established?

Thermodynamics is not concerned with the total energy of the body but only with energy changes taking place during the transformation. The study of thermodynamics is based on three generalisations derived from experimental results. These generalisations are known as first, second and third law of thermodynamics based on human experience and there is no formal proof for them. Scientists are of the view that nothing contrary to these laws will ever occur.

Limitations of thermodynamics: (i) The laws of thermodynamics apply only to the matter in bulk, i.e., macroscopic system and not to individual atoms or molecules of the macroscopic system. Thermodynamics does not deal with internal structure of atoms and molecules. (ii) Thermodynamics can only predict the feasibility or spontaneity of a process under a

given set of conditions but does not tell anything about the rate at which the given process may proceed. It is only concerned with initial and final states of the system. For example, thermodynamics predicts that the reaction between oxygen and hydrogen is possible under ordinary conditions but does not tell whether the reaction is fast or slow.

7.2 TERMS USED IN THERMODYNAMICS

Before we study the laws of thermodynamics, it is necessary to define some of the basic terms which are frequently used in its discussion:

(i) System, Surroundings and Boundary: A system is defined as a specified part of the universe or specified portion of the matter which is under experimental investigation and the rest of the universe, i.e., all other matter which can interact with the system, is surroundings.

Anything which separates system and surroundings is called **boundary**. The boundary may be real or imaginary; it may be rigid or non-rigid; it may be a conductor or a non-conductor of heat. The terms **diathermic wall** and **adiabatic wall** are used for conductor and non-conductor of heat boundaries respectively.

For example, a reaction is carried out in a beaker. The contents of the beaker constitute the system, beaker serves as boundary and the beaker, the air and anything else in the vicinity constitute the surroundings.

(ii) Types of System: There are three types of system:

(a) Isolated system: This type of system has no interaction with its surroundings. The boundary is sealed and insulated. Neither matter nor energy can be exchanged with surroundings. A substance contained in an ideal thermos flask is an example of an isolated system.

(b) Closed system: This type of system can exchange energy in the form of heat, work or radiations but not matter with its surroundings. The boundary between system and surroundings is sealed but not insulated. For example, liquid in contact with vapour in a sealed tube forms a closed system. Heat can be transferred through the walls of the tube to the

surroundings but total amount of matter remains the same as vapours cannot escape.

(c) **Open system:** This type of system can exchange matter as well as energy with surroundings. The boundary is not sealed and not insulated. Sodium reacting with water in an open beaker is an example of open system as hydrogen escapes and heat of the reaction is transferred to the surroundings.

On the basis of composition, there are two types of systems:

(1) **Homogeneous system:** A system is said to be homogeneous when it is completely uniform throughout. A homogeneous system is made of one-phase only. Examples are: a pure single solid, liquid or gas, mixture of gases and a true solution.

(2) **Heterogeneous system:** A system is said to be heterogeneous when it is not uniform throughout, i.e., it consists two or more phases. Examples are: ice in contact with water, two or more immiscible liquids, insoluble solid in contact with a liquid, a liquid in contact with vapour, etc.

(iii) **Thermodynamic Properties:** These are of two types:

(a) **Intensive properties:** The properties which do not depend upon the quantity of matter present in the system or size of the system are called intensive properties. Pressure, temperature, density, specific heat, surface tension, refractive index, viscosity, melting point, boiling point, volume per mole, concentration, etc., are the examples of intensive properties of the system.

(b) **Extensive properties:** The properties whose magnitude depends upon the quantity of matter present in the system are called extensive properties.

Extensive property is an additive property of the system. For a heterogeneous system consisting of several phases, the total value of extensive property will be equal to the sum of contributions from several phases.

The following are some salient features of these properties :

(i) In a system having two or more substances, the extensive property will depend not only on the independent variables but also on the number of moles of different components present in it.

(ii) If an extensive property is expressed per mole or per gram, it becomes intensive property. For example, mass and volume are extensive properties but density (mass per unit volume) and specific volume (volume per unit mass) are intensive properties.

(iii) The product, sum and ratio of intensive properties are also intensive properties. Let X and Y be two intensive properties, then $(X + Y)$; XY ; $\frac{X}{Y}$; $\frac{\partial X}{\partial Y}$ are intensive properties.

(iv) Let X and Y be the two extensive properties, then

(a) $(X + Y)$ will also be an extensive variable.

(b) $\frac{X}{Y}$ and $\frac{\partial X}{\partial Y}$ will be intensive variables.

Extensive and intensive properties

| Intensive properties | Extensive properties |
|----------------------|----------------------|
| Molarity | Heat capacity |
| Molality | Mass |
| Concentration | Volume |

| | |
|---------------------|-------------------|
| Density | Number of moles |
| Temperature | Gibbs free energy |
| Pressure | Enthalpy |
| Mole fraction | Entropy |
| Molar enthalpy | Internal energy |
| Molar entropy | |
| Refractive index | |
| Specific heat | |
| Viscosity | |
| Surface tension | |
| Dielectric constant | |

When the total mass, temperature, volume, number of moles and composition have definite values, the system is said to be in a **definite state**. When there is any change in any one of these properties, it is said that the system has undergone a **change of state**.

(iv) **State Functions or State Variables:** Fundamental properties which determine the state of a system are referred to as **state variables** or **state functions** or **thermodynamic parameters**. The change in the state properties depends only upon the initial and final states of the system, but is independent of the manner in which the change has been brought about. In other words, the state properties do not depend upon a path followed.

Following are the state variables that are commonly used to describe the state of the thermodynamic system:

- | | |
|------------------------|----------------------------|
| 1. Pressure (P) | 2. Temperature (T) |
| 3. Volume (V) | 4. Internal energy (E) |
| 5. Enthalpy (H) | 6. Entropy (S) |
| 7. Free energy (G) | 8. Number of moles (n) |

(v) **Thermodynamic Processes:** When the thermodynamic system changes from one state to another, the operation is called a **process**. The various types of the processes are:

(a) **Isothermal process:** The process is termed **isothermal** if temperature remains fixed, i.e., operation is done at constant temperature. This can be achieved by placing the system in a constant temperature bath, i.e., thermostat. For an isothermal process $dT = 0$, i.e., heat is exchanged with the surroundings and the system is not thermally isolated.

(b) **Adiabatic process:** If a process is carried out under such condition that no exchange of heat takes place between the system and surroundings, the process is termed **adiabatic**. The system is thermally isolated, i.e., $dQ = 0$. This can be done by keeping the system in an insulated container, i.e., thermos flask. In adiabatic process, the temperature of the system varies.

(c) **Isobaric process:** The process is known as **isobaric** in which the pressure remains constant throughout the change, i.e., $dP = 0$.

(d) **Isochoric process:** The process is termed as **isochoric** in which volume remains constant throughout the change, i.e., $dV = 0$.

(e) Cyclic process: When a system undergoes a number of different processes and finally returns to its initial state, it is termed **cyclic process**. For a cyclic process $dE = 0$ and $dH = 0$.

(f) Reversible process: A process which occurs infinitesimally slowly, i.e., opposing force is infinitesimally smaller than driving force and when infinitesimal increase in the opposing force can reverse the process, it is said to be **reversible process**. In fact, a reversible process is considered to proceed from initial state to final state through an infinite series of infinitesimally small stages and at every stage it is virtually in state of equilibrium. A reversible process is an ideal process and cannot be realised in practice.

(g) Irreversible process: When the process goes from initial to final state in single step in finite time and cannot be reversed, it is termed as **irreversible process**. In such a case equilibrium state exists only at the initial and final stages of the process. An irreversible process is spontaneous in nature. It is real and can be performed in practice. All natural processes are irreversible in nature.

| Reversible process | Irreversible process |
|--|--|
| 1. It is an ideal process and takes infinite time. | It is a spontaneous process and takes finite time. |
| 2. The driving force is infinitesimally greater than the opposing force. | The driving force is much greater than the opposing force. |
| 3. It is in equilibrium at all stages. | Equilibrium exists in the initial and final stages only. |
| 4. Work obtained is maximum. | Work obtained is not maximum. |
| 5. It is difficult to realise in practice. | It can be performed in practice. |

Nature of Work and Heat

Work is a mode of energy transfer to or from a system with reference to the surroundings. If an object is displaced through a distance $d x$ against a force of F , then the amount of work done is defined as

$$W = F \times d x$$

There are many types of work and all of them could be expressed as the product of two factors:

- (i) an intensity factor,
- (ii) a capacity factor.

Some of them are:

$$(a) \text{Gravitational work} = (mg) \times h$$

where, m = mass of body, g = acceleration due to gravity, h = height moved.

$$(b) \text{Electrical work} = \text{charge} \times \text{potential}$$

$$= Q \times V$$

where, Q = charge, V = potential gradient.

$$(c) \text{Mechanical work} = P_{\text{ext}} (V_2 - V_1) = P_{\text{ext}} \Delta V$$

where, P_{ext} = external pressure, ΔV = increase or decrease in volume.

Work associated with change in volume of a system against external pressure is called mechanical work.

$$P_{\text{ext}} = \text{intensity factor}$$

$$\Delta V = \text{capacity factor}$$

Work (w) is a path-dependent function, it is a manifestation of energy. Work done on a system increases the energy of the system and work done by the system decreases the energy of the system.

Work done on the system, $w = + \text{ve}$

Work done by the system, $w = - \text{ve}$

Heat may be defined as the quantity of energy which flows between a system and its surroundings on account of temperature difference. Heat always flows from high temperature to low temperature.

$$\text{Heat absorbed or evolved}, \Delta Q = ms \Delta t$$

where, m = mass of substance, s = specific heat

and Δt = temperature difference.

- (i) Heat flowing into the system, ΔQ or $\Delta H = + \text{ve}$.

The process in this case is endothermic in which the temperature of the system is raised and that of the surroundings is lowered.

- (ii) Heat flowing out of the system, ΔQ or $\Delta H = - \text{ve}$.

The process in this case is exothermic in which the temperature of the system is lowered and that of the surroundings is raised.

Units of Heat and Work: The unit of heat is calorie (cal). It is defined as the quantity of heat required to raise the temperature of one gram of water by 1°C .

Since, heat and work are interrelated, SI unit of heat is the joule (J).

$$1 \text{ joule} = 0.2390 \text{ cal}$$

$$1 \text{ calorie} = 4.184 \text{ J}$$

$$1 \text{ kcal} = 4.184 \text{ kJ}$$

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

$$= 1.013 \times 10^9 \text{ erg}$$

$$= 24.206 \text{ cal}$$

SOME SOLVED EXAMPLES

Example 1. A gas expands by 0.5 litre against a constant pressure of one atmosphere. Calculate the work done in joule and calorie.

Solution: Work = $-P_{\text{ext}} \times \text{volume change}$

$$= -1 \times 0.5 = -0.5 \text{ litre-atm}$$

$$= -0.5 \times 101.328 \text{ J} = -50.664 \text{ J}$$

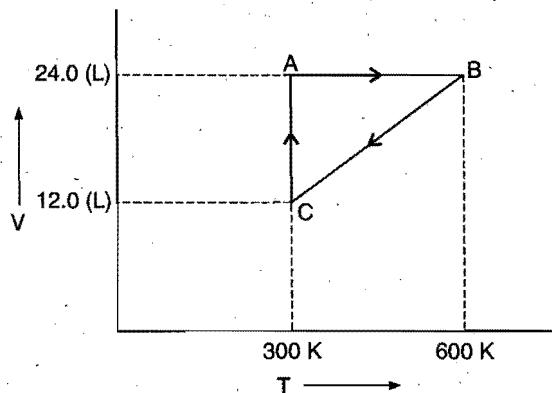
$$0.5 \text{ litre-atm} = -0.5 \times 24.20 \text{ cal} = -12.10 \text{ cal}$$

Example 2. One mole of an ideal gas is put through a series of changes as shown in the graph in which A, B and C mark the three stages of the system. At each stage the variables are shown in the graph.

(a) Calculate the pressure at three stages of the system.

(b) Name the processes during the following changes:

(i) A to B (ii) B to C (iii) C to A and (iv) overall change.



Solution: (a) At stage A:

$$V = 24.0 \text{ L}; T = 300 \text{ K}; n = 1; R = 0.0821 \text{ litre-atm K}^{-1} \text{ mol}^{-1}$$

Substituting these values in the ideal gas equation,

$$PV = nRT,$$

$$P = \frac{1 \times 0.0821 \times 300}{24.0} = 1.026 \text{ atm}$$

At stage B: Volume remains the same but temperature changes from 300 K to 600 K. Thus, according to pressure law, the pressure will be doubled at B with respect to A.

$$\text{Pressure at } B = 2 \times 1.026 = 2.052 \text{ atm}$$

At stage C: Temperature is 300 K and volume is half that of stage A. Thus, according to Boyle's law, the pressure at C will be doubled with respect to A.

$$\text{Pressure at } C = 2 \times 1.026 = 2.052 \text{ atm}$$

(b) (i) During the change from A to B, volume remains constant, the process is **isochoric**.

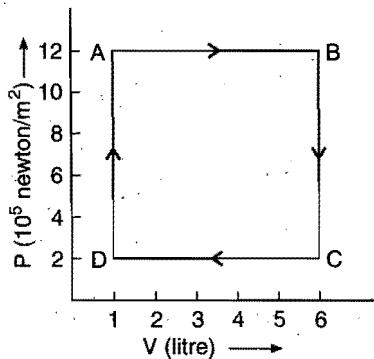
(ii) During the change from B to C the pressure remains constant, the process is **isobaric**.

(iii) During the change from C to A, the temperature remains constant, the process is **isothermal**.

(iv) Overall, the process is **cyclic** as it returns to initial state.

Example 3. The diagram shows a P-V graph of a thermodynamic behaviour of an ideal gas. Find out from this graph (i) work done in the process $A \rightarrow B$, $B \rightarrow C$, $C \rightarrow D$ and $D \rightarrow A$, (ii) work done in the complete cycle $A \rightarrow B \rightarrow C \rightarrow D \rightarrow A$.

Solution: (i) Work done in the process $A \rightarrow B$ (the process is expansion, hence work is done by the gas)



$$= -P \times dV = -12 \times 10^5 \times 5 \times 10^{-3}$$

$$= -6000 \text{ J}$$

Work done in the process $B \rightarrow C$ is zero as volume remains constant.

Work done in the process $C \rightarrow D$ (The process is contraction, hence work is done on the gas)

$$= P \times dV = 2 \times 10^5 \times 5 \times 10^{-3}$$

$$= 1000 \text{ J}$$

(ii) Work done in the process $D \rightarrow A$ is zero as volume remains constant.

$$\text{Net work done in the whole cycle} = -6000 + 1000 = -5000 \text{ J}$$

i.e., net work is done by the gas.

Example 4. Calculate the work done when 1.0 mole of water at 373 K vaporizes against an atmospheric pressure of 1.0 atmosphere. Assume ideal gas behaviour.

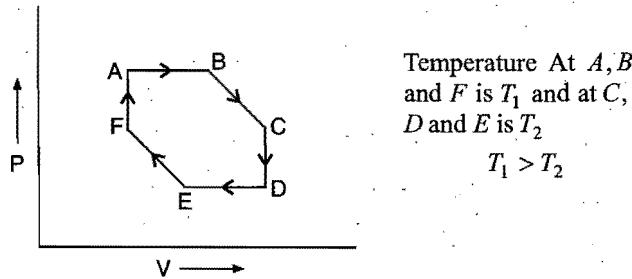
Solution: The volume occupied by water is very small and thus the volume change is equal to the volume occupied by one gram mole of water vapour.

$$V = \frac{nRT}{P} = \frac{1.0 \times 0.0821 \times 373}{1.0} = 31.0 \text{ litre}$$

$$W = -P_{\text{ext}} \times \Delta V = -(1.0) \times (31.0) \text{ litre-atm}$$

$$= -(31.0) \times 101.3 \text{ J} = -3140.3 \text{ J}$$

Example 5. Identify different steps in the following cyclic process:



Solution: (i) $A \rightarrow B$ (Temperature and pressure are constant).

∴ It is **isothermal** and **isobaric** process.

(ii) $B \rightarrow C$: It is adiabatic expansion in which temperature falls from T_1 to T_2 .

(iii) $C \rightarrow D$ (Temperature and volume are constant)

∴ This process is **isothermal** and **isochoric**.

(iv) $D \rightarrow E$ (Temperature and pressure are constant)

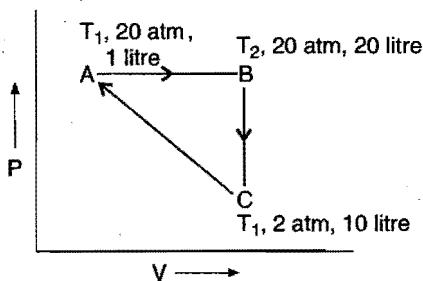
∴ It is **isothermal** and **isobaric** contraction.

(v) $E \rightarrow F$ (It is adiabatic compression in which temperature increases from T_2 to T_1).

(vi) $F \rightarrow A$ (Temperature and volume are constant).

∴ It is **isothermal** and **isochoric** process.

Example 6. One mole of a monoatomic gas is subjected to following cyclic process:



- (a) Calculate T_1 and T_2 .
 (b) Calculate ΔE , q and W in calories in each step of cyclic process.

Solution: (a) At A :

$$\begin{aligned} PV &= nRT \\ 20 \times 1 &= 1 \times 0.0821 \times T_1 \\ T_1 &= 243.6 \text{ K} \end{aligned}$$

At B :

$$\begin{aligned} PV &= nRT \\ 20 \times 10 &= 1 \times 0.0821 \times T_2 \\ T_2 &= 2436.05 \text{ K} \end{aligned}$$

(b) Path AB : Isobaric process ($\Delta E = 0$, $q = W$)

$$\begin{aligned} W &= P\Delta V = 20 \times 9 = 180 \text{ litre-atm} \\ &= \frac{180 \times 101.3}{4.185} \text{ cal} \\ &= 4356.9 \text{ cal} \quad (\text{Work in compression is positive}) \end{aligned}$$

Path BC : Isochoric process

$$\begin{aligned} W &= 0 \\ q_V &= \Delta U = nC_V \Delta T = 1 \times \frac{3}{2} R \times (2436 - 243.6) \\ &= \frac{3}{2} \times 2 \times 2192.4 = 6577.2 \text{ cal} \end{aligned}$$

It is cooling process : $q_V = -6577.2 \text{ cal}$

Path CA: It is isothermal compression ΔE_0

$$\begin{aligned} q &= W = 2.303 nRT \log \frac{V_2}{V_1} \\ q &= 2.303 \times 1 \times 2 \times \log \frac{10}{1} = 1122.02 \text{ cal} \end{aligned}$$

3 INTERNAL ENERGY

Every system having some quantity of matter is associated with a definite amount of energy. This energy is known as internal energy. The exact value of this energy is not known as it includes all types of energies of molecules constituting the given mass of matter such as translational, vibrational, rotational, the kinetic and potential energy of the nuclei and electrons within the individual molecules and the manner in which the molecules are linked together, etc. The internal energy is denoted by E .

$$E = E_{\text{translational}} + E_{\text{rotational}} + E_{\text{vibrational}} + E_{\text{bonding}} + E_{\text{electronic}} + \dots$$

Accurate measurements of some forms of energy which

*The word internal is often omitted and the word energy implies internal energy of a system.

contribute to the absolute value of internal energy for a given substance in a given state is impossible. But one thing is certain that the internal energy of a particular system is a definite quantity at the given moment, irrespective of the manner by which it has been obtained. Internal energy like temperature, pressure, volume, etc., is a state function, i.e., total of all possible kinds of energy of a system is called its internal energy*.

It is neither possible nor necessary to calculate the absolute value of internal energy of a system. In thermodynamics, one is concerned only with energy change which occurs when the system moves from one state to another. Let ΔE be the difference of energy of the initial state (E_i) and the final state (E_f), then

$$\Delta E = E_f - E_i$$

ΔE is positive if $E_f > E_i$ and negative if $E_f < E_i$.

A system may transfer energy to or from the surroundings as heat or work or both.

Characteristics of Internal Energy

- (i) Internal energy of a system is an extensive property.
- (ii) Internal energy is a state property.
- (iii) The change in the internal energy does not depend on the path by which the final state is reached.
- (iv) There is no change in internal energy in a cyclic process.

Thermal Equilibrium and Zeroth Law of Thermodynamics

When a hot body is kept in contact with a cold body, the cold body warms up and the hot body cools down. The internal energy of the hot body decreases and that of cold body increases. The transfer of energy from the hot body to a cold body is a non-mechanical process. The energy that is transferred from one body to the other, without any mechanical work involved, is called heat.

Two bodies are said to be in thermal equilibrium if no transfer of heat takes place when they are placed in contact.

The temperature concept can be stated precisely by the fact that systems in thermal equilibrium with each other have the same temperature.

Courses of thermodynamics usually deal with the three laws : the first, second and third laws, which constitute the subject matter of thermodynamics. However, at present an ever increasing use is made in thermodynamics of the law of thermal equilibrium formulated by R. Fowler in 1931, i.e., the Zeroth law of thermodynamics. This law was formulated after the first and the second laws had been enunciated.

This law states : If two systems are in thermal equilibrium with a third system, they are also in thermal equilibrium with each other.

Conversely, the law can be stated as follows :

If three or more systems are in thermal contact with each other by means of diathermal walls and are all in thermal equilibrium together, then any two systems taken separately are in thermal equilibrium with each other.

Now let us consider three systems A, B and C as shown in Fig. 7.1. It is an experimental fact that if system A is in thermal

equilibrium with system *C* and system *B* is also in thermal equilibrium with system *C*, then *A* and *B* are in thermal equilibrium with each other.

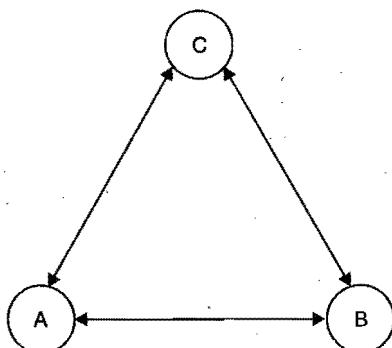


Fig. 7.1 Systems in thermal equilibrium

7.4 FIRST LAW OF THERMODYNAMICS

This law has been stated in various forms but is merely the law of conservation of energy. It was given by **Robert Mayer** and **Helmholtz**.

- (i) Energy cannot be created or destroyed but it can be converted from one form to another.
- (ii) The total energy of the universe is constant.
- (iii) Whenever a quantity of one kind of energy disappears, an exactly equivalent quantity of energy in some other form must appear.
- (iv) It is impossible to construct a perpetual motion machine which could produce work without consuming energy.
- (v) The total energy of an isolated system remains constant though it may change from one form to another.

When a system is changed from initial state to the final state, it undergoes a change in the internal energy from E_i to E_f . Thus, ΔE can be written as:

$$\Delta E = E_f - E_i$$

The change in internal energy can be brought about in two ways:

- (a) Either by allowing the heat to flow into the system (absorption) or out of the system (evolution).
- (b) By doing work on the system or the work done by the system.

Consider a system whose internal energy is E_1 . If the system is supplied q amount of heat, the internal energy of the system will become $E_1 + q$. Now if work w is also done on the system, the final internal energy becomes E_2 . Thus,

$$E_2 = E_1 + q + w$$

or $E_2 - E_1 = q + w$

or $\Delta E = q + w$

This is the mathematical statement of the first law of thermodynamics. In this statement, q is the heat absorbed and w is the work done on the system.

In case q is the heat absorbed and w the work done by the system, then the relationship becomes

$$\Delta E = q + (-w) = q - w$$

The first law of thermodynamics may also be stated as:

The net energy change of a closed system is equal to heat absorbed plus the work done on the system.

Or

The net energy change of a closed system is equal to heat absorbed minus the work done by the system.

Or

It is impossible to construct a mobile or perpetual machine that can work without consumption of any fuel energy.

Example 7. If 500 calorie of heat energy are added to a system and the system does 350 calorie of work on the surroundings, what is the energy change of the system?

Solution: Heat absorbed, $q = 500$ cal

Work done by the system, $w = -350$ cal

Applying the first law of thermodynamics,

$$\Delta E = q + w = 500 + (-350) = 150 \text{ calorie}$$

Example 8. If 100 calorie of heat are added to the same system as in example 1 and a work of 50 calorie is done on the system, calculate the energy change of the system.

Solution: Heat absorbed, $q = 100$ cal

Work done on the system, $w = +50$ cal

Applying the first law of thermodynamics,

$$\Delta E = q + w = (100 + 50) = 150 \text{ calorie}$$

In the above two examples, the final state is same but the paths adopted are different. Thus, the change in energy of the system depends on the initial and final states but does not depend on the path by which the final state has reached, q and w are, therefore, not state functions but ΔE is a state function.

Some useful conclusions drawn from the first law:

$$\Delta E = q + w$$

(i) When a system undergoes a change $\Delta E = 0$, i.e., there is no increase or decrease in the internal energy of the system, the first law of thermodynamics reduces to

$$0 = q + w$$

or $q = -w$

(heat absorbed from surroundings = work done by the system)

or $w = -q$

(heat given to surroundings = work done on the system)

(ii) If no work is done, $w = 0$ and the first law reduces to

$$\Delta E = q$$

i.e., increase in internal energy of the system is equal to the heat absorbed by the system or decrease in internal energy of the system is equal to heat lost by the system.

(iii) If there is no exchange of heat between the system and surroundings, $q = 0$, the first law reduces to

$$\Delta E = w$$

It shows that if work is done on the system, its internal energy will increase or if work is done by the system, its internal energy will decrease. This occurs in an adiabatic process.

(iv) In case of gaseous system, if a gas expands against the constant external pressure, P , let the volume change be ΔV . The mechanical work done by the gas is equal to $-P \times \Delta V$.

Substituting this value in $\Delta E = q + w$,

$$\Delta E = q - P \Delta V$$

When

$$\Delta V = 0,$$

$$\Delta E = q \text{ or } q_V$$

The symbol q_V indicates the heat change at constant volume.

Example 9. A gas contained in a cylinder fitted with a frictionless piston expands against a constant pressure 1 atmosphere from a volume of 4 litre to a volume of 14 litre. In doing so, it absorbs 800 J thermal energy from surroundings. Determine ΔE for the process.

Solution: Given, $q = 800 \text{ J}$

$$\Delta V = (14 - 4) = 10 \text{ litre}$$

$$w = -P \times \Delta V = -1 \times 10 = -10 \text{ litre-atm}$$

But $0.082 \text{ litre-atm} = 1.987 \text{ cal}$

$$\text{So, } w = -\frac{10 \times 1.987}{0.082} = -242.3 \text{ cal}$$

But $1 \text{ calorie} = 4.184 \text{ J}$

$$\text{So, } w = -242.3 \times 4.184 = -1013.7 \text{ J}$$

Substituting the values in equation,

$$\Delta E = q + w = (800 - 1013.7) = -213.7 \text{ J}$$

7.5 ENTHALPY

Heat content of a system at constant pressure is called **enthalpy** denoted by ' H '.

From first law of thermodynamics;

$$Q = E + PV \quad \dots \text{(i)}$$

Heat change at constant pressure can be given as

$$\Delta Q = \Delta E + P \Delta V \quad \dots \text{(ii)}$$

At constant pressure heat can be replaced by enthalpy.

$$\Delta H = \Delta E + P \Delta V \quad \dots \text{(iii)}$$

Constant pressures are common in chemistry as most of the reactions are carried out in open vessels.

At constant volume, $\Delta V = 0$; thus equation (ii) can be written as

$$\Delta Q = \Delta E$$

$\therefore \Delta H =$ Heat change or heat of reaction (in chemical process) at constant pressure

$\Delta E =$ Heat change or heat of reaction at constant volume.

(i) In case of solids and liquids participating in a reaction,

$$\Delta H \approx \Delta E \quad (P \Delta V \approx 0)$$

(ii) Difference between ΔH and ΔE is significant when gases are involved in a chemical reaction.

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

$$\Delta H = \Delta E + \Delta n RT$$

Here,

$\Delta n =$ Number of gaseous moles of products – Number of gaseous moles of reactants.

Using the above relation we can interrelate heats of reaction at constant pressure and at constant volume.

7.6 HEAT CAPACITY

Heat capacity of a system is defined as the quantity of heat required to raise the temperature of the system by one degree. Let a very small quantity of heat dq be given to a system and the temperature of the system rises by dT .

$$\text{Thus, } \text{Heat capacity} = \frac{dq}{dT}$$

The heat capacity of a system, particularly in a gaseous system, determined at constant volume, is different from that determined at constant pressure.

At constant volume, $q = \Delta E$

$$\text{So, Heat capacity at constant volume, } C_V = \left(\frac{\partial E}{\partial T} \right)_V$$

At constant pressure, $q = \Delta E + P \Delta V = \Delta H$

$$\text{So, Heat capacity at constant pressure, } C_P = \left(\frac{\partial H}{\partial T} \right)_P$$

For 1 mole of a gas, heat capacities at constant volume and constant pressure are denoted by C_V and C_P , respectively. These are termed as molar heat capacities. Thus, for 1 mole of a gas,

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V$$

$$\text{and } C_P = \left(\frac{\partial H}{\partial T} \right)_P$$

The difference between C_P and C_V is equal to the work done by 1 mole of gas in expansion when heated through 1°C .

Work done by the gas at constant pressure = $P \Delta V$.

For 1 mole of gas $PV = RT$.

When temperature is raised by 1°C , the volume becomes $V + \Delta V$;

$$\text{So, } P(V + \Delta V) = R(T + 1)$$

$$\text{or } P \Delta V = R$$

$$\text{Hence, } C_P - C_V = P \Delta V = R$$

Ratio of heat capacity $\left(\gamma = \frac{C_P}{C_V} \right)$ depends on atomicity of gas.

| Atomicity | C_V | $C_P = C_V + R$ | $\gamma = \frac{C_P}{C_V}$ |
|---|----------------|-----------------|-------------------------------------|
| Monoatomic He, Ne, Ar etc. | $\frac{3}{2}R$ | $\frac{5}{2}R$ | $\gamma = \frac{5/2R}{3/2R} = 1.66$ |
| Diatomeric O ₂ , N ₂ , H ₂ , Cl ₂ | $\frac{5}{2}R$ | $\frac{7}{2}R$ | $\gamma = \frac{7/2R}{5/2R} = 1.40$ |
| Tri and polyatomic CO ₂ , NH ₃ , SO ₃ , NO ₂ , CH ₄ etc. | 3R | 4R | $\gamma = \frac{4R}{3R} = 1.33$ |

Let n_1 and n_2 moles of two non-reacting gases A and B are mixed then heat capacity of the mixture may be calculated as.

$$(C_V)_{\text{mixture}} = \frac{n_1 (C_V)_1 + n_2 (C_V)_2}{n_1 + n_2}$$

7.7 EXPANSION OF AN IDEAL GAS

(i) Isothermal Expansion

In an isothermal expansion, heat is allowed to flow into or out of the system so that temperature remains constant throughout the process of expansion. Since, for an ideal gas, the internal energy, ΔE , depends only on temperature, it follows that at constant temperature, the internal energy of the gas remains constant, i.e., ΔE is zero.

$$\Delta E = 0$$

According to first law of thermodynamics,

$$\Delta E = q + w$$

Since, for isothermal process, $\Delta E = 0$, hence

$$q = -w$$

This shows that in isothermal expansion, the work is done by the system at the expense of heat absorbed. The magnitude of q or w depends on the manner in which the process of expansion is carried out, i.e., whether it is carried reversibly or irreversibly.

Calculation of ΔH can be done according to the following equation:

$$H = E + PV$$

or

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

or

$$\Delta H = \Delta E + \Delta(nRT)$$

Since, for isothermal process, ΔE and ΔT are zero respectively, hence,

$$\Delta H = 0$$

Work done in reversible isothermal expansion

Consider an ideal gas enclosed in a cylinder fitted with a weightless and frictionless piston. The cylinder is not insulated. The external pressure, P_{ext} , is equal to pressure of the gas, P_{gas} . Let it be P .

$$P_{\text{ext}} = P_{\text{gas}} = P$$

If the external pressure is decreased by an infinitesimal amount dP , the gas will expand by an infinitesimal volume, dV . As a result of expansion, the pressure of the gas within the cylinder falls to $P_{\text{gas}} - dP$, i.e., it becomes again equal to the external pressure and, thus, the piston comes to rest. Such a process is repeated for a number of times, i.e., in each step the gas expands by a volume dV .

Since, the system is in thermal equilibrium with the surroundings, the infinitesimally small cooling produced due to expansion is balanced by the absorption of heat from the

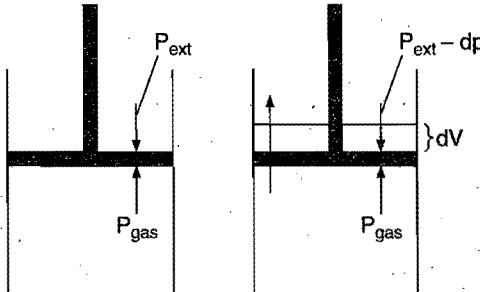


Fig. 7.2

surroundings and the temperature remains constant throughout the expansion.

The work done by the gas in each step of expansion can be given as,

$$d_w = -(P_{\text{ext}} - dP) dV = -P_{\text{ext}} \cdot dV = -P dV$$

$dP \cdot dV$, the product of two infinitesimal quantities, is neglected.

The total amount of work done by the isothermal reversible expansion of the ideal gas from volume V_1 to volume V_2 is, therefore,

$$w = - \int_{V_1}^{V_2} P dV$$

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

$$\text{So, } w = -nRT \int_{V_1}^{V_2} \frac{dV}{V}$$

$$\text{Integrating, } w = -nRT \log_e \frac{V_2}{V_1} = -2.303nRT \log \frac{V_2}{V_1}$$

At constant temperature, according to Boyle's law,

$$P_1 V_1 = P_2 V_2$$

$$\frac{V_2}{V_1} = \frac{P_1}{P_2}$$

$$\text{So, } w = -2.303nRT \log \frac{P_1}{P_2}$$

Isothermal compression work of an ideal gas may be derived similarly and it has exactly the same value with positive sign.

$$w_{\text{compression}} = 2.303nRT \log \frac{V_1}{V_2} = 2.303nRT \log \frac{P_2}{P_1}$$

Work done in irreversible isothermal expansion

Two types of irreversible isothermal expansions are observed, i.e., (i) Free expansion and (ii) Intermediate expansion. In free expansion, the external pressure is zero, i.e., work done is zero when gas expands in vacuum. In intermediate expansion, the external pressure is less than gas pressure. So, the work done when volume changes from V_1 to V_2 is given by

$$w = - \int_{V_1}^{V_2} P_{\text{ext}} \times dV = -P_{\text{ext}} (V_2 - V_1)$$

Since, P_{ext} is less than the pressure of the gas, the work done during intermediate expansion is numerically less than the work done during reversible isothermal expansion in which P_{ext} is almost equal to P_{gas} .

Maximum work: The work done by the system always depends upon the external pressure. The higher the value of P_{ext} , the more work is done by the gas. As P_{ext} cannot be more than P_{gas} , otherwise compression will occur, thus the largest value of P_{ext} can be equal to P_{gas} . Under this condition when expansion occurs, the maximum work is done by the gas on the surroundings.

(ii) Adiabatic Expansion

In adiabatic expansion, no heat is allowed to enter or leave the system, hence, $q = 0$. When this value is substituted in first law of thermodynamics, $\Delta E = q + w$, we get $\Delta E = w$.

In expansion, work is done by the system on the surroundings, hence, w is negative. Accordingly ΔE is also negative, i.e.,

internal energy decreases and therefore, the temperature of the system falls. In case of compression, ΔE is positive, i.e., internal energy increases and therefore, the temperature of the system rises.

The molar specific heat capacity at constant volume of an ideal gas is given by

$$C_V = \left(\frac{dE}{dT} \right)_V$$

or $dE = C_V \cdot dT$... (i)

and for finite change $\Delta E = C_V \Delta T$... (ii)

So, $w = \Delta E = C_V \Delta T$... (iii)

The value of ΔT depends upon the process whether it is reversible or irreversible.

Reversible adiabatic expansion

Let P be the external pressure and ΔV the increase in volume. Thus, the work done by the system is

$$w = -P \Delta V \quad \dots (\text{iv})$$

If ΔT is the fall in temperature, then

$$C_V \Delta T = -P \Delta V \quad \dots (\text{v})$$

For very small change in reversible process,

$$C_V dT = -P dV = -\frac{RT}{V} \cdot dV \quad (\text{for 1 mole of the gas})$$

$$C_V \cdot \frac{dT}{T} = -R \cdot \frac{dV}{V} \quad \dots (\text{vi})$$

Integrating the above equation between temperatures T_1 and T_2 when corresponding values are V_1 and V_2 ,

$$C_V \int_{T_1}^{T_2} \frac{dT}{T} = -R \int_{V_1}^{V_2} \frac{dV}{V}$$

$$C_V \log_e \frac{T_2}{T_1} = -R \log_e \frac{V_2}{V_1} = R \log_e \frac{V_1}{V_2}$$

or $\log \frac{T_2}{T_1} = -\frac{R}{C_V} \log \frac{V_2}{V_1} = \frac{R}{C_V} \log \frac{V_1}{V_2} \quad \dots (\text{vii})$

We know that, $C_P - C_V = R$

$$\frac{C_P}{C_V} - 1 = \frac{R}{C_V}$$

or $(\gamma - 1) = \frac{R}{C_V}$

Putting the value of $\frac{R}{C_V}$ in eq. (vii),

$$\begin{aligned} \log \frac{T_2}{T_1} &= (\gamma - 1) \log \frac{V_1}{V_2} \\ &= \log \left(\frac{V_1}{V_2} \right)^{\gamma-1} \end{aligned} \quad \dots (\text{viii})$$

or $\frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{\gamma-1} \quad \dots (\text{ix})$

or $\frac{T_1}{T_2} = \left(\frac{V_2}{V_1} \right)^{\gamma-1} \quad \dots (\text{x})$

or $\frac{P_1 V_1}{P_2 V_2} = \left(\frac{V_2}{V_1} \right)^{\gamma-1} \quad \dots (\text{xii})$

or $P_1 V_1^{\gamma} = P_2 V_2^{\gamma} \quad \dots (\text{xiii})$

$P V^{\gamma} = \text{constant}$... (xiii)

Thus, knowing γ, V_1, V_2 and initial temperature, T_1 , the final temperature, T_2 , can be readily evaluated.

Modifying the eq. (x),

$$\frac{T_1}{T_2} = \left(\frac{P_2}{\frac{RT_1}{P_1}} \right)^{\gamma-1} = \left(\frac{P_1}{P_2} \cdot \frac{T_2}{T_1} \right)^{\gamma-1}$$

or $\left(\frac{T_1}{T_2} \right)^{\gamma} = \left(\frac{P_1}{P_2} \right)^{\gamma-1} = \left(\frac{P_2}{P_1} \right)^{1-\gamma} \quad \dots (\text{xiii})$

Thus, knowing γ, P_1, P_2 and initial temperature, the final temperature, T_2 , can be evaluated.

From eq. (v),

$$\text{Work done} = C_V \cdot \Delta T = C_V (T_2 - T_1) = \frac{R}{(\gamma - 1)} (T_2 - T_1)$$

$$\text{For } n \text{ moles} = \frac{nR}{(\gamma - 1)} (T_2 - T_1)$$

Irreversible adiabatic expansion

In free expansion, the external pressure is zero, i.e., work done is zero. Accordingly, ΔE which is equal to w is also zero. If ΔE is zero, ΔT should be zero. Thus, in free expansion (adiabatically), $\Delta T = 0, \Delta E = 0, w = 0$ and $\Delta H = 0$.

In intermediate expansion, the volume changes from V_1 to V_2 against external pressure, P_{ext} .

$$w = -P_{\text{ext}} (V_2 - V_1) = -P_{\text{ext}} \left(\frac{RT_2}{P_2} - \frac{RT_1}{P_1} \right)$$

$$= -P_{\text{ext}} \left(\frac{T_2 P_1 - T_1 P_2}{P_1 P_2} \right) \times R$$

or $w = C_V (T_2 - T_1) = -RP_{\text{ext}} \left(\frac{T_2 P_1 - T_1 P_2}{P_1 P_2} \right)$

| Process | Condition | Heat change q | Internal energy change ΔU | Work done |
|--------------------------|------------------------------|-----------------|-----------------------------------|--|
| Free expansion Isochoric | (U) constant (V) constant | — ΔU | 0 $nC_V \Delta T$ | 0 as $P = 0$ 0 as $\Delta V = 0$ |
| Isothermal | (T) constant | $-W$ | 0 | $2.303 nRT \log \left(\frac{V_2}{V_1} \right)$ $= 2.303 nRT \log \left(\frac{P_1}{P_2} \right)$ |

| | | | | |
|----------------|--------------|-----------------|-----------------|---|
| Isobaric | (P) constant | $nC_P \Delta T$ | $nC_V \Delta T$ | $P(V_2 - V_1)$ $= nR(T_2 - T_1)$ |
| Adiabatic | (q) constant | 0 | -W | $C_V(T_1 - T_2)$ $= \frac{nR}{\gamma - 1}$ $(T_1 - T_2)$ $= \frac{1}{\gamma - 1}$ $(P_1V_1 - P_2V_2)$ |
| Cyclic process | — | W | 0 | Area of cycle |

7.8 GRAPHICAL REPRESENTATION OF VARIOUS THERMODYNAMIC PROCESSES AND THE CALCULATION OF WORK DONE BY GRAPHICAL METHODS

1. Graphically, different processes can be represented as follows.

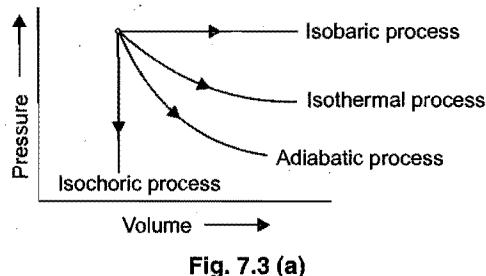


Fig. 7.3 (a)

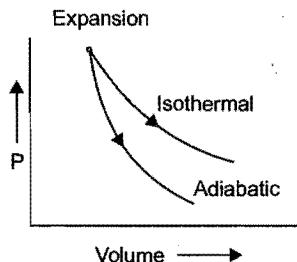


Fig. 7.3 (b)

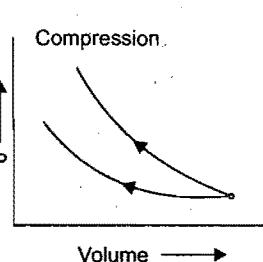
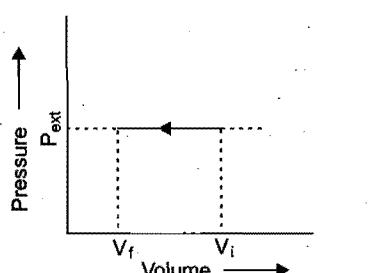


Fig. 7.3 (c)

2. Let a gas is compressed from V_i or V_f by an external pressure of P_{ext} . The work done on the gas can be calculated by the shaded area of the graph represented in following Fig. 7.4.

$$\text{Work done on the gas, } w = -P_{ext}(V_f - V_i) \\ = +\text{ve work,} \quad \text{Since } V_f < V_i$$

Fig. 7.4 Single step compression of ideal gas against external pressure P_{ext}

3. Let compression of gas takes place from volume V_i to V_f in the finite number of stages then the work done on the gas can be calculated by summing up the work of all stages.

Work done on the gas = Shaded area of the diagram.

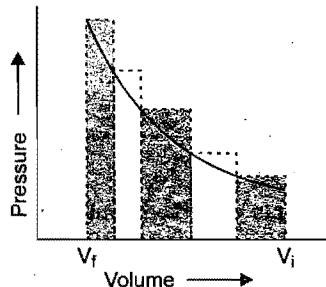


Fig. 7.5 Indicator diagram (P-V) plot in which the compression took place in the finite number of steps with varying pressure

4. Graphically, the work of expansion can also be determined. In case, if a graph is plotted between P and V , then the area under the curve gives the external work done by the gas.

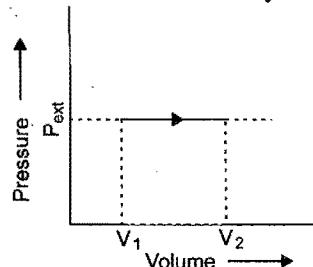


Fig. 7.6 Shaded area gives the work done by the gas when pressure remains constant

$$w_{exp} = -P_{ext}(V_2 - V_1) \\ = -\text{ve work}$$

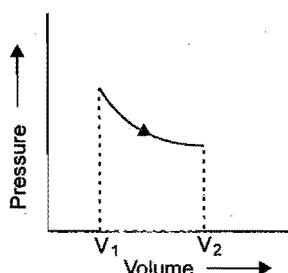


Fig. 7.7 Shaded area represents the work done by the gas when both pressure and volume vary

5. Work done by a gas undergoing cyclic process : It is determined with the help of following three graphs.

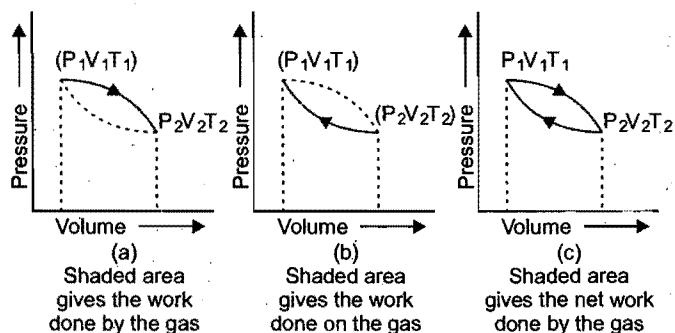


Fig. 7.8 Complete cyclic process of a gas

6. Work done by the gas in a closed path ABCA.

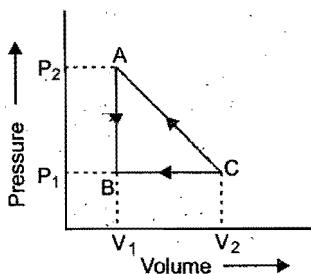


Fig. 7.9 The gas in closed cyclic process ABCA

Work done = Area of shaded triangle

$$\begin{aligned} &= \frac{1}{2} \times \text{Length of base} \times \text{Length of perpendicular} \\ &= \frac{1}{2} \times (V_2 - V_1) (P_2 - P_1) \end{aligned}$$

7. Let a system of gas passes from initial state A to B in following three ways. The work done by the gas will be calculated by the shaded area.

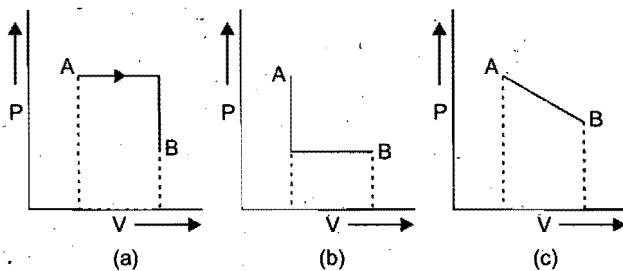


Fig. 7.10 Graphical proof that the work is not a state function

8. Work done in clockwise and anti-clockwise cyclic process :

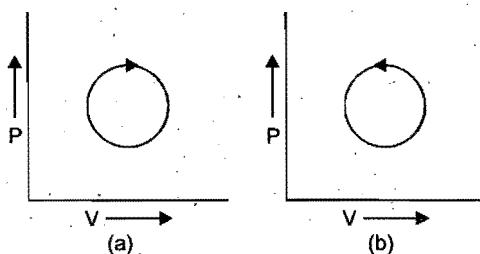


Fig. 7.11 Representation of closed cyclic process in clockwise and anti-clockwise direction

Shaded area represents the net work done in the cyclic process.

Case I : If the cyclic process is in clockwise direction then work done will be negative because the net work will be done by the system.

Case II : If the cyclic process is in anti-clockwise direction then work done will be positive because the net work is done on the system.

9. If the state of a system changes in such a way that its volume remains constant, the process is called isochoric. Following three plots represent isochoric process.

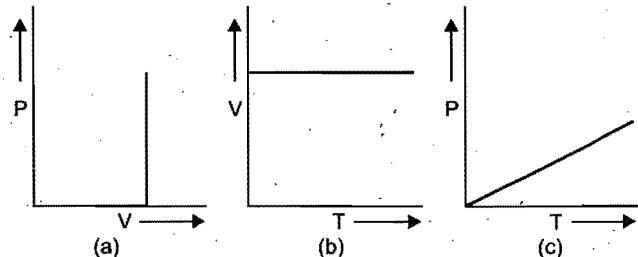


Fig. 7.12 Isochores of Ideal Gas

10. If the state of system changes in such a way that pressure is constant, the process is called isobaric.

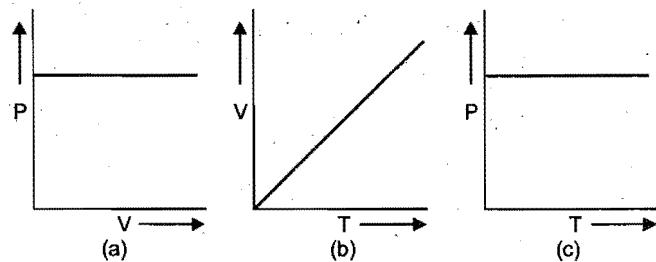


Fig. 7.13 Isobars of Ideal Gas

11. If the state of a system changes in such a way that temperature remains constant, the process is called isothermal.

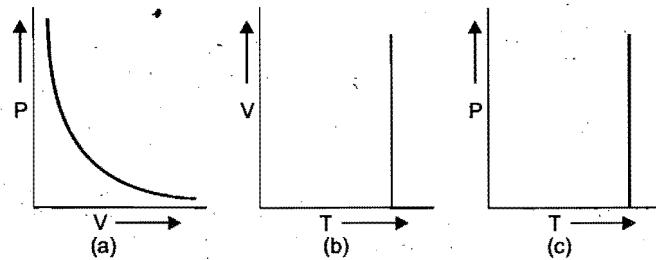


Fig. 7.14 Isotherm of Ideal Gas

7.9 JOULE-THOMSON EFFECT

An ideal gas is defined as the gas in which intermolecular forces of attraction are absent. If such a gas expands into vacuum adiabatically, no cooling is produced in the process, i.e., there is no change in the internal energy which only depends upon the temperature.

However, when a real gas is forced through a porous plug into a region of low pressure, it is found that due to expansion, the gas on the side of low pressure gets cooled. The greater the difference in pressure on the two sides, the higher shall be difference in temperature.

The phenomenon of producing lowering of temperature when a gas is made to expand adiabatically from a region of high pressure into a region of low pressure, is known as Joule-Thomson effect.

The experimental set-up is shown in Fig. 7.15. It consists of a thermally insulated tube fitted with a porous plug and two weightless and frictionless pistons X and Y . Two sensitive thermometers are fitted on both the sides of the porous plug to record temperature.

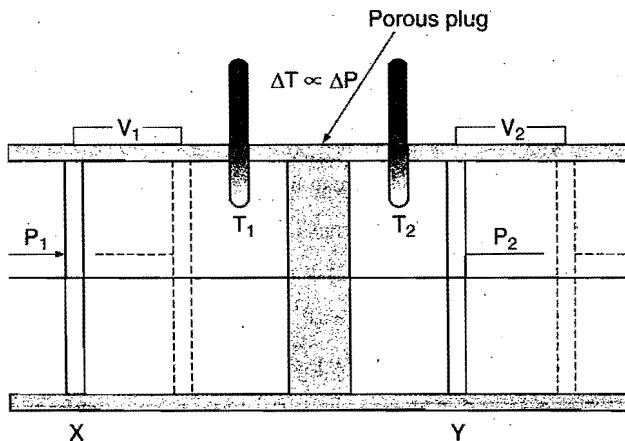


Fig. 7.15

Consider that a certain amount of the gas is passed through the porous plug by slow movement of piston X , i.e., a volume V_1 of the gas at pressure P_1 be forced through the plug on the left side of the plug. The gas in the right hand chamber is allowed to expand to volume V_2 and pressure P_2 by moving the piston Y . The change in temperature is recorded from the thermometers.

Most of the gases are found to undergo cooling on expansion through the porous plug. However, helium and hydrogen are exceptions as these get warmed.

The gas is compressed on left hand side. Thus, work is done on the gas. It is equal to $P_1 V_1$. The work done on right hand side by the gas is equal to $P_2 V_2$.

$$\text{Total work done by the gas} = P_1 V_1 - P_2 V_2$$

As $q = 0$, the work done by the gas lowers its internal energy and consequently temperature falls.

$$\Delta E = P_1 V_1 - P_2 V_2$$

$$E_2 - E_1 = P_1 V_1 - P_2 V_2$$

$$(E_2 + P_2 V_2) - (E_1 + P_1 V_1) = 0$$

or

$$H_2 - H_1 = 0$$

$$\Delta H = 0$$

Thus, Joule-Thomson effect occurs at constant enthalpy.

Joule-Thomson Coefficient

The number of degrees of temperature change produced per atmospheric drop in pressure under constant enthalpy conditions when the gas is allowed to expand through porous plug is called **Joule-Thomson coefficient**. It is denoted by μ .

$$\mu = \frac{dT}{dP}$$

When μ has positive value, the gas cools on expansion. If it has negative value, the gas warms on expansion. Every gas has a definite value of temperature when the sign changes from negative to positive. This temperature is termed **inversion**

temperature. Most of the gases have inversion temperature near about room temperature and thus cool at room temperature when expansion is done. However, the inversion temperature for H_2 is $-80^\circ C$. Thus, at room temperature hydrogen warms on expansion. In order to produce further cooling by Joule-Thomson effect in hydrogen, it is necessary that it should be first cooled to $-80^\circ C$ by other cooling devices.

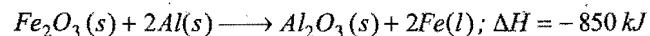
The value of inversion temperature has been calculated by using van der Waals' equation,

$$T_i = \frac{2a}{Rb}$$

Thus, inversion temperature depends upon van der Waals' constants a and b of the gas.

Some Solved Examples

Example 10. 1 mole of Fe_2O_3 and 2 mole of Al are mixed at temperature $25^\circ C$ and the reaction is completed to give :



The liberated heat is retained within the products, whose combined specific heat over a wide temperature range is about $0.8 \text{ J g}^{-1} \text{ K}^{-1}$. The melting point of iron is $1530^\circ C$. Show that the quantity of heat liberated is sufficient to raise the temperature of the product to the melting point of iron in order to get it welded.

Solution: Mass of products

$$= \text{Mass of one mole } Al_2O_3 + \text{Mass of two mole Fe}$$

$$= 214 \text{ g}$$

$$q = ms \Delta T = 214 \times 0.8 \times (1803 - 298)$$

$$= 257656 \text{ J} = 257.656 \text{ kJ}$$

Heat required is less than heat released, hence the temperature can be easily raised to the required value.

Example 11. Calculate w and ΔE for the conversion of 0.5 mole of water at $100^\circ C$ to steam at 1 atm pressure. Heat of vaporisation of water at $100^\circ C$ is 40670 J mol^{-1} .

Solution: Volume of 0.5 mole of steam at 1 atm pressure

$$= \frac{nRT}{P} = \frac{0.5 \times 0.0821 \times 373}{1.0} = 15.3 \text{ L}$$

$$\text{Change in volume} = \text{Vol. of steam} - \text{Vol. of water}$$

$$= 15.3 - \text{negligible} = 15.3 \text{ L}$$

Work done by the system,

$$w = P_{\text{ext}} \times \text{volume change}$$

$$= 1 \times 15.3 = 15.3 \text{ litre-atm}$$

$$= 15.3 \times 101.3 \text{ J} = 1549.89 \text{ J}$$

' w ' should be negative as the work has been done by the system on the surroundings.

$$w = -1549.89 \text{ J}$$

Heat required to convert 0.5 mole of water at $100^\circ C$ to steam

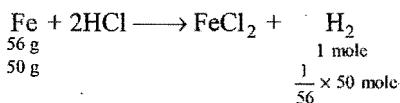
$$= 0.5 \times 40670 \text{ J} = 20335 \text{ J}$$

According to first law of thermodynamics,

$$\Delta E = q + w = 20335 - 1549.89 = 18785.11 \text{ J}$$

Example 12. Calculate the work done when 50 g of iron is dissolved in HCl at 25°C in (i) a closed vessel and (ii) an open beaker when the atmospheric pressure is 1 atm.

Solution: (i) When the reaction is carried in a closed vessel, the change in volume is zero. Hence, the work done by the system will be zero. (ii) When iron dissolves in HCl, hydrogen is produced.



Volume of hydrogen produced at 25°C

$$= \frac{nRT}{P} = \frac{50}{56} \times \frac{0.0821 \times 298}{1} = 21.84 \text{ L}$$

This is equal to volume change when the reaction is carried in open beaker.

Work done by the system $= -P \Delta V = -1.0 \times 21.84$

$$= -21.84 \text{ litre-atm} = -2212.39 \text{ J}$$

Example 13. 5 mole of oxygen are heated at constant volume from 10°C to 20°C. What will be the change in the internal energy of gas? The molar heat of oxygen at constant pressure, $C_p = 7.03 \text{ cal mol}^{-1} \text{ deg}^{-1}$ and $R = 8.31 \text{ J mol}^{-1} \text{ deg}^{-1}$.

$$\begin{aligned} \text{Solution: } R &= 8.31 \text{ J mol}^{-1} \text{ deg}^{-1} = \frac{8.31}{4.18} \text{ cal mol}^{-1} \text{ deg}^{-1} \\ &= 1.99 \text{ cal mol}^{-1} \text{ deg}^{-1} \end{aligned}$$

We know that, $C_p - C_v = R$

$$\text{or } C_v = C_p - R = 7.03 - 1.99 = 5.04 \text{ cal mol}^{-1} \text{ deg}^{-1}$$

Heat absorbed by 5 mole of oxygen in heating from 10°C to 20°C

$$= 5 \times C_v \times \Delta T = 5 \times 5.04 \times 10 = 252 \text{ cal}$$

Since, the gas is heated at constant volume, no external work is done,

$$\text{i.e., } w = 0$$

So, change in internal energy will be equal to heat absorbed,

$$\Delta E = q + w = 252 + 0 = 252 \text{ cal}$$

Example 14. Calculate the amount of work done by 2 mole of an ideal gas at 298 K in reversible isothermal expansion from 10 litre to 20 litre.

Solution: Amount of work done in reversible isothermal expansion,

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

Given, $n = 2$, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$, $T = 298 \text{ K}$, $V_2 = 20 \text{ L}$ and $V_1 = 10 \text{ L}$.

Substituting the values in above equation,

$$\begin{aligned} w &= -2.303 \times 2 \times 8.314 \times 298 \log \frac{20}{10} \\ &= -2.303 \times 2 \times 8.314 \times 298 \times 0.3010 = -3434.9 \text{ J} \end{aligned}$$

i.e., work is done by the system.

Example 15. 5 moles of an ideal gas expand isothermally and reversibly from a pressure of 10 atm to 2 atm at 300 K. What is the largest mass which can be lifted through a height of 1 metre in this expansion?

Solution: Work done by the system

$$\begin{aligned} &= -nRT \log_e \frac{P_1}{P_2} = -2.303nRT \log \frac{P_1}{P_2} \\ &= -2.303 \times 5 \times 8.314 \times 300 \log \frac{10}{2} = -20.075 \times 10^3 \text{ J} \end{aligned}$$

Let M be the mass which can be lifted through a height of 1 m.

Work done in lifting the mass

$$= Mgh = M \times 9.8 \times 1 \text{ J}$$

$$\text{So, } M \times 9.8 = 20.075 \times 10^3$$

$$M = 2048.469 \text{ kg}$$

Example 16. Two moles of an ideal monoatomic gas at NTP are compressed adiabatically and reversibly to occupy a volume of 4.48 dm³. Calculate the amount of work done, ΔE , final temperature and pressure of the gas. C_V for ideal gas = $12.45 \text{ J K}^{-1} \text{ mol}^{-1}$.

Solution: For an ideal gas, $\gamma = \frac{C_p}{C_v} = 1.667$

Initial volume, $V_1 = 2 \times 22.4 = 44.8 \text{ dm}^3$

Initial pressure, $P_1 = 1 \text{ atm}$

Initial temperature, $T_1 = 273 \text{ K}$

Final volume, $V_2 = 4.48 \text{ dm}^3$

Let the final pressure be P_2 and temperature be T_2 .

Applying $P_1 V_1^\gamma = P_2 V_2^\gamma$

$$\text{or } \frac{P_1}{P_2} = \left(\frac{V_2}{V_1} \right)^\gamma = \left(\frac{4.48}{44.8} \right)^{1.667}$$

$$\text{or } \frac{P_2}{P_1} = (10)^{1.667}$$

$$P_2 = (10)^{1.667} (P_1 = 1 \text{ given})$$

$$\log P_2 = 1.667 \log 10 = 1.667$$

$$P_2 = \text{antilog } 1.667 = 46.45 \text{ atm}$$

$$\begin{aligned} \text{Final temperature } &= \frac{\dot{P}_2 V_2}{P_1 V_1} \cdot T_1 = \frac{46.45 \times 4.48}{1 \times 44.8} \times 273 \\ &= 1268 \text{ K} \end{aligned}$$

Work done on the system = $n \cdot C_V \cdot \Delta T$

$$= 2 \times 12.45 \times (1268 - 273)$$

$$= 2 \times 12.45 \times 995 = 24775.5 \text{ J}$$

From the first law of thermodynamics,

$$\Delta E = q + w = 0 + 24775.5 = 24775.5 \text{ J}$$

Example 17. A certain volume of dry air at NTP is expanded reversibly to four times its volume (a) isothermally (b) adiabatically. Calculate the final pressure and temperature in each case, assuming ideal behaviour.

$$\left(\frac{C_p}{C_v} \text{ for air} = 1.4 \right)$$

Solution: Let V_1 be the initial volume of dry air at NTP.

(a) Isothermal expansion: During isothermal expansion, the temperature remains the same throughout. Hence, final temperature will be 273 K.

Since,

$$P_1 V_1 = P_2 V_2$$

$$P_2 = \frac{P_1 V_1}{V_2} = \frac{1 \times V_1}{4V_1} = 0.25 \text{ atm}$$

(b) Adiabatic expansion:

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

$$\frac{273}{T_2} = \left(\frac{4V_1}{V_1} \right)^{1.4-1} = 4^{0.4}$$

$$T_2 = \frac{273}{4^{0.4}} = 156.79 \text{ K}$$

Final pressure: $\frac{P_1}{P_2} = \left(\frac{V_2}{V_1} \right)^\gamma$

$$\frac{1}{P_2} = \left(\frac{4V_1}{V_1} \right)^{1.4} = 4^{1.4}$$

$$P_2 = \frac{1}{4^{1.4}} = 0.143 \text{ atm}$$

Example 18. Calculate q , w , ΔE and ΔH for the reversible isothermal expansion of one mole of an ideal gas at 127°C from a volume of 10 dm^3 to 20 dm^3 .

Solution: Since, the process is isothermal,

$$\Delta E = \Delta H = 0$$

From first law of thermodynamics,

$$\Delta E = q + w = 0$$

$$q = -w$$

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

$$= -2.303 \times 1 \times 8.314 \times 400 \log \frac{20}{10}$$

$$= -2.303 \times 1 \times 8.314 \times 400 \times 0.3010$$

$$= -2305.3 \text{ J} \quad (\text{Work is done by the system})$$

$$q = -w = 2305.3 \text{ J} \quad (\text{Heat is absorbed by the system})$$

Example 19. A gas expands from a volume of 3.0 dm^3 to 5.0 dm^3 against a constant pressure of 3.0 atm . The work done during expansion is used to heat 10.0 mole of water of

temperature 290.0 K . Calculate the final temperature of water (specific heat of water = $4.184 \text{ JK}^{-1} \text{ g}^{-1}$). (IIT 1993)

Solution: Work done = $P \times dV = 3.0 \times (5.0 - 3.0)$

$$= 6.0 \text{ litre-atm} = 6.0 \times 101.3 \text{ J}$$

$$= 607.8 \text{ J}$$

Let ΔT be the change in temperature.

$$\text{Heat absorbed} = m \times s \times \Delta T$$

$$= 10.0 \times 18 \times 4.184 \times \Delta T$$

$$\text{Given,} \quad P \times dV = m \times s \times \Delta T$$

$$\text{or} \quad \Delta T = \frac{P \times dV}{m \times s} = \frac{607.8}{10.0 \times 18.0 \times 4.184} = 0.807$$

$$\text{Final temperature} = 290 + 0.807 = 290.807 \text{ K}$$

Example 20. 10 g of argon gas is compressed isothermally and reversibly at a temperature of 27°C from 10 litre to 5 litre . Calculate q , w , ΔE and ΔH for this process.

$$R = 2 \text{ cal K}^{-1} \text{ mol}^{-1}, \log 2 = 0.30. \text{ Atomic weight of Ar} = 40. \quad (\text{IIT 1997})$$

$$\text{Solution: } w = -2.303nRT \log \frac{V_2}{V_1}$$

$$= -2.303 \times \frac{10}{40} \times 2 \times 300 \log \frac{5}{10} = 103.635 \text{ cal}$$

$$\Delta E = 0$$

$$q = \Delta E - w$$

$$q = -w = -103.635 \text{ cal}$$

Example 21. Calculate the maximum work done in expanding 16 g of oxygen at 300 K and occupying a volume of 5 dm^3 isothermally until the volume becomes 25 dm^3 .

Solution: Reversible work is maximum work.

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

$$= 2.303 \times \frac{16}{32} \times 8.314 \times 300 \log \frac{25}{5} = 2.01 \times 10^3 \text{ joule}$$

Example 22. How much heat is required to change 10 g ice at 0°C to steam at 100°C ? Latent heat of fusion and vaporization for H_2O are 80 cal/g and 540 cal/g , respectively. Specific heat of water is 1 cal/g .

Solution: Total heat absorbed

$$= \Delta H_{\text{fusion}} + \Delta H_{\text{temp. rise}} + \Delta H_{\text{vap.}}$$

$$= 10 \times 80 + 10 \times 1 \times 100 + 10 \times 540 = 7200 \text{ cal}$$

Example 23. A swimmer coming out of a pool is covered with a film of water weighing about 80 g . How much heat must be supplied to evaporate this water?

Solution: $q = mL$

$$= \frac{80}{18} \times 40.79 \\ = 181.28 \text{ kJ}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

1. 5 moles of an ideal gas at 27°C expands isothermally and reversibly from a volume of 6 L to 60 L. The work done in kJ is:

(a) -14.7 (b) -28.72 (c) +28.72 (d) -56.72

[Ans. (b)]

[Hint: $w = -2.303nRT \log \frac{V_2}{V_1}$

$$= -2.303 \times 5 \times 8.314 \times 300 \log \frac{60}{6}$$

$$= -28.72 \text{ kJ}$$

2. 10 moles of an ideal gas confined to a volume of 10 L is released into atmosphere at 300 K where the pressure is 1 bar. The work done by the gas is:

($R = 0.083 \text{ L bar K}^{-1} \text{ mol}^{-1}$)

(a) 249 L bar (b) 259 L bar (c) 239 L bar (d) 220 L bar

[Ans. (c)]

[Hint: Initial volume, $V_1 = 10 \text{ L}$

$$V_2 (\text{final}) = \frac{nRT}{P} = \frac{10 \times 0.083 \times 300}{1} = 249 \text{ L}$$

$$W = P \Delta V = 1 \times (249 - 10)$$

$$= 239 \text{ L bar}$$

3. 1 litre-atm work is approximately equal to:

(a) 101.3 J (b) 8.314 J (c) 931 J (d) 19.2 J

[Ans. (a)]

[Hint: 0.0821 litre-atm = 8.314 J (values of gas constant)]

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

4. A system absorbs 20 kJ heat and also does 10 kJ of work. The net internal energy of the system:

(a) increases by 10 kJ (b) decreases by 10 kJ
(c) increases by 30 kJ (d) decreases by 30 kJ

[Ans. (a)]

[Hint: $\Delta U = q + w = 20 - 10 = 10 \text{ kJ}$]

5. One mole of a gas is heated at constant pressure to raise its temperature by 1°C. The work done in joules is:

(a) -4.3 (b) -8.314
(c) -16.62 (d) unpredictable

[Ans. (b)]

[Hint: $w = -nR \Delta T$ or $w = -P \Delta V$

$$= -1 \times 8.314 \times 1 = -P \left(\frac{nRT_2}{P} - \frac{nRT_1}{P} \right)$$

$$= -8.314 \text{ J}$$

6. In open system:

(a) there will be exchange of both matter and energy
(b) there will be no exchange of matter and energy
(c) there will be exchange of energy only
(d) there will be exchange of matter only

[Ans. (a)]

[Hint: Open system has imaginary boundary, therefore, both energy and mass can be exchanged.]

7.10 THERMOCHEMISTRY

Thermochemistry is a branch of physical chemistry which is concerned with energy changes accompanying chemical transformations. It is also termed as chemical energetics. It is based on the first law of thermodynamics.

Chemical reactions are accompanied by evolution or absorption of heat energy. When reactants combine together to form new products, there is readjustment of energies. During a chemical reaction, the chemical bonds between atoms in the reactant molecules are rearranged in the product molecules, i.e., chemical bonds in the reactants are broken down and new chemical bonds are formed in the products. Energy is needed to break the bonds of reactants and energy is released in the formation of new bonds of products.

Exothermic Reactions

Heat is evolved in these chemical reactions. It is possible when the bond energy of reactants is less than the bond energy of products.

At constant pressure,

$$\Delta H = (H_P - H_R) = -\text{ve}, \quad \text{i.e., } H_P < H_R$$

At constant volume,

$$\Delta E = (E_P - E_R) = -\text{ve}, \quad \text{i.e., } E_P < E_R$$

Endothermic Reactions

Heat is absorbed in these chemical reactions. It is possible when the bond energy of reactants is greater than the bond energy of products.

At constant pressure,

$$\Delta H = H_P - H_R = +\text{ve}, \quad \text{i.e., } H_P > H_R$$

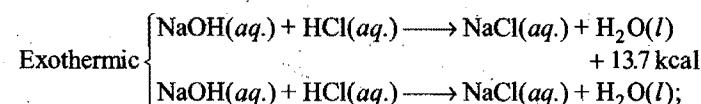
At constant volume,

$$\Delta E = E_P - E_R = +\text{ve}, \quad \text{i.e., } E_P > E_R$$

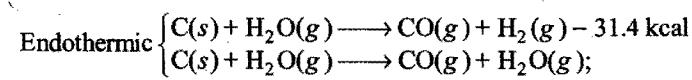
Sign conventions:

| | ΔQ | ΔE | ΔH |
|-------------|------------|------------|------------|
| Exothermic | (-) | (-) | (-) |
| Endothermic | (+) | (+) | (+) |

Exothermic and endothermic chemical equations can be represented as:



$$\Delta H = -13.7 \text{ kcal}$$



$$\Delta H = +31.4 \text{ kcal}$$

7.11 HEAT OF REACTION OR ENTHALPY OF REACTION

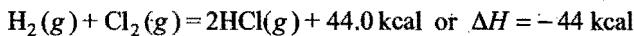
Heat of reaction is defined as the amount of heat evolved or absorbed when quantities of the substances indicated by the chemical equation have completely reacted. The heat of reaction

(or enthalpy of reaction) is actually the difference between the enthalpies of the products and the reactants when the quantities of the reactants indicated by the chemical equation have completely reacted. Mathematically,

Enthalpy of reaction (or heat of reaction)

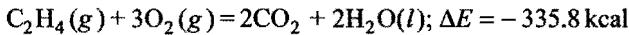
$$= \Delta H = \Sigma H_P - \Sigma H_R$$

For example, the equation



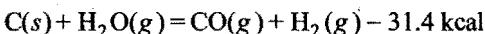
indicates that when 2 g of hydrogen (1 mole) completely reacts with 71 g of chlorine (1 mole) to form 73 g of HCl (2 mole), the amount of heat evolved is 44.0 kcal or the enthalpy decreases by 44.0 kcal or the reacting system loses 44.0 kcal of heat or the enthalpy change of the reaction, $\Delta H = -44.0 \text{ kcal}$.

Consider the following reaction:



The equation indicates that reaction has been carried between 1 mole of C_2H_4 and 3 mole of oxygen at constant volume and $25^\circ C$. The heat evolved is 335.8 kcal or the internal energy of the system decreases by 335.8 kcal.

Consider another reaction:



or $\Delta H = 31.4 \text{ kcal}$

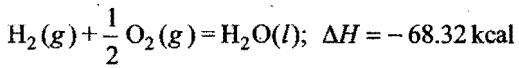
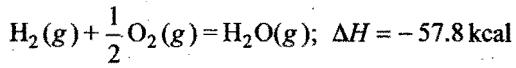
This reaction indicates that 1 mole of carbon (12 g) reacts with 1 mole of steam (18 g) to form 1 mole of CO and 1 mole of hydrogen and 31.4 kcal of heat is absorbed. The enthalpy of the system increases by 31.4 kcal or the total enthalpy of the products is 31.4 kcal more than the enthalpy of reactants.

Factors which Influence the Heat of Reaction

There are a number of factors which affect the magnitude of heat of reaction.

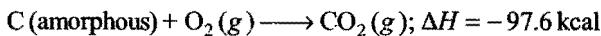
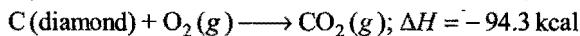
(i) Physical state of reactants and products: Heat energy is involved for changing the physical state of a chemical substance. For example, in the conversion of water into steam, heat is absorbed and heat is evolved when steam is condensed.

Considering the following two reactions:

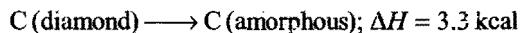


It is observed that there is difference in the value of ΔH if water is obtained in gaseous or liquid state. ΔH value in second case is higher because heat is evolved when steam condenses. Hence, physical state always affects the heat of reaction.

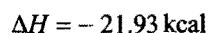
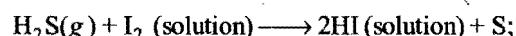
(ii) Allotropic forms of the element: Heat energy is also involved when one allotropic form of an element is converted into another. Thus, the value of ΔH depends on the allotropic form used in the reaction. For example, the value of ΔH is different when carbon in the form of diamond or in amorphous form is used.



The difference between the two values is equal to the heat absorbed when 12 g of diamond is converted into 12 g of amorphous carbon. This is termed as **heat of transition**.



(iii) Enthalpies of solution: Enthalpies of reaction differ when in one case dry substances react and in another case when the same substances react in solution. For example, in the reaction between hydrogen sulphide and iodine,



(iv) Temperature: Heat of reaction or enthalpy of reaction also depends on the temperature at which the reaction is carried out. This is due to variation in the heat capacity of the system with temperature. Due to this reason, enthalpies of reaction are calculated and expressed at a standard temperature of $25^\circ C$ or 298 K. However, if the reaction is not carried out at $25^\circ C$, the temperature at which the reaction is performed, is indicated.

(v) Reaction carried out at constant pressure or constant volume: When a chemical reaction occurs at constant volume, the heat change is called the enthalpy of reaction at constant volume. However, most of the reactions are carried out at constant pressure; the enthalpy change is then termed as the enthalpy of reaction at constant pressure. The difference in the values is negligible when solids and liquids are involved in a chemical change. But, in reactions which involve gases, the difference in two values is considerable. For this purpose see section 7.5.

$$\Delta E + \Delta nRT = \Delta H$$

or

$$q_V + \Delta nRT = q_P$$

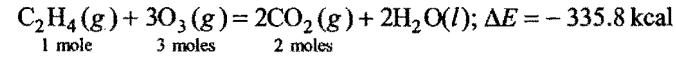
q_V = heat change at constant volume,

q_P = heat change at constant pressure.

Δn = total number of moles of products – total number of moles of reactants

Example 24. The heat of combustion of ethylene at $18^\circ C$ and at constant volume is -335.8 kcal when water is obtained in liquid state. Calculate the heat of combustion at constant pressure and at $18^\circ C$.

Solution: The chemical equation for the combustion of C_2H_4 is



$$\text{No. of moles of reactants} = (1+3) = 4$$

$$\text{No. of moles of products} = 2$$

$$\text{So, } \Delta n = (2-4) = -2$$

$$\text{Given, } \Delta E = -335.8 \text{ kcal}, \Delta n = -2, R = 2 \times 10^{-3} \text{ kcal}$$

and

$$T = (18+273) = 291 \text{ K}$$

Applying

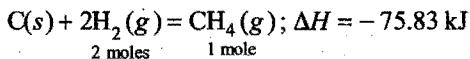
$$\Delta H = \Delta E + \Delta nRT$$

$$= -335.8 + (-2)(2 \times 10^{-3})(291)$$

$$= -336.964 \text{ kcal}$$

Example 25. The enthalpy of formation of methane at constant pressure and 300 K is -75.83 kJ. What will be the heat of formation at constant volume? ($R = 8.3 \text{ J K}^{-1} \text{ mol}^{-1}$)

Solution: The equation for the formation of methane is



$$\Delta n = (1 - 2) = -1$$

Given, $\Delta H = -75.83 \text{ kJ}$, $R = 8.3 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}$, $T = 300 \text{ K}$

Applying $\Delta H = \Delta E + \Delta nRT$

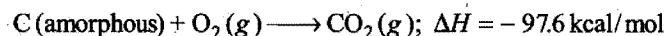
$$-75.83 = \Delta E + (-1)(8.3 \times 10^{-3})(300)$$

$$\begin{aligned} \text{So, } \Delta E &= -75.83 + 2.49 \\ &= -73.34 \text{ kJ} \end{aligned}$$

12 ENTHALPY OF FORMATION OR HEAT OF FORMATION

The process in which a compound is formed from its constituent elements in their standard state is called **formation**.

The amount of heat absorbed or evolved when 1 mole of the substance is directly obtained from its constituent elements is called **heat of formation**.



Enthalpy of formation of CO_2 is -97.6 kcal

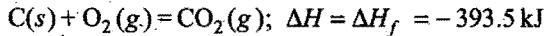


Thus, enthalpy of formation of HCl is -22 kcal per mol.

Standard enthalpy of formation: The enthalpy of formation depends upon the conditions of formation, i.e., temperature, pressure and physical states (gas, solid or liquid) or allotropic state of the reactants. If all substances of the chemical reaction are in their standard states (i.e., at 25°C or 298 K and 1 atmospheric pressure), the heat of formation or enthalpy of formation is called **standard heat of formation or standard enthalpy of formation**. It is denoted by ΔE_f° (volume constant) or ΔH_f° (pressure constant).

It is very difficult to determine absolute values of enthalpies of substances. However, relative enthalpies of substances can be determined if the enthalpies of free elements at 25°C and 1 atmospheric pressure are taken arbitrarily as zero.

Consider the reaction between carbon and oxygen at 25°C to form carbon dioxide under atmospheric pressure.



$$\Delta H_f = \Delta H = H_P - H_R = -393.5 \text{ kJ}$$

$H_R = 0$, i.e., enthalpies of free elements are taken as zero.

So, $\Delta H_f = \Delta H = H_P = \text{enthalpy of CO}_2 = -393.5 \text{ kJ}$

Thus, $\Delta H_f^\circ = -393.5 \text{ kJ}$.

The compounds which have positive enthalpies of formation are called **endothermic compounds** and are less stable than the reactants. The compounds which have negative enthalpies of formation are known as **exothermic compounds** and are more stable than reactants.

The knowledge of standard heats of formation of various substances can be used to calculate the heats of reactions under standard conditions, i.e., ΔH° .

$$\Delta H^\circ \text{ for the reaction} = \left[\begin{array}{l} \text{Sum of the standard} \\ \text{heats of formation} \\ \text{of products} \end{array} \right] - \left[\begin{array}{l} \text{Sum of the standard} \\ \text{heats of formation} \\ \text{of reactants} \end{array} \right]$$

$$\text{i.e., } \Delta H^\circ = \sum \Delta H_f^\circ (\text{products}) - \sum \Delta H_f^\circ (\text{reactants})$$

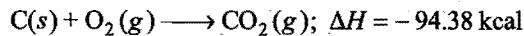
The heats of formation of all the elements in their standard states are arbitrarily assumed to be zero.

Intrinsic energy: It may be defined as:

Intrinsic energy = Heat of formation

"Additional amount of energy which one gram mole of the compound possesses above that of its constituent elements."

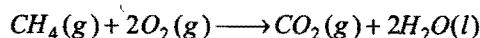
Let us consider the combustion of carbon.



When 1 mole CO_2 is formed, 94.38 kcal heat is evolved. It means, energy content of CO_2 is less than energy content of $\text{C}(s)$ and $\text{O}_2(g)$ by 94.38 kcal. Thus, intrinsic energy of CO_2 is 94.38 kcal.

If we assume that intrinsic energy of elements is zero, then intrinsic energy of compound may be calculated in the form of heat of formation. Hence, intrinsic energy may not be considered as internal energy of the compound.

Example 26. Calculate the enthalpy change for the following reaction:



given, enthalpies of formation of CH_4 , CO_2 and H_2O are $-74.8 \text{ kJ mol}^{-1}$, $-393.5 \text{ kJ mol}^{-1}$ and $-286.2 \text{ kJ mol}^{-1}$ respectively.

Solution:

$$\begin{aligned} \Delta H^\circ &= \Delta H_f^\circ (\text{products}) - \Delta H_f^\circ (\text{reactants}) \\ &= [\Delta H_f^\circ (\text{CO}_2) + 2\Delta H_f^\circ (\text{H}_2\text{O})] - [\Delta H_f^\circ (\text{CH}_4) + 2\Delta H_f^\circ (\text{O}_2)] \\ &= [-393.5 + 2 \times (-286.2)] - [-74.8 + 2 \times 0] \\ &= -393.5 - 572.4 + 74.8 \\ &= -891.1 \text{ kJ} \end{aligned}$$

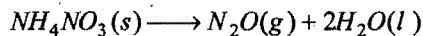
Example 27. The standard heats of formation at 298 K for $\text{CCl}_4(g)$, $\text{H}_2\text{O}(g)$, $\text{CO}_2(g)$ and $\text{HCl}(g)$ are -25.5 , -57.8 , -94.1 and $-22.1 \text{ kcal mol}^{-1}$ respectively. Calculate ΔH_{298}° for the reaction.



Solution:

$$\begin{aligned} \Delta H^\circ &= \Delta H_f^\circ (\text{products}) - \Delta H_f^\circ (\text{reactants}) \\ &= [\Delta H_f^\circ (\text{CO}_2) + 4\Delta H_f^\circ (\text{HCl})] - [\Delta H_f^\circ (\text{CCl}_4) + 2\Delta H_f^\circ (\text{H}_2\text{O})] \\ &= [-94.1 + 4 \times (-22.1)] - [-25.5 + 2 \times (-57.8)] \\ &= -94.1 - 88.4 + 25.5 + 115.6 \\ &= -182.5 + 141.1 = -41.4 \text{ kcal} \end{aligned}$$

Example 28. The molar heat of formation of $\text{NH}_4\text{NO}_3(s)$ is -367.5 kJ and those of $\text{N}_2\text{O}(g)$ and $\text{H}_2\text{O}(l)$ are $+81.46 \text{ kJ}$ and -285.78 kJ respectively at 25°C and 1 atmospheric pressure. Calculate the ΔH and ΔE for the reaction,



$$\text{Solution: } \Delta H^\circ = \Delta H_f^\circ(\text{products}) - \Delta H_f^\circ(\text{reactants})$$

$$\begin{aligned} &= [\Delta H_f^\circ(\text{N}_2\text{O}) + 2 \times \Delta H_f^\circ(\text{H}_2\text{O})] - [\Delta H_f^\circ(\text{NH}_4\text{NO}_3)] \\ &= 81.46 + 2 \times (-285.78) - (-367.5) \\ &= 81.46 - 571.56 + 367.5 \\ &= -122.56 \text{ kJ} \end{aligned}$$

$$\text{We know that, } \Delta H = \Delta E + \Delta nRT$$

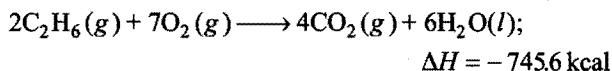
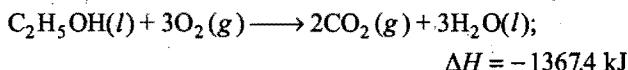
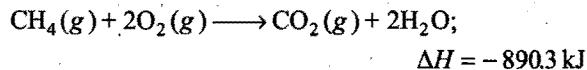
$$\text{or } \Delta E = \Delta H - \Delta nRT$$

$$\Delta n = 1; R = 8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}; T = 298 \text{ K}$$

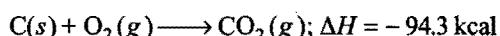
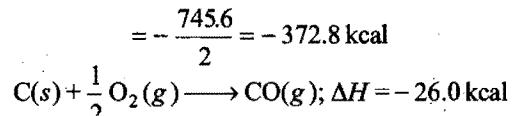
$$\begin{aligned} \Delta E &= -122.56 - (1)(8.314 \times 10^{-3})(298) \\ &= -122.56 - 2.477 \\ &= -125.037 \text{ kJ} \end{aligned}$$

7.13 ENTHALPY OF COMBUSTION OR HEAT OF COMBUSTION

Enthalpy of combustion is the amount of heat evolved or decrease in enthalpy when 1 mole of the substance (compound or element) is completely oxidised. The enthalpy of combustion, i.e., ΔH is always negative. For example,



Since, 2 mole of C_2H_6 are involved, hence enthalpy of combustion of ethane



The enthalpy of combustion of carbon is not -26.0 kcal as combustion is not complete because carbon monoxide can further be oxidised to carbon dioxide. The enthalpy of combustion of carbon is thus -94.3 kcal .

The enthalpies of combustion have a number of applications. Some of these are described below:

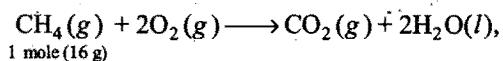
(i) **Calorific values of foods and fuels:** Energy is needed for the working of all machines. Even human body is no exception. Coal, petroleum, natural gas, etc., serve as the principal sources of energy for man-made machines, the food which we eat serves as a source of energy to our body. These substances undergo oxidation or combustion and release energy.

These substances are, therefore, termed as fuels. An adult requires 2500 to 3000 kcal of energy per day. Since, the values of enthalpies of combustion of different food articles are known, it becomes easy to calculate our daily requirements and thus select the articles of food so as to secure a balanced diet.

The grading of food articles and various fuels can be done on the basis of the values of enthalpies of combustion.

The energy released by the combustion of foods or fuels is usually compared in terms of their combustion energies per gram. It is known as calorific value. The amount of heat produced in calorie or joule when one gram of a substance (food or fuel) is completely burnt or oxidised.

When methane burns, $890.3 \text{ kJ mol}^{-1}$ of energy is released.



$$\Delta H_{\text{CH}_4} = -890.3 \text{ kJ}$$

$$\text{So, the calorific value of methane} = -\frac{890.3}{16} = -55.6 \text{ kJ/g}$$

Calorific values of some important foodstuffs and fuels are given below:

| Fuel | Calorific value (kJ/g) | Food | Calorific value (kJ/g) |
|----------|------------------------|--------|------------------------|
| Wood | 17 | Milk | 3.1 |
| Charcoal | 33 | Egg | 6.7 |
| Kerosine | 48 | Rice | 16.7 |
| Methane | 55 | Sugar | 17.3 |
| LPG | 55 | Butter | 30.4 |
| Hydrogen | 150 | Ghee | 37.6 |

Out of the fuels listed, hydrogen has the highest calorific value. However, it is not used as domestic or industrial fuel due to some technical problems. Of the various constituents of our food, fats and carbohydrates serve as the main sources of energy. The calorific value of proteins is quite low.

(ii) **Enthalpies of formation:** Enthalpies of formation of various compounds, which are not directly obtained, can be calculated from the data of enthalpies of combustions easily by the application of Hess's law.

$$\text{Heat of reaction} = \Sigma \text{Heat of combustion of reactants}$$

$$- \Sigma \text{Heat of combustion of products}$$

SOME SOLVED EXAMPLES

Example 29. The heats of combustion of CH_4 and C_4H_{10} are $-890.3 \text{ kJ mol}^{-1}$ and $-2878.7 \text{ kJ mol}^{-1}$ respectively. Which of the two has greater efficiency as fuel per gram?

Solution: Molar mass of methane = 16

$$\text{Heat produced per gram of methane} = -\frac{890.3}{16} = -55.64 \text{ kJ}$$

$$\text{Molar mass of butane} = 58$$

$$\text{Heat produced per gram of butane} = -\frac{2878.7}{58} = -49.63 \text{ kJ}$$

Thus, methane has greater fuel efficiency than butane.

Example 30. In a Gobar gas plant, gobar gas is formed by bacterial fermentation of animal refuse. It mainly contains methane and its heat of combustion is -809 kJ mol^{-1} according to following equation:



How much gobar gas would have to be produced per day for a small village of 50 families, if it is assumed that each family requires 20,000 kJ of energy per day? The methane content in gobar gas is 80% by mass.

Solution: Energy consumption of 50 families per day

$$= 50 \times 20,000 \text{ kJ} = 1 \times 10^6 \text{ kJ}$$

809 kJ of energy is obtained by burning methane = 16 g

$1 \times 10^6 \text{ kJ}$ of energy will be obtained by burning methane

$$\begin{aligned} &= \frac{16}{809} \times 10^6 = 1.98 \times 10^4 \text{ g} \\ &= 19.8 \text{ kg} \end{aligned}$$

Since, methane content in gobar gas is 80% by mass, hence, the mass of gobar gas needed

$$= \frac{100}{80} \times 19.8 = 24.75 \text{ kg}$$

Example 31. The standard molar heats of formation of ethane, carbon dioxide and liquid water are -21.1 , -94.1 and -68.3 kcal respectively. Calculate the standard molar heat of combustion of ethane.

Solution: The required chemical equation for combustion of ethane is



The equation involves 2 moles of C_2H_6 ; heat of combustion of ethane will be $= \frac{\Delta H^\circ}{2}$

$$\Delta H^\circ = \Delta H_f^\circ(\text{products}) - \Delta H_f^\circ(\text{reactants})$$

$$\begin{aligned} &= [4 \times \Delta H_f^\circ(\text{CO}_2) + 6 \times \Delta H_f^\circ(\text{H}_2\text{O})] - [2 \times \Delta H_f^\circ(\text{C}_2\text{H}_6) + 7 \times \Delta H_f^\circ(\text{O}_2)] \\ &= [4 \times (-94.1) + 6 \times (-68.3)] - [2 \times (-21.1) + 7 \times 0] \\ &= -376.4 - 409.8 + 42.2 \\ &= -744.0 \text{ kcal} \end{aligned}$$

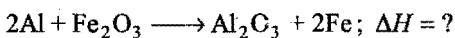
$$\frac{\Delta H^\circ}{2} = \text{Heat of combustion of ethane} = -\frac{744.0}{2} = -372.0 \text{ kcal}$$

Example 32. An intimate mixture of ferric oxide and aluminium is used as solid fuel in rockets. Calculate the fuel value per cm^3 of the mixture. Heats of formation and densities are as follows:

$$H_f(\text{Al}_2\text{O}_3) = -399 \text{ kcal mol}^{-1}; H_f(\text{Fe}_2\text{O}_3) = -199 \text{ kcal mol}^{-1}$$

$$\text{Density of } \text{Fe}_2\text{O}_3 = 5.2 \text{ g/cm}^3; \text{ Density of Al} = 2.7 \text{ g/cm}^3$$

Solution: The required equation is:



$$\Delta H = \Delta H_f(\text{products}) - \Delta H_f(\text{reactants})$$

$$= [\Delta H_f(\text{Al}_2\text{O}_3) + 2\Delta H_f(\text{Fe})] - [2\Delta H_f(\text{Al}) + \Delta H_f(\text{Fe}_2\text{O}_3)]$$

$$= (-399 + 2 \times 0) - [2 \times 0 + (-199)]$$

$$= -399 + 199 = -200 \text{ kcal}$$

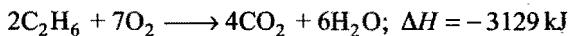
$$\text{At. mass of aluminium} = 27, \text{ Mol. mass of Fe}_2\text{O}_3 = 160$$

$$\text{Volume of reactants} = \frac{160}{5.2} + \frac{2 \times 27}{2.7} = 50.77 \text{ cm}^3$$

$$\text{Fuel value per cm}^3 = \frac{200}{50.77} = 3.92 \text{ kcal}$$

Example 33. When 2 mole of C_2H_6 are completely burnt, 3129 kJ of heat is liberated. Calculate the heat of formation of C_2H_6 . ΔH_f for CO_2 and H_2O are -395 kJ and -286 kJ respectively.

Solution: The equation for the combustion of C_2H_6 is:



$$\Delta H = \Delta H_f(\text{products}) - \Delta H_f(\text{reactants})$$

$$\begin{aligned} &= [4 \times \Delta H_f(\text{CO}_2) + 6 \times \Delta H_f(\text{H}_2\text{O})] - [2 \times \Delta H_f(\text{C}_2\text{H}_6) + 7 \times \Delta H_f(\text{O}_2)] \\ &= [4 \times (-395) + 6 \times (-286)] - [2 \times \Delta H_f(\text{C}_2\text{H}_6) + 7 \times 0] \end{aligned}$$

or

$$2 \times \Delta H_f(\text{C}_2\text{H}_6) = -167$$

$$\text{So, } \Delta H_f(\text{C}_2\text{H}_6) = -\frac{167}{2} = -83.5 \text{ kJ}$$

Example 34. The standard heats of formation of $\text{CH}_4(g)$, $\text{CO}_2(g)$ and $\text{H}_2\text{O}(g)$ are -76.2 , -398.8 and $-241.6 \text{ kJ mol}^{-1}$ respectively. Calculate the amount of heat evolved by burning 1 m^3 of methane measured under normal conditions. (IIT 1990)

Solution: The required equation for the combustion of methane is:



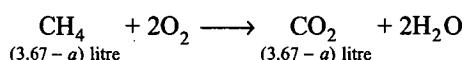
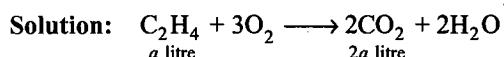
$$\Delta H = \Delta H_f(\text{products}) - \Delta H_f(\text{reactants})$$

$$\begin{aligned} &= \Delta H_f(\text{CO}_2) + 2 \times \Delta H_f(\text{H}_2\text{O}) - \Delta H_f(\text{CH}_4) - 2 \times \Delta H_f(\text{O}_2) \\ &= -398.8 - 2 \times 241.6 - (-76.2) - 2 \times 0 \\ &= -805.8 \text{ kJ mol}^{-1} \end{aligned}$$

Heat evolved by burning 22.4 litre (1 mole) methane = -805.8 kJ . So, heat evolved by burning 1000 litre (1 m^3) methane

$$= \frac{-805.8}{22.4} \times 1000 = -35973.2 \text{ kJ}$$

Example 35. A gas mixture of 3.67 litre of ethylene and methane on complete combustion at 25°C produces 6.11 litre of CO_2 . Find out the heat evolved on burning 1 litre of the gas mixture. The heats of combustion of ethylene and methane are -1423 and -891 kJ mol^{-1} at 25°C . (IIT 1991)



Given, $2a + 3.67 - a = 6.11$

$$a = 2.44 \text{ litre}$$

Volume of ethylene in mixture = 2.44 litre

Volume of methane in mixture = 1.23 litre

$$\text{Volume of ethylene in 1 litre mixture} = \frac{2.44}{3.67} = 0.6649 \text{ litre}$$

$$\text{Volume of methane in 1 litre mixture} = \frac{1.23}{3.67} = 0.3351 \text{ litre}$$

24.45 litre of a gas at 25° C correspond to 1 mole.

Thus, heat evolved by burning 0.6649 litre of ethylene

$$= -\frac{1423}{24.5} \times 0.6649 = -38.69 \text{ kJ}$$

and heat evolved by burning 0.3351 litre of methane

$$= -\frac{891}{24.45} \times 0.3351 = -12.21 \text{ kJ}$$

So, total heat evolved by burning 1 litre of mixture

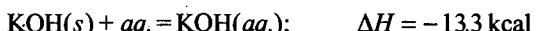
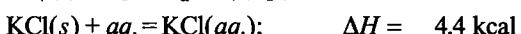
$$= -38.69 - 12.21$$

$$= -50.90 \text{ kJ}$$

7.14 ENTHALPY OF SOLUTION OR HEAT OF SOLUTION

The amount of heat evolved or absorbed when 1 mole solute is dissolved in excess of solvent (about 200 mole) is called **heat of solution**.

Some examples, of heat of solution are:



Heat of ideal solution is taken zero.

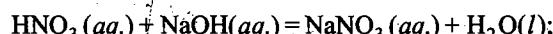
Generally, dissolution of substances in a solvent is a disintegration process. This process needs energy. In such cases, energy is absorbed, i.e., ΔH is positive. But in some cases, besides the process of breaking or ionisation, there is hydrate formation. During hydration heat is evolved. The net result is that heat is either evolved or absorbed. There are also cases in which heat of separation of ions is just equal to the heat of hydration and there is very little heat effect as in the case of sodium chloride. The heat of solution of NaCl is very small as the heat of ionisation is nearly equal to the heat of hydration.

7.15 ENTHALPY OF NEUTRALISATION OR HEAT OF NEUTRALISATION

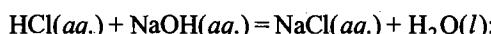
The heat of neutralisation (or enthalpy of neutralisation) is defined as the heat evolved or decrease in enthalpy when 1 gram

equivalent of an acid is neutralised by 1 gram equivalent of a base in dilute solution. Some examples are:

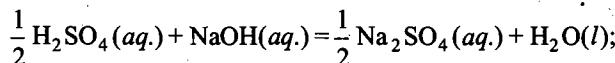
Strong acid + Strong base = Salt + Water; $\Delta H = -13.7 \text{ kcal}$



$$\Delta H = -13.7 \text{ kcal}$$

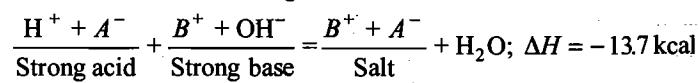


$$\Delta H = -13.75 \text{ kcal}$$

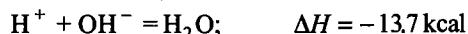


$$\Delta H = -13.7 \text{ kcal}$$

It is observed that heat of neutralisation of a strong acid against a strong base is always nearly the same, i.e., 13.7 kcal or 57 kJ, no matter what acid or base is employed. This constant value is explained with the help of theory of ionisation. Both acid and base are present in aqueous solution in the form of ions and when mixed, the following reaction occurs:

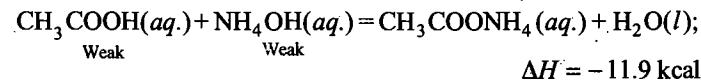
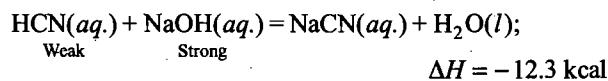
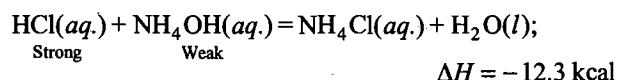


Cancelling the ions which are common on both the sides,

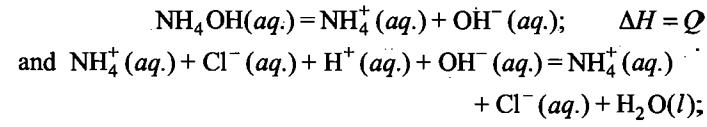


Thus, heat of neutralisation of a strong acid and a strong base is merely the heat of formation of water from H^+ and OH^- ions. This is the common reaction whenever a strong acid and a strong base are mixed and that is why the heat of neutralisation is same.

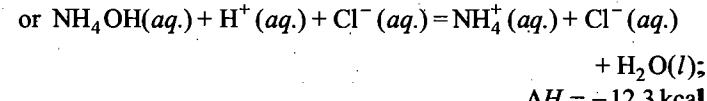
However, when a strong acid and a weak base or a weak acid and a strong base or a weak acid and a weak base are mixed in equivalent amount, the heat evolved or change in enthalpy is less than 13.7 kcal. This is shown in the following examples:



The reason for the lower value is that part of the heat energy evolved is utilised in the complete ionisation of a weak acid or a weak base or both. Hence, the net heat of neutralisation is less than 13.7 kcal. The neutralisation of NH_4OH with HCl can be explained in the following way:



$$\Delta H = -13.7 \text{ kcal}$$



$$\Delta H = -12.3 \text{ kcal}$$

$$\text{So, } Q - 13.7 = -12.3$$

$$\text{or } Q = 13.7 - 12.3 = 1.4 \text{ kcal}$$

Hence, 1.4 kcal of heat energy is absorbed for ionisation of NH_4OH which get subtracted from 13.7 kcal. Thus, the observed value of heat of neutralisation is not -13.7 kcal but -12.3 kcal .

Determination of Heat of Neutralisation

The heat of neutralisation of an acid or base can be easily determined in the laboratory with the help of polythene or polystyrene bottle. Bottle is fitted with rubber cork through which a thermometer and a stirrer are fitted as shown in the Fig. 7.16. 100 mL each of acid and alkali of equal normality are taken in separate bottles. The temperature of each solution is regularly recorded. When constant temperature is attained, the alkali solution is added to the acid solution. The mixture is quickly stirred and the maximum temperature attained is noted.

Calculations:

Suppose, the initial temperature of acid and base = T_1

Final temperature of solution after mixing = T_2

Rise in temperature = $T_2 - T_1$

For the purpose of simplicity, the heat capacity of the bottle may be neglected as it is very small in comparison to that of solution. The specific heat capacity of the solution is assumed to be the same as that of water.

Q = Heat change in reaction = Mass of solution

$$\times \text{sp. heat} \times (T_2 - T_1)$$

Q is the heat evolved by the neutralisation.

$$\text{Therefore, the enthalpy of neutralisation} = \frac{Q}{100} \times 1000 \times \frac{1}{x}$$

where, x = normality of the acid or base.

Example 36. 150 mL of 0.5 N nitric acid solution at 25.35°C was mixed with 150 mL of 0.5 N sodium hydroxide solution at the same temperature. The final temperature was recorded to be 28.77°C . Calculate the heat of neutralisation of nitric acid with sodium hydroxide.

Solution: Total mass of solution = $150 + 150 = 300 \text{ g}$

$$Q = \text{Total heat produced} = 300 \times (28.77 - 25.35) \text{ cal}$$

$$= 300 \times 3.42 = 1026 \text{ cal}$$

$$\text{Heat of neutralisation} = \frac{Q}{150} \times 1000 \times \frac{1}{0.5}$$

$$= \frac{1026}{150} \times 1000 \times \frac{1}{0.5} = 13.68 \text{ kcal}$$

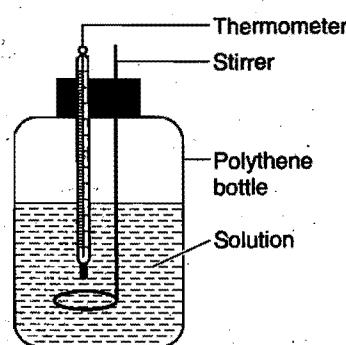
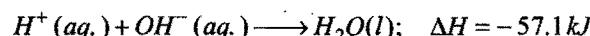


Fig. 7.16

Since, heat is liberated, heat of neutralisation should be negative.

So, heat of neutralisation = -13.68 kcal .

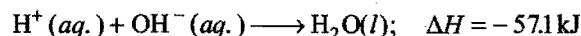
Example 37. Whenever an acid is neutralised by a base, the net reaction is



Calculate the heat evolved for the following experiments:

- (i) 0.50 mole of HCl solution is neutralised by 0.50 mole of NaOH solution.
- (ii) 0.50 mole of HNO_3 solution is mixed with 0.30 mole of KOH solution.
- (iii) 100 mL of 0.2 M HCl is mixed with 100 mL of 0.3 M NaOH solution.
- (iv) 400 mL of 0.2 M H_2SO_4 is mixed with 600 mL of 0.1 M KOH solution.

Solution: According to the reaction,



when 1 mole of H^+ ions and 1 mole of OH^- ions are neutralised, 1 mole of water is formed and 57.1 kJ of energy is released.

$$(i) \quad 0.50 \text{ mole HCl} \equiv 0.50 \text{ mole H}^+ \text{ ions}$$

$$0.50 \text{ mole NaOH} \equiv 0.50 \text{ mole OH}^- \text{ ions}$$

On mixing, 0.50 mole of water is formed.

Heat evolved for the formation of 0.50 mole of water

$$= 57.1 \times 0.5 = 28.55 \text{ kJ}$$

$$(ii) \quad 0.50 \text{ mole HNO}_3 \equiv 0.50 \text{ mole H}^+ \text{ ions}$$

$$0.30 \text{ mole KOH} \equiv 0.30 \text{ mole OH}^- \text{ ions}$$

i.e., 0.30 mole of H^+ ions react with 0.30 mole of OH^- ions to form 0.30 mole of water molecules.

Heat evolved in the formation of 0.3 mole of water

$$= 57.1 \times 0.3 = 17.13 \text{ kJ}$$

$$(iii) \quad 100 \text{ mL of 0.2 M HCl will give}$$

$$\left(\frac{0.2}{1000} \times 100 \right) = 0.02 \text{ mole of H}^+ \text{ ions}$$

and 100 mL of 0.3 M NaOH will give

$$\left(\frac{0.3}{1000} \times 100 \right) = 0.03 \text{ mole of OH}^- \text{ ions}$$

i.e., 0.02 mole of H^+ ions react with 0.02 mole of OH^- ions to form 0.02 mole of water molecules.

Heat evolved in the formation of 0.02 mole of water

$$= 0.02 \times 57.1 = 1.142 \text{ kJ}$$

$$(iv) \quad 400 \text{ mL of 0.2 M H}_2\text{SO}_4 \text{ will give}$$

$$\left(\frac{2 \times 0.2}{1000} \times 400 \right) = 0.16 \text{ mole of H}^+ \text{ ions}$$

and 600 mL of 0.1 M KOH will give

$$\left(\frac{0.1}{1000} \times 600 \right) = 0.06 \text{ mole of OH}^- \text{ ions}$$

i.e., 0.06 mole of H^+ ions react with 0.06 mole of OH^- ions to form 0.06 mole of water molecules.

Heat evolved in the formation of 0.06 mole of water

$$= 0.06 \times 57.1 = 3.426 \text{ kJ}$$

Example 38. 100 cm³ of 0.5 N HCl solution at 299.95 K were mixed with 100 cm³ 0.5 N NaOH solution at 299.75 K in a thermos flask. The final temperature was found to be 302.65 K. Calculate the enthalpy of neutralisation of HCl. Water equivalent of thermos flask is 44 g.

Solution: The initial average temperature of the acid and the base

$$= \frac{299.95 + 299.75}{2} = 299.85 \text{ K}$$

$$\text{Rise in temperature} = (302.65 - 299.85) = 2.80 \text{ K}$$

Heat evolved during neutralisation

$$= (100 + 100 + 44) \times 4.184 \times 2.8 = 2858.5 \text{ J}$$

$$\therefore \text{Enthalpy of neutralisation} = -\frac{2858.5}{100} \times 1000 \times \frac{1}{0.50} \\ = -57.17 \text{ kJ}$$

Example 39. When a student mixed 50 mL of 1 M HCl and 50 mL of 1 M NaOH in a coffee cup calorimeter, the temperature of the resultant solution increases from 21°C to 27.5°C. Assuming that the calorimeter absorbs only a negligible quantity of heat, that the total volume of solution is 100 mL, its density 1 g mL⁻¹ and that its specific heat is 4.18 J/g. Calculate :

- (a) the heat change during mixing,
- (b) the enthalpy change for the reaction,



Solution: (a) Number of moles of HCl and NaOH added

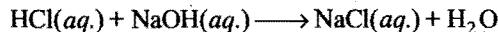
$$= \frac{MV}{1000} = \frac{1 \times 50}{1000} = 0.05$$

$$\text{Mass of mixture} = V \times d = 100 \times 1 = 100 \text{ g}$$

$$\text{Heat evolved, } q = ms \Delta T = 100 \times 4.18 \times (27.5 - 21.0)$$

$$= 100 \times 4.18 \times 6.5 \text{ J} = 2717 \text{ J} = 2.717 \text{ kJ}$$

(b) The involved reaction is:



ΔH = Heat evolved per mol

$$= \frac{-2.717}{0.05} = -54.34 \text{ kJ}$$

Example 40. The enthalpies of neutralisation of a strong acid HA and weaker acid HB by NaOH are -13.7 and -12.7 kcal/eq. When one equivalent of NaOH is added to a mixture containing 1 equivalent of HA and HB; the enthalpy change was -13.5 kcal. In what ratio is the base distributed between HA and HB?

Solution: Let x equivalent of HA and y equivalent of HB are taken in the mixture

$$x + y = 1 \quad \dots \text{(i)}$$

$$x \times 13.7 + y \times 12.7 = 13.5 \quad \dots \text{(ii)}$$

Solving eqs. (i) and (ii), we get

$$x = 0.8, y = 0.2$$

$$x : y = 4 : 1$$

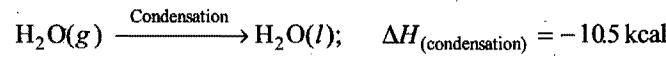
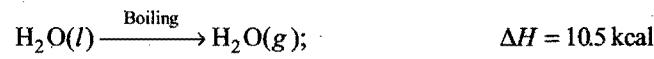
7.16 ENTHALPIES OF PHYSICAL CHANGES (Phase Changes)

Heat energy is involved whenever a physical state of a substance is changed. Some important enthalpies of physical changes are defined below:

(i) Enthalpy of fusion: It is the enthalpy change in converting 1 mole of the substance from solid state to liquid state at its melting point. The enthalpy of fusion equals latent heat of fusion per gram multiplied by the molecular mass. The value of enthalpy of fusion gives an idea about the strength of the intermolecular forces operating in a solid. The values of enthalpies of fusion for ionic solids are much more than molecular solids in which molecules are held together by weak van der Waals' forces.



(ii) Enthalpy of vaporization: It is the enthalpy change in converting 1 mole of the substance from liquid state to gaseous state (or vapour state) at its boiling point.



Enthalpy of vaporization of a liquid gives an idea about the strength of intermolecular forces operating between the molecules of the liquid.

(iii) Enthalpy of sublimation: Sublimation is the process in which a solid on heating is directly converted into vapour state. It is the heat change in converting 1 mole of a solid directly into its vapour at a given temperature below its melting point.



The enthalpy of sublimation of a solid is equal to the sum of enthalpy of fusion and enthalpy of vaporization.

$$\Delta H_{\text{sublimation}} = \Delta H_{\text{fus}} + \Delta H_{\text{vap}}$$

7.17 HESS'S LAW (The Law of Constant Heat Summation)

This law was presented by Hess in 1840. According to this law, if a chemical reaction can be made to take place in a number of ways in one or in several steps, the total enthalpy change (total heat change) is always the same, i.e., the total enthalpy change is independent of intermediate steps involved in the change. The enthalpy change of a chemical reaction depends on the initial and final stages only. Let a substance A be changed in three steps to D with enthalpy change from A to

$B \Delta H_1$ calorie, from B to $C \Delta H_2$ calorie and from C to $D \Delta H_3$ calorie. Total enthalpy change from A to D will be equal to the sum of enthalpies involved in various steps.

Total enthalpy change

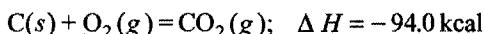
$$\Delta H_{\text{steps}} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

Now if D is directly converted into A , let the enthalpy change be ΔH_{direct} . According to Hess's law $\Delta H_{\text{steps}} + \Delta H_{\text{direct}} = 0$, i.e., ΔH_{steps} must be equal to ΔH_{direct} numerically but with opposite sign. In case it is not so, say ΔH_{steps} (which is negative) is more than ΔH_{direct} (which is positive), then in one cycle, some energy will be created which is not possible on the basis of first law of thermodynamics. Thus, ΔH_{steps} must be equal to ΔH_{direct} numerically.

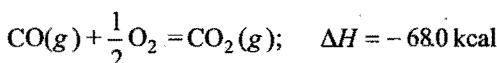
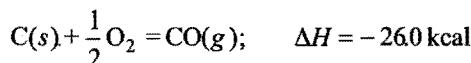
Hess's law can also be verified experimentally with the help of following examples:

(i) Formation of carbon dioxide from carbon:

First method: Carbon is directly converted into $\text{CO}_2(g)$.



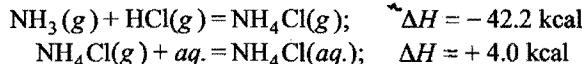
Second method: Carbon is first converted into $\text{CO}(g)$ and then $\text{CO}(g)$ into $\text{CO}_2(g)$, i.e., conversion has been carried in two steps:



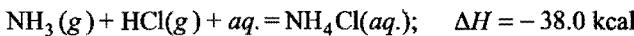
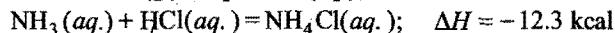
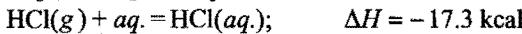
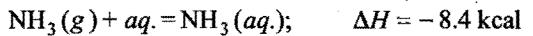
Total enthalpy change $\text{C}(s)$ to $\text{CO}_2(g)$; $\Delta H = -94.0 \text{ kcal}$

(ii) Formation of ammonium chloride from ammonia and hydrochloric acid:

First method:



Second method:



Conclusions

- (i) The heat of formation of compounds is independent of the manner of its formation.
- (ii) The heat of reaction is independent of the time consumed in the process.
- (iii) The heat of reaction depends on the sum of enthalpies of products minus sum of the enthalpies of reactants.
- (iv) Thermochemical equations can be added, subtracted or multiplied like algebraic equations.

Applications of Hess's Law

- (i) For the determination of enthalpies of formation of those compounds which cannot be prepared directly from the elements easily using enthalpies of combustion of compounds.

(ii) For the determination of enthalpies of extremely slow reactions.

(iii) For the determination of enthalpies of transformation of one allotropic form into another.

(iv) For the determination of bond energies.

$$\Delta H_{\text{reaction}} = \sum \text{Bond energies of reactants}$$

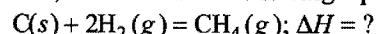
$$- \sum \text{Bond energies of products}$$

(v) For the determination of resonance energy.

(vi) For the determination of lattice energy.

Thermochemical calculations: For making thermochemical calculations, the following points are kept in mind:

(i) Write down the required thermochemical equation. For example, if heat of formation of methane is to be determined, write down the following equation:



(ii) Try to obtain the required equation from the given data. This can be done in two ways:

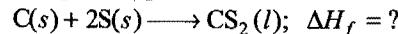
(a) By adding, subtracting and multiplying the various given thermochemical equations. Or

(b) Heat of reaction = Total enthalpies of products – Total enthalpies of reactants

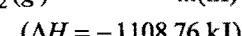
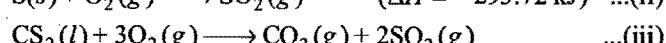
Note: In case of calculation of heat of formation, the enthalpies of free elements can be arbitrarily fixed as zero at 25°C and 1 atmospheric pressure.

Example 41. Calculate the standard heat of formation of carbon disulphide (l). Given that the standard heats of combustion of carbon (s), sulphur (s) and carbon disulphide (l) are -393.3 , 293.7 and $-1108.76 \text{ kJ mol}^{-1}$ respectively.

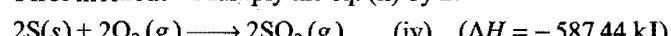
Solution: Required equation is



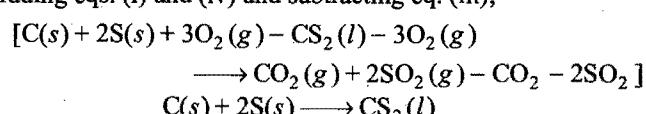
Given,



First method: Multiply the eq. (ii) by 2.



Adding eqs. (i) and (iv) and subtracting eq. (iii),

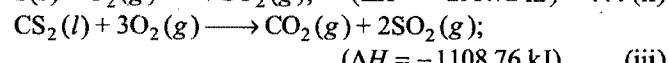


This is the required equation.

$$\text{Thus, } \Delta H_f = -393.3 - 587.44 + 1108.76 = 128.02 \text{ kJ}$$

Standard heat of formation of $\text{CS}_2(l) = 128.02 \text{ kJ}$

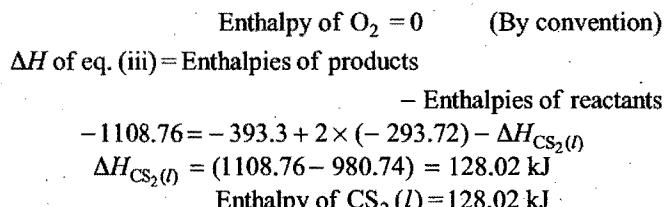
Second method:



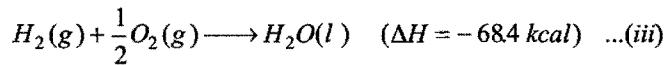
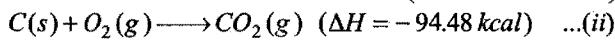
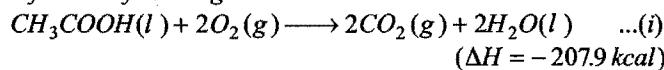
From eqs. (i) and (ii),

$$\text{Enthalpy of CO}_2 = -393.3 \text{ kJ}$$

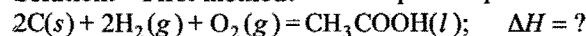
$$\text{Enthalpy of SO}_2 = -293.72 \text{ kJ}$$



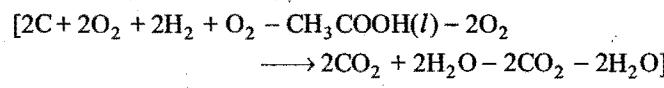
Example 42. Calculate the heat of formation of acetic acid from the following data:



Solution: First method: The required equation is

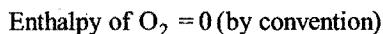
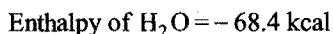
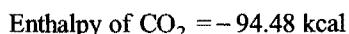


This equation can be obtained by multiplying eq. (ii) by 2 and also eq. (iii) by 2 and adding both and finally subtracting eq. (i).

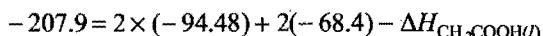


$$\begin{aligned}\Delta H_{CH_3COOH(l)} &= 2 \times (-94.48) + 2 \times (-68.4) - (-207.9) \\ &= -188.96 - 136.8 + 207.9 \\ &= -325.76 + 207.9 = -117.86 \text{ kcal}\end{aligned}$$

Second method: From eqs. (ii) and (iii)



ΔH of eq. (i) = Enthalpies of products - Enthalpies of reactants

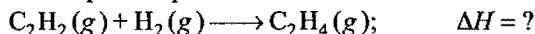


$$\begin{aligned}\Delta H_{CH_3COOH(l)} &= -188.96 - 136.8 + 207.9 \\ &= -325.76 + 207.9 = -117.86 \text{ kcal}\end{aligned}$$

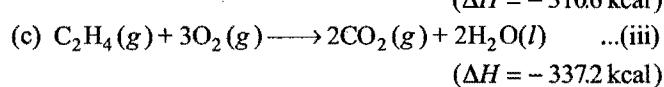
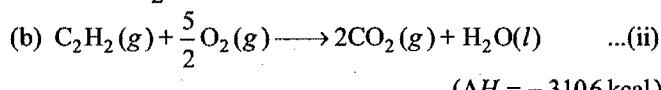
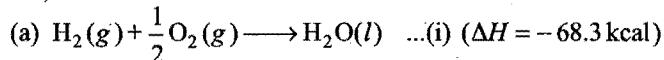
Example 43. Given the following standard heats of reactions :

(a) heat of formation of water = -68.3 kcal, (b) heat of combustion of C_2H_2 = -310.6 kcal and (c) heat of combustion of ethylene = -337.2 kcal. Calculate the heat of the reaction for the hydrogenation of acetylene at constant volume and at $25^\circ C$.

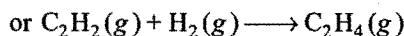
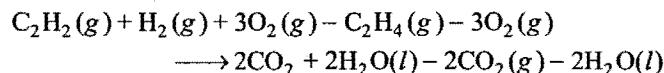
Solution: The required equation is



Given,



The required equation can be achieved by adding eqs. (i) and (ii) and subtracting (iii).



$$\Delta H = -68.3 - 310.6 - (-337.2) = -378.9 + 337.2 = -41.7 \text{ kcal}$$

We know that,

$$\Delta H = \Delta E + \Delta nRT$$

or

$$\Delta E = \Delta H - \Delta nRT$$

$$\Delta n = (1 - 2) = -1, R = 2 \times 10^{-3} \text{ kcal mol}^{-1} \text{ K}^{-1}$$

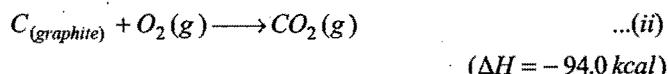
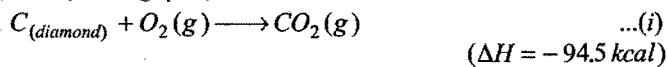
$$\text{and} \quad T = (25 + 273) = 298 \text{ K}$$

Substituting the values in above equation,

$$\Delta E = -41.7 - (-1)(2 \times 10^{-3})(298)$$

$$= -41.7 + 0.596 = -41.104 \text{ kcal}$$

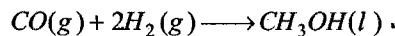
Example 44. Determine the heat of transformation of $C_{(diamond)} \rightarrow C_{(graphite)}$ from the following data:



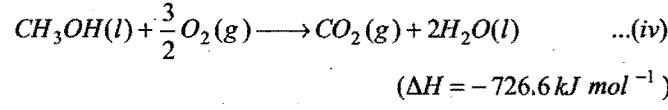
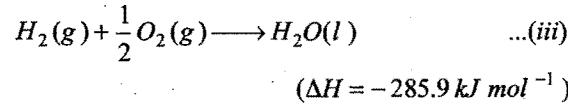
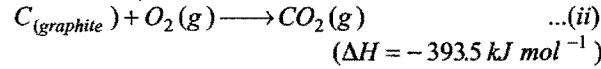
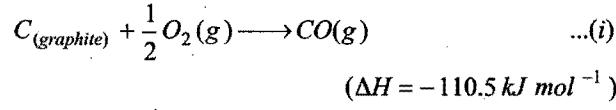
Solution: Subtracting eq. (ii) from (i), the required equation is obtained.

$$\begin{aligned}\Delta H_{\text{transformation}} &= -94.5 - (-94.0) \\ &= -94.5 + 94.0 = -0.5 \text{ kcal}\end{aligned}$$

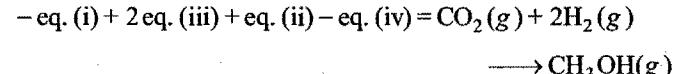
Example 45. Methanol can be prepared synthetically by heating carbon monoxide and hydrogen gases under pressure in the presence of a catalyst. The reaction is



Determine the enthalpy of this reaction by an appropriate combination of the following data:

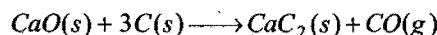


Solution: The required equation can be obtained in the following manner:



$$\text{So, } \Delta H = 110.5 - 571.8 - 393.5 + 726.6 = -128.2 \text{ kJ mol}^{-1}$$

Example 46. How much heat will be required to make 2 kg of calcium carbide (CaC_2) according to the following reaction?



The heats of formation of $\text{CaO}(s)$, $\text{CaC}_2(s)$ and $\text{CO}(g)$ are -151.6 , -14.2 and -26.4 kcal respectively.

$$\begin{aligned}\text{Solution: } \Delta H &= \Sigma \Delta H_f^\circ (\text{products}) - \Sigma \Delta H_f^\circ (\text{reactants}) \\ &= [\Delta H_f^\circ (\text{CaC}_2) + \Delta H_f^\circ (\text{CO})] - [\Delta H_f^\circ (\text{CaO}) + 3\Delta H_f^\circ (\text{C})] \\ &= [-14.2 - 26.4] - [-151.6 + 3 \times 0] \\ &= -40.6 + 151.6 = 111.0 \text{ kcal}\end{aligned}$$

For formation of 64 g of CaC_2 111.0 kcal of heat is required.

So, heat required for making 2000 g of

$$\text{CaC}_2 = \frac{111.0}{64} \times 2000 = 3468.75 \text{ kcal}$$

7.18 INFLUENCE OF TEMPERATURE ON THE HEAT OF REACTION OR KIRCHHOFF'S EQUATION

Let us consider a reaction occurring at constant pressure. Heat of reaction at constant pressure may be given as:

$$\Delta H = H_P - H_R$$

Differentiating the above equation with respect to ' T ' at constant pressure, we get:

$$\begin{aligned}\left(\frac{d\Delta H}{dT} \right)_P &= \left(\frac{dH_P}{dT} \right)_P - \left(\frac{dH_R}{dT} \right)_P \\ &= (C_P)_P - (C_P)_R = \Delta C_P\end{aligned}$$

$$\text{or } d(\Delta H) = \Delta C_P dT$$

Integrating above differential equation within proper limit, we get:

$$\begin{aligned}\int_{T_1}^{T_2} d\Delta H &= \Delta C_P \int_{T_1}^{T_2} dT \\ \Delta H_{T_2} - \Delta H_{T_1} &= \Delta C_P (T_2 - T_1) \\ \frac{\Delta H_{T_2} - \Delta H_{T_1}}{T_2 - T_1} &= \Delta C_P\end{aligned}$$

Above equation is **Kirchhoff's equation**. It is used to calculate heat of reaction at a temperature provided it is known at another temperature.

Change in heat of reaction due to per degree change in temperature is equivalent to heat capacity difference between reactant and product.

Kirchhoff's equation at constant volume may be given as:

$$\frac{\Delta E_{T_2} - \Delta E_{T_1}}{T_2 - T_1} = \Delta C_V$$

7.19 BOND ENERGY OR BOND ENTHALPIES

When a bond is formed between atoms, energy is released. Obviously same amount of energy will be required to break the

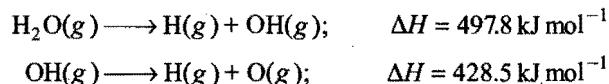
bond. The energy required to break the bond is termed bond dissociation energy. The more precise definition is:

The amount of energy required to break one mole of bond of a particular type between the atoms in the gaseous state, i.e., to separate the atoms in the gaseous state under 1 atmospheric pressure and the specified temperature is called bond dissociation energy. For example,

| | |
|---|---|
| $\text{H} - \text{H}(g) \rightarrow 2\text{H}(g);$ | $\Delta H = +433 \text{ kJ mol}^{-1}$ |
| $\text{Cl} - \text{Cl}(g) \rightarrow 2\text{Cl}(g);$ | $\Delta H = +242.5 \text{ kJ mol}^{-1}$ |
| $\text{H} - \text{Cl}(g) \rightarrow \text{H}(g) + \text{Cl}(g);$ | $\Delta H = +431 \text{ kJ mol}^{-1}$ |
| $\text{I} - \text{I}(g) \rightarrow 2\text{I}(g);$ | $\Delta H = +15.1 \text{ kJ mol}^{-1}$ |
| $\text{H} - \text{I}(g) \rightarrow \text{H}(g) + \text{I}(g);$ | $\Delta H = +299 \text{ kJ mol}^{-1}$ |

The bond dissociation energy of a diatomic molecule is also called bond energy. However, the bond dissociation energy depends upon the nature of bond and also the molecule in which the bond is present. When a molecule of a compound contains more than one bond of the same kind, the average value of the dissociation energies of a given bond is taken. This average bond dissociation energy required to break each bond in a compound is called bond energy.*

Consider the dissociation of water molecule which consists of two O—H bonds. The dissociation occurs in two stages.



The average of these two bonds dissociation energies gives the value of bond energy of O—H.

$$\text{Bond energy of O—H bond} = \frac{497.8 + 428.5}{2} = 463.15 \text{ kJ mol}^{-1}$$

Similarly, the bond energy of N—H bond in NH_3 is equal to one-third of the energy of dissociation of NH_3 and those of C—H bond in CH_4 is equal to one-fourth of the energy of dissociation of CH_4 .

$$\text{Bond energy C—H} = \frac{1664}{4} = 416 \text{ kJ mol}^{-1}$$



Application of Bond Energy

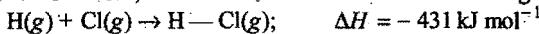
- Heat of a reaction = Σ Bond energy of reactants — Σ Bond energy of products

Note: In case of atomic species, bond energy is replaced by heat of atomization.

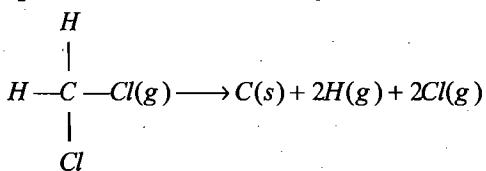
- Determination of resonance energy:** When a compound shows resonance, there is considerable difference between the heat of formation as calculated from bond energies and that determined experimentally.

Resonance energy = Experimental or actual heat of formation — Calculated heat of formation.

*Bond energy is also called, the heat of formation of the bond from gaseous atoms constituting the bond with reverse sign.



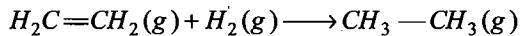
$$\text{Bond energy of H—Cl} = -(\text{enthalpy of formation}) = -(-431) = +431 \text{ kJ mol}^{-1}$$

SOME SOLVED EXAMPLES**Example 47.** Calculate the ΔH of the reaction,

Bond energy for C—H bond and C—Cl bond are 415 kJ and 326 kJ respectively.

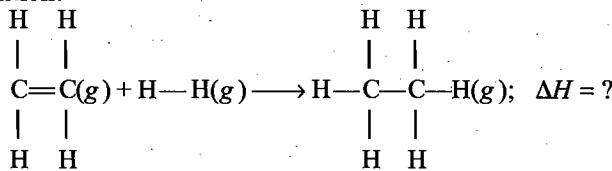
Solution: $\Delta H = \text{Sum of bond energies of reactants}$

$$\begin{aligned} & - \text{Sum of bond energies of products} \\ & = [2 \times (\text{C—H}) + 2 \times (\text{C—Cl})] - 0 \\ & \quad (\text{All the products are free atoms}) \\ & = 2 \times 415 + 2 \times 326 \\ & = 830 + 652 = 1482 \text{ kJ} \end{aligned}$$

Example 48. Calculate the enthalpy of the following reaction:

The bond energies of C—H, C—C, C=C and H—H are 99, 83, 147 and 104 kcal respectively.

Solution: The reaction is:

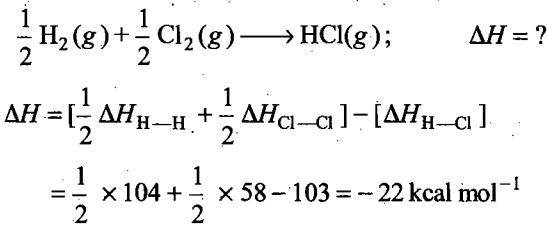


$\Delta H = \text{Sum of bond energies of reactants}$

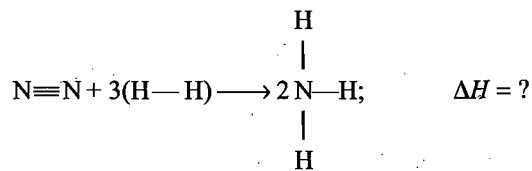
$$\begin{aligned} & - \text{Sum of the bond energies of products} \\ & = [\Delta H_{\text{C=C}} + 4 \times \Delta H_{\text{C—H}} + \Delta H_{\text{H—H}}] \\ & \quad - [\Delta H_{\text{C—C}} + 6 \times \Delta H_{\text{C—H}}] \\ & = (147 + 4 \times 99 + 104) - (83 + 6 \times 99) = -30 \text{ kcal} \end{aligned}$$

Example 49. The bond dissociation energies of gaseous H_2 , Cl_2 and HCl are 104, 58 and 103 kcal mol^{-1} respectively. Calculate the enthalpy of formation of $HCl(g)$.

Solution: The required equation is

**Example 50.** Calculate the enthalpy of formation of ammonia from the following bond energy data:

(N—H) bond = 389 kJ mol^{-1} ; (H—H) bond = 435 kJ mol^{-1} and (N≡N) bond = 945.36 kJ mol^{-1} .

Solution:

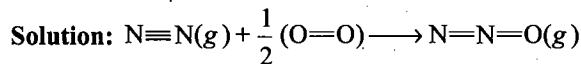
$$\begin{aligned} \Delta H &= [\Delta H_{(N \equiv N)} + 3 \times \Delta H_{(H-H)}] - [6 \Delta H_{(N-H)}] \\ &= 945.36 + 3 \times 435.0 - 6 \times 389.0 = -83.64 \text{ kJ} \end{aligned}$$

$$\text{Heat of formation of } NH_3 = \frac{\Delta H}{2} = -\frac{83.64}{2} = -41.82 \text{ kJ mol}^{-1}$$

Example 51. Calculate the resonance energy of N_2O from the following data:

$$\Delta H_f^{\circ} \text{ of } N_2O = 82 \text{ kJ mol}^{-1}$$

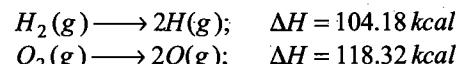
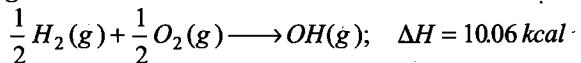
Bond energy of $N \equiv N$, $N=N$, $O=O$ and $N=O$ bonds is 946, 418, 498 and 607 kJ mol^{-1} respectively. (IIT 1991)



$$\begin{aligned} \Delta H_{f(N_2O)} &= [\Delta H_{(N \equiv N)} + \frac{1}{2} \Delta H_{(O=O)}] - [\Delta H_{(N=O)} + \Delta H_{(N=N)}] \\ &= (946 + \frac{1}{2} \times 498) - (607 + 418) \\ &= 946 + 249 - 607 - 418 \\ &= 1195 - 1025 = 170 \text{ kJ mol}^{-1} \end{aligned}$$

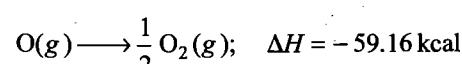
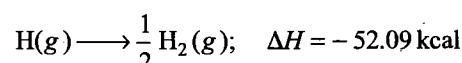
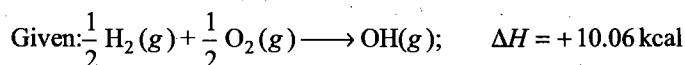
Resonance energy = Observed heat of formation

$$\begin{aligned} & \sim \text{Calculated heat of formation} \\ & = 82 \sim 170 = 88 \text{ kJ mol}^{-1} \end{aligned}$$

Example 52. The enthalpies for the following reactions at 25°C are given:

Calculate the O—H bond energy in the OH group.

Solution: Required equation is

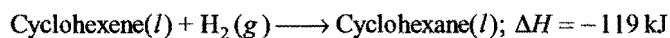


Adding, $H(g) + O(g) \longrightarrow OH(g); \quad \Delta H = -101.19 \text{ kcal}$

Example 53. The standard molar enthalpies of formation of cyclohexane (l) and benzene (l) at 25°C are -156 and +49 kJ mol^{-1} respectively. The standard enthalpy of hydrogenation of cyclohexene (l) at 25°C is -119 kJ mol^{-1} . Use these data to estimate the magnitude of resonance energy of benzene.

(IIT 1996)

Solution:



Enthalpy of formation of cyclohexane(l) = -156 kJ mol^{-1}

$$\begin{aligned} \text{So, enthalpy of formation of cyclohexane} &= -156 - (-119) \text{ kJ} \\ &= -37 \text{ kJ mol}^{-1} \end{aligned}$$

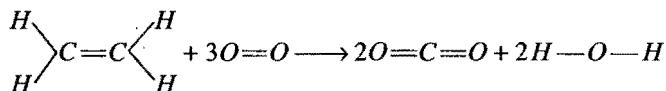
Since, $\Delta H_{\text{cyclohexane}}$ is -156 kJ mol^{-1} , we can say that for every double bond the energy decreases by an amount $+119 \text{ kJ mol}^{-1}$ and therefore for the introduction of three double bonds (present in benzene ring) the energy required

$$= 3 \times 119 \text{ kJ mol}^{-1} = 357 \text{ kJ mol}^{-1}$$

$$\begin{aligned} \text{Hence, theoretical } \Delta H_f \text{ for benzene} &= (357 - 156) \text{ kJ mol}^{-1} \\ &= 201 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Resonance energy} &= \text{Theoretical } \Delta H_f - \text{Observed } \Delta H_f \\ &= (201 - 49) \text{ kJ mol}^{-1} = 152 \text{ kJ mol}^{-1} \end{aligned}$$

Example 54. Calculate heat of combustion of ethene:



from bond energy data: C=C, C—H, O=O, C=O, O—H

$$\text{BE kJ mol}^{-1}: \quad 619 \quad 414 \quad 499 \quad 724 \quad 460$$

Solution:

ΔH = Sum of bond energies of reactants

$$\begin{aligned} &\quad - \text{Sum of bond energies of products} \\ &= [\Delta H_{(\text{C=C})} + 4\Delta H_{(\text{C-H})} + 3 \times \Delta H_{(\text{O=O})}] \\ &\quad - [4 \times \Delta H_{(\text{C=O})} + 4 \times \Delta H_{(\text{O-H})}] \\ &= [619 + 4 \times 414 + 3 \times 499] - [4 \times 724 + 4 \times 460] \\ &= -964 \text{ kJ mol}^{-1} \end{aligned}$$

Example 55. Using the data (all values are in kilocalorie per mole at 25°C) given below, calculate the bond energy of C—C and C—H bonds.

$$\Delta H^{\circ}_{\text{combustion of ethane}} = -372.0$$

$$\Delta H^{\circ}_{\text{combustion of propane}} = -530.0$$

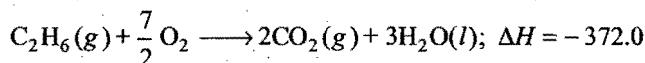
$$\Delta H^{\circ} \text{ for } \text{C}_{(\text{graphite})} \longrightarrow \text{C}(g) = +172.0$$

$$\text{Bond energy of H—H bond} = +104.0$$

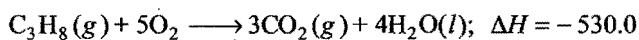
$$\Delta H^{\circ}_f \text{ of } \text{H}_2\text{O}(l) = -68.0$$

$$\Delta H^{\circ}_f \text{ of } \text{CO}_2(g) = -94.0$$

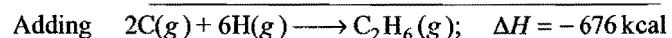
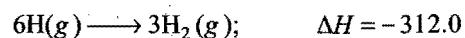
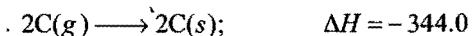
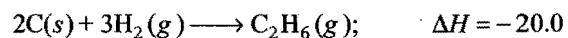
Solution:



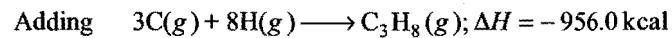
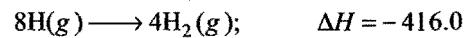
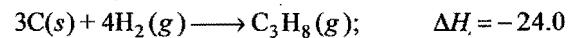
$$\Delta H^{\circ}_f(\text{C}_2\text{H}_6) = 2 \times (-94.0) + 3 \times (-68.0) + 372.0 = -20 \text{ kcal}$$



$$\Delta H^{\circ}_f(\text{C}_3\text{H}_8) = 2 \times (-94.0) + 4 \times (-68.0) + 530.0 = -24 \text{ kcal}$$



So, enthalpy of formation of 6C—H bonds and one C—C bond is -676.0 kcal .



So, enthalpy of formation of 8C—H and 2C—C bonds is -956 kcal .

Let the bond energy of C—C be x and of C—H be y kcal.

$$\text{In ethane} \quad x + 6y = 676$$

$$\text{In propane} \quad 2x + 8y = 956$$

$$\text{On solving,} \quad x = 82 \text{ and } y = 99$$

Thus, bond energy of C—C = 82 kcal and
bond energy of C—H = 99 kcal

Example 56. Using the bond enthalpy data given below, calculate the enthalpy of formation of acetone (g).

$$\text{Bond energy C—H} = 413.4 \text{ kJ mol}^{-1};$$

$$\text{Bond energy C—C} = 347.0 \text{ kJ mol}^{-1};$$

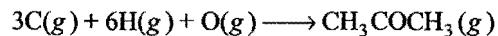
$$\text{Bond energy C=O} = 728.0 \text{ kJ mol}^{-1};$$

$$\text{Bond energy O=O} = 495.0 \text{ kJ mol}^{-1};$$

$$\text{Bond energy H—H} = 435.8 \text{ kJ mol}^{-1};$$

$$\Delta H_{\text{sub}}^{\circ} \text{C}(s) = 718.4 \text{ kJ mol}^{-1}$$

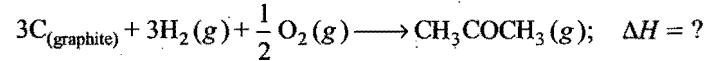
Solution:



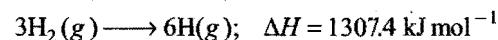
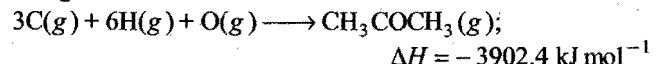
In acetone, six C—H bonds, one C=O bond and two C—C bonds are present. Energy released in the formation of these bonds is

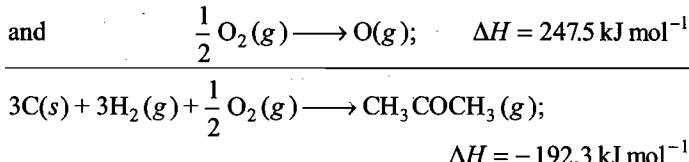
$$= -6 \times 413.4 - 728.0 - 2 \times 347.0 = -3902.4 \text{ kJ mol}^{-1}$$

The equation of the enthalpy of formation of acetone is



This equation can be obtained from the following equations by adding:



**ILLUSTRATIONS OF OBJECTIVE QUESTIONS**

7. ΔH_f° 298 K of methanol is given by the chemical equation:
(AIIMS 2005)

- (a) $\text{CH}_4(g) + \frac{1}{2} \text{O}_2(g) \longrightarrow \text{CH}_3\text{OH}(g)$
 (b) C (graphite) + $\frac{1}{2} \text{O}_2(g) + 2\text{H}_2(g) \longrightarrow \text{CH}_3\text{OH}(l)$
 (c) C (diamond) + $\frac{1}{2} \text{O}_2(g) + 2\text{H}_2(g) \longrightarrow \text{CH}_3\text{OH}(l)$
 (d) $\text{CO}(g) + 2\text{H}_2(g) \longrightarrow \text{CH}_3\text{OH}(l)$

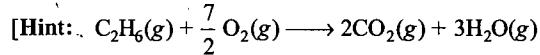
[Ans. (b)]

[Hint: In the process of formation, the compound must be formed from constituent elements in their standard state.]

8. The standard molar heat of formation of ethane, CO_2 and $\text{H}_2\text{O}(l)$ are respectively -21.1, -94.1 and -68.3 kcal. The standard molar heat of combustion of ethane will be:

- (a) -372 kcal (b) -240 kcal
 (c) 162 kcal (d) 183.5 kcal

[Ans. (a)]



$$\Delta H = 2\Delta H_f^\circ(\text{CO}_2) + 3\Delta H_f^\circ(\text{H}_2\text{O}) - \Delta H_f^\circ(\text{C}_2\text{H}_6)$$

$$= 2(-94.1) + 3(-68.3) - (-21.1) = -372 \text{ kcal}]$$

9. When ethyne is passed through a red hot tube, then formation of benzene takes place:

$$\Delta H_f^\circ(\text{C}_2\text{H}_2)(g) = 230 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\circ(\text{C}_6\text{H}_6)(g) = 85 \text{ kJ mol}^{-1}$$

Calculate the standard heat of trimerisation of ethyne to benzene.

- (a) 205 kJ mol^{-1} (b) 605 kJ mol^{-1}
 (c) -605 kJ mol^{-1} (d) -205 kJ mol^{-1}

[Ans. (c)]

[Hint: $\Delta H_{\text{reaction}} = \Delta H_f^\circ(\text{C}_6\text{H}_6) - 3\Delta H_f^\circ(\text{C}_2\text{H}_2)$
 $= 85 - 3(230)$
 $= -605 \text{ kJ mol}^{-1}$]

10. $\text{F}_2(g) + 2\text{HCl}(g) \longrightarrow 2\text{HF}(g) + \text{Cl}_2(g); \Delta H^\circ = -352.18 \text{ kJ}$

$$\Delta H_f^\circ(\text{HF}) = -268.3 \text{ kJ}$$

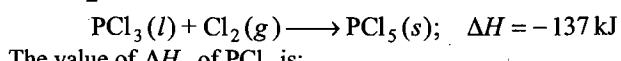
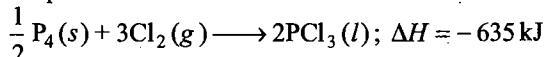
The heat of formation of HCl will be:

- (a) -22 kJ mol^{-1} (b) 88 kJ mol^{-1}
 (c) -92.21 kJ mol^{-1} (d) -183.8 kJ mol^{-1}

[Ans. (c)]

[Hint: $\Delta H_{\text{reaction}}^\circ = 2\Delta H_f^\circ(\text{HF}) - 2\Delta H_f^\circ(\text{HCl})$
 $-352.18 = 2 \times (-268.3) - 2x$
 $2x = 2(-268.3) + 352.18$
 $x = -92.21 \text{ kJ mol}^{-1}$]

11. Given two processes:

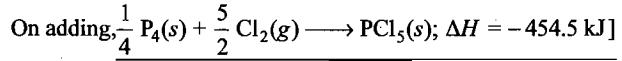
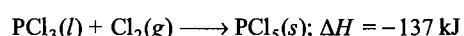


The value of ΔH_f° of PCl_5 is:

- (a) 454.5 kJ mol^{-1} (b) -454.5 kJ
 (c) -772 kJ mol^{-1} (d) -498 kJ mol^{-1}

[Ans. (b)]

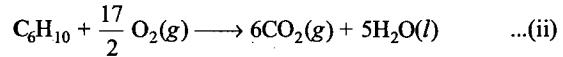
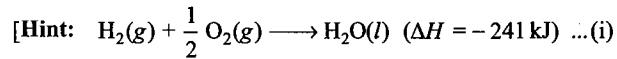
[Hint: $\frac{1}{4} \text{P}_4(s) + \frac{3}{2} \text{Cl}_2(g) \longrightarrow \text{PCl}_5(l); \Delta H = -\frac{635}{2} \text{ kJ}$



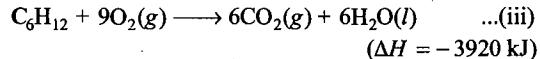
12. The enthalpy of combustion at 25°C of H_2 , cyclohexane (C_6H_{12}) and cyclohexene (C_6H_{10}) are -241, -3920 and -3800 kJ/mol respectively. The heat of hydrogenation of cyclohexene is: [CBSE (Med.) 2006]

- (a) -121 kJ/mol (b) +121 kJ/mol
 (c) -242 kJ/mol (d) +242 kJ/mol

[Ans. (a)]



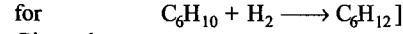
$$(\Delta H = -3800 \text{ kJ})$$



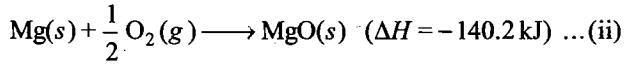
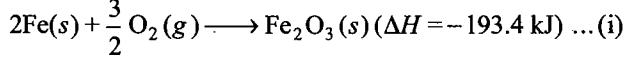
$$(\Delta H = -3920 \text{ kJ})$$

Eq. (i) + eq. (ii) - eq. (iii) gives

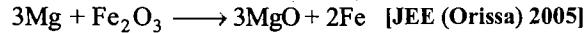
$$\Delta H = -241 - 3800 - (-3920) = -121 \text{ kJ}$$



Given that:



What is ΔH of the reaction?

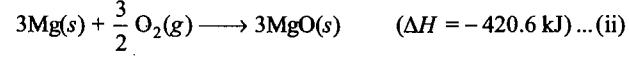
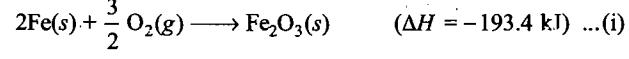


- (a) -227.2 kJ (b) -272.3 kJ

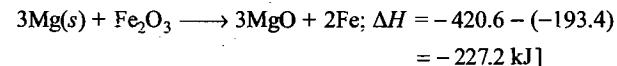
- (c) 227.2 kJ (d) 272.3 kJ

[Ans. (a)]

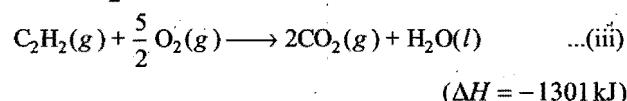
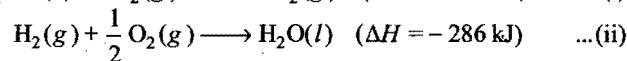
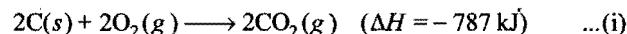
[Hint: Subtracting equation 1st from 2nd multiplied by 3,



Subtracting eq. (i) from (ii),



14. Given that:

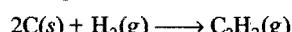


Heat of formation of acetylene is: [JEE (Orissa) 2005]

- (a) -1802 kJ (b) +1802 kJ
 (c) -800 kJ (d) +228 kJ

[Ans. (d)]

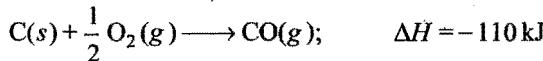
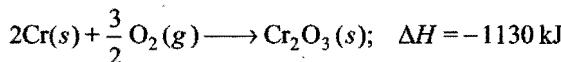
[Hint: Required equation is:



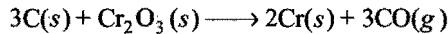
Eq. (i) + eq. (ii) - eq. (iii) gives

$$\begin{aligned} \Delta H &= (-787) + (-286) - (-1301) \\ &= +228 \text{ kJ} \end{aligned}$$

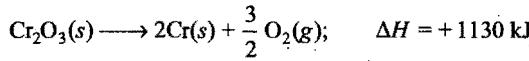
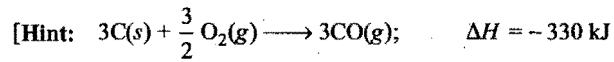
15. The enthalpy changes for two reactions are given by the equations:



What is the enthalpy change in kJ for the following reaction?



- (a) -1460 kJ (b) -800 kJ (c) +800 kJ (d) +1020 kJ
 (e) +1460 kJ
 [Ans. (c)]



On adding, $3\text{C}(s) + \text{Cr}_2\text{O}_3(s) \longrightarrow 2\text{Cr}(s) + 3\text{CO}(g); \quad \Delta H = 800 \text{ kJ}$

16. The enthalpy change ΔH for the neutralisation of 1 M HCl by caustic potash in dilute solution at 298 K is: (DPMT 2005)

- (a) 68 kJ (b) 65 kJ
 (c) 57.3 kJ (d) 50 kJ

[Ans. (c)]

[Hint: Since, both HCl and KOH are strong, 57.3 kJ heat will be released.]

17. Enthalpy of neutralisation of the reaction between CH_3COOH (*aq.*) and NaOH (*aq.*) is -13.2 kcal eq^{-1} and that of the reaction between H_2SO_4 (*aq.*) and KOH (*aq.*) is -13.7 kcal eq^{-1} . The enthalpy of dissociation of CH_3COOH (*aq.*) is:

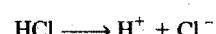
- (a) -0.5 kcal eq^{-1} (b) +0.5 kcal eq^{-1}
 (c) -26.9 kcal eq^{-1} (d) +13.45 kcal eq^{-1}
 [Ans. (b)]

[Hint: Dissociation enthalpy of $\text{CH}_3\text{COOH} = 13.7 - 13.2 = 0.5 \text{ kcal eq}^{-1}$. Thus, 0.5 kcal eq^{-1} heat will be used to dissociate CH_3COOH completely.]

18. Calculate the enthalpy change when 50 mL of 0.01 M $\text{Ca}(\text{OH})_2$ reacts with 25 mL of 0.01 M HCl. Given that ΔH° neutralisation of a strong acid and a strong base is 140 kcal mol^{-1}

- (a) 14 kcal (b) 35 cal (c) 10 cal (d) 7.5 cal
 [Ans. (b)]

[Hint: Number of moles of HCl = $\frac{MV}{1000} = \frac{0.01 \times 25}{1000}$
 $= 25 \times 10^{-5}$



$$n_{\text{H}^+} = 25 \times 10^{-5}$$

$$\text{Number of moles of } \text{Ca}(\text{OH})_2 = \frac{MV}{1000} = \frac{0.01 \times 50}{1000} = 50 \times 10^{-5}$$

$$n_{\text{OH}^-} = 2 \times 50 \times 10^{-5} = 10^{-3}$$

In the process of neutralisation 25×10^{-5} mole H^+ will be completely neutralised

$$\therefore \Delta H = 140 \times 25 \times 10^{-5} \text{ kcal} = 0.035 \text{ kcal} = 35 \text{ cal}$$

19. Equal volumes of 1 M HCl and 1 M H_2SO_4 are neutralised by 1 M NaOH solution and x and y kJ/ equivalent of heat are liberated respectively. Which of the following relations is correct?

- (a) $x = 2y$ (b) $x = 3y$ (c) $x = 4y$ (d) $x = \frac{1}{2}y$
 [Ans. (d)]

[Hint: Since, H_2SO_4 gives 2 moles H^+ while HCl gives 1 mole H^+ from 1 mole after ionisation. Hence, H_2SO_4 will release double amount of heat as compared to HCl,

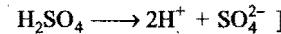
$$\text{i.e., } y = 2x \text{ or } x = \frac{y}{2}$$

20. Which of the following acid will release maximum amount of heat when completely neutralised by strong base NaOH?

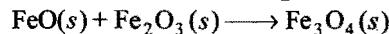
- (a) 1 M HCl (b) 1 M HNO_3
 (c) 1 M HClO_4 (d) 1 M H_2SO_4

[Ans. (d)]

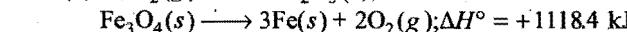
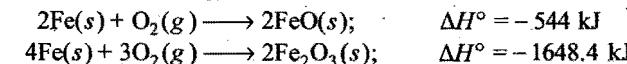
[Hint: Ionisation of H_2SO_4 gives double amount of H^+ ions as compared to other acids.



21. Determine the heat of the following reaction:

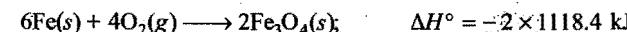
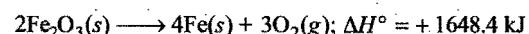
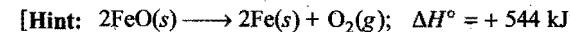


Given informations:

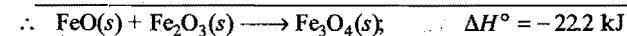


- (a) -1074 kJ (b) -22.2 kJ (c) +249.8 kJ (d) +2214.6 kJ

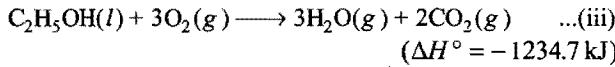
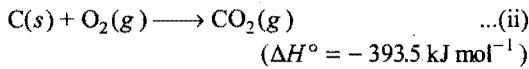
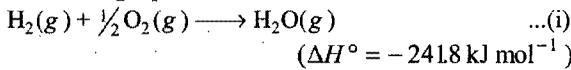
[Ans. (b)]



On adding,



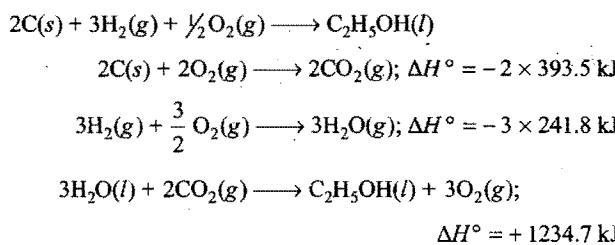
22. Calculate the enthalpy of formation of ΔH_f for C_2H_5OH from tabulated data and its heat of combustion as represented by the following equations:



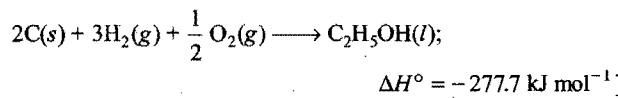
- (a) $-2747.1 \text{ kJ mol}^{-1}$ (b) $-277.7 \text{ kJ mol}^{-1}$
 (c) $277.7 \text{ kJ mol}^{-1}$ (d) $2747.1 \text{ kJ mol}^{-1}$

[Ans. (b)]

[Hint: Required equation:



On adding,



23. Which of the following methods for calculation of heat of a reaction is not correct?

- (a) $\Delta H_{\text{reaction}} = \sum \Delta H_f^{\circ} \text{ products} - \sum \Delta H_f^{\circ} \text{ reactants}$
 (b) $\Delta H_{\text{reaction}} = \sum (\text{BE})_{\text{reactants}} - \sum (\text{BE})_{\text{products}}$
 (c) $\Delta H_{\text{reaction}} = \sum \Delta H_{\text{comb. (reactants)}} - \sum \Delta H_{\text{comb. (products)}}$
 (d) $\Delta H_{\text{reaction}} = \sum \Delta H_{\text{solution (reactants)}} - \sum \Delta H_{\text{solution (products)}}$

[Ans. (d)]

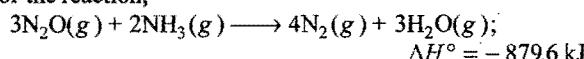
24. Heat of combustion of diamond and graphite are -94.5 kcal and -94 kcal/mol respectively. What will be the heat of transition from diamond to graphite?

- (a) -0.5 kcal (b) $+0.5 \text{ kcal}$ (c) 1 kcal (d) -1 kcal

[Ans. (b)]

[Hint: $\Delta H = \Delta H_{\text{comb. (diamond)}} - \Delta H_{\text{comb. (graphite)}}$]

25. For the reaction,



If $\Delta H_f^{\circ}[NH_3(g)] = -45.9 \text{ kJ mol}^{-1}$;

$\Delta H_f^{\circ}[H_2O(g)] = -241.8 \text{ kJ mol}^{-1}$

then $\Delta H_f^{\circ}[N_2O(g)]$ will be:

- (a) $+246 \text{ kJ}$ (b) $+82 \text{ kJ}$
 (c) -82 kJ (d) -246 kJ

[Ans. (b)]

[Hint: $\Delta H_{\text{reaction}} = \sum \Delta H_f^{\circ} \text{ (products)} - \sum \Delta H_f^{\circ} \text{ (reactants)}$

$$= 4 \Delta H_f^{\circ}[N_2] + 3 \Delta H_f^{\circ}[H_2O] - [3 \Delta H_f^{\circ}[N_2O] + 2 \Delta H_f^{\circ}[NH_3]]$$

26. The bond energies of $C=C$ and $C-C$ at 298 K are 590 and 331 kJ mol^{-1} respectively. The enthalpy of polymerisation per mole of ethylene is:

- (a) -70 kJ (b) -72 kJ (c) 72 kJ (d) -68 kJ

[Ans. (b)]

[Hint: The polymerisation of ethene may be represented as

$$nCH_2 = CH_2 \longrightarrow \{CH_2 - CH_2\}_n$$

one mole of $C=C$ bond is decomposed and two moles of $C-C$ bonds are formed per mole of ethene.

$$\therefore \Delta H = 590 - 2 \times 331 = -72 \text{ kJ per mol of ethylene.]}$$

27. For the reaction,

$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g); \Delta H = -571 \text{ kJ}$
 bond energy of $(H-H) = 435 \text{ kJ}$; of $(O=O) = 498 \text{ kJ}$; then calculate the average bond energy of $(O-H)$ bond using the above data. (DCE 2005)

- (a) 484 kJ (b) -484 kJ (c) 271 kJ (d) -271 kJ

[Ans. (a)]

[Hint: $2(H-H) + O=O \longrightarrow 2(H-O-H)$

$$\Delta H = \sum (\text{BE})_{\text{reactants}} - \sum (\text{BE})_{\text{products}}$$

$$-571 = [2 \times 435 + 498] - 4 \times (\text{BE})_{O-H}$$

$$(\text{BE})_{O-H} = \frac{2 \times 435 + 498 + 571}{4} \approx 484 \text{ kJ}]$$

28. Use the bond energies in the table to estimate ΔH for this reaction:



| Bond | $C-C$ | $C=C$ | $C-Cl$ | $C-H$ | $Cl-Cl$ |
|-------------------------|-------|-------|--------|-------|---------|
| Bond energy (kJ/mol) | 347 | 612 | 331 | 414 | 243 |

- (a) $\Delta H = -684 \text{ kJ}$ (b) $\Delta H = -154 \text{ kJ}$

- (c) $\Delta H = +89 \text{ kJ}$ (d) $\Delta H = +177 \text{ kJ}$

[Ans. (b)]

[Hint:

$$\Delta H_{\text{reaction}} = \sum (\text{BE})_{\text{reactants}} - \sum (\text{BE})_{\text{products}}$$

$$= [(BE)_{C=C} + 4(BE)_{C-H} + (BE)_{Cl-Cl}]$$

$$- [4(BE)_{C-H} + 2(BE)_{C-Cl} + (BE)_{C-C}]$$

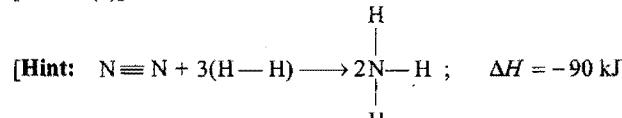
$$= [(BE)_{C=C} + (BE)_{Cl-Cl}] - [2(BE)_{C-Cl} + (BE)_{C-C}]$$

$$= [612 + 243] - [2 \times 331 + 347] = -154 \text{ kJ}]$$

29. Heat of formation of 2 moles of $NH_3(g)$ is -90 kJ ; bond energies of $H-H$ and $N-H$ bonds are 435 kJ and 390 kJ mol^{-1} respectively. The value of the bond energy of $N \equiv N$ will be:

- (a) -472.5 kJ (b) -945 kJ (c) 472.5 kJ (d) 945 kJ mol^{-1}

[Ans. (d)]



$$\Delta H_{\text{reaction}} = \sum (\text{BE})_{\text{reactants}} - \sum (\text{BE})_{\text{products}}$$

$$-90 = [(BE)_{N \equiv N} + 3(BE)_{H-H}] - [6(BE)_{N-H}]$$

$$-90 = x + 3 \times 435 - 6 \times 390$$

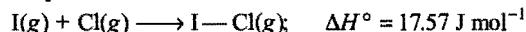
$$x = 945 \text{ kJ mol}^{-1}]$$

30. If values of ΔH_f° of $\text{ICl}(g)$, $\text{Cl}(g)$ and $\text{I}(g)$ are respectively 17.57 , 121.34 , $106.96 \text{ J mol}^{-1}$. The value of I—Cl (bond energy) in J mol^{-1} is:

(a) 17.57 (b) 210.73 (c) 35.15 (d) 106.96

[Ans. (b)]

[Hint: The process will be:



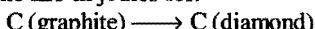
ΔH = Heat of atomisation of $\text{I}(g)$ and $\text{Cl}(g)$

- Bond energy of I—Cl bond

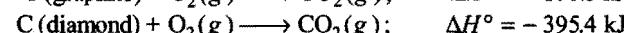
$$17.57 = 121.34 + 106.96 - x$$

$$x = 210.73 \text{ J mol}^{-1}$$

31. Calculate the ΔH in joules for:



from the following data:

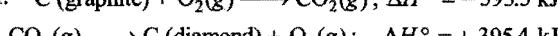


[CET (J&K) 2006]

$$(a) 1900 \quad (b) -788.9 \times 10^3$$

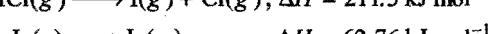
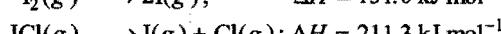
$$(c) 190000 \quad (d) +788.9 \times 10^3$$

[Ans. (a)]



On adding, $\text{C (graphite)} \longrightarrow \text{C (diamond)}; \Delta H^\circ = +1900 \text{ J}$
 $= +1.9 \text{ kJ}]$

32. The enthalpy changes for the following processes are listed below:



Given that, the standard states for iodine and chlorine are $\text{I}_2(s)$ and $\text{Cl}_2(g)$, the standard enthalpy of formation for $\text{ICl}(g)$ is :

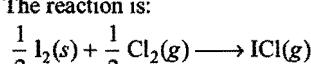
(AIEEE 2006)

$$(a) -14.6 \text{ kJ mol}^{-1} \quad (b) -16.8 \text{ kJ mol}^{-1}$$

$$(c) +16.8 \text{ kJ mol}^{-1} \quad (d) +244.8 \text{ kJ mol}^{-1}$$

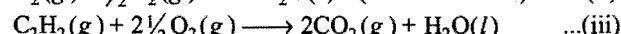
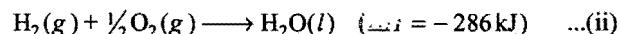
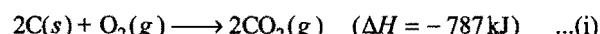
[Ans. (c)]

[Hint: The reaction is:



$$\begin{aligned} \Delta_f H_{\text{ICl}} &= \left[\frac{1}{2} \Delta H_{\text{I}_2(s) \rightarrow \text{I}_2(g)} + \frac{1}{2} \Delta H_{\text{Cl}_2(g)} \right. \\ &\quad \left. + \frac{1}{2} \Delta H_{\text{Cl—Cl}} \right] - [\Delta H_{\text{I—Cl}}] \\ &= \left[\frac{1}{2} \times 62.76 + \frac{1}{2} \times 151 + \frac{1}{2} \times 242.3 \right] - [211.3] \\ &= 16.73 \text{ kJ mol}^{-1} \end{aligned}$$

33. Given that:



$(\Delta H = -1310 \text{ kJ})$

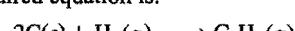
The heat of formation of acetylene is: (VITEEE 2007)

$$(a) -1802 \text{ kJ mol}^{-1} \quad (b) +1802 \text{ kJ mol}^{-1}$$

$$(c) +237 \text{ kJ mol}^{-1} \quad (d) -800 \text{ kJ mol}^{-1}$$

[Ans. (c)]

[Hint: Required equation is:



It can be obtained by adding eqs. (i) and (ii) and then subtracting eq. (iii) from it.

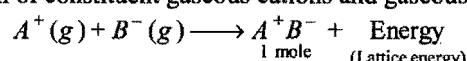
Heat of formation of acetylene

$$= (-787) + (-286) - (-1310)$$

$$= +237 \text{ kJ mol}^{-1}$$

7.20 DETERMINATION OF LATTICE ENERGY (Born-Haber Cycle)

Lattice energy of an ionic compound is defined as the amount of energy released when one mole of the compound is formed by the interaction of constituent gaseous cations and gaseous anions.



It is represented by the symbol, U . It is given negative sign as the energy is always released. Since, it is difficult to find the lattice energy by direct experiment, it is generally calculated by indirect method known as **Born-Haber cycle** which is based on Hess's law. The cycle can be easily explained by taking the example of the formation of sodium chloride (NaCl). The formation of sodium chloride can be schematically represented as:

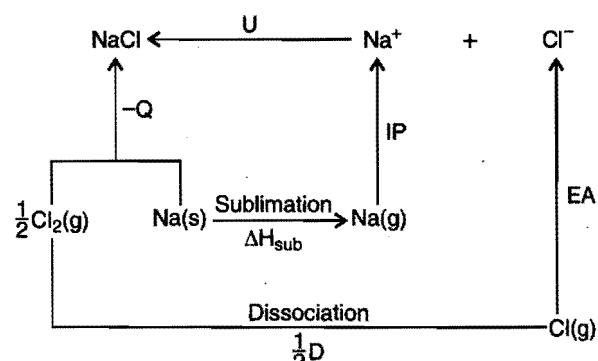


Fig. 7.17

The formation of sodium chloride can occur either by direct combination of sodium(s) and chlorine(g) or in various steps.

Let the heat of formation of sodium chloride by direct combination be $-Q$.

The various steps in the formation of NaCl are the following: In each step, either energy is absorbed or released.

| Steps involved | Energy change |
|---|--------------------------|
| (a) Solid sodium changes into gaseous sodium. Energy is absorbed. It is sublimation energy. $\text{Na}(s) + \text{sublimation energy} \rightarrow \text{Na}(g)$ | $+\Delta H_{\text{sub}}$ |
| (b) Gaseous sodium atoms change into gaseous sodium ions. In this step, energy equivalent to ionisation potential is absorbed. $\text{Na}(g) + IP \rightarrow \text{Na}^+(g) + e^-$ | $+IP$ |
| (c) Half mole of molecular chlorine dissociate into one mole of gaseous atomic chlorine. In this step, energy equivalent to one half of the dissociation energy is absorbed. $\frac{1}{2} \text{Cl}_2(g) + \frac{1}{2} D = \text{Cl}(g)$ | $+\frac{1}{2} D$ |
| (d) Gaseous chlorine atoms change into chloride ions by acceptance of electrons. In this process, energy equivalent to electron affinity is released. $\text{Cl}(g) + e^- \rightarrow \text{Cl}^-(g) + EA$ | $-EA$ |
| (e) Sodium and chlorine ions are held together by electrostatic forces to form Na^+Cl^- . The energy equivalent to lattice energy is released. | U |

Total energies involved in the above five steps

$$= \Delta H_{\text{sub}} + \frac{1}{2} D + IP - EA + U$$

Thus, according to Hess's law

$$-Q = \Delta H_{\text{sub}} + \frac{1}{2} D + IP - EA + U$$

Example 57. Calculate the lattice energy for the reaction,
 $\text{Li}^+(g) + \text{Cl}^-(g) \rightarrow \text{LiCl}(s)$

from the following data:

$$\Delta H_{\text{sub(Li)}} = 160.67 \text{ kJ mol}^{-1}; \frac{1}{2} D(\text{Cl}_2) = 122.17 \text{ kJ mol}^{-1}$$

$$IP(\text{Li}) = 520.07 \text{ kJ mol}^{-1}; EA(\text{Cl}) = -365.26 \text{ kJ mol}^{-1}$$

$$\text{and } \Delta H_f^\circ(\text{LiCl}) = -401.66 \text{ kJ mol}^{-1}.$$

Solution: Applying the equation

$$-Q = \Delta H + \frac{1}{2} D + IP - EA + U$$

and substituting the respective values,

$$-401.66 = 160.67 + 122.17 + 520.07 - 365.26 + U$$

$$U = -839.31 \text{ kJ mol}^{-1}$$

Example 58. When a mole of crystalline sodium chloride is prepared, 410 kJ of heat is produced. The heat of sublimation of sodium metal is 180.8 kJ. The heat of dissociation of chlorine gas into atoms is 242.7 kJ. The ionisation energy of Na and electron affinity of Cl are 493.7 kJ and -368.2 kJ respectively. Calculate the lattice energy of NaCl.

Solution: Applying the equation

$$-Q = \Delta H_{\text{sub}} + \frac{1}{2} D + IP - EA + U$$

and substituting the respective values,

$$-410 = 108.8 + \frac{1}{2} \times 242.7 + 493.7 - 368.2 + U$$

$$U = -765.65 \text{ kJ mol}^{-1}$$

7.21 EXPERIMENTAL DETERMINATION OF THE HEAT OF REACTION

The heat evolved or absorbed in a chemical reaction is measured by carrying out the reaction in an apparatus called **calorimeter**. The principle of measurement is that heat given out is equal to heat taken, i.e.,

$$Q = (W + m) \times s \times (T_2 - T_1),$$

where, Q is the heat of the reaction (given out), W is the water equivalent of the calorimeter and m is the mass of liquid in the calorimeter and s its specific heat, T_2 is the final temperature and T_1 the initial temperature of the system. Different types of calorimeters are used but two of the common types are:

- (i) Water calorimeter and
- (ii) Bomb calorimeter

(i) Water calorimeter

It is a simple form of a calorimeter which can be conveniently used in the laboratory. It is shown in Fig. 7.18.

It consists of a large vessel A in which a calorimeter B is held on corks. In between the calorimeter and the vessel, there is a packing of an insulating material such as cotton wool. Inside the calorimeter there are holes through which a thermometer, a stirrer and the boiling tube containing reacting substances are fitted. A known amount of water is taken in the calorimeter. Known

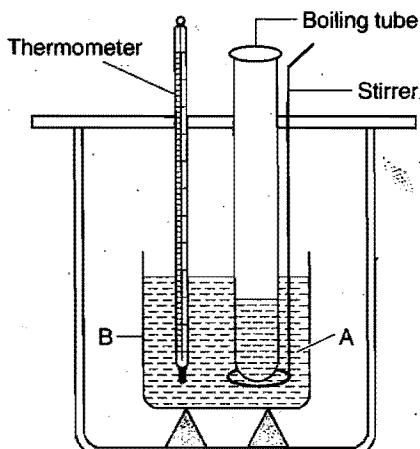


Fig. 7.18

amounts of reacting substances are taken in the boiling tube. The heat evolved during the reaction will be absorbed by the water. The rise in temperature is recorded with the help of thermometer. The heat evolved is then calculated from the formula

$$(W + m) \times s \times (T_2 - T_1)$$

(ii) Bomb calorimeter

This is commonly used to find the heat of combustion of organic substances. It consists of a sealed combustion chamber, called a bomb. A weighed quantity of the substance in a dish along with oxygen under about 20 atmospheric pressure is placed in the bomb which is lowered in water contained in an insulated copper vessel. The vessel is fitted with a stirrer and a sensitive thermometer. The arrangement is shown in Fig. 7.19.

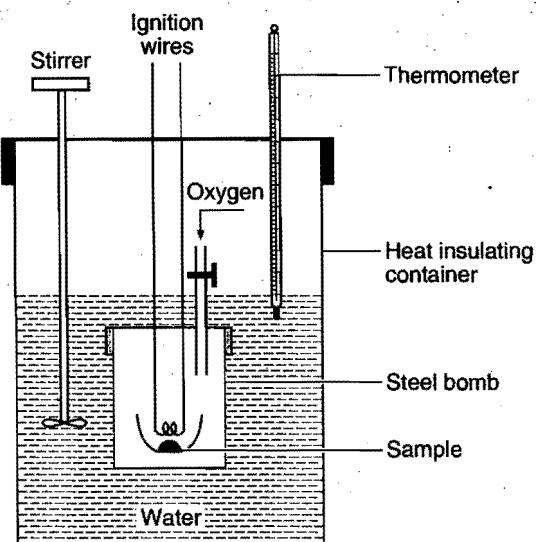


Fig. 7.19

The temperature of the water is noted and the substance is ignited by an electric current. After combustion, the rise in temperature of the system is noted. The heat of combustion can be calculated from the heat gained by water and calorimeter.

Since, the reaction in a bomb calorimeter proceeds at constant volume, the heat of combustion measured is ΔE .

$$\Delta E = \frac{(W + m)(T_2 - T_1) \times s}{w_1} \times M \text{ kcal}$$

Where, M is the molecular mass of the substance and w_1 is the mass of substance taken.

ΔH can be calculated from the relation,

$$\Delta H = \Delta E + \Delta nRT$$

Example 59. 0.5 g of benzoic acid was subjected to combustion in a bomb calorimeter at 15°C when the temperature of the calorimeter system (including water) was found to rise by 0.55°C. Calculate the heat of combustion of benzoic acid (i) at constant volume and (ii) at constant pressure. The thermal capacity of the calorimeter including water was found to be 23.85 kJ.

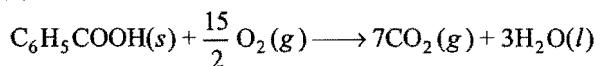
Solution: (i) Heat of combustion at constant volume, ΔE

$$= \text{Heat capacity of calorimeter and its contents} \\ \times \text{rise in temperature} \times \frac{\text{Mol. mass of compound}}{\text{Mass of compound}}$$

$$= 23.85 \times 0.55 \times \frac{122}{0.5} = 3200.67 \text{ kJ}$$

$$\text{i.e., } \Delta E = -3200.67 \text{ kJ mol}^{-1}$$

$$\text{(ii) We know that, } \Delta H = \Delta E + \Delta nRT$$



$$\Delta n = 7 - 7.5 = -0.5; R = 8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}; T = 288 \text{ K}$$

Substituting the values in the above equation,

$$\begin{aligned} \Delta H &= -3200.67 + 8.314 \times 10^{-3} \times (-0.5) \times 288 \\ &= -3200.67 - 1.197 = -3201.867 \text{ kJ mol}^{-1} \end{aligned}$$

Example 60. A sample of 0.16 g CH_4 was subjected to combustion at 27°C in a bomb calorimeter. The temperature of the calorimeter system (including water) was found to rise by 0.5°C. Calculate the heat of combustion of methane at (i) constant volume and (ii) constant pressure. The thermal capacity of calorimeter system is 17.7 kJ K^{-1} and $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

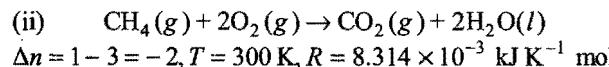
(IIT 1998)

Solution: (i) Heat of combustion at constant volume, ΔE
 $= \text{Heat capacity of calorimeter system} \times \text{rise in temperature}$

$$\times \frac{\text{Mol. mass of compound}}{\text{Mass of compound}}$$

$$= 17.7 \times 0.5 \times \frac{16}{0.16} = 885$$

$$\text{i.e., } \Delta E = -885 \text{ kJ mol}^{-1}$$



$$\begin{aligned} \Delta H &= \Delta E + \Delta nRT \\ &= -885 + (-2) \times 8.314 \times 10^{-3} \times 300 \\ &= -885 - 4.988 = -889.988 \text{ kJ mol}^{-1} \end{aligned}$$

Example 61. The heat of combustion of ethane gas is -368 kcal/mol. Assuming that 60% of heat is useful, how many m^3 of ethane measured at NTP must be burned to supply heat to convert 50 kg of water at 10°C to steam at 100°C?

Solution: Heat required per gram of water

$$= (90 + 540) \text{ cal} = 630 \text{ cal}$$

Total heat needed for 50 kg of water

$$= 50 \times 10^3 \times 630 \text{ cal}$$

As the efficiency is 60%, the actual amount of heat required

$$= \frac{50 \times 10^3 \times 630}{60} \times 100 = 52500 \text{ kcal}$$

No. of mole of ethane required to produce 52500 kcal

$$= \frac{52500}{368} = 142.663 \text{ mole}$$

$$\begin{aligned} \text{Volume of 142.663 mole at NTP} &= 142.663 \times 22.4 \\ &= 3195.65 \text{ litre} = 3.195 \text{ m}^3 \end{aligned}$$

7.22 LIMITATIONS OF FIRST LAW OF THERMODYNAMICS

The essence of first law of thermodynamics is that all physical and chemical processes occur in such a way that the total energy of the system and surroundings is constant. The law correlates the

various forms of energy, i.e., their interconversion into one another in exactly equivalent amounts. The law has stood the test of time as no transformation has violated the principle of conservation of energy. However, the first law of thermodynamics has a number of limitations.

1. The law does not give any information about the direction in which flow of energy takes place. For example, if two systems *A* and *B* which are capable of exchanging heat are brought in contact with each other, the first law of thermodynamics will only tell us that one system loses energy and other system gains the same amount of energy. But the law fails to tell whether the heat will flow from system *A* to *B* or from system *B* to *A*. In order to predict the direction of the flow of heat, one more parameter, i.e., temperature is required. The heat actually flows from a system which has higher temperature. The process continues till both the systems attain the same temperature. The law fails to answer why heat energy does not flow from cold system to hot system though the energy is conserved in this way also.
2. The law does not explain why the chemical reactions do not proceed to completion.
3. The law does not explain why natural spontaneous processes are irreversible.
4. The law does not contradict the existence of self-acting refrigerator.
5. The law does not contradict the existence of 100% efficient engine.
6. The difference between spontaneous and non-spontaneous processes is insignificant in view of the first law.

The answers to above limitations are provided by second law of thermodynamics. However, before we study this law, let us understand the terms **spontaneous**, **entropy** and **free energy**.

7.23 SPONTANEOUS AND NON-SPONTANEOUS PROCESSES

One of the main objectives in studying thermodynamics, as far as chemists are concerned, is to be able to predict whether or not a reaction will occur when reactants are brought together under a special set of conditions (for example, at a certain temperature, pressure and concentration). A reaction that occurs under the given set of conditions is called a **spontaneous reaction**. If a reaction does not occur under specified conditions, it is said to be **non-spontaneous**.

The term spontaneity means the feasibility of a process. In nature, we observe many processes which occur of their own. For example, water flows down the hill without the help of any external agency, heat flows from a conductor at high temperature to another at low temperature, electricity flows from high potential to low potential. There are processes which require some initiation before they can proceed. But once initiated, they proceed by themselves. The burning of carbon, burning of fuels and petrol, etc., require some initiation. These processes are termed as spontaneous on account of their feasibility, i.e., these can occur without the help of external work.

A process which has an urge or a natural tendency to occur either of its own or after proper initiation under the given set of conditions is known as spontaneous process.

Spontaneous process does not mean that it takes place **instantaneously**. It simply implies that the process has an urge to take place and is practically feasible. The actual speed of the process may vary from very low to extremely fast. The rusting of iron is a slow spontaneous process while the neutralisation reaction between an acid and an alkali is a fast spontaneous process. It is a matter of experience also that all natural processes are spontaneous and are **irreversible**, i.e., move in one direction only. The reverse process which can be termed as non-spontaneous can be made to occur only by supplying external energy. For example, water can be made to flow upward by the use of some external agency or energy is always required to lift the ball from the ground. The natural (spontaneous) processes follow a non-equilibrium path and as such are irreversible but these processes proceed up to establishment of equilibrium. At equilibrium state, the process stops to occur any further. Heat flows from a hotter body to a colder body till the temperature of both bodies becomes equal; there is no further flow of heat and we say that the system has attained equilibrium. Some of the familiar examples of spontaneous processes are listed below:

(a) Spontaneous processes where no initiation is required

- (i) Dissolution of sugar or salt in water

$$\text{Sugar} + \text{water} \longrightarrow \text{Aqueous solution of sugar}$$

$$\text{Salt} + \text{water} \longrightarrow \text{Aqueous solution of salt}$$
- (ii) Evaporation of water from water reservoirs such as ponds, lakes, rivers, sea, open vessels, etc.

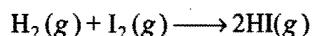
$$\text{H}_2\text{O}(l) \longrightarrow \text{H}_2\text{O}(g)$$

(iii) Flow of heat from a hot body to a cold body.

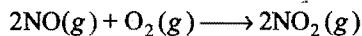
(iv) Mixing of different gases.

(v) Flow of water down a hill.

(vi) Reaction between $\text{H}_2(g)$ and $\text{I}_2(g)$ to form $\text{HI}(g)$.



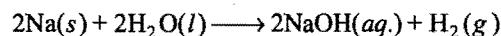
(vii) Reaction between nitric oxide gas and oxygen to form nitrogen dioxide.



(viii) Melting of ice into water.



(ix) A piece of sodium metal reacts violently with water to form sodium hydroxide and hydrogen gas.

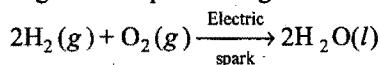


(x) When a zinc rod is dipped in an aqueous solution of copper sulphate, copper is precipitated.

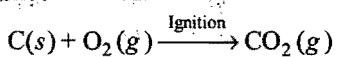


(b) Spontaneous processes where initiation is required

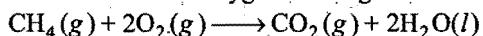
- (i) Reaction between H_2 and O_2 : This reaction is initiated by passing electric spark through the mixture.



- (ii) Coal burns in oxygen or air when ignited. Coal keeps on burning once initiated.

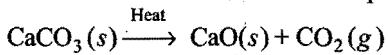


- (iii) Methane burns with oxygen when ignited.



- (iv) A candle made up of wax burns only when ignited.

- (v) Calcium carbonate evolves carbon dioxide upon heating.



A process which can neither occur by itself nor by initiation is called a non-spontaneous process.

Or

A process which has no natural tendency or urge to occur is said to be a non-spontaneous process.

Few examples of non-spontaneous processes are:

- (i) Flow of heat from a cold body to a hot body.
- (ii) Dissolution of gold or silver in water.
- (iii) Flow of water from ground to overhead tank.
- (iv) Hydrolysis of sodium chloride.
- (v) Decomposition of water into hydrogen and oxygen.
- (vi) Diffusion of gas from a low pressure to a high pressure.

It is not always true that non-spontaneous processes do not occur at all. Many of the non-spontaneous processes or changes can be made to take place when energy from some external source is supplied continuously throughout the change. (However, the processes that occur spontaneously in one direction cannot, under the same conditions, also take place spontaneously in the opposite direction). For example, the decomposition of water into hydrogen and oxygen (non-spontaneous process) can occur when electrical energy is supplied to water. The process stops when the passage of electrical energy is stopped.

Driving force for a spontaneous process: After having learnt about spontaneous processes, a very obvious question arises in our minds that why some processes are spontaneous? Obviously there must be some kind of driving force which is responsible for driving the process or a reaction in a particular direction.

The force which is responsible for the spontaneity of a process is called the driving force.

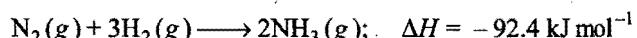
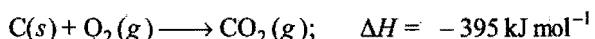
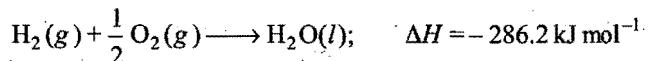
Let us now discuss the nature of the driving force.

1. Tendency to acquire minimum energy: We know that, *lesser is the energy, greater is the stability*. Thus, every system tends to acquire minimum energy. For example:

- (i) Heat flows from high temperature to low temperature so that heat content of hot body becomes minimum.
- (ii) Water flows down a hill or a slope to have minimum energy (potential).
- (iii) A wound watch spring tends to unwind so that mechanical energy of watch becomes minimum.

All the above processes are spontaneous because of a tendency to acquire minimum energy.

It has been observed that most of the spontaneous chemical reactions are exothermic. For example:



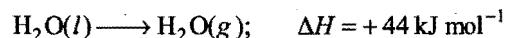
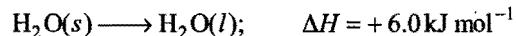
In exothermic reactions, heat is evolved from the system, i.e., energy is lowered. Thus, exothermic reactions occur spontaneously on account of decrease in enthalpy of system ($\Delta H = -ve$).

Hence, it can be concluded that the negative value of ΔH may be the criterion of spontaneity.

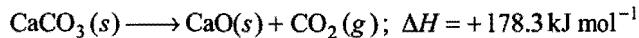
Limitations of the criterion for minimum energy

(a) Spontaneous endothermic reactions or processes: A number of endothermic reactions and processes are known which are spontaneous, i.e., when ΔH is +ve. Some examples are given below:

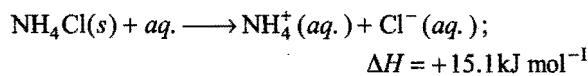
(i) Evaporation of water or melting of ice takes place by absorption of heat from surroundings, i.e., these processes are endothermic ($\Delta H = +ve$).



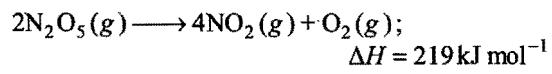
(ii) The decomposition of CaCO_3 is non-spontaneous at room temperature but becomes spontaneous when the temperature is raised.



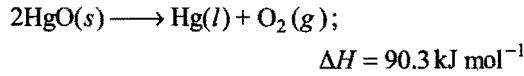
(iii) Compounds like NH_4Cl , KCl , etc., dissolve in water by absorption of heat from water. Temperature of the water decreases.



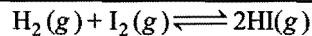
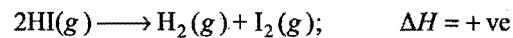
(iv) Dinitrogen pentoxide (N_2O_5) decomposes spontaneously at room temperature into NO_2 and O_2 , although the reaction is highly endothermic.

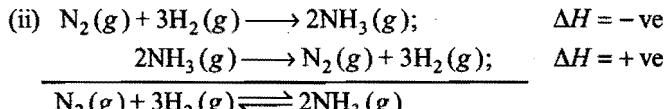


(v) The decomposition of HgO becomes spontaneous on heating.



(b) Occurrence of reversible reactions: A large number of reactions are reversible in nature. In these reactions, both forward and backward reactions occur simultaneously in spite of the fact that one reaction is exothermic ($\Delta H = -ve$) and other endothermic ($\Delta H = +ve$).





(c) Reactions having zero ΔH : A number of reactions are known in which neither energy is evolved nor absorbed, but these are spontaneous. For example, esterification of acetic acid is a spontaneous process. ΔH of this reaction is zero.



(d) Exothermic reactions fail to achieve completion: Every exothermic reaction rarely proceeds to completion even though ΔH remains negative throughout. In fact, all spontaneous reactions proceed in a direction until an equilibrium is attained.

Since, some spontaneous reactions are exothermic and others are endothermic, it is clear that enthalpy alone cannot account for spontaneity. There must be some other factor responsible for spontaneity or feasibility of a process.

2. Tendency to acquire maximum randomness: There is another natural tendency that must be taken into account to predict the direction of spontaneity.

Nature tends to move spontaneously from a state of lower probability to one of higher probability, i.e., things tend to change from organized to disorganized. To illustrate what this statement means, we consider a spontaneous process of intermixing of two inert gases for which ΔH is zero. Two different inert gases, let us say helium (He) and neon (Ne), are originally contained in different glass bulbs, separated by a stopcock as shown in Fig. 7.20(a). To make the system as closed one, the entire system is perfectly insulated.

When the valve is opened, the intermixing of the two inert gases occurs due to diffusion into one another. As the gases are inert, there is no chemical interaction between them, the heat change during intermixing is negligible. The process of intermixing is a spontaneous process. If the process is examined critically, it is observed that when the valve is opened, both the gases are provided larger volume to occupy, i.e., each gas achieves its own most probable distribution, independent of the presence of other gas. The final distribution is clearly much more probable than the initial distribution. There is, however, another

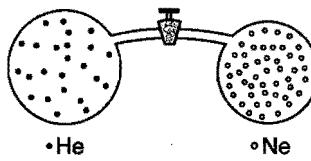


Fig. 7.20 (a)
Inert gases before mixing

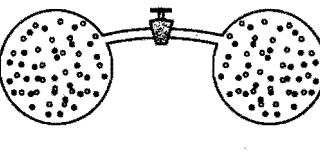


Fig. 7.20 (b)
Inert gases after mixing

useful way of looking at this process. The system has gone from a highly ordered state (all the helium molecules on the left, all the neon molecules on the right) to a more disordered or random state. Mixed gases cannot be separated on their own. Thus, diffusion is a spontaneous process acquiring more randomness.

In general, nature tends to move spontaneously from more ordered to more random states, or a process proceeds

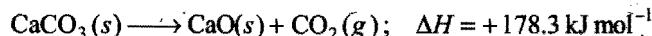
spontaneously in a direction in which randomness of the system increases.

Another example of achieving more randomness is the sugar dissolving in water. Before the solid sugar dissolves, the sugar molecules are organized in a crystal. As the molecules dissolve, they become distributed randomly and uniformly throughout the liquid. The opposite process never occurs, i.e., sugar cubes do not form from the solution.

Thus, the second factor which is responsible for the spontaneity of a process is the tendency to acquire maximum randomness.

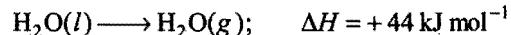
On the basis of second factor we may also explain the spontaneity of endothermic processes.

(i) *Decomposition of calcium carbonate:*



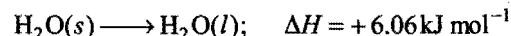
This process is spontaneous because the gaseous CO_2 produced is more random than solid calcium carbonate.

(ii) *Evaporation of water:*

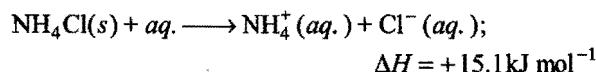


The gaseous state of a substance is more random than the liquid state. Thus, evaporation of water is spontaneous which proceeds in the direction of more randomness.

Similarly, fusion of ice is also spontaneous because the process again proceeds in the direction of more random state, i.e., liquid state is more random in comparison to solid state.

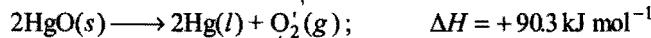


(iii) *Dissolution of NH_4Cl in water:*



When solid $\text{NH}_4\text{Cl}(s)$ is dissolved in water, its ions become free. Free ions move randomly in all directions. Thus, the solution is a more random state as compared to solid NH_4Cl . Thus, the process of dissolution will be spontaneous because randomness increases on dissolution.

(iv) *Decomposition of mercuric oxide:*



Here again the process will be spontaneous because the product is more random than reactant due to presence of gaseous O_2 .

Limitations of the criterion for maximum randomness: Like energy factor, the randomness factor has also certain limitations. For example, in the liquefaction of a gas or in the solidification of a liquid, the randomness of the particles decreases but still these processes are spontaneous. Thus, like energy factor, randomness alone cannot be the sole criterion for the spontaneity of a process.

Overall tendency as driving force for a spontaneous process

From the above discussion, it is apparent that the spontaneous processes occur because of the two tendencies:

- Tendency of a system to achieve a state of minimum energy.

- (ii) Tendency of a system to achieve a state of maximum randomness.

The overall tendency of a process to be spontaneous depends on the resultant of the above two factors. The resultant of the two tendencies or overall tendency for a process to occur is termed the **driving force**.

Here, it should be noted that these tendencies are independent of each other. Both may act in the same or in opposite directions in a process.

Case I: When enthalpy factor is absent then randomness factor decides spontaneity of a process.

Case II: When randomness factor is absent then enthalpy or energy factor decides spontaneity of a process.

Case III: When both factors take place simultaneously then magnitude of the tendencies becomes important to decide spontaneity.

7.24 ENTROPY

Why do systems tend to move spontaneously to a state of maximum randomness or disorder? The answer is that a disordered state is more probable than an ordered state because the disordered state can be achieved in more ways. The following example illustrates the point. Suppose that you shake a box containing 10 identical coins and then count the number of heads (H) and tails (T). It is very unlikely that all the 10 coins will come up heads; i.e., perfectly ordered arrangement is much less probable than the totally disordered state in which heads and tails come up randomly. The perfectly ordered state of 10 heads can be achieved in only one way and the totally disordered state can be achieved in 2^{10} (1024) ways, i.e., the totally disordered state is 2^{10} times more probable than the perfectly ordered state. If the box contained 1 mol of coins, the perfectly ordered state would be only one, but the disordered states would be much higher ($2^{N_A} = 2^{6.02 \times 10^{23}}$). It is thus, concluded that a change which brings about randomness is more likely to occur than one that brings about order. The extent of disorder or randomness is expressed by a property known as **entropy**.

Entropy is a thermodynamic state quantity which is a measure of randomness or disorder of the molecules of the system.

Entropy is represented by the symbol 'S'. It is difficult to define the actual entropy of a system. It is more convenient to define the change of entropy during a change of state. The change in entropy from initial to final state of a system is represented by ΔS . The entropy is a state function and depends only on the initial and final states of the system.

$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$

When $S_{\text{final}} > S_{\text{initial}}$, ΔS is positive.

For a chemical reaction,

$$\Delta S = S_{(\text{products})} - S_{(\text{reactants})}$$

Mathematical Definition of Entropy

The entropy change of a system may be defined as the integral of all the terms involving heat exchanged (q) divided by the absolute temperature (T) during each infinitesimally small change of the process carried out reversibly at constant temperature (isothermally).

$$\int dS = \frac{1}{T} \int \delta q_{\text{rev}}$$

$$\text{or } \Delta S = \frac{q_{\text{rev}}}{T} \quad \dots (i)$$

If heat is absorbed, then ΔS is positive (increase in entropy). If heat is evolved, ΔS is negative (decrease in entropy). The value of ΔS , like ΔE and ΔH , is a definite quantity and depends on the initial and final states of the system. It is independent of the manner in which the change has been brought about, i.e., whether the change has been brought about reversibly or irreversibly.

Several factors influence the amount of entropy that a system has in a particular state. In general,

- (i) The value of entropy depends on the mass of the system. Hence, it is an extensive property.
- (ii) A liquid has a higher entropy than the solid from which it is formed. In a solid, the atoms, molecules or ions are fixed in position; in the liquid, these particles are free to move past one another, i.e., liquid structure is more random and the solid more ordered.
- (iii) A gas has a higher entropy than the liquid from which it is formed. When vaporization occurs, the particles acquire greater freedom to move about.
- (iv) Increasing temperature of a substance increases its entropy. Raising the temperature increases the kinetic energy of the molecules (atoms or ions) and hence their freedom of motion. In the solid, the molecules vibrate with a greater amplitude at higher temperatures. In a liquid or a gas, they move about more rapidly. In other words, the more heat the system absorbs, the more disordered it becomes. Furthermore, if heat is absorbed at low temperature, it becomes more disordered than when the same amount of heat is added at higher temperature.

Units of Entropy and Entropy Change

Since, entropy change is expressed by a heat term divided by temperature, it is expressed in terms of calories per degree, i.e., cal K⁻¹. In SI units, the entropy change is expressed in terms of joules per degree, i.e., JK⁻¹. Entropy is an extensive property, i.e., it depends on the mass of the substance; hence units of entropy are expressed as cal deg⁻¹ mol⁻¹ (cal K⁻¹ mol⁻¹) or joule deg⁻¹ mol⁻¹ (JK⁻¹ mol⁻¹).

Spontaneity in Terms of Entropy Change

In an isolated system, such as mixing of gases, there is no exchange of energy or matter between the system and surroundings. However, the mixing of gases is accompanied by randomness, i.e., there is increase in entropy. Therefore, it can be

stated that for a spontaneous process in an isolated system, the change in entropy is positive, i.e., $\Delta S > 0$.

However, if a system is not isolated, the entropy changes of both the system and surroundings are to be taken into account because system and surroundings together constitute the **isolated system**. Thus, the total entropy change (ΔS_{total}) is sum of the change in entropy of the system (ΔS_{system}) and the change in entropy of the surroundings ($\Delta S_{\text{surroundings}}$), i.e.,

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \quad \dots (\text{ii})$$

For a spontaneous process, ΔS_{total} must be positive, i.e.,

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0 \quad \dots (\text{iii})$$

ΔS_{total} is also termed as $\Delta S_{\text{universe}}$.

During a spontaneous process, the entropy of the system goes on increasing till the system attains the equilibrium state, i.e., entropy of the system becomes maximum and, therefore, no more increase in the entropy of the system is possible. The mathematical condition for equilibrium is,

$$\Delta S = 0 \text{ (at equilibrium for an isolated system)} \quad \dots (\text{iv})$$

If ΔS_{total} is negative, the direct process is non-spontaneous whereas the reverse process is spontaneous.

This can be illustrated by considering the entropy changes in the conversion of water to ice at three different temperatures. The relevant entropy changes for the system and surroundings and total change are given in the following table:

| Temperature °C | Temperature K | ΔS_{system} $\text{J K}^{-1} \text{ mol}^{-1}$ | $\Delta S_{\text{surrounding}}$ $\text{J K}^{-1} \text{ mol}^{-1}$ | ΔS_{total} $\text{J K}^{-1} \text{ mol}^{-1}$ |
|-------------------|------------------|--|---|---|
| -1 | 272 | -21.85 | +21.93 | +0.08 |
| 0 | 273 | -21.99 | +21.99 | 0.00 |
| +1 | 274 | -22.13 | +22.05 | -0.08 |

$$\text{At } 272 \text{ K: } \Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

$$= -21.85 + 21.93 = +0.08 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\therefore \Delta S_{\text{process}} > 0 \text{ at } 272 \text{ K}$$

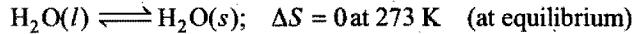
Thus, freezing of ice at 272 K, $\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(s)$ will be spontaneous.

$$\text{At } 273 \text{ K: } \Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

$$= -21.99 + 21.99 = 0$$

$$\Delta S_{\text{total}} = 0$$

Thus, at this temperature, water and ice will be at equilibrium.

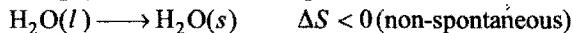


$$\text{At } 274 \text{ K: } \Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

$$= -22.13 + 22.05 = -0.08 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta S < 0$$

Thus, freezing of water will be non-spontaneous at 274 K.



Entropy Change in Reversible Process

Consider an isothermal reversible process. In this process, let the system absorb q amount of heat from surroundings at temperature T . The increase in the entropy of the system will be

$$\Delta S_{\text{system}} = + \frac{q}{T}$$

On the other hand, surroundings lose the same amount of heat at the same temperature. The decrease in the entropy of the surroundings will

$$\Delta S_{\text{surroundings}} = - \frac{q}{T}$$

Total change in entropy = entropy change in system + entropy change in surroundings

$$\begin{aligned} \Delta S_{\text{total}} &= \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \\ &= \frac{q}{T} - \frac{q}{T} = 0 \end{aligned}$$

When the reversible process is **adiabatic**, there will be no heat exchange between system and surroundings, i.e., $q = 0$

$$\begin{aligned} \Delta S_{\text{system}} &= 0, \Delta S_{\text{surroundings}} = 0 \\ \Delta S_{\text{total}} &= \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0 \end{aligned}$$

Entropy Change in Irreversible Processes

Consider a system at higher temperature T_1 and its surroundings at lower temperature T_2 . 'q' amount of heat goes irreversibly from system to surroundings.

$$\therefore \Delta S_{\text{system}} = - \frac{q}{T_1}$$

$$\Delta S_{\text{surroundings}} = + \frac{q}{T_2}$$

$$\begin{aligned} \Delta S_{\text{process}} &= \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \\ &= - \frac{q}{T_1} + \frac{q}{T_2} = q \left[\frac{T_1 - T_2}{T_1 T_2} \right] \end{aligned}$$

But $T_1 > T_2$, $\therefore T_1 - T_2 = +\text{ve}$

or $\Delta S_{\text{process}} > 0$

Hence, entropy increases in an irreversible process.

Entropy Change for Ideal Gases

Change in entropy for an ideal gas under different conditions may be calculated as:

(i) When changes from initial state (1) to final state (2):

$$\Delta S = 2.303nC_V \log \left(\frac{T_2}{T_1} \right) + 2.303nR \log \left(\frac{V_2}{V_1} \right)$$

(when T and V are variables)

$$\Delta S = 2.303nC_P \log \left(\frac{T_2}{T_1} \right) + 2.303nR \log \left(\frac{P_1}{P_2} \right)$$

(when T and P are variables)

(ii). Entropy change for isothermal process:

$$\Delta S = 2.303nR \log \left(\frac{V_2}{V_1} \right)$$

$$\Delta S = 2.303nR \log \left(\frac{P_1}{P_2} \right)$$

(iii) *Entropy change for isobaric process (at constant pressure):*

$$\Delta S = 2.303nC_P \log \left(\frac{T_2}{T_1} \right)$$

$$\Delta S = 2.303nC_P \log \left(\frac{V_2}{V_1} \right)$$

(iv) *Entropy change for isochoric process (at constant volume):*

$$\Delta S = 2.303nC_V \log \left(\frac{T_2}{T_1} \right)$$

$$\Delta S = 2.303nC_V \log \left(\frac{P_2}{P_1} \right)$$

(v) *Entropy change in mixing of ideal gases:* Let n_1 mole of gas A and n_2 mole of gas B are mixed; then total entropy change can be calculated as:

$$\Delta S = -2.303R[n_1 \log x_1 + n_2 \log x_2]$$

x_1, x_2 are mole fractions of gases A and B,

$$i.e., \quad x_1 = \frac{n_1}{n_1 + n_2}; x_2 = \frac{n_2}{n_1 + n_2}$$

$$\Delta S/\text{mol} = -2.303R \left[\frac{n_1}{n_1 + n_2} \log x_1 + \frac{n_2}{n_1 + n_2} \log x_2 \right]$$

$$\Delta S/\text{mol} = -2.303R[x_1 \log x_1 + x_2 \log x_2]$$

Entropy change in adiabatic expansion will be zero, $\Delta S = 0$.

Physical Significance of Entropy at a Glance

1. **Entropy as unavailable energy:** Entropy is unavailable energy of the system.

$$\text{Entropy} = \frac{\text{Unavailable energy}}{\text{Temperature in K}}$$

2. **Entropy and randomness:** Entropy is a measure of disorderliness or randomness in the system. Increase in entropy means change from an ordered to less ordered (or disordered) state.

3. **Entropy and probability:** Entropy may be defined as a function of probability of the thermodynamic state. Since, we know that both the entropy and thermodynamic probability increase simultaneously in a process, hence the state of equilibrium is the state of maximum probability.

Characteristics of Entropy

The important characteristics of entropy are summarised below:

(i) Entropy is an extensive property. It is difficult to determine the absolute value of entropy of a substance

but its value depends on mass of the substance present in the system.

- (ii) Entropy of a system is a state function. It depends on the state variables such as T, P, V and n which govern the state of the system.
- (iii) The change in entropy taking place in going from one state to another state does not depend on the path adopted. It actually depends on the final and initial states of the system.

Change in entropy, $\Delta S = S_{\text{final}} - S_{\text{initial}}$

- (iv) The entropy change for a cyclic process is zero.
- (v) The entropy change in the equilibrium state is zero ($\Delta S = 0$).
- (vi) For natural processes, entropy of universe is increasing.

$$\Delta S_{\text{universe}} > 0$$

- (vii) In a reversible process, ΔS_{total} or $\Delta S_{\text{universe}} = 0$ and therefore

$$\Delta S_{\text{system}} = -\Delta S_{\text{surroundings}}$$

- (viii) For adiabatic reversible process,

$$\Delta S_{\text{system}} = \Delta S_{\text{surroundings}} = \Delta S_{\text{total}} = 0$$

In a spontaneous (irreversible process),

$$\Delta S_{\text{total}} \text{ or } \Delta S_{\text{universe}} > 0,$$

i.e., in spontaneous processes, there is always increase in entropy of the universe.

7.25 ENTROPY CHANGE DURING PHASE TRANSITIONS

Solid, liquid and gas are the three forms of a matter. The change of a substance from one form to another is known as **phase transformation**. Such changes occur at definite temperatures and are accompanied by entropy change. During these transformations either heat is absorbed or evolved, i.e., the entropy either increases or decreases accordingly.

The entropy change for these transformations is given by

$$\Delta S_{\text{trans}} = \frac{q_{\text{rev}}}{T}$$

where, q_{rev} is the heat absorbed or evolved and T is the temperature of transition. q_{rev} is actually the molar enthalpy change of the substance.

(i) **Entropy of fusion:** The entropy of fusion is defined as the change in entropy when one mole of a solid substance changes into liquid form at the melting temperature.

The heat absorbed is equal to the latent heat of fusion

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

For example, when ice melts, the change in entropy is given by

$$\begin{aligned} \Delta S_{\text{fusion (ice)}} &= S_{\text{water}} - S_{\text{ice}} = \frac{\Delta H_{\text{fusion}}}{T_f} = \frac{6000 \text{ J mol}^{-1}}{273} \\ &= 21.98 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

(ii) Entropy of vaporisation: It is defined as the change in entropy when one mole of the liquid substance changes into vapours (gas) at its boiling point.

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

Where, ΔH_{vapour} is the latent heat of vaporisation and T_{bp} is the boiling point.

For example, when water is converted into steam, the change in entropy is given by

$$\Delta S_{\text{vapour (water)}} = S_{\text{steam}} - S_{\text{water}} = \frac{\Delta H_{\text{vapour}}}{T_{\text{bp}}} = \frac{40626 \text{ J mol}^{-1}}{373} \\ = 108.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

(iii) Entropy of sublimation: Sublimation involves the direct conversion of a solid into its vapour. The entropy of sublimation is defined as the change in entropy when one mole of a solid changes into vapour at a particular temperature.

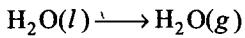
$$\Delta S_{\text{sub}} = S_{\text{vapour}} - S_{\text{solid}} = \frac{\Delta H_{\text{sub}}}{T}$$

Where, ΔH_{sub} = heat of sublimation at temperature T .

SOME SOLVED EXAMPLES

Example 62. The enthalpy change, for the transition of liquid water to steam, ΔH_{vapour} is 40.8 kJ mol^{-1} at 373 K . Calculate entropy change for the process.

Solution: The transition under consideration is:



We know that, $\Delta S_{\text{vapour}} = \frac{\Delta H_{\text{vapour}}}{T}$

Given, $\Delta H_{\text{vapour}} = 40.8 \text{ kJ mol}^{-1}$
 $= 40.8 \times 1000 \text{ J mol}^{-1}$
 $T = 373 \text{ K}$

Thus, $\Delta S_{\text{vapour}} = \frac{40.8 \times 1000}{373} = 109.38 \text{ J K}^{-1} \text{ mol}^{-1}$

Example 63. What is entropy change for the conversion of one gram of ice to water at 273 K and one atmospheric pressure? ($\Delta H_{\text{fusion}} = 6.025 \text{ kJ mol}^{-1}$)

Solution: $\Delta H_{\text{fusion}} = 6.025 \times 1000 \text{ J mol}^{-1}$
 $= \frac{6025}{18} \text{ J g}^{-1} = 334.72 \text{ J g}^{-1}$
 $\Delta S_{\text{fusion}} = \frac{\Delta H_{\text{fusion}}}{T_f}$
 $= \frac{334.72}{273} = 1.226 \text{ J K}^{-1} \text{ g}^{-1}$

Example 64. Calculate the enthalpy of vaporisation per mole for ethanol. Given, $\Delta S = 109.8 \text{ J K}^{-1} \text{ mol}^{-1}$ and boiling point of ethanol is 78.5°C .

Solution: We know that,

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

Given,

$$\Delta S_{\text{vapour}} = 109.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$T_{\text{bp}} = 78.5 + 273 = 351.5 \text{ K}$$

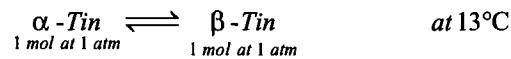
Substituting these values in above equation, we get

$$109.8 = \frac{\Delta H_{\text{vapour}}}{351.5}$$

$$\Delta H_{\text{vapour}} = 38594.7 \text{ J mol}^{-1}$$

$$= 38.594 \text{ kJ mol}^{-1}$$

Example 65. Calculate the entropy change for the following reversible process:



$$(\Delta H_{\text{trans}} = 2090 \text{ J mol}^{-1})$$

Solution: $\Delta S_{\text{trans}} = \frac{\Delta H_{\text{trans}}}{T} = \frac{2090}{286}$
 $= 7.3076 \text{ J K}^{-1} \text{ mol}^{-1}$

Example 66. At 0°C , ice and water are in equilibrium and enthalpy change for the process $\text{H}_2\text{O}(s) \rightleftharpoons \text{H}_2\text{O}(l)$ is 6 kJ mol^{-1} . Calculate the entropy change for the conversion of ice into liquid water.

Solution: We know that for the process of fusion,

$$\text{H}_2\text{O}(s) \rightleftharpoons \text{H}_2\text{O}(l)$$

$$\Delta S_{\text{fusion}} = \frac{\Delta H_{\text{fusion}}}{T_f}$$

$$= \frac{6 \times 1000}{273} = 21.98 \text{ J K}^{-1} \text{ mol}^{-1}$$

Example 67. The enthalpy of vaporisation of liquid diethyl ether $(\text{C}_2\text{H}_5)_2\text{O}$ is 26 kJ mol^{-1} at its boiling point 35°C . Calculate ΔS° for conversion of:

- (a) liquid to vapour,
- (b) vapour to liquid at 35°C .

Solution: (a) $\Delta S_{\text{vaporisation}} = \frac{\Delta H_{\text{vaporisation}}}{T_{\text{bp}}} = \frac{26000}{308}$
 $= 84.42 \text{ J K}^{-1} \text{ mol}^{-1}$

(b) $\Delta S_{\text{condensation}} = -\Delta S_{\text{vaporisation}}$
 $= -84.42 \text{ J K}^{-1} \text{ mol}^{-1}$

Example 68. Calculate entropy change when 10 moles of an ideal gas expands reversibly and isothermally from an initial volume of 10 litre to 100 litre at 300 K .

Solution: $\Delta S = 2.303nR \log \left(\frac{V_2}{V_1} \right)$
 $= 2.303 \times 10 \times 8.314 \log \left(\frac{100}{10} \right)$
 $= 191.24 \text{ J K}^{-1}$

Example 69. Oxygen gas weighing 64 g is expanded from 1 atm to 0.25 atm at 30°C. Calculate entropy change, assuming the gas to be ideal.

$$\text{Solution: } n = \frac{w}{\text{m.wt.}} = \frac{64}{32} = 2$$

$$\Delta S = 2.303nR \log \left(\frac{P_1}{P_2} \right)$$

$$= 2.303 \times 2 \times 8.314 \log \left(\frac{1}{0.25} \right) \\ = 23.053 \text{ J K}^{-1}$$

Example 70. Calculate the change in entropy when 1 mole nitrogen gas expands isothermally and reversibly from an initial volume of 1 litre to a final volume of 10 litre at 27°C.

$$\text{Solution: } \Delta S = 2.303 nR \log \left(\frac{V_2}{V_1} \right)$$

$$= 2.303 \times 1 \times 8.314 \log \left(\frac{10}{1} \right) \\ = 19.12 \text{ J K}^{-1}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

34. For a liquid, enthalpy of fusion is 1.435 kcal mol⁻¹ and molar entropy change is 5.26 cal mol⁻¹ K⁻¹. The melting point of the liquid is:

- (a) 0°C (b) -273°C
 (c) 173 K (d) 100°C

[Ans. (a)]

$$[\text{Hint: } \Delta S_{\text{fusion}} = \frac{\Delta H_{\text{fusion}}}{T_{\text{mp}}}]$$

$$5.26 = \frac{1.435 \times 1000}{T_{\text{mp}}}$$

$$T_{\text{mp}} = \frac{1435}{5.26} = 273 \text{ K, i.e., } 0^\circ\text{C}$$

35. Latent heat of vaporisation of water is 540 cal g⁻¹ at 100°C. Calculate the entropy change when 1000 g water is converted to steam at 100°C.

- (a) 1447 cal (b) 2447 cal (c) 3447 cal (d) 4447 cal

[Ans. (a)]

$$[\text{Hint: } \Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T} = \frac{540 \times 1000}{373} = 1447 \text{ cal}]$$

36. Enthalpy of fusion of water is 6.01 kJ mol⁻¹. The entropy change of 1 mole of ice at its melting point will be:

- (a) 22 kJ mol⁻¹ (b) 109 kJ mol⁻¹
 (c) 44 kJ mol⁻¹ (d) 11 kJ mol⁻¹

[Ans. (a)]

$$[\text{Hint: } \Delta S_{\text{fusion}} = \frac{\Delta H_{\text{fusion}}}{T_{\text{mp}}} = \frac{6.01 \times 1000}{273} = 22 \text{ kJ mol}^{-1}]$$

37. For spontaneous process:

- | | |
|-----------------------------------|-----------------------------------|
| (a) $\Delta S_{\text{total}} = 0$ | (b) $\Delta S_{\text{total}} > 0$ |
| (c) $\Delta S_{\text{total}} < 0$ | (d) none of these |

[Ans. (b)]

[Hint: $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$

= +ve for spontaneous process]

38. Melting point of a solid is x K and its latent heat of fusion is 600 cal mol⁻¹. The entropy change for fusion of 1 mol solid is 2 cal mol⁻¹ K⁻¹. The value of x will be:

- (a) 100 K (b) 200 K (c) 300 K (d) 400 K

[Ans. (c)]

[Hint: $\frac{\Delta H_{\text{fusion}}}{T_{\text{mp}}} = \Delta S_{\text{fusion}}$

$$\frac{600}{T} = 2$$

$$T = 300 \text{ K}$$

39. The entropy change involved in the conversion of 1 mole of liquid water at 373 K to vapour at the same temperature will be:

$$\Delta H_{\text{vap}} = 2.257 \text{ kJ/g}$$

- | | |
|--------------|--------------|
| (a) 0.119 kJ | (b) 0.109 kJ |
| (c) 0.129 kJ | (d) 0.120 kJ |

[PMT (MP) 2007]

[Ans. (b)]

$$[\text{Hint: } \Delta S = \frac{\Delta H_{\text{vap}}}{T} = \frac{2.257 \times 18}{373} = 0.109 \text{ kJ/g}]$$

7.26 SECOND LAW OF THERMODYNAMICS

The second law of thermodynamics tells us whether a given process can occur spontaneously and to what extent. It also helps us to calculate the maximum fraction of heat that can be converted into work in a given process.

The second law of thermodynamics like first law is a postulate and has not been derived from any prior concepts. It is stated in various forms. However, all the statements of second law have the same meaning.

1. Clausius statement: "It is impossible to construct a machine that is able to convey heat by a cyclic process from a colder to a hotter body unless work is done on the machine by some outside agency."

It means that work can always be completely converted into heat but heat cannot be converted completely into work without leaving some permanent change in the system or surroundings. For example, heat produced in heat engine is never fully utilized, as part of it is always lost to surroundings or in overcoming friction, etc. Thus, it can be said that *the complete conversion of heat into work is impossible without leaving some effect elsewhere.*

Or

It is not possible to convert heat into work without compensation.

Or

All forms of energy can be converted into heat energy but heat cannot be converted into other forms of energy fully by any process.

The other similar statements are:

2. Thomson statement: *The heat of the coldest body among those participating in a cyclic process cannot serve as a source of work.*

3. Kelvin-Planck statement: *It is impossible by means of inanimate material agency to derive mechanical work or effort from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects.*

4. It is impossible to construct a heat engine of 100% thermal efficiency.

5. Ludwig Boltzmann statement: In 1886, Ludwig Boltzmann gave a most useful statement of the second law of thermodynamics. *Nature tends to pass from a less probable to more probable state.*

The connection between entropy and the spontaneity of a reaction or a process is expressed by the second law of thermodynamics in a number of ways.

6. All spontaneous processes or naturally occurring processes are thermodynamically irreversible. Without the help of an external agency, a spontaneous process cannot be reversed.

For example, the mixing of non-reacting gases is a spontaneous process. But these cannot be separated from the mixture without the application of special methods.

Heat energy can flow from a hot body to a cold body of its own (spontaneously) but not from a cold body to a hot body unless the former is heated.

7. The entropy of the universe increases in a spontaneous process and remains unchanged in an equilibrium process.

Since, the universe is made up of the system and the surroundings, the entropy change in the universe ($\Delta S_{\text{universe}}$) for any process is the sum of the entropy changes in the system (ΔS_{system}) and in the surroundings ($\Delta S_{\text{surroundings}}$). Mathematically, the second law of thermodynamics can be expressed as:

A spontaneous process:

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$$

An equilibrium process:

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0$$

For a spontaneous process, the law says that $\Delta S_{\text{universe}}$ must be greater than zero, but it does not place a restriction on either ΔS_{system} or $\Delta S_{\text{surroundings}}$. Thus, it is possible for either ΔS_{system} or $\Delta S_{\text{surroundings}}$ to be negative, as long as the sum of these two quantities is greater than zero. For an equilibrium process, $\Delta S_{\text{universe}}$ is zero, i.e., ΔS_{system} and $\Delta S_{\text{surroundings}}$ must be equal in magnitude but opposite in sign.

Thus, *the entropy of the universe is continuously increasing*. The main ideas of the first and second law of thermodynamics may be summarised as:

First law states that the energy of the universe is constant whereas the second law states that the entropy of the universe is continuously increasing and tends to a maximum.

First law deals with the conservation of energy whereas the second law tells the direction of flow of energy.

For a reversible process,

$$dS = \frac{dq}{T} \quad \text{or} \quad dq = T dS$$

For an irreversible process,

$$\therefore dS > \frac{dq}{T}$$

$$dS \geq \frac{dq}{T}$$

This is the mathematical statement of second law of thermodynamics.

$dq = dE + P dV$ This is the mathematical statement of first law of thermodynamics

Combining both the laws of a reversible process,

$$T dS = dE + P dV$$

7.27 GIBBS FREE ENERGY, (G), CHANGE IN FREE ENERGY AND SPONTANEITY

As discussed earlier, there are two thermodynamic quantities that affect reaction spontaneity. One of these is enthalpy, H ; the other is the entropy, S . The problem is to put these two quantities together in such a way as to arrive at a single function whose sign will determine whether a reaction is spontaneous. This problem was first solved more than a century ago by J. Willard Gibbs, who introduced a new quantity, now called the **Gibbs free energy** and given the symbol, G . Gibbs showed that for a reaction taking place at constant pressure and constant temperature, ΔG represents that portion of the total energy change that is available (i.e., free) to do useful work. If, for example, ΔG for a reaction is -300 kJ , it is possible to obtain 300 kJ of useful work from the reaction. Conversely, if ΔG is $+300 \text{ kJ}$, at least that much energy in the form of work must be supplied to make the reaction to take place. Gibbs free energy of a system is defined as:

"The thermodynamic quantity of the system, the decrease in whose value during a process is equal to useful work done by the system."

Mathematically, it may be defined as:

$$G = H - TS \quad \dots (i)$$

where, H = enthalpy; S = entropy and T = absolute temperature.

$$\text{We know that, } H = E + PV \quad \dots (ii)$$

From eqs. (i) and (ii),

$$G = E + PV - TS$$

Free energy change at constant temperature and pressure can be given as:

$$\begin{aligned} \Delta G &= \Delta E + P \Delta V - T \Delta S \\ \Delta G &= \Delta H - T \Delta S \end{aligned} \quad \dots (iii)$$

(Gibbs-Helmholtz equation)

Here, $\Delta H = \Delta E + P \Delta V$

Gibbs-Helmholtz equation is used to discuss the **driving force**, i.e., the overall criterion of spontaneity.

[Note: Since, ' H ' and ' S ' are extensive property hence ' G ' will also be an extensive property. Moreover, Gibbs function ' G ' is a state function.]

Free Energy Change and Spontaneity

Let us consider a system which is not isolated from its surroundings. In this case, total entropy change can be calculated as:

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \quad \dots (\text{i})$$

Let us consider the process at constant temperature and pressure. Let q_P amount of heat be given by the system to the surroundings.

$$(q_P)_{\text{surroundings}} = -(q_P)_{\text{system}} = -\Delta H_{\text{system}}$$

$$\Delta S_{\text{surroundings}} = \frac{(q_P)_{\text{surroundings}}}{T} = \frac{-\Delta H_{\text{system}}}{T} \quad \dots (\text{ii})$$

From equations (i) and (ii),

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

or $T \Delta S_{\text{total}} = T \Delta S_{\text{system}} - \Delta H_{\text{system}} \quad \dots (\text{iii})$

or $-T \Delta S_{\text{total}} = \Delta H_{\text{system}} - T \Delta S_{\text{system}} \quad \dots (\text{iv})$

According to Gibbs-Helmholtz equation,

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

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

From equations (iii) and (iv),

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

We know that for spontaneous process, $\Delta S_{\text{total}} > 0$

$\therefore \Delta G = -ve$ for spontaneous process.

Thus, for spontaneous process $T \Delta S_{\text{total}}$ should be positive or ΔG should be negative.

Case I: Let entropy and energy, both factors are favourable process, i.e., $\Delta H = -ve$ and $T \Delta S = +ve$

$$\therefore \text{From } \Delta G = \Delta H - T \Delta S$$

$$= (-ve) - (+ve) = -ve$$

Thus, $\Delta G = -ve$ for spontaneous process.

Case II: Let both energy and entropy factors oppose a process, i.e., $\Delta H = +ve$, $T \Delta S = -ve$.

$$\therefore \text{From } \Delta G = \Delta H - T \Delta S$$

$$= +ve - (-ve) = +ve$$

Thus, ΔG is positive for a non-spontaneous process.

Case III: Let both tendencies be equal in magnitude but opposite, i.e.,

$$\Delta H = +ve \text{ and } T \Delta S = +ve \text{ and } \Delta H = T \Delta S$$

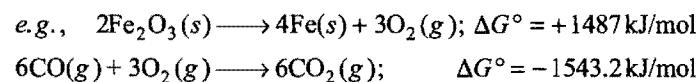
$$\therefore \text{From } \Delta G = \Delta H - T \Delta S$$

$$= 0$$

In this condition, the process is said to be at equilibrium.

Coupled Reactions

We know that the reactions which have $\Delta G = +ve$ are non-spontaneous. However, such reactions can be made spontaneous when coupled with a reaction having very large negative free energy of reaction,



On adding, $2\text{Fe}_2\text{O}_3(s) + 6\text{CO}(g) \rightarrow 4\text{Fe}(s) + 6\text{CO}_2(g);$

$$\Delta G^\circ = -52.2 \text{ kJ/mol}$$

Thus, both reactions proceed simultaneously.

The free energy of a reaction is the chemical analogue of potential energy of mechanical systems. A body moves in the direction in which there is decrease in potential energy. Similarly, in chemical system, the substance moves in a direction in which there is decrease in free energy, i.e., ΔG is negative.

In a chemical reaction, $\Delta G = G_{\text{products}} - G_{\text{reactants}}$. Thus, spontaneous changes occur with a decrease in free energy, i.e., ΔG is negative.

To sum up, the criteria for spontaneity of a process in terms of ΔG is as follows:

- If ΔG is negative, the process is spontaneous.
- If ΔG is zero, the system is in equilibrium. The process does not occur.
- If ΔG is positive, the process does not occur in the forward direction. It may occur in the backward direction.

Conditions for ΔG to be negative or the process to be spontaneous

We know that, $\Delta G = \Delta H - T \Delta S$

| ΔH | $T \Delta S$ | Conditions | ΔG |
|-----------------------|-----------------------|-----------------------------|-----------------|
| -ve (favourable) | +ve (favourable) | (any) | -ve spontaneous |
| -ve (favourable) | -ve (unfavourable) | $ \Delta H > (T \Delta S)$ | -ve spontaneous |
| +ve (unfavourable) | +ve (favourable) | $ T \Delta S > \Delta H $ | -ve spontaneous |

Role of Temperature on Spontaneity

In Gibbs-Helmholtz equation:

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

not only ΔH and ΔS but also temperature ' T ' is a determining factor for spontaneity, i.e., for ΔG to be -ve. Let us discuss exothermic and endothermic reactions to show the influence of temperature.

1. Exothermic processes: In exothermic reactions, $\Delta H = -ve$ (favourable condition)

Case I: When $T \Delta S$ is positive, i.e., favourable, then ΔG will be negative and the process will be spontaneous at all temperatures.

Case II: When $T \Delta S$ is negative, i.e., unfavourable, then ΔG will be negative when $|\Delta H| > |T \Delta S|$. To reduce the magnitude of $T \Delta S$, the temperature should be low. Thus, *exothermic reactions can be made favourable (when $T \Delta S = -ve$) by lowering the temperature*.

2. Endothermic reactions: In endothermic reactions, $\Delta H = +ve$ (unfavourable conditions).

In case of endothermic reactions, ΔG will be negative when $|\Delta H| < |T \Delta S|$. To increase the magnitude of $T \Delta S$, temperature

(T) should be increased. Thus, endothermic reactions can be made favourable by increasing the temperature.

Thus, temperature also plays an important role in deciding the spontaneity of a reaction. A reaction which is non-spontaneous at low temperature becomes spontaneous at high temperature and vice-versa.

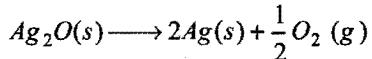
Sign of ΔH , ΔG and ΔS and prediction of spontaneity

| ΔH | ΔS | ΔG | Remarks |
|------------|------------|---|-------------------------------------|
| -ve | +ve | -ve | Spontaneous at all temperatures |
| -ve | -ve | -ve (at low temperature) +ve (at high temperature) | Spontaneous Non-spontaneous |
| +ve | +ve | +ve (at low temperature) -ve (at high temperature) | Non-spontaneous Spontaneous |
| +ve | -ve | +ve | Non-spontaneous at all temperatures |

| ΔH | | | |
|------------|-----|---|--|
| | | $+$ | $-$ |
| ΔS | $+$ | Spontaneous at high temperature and non-spontaneous at low temperatures | Spontaneous at all temperatures |
| | - | Non-spontaneous at all temperatures | Non-spontaneous at high temperatures and spontaneous at low temperatures |

••••• SOME SOLVED EXAMPLES •••••

Example 71. ΔH and ΔS for the reaction,



are 30.56 kJ mol^{-1} and $66.0\text{ J K}^{-1}\text{ mol}^{-1}$ respectively. Calculate the temperature at which free energy change for the reaction will be zero. Predict whether the forward reaction will be favoured above or below this temperature.

Solution: We know that,

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

At equilibrium, $\Delta G = 0$

so that $0 = \Delta H - T \Delta S$

$$T = \frac{\Delta H}{\Delta S}$$

Given that, $\Delta H = 30.56\text{ kJ mol}^{-1}$

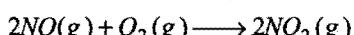
$$= 30560\text{ J mol}^{-1}$$

$$\Delta S = 66.0\text{ J K}^{-1}\text{ mol}^{-1}$$

$$T = \frac{30560}{66} = 463\text{ K}$$

Above this temperature, ΔG will be negative and the process will be spontaneous in forward direction.

Example 72. For the reaction,



Calculate ΔG at 700 K when enthalpy and entropy changes are $-113.0\text{ kJ mol}^{-1}$ and $-145\text{ J K}^{-1}\text{ mol}^{-1}$ respectively.

Solution: We know that, $\Delta G = \Delta H - T \Delta S$

Given,

$$\Delta H = -113\text{ kJ mol}^{-1}$$

$$= -113000\text{ J mol}^{-1}$$

$$\Delta S = -145\text{ J K}^{-1}\text{ mol}^{-1}$$

$$T = 700\text{ K}$$

Substituting these values in the above equation,

$$\text{we get } \Delta G = -113000 - 700 \times (-145)$$

$$= -11500\text{ J mol}^{-1}$$

$$= -11.5\text{ kJ mol}^{-1}$$

Example 73. In the reaction $A^+ + B \longrightarrow A + B^+$, there is no entropy change. If enthalpy change is 22 kJ of A^+ , calculate ΔG for the reaction.

Solution: For the given reaction,

$$\Delta H = 22\text{ kJ}, \Delta S = 0$$

∴ From,

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

$$\Delta G = 22 - T \times 0 = 22\text{ kJ mol}^{-1}$$

Example 74. ΔH and ΔS for the reaction $Br_2(l) + Cl_2(g) \rightarrow 2BrCl(g)$ are 29.37 kJ and 104.0 J K^{-1} respectively. Above what temperature will this reaction become spontaneous?

Solution: According to Gibbs-Helmholtz equation,

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

For spontaneous process, $\Delta G < 0$

i.e.,

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

$$T \Delta S > \Delta H$$

$$T > \frac{\Delta H}{\Delta S}$$

$$T > \frac{29.37 \times 1000}{104}$$

$$T > 282.4\text{ K}$$

Example 75. Calculate the temperature at which liquid water will be in equilibrium with water vapour.

$$\Delta H_{vap} = 40.73\text{ kJ mol}^{-1} \text{ and } \Delta S_{vap} = 0.109\text{ kJ mol}^{-1}\text{ K}^{-1}$$

Solution: Given, $\Delta H = 40.73\text{ kJ mol}^{-1}$

$$\Delta S = 0.109\text{ kJ mol}^{-1}\text{ K}^{-1}$$

and

$$\Delta G = 0$$

Applying

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

$$0 = 40.73 - T \times 0.109$$

$$T = \frac{40.73}{0.109} = 373.6\text{ K}$$

Example 76. Zinc reacts with dilute hydrochloric acid to give hydrogen at 17°C . The enthalpy of the reaction is $-12.55\text{ kJ mol}^{-1}$ of zinc and entropy change equals $5.0\text{ J K}^{-1}\text{ mol}^{-1}$ for the reaction. Calculate the free energy change and predict whether the reaction is spontaneous or not.

Solution: Given, $\Delta H = -12.55 \text{ kJ mol}^{-1}$

$$\begin{aligned}\Delta S &= 5.0 \text{ J K}^{-1} \text{ mol}^{-1} \\ &= 0.005 \text{ kJ K}^{-1} \text{ mol}^{-1}\end{aligned}$$

$$T = 17 + 273 = 290 \text{ K}$$

Applying

$$\begin{aligned}\Delta G &= \Delta H - T \Delta S \\ &= -12.55 - 0.005 \times 290 \\ &= -12.55 - 1.45 = -14.00 \text{ kJ mol}^{-1}\end{aligned}$$

Since, ΔG is negative, the reaction will be spontaneous.

Example 77. ΔH and ΔS for the system $H_2O(l) \rightleftharpoons H_2O(g)$ at 1 atmospheric pressure are $40.63 \text{ kJ mol}^{-1}$ and $108.8 \text{ J K}^{-1} \text{ mol}^{-1}$ respectively. Calculate the temperature at which the rates of forward and backward reactions will be the same. Predict the sign of free energy for this transformation above this temperature.

Solution: Given, $\Delta H = 40.63 \text{ kJ mol}^{-1}$

$$\Delta S = 108.8 \text{ J K}^{-1} \text{ mol}^{-1} = 0.1088 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$\Delta G = 0$$

(when the system is in equilibrium)

Applying

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

$$0 = 40.63 - T \times 0.1088$$

$$T = \frac{40.63}{0.1088} = 373.4 \text{ K}$$

The sign of ΔG above 373 K , i.e., say 374 K , may be calculated as follows:

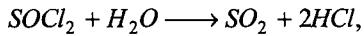
Again applying $\Delta G = \Delta H - T \Delta S$

$$= 40.63 - 374 \times 0.1088$$

$$= 40.63 - 40.69 = -0.06 \text{ kJ}$$

ΔG will be negative; hence, the reaction will be spontaneous.

Example 78. For the reaction,



the enthalpy of reaction is 49.4 kJ and the entropy of reaction is 336 J K^{-1} . Calculate ΔG at 300 K and predict the nature of the reaction.

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

$$= 49.4 - (300 \times 336 \times 10^{-3})$$

$$= -51.4 \text{ kJ}$$

Since, the free energy change is negative, the given reaction is spontaneous.

Example 79. The standard enthalpy and entropy changes for the reaction in equilibrium for the forward direction are given below:



$$\Delta H_{300K}^{\circ} = -41.16 \text{ kJ mol}^{-1}$$

$$\Delta S_{300K}^{\circ} = -4.24 \times 10^{-2} \text{ kJ mol}^{-1}$$

$$\Delta H_{1200K}^{\circ} = -32.93 \text{ kJ mol}^{-1}$$

$$\Delta S_{1200K}^{\circ} = -2.96 \times 10^{-2} \text{ kJ mol}^{-1}$$

Calculate K_P at each temperature and predict the direction of reaction at 300 K and 1200 K , when $P_{CO} = P_{CO_2} = P_{H_2} = P_{H_2O} = 1 \text{ atm}$ at initial state.

Solution: At 300 K : $\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$

$$= -41.16 - 300 \times (-4.24 \times 10^{-2})$$

$$= -28.44 \text{ kJ}$$

Since, ΔG° is negative hence reaction is spontaneous in forward direction,

$$\Delta G^{\circ} = -2.303 RT \log K_P$$

$$-28.44 = -2.303 \times 8.314 \times 10^{-3} \times 300 \log K_P$$

$$K_P = 8.93 \times 10^4$$

At 1200 K : $\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$

$$= -32.93 - 1200(-2.96 \times 10^{-2}) = +2.59 \text{ kJ}$$

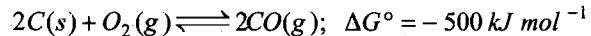
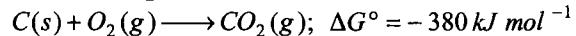
Positive value of ΔG° shows that the reaction is spontaneous in backward direction

$$\Delta G^{\circ} = -2.303 RT \log K_P$$

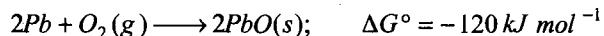
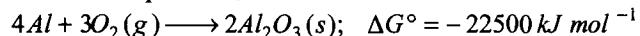
$$2.59 = -2.303 \times 8.314 \times 10^{-3} \times 1200 \log K_P$$

$$K_P = 0.77$$

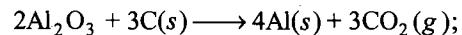
Example 80. The standard Gibbs free energies for the reactions at 1773 K are given below:



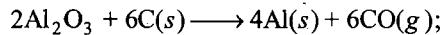
Discuss the possibility of reducing Al_2O_3 and PbO with carbon at this temperature,



Solution: Let us consider the reduction of Al_2O_3 by carbon:



$$\Delta G^{\circ} = -380 \times 3 + (22500) = +21360 \text{ kJ}$$



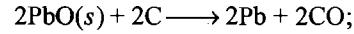
$$\Delta G^{\circ} = -500 \times 3 + 22500 = +21000 \text{ kJ}$$

Positive values of ΔG° show that the reduction of Al_2O_3 is not possible by any of the above methods.

Now, let us consider the reduction of PbO .



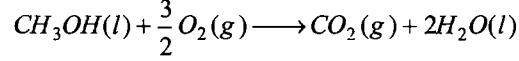
$$\Delta G^{\circ} = +120 + (-380) = -260 \text{ kJ}$$



$$\Delta G^{\circ} = +120 + (-500) = -380 \text{ kJ}$$

Negative value of ΔG° shows that the process is spontaneous and PbO can be reduced by carbon.

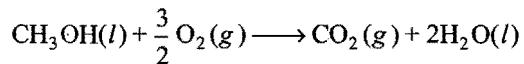
Example 81. In a fuel cell, methanol is used as fuel and oxygen gas is used as an oxidiser. The reaction is:



Calculate standard Gibbs free energy change for the reaction that can be converted into electrical work. If standard enthalpy of combustion for methanol is -726 kJ mol^{-1} ; calculate the efficiency of conversion of Gibbs energy into useful work.

ΔG_f° for CO_2 , H_2O , CH_3OH , O_2 are -394.36 ; -237.13 ; -166.27 and zero respectively.

Solution: The reaction for combustion of methanol is:



$$\begin{aligned}\Delta G_{\text{reaction}}^\circ &= [\Delta G_f^\circ \text{ CO}_2(g) + 2 \Delta G_f^\circ \text{ H}_2\text{O}(l)] \\ &\quad - [\Delta G_f^\circ \text{ CH}_3\text{OH}(l) + \frac{3}{2} \Delta G_f^\circ \text{ O}_2(g)] \\ &= [-394.36 + 2(-237.13)] - [-166.27 + 0] \\ &= -702.35 \text{ kJ mol}^{-1}\end{aligned}$$

Efficiency of conversion of Gibbs free energy into useful work

$$\begin{aligned}&= \frac{\Delta G_{\text{reaction}}^\circ \times 100}{\Delta H_{\text{reaction}}} \\ &= \frac{-702.35 \times 100}{-726} = 96.7\%\end{aligned}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

40. The free energy for a reaction having $\Delta H = 31400 \text{ cal}$, $\Delta S = 32 \text{ cal K}^{-1} \text{ mol}^{-1}$ at 1000°C is: [JEE (Orissa) 2005]
 (a) -9336 cal (b) -7386 cal (c) -1936 cal (d) $+9336 \text{ cal}$
 [Ans. (a)]

[Hint: $\Delta G = \Delta H - T \Delta S = 31400 - 1273 \times 32 = -9336 \text{ cal}$]

41. $\text{F}_2\text{C}=\text{CF}-\text{CF}=\text{CF}_2 \longrightarrow \text{F}_2\text{C} \begin{array}{c} | \\ \text{FC}=\text{CF} \end{array} \text{F}_2$

For this reaction (ring closure), $\Delta H = -49 \text{ kJ mol}^{-1}$, $\Delta S = -40.2 \text{ J K}^{-1} \text{ mol}^{-1}$. Upto what temperature is the forward reaction spontaneous?

- (a) 1492°C (b) 1219°C (c) 946°C (d) 1080°C

[Ans. (c)]

[Hint: For spontaneous process,

$$\Delta G = \Delta H - T \Delta S \text{ (should be negative)}$$

$$T > \frac{\Delta H}{\Delta S}$$

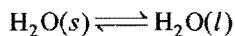
$$T > \frac{-49 \times 1000}{-40.2}$$

$$T > 1219 \text{ K, i.e., } 946^\circ\text{C}]$$

42. For the equilibrium reaction, the value of Gibbs free energy change is: (DCE 2005)
 (a) > 0 (b) < 0 (c) $= 0$ (d) $\neq 0$
 [Ans. (c)]

[Hint: $\Delta G = 0$ at equilibrium]

43. At 0°C , ice and water are in equilibrium and $\Delta H = 6 \text{ kJ mol}^{-1}$. For this process:



The values of ΔS and ΔG for conversion of ice into liquid water at 0°C are:

- (a) $-21.9 \text{ J K}^{-1} \text{ mol}^{-1}$ and 0 (b) $0.219 \text{ J K}^{-1} \text{ mol}^{-1}$ and 0
 (c) $21.9 \text{ J K}^{-1} \text{ mol}^{-1}$ and 0 (d) $0.0219 \text{ J K}^{-1} \text{ mol}^{-1}$ and 0

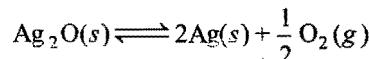
[Ans. (c)]

[Hint: $\Delta G = 0$,

$$\therefore \Delta H - T \Delta S = 0$$

$$\Delta S = \frac{\Delta H}{T} = \frac{6000}{273} = 21.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

44. For a reaction:



ΔH , ΔS and T are $40.63 \text{ kJ mol}^{-1}$, $108.8 \text{ J K}^{-1} \text{ mol}^{-1}$ and 373.4 K respectively. Predict the feasibility of the reaction.

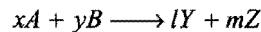
- (a) feasible (b) non-feasible
 (c) remains at equilibrium (d) not predicted

[Ans. (c)]

[Hint: $\Delta G = \Delta H - T \Delta S$

$$= 40.63 \times 1000 - 373.4 \times 108.8 = 0$$

45. For the homogeneous reactions:



$$\Delta H = -30 \text{ kJ mol}^{-1}, \Delta S = -100 \text{ J K}^{-1} \text{ mol}^{-1}$$

At what temperature the reaction is at equilibrium?

[PMT (Kerala) 2006]

- (a) 50°C (b) 250°C (c) 100 K (d) 27°C

(e) 500 K

[Ans. (d)]

[Hint: $\Delta G = \Delta H - T \Delta S$

At equilibrium, $\Delta G = 0$

$$\therefore T = \frac{\Delta H}{\Delta S} = \frac{-30 \times 1000}{-100} = 300 \text{ K, i.e., } 27^\circ\text{C}]$$

46. For the reaction $\text{CO}(g) + \frac{1}{2} \text{O}_2(g) \longrightarrow \text{CO}_2(g)$, ΔH and

ΔS are $+283 \text{ kJ}$ and $-87 \text{ J K}^{-1} \text{ mol}^{-1}$ respectively. It was intended to carry out this reaction at 1000°C , 1500°C , 3000°C and 3500°C . At which of these temperatures would this reaction be thermodynamically spontaneous? [PMT (Kerala) 2006]

- (a) 1500°C and 3500°C (b) 3000°C and 3500°C
 (c) 1000°C , 1500°C and 3000°C (d) 1500°C , 3000°C and 3500°C
 (e) At all of the above temperatures

[Ans. (c)]

[Hint: $\Delta G = \Delta H - T \Delta S$

$$\begin{aligned}\text{At } 1000^\circ\text{C, } \Delta G &= 283 - (-1000 \times 0.087) \text{ (Spontaneous)} \\ &= -196\end{aligned}$$

$$\begin{aligned}\text{At } 1500^\circ\text{C, } \Delta G &= 283 - (-1500 \times 0.087) \text{ (Spontaneous)} \\ &= -152.5\end{aligned}$$

$$\begin{aligned}\text{At } 3000^\circ\text{C, } \Delta G &= 283 - (-3000 \times 0.087) \text{ (Spontaneous)} \\ &= -22\end{aligned}$$

$$\begin{aligned}\text{At } 3500^\circ\text{C, } \Delta G &= 283 - (-3500 \times 0.087) \text{ (Non-spontaneous)} \\ &= +21.5\end{aligned}$$

47. For a reaction,

$$\Delta H = +29 \text{ kJ mol}^{-1}; \Delta S = -35 \text{ J K}^{-1} \text{ mol}^{-1}$$

at what temperature, the reaction will be spontaneous?

[PMT (Haryana) 2007]

- (a) 828.7°C
 (b) 828.7 K
 (c) Spontaneous at all temperature
 (d) Not possible
- [Ans. (d)]

[Hint: $\Delta G = \Delta H - T \Delta S$

When $\Delta H = +$ ve, $\Delta S = -$ ve then ΔG will be positive and the reaction is non-spontaneous.]

7.28 STANDARD FREE ENERGY CHANGE

Just like enthalpy and internal energies, we cannot determine absolute value of Gibbs free energy. The standard free energy change can be determined and it is defined as *the free energy change for a process at 298 K and 1 atm pressure in which the reactants in their standard state are converted to products in their standard state*. It is denoted as ΔG° ; it can be related to standard enthalpy and entropy change in the following manner:

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

Like that of ΔH° , ΔG° can be calculated from the standard free energies of formation of the products and the reactants.

$$\begin{aligned} \Delta G^\circ &= \Sigma G_f^\circ (\text{products}) - \Sigma G_f^\circ (\text{reactants}) \\ &= \left[\begin{array}{l} \text{Sum of standard free} \\ \text{energies of formation} \end{array} \right] - \left[\begin{array}{l} \text{Sum of standard free} \\ \text{energies of formation} \\ \text{of products} \end{array} \right] \end{aligned}$$

Let us consider a general reaction:



$$\begin{aligned} \Delta G^\circ &= \Sigma G_f^\circ (\text{products}) - \Sigma G_f^\circ (\text{reactants}) \\ &= [n_3 G_f^\circ (L) + n_4 G_f^\circ (M)] - [n_1 G_f^\circ (A) + n_2 G_f^\circ (B)] \end{aligned}$$

The standard free energy of formation (ΔG_f°) may be defined as *the free energy change when 1 mole of a compound is formed from its constituent elements in their standard state. The standard free energy of formation of an element in its standard state is assumed to be zero*.

Standard Gibbs Free Energy of Formation (kJ mol^{-1} at 298 K)

| | | | |
|---------------------------------|--------|-------------------------------------|---------|
| HCl | -95.27 | C_2H_8 (iso-butene) | 294 |
| H_2O | -228.6 | BaO | -528.4 |
| H_2O_2 | -103.3 | BaCO_3 | -1139 |
| CO | -137.3 | BaSO_4 | -1465 |
| CO_2 | -394.4 | CaO | -604.2 |
| SO_2 | -300.4 | $\text{Ca}(\text{OH})_2$ | -896.6 |
| SO_3 | -370.4 | CaCO_3 | -1129 |
| NO_2 | 51.84 | CuO | -127 |
| N_2O | 104 | NaCl | -384.0 |
| NH_3 | -16.6 | KCl | -408.3 |
| O_3 | 163.4 | NH_4Cl | -203.0 |
| NO | 86.69 | Al_2O_3 | -1582.4 |
| CH_4 | -50.79 | Fe_2O_3 | -741.0 |
| C_2H_6 (ethane) | 229 | ZnO | -318.2 |

| | | | |
|---|-------|---------------------------------|--------|
| C_3H_8 (propane) | 270 | SiO_2 | -805 |
| C_4H_{10} (<i>n</i> -butane) | 310 | PbO_2 | -219 |
| C_4H_{10} (<i>iso</i> -butane) | 310 | CH_3OH | -166.2 |
| C_2H_2 (acetylene) | 209.2 | $\text{C}_2\text{H}_5\text{OH}$ | -174.8 |
| C_2H_4 (ethylene) | 219.4 | C_6H_6 | -124.5 |
| C_3H_6 (propylene) | 266.9 | CH_3COOH | -392 |
| C_4H_8 (1-butene) | 307.4 | | |

Example 82. Will the reaction,



proceed spontaneously in the forward direction at 298 K, $\Delta G_f^\circ \text{HI}(g) = 1.8 \text{ kJ mol}^{-1}$, $\Delta G_f^\circ \text{H}_2\text{S}(g) = 33.8 \text{ kJ mol}^{-1}$?

Solution:

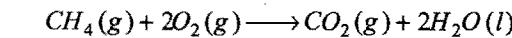
$$\Delta G^\circ = \Sigma G_f^\circ (\text{products}) - \Sigma G_f^\circ (\text{reactants})$$

$$= [2G_f^\circ \text{HI}(g) + G_f^\circ \text{S}(s)] - [1 \times G_f^\circ \text{I}_2(s) + G_f^\circ \text{H}_2\text{S}(g)]$$

$$= [2 \times 1.8 + 0] - [0 + 33.8] = -30.2 \text{ kJ}$$

-ve value shows that the process is spontaneous in forward direction.

Example 83. Compute the standard free energy of the reaction at 27°C for the combustion of methane using the given data:



| Species | CH_4 | O_2 | CO_2 | H_2O |
|--|---------------|--------------|---------------|----------------------|
| $\Delta H_f^\circ / (\text{kJ mol}^{-1})$ | -74.8 | — | -393.5 | -285.8 |
| $S^\circ / (\text{J K}^{-1} \text{ mol}^{-1})$ | 186 | 205 | 214 | 70 |

$$\begin{aligned} \text{Solution: } \Delta H^\circ &= \Delta H_f^\circ (\text{CO}_2) + 2\Delta H_f^\circ (\text{H}_2\text{O}) - \Delta H_f^\circ (\text{CH}_4) \\ &= -393.5 + 2 \times (-285.8) - (-74.8) \\ &= -890 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta S^\circ &= S^\circ (\text{CO}_2) + 2S^\circ (\text{H}_2\text{O}) - S^\circ (\text{CH}_4) - 2S^\circ (\text{O}_2) \\ &= 214 + 2 \times 70 - 186 - 2 \times 205 \\ &= -242 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T \Delta S^\circ \\ &= -890 - 300 \times (-242 \times 10^{-3}) \\ &= -890 + 72.6 = -817.4 \text{ kJ mol}^{-1} \end{aligned}$$

7.29 RELATIONSHIP BETWEEN STANDARD FREE ENERGY CHANGE (ΔG°) AND EQUILIBRIUM CONSTANT

For any reversible reaction, $A + B \rightleftharpoons C + D$, the free energy change and standard free energy change are related with each other by the following relation:

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

where, R is universal constant; T is temperature and Q is reaction quotient $Q = \frac{[C][D]}{[A][B]}$.

At equilibrium state, $\Delta G = 0$ and $Q = K_{eq}$

$$0 = \Delta G^\circ + RT \log_e K_{eq}$$

$$\text{or } \Delta G^\circ = -RT \log_e K_{eq}$$

$$\text{or } \Delta G^\circ = -2.303RT \log K_{\text{eq}}$$

This equation helps in the calculation of K_{eq} if ΔG° of the reaction is known and vice-versa. The value of K_{eq} can give an idea about the extent of chemical reaction before the equilibrium is attained.

Alternatively,

$$K = e^{-\Delta G^\circ/RT}$$

Equilibrium constant of unity implies that standard free energy change ΔG° is zero and that the positive values of ΔG° implies the equilibrium constant to be less than unit.

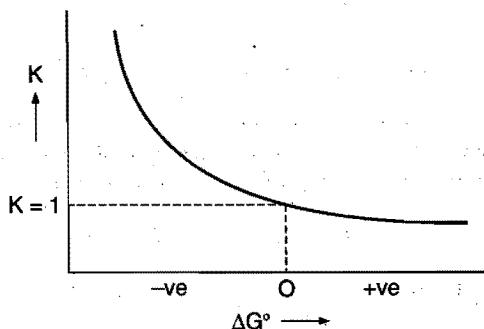


Fig. 7.21 Variation of equilibrium constant against standard free energy change

If we draw a graph of free energy against extent of reaction, we get U-shaped graph Fig. 7.22.

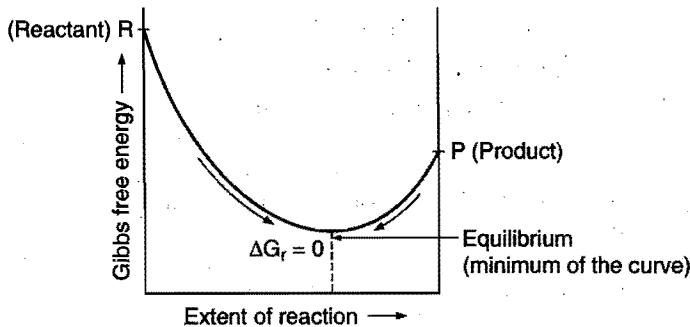


Fig. 7.22 Plot of free energy against extent of reaction

If the minimum in the curve lies closer to products, it means that reaction is in favour of products ($K \ggg 1$). The reaction in this case will be closer to completion. On the other hand, if the

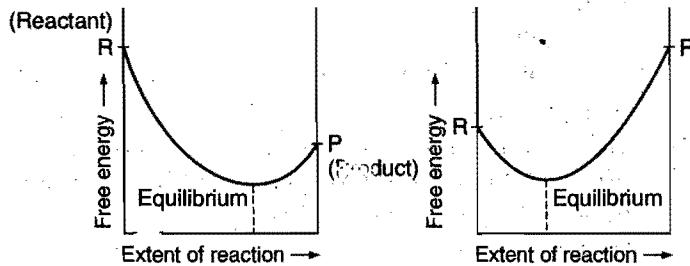
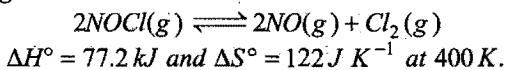


Fig. 7.23 Prediction of extent of reaction by the plot of free energy against extent of reaction

minimum in the curve lies closer to the reactants, the reaction favours reactants ($K \lll 1$). The reaction in this case will be farthest from completion. (See, Fig. 7.23)

Example 84. What is the equilibrium constant K_c for the following reaction at 400 K?



Solution: According to Gibbs-Helmholtz equation,

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= 77.2 - 400 \times 122 \times 10^{-3} \\ &= 28.4 \text{ kJ} = 28.4 \times 10^3 \text{ J} \end{aligned}$$

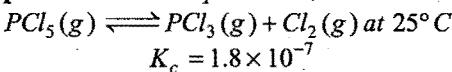
We know that, $\Delta G^\circ = -2.303RT \log K_c$

$$\therefore \log K_c = \frac{-\Delta G^\circ}{2.303RT} = -\frac{28.4 \times 10^3}{2.303 \times 8.314 \times 400}$$

$$= -3.7081$$

$$K_c = \text{antilog } (-3.7081) = 1.958 \times 10^{-4}$$

Example 85. For the equilibrium,

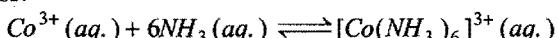


Calculate ΔG° for the reaction ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$).

Solution: We know that,

$$\begin{aligned} \Delta G^\circ &= -2.303RT \log K_c \\ &= -2.303 \times 8.314 \times 298 \log (1.8 \times 10^{-7}) \\ &= 38484 \text{ J mol}^{-1} = 38.484 \text{ kJ mol}^{-1} \end{aligned}$$

Example 86. The equilibrium constant at $25^\circ C$ for the process:



is 2×10^7 .

Calculate the value of ΔG° at $25^\circ C$. ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)

In which direction, the reaction is spontaneous when the reactants and products are in standard state?

Solution: We know that, $\Delta G^\circ = -2.303RT \log K_c$

Given, $K_c = 2 \times 10^7$, $T = 298 \text{ K}$, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

Thus, from above equation,

$$\begin{aligned} \Delta G^\circ &= -2.303 \times 8.314 \times 298 \log 2 \times 10^7 \\ &= -12023.4 \text{ J} = -12.023 \text{ kJ} \end{aligned}$$

Example 87. The equilibrium constant for the reaction,



is 73. Calculate the value of the standard free energy change ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$).

Solution: We know that, $\Delta G^\circ = -2.303RT \log K_c$

Given, $K_c = 73$, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$, $T = 298 \text{ K}$

∴ From above equation,

$$\begin{aligned} \Delta G^\circ &= -2.303 \times 8.314 \times 298 \log 73 \\ &= -10.632 \text{ kJ} \end{aligned}$$

Example 88. For the water gas reaction,



the standard Gibbs free energy of reaction (at 1000 K) is -8.1 kJ/mol . Calculate its equilibrium constant.

Solution: We know that,

$$K = \text{antilog} \left(\frac{-\Delta G^\circ}{2.303RT} \right) \quad \dots \text{(i)}$$

Given that, $\Delta G^\circ = -8.1 \text{ kJ/mol}$

$$R = 8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$T = 1000 \text{ K}$$

Substituting these values in eq. (i), we get

$$K = \text{antilog} \left[\frac{-(-8.1)}{2.303 \times 8.314 \times 10^{-3} \times 1000} \right]$$

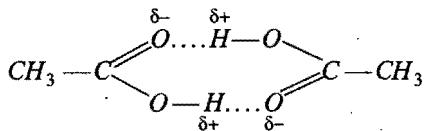
$$K = 2.65$$

Example 89. Calculate ΔG° for the conversion of oxygen to ozone, $(3/2)O_2(g) \rightleftharpoons O_3(g)$ at 298 K, if K_p for this conversion is 2.47×10^{-29} .

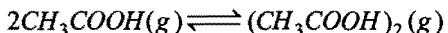
Solution: We know that,

$$\begin{aligned} \Delta G^\circ &= -2.303RT \log K_p \\ &= -2.303 \times 8.314 \times 298 \log 2.47 \times 10^{-29} \\ &= 163228 \text{ J/mol} \\ &= 163.228 \text{ kJ/mol} \end{aligned}$$

Example 90. Acetic acid CH_3COOH can form a dimer $(CH_3COOH)_2$ in the gas phase. The dimer is held together by two H-bonds with a total strength of 66.5 kJ per mol of dimer



If at 25°C, the equilibrium constant for the dimerization is 1.3×10^3 . Calculate ΔS° for the reaction:



Solution: $\Delta G^\circ = -2.303 RT \log K$

$$\begin{aligned} &= -2.303 \times 8.314 \times 298 \log (1.3 \times 10^3) \\ &= -17767.688 \text{ J} = -17.767 \text{ kJ} \end{aligned}$$

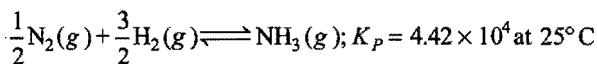
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$-17.767 = -66.5 - 298 \times \Delta S^\circ$$

$$\Delta S^\circ = \frac{-66.5 + 17.767}{298} = -0.163 \text{ kJ}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

48. What is ΔG° for this reaction?



- (a) $-26.5 \text{ kJ mol}^{-1}$ (b) $-11.5 \text{ kJ mol}^{-1}$
 (c) -2.2 kJ mol^{-1} (d) $-0.97 \text{ kJ mol}^{-1}$
 [Ans. (a)]

[Hint: $\Delta G^\circ = -2.303RT \log K_p$

$$\begin{aligned} &= -2.303 \times 8.314 \times 298 \log (4.42 \times 10^4) \\ &= -26.5 \text{ kJ mol}^{-1} \end{aligned}$$

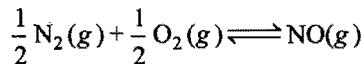
49. What is the sign of ΔG° and the value of K for an electrochemical cell for which $E_{cell}^\circ = 0.80 \text{ volt}$?

| ΔG° | K |
|------------------|-------|
| (a) - | > 1 |
| (b) + | > 1 |
| (c) + | < 1 |
| (d) - | < 1 |

[Ans. (a)]

[Hint: $\Delta G^\circ = -nFE^\circ$; $\Delta G^\circ = -2.303RT \log K$]

50. The free energy of formation of NO is 78 kJ mol^{-1} at the temperature of an automobile engine (1000 K). What is the equilibrium constant for this reaction at 1000 K ?



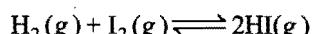
- (a) 8.4×10^{-5} (b) 7.1×10^{-9}
 (c) 4.2×10^{-10} (d) 1.7×10^{-19}

[Ans. (a)]

[Hint: $K = \text{antilog} \left[\frac{-\Delta G^\circ}{2.303RT} \right]$

$$\begin{aligned} &= \text{antilog} \left[\frac{-78 \times 1000}{2.303 \times 8.314 \times 1000} \right] \\ &= 8.4 \times 10^{-5} \end{aligned}$$

51. Equilibrium constant for the reaction:



is $K_c = 50$ at $25^\circ C$.

The standard Gibbs free energy change for the reaction will be:

- (a) -6.964 kJ (b) -9.694 kJ
 (c) -4.964 kJ (d) -6.496 kJ

[Ans. (b)]

[Hint: $\Delta G^\circ = -2.303RT \log K_c$

$$\begin{aligned} &= -2.303 \times 8.314 \times 298 \log 50 \\ &= -9694 \text{ J} = -9.694 \text{ kJ} \end{aligned}$$

52. Standard Gibbs free energy change ΔG° for a reaction is zero. The value of the equilibrium constant will be:

- (a) 10 (b) 1 (c) 100 (d) ∞

[Ans. (b)]

[Hint: $\Delta G^\circ = -2.303RT \log K$

When $K = 1$, $\Delta G^\circ = 0$]

53. The standard free energy change of a reaction is $\Delta G^\circ = -115 \text{ kJ}$ at 298 K . Calculate the equilibrium constant K_p in $\log K_p$. ($R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$)

- (a) 20.16 (b) 2.303 (c) 2.016 (d) 13.83
 (VITEEE 2008)

[Ans. (a)]

$$\begin{aligned} \text{[Hint: } \log K_P &= \frac{-\Delta G^\circ}{2.303 RT} \\ &= \frac{-(-115 \times 1000)}{2.303 \times 8.314 \times 298} \\ &= 20.16] \end{aligned}$$

7.30 PHYSICAL SIGNIFICANCE OF GIBBS FREE ENERGY CHANGE (Free Energy and Useful Work)

According to first law of thermodynamics,

$$\Delta E = q - w \quad \dots (\text{i})$$

(-ve sign as the work is done by system)

Here, q is heat absorbed by the system and w is the work done by the system while ΔE is the change in internal energy. The work (w) actually includes two types of work, i.e., $w_{\text{expansion}}$ (or $P\Delta V$) and $w_{\text{non-expansion}}$ (useful work). The two types of works can be understood by taking an example of the electrolysis of water to form $H_2(g)$ and $O_2(g)$ leading to an increase in the volume of the system. The work non-expansion (non-mechanical) is done to cause the decomposition of water while the work expansion (mechanical) is due to expansion in volume of the system. Thus, the electrical work is called non-pressure-volume work or non-expansion work or non-mechanical work. The non-expansion work is also known as useful work. Thus,

$$\begin{aligned} \Delta E &= q - w_{\text{expansion}} - w_{\text{non-expansion}} \quad \dots (\text{ii}) \\ &= q - P \Delta V - w_{\text{non-expansion}} \quad (\because w_{\text{expansion}} = P \Delta V) \end{aligned}$$

$$\text{or } q = \Delta E + P\Delta V + w_{\text{non-expansion}} \quad \dots (\text{iii})$$

We know that,

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

$$\text{or } q = \Delta H + w_{\text{non-expansion}} \quad \dots (\text{iv})$$

According to second law of thermodynamics, for a reversible change taking place at constant temperature, T

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

$$\text{or } q_{\text{rev.}} = T \Delta S \quad \dots (\text{v})$$

Substituting in equation (iv)

$$T \Delta S = \Delta H + w_{\text{non-expansion}} \quad \dots (\text{vi})$$

$$\text{or } \Delta H - T \Delta S = -w_{\text{non-expansion}}$$

$$\text{or } \Delta G = -w_{\text{non-expansion}} \quad (\because \Delta H - T \Delta S = \Delta G)$$

$$\text{or } -\Delta G = w_{\text{non-expansion}} = w_{\text{useful work}} \quad \dots (\text{vii})$$

Thus, the decrease in Gibbs free energy is a measure of useful work or non-expansion work done by the system. The greater the free energy change, the greater is the amount of work that can be obtained from the process. This relation is useful in assessing the electrical work that may be produced by electrochemical cells and fuel cells.

Free Energy Change and Electrical Work Done in a Cell

Free energy change in electrochemical cells is related to the electrical work done in the cell.

ΔG and emf of the cell (E°) are related by the following relation:

$$\Delta G = -nFE$$

where, F = faraday = 96500 coulomb

E = emf of the cell

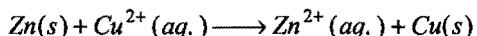
n = Number of moles of electrons involved in balanced electrochemical reaction

If the reactants and products are in their standard states, then

$$\Delta G^\circ = -nFE^\circ$$

when E° = standard emf of the cell.

Example 91. The emf of the cell reaction,



is 1.1 V. Calculate free energy change for the reaction. If enthalpy of the reaction is $-216.7 \text{ kJ mol}^{-1}$, calculate the entropy change for the reaction.

Solution: $-\Delta G^\circ = n \times F \times E^\circ = 2 \times 96500 \times 1.1 = 212.3 \text{ kJ}$

$$\Delta G^\circ = -212.3 \text{ kJ mol}^{-1}$$

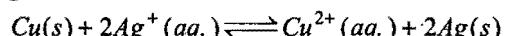
$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = \frac{-216.7 - (-212.3)}{298}$$

$$= -0.01476 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$= -14.76 \text{ J K}^{-1} \text{ mol}^{-1}$$

Example 92. Calculate equilibrium constant for the following reaction:



At 25°C , $E_{\text{cell}}^\circ = 0.47 \text{ volt}$, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$, $F = 96500 \text{ coulomb}$.

Solution: Let us apply Nernst equation at equilibrium

$$E_{\text{cell}}^\circ = \frac{0.0591}{n} \log K_c$$

$$0.47 = \frac{0.0591}{2} \log K_c$$

$$K_c = \text{antilog} \left[\frac{0.47 \times 2}{0.0591} \right]$$

$$= 8.5 \times 10^{15}$$

7.31 ABSOLUTE ENTROPIES AND THIRD LAW OF THERMODYNAMICS

Third law of Thermodynamics was given by T.W. Richards, Walter Nernst and Max Planck. Some statements for third law of thermodynamics are given below:

Statement-1. "Every substance has a finite positive entropy but at the absolute zero temperature the entropy may become zero and does so become in the case of perfectly crystalline solids."

Because

Statement-2. "Entropy of a solid or liquid approaches zero at the absolute zero of temperature."

It can be mathematically expressed as

$$\lim_{T \rightarrow 0 \text{ K}} S \rightarrow 0$$

Because

Statement-3. "It is impossible by any method, no matter how idealised it is, to reduce the temperature of any system to the absolute zero in a finite number of operations."

Application of Third Law of Thermodynamics

The third law of thermodynamics has been useful in calculating the absolute entropies of solids, liquids and gases at different temperatures. Moreover, this law is also useful to calculate entropy changes of a chemical or physical process. Let us calculate absolute entropy.

$$dS = \frac{dQ}{T}$$

$$dS = C_P \frac{dT}{T}$$

On integrating the above equation between temperature limits of 0 and T K, we get

$$S_T - S_0 = \int_0^T C_P \frac{dT}{T}$$

$$\text{or } S_T - S_0 = \int_0^T C_P d \ln T$$

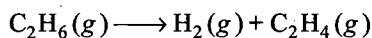
From third law of thermodynamics, $S_0 = 0$

$$\therefore S_T = \int_0^T C_P d \ln T$$

When entropy of one mole of a substance is expressed at 298 K and 1 atm pressure, it is called standard entropy of that substance. It is denoted by S° . The standard entropy change ΔS° for a chemical reaction can be calculated as

$$\begin{aligned} \Delta S^\circ &= \sum S^\circ_{(\text{products})} - \sum S^\circ_{(\text{reactants})} \\ &= [\text{Sum of the standard entropies of products}] - [\text{Sum of the standard entropies of reactants}] \end{aligned}$$

e.g., in the reaction:



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

$$= [S^\circ_{\text{H}_2} + S^\circ_{\text{C}_2\text{H}_4}] - [S^\circ_{\text{C}_2\text{H}_6}]$$

Standard molar entropies in J/K mol at 298 K

| Solids | Entropy | Solids | Entropy |
|--------------------------------|---------|-------------------------------|---------|
| C (graphite) | 5.7 | N ₂ | 191.6 |
| C (diamond) | 2.4 | O ₂ | 205.1 |
| Fe | 27.3 | CO ₂ | 213.7 |
| Pb | 64.8 | NO ₂ | 240.1 |
| Cu | 33.1 | N ₂ O ₄ | 304.3 |
| Al | 96.2 | NH ₃ | 192.3 |
| Fe ₂ O ₃ | 87.4 | CH ₄ | 186.2 |

| | | | |
|---|-------|----------------------------------|-------|
| CuSO ₄ · 5H ₂ O | 300.4 | Hg | 76.0 |
| C ₁₂ H ₂₂ O ₁₁ (sucrose) | 360.8 | H ₂ O | 69.9 |
| CaO | 39.8 | C ₂ H ₅ OH | 160.7 |
| CaCO ₃ (calcite) | 92.9 | C ₆ H ₆ | 173.3 |
| H ₂ | 130.7 | CH ₃ COOH | 159.8 |

Tephigraph

Graph of entropy of a substance against temperature is called tephigraph. In the following graph variation of entropy with temperature is represented:

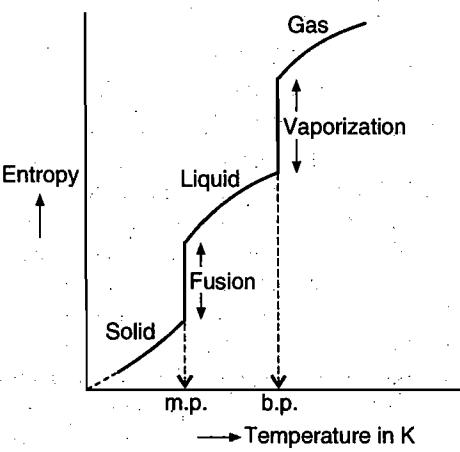
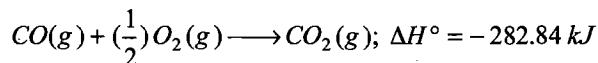


Fig. 7.24

From the graph it is clear that entropy of a substance increases with increase in temperature; there is sudden change in entropy at the stage of phase transformation.

Example 93. Calculate ΔG° for the following reaction:



Given,

$$S^\circ_{\text{CO}_2} = 213.8 \text{ J K}^{-1} \text{ mol}^{-1}, S^\circ_{\text{CO}(g)} = 197.9 \text{ J K}^{-1} \text{ mol}^{-1},$$

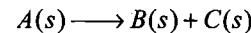
$$S^\circ_{\text{O}_2} = 205.0 \text{ J K}^{-1} \text{ mol}^{-1}.$$

$$\begin{aligned} \text{Solution: } \Delta S^\circ &= \sum S^\circ_{(\text{products})} - \sum S^\circ_{(\text{reactants})} \\ &= [S^\circ_{\text{CO}_2}] - [S^\circ_{\text{CO}} + \frac{1}{2} S^\circ_{\text{O}_2}] \\ &= 213.8 - [197.9 + \frac{1}{2} 205] \\ &= -86.6 \text{ J K}^{-1} \end{aligned}$$

According to Gibbs-Helmholtz equation,

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T \Delta S^\circ \\ &= -282.84 - 298 \times (-86.6 \times 10^{-3}) \\ &= -282.84 + 25.807 \\ &= -257.033 \text{ kJ} \end{aligned}$$

Example 94. For the reaction;



calculate the entropy change at 298 K and 1 atm if absolute entropies (in $\text{J K}^{-1} \text{ mol}^{-1}$) are:

$$A = 130, B = 203, C = 152$$

Solution:

$$\begin{aligned}\Delta S^\circ &= \Sigma S^\circ_{\text{(products)}} - \Sigma S^\circ_{\text{(reactants)}} \\ &= [S_B^\circ + S_C^\circ] - [S_A^\circ] \\ &= [203 + 152] - [130] \\ &= 225 \text{ J K}^{-1}\end{aligned}$$

7.32 CONVERSION OF HEAT INTO WORK—THE CARNOT CYCLE

Carnot, a French engineer, in 1824, employed merely theoretical and an imaginary reversible cycle known as Carnot cycle to demonstrate the maximum convertibility of heat into work.

The system consists of one mole of an ideal gas enclosed in a cylinder fitted with a piston which is subjected to a series of four successive operations. The four operations are:

- (i) Isothermal reversible expansion
- (ii) Adiabatic reversible expansion
- (iii) Isothermal reversible compression
- (iv) Adiabatic reversible compression

The four operations have been shown in Fig. 7.25.

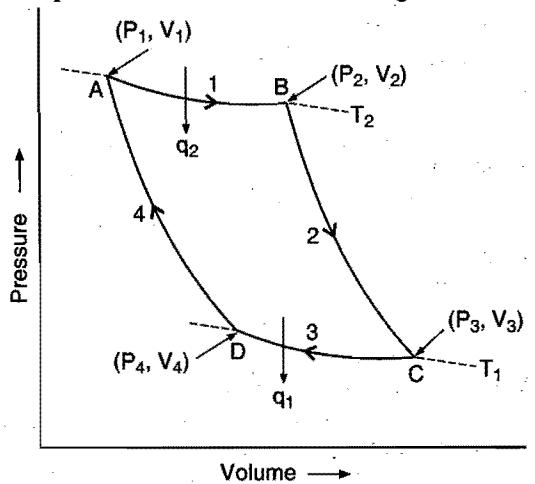


Fig. 7.25

First operation—Isothermal reversible expansion

The gas is allowed to expand reversibly and isothermally at the temperature T_2 through AB path. The volume V_1 (point A) increases to volume V_2 (point B). In this operation, let the heat absorbed by the system be q_2 (+ve) and the work done by the system on the surroundings be w_1 (-ve).

Since, the expansion is isothermal, $\Delta E = 0$. The heat absorbed, q_2 , should be equal to the work done by the system on the surroundings, i.e.,

$$q_2 = -w_1 = RT_2 \log_e \frac{V_2}{V_1} \quad \dots (\text{i})$$

Second operation—Adiabatic reversible expansion

The gas is now allowed to expand reversibly and adiabatically through BC path. The volume increases from V_2 (point B) to

volume V_3 (point C). In this operation, no heat is absorbed and thus, the work, w_2 , is done by the system at the expense of internal energy, i.e., the temperature of the system falls from temperature T_2 to temperature T_1 .

$$\Delta E = -w_2 = -C_V (T_2 - T_1) \quad \dots (\text{ii})$$

Third operation—Isothermal reversible compression

The gas at point C is subjected to reversible isothermal compression at temperature T_1 . The path followed is CD when the volume decreases from V_3 to V_4 (point D). In this operation work is done on the system and heat q_1 is given out by the system to surroundings.

$$-q_1 = w_3 = RT_1 \log_e \frac{V_4}{V_3} \quad \dots (\text{iii})$$

Fourth operation—Adiabatic reversible compression

Finally, the gas at point D is subjected to reversible adiabatic compression through the path DA at temperature T_1 . The volume changes from V_4 to V_1 , i.e., the original volume is restored. The temperature increases from T_1 to T_2 (original temperature). The work done increases the internal energy of the system as $q = 0$.

$$w_4 = C_V (T_2 - T_1) \quad \dots (\text{iv})$$

The net heat absorbed, q , by the ideal gas in the cycle is given by

$$\begin{aligned}q &= q_2 + (-q_1) = RT_2 \log_e \frac{V_2}{V_1} + RT_1 \log_e \frac{V_4}{V_3} \\ &= RT_2 \log_e \frac{V_2}{V_1} - RT_1 \log_e \frac{V_3}{V_4} \quad \dots (\text{v})\end{aligned}$$

According to the expression governing adiabatic changes,

$$\frac{T_2}{T_1} = \left(\frac{V_3}{V_2} \right)^{\gamma-1} \quad (\text{For adiabatic expansion})$$

$$\frac{T_1}{T_2} = \left(\frac{V_1}{V_4} \right)^{\gamma-1} \quad (\text{For adiabatic compression})$$

$$\text{or } \frac{V_3}{V_2} = \frac{V_4}{V_1}$$

$$\text{or } \frac{V_2}{V_1} = \frac{V_3}{V_4}$$

Substituting the value of $\frac{V_3}{V_2}$ in eq. (v),

$$\begin{aligned}q &= q_2 - q_1 = RT_2 \log_e \frac{V_2}{V_1} - RT_1 \log_e \frac{V_2}{V_1} \\ &= R(T_2 - T_1) \log_e \frac{V_2}{V_1} \quad \dots (\text{vi})\end{aligned}$$

Similarly, net work done by the gas is given by

$$w = -w_1 - w_2 + w_3 + w_4$$

$$\begin{aligned}
 &= RT_2 \log_e \frac{V_2}{V_1} - C_V (T_2 - T_1) \\
 &\quad + RT_1 \log_e \frac{V_4}{V_3} - C_V (T_2 - T_1) \\
 &= RT_2 \log_e \frac{V_2}{V_1} - RT_1 \log_e \frac{V_3}{V_4} \\
 &= RT_2 \log_e \frac{V_2}{V_1} - RT_1 \log_e \frac{V_2}{V_1} \\
 &= R(T_2 - T_1) \log_e \frac{V_2}{V_1} \quad \dots \text{(vii)}
 \end{aligned}$$

Thus, $q = w$. For cyclic process, the essential condition is that net work done is equal to heat absorbed. This condition is satisfied in a Carnot cycle.

Calculation of thermodynamic efficiency of Carnot engine

Total work done from eq. (vii),

$$w = R(T_2 - T_1) \log_e \frac{V_2}{V_1}$$

and the heat absorbed at temperature T_2 from eq. (i),

$$q_2 = RT_2 \log_e \frac{V_2}{V_1}$$

Dividing both equations,

$$\frac{w}{q_2} = \frac{T_2 - T_1}{T_2} = \text{Thermodynamic efficiency}$$

Thus, the larger the temperature difference between high and low temperature reservoirs, the more the heat converted into work by the heat engine.

Since, $\frac{T_2 - T_1}{T_2} < 1$, it follows that $w < q_2$. This means that only

a part of heat absorbed by the system at the higher temperature is transformed into work. The rest of the heat is given out to surroundings. The efficiency of the heat engine is always less than 1. This has led to the following enunciation of the second law of thermodynamics.

It is impossible to convert heat into work without compensation.

Example 95. Calculate the maximum efficiency of an engine operating between 100°C and 25°C .

Solution: Efficiency = $\frac{T_2 - T_1}{T_2}$

$$T_2 = 100 + 273 = 373 \text{ K}$$

$$T_1 = 25 + 273 = 298 \text{ K}$$

$$\text{Efficiency} = \frac{373 - 298}{373} = \frac{75}{373} = 0.20 = 20\%$$

Example 96. Heat supplied to a Carnot engine is 453.6 kcal. How much useful work can be done by the engine which works between 10°C and 100°C ?

Solution: $T_2 = 100 + 273 = 373 \text{ K}$; $T_1 = 10 + 273 = 283 \text{ K}$;

$$q_2 = 453.6 \times 4.184 = 1897.86 \text{ kJ}$$

We know that,

$$\begin{aligned}
 w &= q_2 \cdot \frac{T_2 - T_1}{T_2} \\
 &= 1897.86 \times \frac{(373 - 283)}{373} \\
 &= \frac{1897.86 \times 90}{373} = 457.92 \text{ kJ}
 \end{aligned}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

54. For which of the following reactions, the entropy change will be positive? [JEE (WB) 2008]

- (a) $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)$
- (b) $\text{HCl}(g) + \text{NH}_3(g) \rightleftharpoons \text{NH}_4\text{Cl}(s)$
- (c) $\text{NH}_4\text{NO}_3(s) \rightleftharpoons \text{N}_2\text{O}(g) + 2\text{H}_2\text{O}(g)$
- (d) $\text{MgO}(s) + \text{H}_2(g) \rightleftharpoons \text{Mg}(s) + \text{H}_2\text{O}(l)$

[Ans. (c)]

[Hint: $\Delta n_g = 3 - 0 = 3$,

Since $\Delta n_g > 0$, there will be increase in entropy change.]

55. If an endothermic reaction occurs spontaneously at constant temperature T and pressure P , then which of the following is true? [VITEEE 2008]

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

[Ans. (c)]

[Hint: $\Delta S = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$

$\Delta S > 0$ for spontaneous process.]

56. Which is the correct expression that relates changes of entropy with the change of pressure for an ideal gas at constant temperature, among the following? [PET (MP) 2008]

- (a) $\Delta S = nRT \ln \frac{P_2}{P_1}$
- (b) $\Delta S = T(P_2 - P_1)$
- (c) $\Delta S = nR \ln \left(\frac{P_1}{P_2} \right)$
- (d) $\Delta S = 2.303 nRT \ln \left(\frac{P_1}{P_2} \right)$

[Ans. (c)]

[Hint: From first law, $\Delta U = q - W$

$$0 = q - W \quad (\text{for isothermal process})$$

$$q = W = PdV$$

$$dS = \frac{q}{T} = \frac{PdV}{T}$$

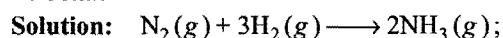
$$dS = nR \frac{dV}{V}$$

On integration, $\Delta S = nR \ln \left(\frac{V_2}{V_1} \right)$

$\Delta S = nR \ln \left(\frac{P_1}{P_2} \right)$. Since $P_1 V_1 = P_2 V_2$ according to Boyle's law.]

MISCELLANEOUS NUMERICAL EXAMPLES

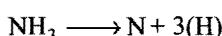
Example 1. Bond dissociation enthalpies of $H_2(g)$ and $N_2(g)$ are $436.0 \text{ kJ mol}^{-1}$ and $941.8 \text{ kJ mol}^{-1}$ and enthalpy of formation of $NH_3(g)$ is -46 kJ mol^{-1} . What is enthalpy of atomization of $NH_3(g)$? What is the average bond enthalpy of N—H bond?



$$\Delta H = -2 \times 46 \text{ kJ/mol}$$

$$\begin{aligned}\Delta H &= \Sigma(\text{BE})_R - \Sigma(\text{BE})_P \\ &= (941.8 + 3 \times 436) - (6x) = -2 \times 46 \\ &\quad (\text{Here, } x = \text{BE of N—H bonds})\end{aligned}$$

$$x = 390.3 \text{ kJ mol}^{-1}$$



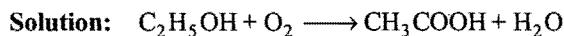
$$\text{Heat of atomization} = 3 \times 390.3 = 1170.9 \text{ kJ mol}^{-1}$$

Example 2. Ethanol was oxidised to acetic acid in a catalyst chamber at $18^\circ C$. Calculate the rate of removal of heat to maintain the reaction chamber at $18^\circ C$ with the feed rate of 30 kg per hour ethanol along with excess oxygen to the system at $18^\circ C$, given that a 42 mole per cent yield based on ethanol is obtained. Given that,

$$\Delta H_{f H_2O(l)} = -68.4 \text{ kcal mol}^{-1}$$

$$\Delta H_{f C_2H_5OH(l)} = -66 \text{ kcal mol}^{-1}$$

$$\Delta H_{f CH_3COOH(l)} = -118 \text{ kcal mol}^{-1}$$

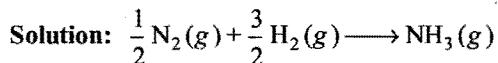
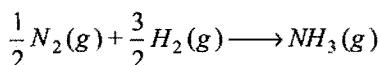


$$\Delta H = \Sigma(H_f)_P - \Sigma(H_f)_R = (-118 - 68.4) - (-66) = -120.4 \text{ kcal}$$

Yield is 42%. Thus, energy produced per hour will be

$$= \frac{120.4 \times 42 \times 30000}{100 \times 46} = 32979.13 \text{ kcal hour}^{-1}$$

Example 3. The standard heat of formation listed for gaseous NH_3 is -11.02 kcal/mol at 298 K . Given that at 298 K , the constant pressure heat capacities of gaseous N_2 , H_2 and NH_3 are respectively 6.96 , 6.89 , 8.38 cal/mol . Determine ΔH_{298K}° and ΔH_{773K}° for the reaction,



$$\begin{aligned}\Delta H_{298K} &= \Sigma(H_f)_P - \Sigma(H_f)_R = (-11.02 - 0) \\ &= -11.02 \text{ kcal mol}^{-1}\end{aligned}$$

$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_P$$

$$\frac{\Delta H_2 - (-11.02)}{773 - 298} = (8.38 - \frac{1}{2} \times 6.96 - \frac{3}{2} \times 6.89) \times 10^{-3}$$

$$\Delta H_2 = -13.6 \text{ kcal mol}^{-1}$$

Example 4. The heat of combustion of glycogen is about 476 kJ/mol of carbon. Assume that average rate of heat loss by an adult male is 150 watt . If we were to assume that all the heat comes from oxidation of glycogen, how many units of glycogen ($1 \text{ mole carbon per unit}$) must be oxidised per day to provide for this heat loss?

Solution: Total energy required in the day

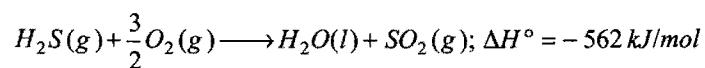
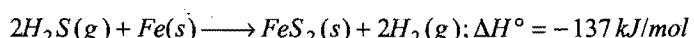
$$\begin{aligned}&= \frac{150 \times 24 \times 60 \times 60}{1000} \text{ kJ} \quad (1 \text{ watt} = \text{J sec}^{-1}) \\ &= 12960 \text{ kJ}\end{aligned}$$

$$\text{Units of glycogen required} = \frac{12960}{476} = 27.22 \text{ units}$$

Example 5. At $25^\circ C$, the following heat of formations are given :

| Compound | $SO_2(g)$ | $H_2O(l)$ |
|-----------------------------------|-----------|-----------|
| $\Delta H_f^\circ \text{ kJ/mol}$ | -296.81 | -285.83 |

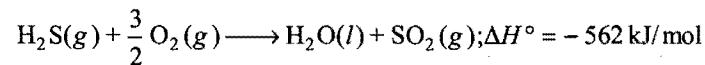
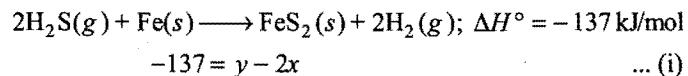
For the reactions at $25^\circ C$,



Calculate heat of formation of $H_2S(g)$ and $FeS_2(s)$ at $25^\circ C$.

Solution: Heat of formation of $H_2S = x \text{ kJ/mol}$

Heat of formation of $FeS_2 = y \text{ kJ/mol}$



$$-562 = -285.83 - 296.81 - x \quad \dots (ii)$$

$$\text{From eq. (ii), } x = -20.64 \text{ kJ mol}^{-1}$$

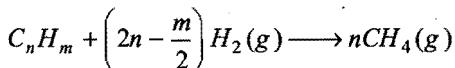
From eq. (i), we get

$$y = 2x - 137 = 2(-20.64) - 137 = -178.28 \text{ kJ mol}^{-1}$$

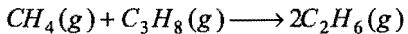
$$\Delta H_{f H_2S} = 20.64 \text{ kJ/mol}$$

$$\Delta H_{f FeS_2} = -178 \text{ kJ/mol}$$

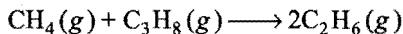
Example 6. The "heat of total cracking" of hydrocarbons ΔH_{TC} is defined as ΔH at 298.15 K and 101.325 kPa for the process below:



Given that, ΔH_{TC} is -65.2 kJ for C_2H_6 and -87.4 kJ for C_3H_8 , calculate ΔH for



Solution: ΔH_{TC} of $CH_4 = 0$



$$\Delta H = 2\Delta H_{TC}(C_2H_6) - \Delta H_{TC}(C_3H_8)$$

$$= 2(-65.2) - (-87.4) = -43\text{ kJ}$$

Example 7. A constant pressure calorimeter consists of an insulated beaker of mass 92 g made up of glass with heat capacity $0.75\text{ J K}^{-1}\text{ g}^{-1}$. The beaker contains 100 mL of 1 M HCl at 22.6°C to which 100 mL of 1 M $NaOH$ at 23.4°C is added. The final temperature after the reaction is complete at 29.3°C . What is ΔH per mole for this neutralization reaction? Assume that the heat capacities of all solutions are equal to that of same volumes of water.

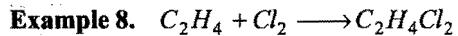
Solution: Initial average temperature of the acid and base

$$= \frac{22.6 + 23.4}{2} = 23.0^\circ\text{C}$$

$$\text{Rise in temperature} = (29.3 - 23.0) = 6.3^\circ\text{C}$$

$$\begin{aligned} \text{Total heat produced} &= (92 \times 0.75 + 200 \times 4.184) \times 6.3 \\ &= (905.8) \times 6.3 = 5706.54\text{ J} \end{aligned}$$

$$\begin{aligned} \text{Enthalpy of neutralization} &= -\frac{5706.54}{100} \times 1000 \times 1 \\ &= -57065.4\text{ J} = -57\text{ kJ} \end{aligned}$$



$$\Delta H = -270.6\text{ kJ mol}^{-1} K^{-1}; \Delta S = -139\text{ JK}^{-1}$$

(i) Is the reaction favoured by entropy, enthalpy both or none?

(ii) Find ΔG if $T = 300\text{ K}$.

[CBSE (Mains) 2005]

Solution: (i) Since, $\Delta H = -$ ve, exothermic process and is favoured, i.e., it will be spontaneous.

$$(ii) \quad \Delta G = \Delta H - T\Delta S$$

$$= -270.6 \times 1000 - 300 \times (-139)$$

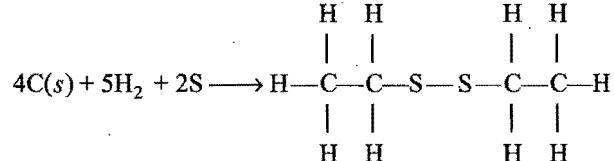
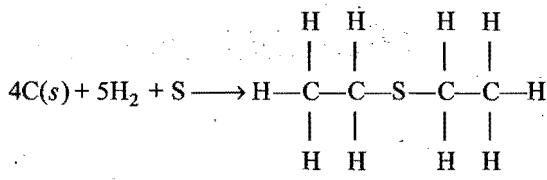
$$= -228900\text{ J}$$

$$= -228.9\text{ kJ}$$

Example 9. Find bond enthalpy of $S-S$ bond from the following data:



Solution:



$$\Delta H = \Sigma(\text{BE})_R - \Sigma(\text{BE})_P$$

(i) -147.2 = Heat of atomization of $4C, 10H, 1S$

$-$ BE of $10(C-H), 2(C-S), 2(C-C)$

(ii) -201.9 = Heat of atomization of $4C, 10H, 2S$

$-$ BE of $10(C-H), 2(C-S), 2(C-C), (S-S)$

Subtracting (i) from (ii),

$$\begin{aligned} -201.9 + 147.2 &= \text{Heat of atomization of } 1S - \text{BE of } (S-S) \\ &= 222.8\text{ kJ} - \text{BE of } (S-S) \end{aligned}$$

$$\text{BE of } (S-S) = 277.5\text{ kJ}$$

Example 10. A natural gas may be assumed to be a mixture of methane and ethane only. On complete combustion of 10 litre of gas at STP, the heat evolved was 474.6 kJ . Assuming $\Delta H_{comb} CH_4(g) = -894\text{ kJ mol}^{-1}$ and $\Delta H_{comb} C_2H_6 = -1500\text{ kJ}$. Calculate the percentage composition of the mixture by volume.

Solution:

$$x \text{ litre} \longrightarrow CH_4; \text{ mole of } CH_4 = x/22.4$$

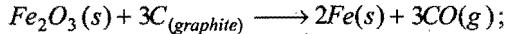
$$(10-x) \text{ litre} \longrightarrow C_2H_6; \text{ mole of } C_2H_6 = (10-x)/22.4$$

$$\text{Heat evolved} = \frac{x}{22.4} \times 894 + \frac{(10-x)}{22.4} \times 1500$$

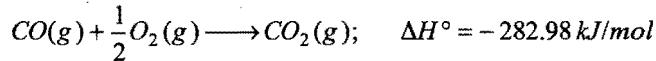
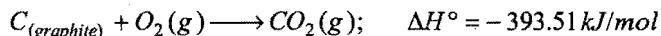
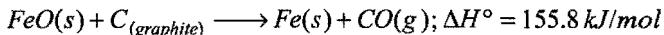
$$474.6 = \frac{x}{22.4} \times 894 + \frac{(10-x)}{22.4} \times 1500$$

$$x = 0.745, \quad \% CH_4 = 74.5\%$$

Example 11. From the data at 25°C :

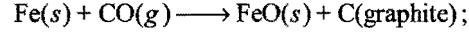


$$\Delta H^\circ = 492.6\text{ kJ/mol}$$

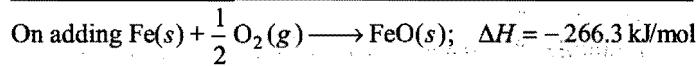
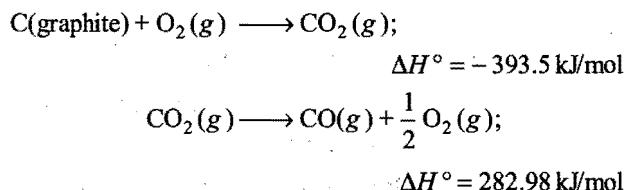


Calculate standard heat of formation of $FeO(s)$ and $Fe_2O_3(s)$.

Solution:



$$\Delta H^\circ = -158.88\text{ kJ/mol}$$



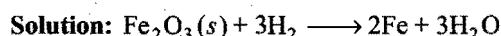
Similarly we may calculate heat of formation of Fe_2O_3 .

Example 12. Calculate, the ΔH at 85°C for the reaction:



The data are: $\Delta H_{298}^\circ = -33.29 \text{ kJ/mol}$ and

| Substance | $\text{Fe}_2\text{O}_3(s)$ | $\text{Fe}(s)$ | $\text{H}_2\text{O}(l)$ | $\text{H}_2(g)$ |
|-----------------------------|----------------------------|----------------|-------------------------|-----------------|
| $C_P^\circ \text{ J/K mol}$ | 103.8 | 25.1 | 75.3 | 28.8 |



$$\begin{aligned} \Delta C_P &= (C_P)_P - (C_P)_R \\ &= (2 \times 25.1 + 3 \times 75.3) - (103.8 + 3 \times 28.8) \\ &= 276.1 - 190.2 = 85.9 \text{ J} \end{aligned}$$

$$\frac{\Delta H_{T_2} - \Delta H_{T_1}}{T_2 - T_1} = \Delta C_P$$

$$\frac{\Delta H_{358} - (-33.29)}{358 - 298} = 85.9 \times 10^{-3}$$

$$\Delta H_{358} = -28.14 \text{ kJ/mol}$$

Example 13. The standard heats of formation at 298K for $\text{CCl}_4(g)$, $\text{H}_2\text{O}(g)$, $\text{CO}_2(g)$ and $\text{HCl}(g)$ are -25.5 , -57.8 , -94.1 and $-22.1 \text{ kcal mol}^{-1}$ respectively, calculate $\Delta H_{298\text{K}}^\circ$ for the reaction:



[BCECE (Mains) 2005]

Solution:

$\Delta H_{\text{reaction}} = \Sigma \text{Heat of formation of products}$

$- \Sigma \text{Heat of formation of reactants}$

$$\begin{aligned} &= [\Delta H_f(\text{CO}_2) + 4 \Delta H_f(\text{HCl})] - [\Delta H_f(\text{CCl}_4) + 2 \Delta H_f(\text{H}_2\text{O})] \\ &= [-94.1 + 4 \times (-22.1)] - [-25.5 + 2 \times (-57.8)] \\ &= -41.4 \text{ kcal} \end{aligned}$$

Example 14. Calculate Q , W , ΔE and ΔH for the isothermal reversible expansion of 1 mole of an ideal gas from an initial pressure of 1.0 bar to a final pressure of 0.1 bar at a constant temperature of 273K . (IIT 2000)

Solution: In isothermal process as temperature remains constant both ΔE and ΔH are zero.

$$\Delta E = 0; \quad \Delta H = 0$$

Applying first law of thermodynamics,

$$\Delta E = W + Q$$

$$0 = W + Q$$

$$\begin{aligned} \text{or} \quad Q &= -W = -2.303 nRT \log \left(\frac{P_1}{P_2} \right) \\ &= -2.303 \times 1 \times 8.314 \times 273 \log \left(\frac{1}{0.1} \right) \\ &= 5227.169 \text{ J} = 5.227 \text{ kJ} \end{aligned}$$

Example 15. A sample of argon at 1 atm pressure and 27°C expands reversibly and adiabatically from 1.25 dm^3 to 2.50 dm^3 . Calculate the enthalpy change in this process. $C_{v.m.}$ for argon is $12.48 \text{ J K}^{-1} \text{ mol}^{-1}$. (IIT 2000)

Solution: Number of moles of argon present in the sample

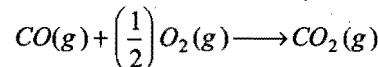
$$\frac{PV}{RT} = \frac{1.25 \times 1}{0.0821 \times 300} = 0.05075$$

For adiabatic expansion,

$$\begin{aligned} \frac{T_1}{T_2} &= \left(\frac{V_2}{V_1} \right)^{r-1} \\ \text{or} \quad \frac{300}{T_2} &= \left(\frac{2.50}{1.25} \right)^{1.66-1} \\ \text{or} \quad T_2 &= 188.55 \text{ K} \\ C_P &= C_V + R \\ &= 12.48 + 8.314 \\ &= 20.794 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

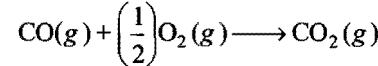
$$\begin{aligned} \Delta H &= n \times C_P \times \Delta T \\ &= 0.05075 \times 20.794 \times (300 - 188.55) \\ &= 117.6 \text{ J} \end{aligned}$$

Example 16. Show that the reaction,



at 300K is spontaneous and exothermic, when the standard entropy change is $-0.094 \text{ kJ mol}^{-1} \text{ K}^{-1}$. The standard Gibb's free energies of formation for CO_2 and CO are -394.4 and $-137.2 \text{ kJ mol}^{-1}$ respectively. (IIT 2000)

Solution: The given reaction is,



$$\begin{aligned} \Delta G^\circ (\text{for reaction}) &= G_{\text{CO}_2}^\circ - G_{\text{CO}}^\circ - \left(\frac{1}{2} \right) G_{\text{O}_2}^\circ \\ &= -394.4 - (-137.2) - 0 \\ &= -257.2 \text{ kJ mol}^{-1} \end{aligned}$$

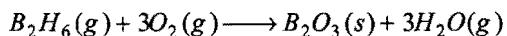
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$-257.2 = \Delta H^\circ - 298 \times (0.094)$$

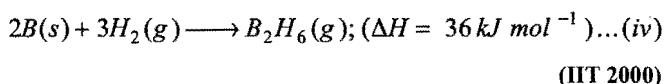
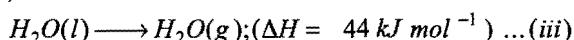
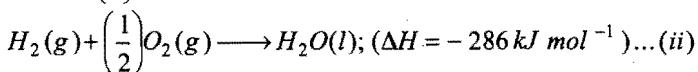
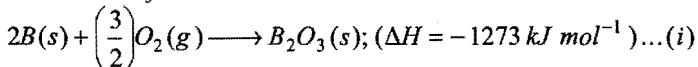
$$\text{or} \quad \Delta H^\circ = -288.2 \text{ kJ}$$

ΔG° is $-ve$, hence the process is spontaneous, and ΔH° is also $-ve$, hence the process is also exothermic.

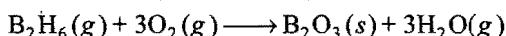
Example 17. Diborane is a potential rocket fuel which undergoes combustion according to the reaction,



From the following data, calculate the enthalpy change for the combustion of diborane:



Solution: The required equation,



can be obtained from

$$\begin{aligned} &\text{eq. (i)} + 3\text{eq. (ii)} + 3\text{eq. (iii)} - \text{eq. (iv)} \\ &= -1273 - 858 + 132 - 36 \\ &= -2035 \text{ kJ mol}^{-1} \end{aligned}$$

i.e., Enthalpy of combustion of diborane is $-2035 \text{ kJ mol}^{-1}$.

Example 18. An insulated container contains 1 mole of a liquid, molar volume 100 mL at 1 bar. When liquid is steadily passed to 100 bar, volume decreases to 99 mL. Find ΔH and ΔU for the process. [IIT 2004 (Memory based)]

Solution: From first law of thermodynamics:

$$\begin{aligned} \Delta U &= q + W \\ \Delta U &= q + P \Delta V = 0 + \{-100(99 - 100)\} \\ &= 100 \text{ bar mL} \\ \Delta H &= \Delta U + (P_2V_2 - P_1V_1) \\ &= 100 + (100 \times 99 - 1 \times 100) \\ &= 9900 \text{ bar mL} \end{aligned}$$

Example 19. In the following equilibrium:



when 5 moles of each are taken and temperature is kept at 298 K, the total pressure was found to be 20 bar.

Given: $\Delta G_f^\circ N_2O_4 = 100 \text{ kJ}$

$\Delta G_f^\circ NO_2 = 50 \text{ kJ}$

(i) Find ΔG of the reaction at 298 K.

(ii) Find the direction of the reaction.

[IIT 2004 (Memory based)]

Solution: The reaction is:



Since, number of moles of both N_2O_4 and NO_2 are same hence their partial pressure will also be same.

$$P_{N_2O_4} = P_{NO_2} = \frac{20}{2} = 10 \text{ bar}$$

$$Q_P = \frac{[P_{NO_2}]^2}{[P_{N_2O_4}]} = \frac{10^2}{10} = 10 \text{ bar}$$

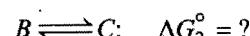
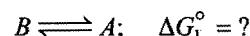
$$\Delta G_{\text{reaction}}^\circ = 2\Delta G_f^\circ NO_2 - \Delta G_f^\circ N_2O_4$$

$$= 2 \times 50 - 100 = 0$$

$$\begin{aligned} \text{We know that, } \Delta G &= \Delta G^\circ - 2.303 RT \log Q \\ &= 0 - 2.303 \times 8.314 \times 298 \log 10 \\ &= -5705 \text{ J} \end{aligned}$$

Since, ΔG is negative hence reaction will be spontaneous in forward direction.

Example 20. When 1-pentyne (*A*) is treated with 4*N* alcoholic KOH at 175°C, it is slowly converted into an equilibrium mixture of 1.3% of 1-pentyne (*A*), 95.2% 2-pentyne (*B*) and 3.5% of 1,2-pentadiene (*C*). The equilibrium was maintained at 175°C. Calculate ΔG° for the following equilibria:



From the calculated value of ΔG_1° and ΔG_2° indicate the order of stability of (*A*), (*B*) and (*C*). Write a reasonable reaction mechanism showing all intermediates leading to (*A*), (*B*) and (*C*). (IIT 2001)

Solution: Pentyne-1 \rightleftharpoons Pentyne-2 + 1, 2-pentadiene

$$\begin{array}{ccc} (A) & (B) & (C) \\ t_{\text{eq}} & 1.3 & 95.2 & 3.5 \end{array}$$

$$K_{\text{eq}} = \frac{[B][C]}{[A]} = \frac{95.2 \times 3.5}{1.3} = 256.31$$



$$K_1 = \frac{[A]}{[B]} = \frac{[C]}{K_{\text{eq}}} = \frac{3.5}{256.31} = 0.013$$

$$\Delta G_1^\circ = -2.303RT \log K_1$$

$$\begin{aligned} &= -2.303 \times 8.314 \times 448 \log 0.013 \\ &= 16178 \text{ J} = 16.178 \text{ kJ} \end{aligned}$$

for



$$K_2 = \frac{[C]}{[B]} = \frac{K_{\text{eq}}[A]}{[B]^2} = \frac{256.31 \times 1.3}{(95.2)^2} = 0.037$$

$$\Delta G_2^\circ = -2.303RT \log K_2$$

$$\begin{aligned} &= -2.303 \times 8.314 \times 448 \log 0.037 \\ &= 12282 \text{ J} = 12.282 \text{ kJ} \end{aligned}$$

Stability will lie in the order

$$B > C > A$$

Example 21. Two moles of a perfect gas undergo the following process:

(a) A reversible isobaric expansion from (1 atm 20 L) to (1 atm 40 L).

(b) A reversible isochoric change of state from (1 atm 40 L) to (0.5 atm 40 L).

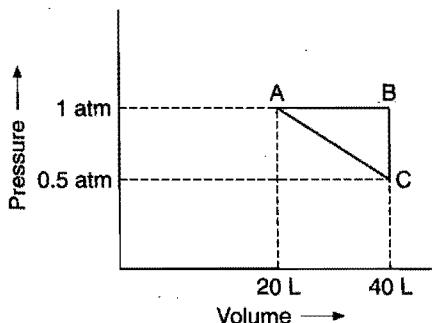
(c) A reversible isothermal compression from (0.5 atm 40 L) to (1 atm 20 L).

(i) Sketch with labels each of the process on the same P-V diagram.

(ii) Calculate the total work (W) and the total heat change (q) involved in the above process.

(iii) What will be the value of ΔU , ΔH and ΔS for the overall process? (IIT 2002)

Solution:



$AB \rightarrow$ Isobaric process

$BC \rightarrow$ Isochoric process

$CA \rightarrow$ Isothermal compression

$$\text{Total work} = W_{AB} + W_{BC} + W_{CA}$$

$$= -P \times \Delta V + 0 + 2.303 nRT \log\left(\frac{V_2}{V_1}\right)$$

$$= -1 \times 20 \times 101.3 + 0$$

$$+ 2.303 \times 2 \times 8.314 \times T \log\left(\frac{40}{20}\right) \quad \dots (1)$$

$$PV = nRT \text{ (At } A)$$

$$1 \times 20 = 2 \times 0.0821 \times T$$

$$T = \frac{20}{2 \times 0.0821} = 121.8 \text{ K}$$

From eq. (1),

$$\text{Total work} = -2026 + 2.303 \times 2 \times 8.314 \times 121.8 \log 2$$

$$= -622.06 \text{ J}$$

$$W = q = -622.06 \text{ J}$$

In cyclic process:

$$\Delta U = 0, \Delta H = 0 \text{ and } \Delta S = 0$$

SUMMARY AND IMPORTANT POINTS TO REMEMBER

1. Thermodynamics: It is the branch of science which deals with all changes in energy or transfer of energy that accompany physical and chemical processes. It is not concerned with the total energy of body but only with energy changes taking place. The laws of thermodynamics apply only to matter in bulk, i.e., to macroscopic system and not to individual atoms or molecules.

2. Terms used in thermodynamics:

(a) System, surroundings and boundary: A **system** is defined as a specified part of the universe which is under experimental investigation and the rest of the universe which can interact with the system is **surroundings**. Anything which separates system and surroundings is called **boundary**. It may be real or imaginary, conductor or non-conductor.

(b) Types of system: There are three types of system:

(i) Isolated system is one which has no interaction with its surroundings. The boundary is sealed and insulated. Neither matter nor energy can be exchanged with surroundings. **(ii) Closed system** is one which can exchange energy but not matter with surroundings. **(iii) Open system** is one which can exchange matter as well as energy with surroundings. A system is said to be **homogeneous** if it is made of one-phase only. A system is said to be **heterogeneous** when it consists of two or more phases.

(c) Thermodynamic properties: These are of two types: **(i) Intensive properties** are those which do not depend upon the quantity of matter present in the system such as pressure, temperature, specific heat, surface tension, viscosity, melting and

boiling points, etc. **(ii) Extensive properties** are those whose magnitude depends upon the quantity of matter present in the system such as volume, total energy, enthalpy, entropy, etc.

(d) State variables: The fundamental properties which determine the state of the system are termed **state variables**. The change in state property depends only upon the initial and final states of the system, i.e., do not depend on the path followed. Pressure, volume, temperature, internal energy, enthalpy, entropy, force, energy and number of moles are the state variables.

(e) Thermodynamic equilibrium: A system in which the fundamental properties do not undergo any change with time is said to be in thermodynamic equilibrium. Actually the system should be in thermal equilibrium, mechanical equilibrium and chemical equilibrium.

(f) Thermodynamic processes: When the system changes from one state to another, the operation is called a **process**. The various types of processes are:

(i) Isothermal: Temperature remains fixed, i.e., $dT = 0$. This is achieved by placing the system in a thermostat.

(ii) Adiabatic: When no exchange of heat occurs between the system and surroundings, i.e., the system is thermally isolated ($dq = 0$).

(iii) Isobaric: Pressure remains constant throughout the change, i.e., $dP = 0$.

(iv) Isochoric: Volume remains constant throughout the change, i.e., $dV = 0$.

(v) **Cyclic:** When a system undergoes a number of different processes and finally returns to initial state, $dE = 0$ and $dH = 0$

(vi) **Reversible:** A process which occurs infinitesimally slowly and at every small change it is virtually in a state of equilibrium. It takes infinite time.

(vii) **Irreversible:** When the process goes from initial to final state in single step in finite time. All natural processes are irreversible.

3. Nature of work and heat: Work is a mode of transfer of energy to or from a system with reference to surroundings. If an object is displaced through a distance dx against a constant force F , then the amount of work which has to be done is equal to $F \times dx$. The mechanical work or pressure volume work is equal to $P_{\text{ext}}(V_2 - V_1)$ or $P \times dV$. The work done on the system increases its energy while work done by the system decreases its energy. On this basis, the work done has the sign convention.

$$\text{Work done by the system} = -w$$

$$\text{Work done on the system} = +w$$

The unit of work is erg. It is very small. The bigger unit is joule or kilojoule.

$$1 \text{ joule} = 10^7 \text{ ergs}; 1 \text{ kJ (kilojoule)} = 1000 \text{ J}$$

Heat is the quantity of energy which flows between system and surroundings on account of temperature difference. It is equal to $m \times s \times \Delta t$ where m is the mass, s is the specific heat and Δt is the temperature difference. The sign convention for heat is:

$$\text{Heat gained by system} = +q$$

$$\text{Heat lost by system} = -q$$

The unit of heat is calorie (cal). Since, heat and work are correlated the SI unit of heat is joule.

$$1 \text{ joule} = 0.2390 \text{ cal}$$

$$1 \text{ calorie} = 4.184 \text{ J}$$

$$1 \text{ kcal} = 4.184 \text{ kJ}$$

$$1 \text{ litre-atm} = 101.3 \text{ J} = 1.013 \times 10^9 \text{ erg} = 24.206 \text{ cal}$$

4. Internal energy: Sum of all forms of energy that a system possesses is termed internal energy. It is denoted by E . It is an extensive property. It is also a state property.

$$E = E_{\text{translational}} + E_{\text{rotational}} + E_{\text{vibrational}} + E_{\text{bonding}} + E_{\text{electronic}} + \dots$$

The internal energy of a particular system is a definite quantity but it is impossible to determine its exact value. It is a state function. In thermodynamics, one is concerned only with energy change which occurs when the system moves from one state to another, i.e., $\Delta E = E_f - E_i$. ΔE is +ve if $E_f > E_i$ and negative if $E_f < E_i$. ΔE does not depend on the path by which final state is achieved. For a cyclic process, $\Delta E = 0$.

5. First law of thermodynamics: Energy can neither be created nor destroyed but it can be converted from one form to another.

Or

The energy of the universe is constant.

Or

Total energy of an isolated system remains constant, though it may change from one form to another.

When heat energy (q) is given to a system and work (w) is also done on it, its energy increases from E_1 to E_2 .

$$E_2 = E_1 + q + w \quad \text{or} \quad E_2 - E_1 = q + w \quad \text{or} \quad \Delta E = q + w$$

In case heat energy (q) is given to a system and work (w) is done by the system then

$$\Delta E = q + (-w) = q - w$$

6. Enthalpy or heat content: The quantity $E + PV$ is known as enthalpy or heat content. It is denoted by H . It represents the total energy stored in a system.

$$\Delta E = q - P(V_2 - V_1) \quad \text{or} \quad E_2 - E_1 = q - PV_2 + PV_1$$

$$\text{or} \quad (E_2 + P_2 V_2) - (E_1 + P_1 V_1) = q \quad \text{or} \quad H_2 - H_1 = q$$

$$\text{or} \quad \Delta H = q \quad \text{or} \quad \Delta E + P \Delta V = \Delta H = q_P$$

$$\text{when } V_2 = V_1, \text{ i.e., } \Delta V = 0, \Delta E = q_V$$

$$q_V + \Delta n RT = q_P \quad \text{in the case of gases}$$

where, Δn = total number of moles of products – total number

of moles of reactants

7. Heat capacity: It is the quantity of heat required to raise the temperature of the system by one degree.

$$\text{Heat capacity} = \frac{dq}{dT}$$

In the case of gases,

$$C_V \text{ (at constant volume)} = \left(\frac{\partial E}{\partial T} \right)_V$$

= Molar heat capacity at constant volume

$$\text{and } C_P \text{ (at constant pressure)} = \left(\frac{\partial H}{\partial T} \right)_P$$

= Molar heat capacity at constant pressure

$$C_P - C_V = R$$

8. Isothermal expansion of an ideal gas: The expansion in an ideal gas at constant temperature can be done reversibly or irreversibly.

w = Work done by gas in reversible expansion

$$= -2.303nRT \log \frac{V_2}{V_1} = -2.303nRT \log \frac{P_1}{P_2}$$

q = Heat absorbed from surroundings

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

w = Work done by gas in irreversible expansion

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

Maximum work is done in reversible isothermal expansion. In isothermal process, $\Delta E = 0$ and $\Delta H = 0$.

Adiabatic expansion of an ideal gas: q in the process is zero, hence $\Delta E = w$. Work is done by the gas during expansion at the expense of internal energy. In expansion, ΔE decreases while in compression ΔE increases.

$$\Delta E = w = C_V \times \Delta T$$

The value of ΔT depends upon the process whether carried reversibly or irreversibly. The following relationships are followed by an ideal gas under adiabatic conditions:

$$PV^\gamma = \text{constant} \quad \left(\gamma = \frac{C_p}{C_v} \right)$$

$$\left(\frac{T_1}{T_2} \right)^\gamma = \left(\frac{P_1}{P_2} \right)^{\gamma-1} = \left(\frac{P_2}{P_1} \right)^{1-\gamma}$$

9. Joule-Thomson effect: The phenomenon of producing lowering of temperature when a gas is made to expand adiabatically from a region of high pressure into a region of low pressure, is known as Joule-Thomson effect. This effect is observed below the inversion temperature of a gas. The inversion temperature of a gas depends upon the van der Waals' constants of a gas. It is expressed in terms of van der Waals' constants 'a' and 'b' as:

$$T_i = \frac{2a}{Rb}$$

10. Thermochemistry: It is concerned with heat changes accompanying physical and chemical transformations. It is also termed as chemical energetics. It is based on the first law of thermodynamics. If E_1 and E_2 represent total energies associated with reactants and products respectively, three cases may arise:

Case I: $E_1 = E_2$. Neither heat is evolved nor absorbed. Such reactions are very rare.

Case II: $E_1 > E_2$. The difference ($E_1 - E_2$) of energy will be evolved, i.e., heat is evolved.

Case III: $E_1 < E_2$. The difference ($E_2 - E_1$) of energy will be absorbed, i.e., heat is absorbed.

11. Exothermic reactions: Reactions which occur with evolution of heat

$$H_{\text{products}} < H_{\text{reactants}}, \quad \text{i.e.,} \quad \Delta H = -\text{ve}$$

Endothermic reactions: Reactions which occur with absorption of heat

$$H_{\text{products}} > H_{\text{reactants}}, \quad \text{i.e.,} \quad \Delta H = +\text{ve}$$

| Sign conventions | q | ΔE | ΔH |
|------------------|-----|------------|------------|
| Exothermic | (-) | (-) | (-) |
| Endothermic | (+) | (+) | (+) |

12. Heat of reaction or enthalpy of reaction: The amount of heat evolved or absorbed when quantities of the substances indicated by chemical equation have completely reacted, it is represented as ΔH .

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

The factors which affect the magnitude of heat of reaction are :

- (i) Physical state of reactants and products
- (ii) Allotropic forms of the elements
- (iii) Reaction carried at constant pressure or constant volume ($\Delta H = \Delta E + \Delta nRT$)
- (iv) Enthalpy of solution
- (v) Temperature at which the reaction is carried out.

13. Heat of formation or enthalpy of formation: It is the amount of heat evolved or absorbed when one gram mole of substance is directly obtained from its constituent elements. It is represented as ΔH_f .

If all the substances of the chemical reaction are in their standard states (i.e., at 25°C or 298K and one atmospheric pressure), the heat of reaction or formation is called standard heat of reaction or formation respectively. These are denoted as ΔH° or ΔH_f° respectively. The enthalpies of free elements at standard conditions are taken arbitrary as zero.

The compounds which have positive enthalpies of formation are called endothermic compounds (less stable) and which have negative enthalpies of formation are called exothermic compounds (stable).

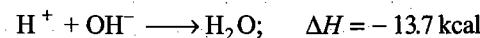
14. Heat of combustion or enthalpy of combustion: It is the amount of heat evolved when one mole of the substance is completely oxidised. It has a number of applications:

- (i) Determination of calorific values of foods and fuels.
- (ii) Enthalpy of formation can be determined by application of Hess's law.
- (iii) Structural problems can be evaluated.

15. Enthalpy of hydrogenation: The enthalpy change associated when one mole of an unsaturated organic compound is fully hydrogenated.

16. Enthalpy of solution: The amount of heat evolved or absorbed when one mole of the substance is dissolved in excess of water so that further dilution does not bring any heat change.

17. Enthalpy or heat of neutralisation: The amount of heat evolved when one gram equivalent of an acid is neutralised by one gram equivalent of a base in dilute solution. Heat of neutralisation of a strong acid against a strong base is always constant, i.e., 13.7 kcal or 57.1 kJ . It is due to common reaction between H^+ and OH^- ions. The heat of formation of water from these ions is 13.7 kcal .



In the case of weak acids and weak bases, the heat of neutralisation is always less than 13.7 kcal because some of the evolved heat energy is utilised in bringing about complete ionisation of acid or base in solution.

18. Enthalpy of fusion: Heat absorbed in converting one mole of solid into liquid at its melting point.

19. Enthalpy of vaporisation: Heat absorbed in converting one mole of a liquid into its vapours at its boiling point.

Enthalpy of sublimation: Heat absorbed in converting one mole of solid directly into its vapour.

20. Laws of thermochemistry:

(i) Lavoisier and Laplace law: The heat which is required to break a compound into its elements is equal to the heat evolved during its formation from its elements.

$$\Delta H_{\text{decomposition}} = -\Delta H_f$$

(ii) **Hess's law (the law of constant heat summation):** If a chemical reaction can be made to take place in a number of ways in one or in several steps, the total change is always the same, i.e., heat change depends upon the initial and final stages only and independent of intermediate steps. The thermochemical equations can be added, subtracted or multiplied by a number to obtain a desired equation.

21. Bond energy: The energy required to break one mole of bond of a particular type is termed bond dissociation energy. It depends upon the nature of bond and also the molecule in which the bond is present. The bond energies can be used for determining heats of reactions.

$$\begin{aligned} \text{[Heat of reaction} &= \text{Sum of bond energies of reactants} \\ &\quad - \text{Sum of bond energies of products]}\end{aligned}$$

The bond energies can also be used for determining resonance energy.

$$\begin{aligned} \text{Resonance energy} &= \text{Observed heat of formation} \\ &\quad - \text{Calculated heat of formation}\end{aligned}$$

22. Experimental determination of heat of reaction: The apparatus used is called calorimeter. Two of the common types of calorimeters are: (i) Water calorimeter (ii) Bomb-calorimeter. The principle of measurement is that heat given out is equal to heat taken, i.e.,

$$Q = (W + m) \times s \times (T_2 - T_1)$$

where, W = Water equivalent of the calorimeter, m = mass of the liquid, s = its sp. heat, T_2 = final temperature and T_1 = initial temperature.

23. Spontaneous process: A process which proceeds of its own accord without any outside help is termed spontaneous process. All natural processes proceed spontaneously and are thermodynamically irreversible.

Driving force: It is the force which makes the process to occur by itself. It is the resultant of two basic tendencies:

- (i) Tendency to attain a state of minimum energy.
- (ii) Tendency to attain a state of maximum randomness.

The disorder or randomness in a system is measured in terms of a thermodynamic property known as **entropy**. The absolute

value of entropy cannot be determined. The change in entropy is denoted by ΔS .

$$\Delta S = \frac{q_{\text{reversible}}}{T}$$

where, q is the heat supplied at temperature T .

$\Delta S = +$ indicates increase in randomness whereas, $\Delta S = -$ indicates the decrease in randomness.

$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$

24. Free energy: Free energy change, ΔG , was introduced by Gibbs. The Gibbs-Helmholtz equation is:

$$\Delta G = \Delta H - T \Delta S \quad \text{or} \quad G = H - TS$$

and

$$\Delta G = G_{\text{products}} - G_{\text{reactants}}$$

where, G is known as free energy. This is the maximum energy available to a system during a process which can be converted into useful work.

Negative value of ΔG indicates that the process is spontaneous. Zero value means that there is a state of equilibrium.

25. Second law of thermodynamics: It is impossible to construct a machine that is able to convey heat by a cyclic process from a colder to a hotter body unless work is done on the machine by some outside agency.

Or

Work can always be converted into heat but the conversion of heat into work does not take place under all conditions.

26. Carnot cycle: It demonstrates the maximum convertibility of heat into work in a theoretical and an imaginary cycle.

$$\text{Thermodynamic efficiency} = \frac{W}{q_2} = \frac{T_2 - T_1}{T_2}$$

The efficiency of a heat engine is always less than 1.

27. Third law of thermodynamics: The entropy of all pure crystals is zero at the absolute zero of temperature.

Questions

1. Matrix-Matching Problems (For IIT Aspirants):

[A] Match the List-I with List-II:

| List-I | List-II |
|---|---|
| (a) $\Delta S_{\text{system}} > 0$ (Isolated system) | (p) Spontaneous |
| (b) $\Delta G < 0$ | (q) Non-spontaneous photochemical reaction |
| (c) $\Delta S_{\text{Total}} = 0$ | (r) Equilibrium |
| (d) $(\Delta G)_{TP} > 0$ | (s) Non-spontaneous |

[B] Match the Column-I with Column-II:

| Column-I | Column-II |
|--|--|
| (a) Isothermal process (reversible) | (p) $W = 2.303nRT \log \left(\frac{P_1}{P_2} \right)$ |
| (b) Adiabatic process | (q) $PV^\gamma = \text{constant}$ |
| (c) $W = \frac{nR}{r-1} (T_2 - T_1)$ | (r) $W = 2.303nRT \log \left(\frac{V_2}{V_1} \right)$ |
| (d) Irreversible isothermal process | (s) $W = -P_{\text{ext}} (V_2 - V_1)$ |

[C] Match the physical properties in List-I with their relations in List-II:

| List-I (Quantity) | List-II (Relation) |
|-----------------------------|--|
| (a) ΔG | (p) $-nFE$ or $-nFE^\circ$ |
| (b) ΔG° | (q) $\Delta H - T \Delta S$ |
| (c) W or W_{max} | (r) $-RT \log_e K$ |
| (d) ΔS° | (s) $2.303nR \log_{10} \left(\frac{V_2}{V_1} \right)$ |

[D] Match the Column-I with Column-II:

| Column-I (Gas) | Column-II (Thermodynamic property) |
|---|---------------------------------------|
| (a) O ₂ | (p) $\gamma = 1.4$ |
| (b) N ₂ | (q) $C_P = \frac{7}{2} R$ |
| (c) CO ₂ , CH ₄ | (r) $\frac{23}{6} R$ |
| (d) 1 mol O ₂ + 2 mol O ₃ | (s) $\gamma = 1.33$ |

Here: C_P = Heat capacity at constant pressure

$$\gamma = C_P/C_V$$

[E] Match the reactions in Column-I with relations of Column - II:

| Column-I (Reaction) | Column-II (Relation) |
|---|--|
| (a) H ₂ (g) + Cl ₂ (g) → 2HCl(g) | (p) $\Delta H = \Delta U + RT$ |
| (b) N ₂ (g) + O ₂ (g) ⇌ 2NO(g) | (q) $\Delta H = \Delta U$ |
| (c) H ₂ (g) + I ₂ (g) ⇌ 2HI(g) | (r) $\Delta H = \Delta U - 2RT$ |
| (d) N ₂ (g) + 3H ₂ (g) ⇌ 2NH ₃ (g) | (s) Forward shift by increasing pressure |

[F] Match the processes of Column-I with entropy or enthalpy changes in Column-II:

| Column-I | Column-II |
|---|--------------------|
| (a) N ₂ (g) + O ₂ (g) → 2NO(g) | (p) $\Delta S = 0$ |
| (b) 2KI(aq.) + HgI ₂ (aq.) → K ₂ [HgI ₄](aq.) | (q) $\Delta S < 0$ |
| (c) PCl ₃ (g) + Cl ₂ (g) → PCl ₅ (g) | (r) $\Delta H > 0$ |
| (d) NH ₃ (g) + HCl(g) → NH ₄ Cl(s) | (s) $\Delta H < 0$ |

[G] Match the List-I with List-II:

| List-I (Reaction) | List-II (Process) |
|---|----------------------------------|
| (a) C(s) + $\frac{1}{2}$ O ₂ (g) → CO(g) | (p) Combustion |
| (b) CO(g) + $\frac{1}{2}$ O ₂ (g) → CO ₂ (g) | (q) Neutralization |
| (c) NaOH(aq.) + HCl(aq.) → NaCl(aq.) + H ₂ O | (r) Process of formation |
| (d) H ₂ (g) + $\frac{1}{2}$ O ₂ (g) → H ₂ O(l) | (s) Reaction of apollo fuel cell |

[H] Match the relations of Column-I with their names in Column-II:

| Column-I | Column-II |
|---|---|
| (a) $\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_P$ | (p) Trouton equation |
| (b) $\frac{\Delta U_2 - \Delta U_1}{T_2 - T_1} = \Delta C_V$ | (q) Effect of temperature on the heat of reaction |
| (c) $\frac{\Delta H_{\text{fusion}}}{T_{\text{mp}}} = \Delta S_{\text{fusion}}$ | (r) Kirchhoff's equation |
| (d) $\lim_{T \rightarrow 0 \text{ K}} S \rightarrow 0$ | (s) Third law of thermodynamics |

[I] Match the Column-I with Column-II:

| Column-I | Column-II |
|--|---------------------------------------|
| (a) Amount of heat required to raise the temperature of 1 mol substance by 1°C | (p) Specific heat \times molar mass |
| (b) $\frac{\Delta H}{\Delta T}$ or $\frac{\Delta U}{\Delta T}$ | (q) Heat capacity = C, C_p or C_v |
| (c) Heat evolved in the combustion of 1 g of a substance | (r) Electron gain enthalpy |
| (d) Heat evolved when an extra electron is added to valence shell of an isolated gaseous atom | (s) Calorific value |

[J] Match the Column-I with Column-II :

| Column-I | Column-II |
|--|---|
| (a) $\Delta H = + \text{ve}, \Delta S = + \text{ve}$ | (p) Spontaneous at all temperature |
| (b) $\Delta H = - \text{ve}, \Delta S = + \text{ve}$ | (q) Non-spontaneous at all temperature |
| (c) $\Delta H = + \text{ve}, \Delta S = - \text{ve}$ | (r) Non-spontaneous at high temperature |
| (d) $\Delta H = - \text{ve}, \Delta S = - \text{ve}$ | (s) Spontaneous at high temperature |

Answers

1. [A] (a—p); (b—p, q); (c—r); (d—s)
- [B] (a—p, r); (b—q); (c—q); (d—s)
- [C] (a—p, q); (b—p, r); (c—p); (d—s)
- [D] (a—p, q); (b—p, q); (c—s); (d—r)
- [E] (a—q); (b—q); (c—p); (d—r, s)
- [F] (a—p, r); (b—q, s); (c—q, r); (d—q, s)

- [G] (a—p, r); (b—p); (c—q); (d—p, r, s)
- [H] (a—q, r); (b—q, r); (c—p); (d—s)
- [I] (a—p, q); (b—p, q); (c—s); (d—r)
- [J] (a—s); (b—p); (c—q); (d—r)

● PRACTICE PROBLEMS ●

1. Write 'yes' if heat, work or matter are able to cross the boundary of the corresponding system and 'no' if passage is forbidden:

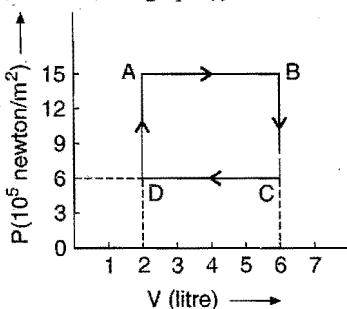
| Property | Open system | Close system | Isolated system | Adiabatic system |
|----------|-------------|--------------|-----------------|------------------|
| Heat | Yes/No | Yes/No | Yes/No | Yes/No |
| Work | Yes/No | Yes/No | Yes/No | Yes/No |
| Matter | Yes/No | Yes/No | Yes/No | Yes/No |

2. Which of the following are state functions?

- (i) Q (ii) W (iii) $Q + W$ (iv) $Q - W$ (v) Q_V (vi) Q_P
- (vii) $\frac{Q}{W}$ (viii) $\frac{Q}{T}$ (ix) $\frac{\Delta H}{T}$ (x) $E + PV$ (xi) $E - PV$

[Ans. (iv), (v), (vi), (viii), (ix), (x).]

3. In the adjoining diagram, the P - V graph of an ideal gas is shown. Find out from the graph (i) Work done in taking the gas



from the state $A \rightarrow B$ (ii) Work done in taking the gas from $B \rightarrow C$ (iii) Work done in a complete cycle. ($1 \text{ litre} = 10^{-3} \text{ m}^3$)

[Ans. (i) $-60 \times 10^2 \text{ J}$ (ii) zero (iii) $36 \times 10^2 \text{ J}$, i.e., net work is done by the gas.]

4. A sample of a gas contracts 200 cm^3 by an average of 0.5 atmosphere while 8.5 J heat flows out into the surroundings. What is the change in energy of the system?

(1 litre-atm = 101.3 J)

[Ans. Energy of the system increases by 1.63 J]

5. Calculate the pressure-volume work done by the system when the gas expands from 1.0 litre to 2.0 litre against a constant external pressure of 10 atmospheres. Express the answer in calorie and joule.

[Ans. -10 litre-atm , -242.2 cal , -1013.28 J]

6. A sample of a gas in a cylinder contracts by 7.5 litre at a constant pressure of 5.0 atmosphere. How much work is done on the gas by the surroundings?

[Ans. 37.5 litre-atm or 3801.75 J]

7. A sample of a gas expands from 200 cm^3 to 500 cm^3 against an average pressure of 750 torr while 1.5 J heat flows into the system. What is the change in energy of the system? (1 litre-atm = 101.3 J)

[Ans. Energy of the system is decreased by 28.5 J ; $\Delta E = -28.5 \text{ J}$]

8. Calculate the work done when 65.38 g of zinc dissolves in hydrochloric acid in an open beaker at 300 K. (At. mass of Zn = 65.38)

- [Ans. - 2494.2 J, i.e., work is done by the system]
9. 6 moles of an ideal gas expand isothermally and reversibly from a volume of 1 dm^3 to a volume of 10 dm^3 at 27°C . What is the maximum work done? Express your answer in joule.
 [Ans. - 34464.8 J, work is done by the system]
10. 1 mole of an ideal gas at 25°C is allowed to expand reversibly at constant temperature from a volume of 10 litre to 20 litre. Calculate the work done by the gas in joule and calorie.
 [Ans. - 1717.46 J or -411 cal, i.e., work is done by the gas]
11. Find the work done when 1 mole of the gas is expanded reversibly and isothermally from 5 atm to 1 atm at 25°C .
 [Ans. - 3984 J]
 [Hint: Use $w = -2.303 nRT \log \frac{P_1}{P_2}$]
12. How much energy is absorbed by 10 moles of an ideal gas if it expands from an initial pressure of 8 atmosphere to 4 atmosphere at a constant temperature of 27°C ? ($R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$)
 [Ans. $1.728 \times 10^4 \text{ J}$]
 [Hint: In isothermal process, $\Delta E = 0$, so q (heat absorbed) = $-w$. Thus, apply the equation $q = 2.303nRT \log \frac{P_1}{P_2}$]
13. A given mass of a gas at 0°C is compressed reversibly and adiabatically to a pressure 20 times the initial value. Calculate the final temperature of the gas. $\left[\frac{C_P}{C_V} = 1.42 \right]$
 [Ans. $T_2 = 662.2 \text{ K}$]
 [Hint: Apply the formula $\left(\frac{T_1}{T_2} \right)^\gamma = \left(\frac{P_2}{P_1} \right)^{1-\gamma}$]
14. 3 moles of hydrogen are compressed isothermally and reversibly from 60 dm^3 to 20 dm^3 and 8.22 kJ of work is done on it. Assuming ideal behaviour, calculate the temperature of the gas.
 [Ans. 300 K]
15. To what pressure must a certain ideal gas ($\gamma = 1.4$) at 373 K and 1 atmospheric pressure be compressed adiabatically in order to raise its temperature to 773 K?
 [Ans. 7.89 atm]
16. 1 mole of an ideal gas ($C_V = 12.55 \text{ J K}^{-1} \text{ mol}^{-1}$) at 300 K is compressed adiabatically and reversibly to one-fourth of its original volume. What is the final temperature of the gas?
 [Ans. 752 K]
17. Calculate q , w , ΔE and ΔH for the reversible isothermal expansion of 1 mole of ideal gas at 27°C from a volume of 10 dm^3 to a volume of 20 dm^3 .
 [Ans. $q = -w = 1729 \text{ J}$]
18. Calculate the internal energy change for the process in which 1.0 kcal of heat is added to 1.2 litre of O_2 gas in a cylinder at constant pressure of 1.0 atm and the volume changes to 1.5 litre.
 [Ans. 0.993 kcal]
19. Calculate ΔE and ΔH when 10 dm^3 of helium at NTP is heated in a cylinder to 100°C , assuming that the gas behaves ideally. ($C_V = 3/2R$)
 [Ans. $\Delta E = 556.74 \text{ J}$
 $\Delta H = 927.9 \text{ J}$]
 [Hint: $\Delta E = n \cdot C_V \cdot \Delta T$ and $\Delta H = n \cdot C_P \cdot \Delta T$
 $= \frac{10}{22.4} \times \frac{3}{2} \times 8.314 \times 100 = \frac{10}{22.4} \times \frac{5}{2} \times 8.314 \times 100$
 $= 556.74 \text{ J} = 927.9 \text{ J}]$
20. For the conversion of 1 mole of $\text{SO}_2(g)$ into $\text{SO}_3(g)$ the enthalpy of reaction at constant volume, ΔE , at 298 K is -97.027 kJ. Calculate the enthalpy of reaction, ΔH , at constant pressure.
 [Ans. $\Delta H = -98.267 \text{ kJ}$]
 [Hint: Use the reaction,
 $\text{SO}_2(g) + \frac{1}{2} \text{O}_2(g) \longrightarrow \text{SO}_3(g)$, $\Delta n = 1 - \frac{3}{2} = -\frac{1}{2}$]
21. The heat liberated on complete combustion of 7.8 g benzene is 327 kJ. This heat has been measured at constant volume and at 27°C . Calculate the heat of combustion of benzene at constant pressure. ($R = 8.3 \text{ JK}^{-1} \text{ mol}^{-1}$) (IIT 1996)
 [Ans. -3273.7 kJ mol $^{-1}$]
22. 1 mole of naphthalene (C_{10}H_8) was burnt in oxygen gas at 25°C at constant volume. The heat evolved was found to be 5138.8 kJ. Calculate the heat of reaction at constant pressure. ($R = 8.3 \text{ JK}^{-1} \text{ mol}^{-1}$)
 [Ans. 5143.8 kJ]
 [Hint: Water is present in liquid state at 25°C and naphthalene in solid state.]
23. The enthalpy of formation of methane at constant pressure and 300 K is -75.83 kJ. What will be the heat of formation at constant volume? ($R = 8.3 \text{ JK}^{-1} \text{ mol}^{-1}$)
 [Ans. -73.34 kJ]
24. The heat change for the reaction,
 $\text{N}_2(g) + 3\text{H}_2(g) \longrightarrow 2\text{NH}_3(g)$
 is -92.2 kJ. Calculate the heat of formation of ammonia.
 [Ans. -46.1 kJ mol $^{-1}$]
25. ΔH° for the reaction,
 $4\text{S}(s) + 6\text{O}_2(g) \longrightarrow 4\text{SO}_3(g)$
 is -1583.2 kJ. Calculate ΔH_f° of sulphur trioxide.
 [Ans. -395.8 kJ]
26. Calculate the heat change in the reaction,
 $4\text{NH}_3(g) + 3\text{O}_2(g) \longrightarrow 2\text{N}_2(g) + 6\text{H}_2\text{O}(l)$
 at 298 K given that heats of formation at 298 K for $\text{NH}_3(g)$ and $\text{H}_2\text{O}(l)$ are -46.0 and -286.0 kJ mol $^{-1}$ respectively.
 [Ans. $\Delta H^\circ = -1532 \text{ kJ}$]
27. Calculate the heat of combustion of 1 mole of $\text{C}_2\text{H}_4(g)$ to form $\text{CO}_2(g)$ and $\text{H}_2\text{O}(g)$ at 398 K and 1 atmosphere, given that the heats of formation of $\text{CO}_2(g)$, $\text{H}_2\text{O}(g)$ and $\text{C}_2\text{H}_4(g)$ are -94.1, -57.8 and +12.5 kcal mol $^{-1}$ respectively.
 [Ans. -316.3 kcal]

28. The heats of combustion of $\text{CH}_4(g)$ and $\text{C}_2\text{H}_6(g)$ are -890.3 and $-1560 \text{ kJ mol}^{-1}$ respectively. Which has higher calorific value?

[Ans. Methane has higher calorific value.]

29. The heat of combustion of butane is 2880 kJ mol^{-1} . What is the heat liberated by burning 1 kg of butane in excess of oxygen supply?

[Ans. 49655 kJ]

30. The heat of formation of $\text{CH}_4(g)$, $\text{C}_2\text{H}_6(g)$ and $\text{C}_4\text{H}_{10}(g)$ are -74.8 , -84.7 and $-126.1 \text{ kJ mol}^{-1}$ respectively. Arrange them in order of their efficiency as fuel per gram. Heats of formation of $\text{CO}_2(g)$ and $\text{H}_2\text{O}(l)$ are -393.5 and $-285.8 \text{ kJ mol}^{-1}$ respectively.

[Ans. $\text{CH}_4 > \text{C}_2\text{H}_6 > \text{C}_4\text{H}_{10}$]

[Hint: First determine heat of combustion in each case and then find the calorific value.]

31. The heat of combustion of carbon to $\text{CO}_2(g)$ is $-393.5 \text{ kJ mol}^{-1}$. Calculate the heat released upon formation of 35.2 g of $\text{CO}_2(g)$ from carbon and oxygen gas.

[Ans. -315 kJ]

32. Calculate ΔH_f° of $\text{C}_6\text{H}_{12}\text{O}_6(s)$ from the following data:

$$\Delta H_{\text{comb}} \text{ of } \text{C}_6\text{H}_{12}\text{O}_6(s) = -2816 \text{ kJ mol}^{-1}, \Delta H_f^\circ \text{ of } \text{CO}_2(g) = -393.5 \text{ kJ mol}^{-1} \text{ and } \Delta H_{f(H_2O)}^\circ = -285.9 \text{ kJ mol}^{-1}.$$

[Ans. $-1260 \text{ kJ mol}^{-1}$]

33. Calculate the amount of heat released when:

(i) 100 mL of 0.2 M HCl solution is mixed with 50 mL of 0.2 M KOH.

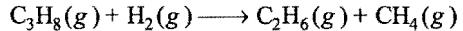
(ii) 200 mL of 0.1 M H_2SO_4 is mixed with 200 mL of 0.2 M KOH solution.

[Ans. (i) 0.57 kJ (ii) 2.18 kJ]

34. When 100 mL each of HCl and NaOH solutions are mixed, 5.71 kJ of heat was evolved. What is the molarity of two solutions? The heat of neutralisation of HCl is 57.1 kJ .

[Ans. 1 M]

35. Determine the enthalpy of the reaction,



at 25°C , using the given heat of combustion values under standard conditions.

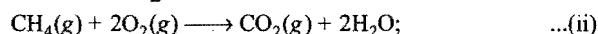
| Compound | $\text{H}_2(g)$ | $\text{CH}_4(g)$ | $\text{C}_2\text{H}_6(g)$ | C (graphite) |
|---------------------------------------|-----------------|------------------|---------------------------|--------------|
| $\Delta H^\circ (\text{kJ mol}^{-1})$ | -285.8 | -890.0 | -1560.0 | -393.5 |

The standard heat of formation of $\text{C}_3\text{H}_8(g)$ is $-103.8 \text{ kJ mol}^{-1}$.

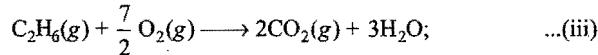
(ITT 1992)

[Ans. -55.7 kJ]

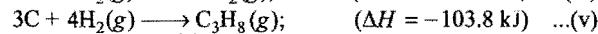
[Hint: $\text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \longrightarrow \text{H}_2\text{O}; (\Delta H = -285.8 \text{ kJ})$... (i)]



$$(\Delta H = -890.0 \text{ kJ})$$



$$(\Delta H = -1560.0 \text{ kJ})$$

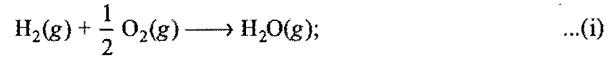


Multiplying eq. (i) by 5 and eq. (iv) by 3 and adding both the equations and subtracting eqs. (ii), (iii) and (v).]

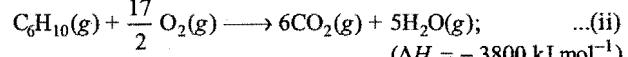
36. The standard enthalpy of combustion at 25°C of hydrogen, cyclohexene (C_6H_{10}) and cyclohexane (C_6H_{12}) are -241 , -3800 and $-3920 \text{ kJ mol}^{-1}$ respectively. Calculate the heat of hydrogenation of cyclohexene. [ISM (Dhanbad) 1992]

[Ans. -121 kJ mol^{-1}]

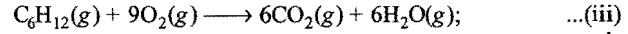
[Hint:



$$(\Delta H = -241 \text{ kJ mol}^{-1})$$

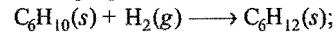


$$(\Delta H = -3800 \text{ kJ mol}^{-1})$$



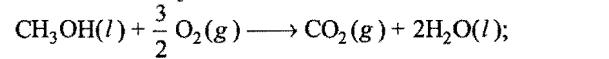
$$(\Delta H = -3920 \text{ kJ mol}^{-1})$$

Adding eqs. (i) and (ii) and subtracting eq. (iii),

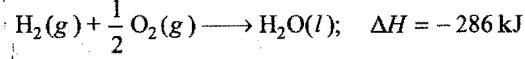
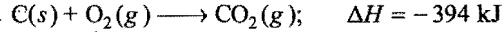


$$\Delta H = -241 - 3800 - (-3920) = -121 \text{ kJ mol}^{-1}]$$

37. From the following data of heats of combustion, find the heat of formation of $\text{CH}_3\text{OH}(l)$:



$$\Delta H = -726 \text{ kJ}$$



[BIT (Ranchi) 1991]

[Ans. -240 kJ mol^{-1}]

38. Calculate the heat of formation of methane, given that heat of formation of water $= -286 \text{ kJ mol}^{-1}$

heat of combustion of methane $= -890 \text{ kJ mol}^{-1}$

heat of combustion of carbon $= -393.5 \text{ kJ mol}^{-1}$

[ISM (Dhanbad) 1991]

[Ans. $-75.5 \text{ kJ mol}^{-1}$]

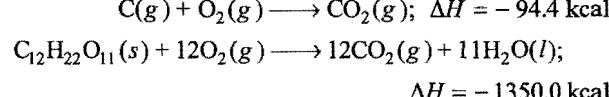
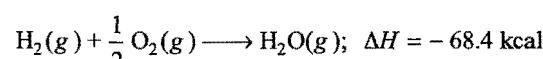
39. Calculate the standard heat of formation of C_{10}H_8 (naphthalene) if standard heat of combustion of naphthalene is -1231.0 kcal at 298 K and standard heat of formation of $\text{CO}_2(g)$ and $\text{H}_2\text{O}(l)$ are -94.0 kcal and -68.4 kcal respectively.

[Ans. 17.4 kcal]

40. The heat of combustion of liquid ethanol is -327.0 kcal . Calculate the heat of formation of ethanol, given that the heats of formation of $\text{CO}_2(g)$ and $\text{H}_2\text{O}(l)$ are -94.0 kcal and -68.4 kcal respectively.

[Ans. -66.2 kcal]

41. Calculate heat of formation of cane sugar from following data:

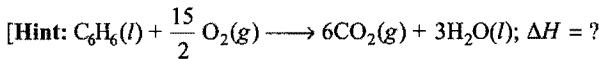


$$\Delta H = -1350.0 \text{ kcal}$$

[Ans. -535.2 kcal]

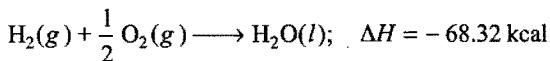
42. The heats of formation of $\text{C}_6\text{H}_6(l)$, $\text{H}_2\text{O}(l)$ and $\text{CO}_2(g)$ are 11.70 , -68.4 and -94.0 kcal respectively. Calculate the heat of combustion of benzene (l).

[Ans. -780.9 kcal]

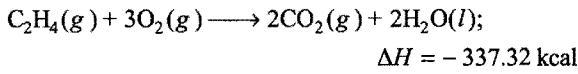


$$\Delta H = 6 \times \Delta H_f(CO_2) + 3 \times \Delta H_f(H_2O) - \Delta H_f(C_6H_6)$$

43. Calculate the heat of hydrogenation of C_2H_2 to C_2H_4 .



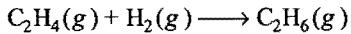
$$\Delta H = -310.61 \text{ kcal}$$



$$\Delta H = -337.32 \text{ kcal}$$

[Ans. -41.61 kcal]

44. Calculate the heat of hydrogenation,



given that, the heat of combustion of ethylene, hydrogen and ethane are -337.0 , -68.4 and -373.0 kcal respectively.

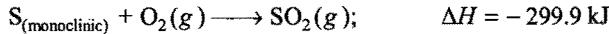
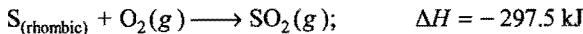
[Ans. -32.4 kcal]

45. If the heat of formation of $Al_2O_3(s)$ and $Cr_2O_3(s)$ are 1596 kJ and 1134 kJ (both exothermic) respectively. Calculate ΔH of the thermite reaction.



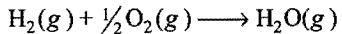
[Ans. -462 kJ]

46. Calculate the enthalpy of transition of rhombic sulphur to monoclinic sulphur from the following data:



[Ans. $+2.4 \text{ kJ}$]

47. Calculate ΔH for the reaction,



given that bond energies of $H-H$ and $O=O$ bond and $O-H$ bond are 433 kJ mol^{-1} , 492 kJ mol^{-1} and 464 kJ mol^{-1} .

[Ans. -249 kJ]

48. Using the bond enthalpy data, calculate ΔH of the following reaction:



given that, bond energies of $Cl-Cl$, $H-Cl$, $O-H$ and $O=O$ are 242.8 , 431.8 , 464 and 442 kJ mol^{-1} respectively.

[Ans. $172.4 \text{ kJ mol}^{-1}$]

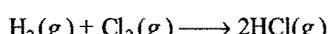
49. Calculate the enthalpy of the reaction,



given that, enthalpy of formation of $SnO_2(s)$ and $H_2O(l)$ are -580.7 kJ and -285.8 kJ respectively.

[Ans. $+9.1 \text{ kJ}$]

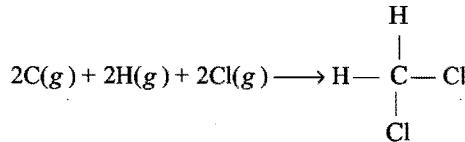
50. Calculate the enthalpy change for the reaction,



given that, bond energies of $H-H$, $Cl-Cl$ and $H-Cl$ are 436 , 243 and 432 kJ mol^{-1} .

[Ans. -185 kJ mol^{-1}]

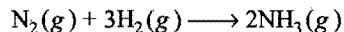
51. Use the bond energy data and calculate the enthalpy change for:



The bond energies of $C-H$ and $C-Cl$ are 413 and 328 kJ mol^{-1} respectively.

[Ans. $-1482 \text{ kJ mol}^{-1}$]

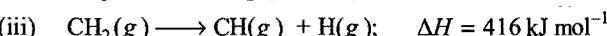
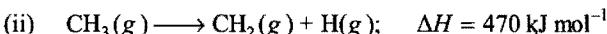
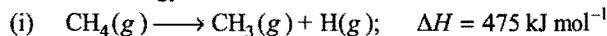
52. Calculate the heat of formation of ammonia from the following data:



The bond energies of $N \equiv N$, $H-H$ and $N-H$ bonds are 226 , 104 and 93 kcal respectively.

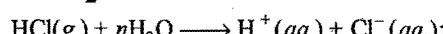
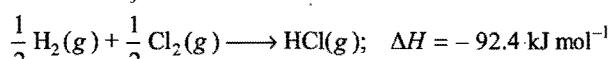
[Ans. -10 kcal]

53. Use the following bond dissociation energies to compute the $C-H$ bond energy in methane:



[Ans. 424 kJ mol^{-1}]

54. Calculate ΔH_f° for chloride ion from the following data:

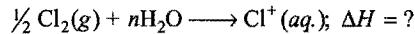


$$\Delta H = -74.8 \text{ kJ mol}^{-1}$$

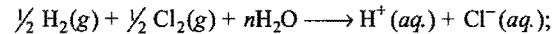
$$\Delta H_f^\circ(H^+ aq.) = 0.0 \text{ kJ mol}^{-1}$$

(III 1992)

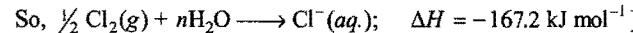
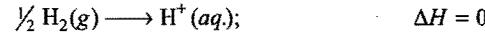
[Hint: Required equation is



Adding both equations.



$$\Delta H = -167.2$$



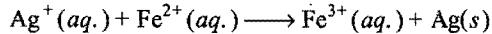
55. The heat of ionisation of formic acid is 1.5 kJ/mol . 9.2 g formic acid on reaction with 7 g ammonium hydroxide gives 10.8 kJ of heat. Calculate the heat of ionisation of ammonium hydroxide. ($1 \text{ cal} = 4.2 \text{ J}$)

[Ans. 2.04 kJ/mol]

56. Assuming that 50% of the heat of useful, how many kg of water at 15°C can be heated to 95.0°C by burning 200 litre of methane measured at NTP? The heat of combustion of methane is $211 \text{ kcal mol}^{-1}$.

[Ans. 11.76 kg]

57. The standard potential for the reaction,



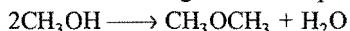
is 0.028 V . What is the standard free energy change for this reaction?

[Ans. $-2.702 \text{ kJ mol}^{-1}$]

58. Calculate the theoretical maximum efficiency of a heat engine operating between 373 K and 173 K.

[Ans. 0.536 or 53.6%]

59. The standard free energy of formation in the gaseous state of methanol, dimethyl ether and water are -38.7 , -27.3 and -54.6 kcal respectively. Is the transformation of methanol to dimethyl ether and water in gaseous state possible?



[Hint: ΔG° for the transformation

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

$= -ve$ (the transformation is possible)]

60. Ethanol boils at 78.4°C and standard enthalpy of vaporization of ethanol is 42.4 kJ mol^{-1} . Calculate the entropy of vaporization of ethanol.

[Ans. $120.9 \text{ J K}^{-1} \text{ mol}^{-1}$]

61. The following data is known about the melting of KCl:

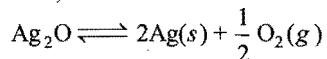
$$\Delta H = 7.25 \text{ kJ mol}^{-1} \text{ and } \Delta S = +0.007 \text{ J K}^{-1} \text{ mol}^{-1}$$

Calculate its melting point.

[Ans. 1035.7 K]

[Hint: At melting point $\Delta G = 0$]

62. For the reaction,



Calculate the temperature at which free energy change is zero. At a temperature lower than this, predict whether the forward or the reverse reaction will be favoured. Give reason.

($\Delta H = +30.56 \text{ kJ}$ and $\Delta S = +0.066 \text{ J K}^{-1} \text{ mol}^{-1}$ at one atmosphere)

[Hint: Calculate T by applying the formula

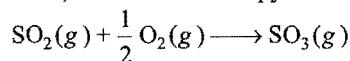
$$\Delta G = \Delta H - T \Delta S \text{ and } \Delta G = 0.$$

Then find the value of ΔG at lower temperature than T . The value of ΔG comes positive; hence, the reverse reaction will be favoured. At temperature higher than T , the reaction is spontaneous.]

63. Calculate the boiling point of the liquid if its entropy of vaporization is $110 \text{ J K}^{-1} \text{ mol}^{-1}$ and the enthalpy of vaporization is $40.85 \text{ kJ mol}^{-1}$.

[Ans. 371.36 K]

64. Using S° values, calculate the entropy of the reaction,

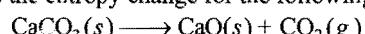


The S° values for SO_2 , O_2 and SO_3 are 248.5 , 205.0 and $256.2 \text{ J K}^{-1} \text{ mol}^{-1}$.

[Ans. $= -94.2 \text{ J K}^{-1} \text{ mol}^{-1}$]

[Hint: $\Delta S_{\text{reaction}}^\circ = \sum S_{\text{products}}^\circ - \sum S_{\text{reactants}}^\circ$]

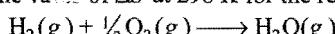
65. Calculate the entropy change for the following reaction:



$$S^\circ \quad 92.9 \quad 39.7 \quad 213.6 \text{ J K}^{-1} \text{ mol}^{-1}$$

[Ans. $+120.4 \text{ J K}^{-1} \text{ mol}^{-1}$]

66. Compute the value of ΔS at 298 K for the reaction,



given that, $\Delta G = -228.6 \text{ kJ}$ and $\Delta H = -241.8 \text{ kJ}$.

[Ans. -44.3 J K^{-1}]

67. An engine operating between 150°C and 25°C takes 500 J heat from a high temperature reservoir. Assuming there is no frictional loss, calculate the work that can be done by the engine.

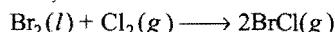
[Ans. 148 J]

68. At 300 K , the standard enthalpies of formation of $\text{C}_6\text{H}_5\text{COOH}(s)$, $\text{CO}_2(g)$ and $\text{H}_2\text{O}(l)$ are -408 , -393 and -286 kJ mol^{-1} respectively. Calculate the heat of combustion of benzoic acid at (i) constant pressure and (ii) constant volume. ($R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$)

(IIT 1995)

[Ans. (i) $\Delta H = -3201 \text{ kJ mol}^{-1}$;
(ii) $\Delta E = -3199.75 \text{ kJ mol}^{-1}$]

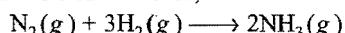
69. For the reaction,



$\Delta H = 29.37 \text{ kJ mol}^{-1}$ and $\Delta S = 104 \text{ J K}^{-1} \text{ mol}^{-1}$. Find the temperature above which the reaction would become spontaneous.

[Ans. Above 282.4 K]

70. For the synthesis of ammonia,



Calculate ΔH° , ΔS° and ΔG° at 300 K using the following data:

| Species | N_2 | H_2 | NH_3 |
|--|--------------|--------------|---------------|
| $\Delta H_f^\circ / (\text{kJ mol}^{-1})$ | 0 | 0 | -46.2 |
| $S^\circ / (\text{J K}^{-1} \text{ mol}^{-1})$ | 191.5 | 130.6 | 192.5 |

[Ans. $\Delta H^\circ = -92.4 \text{ kJ mol}^{-1}$, $\Delta S^\circ = -198.3 \text{ J K}^{-1} \text{ mol}^{-1}$, $\Delta G^\circ = -32.91 \text{ kJ mol}^{-1}$]

71. How much heat is required to change 15.6 g of benzene from liquid into vapour at its boiling point of 80°C ? Entropy of vaporization of benzene is $87 \text{ J K}^{-1} \text{ mol}^{-1}$.

[Ans. 6142.2 J]

72. Calculate the standard free energy change for the combustion of glucose at 298 K , using the given data.



$$\Delta H^\circ = -2820 \text{ kJ mol}^{-1}, \Delta S^\circ = 210 \text{ J K}^{-1} \text{ mol}^{-1}$$

[Ans. $\Delta G^\circ = -2882.58 \text{ kJ mol}^{-1}$]

73. The specific heat at constant volume for a gas is 0.075 cal/g and at constant pressure it is 0.125 cal/g . Calculate:

(i) the molecular weight of gas,

(ii) atomicity of gas.

[Hint: (i) $C_P - C_V = \frac{R}{M}$ where, M = molecular weight of gas

$$0.125 - 0.075 = \frac{1.987}{M}$$

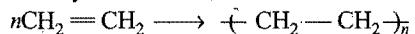
$$M = 39.74 \approx 40$$

$$(ii) \quad \frac{C_P}{C_V} = \gamma$$

$$\therefore \gamma = \frac{0.125}{0.075} = 1.66$$

$\therefore 1.66$ value of γ shows that the gas is monoatomic.]

74. The polymerisation of ethylene to linear polyethylene is represented by the reaction,



where, n has a large integral value. Given that the average enthalpies of bond dissociation for $\text{C}=\text{C}$ and $\text{C}-\text{C}$ at 298 K are +590 and +331 kJ mol^{-1} respectively, calculate the enthalpy of polymerisation per mole of ethylene at 298 K.

(IIT 1994)



There are equal number of $\text{C}-\text{H}$ bonds on both sides but on reactant side there are $n\text{C}=\text{C}$ bonds and on product side $(2n+1)\text{C}-\text{C}$ bonds.

Enthalpy of polymerisation

$$\begin{aligned} &= n\Delta H_{(\text{C}=\text{C})} - (2n+1)\Delta H_{(\text{C}-\text{C})} \\ &= 590n - (2n+1)(331) \\ &= 590n - 662n \quad [2n+1 \rightarrow 2n \text{ as } n \text{ is very large}] \\ &= -72n \text{ kJ} \end{aligned}$$

Enthalpy of polymerisation per mole

$$= \frac{\Delta H}{n} = -\frac{72n}{n} = -72 \text{ kJ mol}^{-1}$$

75. An athlete is given 100 g of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) of energy equivalent to 1560 kJ. He utilises 50% of this gained energy in the event. In order to avoid storage of energy in the body, calculate the mass of water he would need to perspire. The enthalpy of evaporation of water is 44 kJ mol^{-1} .

[Hint: Unused energy = $\frac{1560}{2} = 780 \text{ kJ}$

$$\text{Mass of water needed for perspiration} = 18 \times \frac{780}{44} = 318.96 \text{ g}$$

76. Calculate the entropy of ideal mixing when 2 moles of N_2 , 3 moles of H_2 and 2 moles of NH_3 are mixed at constant temperature, assuming no chemical reaction is occurring.

[Ans. 62.80 J K^{-1}]

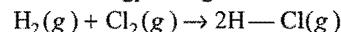
[Hint: Use the relation,

$$\Delta S = -R \sum n_i \log_e x_i$$

when n_i = no. of moles of component

x_i = mole fraction of the component]

77. Calculate free energy change for the reaction:



by using the bond energy and entropy data.

Bond energies of $\text{H}-\text{H}$, $\text{Cl}-\text{Cl}$ and $\text{H}-\text{Cl}$ bonds are 435 kJ mol^{-1} , 240 kJ mol^{-1} and 430 kJ mol^{-1} respectively. Standard entropies of H_2 , Cl_2 and HCl are 130.59, 222.95 and 186.68 $\text{J K}^{-1} \text{ mol}^{-1}$ respectively.

[Ans. 190.9 kJ]

[Hint: ΔG° can be calculated by using:

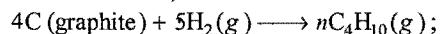
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta H^\circ = \Sigma (\text{BE})_{\text{reactants}} - \Sigma (\text{BE})_{\text{products}} \\ = 435 + 240 - 2 \times 430 = -185 \text{ kJ}$$

$$\begin{aligned} \Delta S^\circ &= \Sigma S^\circ_{\text{products}} - \Sigma S^\circ_{\text{reactants}} \\ &= 2 \times 186.68 - 130.59 - 222.95 \\ &= 19.82 \text{ J K}^{-1} = 19.82 \times 10^{-3} \text{ kJ K}^{-1} \end{aligned}$$

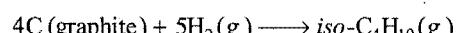
$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= -185 - 298 \times 19.82 \times 10^{-3} = -190.9 \text{ kJ} \end{aligned}$$

78. For the reaction,



$$\Delta H^\circ = -124.73 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ = -365.8 \text{ J K}^{-1} \text{ mol}^{-1}$$



$$\Delta H^\circ = -131.6 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ = -381.079 \text{ J K}^{-1} \text{ mol}^{-1}$$

Indicate whether *normal butane* can be spontaneously converted to *iso-butane* or not.

[Ans. Yes, $\Delta G^\circ = -2.32 \text{ kJ}$]

[Hint: For $n\text{C}_4\text{H}_{10}$,

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= -124.73 - 298(-365.8 \times 10^{-3}) = -15.72 \text{ kJ} \end{aligned}$$

For *iso-butane* ($\text{iso-C}_4\text{H}_{10}$),

$$\begin{aligned} \Delta G^\circ &= -131.6 - 298(-381.079 \times 10^{-3}) \\ &= -18.04 \text{ kJ} \end{aligned}$$

For conversion of $n\text{C}_4\text{H}_{10} \longrightarrow \text{iso-C}_4\text{H}_{10}$,

$$\Delta G^\circ = -18.04 - (-15.72) = -2.32 \text{ kJ}$$

Negative value shows that the process is spontaneous.]

79. The temperature of a bomb calorimeter was found to rise by 1.617 K, when a current of 3.20 amp was passed for 27 sec from a 12 V source. Calculate the calorimeter constant.

[Hint: Energy absorbed by the calorimeter
 $= I \times t \times V = 3.2 \times 27 \times 12 = 1036.8 \text{ J}$

Calorimeter constant (ms) can be calculated as,

$$q = ms \Delta t$$

$$1036.8 = ms \times 1.617$$

$$ms = 641.187 \text{ kJ}$$

80. 1 mole of an ideal gas is allowed to expand isothermally at 27°C until its volume is tripled. Calculate ΔS_{sys} and ΔS_{univ} under the following conditions:

- (a) the expansion is carried out reversibly.
(b) the expansion is a free expansion.

[Ans. (a) $\Delta S_{\text{sys}} = 9.135 \text{ J K}^{-1} \text{ mol}^{-1}$

$$\Delta S_{\text{surr}} = -9.135 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta S_{\text{univ}} = 0$$

$$(b) \Delta S_{\text{univ}} = \Delta S_{\text{sys}} = 9.135 \text{ J K}^{-1} \text{ mol}^{-1}$$

[Hint: (a) In isothermal reversible process:

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

$$q = -W = 2.303RT \log \frac{V_2}{V_1}$$

$$= 2.303 \times 8.314 \times 300 \log 3 = 2740.6 \text{ J mol}^{-1}$$

$$\Delta S_{\text{system}} = \frac{q_{\text{rev}}}{T} = \frac{2740.6}{300} = 9.135 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta S_{\text{surr}} = -\Delta S_{\text{system}} = -9.135 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta S_{\text{univ}} = 0$$

(b) In case of free expansion:

$$\Delta S = 2.303nR \log \left(\frac{V_2}{V_1} \right) = 9.135 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} = 9.135 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta S_{\text{surr}} = 0$$

81. One kilogram water at 0°C is brought into contact with a heat reservoir at 100°C . Find:

- (a) change in entropy when temperature reaches to 100°C .
- (b) what is the change in entropy of reservoir?
- (c) change in entropy of universe.
- (d) the nature of process.

[Ans. (a) 312 cal K^{-1} , (b) $-268.1 \text{ cal K}^{-1}$, (c) 43.9 cal K^{-1}
 (d) spontaneous]

[Hint: (a) $\Delta S = 2.303nC_P \log\left(\frac{T_2}{T_1}\right)$

$$= 2.303 \times \frac{1000}{18} \times 18 \log\left(\frac{373}{273}\right) = 312 \text{ cal K}^{-1}$$

(b) $\Delta S_{\text{reservoir}} = -\frac{\Delta Q}{T}$

$$\Delta Q = ms \Delta t = 1000 \times 1 \times 100 = 10^5 \text{ cal}$$

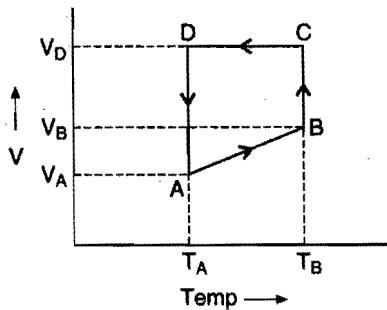
$$\Delta S = \frac{-10^5}{373} = -268.1 \text{ cal K}^{-1}$$

(c) $\Delta S_{\text{universe}} = 312 - 268.1 = 43.9 \text{ cal K}^{-1}$

(d) $\Delta S > 0$, the process will be spontaneous.]

82. A monoatomic ideal gas of two moles is taken through a cyclic process starting from A as shown in figure. The volume ratios are $\frac{V_B}{V_A} = 2$ and $\frac{V_D}{V_A} = 4$. If the temperature T_A at A is 27°C .

Calculate:



- (a) the temperature of gas at B .
- (b) heat absorbed or evolved in each process.
- (c) total work done in cyclic process.

[Hint: $A \rightarrow B$: (It is isobaric process)]

$$\frac{V_A}{T_A} = \frac{V_B}{T_B}$$

$$T_B = \frac{V_B}{V_A} \times T_A = 2 \times 300 = 600 \text{ K}$$

$$q_{AB} = nC_P \Delta T = 2 \times \frac{5}{2} R \Delta T \\ = 2 \times \frac{5}{2} \times 2 \times 300 = 3000 \text{ cal}$$

(Isothermal process)

$$\Delta U = 0$$

$$\therefore q_{BC} = W = 2.303 nRT \log\left(\frac{V_C}{V_B}\right)$$

$$= 2.303 \times 2 \times 2 \times 600 \log \frac{4}{2} \\ = 1.663 \times 10^3 \text{ cal}$$

$C \rightarrow D$: (Isochoric process)

$$q_{CD} = nC_V \Delta T = 2 \times \frac{3}{2} \times 2 (-300) = -1800 \text{ cal}$$

$D \rightarrow A$: (Isothermal process)

$$q_{DA} = 2.303 nRT_A \log\left(\frac{V_A}{V_D}\right) \\ = 2.303 \times 2 \times 2 \times 300 \log \frac{1}{4} \\ = -1.663 \times 10^3 \text{ cal}$$

$$\text{Total heat change} = 3000 + 1.663 \times 10^3 - 1800 - 1.663 \times 10^3 \\ = 1200 \text{ cal}$$

Work done = -1200 cal]

83. The reaction, $\text{SOCl}_2 + \text{H}_2\text{O} \longrightarrow \text{SO}_2 + 2\text{HCl}$ is endothermic by 49.4 kJ and exoergonic by 50.8 kJ . What is the factor that makes the reaction to be spontaneous? Calculate the entropy change at 298 K .

[Ans. $\Delta S^\circ = 0.3362 \text{ kJ K}^{-1}$]

[Hint: Exoergonic means $\Delta G^\circ = -\text{ve}$.

$$\Delta G^\circ = -50.8 \text{ kJ},$$

$$\Delta H^\circ = 49.4 \text{ kJ}$$

Substitute these values in $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ to calculate entropy.

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = \frac{49.4 - (-50.8)}{298} \\ = 0.3362 \text{ kJ K}^{-1}$$

84. What amount of ice will remain when 52 g ice is added to 100 g of water at 40°C ?

Specific heat of water is 1 cal/g and latent heat of fusion of ice is 80 cal/g .

[Ans. 2 g ice]

[Hint: At the stage of thermal equilibrium at 0°C ,

Heat lost by water = Heat absorbed by ice to melt.

$$ms \Delta T = mL$$

$$100 \times 1 \times 40 = m \times 80$$

$$m = 50 \text{ g}$$

$$\text{Remaining ice} = 52 - 50 = 2 \text{ g}$$

85. Calculate the ΔH_f° of $\text{C}_6\text{H}_{12}\text{O}_6(s)$ from the following data:

$$\Delta H_{\text{comb}} [\text{C}_6\text{H}_{12}\text{O}_6(s)] = -2816 \text{ kJ/mol}$$

$$\Delta H_f^\circ \text{ of CO}_2(g) = -393.5 \text{ kJ/mol}$$

$$\Delta H_f^\circ \text{ of H}_2\text{O}(l) = -285.9 \text{ kJ/mol}$$
 [BCECE 2006]

[Ans. -1260 kJ/mol]

86. A liquid freezes into solid ($\Delta H = -500 \text{ J mol}^{-1}$) at 100 K and 1 atm . Find the values of:

(i) Gibbs free energy change

(ii) entropy change.

[CBSE (Mains) 2006]

[Hint: Liquid \rightleftharpoons Solid

(i) $\Delta G = 0$, at equilibrium

$$(ii) \Delta S = \frac{\Delta H}{T} = \frac{-500}{100} = -5 \text{ J K}^{-1} \text{ mol}^{-1}$$

OBJECTIVE QUESTIONS

Set-1: Questions with single correct answer

1. Thermodynamics is concerned with:
 - total energy of a system
 - energy changes in a system
 - rate of a chemical change
 - mass changes in nuclear reactions
2. An isolated system is that system in which:

[PET (MP) 1993]

 - there is no exchange of energy with the surroundings
 - there is exchange of mass and energy with the surroundings
 - there is no exchange of energy and mass with the surroundings
 - there is exchange of mass with the surroundings
3. Identify the intensive property from the following:
 - volume
 - mass
 - enthalpy
 - temperature
4. Which one of the following is an extensive property?

[Comed (Karnataka) 2008]

 - Enthalpy
 - Concentration
 - Density
 - Viscosity
5. For an adiabatic process, which of the following relations is correct?

(CPMT 1990)

 - $\Delta E = 0$
 - $P \Delta V = 0$
 - $q = 0$
 - $q = +w$
6. Which one is true from the following for isobaric process?

[CET (Gujarat) 2008]

 - $\Delta P = 0$
 - $\Delta q = 0$
 - $\Delta H = 0$
 - $\Delta E = 0$
7. For an ideal gas, the value of $\left(\frac{dE}{dV}\right)_T$ is:

[PET (MP) 1993]

 - positive
 - zero
 - negative
 - interchangeable
8. A process, in which pressure remains constant, is called:
 - isochoric process
 - isothermal process
 - adiabatic process
 - isobaric process
9. A process in which volume remains constant, is called:
 - isochoric process
 - isothermal process
 - adiabatic process
 - isobaric process
10. For a cyclic process, the condition is:
 - $\Delta E = 0$
 - $\Delta H = 0$
 - $\Delta E > 0$ and $\Delta H > 0$
 - both $\Delta E = 0$ and $\Delta H = 0$
11. Which one of the following is a state property?
 - Heat
 - Work
 - Internal energy
 - Potential energy
12. Internal energy of a system of molecules is determined by taking into consideration its:
 - kinetic energy
 - vibrational energy
 - rotational energy
 - all kinds of energies present in the molecules
13. A thermodynamic quantity is that:
 - which is used in thermochemistry
 - which obeys all laws of thermodynamics
 - quantity whose value depends only upon the state of the system
 - quantity which is used in measuring thermal change
14. Thermodynamic equilibrium involves:

[CET (Pb.) 1991]

 - chemical equilibrium
 - thermal equilibrium
 - mechanical equilibrium
 - all the three
15. For the reaction of one mole zinc dust with one mole sulphuric acid in a bomb calorimeter, ΔU and w correspond to:

(AIIMS 2005)

 - $\Delta U < 0, w = 0$
 - $\Delta U < 0, w < 0$
 - $\Delta U > 0, w = 0$
 - $\Delta U > 0, w > 0$

[Hint: In bomb calorimeter, $w = 0, \Delta U = q(-ve)\]$
16. A system is provided with 50 joules of heat and the work done on the system is 10 joules. What is the change in internal energy of the system in joules?

[EAMCET (Engg.) 2010]

 - 60
 - 40
 - 50
 - 10
17. During an isothermal expansion of an ideal gas, its:

(CBSE 1991)

 - internal energy increases
 - enthalpy decreases
 - enthalpy remains unaffected
 - enthalpy reduces to zero
18. The work done in ergs for a reversible expansion of one mole of an ideal gas from a volume of 10 litre to 20 litre at 25°C is:

[CMC (Vellore) 1991]

 - $2.303 \times 8.31 \times 10^7 \times 298 \log 2$
 - $2.303 \times 0.0821 \times 298 \log 2$
 - $2.303 \times 0.0821 \times 298 \log 0.5$
 - $2.303 \times 2 \times 298 \log 2$
19. When an ideal gas is compressed adiabatically and reversibly, the final temperature is:
 - higher than the initial temperature
 - lower than the initial temperature
 - the same as initial temperature
 - dependent upon the rate of compression
20. Adiabatic reversible expansion of a gas is represented by:

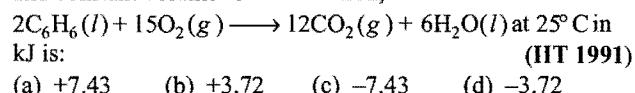
$$(a) \left(\frac{T_1}{T_2}\right)^Y = \left(\frac{P_2}{P_1}\right)^{1-Y}$$
 (b) $\left(\frac{T_1}{T_2}\right) = \left(\frac{P_1}{P_2}\right)^{1-Y}$

$$(c) \left(\frac{T_1}{T_2}\right)^Y = \left(\frac{P_2}{P_1}\right)^{Y-1}$$
 (d) all are correct
21. Total energy change for a reversible isothermal cycle is:
 - always positive
 - zero
 - always negative
 - always 100 kJ per degree
22. "Heat energy cannot be completely transformed into work without producing some change somewhere", is the statement of:

- (a) Hess's law
 (b) first law of thermodynamics
 (c) Kirchhoff's law
 (d) second law of thermodynamics
23. The heat content of the system is called:
 (a) internal energy (b) enthalpy
 (c) free energy (d) entropy
24. If one mole of ammonia and one mole of hydrogen chloride are mixed in a closed container to form ammonium chloride gas, then : (KCET 2008)
 (a) $\Delta H < \Delta U$
 (b) $\Delta H > \Delta U$
 (c) $\Delta H = \Delta U$
 (d) there is no relationship between ΔH and ΔU
25. An exothermic reaction is one in which the reacting substances:
 (a) have same energy as products
 (b) have less energy than the products
 (c) have more energy than the products
 (d) are at higher temperature than the products
26. In endothermic reactions, the reactants:
 (a) have more energy than products
 (b) have as much energy as the products
 (c) are at lower temperature than products
 (d) have less energy than the products
27. Identify the reaction in which the heat liberated corresponds to the heat of formation (ΔH_f): (EAMCET 2006)
 (a) $C(\text{diamond}) + O_2(g) \rightarrow CO_2(g) + \text{heat}$
 (b) $2H_2(g) + O_2(g) \rightarrow 2H_2O(g) + \text{heat}$
 (c) $C(\text{diamond}) + 2H_2(g) \rightarrow CH_4(g) + \text{heat}$
 (d) $S(\text{rhombic}) + O_2(g) \rightarrow SO_2(g) + \text{heat}$
28. In an exothermic reaction, ΔH is:
 (a) positive (b) negative
 (c) zero (d) may be positive or negative
29. Evaporation of water is:
 (a) a process in which neither heat is evolved nor absorbed
 (b) a process accompanied by chemical reaction
 (c) an exothermic change
 (d) an endothermic change
30. An endothermic reaction is one in which:
 (a) heat is converted into electricity
 (b) heat is absorbed
 (c) heat is evolved
 (d) heat changes to mechanical work
31. If total enthalpy of reactants and products is H_R and H_P respectively, then for exothermic reaction:
 (a) $H_R = H_P$ (b) $H_R < H_P$
 (c) $H_R > H_P$ (d) $H_R - H_P = 0$
32. 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 : (DPMT 2009)
 (a) 4.01 kJ (b) -8.02 kJ
 (c) 18.02 kJ (d) -14.01 kJ
 [Hint : $w = 2.303 nRT \log\left(\frac{P_2}{P_1}\right)$
 $= 2.303 \times 1 \times 8.314 \times 300 \log \frac{4}{1}$
 $= 3458.3 \text{ J} = 3.458 \text{ kJ}$]
33. Under which of the following conditions is the relation, $\Delta H = \Delta E + P \Delta V$ valid for a closed system?
 (a) Constant pressure
 (b) Constant temperature
 (c) Constant temperature and pressure
 (d) Constant temperature, pressure and composition
34. Which of the following is an endothermic reaction?
 (a) $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$
 (b) $N_2(g) + O_2(g) \rightarrow 2NO(g)$
 (c) $NaOH(aq.) + HCl(aq.) \rightarrow NaCl(aq.) + H_2O(l)$
 (d) $C_2H_5OH(aq.) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$
35. Which of the following reactions is endothermic?
 (a) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
 (b) $Fe(s) + S(s) \rightarrow FeS(s)$
 (c) $NaOH(aq.) + HCl(aq.) \rightarrow NaCl(aq.) + H_2O(l)$
 (d) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$
36. The formation of water from $H_2(g)$ and $O_2(g)$ is an exothermic process because:
 (a) the chemical energy of $H_2(g)$ and $O_2(g)$ is more than that of water
 (b) the chemical energy of $H_2(g)$ and $O_2(g)$ is less than that of water
 (c) the temperature of $H_2(g)$ and $O_2(g)$ is higher than that of water
 (d) the temperature of $H_2(g)$ and $O_2(g)$ is lower than that of water
37. Which one of the following reactions is an exothermic reaction?
 (a) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
 (b) $N_2(g) + O_2(g) \rightarrow 2NO(g)$
 (c) $2HgO(s) \rightarrow 2Hg(s) + O_2(g)$
 (d) $C(s) + O_2(g) \rightarrow CO_2(g)$
38. Which one of the following is not applicable for a thermochemical equation?
 (a) It tells about physical state of reactants and products
 (b) It tells whether the reaction is spontaneous
 (c) It tells whether the reaction is exothermic or endothermic
 (d) It tells about the allotropic form (if any) of the reactants
39. The enthalpies of all elements in their standard state at 25°C and one atmospheric pressure are:
 (a) same (b) always positive
 (c) always negative (d) zero
40. The heat of reaction does not depend upon:
 (a) physical state of the reactants and products
 (b) whether the reaction has been carried at constant pressure or constant volume
 (c) the manner by which the reaction has been carried
 (d) the temperature at which the reaction has been carried
41. The value of $\Delta H - \Delta U$ for the following reaction at 27°C will be:
 $2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$ [AMU (Medical) 2007]
 (a) $8.314 \times 273 \times (-2)$ (b) $8.314 \times 300 \times (-2)$
 (c) $8.314 \times 273 \times 2$ (d) $8.314 \times 300 \times 2$

42. Since, the enthalpy of the elements in their standard states is taken to be zero, the heat of formation (ΔH_f) of compounds:
 (a) is always negative (b) is always positive
 (c) is zero (d) may be positive or negative

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



44. For a gaseous reaction, $A(g) + 3B(g) \rightarrow 3C(g) + 3D(g)$, ΔE is 17 kcal at 27°C . Assuming $R = 2 \text{ cal K}^{-1} \text{ mol}^{-1}$, the value of ΔH for the above reaction is:
 (a) 15.8 kcal (b) 18.2 kcal
 (c) 20.0 kcal (d) 16.4 kcal

45. Which of the following statements is correct for the reaction,
 $\text{CO}(g) + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{CO}_2(g)$ at constant temperature and pressure?
 (a) $\Delta H = \Delta E$ (b) $\Delta H < \Delta E$
 (c) $\Delta H > \Delta E$ (d) None of these

46. For the reaction, $\text{Ag}_2\text{O}(s) \longrightarrow 2\text{Ag}(s) + \frac{1}{2}\text{O}_2(g)$ which one of the following is true?
 (a) $\Delta H = \Delta E$ (b) $\Delta H < \Delta E$
 (c) $\Delta H > \Delta E$ (d) $\Delta H = \frac{1}{2}\Delta E$

47. Thermochemistry is the study of relationship between heat energy and:
 (a) chemical energy (b) activation energy
 (c) friction energy (d) none of these

48. Assume each reaction is carried out in an open container. For which reaction will $\Delta H = \Delta U$? [CBSE (Med.) 2006]
 (a) $\text{H}_2(g) + \text{Br}_2(g) \longrightarrow 2\text{HBr}(g)$
 (b) $\text{C}(s) + 2\text{H}_2\text{O}(g) \longrightarrow 2\text{H}_2(g) + \text{CO}_2(g)$
 (c) $\text{PCl}_5(g) \longrightarrow \text{PCl}_3(g) + \text{Cl}_2(g)$
 (d) $2\text{CO}(g) + \text{O}_2(g) \longrightarrow 2\text{CO}_2(g)$

49. The enthalpy change in the reaction, $2\text{CO} + \text{O}_2 \longrightarrow 2\text{CO}_2$ is termed as:
 (a) enthalpy of reaction (b) enthalpy of fusion
 (c) enthalpy of formation (d) enthalpy of combustion

50. Reaction, $\text{H}_2(g) + \text{I}_2(g) \longrightarrow 2\text{HI}$; $\Delta H = 12.40 \text{ kcal}$
 According to this, heat of formation of HI will be:

[PET (MP) 1990]

- (a) 12.40 kcal (b) -12.4 kcal
 (c) -6.20 kcal (d) 6.20 kcal

51. For the reactions,
 (i) $\text{H}_2(g) + \text{Cl}_2(g) = 2\text{HCl}(g) + x \text{ kJ}$
 (ii) $\text{H}_2(g) + \text{Cl}_2(g) = 2\text{HCl}(l) + y \text{ kJ}$

which one of the following statements is correct?

[PET (MP) 2007]

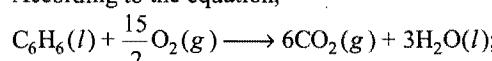
- (a) $x > y$ (b) $x < y$ (c) $x - y = 0$ (d) $x = y$

52. For the reactions,
 (i) $\text{H}_2(g) + \text{Cl}_2(g) = 2\text{HCl}(g) + x \text{ kJ}$
 (ii) $2\text{HCl}(g) = \text{H}_2(g) + \text{Cl}_2(g) - y \text{ kJ}$

which one of the following statements is correct?

- (a) $x - y > 0$ (b) $x - y < 0$
 (c) $x - y = 0$ (d) None of these

53. According to the equation,



$$\Delta H = -3264.4 \text{ kJ mol}^{-1}$$

the energy evolved when 7.8 g benzene is burnt in air will be:

[PET (MP) 1990]

- (a) 163.22 kJ (b) 32.64 kJ (c) 3.264 kJ (d) 326.4 kJ

54. $\Delta H_f(x)$, $\Delta H_f(y)$, $\Delta H_f(R)$ and $\Delta H_f(S)$ denote the enthalpies of formation of x , y , R and S respectively. The enthalpy of the reaction, $x + y \longrightarrow R + S$ is given by:

- (a) $\Delta H_f(x) + \Delta H_f(y)$
 (b) $\Delta H_f(R) + \Delta H_f(S)$
 (c) $\Delta H_f(x) + \Delta H_f(y) - \Delta H_f(R) - \Delta H_f(S)$
 (d) $\Delta H_f(R) + \Delta H_f(S) - \Delta H_f(x) - \Delta H_f(y)$

55. The enthalpy change for the reaction,

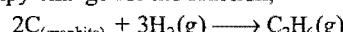


- is called:
 (a) enthalpy of formation (b) enthalpy of combustion
 (c) enthalpy of vaporisation (d) enthalpy of sublimation

56. The heat of combustion of methane is -880 kJ mol^{-1} . If 3.2 g of methane is burnt of heat is evolved.

- (a) 88 kJ (b) 264 kJ (c) 176 kJ (d) 440 kJ

57. The enthalpy change for the reaction,



is called:

- (a) enthalpy of formation (b) enthalpy of combustion
 (c) enthalpy of hydrogenation (d) enthalpy of vaporisation

58. The enthalpy of formation of water from hydrogen and oxygen is $-286.0 \text{ kJ mol}^{-1}$. The enthalpy of decomposition of water into hydrogen and oxygen is kJ mol^{-1} :

- (a) -286.0 (b) -143.0 (c) 286.0 (d) 143.0

59. The heat of combustion of $\text{C}_{(\text{graphite})}$ is $-393.5 \text{ kJ mol}^{-1}$. The heat of formation of CO_2 from graphite is kJ mol^{-1} :
 (a) 393.5 (b) -393.5 (c) -787.0 (d) 787.0

60. The enthalpies of formation of organic compounds are conveniently determined from their:

- (a) boiling points
 (b) melting points
 (c) enthalpies of neutralization
 (d) enthalpies of combustion

61. ΔH combustion of a compound is always:

- (a) positive (b) negative (c) zero (d) uncertain

62. The apparatus used for measuring the heat changes of a reaction is called:

- (a) a thermometer (b) a colorimeter
 (c) a calorimeter (d) none of these

63. The heat of neutralization of any strong acid and strong base is always constant and $\Delta H = -57.3 \text{ kJ}$. This is because:

[Comed (Karnataka) 2008]

- (a) both the acid and base undergo complete ionization.
 (b) during neutralization, salt and water are formed.
 (c) 1 mole of water is formed from H^+ and OH^- ions.
 (d) the reaction is exothermic.

64. The enthalpy of neutralization of oxalic acid by a strong base is $-25.4 \text{ k cal mol}^{-1}$. The enthalpy of neutralization of strong acid and strong base is $-13.7 \text{ kcal eq}^{-1}$. The enthalpy of dissociation of oxalic acid is: (DPMT 2009)

(a) 1 kcal mol^{-1} (b) 2 kcal mol^{-1}
 (c) $18.55 \text{ kcal mol}^{-1}$ (d) $11.7 \text{ kcal mol}^{-1}$

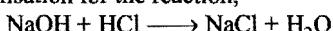
[Hint : Oxalic acid is dibasic acid hence expected heat of neutralization will be $(2 \times -13.7 \text{ kcal})$.

$$\begin{aligned}\text{The dissociation energy of oxalic acid} &= 2 \times 13.7 - 25.4 \\ &= 2 \text{ kcal mol}^{-1}\end{aligned}$$

65. The amount of heat liberated when one mole of NH_4OH reacts with one mole of HCl is: (IIT 1990)

(a) 13.7 kcal (b) more than 13.7 kcal
 (c) less than 13.67 kcal (d) cannot be predicted

66. Heat of neutralisation for the reaction,



is 57.1 kJ mol^{-1} . The heat released when 0.25 mole of NaOH is titrated against 0.25 mole of HCl will be:

(a) 22.5 kJ (b) 57.1 kJ
 (c) 28.6 kJ (d) 14.3 kJ

67. If $\text{H}^+ + \text{OH}^- = \text{H}_2\text{O} + 13.7 \text{ kcal}$, then heat of complete neutralisation of one gram mole of H_2SO_4 with strong base will be: [PMT (MP) 1990]

(a) 13.7 kcal (b) 27.4 kcal
 (c) 6.85 kcal (d) 3.425 kcal

68. In which of the following neutralization reactions, the heat of neutralization will be highest?

(a) HCl and NaOH (b) CH_3COOH and NaOH
 (c) CH_3COOH and NH_4OH (d) HCl and NH_4OH

69. "The enthalpy of formation of a compound is equal in magnitude but of opposite sign to the enthalpy of decomposition of that compound under the same conditions." This law was presented by:

(a) Hess (b) Le Chatelier
 (c) Kirchhoff (d) Lavoisier and Laplace

70. "The change of enthalpy of a chemical reaction is the same whether the reaction takes place in one step or in several steps". This law was presented by:

(a) Hess (b) Le Chatelier
 (c) van't Hoff (d) Kirchhoff

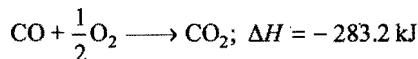
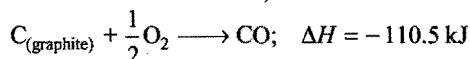
71. The enthalpy change in a reaction does not depend on the:

(a) conditions under which the reaction is carried out
 (b) initial and final enthalpies of the reactants and products
 (c) state of reactants and products
 (d) number of intermediate steps to convert reactants to products

72. Hess's law deals with:

(a) changes in heat of reaction
 (b) rate of reaction
 (c) equilibrium constant
 (d) influence of pressure on volume of a gas

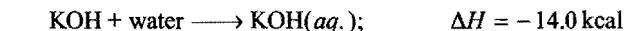
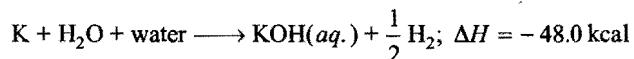
73. From the thermochemical reactions,



the heat of reaction of $\text{C}_{(\text{graphite})} + \text{O}_2 \longrightarrow \text{CO}_2$ is:

(a) $+393.7 \text{ kJ}$ (b) -393.7 kJ (c) -172.7 kJ (d) $+172.7 \text{ kJ}$

74. If $\text{H}_2 + \frac{1}{2}\text{O}_2 \longrightarrow \text{H}_2\text{O}; \quad \Delta H = -68.09 \text{ kcal}$



the heat of formation of KOH is:

(a) $-68.39 + 48 - 14.0$ (b) $-68.39 - 48.0 + 14.0$
 (c) $+68.39 - 48.0 + 14.0$ (d) $+68.39 + 48.0 - 14.0$

75. The enthalpies of combustion of $\text{C}_{(\text{graphite})}$ and $\text{C}_{(\text{diamond})}$ are -393.5 and -395.4 kJ/mol respectively. The enthalpy of conversion of $\text{C}_{(\text{graphite})}$ to $\text{C}_{(\text{diamond})}$ in kJ/mol is:

(a) -1.9 (b) -788.9
 (c) 1.9 (d) 788.9

76. The heat of combustion of yellow phosphorus and red phosphorus are -9.91 kJ and -8.78 kJ respectively. The heat of transition of yellow phosphorus to red phosphorus is:

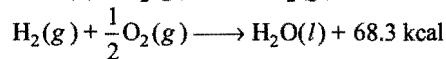
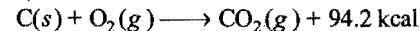
[CEE (Bihar) 1992]

(a) -18.69 kJ (b) $+1.13 \text{ kJ}$
 (c) $+18.69 \text{ kJ}$ (d) -1.13 kJ

77. 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) $(-x - y + z) \text{ kJ}$ (b) $(-z - x + 2y) \text{ kJ}$
 (c) $(-x - 2y - z) \text{ kJ}$ (d) $(-x - 2y + z) \text{ kJ}$

78. Given,



The heat of formation of methane in kcal will be:

[PET (MP) 1990]

(a) 45.9 (b) 47.8 (c) 20.0 (d) 47.3

79. On combustion carbon forms two oxides CO and CO_2 , heat of formation of CO_2 is -94.3 kcal and that of CO is -26.0 kcal . Heat of combustion of carbon is: [EAMCET (Med.) 2010]

(a) -26.0 kcal (b) -68.3 kcal
 (c) -94.3 kcal (d) -120.3 kcal

80. The heat of combustion of ethanol determined in a bomb calorimeter is $-670.48 \text{ kcal mol}^{-1}$ at 298 K . What is ΔE at 298 K for the reaction?

(a) $-760 \text{ kcal mol}^{-1}$ (b) $-670.48 \text{ kcal mol}^{-1}$
 (c) $+760 \text{ kcal mol}^{-1}$ (d) $+670.48 \text{ kcal mol}^{-1}$

81. 1 calorie is equivalent to:

(a) 4.184 J (b) 41.84 J (c) 418.4 J (d) 0.4184 J

82. For an endothermic reaction, where ΔH represents the enthalpy of reaction, the minimum value for the energy of activation will be: [IIT 1991; PET (MP) 1993]

(a) less than ΔH (b) zero
 (c) equal to ΔH (d) more than ΔH

83. If $S + O_2 \rightarrow SO_2; \Delta H = -298.2 \text{ kJ}$
 $SO_2 + \frac{1}{2} O_2 \rightarrow SO_3; \Delta H = -98.7 \text{ kJ}$
 $SO_3 + H_2O \rightarrow H_2SO_4; \Delta H = -130.2 \text{ kJ}$
 $H_2 + \frac{1}{2} O_2 \rightarrow H_2O; \Delta H = -227.3 \text{ kJ}$

the heat of formation of H_2SO_4 will be:

- (a) -754.4 kJ (b) $+320.5 \text{ kJ}$ (c) -650.3 kJ (d) -433.7 kJ

84. Which of the following units represents the largest amount of energy?

- (a) Electron-volt (b) Erg
 (c) Joule (d) Calorie

85. If ΔH_f° for $H_2O_2(l)$ and $H_2O(l)$ are -188 kJ mol^{-1} and -286 kJ mol^{-1} , what will be the enthalpy change of the reaction $2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$? [PMT (MP) 1992]

- (a) 146 kJ mol^{-1} (b) -196 kJ mol^{-1}
 (c) -494 kJ mol^{-1} (d) -98 kJ mol^{-1}

86. The bond dissociation energies for Cl_2 , I_2 and ICl are 242.3, 151 and 211.3 kJ/mol respectively. The enthalpy of sublimation of iodine is 62.8 kJ/mol . What is the standard enthalpy of formation of $ICl(g)$?

- (a) -211.3 kJ/mol (b) -14.6 kJ/mol
 (c) 16.8 kJ/mol (d) 33.5 kJ/mol

[Hint: $Cl_2(g) \rightarrow 2Cl(g); \Delta H_1 = 242.3 \text{ kJ/mol}$
 $I_2(g) \rightarrow 2I(g); \Delta H_2 = 151 \text{ kJ/mol}$
 $ICl(g) \rightarrow I(g) + Cl(g); \Delta H_3 = 211.3 \text{ kJ/mol}$
 $I_2(s) \rightarrow I_2(g); \Delta H_4 = 62.8 \text{ kJ/mol}$

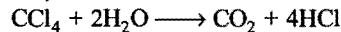
Required equation:

$$\frac{1}{2} I_2(s) + \frac{1}{2} Cl_2(g) \rightarrow ICl(g); \Delta H = ?$$

$$\Delta H = \frac{62.8 + 151 + 242.3}{2} - 211.3$$

$$= 16.75 \text{ kJ/mol}$$

87. Standard heat of formation for CCl_4 , H_2O , CO_2 and HCl at 298K are -25.5 , -57.8 , -94.1 and -22.1 kJ/mol respectively. For the reaction,



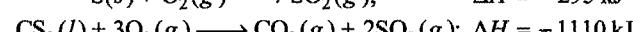
what will be ΔH ? [SCRA 2007]

- (a) 36.4 kJ (b) 20.7 kJ (c) -20.7 kJ (d) -414 kJ

88. Heat of combustion of CH_4 , C_2H_6 , C_2H_4 and C_2H_2 are -212.8 , -373.0 , -337.0 and -310.5 kcal respectively at the same temperature. The best fuel among these gases is:

- (a) CH_4 (b) C_2H_6
 (c) C_2H_4 (d) C_2H_2

89. Given, $C(s) + O_2(g) \rightarrow CO_2(g); \Delta H = -395 \text{ kJ}$
 $S(s) + O_2(g) \rightarrow SO_2(g); \Delta H = -295 \text{ kJ}$



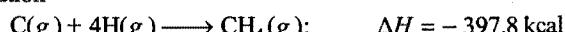
The heat of formation of $CS_2(l)$ is: [CEE (Bihar) 1992]

- (a) 250 kJ (b) 62.5 kJ (c) 31.25 kJ (d) 125 kJ

90. The heats of combustion of rhombic and monoclinic sulphur are -70960 and -71030 calorie respectively. What will be the heat of conversion of rhombic sulphur to monoclinic sulphur?

- (a) -70960 cal (b) -71030 cal
 (c) 70 cal (d) -70 cal

91. The bond dissociation energy of C—H in CH_4 from the equation



is:

- (a) $+99.45 \text{ kcal}$ (b) -99.45 kcal
 (c) $+397.8 \text{ kcal}$ (d) $+198.9 \text{ kcal}$

92. The dissociation energy of CH_4 is $400 \text{ kcal mol}^{-1}$ and that of ethane is $670 \text{ kcal mol}^{-1}$. The C—C bond energy is:

- (a) 270 kcal (b) 70 kcal (c) 200 kcal (d) 240 kcal

93. Heat of reaction at constant volume is measured in the apparatus:

- (a) bomb calorimeter (b) calorimeter
 (c) pycnometer (d) pyrometer

94. When 10 mL of a strong acid is added to 10 mL of an alkali, the temperature rises by 5°C . If 100 mL of the same acid is mixed with 100 mL of the same base, the temperature rise would be:

- (a) 5°C (b) 50°C
 (c) 20°C (d) cannot be predicted

95. Energy required to dissociate 4 g of gaseous hydrogen into free gaseous atoms is 208 kcal at 25°C . The bond energy of H—H bond will be:

- (a) 1.04 cal (b) 10.4 kcal
 (c) 104 kcal (d) 1040 kcal

96. The heat of neutralisation of strong base and strong acid is 57.0 kJ . The heat released when 0.5 mole of HNO_3 solution is added to 0.20 mole of $NaOH$ solution is: [KCET 1993]

- (a) 57.0 kJ (b) 28.5 kJ
 (c) 11.40 kJ (d) 34.9 kJ

97. The enthalpy of combustion of cyclohexane, cyclohexene and H_2 are respectively -3920 , -3800 and -241 kJ mol^{-1} . The heat of hydrogenation of cyclohexene is: [AIIMS 2007]

- (a) -121 kJ mol^{-1} (b) 121 kJ mol^{-1}
 (c) -242 kJ mol^{-1} (d) 242 kJ mol^{-1}

98. If $C(s) + O_2(g) \rightarrow CO_2(g); \Delta H = r$
 and $CO(g) + \frac{1}{2} O_2(g) \rightarrow CO_2(g); \Delta H = s$

then the heat of formation of CO is:

- (a) $r + s$ (b) $r - s$ (c) $s - r$ (d) $r \times s$

99. Given that, heat of neutralisation of strong acid and strong base is 57.1 kJ . Calculate the heat produced when 0.25 mole of HCl is neutralised with 0.25 mole of $NaOH$ in aqueous solution: [CPMT 1990]

- (a) 22.5 kJ (b) 57 kJ
 (c) 14.275 kJ (d) 28.55 kJ

100. Which one of the following values of ΔH° represents that the product is least stable?

- (a) $-94.0 \text{ kcal mol}^{-1}$ (b) $-231.6 \text{ kcal mol}^{-1}$
 (c) $+21.4 \text{ kcal mol}^{-1}$ (d) $+64.8 \text{ kcal mol}^{-1}$

101. The value of ΔH_{O-H} is $109 \text{ kcal mol}^{-1}$. The formation of one mole of water in gaseous state from $H(g)$ and $O(g)$ is accompanied by: [CBSE 1990]

- (a) 218 kcal (b) -109 kcal
 (c) -218 kcal (d) unpredictable

102. Heat of neutralisation of a strong dibasic acid in dilute solution by NaOH is nearly:
 (a) -27.4 kcal/eq (b) -13.7 kcal/eq
 (c) +13.7 kcal/eq (d) -13.7 kcal/mol

103. The enthalpy changes at 298 K in successive breaking of O—H bonds of water are



and $\text{OH}(g) \longrightarrow \text{H}(g) + \text{O}(g); \quad \Delta H = 428 \text{ kJ mol}^{-1}$

The bond enthalpy of O—H bond is:

- (a) 498 kJ mol⁻¹ (b) 428 kJ mol⁻¹
 (c) 70 kJ mol⁻¹ (d) 463 kJ mol⁻¹

104. ΔH and ΔE for the reaction, $\text{S}(s) + \frac{3}{2}\text{O}_2(g) \longrightarrow \text{SO}_3(g)$ are related as:

- (a) $\Delta H = \Delta E - 0.5RT$ (b) $\Delta H = \Delta E - 1.5RT$
 (c) $\Delta H = \Delta E + RT$ (d) $\Delta H = \Delta E + 1.5RT$

105. A spontaneous change is one in which the system suffers:
 (VITEEE 2008)

- (a) an increase in internal energy
 (b) lowering in entropy
 (c) lowering in free energy
 (d) no energy change

106. The free energy change for a reversible reaction at equilibrium is:

- (a) zero (b) positive
 (c) negative (d) none of these

107. In the evaporation of water, the entropy:

- (a) decreases (b) increases
 (c) does not change
 (d) sometimes increases, sometimes decreases

108. In which of the following change entropy decreases?

- (a) Crystallisation of sucrose from solution
 (b) Dissolving sucrose in water
 (c) Melting of ice
 (d) Vaporisation of camphor

109. For the precipitation reaction of Ag^+ ions with NaCl which of the following statements is true?

- (a) ΔH is zero for the reaction
 (b) ΔG is zero for the reaction
 (c) ΔG is negative for the reaction
 (d) ΔG should be equal to ΔH

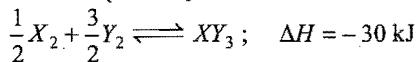
110. If enthalpy of vaporisation of water is 186.5 kJ/mol, the entropy of its vaporisation will be:

- (a) 0.5 (b) 1.0 (c) 1.5 (d) 2.0

111. A reaction is non-spontaneous when: [AMU (Medical) 2006]

- (a) ΔH is +ve, ΔS is -ve
 (b) both ΔH and ΔS are -ve
 (c) ΔH is -ve and ΔS is +ve
 (d) none of the above

112. Standard entropies of X_2 , Y_2 and XY_3 are 60, 40 and 50 $\text{JK}^{-1}\text{mol}^{-1}$ respectively. For the reaction:



to be at equilibrium, the temperature should be :

[CBSE (PMT) 2010]

- (a) 750 K (b) 1000 K
 (c) 1250 K (d) 500 K

$$\begin{aligned} [\text{Hint: } \Delta S &= \sum S_{\text{Products}} - \sum S_{\text{Reactants}} \\ &= 50 - \left[\frac{1}{2} \times 60 + \frac{3}{2} \times 40 \right] \\ &= 50 - (30 + 60) = -40 \text{ JK}^{-1} \text{ mol}^{-1} \end{aligned}$$

At equilibrium, $\Delta G = \Delta H - T\Delta S = 0$

$$\begin{aligned} i.e., \quad \Delta H &= T\Delta S \\ T &= \frac{\Delta H}{\Delta S} = \frac{-30 \times 1000}{-40} = 750 \text{ K} \end{aligned}$$

113. 'At absolute zero the entropy of a perfect crystal is zero.' This statement corresponds to which law of thermodynamics?

- (a) First law (b) Second law
 (c) Third law (d) None of these

114. Unit of entropy is: [PMT (Punjab) 2007]

- (a) $\text{JK}^{-1} \text{ mol}^{-1}$ (b) J mol^{-1}
 (c) $\text{J}^{-1} \text{ K}^{-1} \text{ mol}^{-1}$ (d) JK mol^{-1}

115. Given that $\Delta H_f(H) = 218 \text{ kJ/mol}$, express the H—H bond energy in kcal/mol: [EAMCET 2009]

- (a) 52.15 (b) 911
 (c) 109 (d) 5.2153

116. For which reaction from the following, ΔS will be maximum?

- (a) $\text{Ca}(s) + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{CaO}(s)$
 (b) $\text{CaCO}_3(s) \longrightarrow \text{CaO}(s) + \text{CO}_2(g)$
 (c) $\text{C}(s) + \text{O}_2(g) \longrightarrow \text{CO}_2(g)$
 (d) $\text{N}_2(g) + \text{O}_2(g) \longrightarrow 2\text{NO}(g)$

117. A particular reaction at 27°C for which $\Delta H > 0$ and $\Delta S > 0$ is found to be non-spontaneous. The reaction may proceed spontaneously if:

- (a) the temperature is decreased
 (b) the temperature is kept constant
 (c) the temperature is increased
 (d) it is carried in open vessel at 27°C

118. The least random state of water system is:

- (a) ice (b) liquid water
 (c) steam (d) randomness is same in all

119. Although the dissolution of ammonium chloride in water is an endothermic reaction, even then it is spontaneous because:

- (a) ΔH is positive, ΔS is -ve
 (b) ΔH is +ve, ΔS is zero
 (c) ΔH is positive, $T\Delta S < \Delta H$
 (d) ΔH is +ve, ΔS is positive and $\Delta H < T\Delta S$

120. For an exothermic reaction to be spontaneous:

- (a) temperature must be high
 (b) temperature must be zero
 (c) temperature may have any magnitude
 (d) temperature must be low

121. For the reversible process, the value of ΔS is given by the expression:

- (a) $\frac{q_{\text{rev}}}{T}$ (b) $T - q_{\text{rev}}$
 (c) $q_{\text{rev}} \times T$ (d) $q_{\text{rev}} - T$

122. In an electrochemical cell, if E° is the emf of the cell involving n mole of electrons, then ΔG° is:

(a) $\Delta G^\circ = nFE^\circ$ (b) $\Delta G^\circ = -nFE^\circ$
 (c) $E^\circ = nF \Delta G^\circ$ (d) $\Delta G^\circ = nF/E^\circ$

123. The correct relation between equilibrium constant (K), standard free energy (ΔG°) and temperature (T) is:

[CET (J&K) 2006]

(a) $\Delta G^\circ = RT \ln K$ (b) $K = e^{-\Delta G^\circ/2.303 RT}$
 (c) $\Delta G^\circ = -RT \log K$ (d) $K = 10^{-\Delta G^\circ/2.303 RT}$
 (e) $\Delta G^\circ = R \ln K$

124. The value of entropy in the universe is:

(a) constant (b) decreasing
 (c) increasing (d) zero

125. Which of the following thermodynamic relation is correct?

[JEE (WB) 2010]

(a) $dG = VdP - SdT$ (b) $dU = PdV + TdS$
 (c) $dH = -VdP + TdS$ (d) $dG = VdP + SdT$

[Hint : $dG = dH - TdS - SdT$

$$(G = H - TS)$$

$$dH = dU + PdV + VdP$$

$$(H = U + PV)$$

and $dU = TdS - PdV$

$$\therefore dG = (TdS - PdV) + PdV + VdP - TdS - SdT$$

$$dG = VdP - SdT$$

126. If enthalpies of formation for $C_2H_4(g)$, $CO_2(g)$ and $H_2O(l)$ at $25^\circ C$ and 1 atm pressure be 52, -394 and -286 kJ mol $^{-1}$ respectively, enthalpy of combustion of $C_2H_4(g)$ will be:

(CBSE 1995)

(a) +141.2 kJ mol $^{-1}$ (b) +1412 kJ mol $^{-1}$
 (c) -141.2 kJ mol $^{-1}$ (d) -1412 kJ mol $^{-1}$

127. Identify the correct statement regarding entropy: (CBSE 1998)

(a) at absolute zero, the entropy of a perfectly crystalline substance is + ve.
 (b) at absolute zero, the entropy of a perfectly crystalline substance is zero.
 (c) at $0^\circ C$ the entropy of a perfectly crystalline substance is taken to be zero.
 (d) at absolute zero of temperature the entropy of all crystalline substances is taken to be zero.

128. The enthalpy and entropy change for a chemical reaction are -2.5×10^{-3} cal and 7.4 cal deg $^{-1}$ respectively. Predict whether the nature of reaction at 298 K is: (AFMC 1998)

(a) spontaneous (b) reversible
 (c) irreversible (d) non-spontaneous

129. One mole of an ideal gas at 300 K is expanded isothermally from an initial volume of 1 litre to 10 litre. The ΔE for this process is: ($R = 2 \text{ cal K}^{-1} \text{ mol}^{-1}$) (CBSE 1998)

(a) 163.7 cal (b) 1381.1 cal
 (c) 9 litre-atm (d) zero

130. The latent heat of vaporisation of a liquid at 500 K and 1 atm pressure is 10 kcal/mol. What will be the change in internal energy (ΔE) of 3 moles of liquid at the same temperature?

(CBSE 1998)

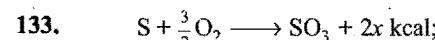
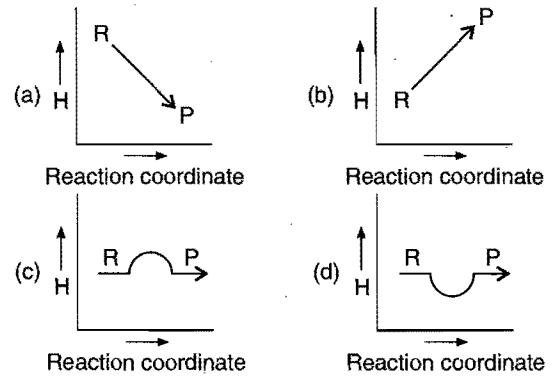
(a) 13.0 kcal (b) -13.0 kcal
 (c) 27.0 kcal (d) -27.0 kcal

131. The enthalpy change of a reaction does not depend on:

(AIIMS 1997)

(a) state of reactants and products
 (b) nature of reactants and products
 (c) different intermediate reactions
 (d) initial and final enthalpy change of reaction

132. Which plot represents an exothermic reaction?

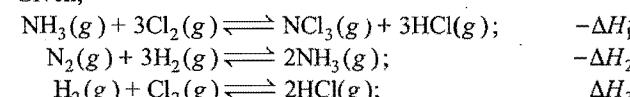


The heat of formation of SO_2 is:

[AIIMS 1997; PET (Kerala) 2008]

(a) $y - 2x$ (b) $2x + y$ (c) $x + y$ (d) $2x / y$

134. Given,



The heat of formation of $NCl_3(g)$ in terms of ΔH_1 , ΔH_2 and ΔH_3 is:

(EAMCET 1998)

$$(a) \Delta H_f = -\Delta H_1 + \frac{1}{2} \Delta H_2 - \frac{3}{2} \Delta H_3$$

$$(b) \Delta H_f = \Delta H_1 + \frac{1}{2} \Delta H_2 - \frac{3}{2} \Delta H_3$$

$$(c) \Delta H_f = \Delta H_1 - \frac{1}{2} \Delta H_2 - \frac{3}{2} \Delta H_3$$

(d) none of the above

135. The word 'standard' in standard molar enthalpy change implies:

(a) temperature 298 K
 (b) pressure 1 atm
 (c) temperature 298 K and pressure 1 atm
 (d) all temperatures and all pressures

136. The heat of formation (ΔH_f°) of $H_2O(l)$ is equal to:

(a) zero
 (b) molar heat of combustion of $H_2(l)$
 (c) molar heat of combustion of $H_2(g)$
 (d) sum of heat of formation of $H_2O(g)$ and $O_2(g)$

137. An example of extensive property is:

(a) temperature (b) internal energy
 (c) viscosity (d) molar heat capacity

138. For a diatomic molecule AB , the electronegativity difference between A and B is $0.2028 \sqrt{\Delta}$ [where, Δ = bond energy of

- AB – geometric mean of the bond energies of A_2 and B_2 . The electronegativities of fluorine and chlorine are 4.0 and 3.0 respectively and the bond energies are of F—F: 38 kcal mol⁻¹ and of Cl—Cl: 58 kcal mol⁻¹. The bond energy of Cl—F is:
- (a) ~ 71 kcal/mol (b) ~ 61 kcal/mol
 (c) ~ 48 kcal/mol (d) ~ 75 kcal/mol
139. The value of ΔH° for the reaction $Cu^+(g) + I^-(g) \rightarrow CuI(g)$ is -446 kJ mol⁻¹. If the ionisation energy of $Cu(g)$ is 745 kJ mol⁻¹ and the electron affinity of $I(g)$ is -295 kJ mol⁻¹, then the value of ΔH° for the formation of one mole of $CuI(g)$ from $Cu(g)$ and $I(g)$ is:
- (a) -446 kJ (b) 450 kJ (c) 594 kJ (d) 4 kJ
140. If the enthalpy change for the reaction,
 $CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g); \Delta H = -25$ kcal,
 Bond energy of C—H is 20 kcal mol⁻¹ greater than the bond energy of C—Cl and bond energies of H—H and H—Cl are same in magnitude, then for the reaction $H_2(g) + Cl_2(g) \rightarrow 2HCl(g), \Delta H = ?$
- (a) -22.5 kcal/mol (b) -20.5 kcal/mol
 (c) -32.5 kcal/mol (d) -12.5 kcal/mol
141. The standard heat of formation of sodium ions in aqueous solution from the following data:
 Heat of formation of $NaOH(aq.)$ at $25^\circ C = -470.7$ kJ
 Heat of formation of $OH^-(aq.)$ at $25^\circ C = -228.8$ kJ
 is:
 (a) -251.9 kJ (b) 241.9 kJ (c) -241.9 kJ (d) 251.9 kJ
142. AB, A_2 and B_2 are diatomic molecules. If the bond enthalpies of A_2, AB and B_2 are in the ratio 1:1:0.5 and the enthalpy of formation of AB from A_2 and B_2 is -100 kJ mol⁻¹, what is the bond enthalpy of A_2 ?
 (a) 400 kJ mol⁻¹ (b) 200 kJ mol⁻¹
 (c) 100 kJ mol⁻¹ (d) 300 kJ mol⁻¹
143. The lattice energy of solid NaCl is 180 kcal per mol. The dissolution of the solid in water in the form of ions is endothermic to the extent of 1 kcal per mol. If the solvation energies of Na^+ and Cl^- ions are in the ratio 6 : 5, what is the enthalpy of hydration of sodium ion?
 (a) -85.6 kcal/mol (b) -97.5 kcal/mol
 (c) 82.6 kcal/mol (d) +100 kcal/mol
144. Which one of the following statements is false?
 [IIT (Screening) 2000, 01]
 (a) Work is a state function
 (b) Temperature is a state function
 (c) Work appears at the boundary of the system
 (d) Change in the state is completely defined when the initial and final states are specified.
145. ΔG° for the reaction $x + y \rightleftharpoons z$ is -4.606 kcal. The value of equilibrium constant of the reaction at $227^\circ C$ is:
 (IIT 1999)
 (a) 100 (b) 10 (c) 2 (d) 0.01
 $(R = 2.0 \text{ cal K}^{-1} \text{ mol}^{-1})$
 [Hint: $\Delta G^\circ = -RT \times 2.303 \times \log K$]
146. The enthalpy of solution of $BaCl_2(s)$ and $BaCl_2 \cdot 2H_2O(s)$ are -20.6 and 8.8 kJ mol⁻¹, respectively. The enthalpy change for the reaction is:
 (IIT 1998)
147. (a) 29.8 kJ (b) -11.8 kJ
 (c) -20.6 kJ (d) -29.4 kJ
148. For the reaction,
 $A(g) + 2B(g) \rightarrow 2C(g) + 3D(g)$
 the value of ΔH at $27^\circ C$ is 19.0 kcal. The value of ΔE for the reaction would be: (Given, $R = 2.0 \text{ cal K}^{-1} \text{ mol}^{-1}$): (IIT 1998)
 (a) 20.8 kcal (b) 19.8 kcal (c) 18.8 kcal (d) 17.8 kcal
149. In thermodynamics, a process is called reversible when:
 [IIT (Screening) 2000, 01]
 (a) surroundings and system change into each other
 (b) there is no boundary between system and surroundings
 (c) the surroundings are always in equilibrium with the system
 (d) the system changes into the surroundings spontaneously
150. The heat liberated when 1.89 g of benzoic acid is burnt in a bomb calorimeter at $25^\circ C$ increases the temperature of 18.94 kg of water by 0.632°C. If the specific heat of water at $25^\circ C$ is 0.998 cal g⁻¹ deg⁻¹, the value of heat of combustion of benzoic acid is:
 (a) 881.1 kcal (b) 771.4 kcal
 (c) 981.1 kcal (d) 871.2 kcal
 [Hint: Heat liberated by 1.89 g of benzoic acid,

$$q = ms\Delta T$$

$$= 18940 \times 0.998 \times 0.632$$

$$= 11946.14 \text{ cal}$$

 Heat liberated by the combustion of
 1 mol benzoic acid, i.e.,
 122 g benzoic acid

$$= \frac{11946.14}{189} \times 122 = 771126.5 \text{ cal}$$

$$= 771.12 \text{ kcal mol}^{-1}]$$
151. One mole of a non-ideal gas undergoes a change state (2 atm, 3 L, 95 K) to (4 atm, 5 L, 245 K) with a change of internal energy, $\Delta U = 30 \text{ L atm}$. The change in enthalpy (ΔH) of the process in L atm.:
 (a) 40.0 (b) 42.3
 (c) 44.0 (d) not defined, because pressure is not constant
 [IIT (S) 2002]
152. Which of the following reactions defines ΔH_f° ?
 [IIT (S) 2003]
 (a) $C_{(\text{diamond})} + O_2(g) \rightarrow CO_2(g)$
 (b) $\frac{1}{2} H_2(g) + \frac{1}{2} F_2(g) \rightarrow HF(g)$
 (c) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$
 (d) $CO(g) + \frac{1}{2} O_2(g) \rightarrow CO_2(g)$
153. If the enthalpies of formation of Al_2O_3 and Cr_2O_3 are -1596 kJ and -1134 kJ respectively, then the value of ΔH for the reaction;
 $2Al + Cr_2O_3 \rightarrow 2Cr + Al_2O_3$ is: (AIIMS 2004)
 (a) -462 kJ (b) -1365 kJ
 (c) -2530 kJ (d) +2530 kJ
 [PMT (Himachal) 2006]
 (a) $\Delta G > 0$ (b) $\Delta G < 0$ (c) $\Delta G = 0$ (d) $\Delta G = T \Delta S$

154. Considering entropy(s) as a thermodynamic parameter, the criterion for the spontaneity of any process is:

[CBSE (PMT) 2004]

- (a) $\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$
- (b) $\Delta S_{\text{system}} - \Delta S_{\text{surroundings}} > 0$
- (c) $\Delta S_{\text{system}} > 0$ only
- (d) $\Delta S_{\text{surroundings}} > 0$ only

155. An ideal gas expands in volume from $1 \times 10^{-3} \text{ m}^3$ to $1 \times 10^{-2} \text{ m}^3$ at 300 K against a constant pressure of $1 \times 10^5 \text{ Nm}^{-2}$. The work done is: [AIEEE 2004]

- (a) -900 J
- (b) -900 kJ
- (c) 270 kJ
- (d) +900 kJ

156. What is the value of internal energy change (ΔU) at 27°C of a gaseous reaction $2A_2(g) + 5B_2(g) \rightarrow 2A_2B_5(g)$ (whose heat change at constant pressure is -50700 J)?

$$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \quad (\text{SCRA 2009})$$

- (a) -50700 J
- (b) -63171 J
- (c) -38229 J
- (d) +38229 J

[Hint: $\Delta H = \Delta U + \Delta n_g RT$

$$-50700 = \Delta U + (-5) \times 8.314 \times 300$$

$$\Delta U = -38229 \text{ J}$$

157. Two mole of an ideal gas is expanded isothermally and reversibly from 1 litre to 10 litre at 300 K. The enthalpy change (in kJ) for the process is: [IIT (S) 2004]

- (a) 11.4 kJ
- (b) -11.4 kJ
- (c) 0 kJ
- (d) 4.8 kJ

158. The enthalpy of vaporization of a liquid is 30 kJ mol^{-1} and entropy of vaporization is $75 \text{ J mol}^{-1} \text{ K}^{-1}$. The boiling point of the liquid at 1 atm is: [IIT (S) 2004]

- (a) 250 K
- (b) 400 K
- (c) 450 K
- (d) 600 K

159. The sublimation energy of $I_2(s)$ is 57.3 kJ/mol and the enthalpy of fusion is 15.5 kJ/mol. The enthalpy of vaporisation of I_2 is: [DCE 2005]

- (a) 41.8 kJ/mol
- (b) -41.8 kJ/mol
- (c) 72.8 kJ/mol
- (d) -72.8 kJ/mol

[Hint: $\Delta H_{\text{sublimation}} = \Delta H_{\text{fusion}} + \Delta H_{\text{vaporation}}$]

160. ΔH and ΔS for a reaction are $+30.558 \text{ kJ mol}^{-1}$ and $0.066 \text{ kJ K}^{-1} \text{ mol}^{-1}$ at 1 atm pressure. The temperature at which free energy change is zero and the nature of the reaction below this temperature is: [PET (Kerala) 2005]

- (a) 483 K, spontaneous
- (b) 443 K, non-spontaneous
- (c) 443 K, spontaneous
- (d) 463 K, non-spontaneous
- (e) 463 K, spontaneous

161. What would be the amount of heat released when an aqueous solution containing 0.5 mole of HNO_3 is mixed with 0.3 mole of OH^- (enthalpy of neutralisation is -57.1 kJ)?

[PET (Kerala) 2005]

- (a) 28.5 kJ
- (b) 17.1 kJ
- (c) 45.7 kJ
- (d) 1.7 kJ
- (e) 2.85 kJ

[Hint: 0.3 mole OH^- ion will be completely neutralised,

$$\therefore \Delta H = -57.1 \times 0.3 = -17.13 \text{ kJ}$$

162. A process in which the system does not exchange heat with the surroundings is known as: [CET (J&K) 2005]

- (a) isothermal
- (b) isobaric
- (c) isochoric
- (d) adiabatic

163. The entropy of a crystalline substance at absolute zero on the basis of third law of thermodynamics should be taken as:

[CET (J&K) 2005]

- (a) 100
- (b) 50

- (c) zero
- (d) different for different substances

164. Which of the following expressions is correct?

[JEE (Orissa) 2005]

(a) $\Delta G^\circ = -nFE^\circ$

(b) $\Delta G^\circ = +nFE^\circ$

(c) $\Delta G^\circ = -2.303RTnFE_{\text{cell}}^\circ$

(d) $\Delta G^\circ = -nF \log K_c$

165. Consider the reaction, $\text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g)$; carried out at constant temperature and pressure. If ΔH and ΔU are enthalpy change and internal energy change respectively, which of the following expressions is true?

[AIEEE 2005]

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

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

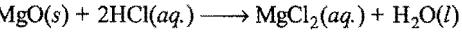
(c) $\Delta H < \Delta U$

(d) $\Delta H > \Delta U$

[Hint: $\Delta H = \Delta U + \Delta nRT$, $\Delta n = 2 - 4 = -2$

$$\therefore \Delta H < \Delta U$$

166. The absolute enthalpy of neutralisation of the reaction,



will be:

(a) -57.33 kJ mol⁻¹

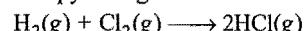
(b) greater than -57.33 kJ mol⁻¹

(c) less than -57.33 kJ mol⁻¹

(d) 57.33 kJ mol⁻¹

[Hint: Since, MgO is an oxide of a weak base, hence its neutralisation will evolve the heat less than 57.33 kJ mol⁻¹]

167. The entropy values (in $\text{J K}^{-1} \text{ mol}^{-1}$) of $\text{H}_2(g) = 130.6$, $\text{Cl}_2(g) = 223$ and $\text{HCl}(g) = 186.7$ at 298 K and 1 atm pressure are given. Then entropy change for the reaction,



is:

[BHU (Pre) 2005]

(a) +540.3

(b) +727.3

(c) -166.9

(d) +19.8

168. A mixture of 2 mole of $\text{CO}(g)$ and one mole of O_2 , in a closed vessel, is ignited to convert the carbon monoxide to carbon dioxide. If ΔH and ΔU are enthalpy and internal energy change, then:

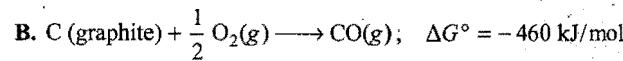
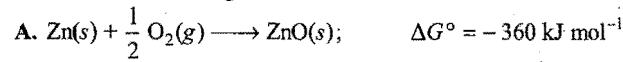
(a) $\Delta H > \Delta U$

(b) $\Delta H < \Delta U$

(c) $\Delta H = \Delta U$

(d) the relationship depends on the capacity of the vessel

169. Consider the following reactions at 1000°C:



Choose the correct statement at 1000°C:

[PMT (Kerala) 2006]

(a) zinc can be oxidised by carbon monoxide.

(b) ZnO can be reduced by graphite.

(c) both (a) and (b) are true.

(d) both (a) and (b) are false.

(e) carbon monoxide can be reduced by zinc.

170. Which one of the following equations does not correctly represent the first law of thermodynamics for the given process?

[PET (Kerala) 2006]

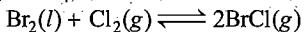
- (a) Isothermal process : $q = -w$
 (b) Cyclic process : $q = -w$
 (c) Isochoric process : $\Delta U = q$
 (d) Adiabatic process : $\Delta U = -w$
 (e) Expansion of gas into vacuum : $\Delta U = q$
- [Hint: In adiabatic process : $q = 0$]

$$\therefore \text{From } \Delta U = q - w$$

Work is done by the system,

$$\Delta U = -w \quad [\text{for adiabatic process}]$$

171. The enthalpy and entropy changes for the reaction:



are 30 kJ mol^{-1} and $105 \text{ J K}^{-1} \text{ mol}^{-1}$ respectively. The temperature at which the reaction will be in equilibrium is:

[CBSE (Med.) 2006]

- (a) 285.7 K (b) 273 K (c) 450 K (d) 300 K

172. $(\Delta H - \Delta U)$ for the formation of carbon monoxide (CO) from its element at 298 K is: ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)

(AIEEE 2006)

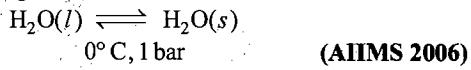
- (a) $-1238.78 \text{ J mol}^{-1}$ (b) $1238.78 \text{ J mol}^{-1}$
 (c) $-2477.57 \text{ J mol}^{-1}$ (d) $2477.57 \text{ J mol}^{-1}$

[Hint: $\text{C}(s) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{CO}(g)$ $\Delta n_g = 1 - \frac{1}{2} = \frac{1}{2}$

$$\Delta H - \Delta U = \Delta nRT$$

$$= \frac{1}{2} \times 8.314 \times 298 = 1238.786 \text{ J mol}^{-1}$$

173. For a phase change:



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

174. We can drive any thermodynamically forbidden reaction in the desired direction by coupling with: [PET (Kerala) 2006]

- (a) highly exothermic reaction
 (b) highly endothermic reaction
 (c) highly exergonic reaction
 (d) highly endergonic reaction
 (e) reaction with large positive ΔS values

175. Given that, bond energies of $\text{H} - \text{H}$ and $\text{Cl} - \text{Cl}$ are 430 kJ/mol and 240 kJ/mol respectively. ΔH_f for HCl is -90 kJ/mol . Bond enthalpy of HCl is: [CBSE (Med.) 2007]

- (a) 380 kJ mol^{-1} (b) 425 kJ mol^{-1}
 (c) 245 kJ mol^{-1} (d) 290 kJ mol^{-1}

176. The amount of heat released, when 20 mL of 0.5 M NaOH is mixed with 100 mL of 0.1 M HCl , is $x \text{ kJ}$. The heat of neutralization (in kJ mol^{-1}) is: [BHU (Mains) 2007]

- (a) $-100x$ (b) $-50x$ (c) $+100x$ (d) $+50x$

[Hint: Number of moles of $\text{NaOH} = \frac{MV}{1000} = \frac{0.5 \times 20}{1000} = 0.01$

$$\text{Number of moles of HCl} = \frac{MV}{1000} = \frac{0.1 \times 100}{1000} = 0.01$$

$$\text{Heat of neutralization} = \frac{-x}{0.01} = -100x$$

177. In the conversion of limestone to lime,
 $\text{CaCO}_3(s) \rightarrow \text{CaO}(s) + \text{CO}_2(g)$
 the values of ΔH° and ΔS° are $+179.1 \text{ kJ mol}^{-1}$ and

$160.2 \text{ JK}^{-1} \text{ mol}^{-1}$ respectively at 298 K and 1 bar . Assuming that, ΔH° and ΔS° do not change with temperature; temperature above which conversion of limestone to lime will be spontaneous is: [AIEEE 2007]

- (a) 1118 K (b) 1008 K (c) 1200 K (d) 845 K
178. Assuming that, water vapour is an ideal gas, the internal energy change (ΔU) when 1 mol of water is vaporised at 1 bar pressure and 100°C , (given: molar enthalpy of vaporisation of water at 1 bar and $373\text{K} = 41 \text{ kJ mol}^{-1}$ and $R = 8.3 \text{ JK}^{-1} \text{ mol}^{-1}$) will be:

(AIEEE 2007)

- (a) $41.00 \text{ kJ mol}^{-1}$ (b) $4.100 \text{ kJ mol}^{-1}$
 (c) $3.7904 \text{ kJ mol}^{-1}$ (d) $37.904 \text{ kJ mol}^{-1}$

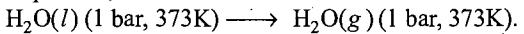
[Hint: $\Delta U = \Delta H - \Delta nRT$

$$= 41000 - 1 \times 8.314 \times 373$$

$$= 37898.878 \text{ J mol}^{-1}$$

$$= 37.9 \text{ kJ mol}^{-1}$$

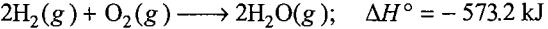
179. For the process,



The correct set of thermodynamic parameters is: [IIT 2007]

- (a) $\Delta G = 0, \Delta S = +\text{ve}$ (b) $\Delta G = 0, \Delta S = -\text{ve}$
 (c) $\Delta G = +\text{ve}, \Delta S = 0$ (d) $\Delta G = -\text{ve}, \Delta S = +\text{ve}$

180. For the reaction,



The heat of decomposition of water per mol is:

(MHT-CET 2007)

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

181. The free energy change $\Delta G = 0$, when: [CET (J&K) 2007]

- (a) the reactants are completely consumed
 (b) a catalyst is added
 (c) the system is at equilibrium
 (d) the reactants are initially mixed

182. In a closed container, a liquid is stirred with a paddle to increase the temperature, which of the following is true?

(PMT (Pb.) 2007)

- (a) $\Delta U = \Delta W \neq 0, q = 0$ (b) $\Delta U = W = 0, q \neq 0$
 (c) $\Delta U = 0, W = q \neq 0$ (d) $W = 0, \Delta U = q \neq 0$

183. For the gas phase reaction,



Which of the following conditions are correct?

[CBSE-PMT (Pre) 2008]

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

184. Which of the following is correct? [BHU (Screening) 2008]

- (a) $C_V = \left(\frac{\partial U}{\partial T}\right)_P$ (b) $C_P = \left(\frac{\partial H}{\partial T}\right)_V$
 (c) $C_P - C_V = R$ (d) $\left(\frac{\partial U}{\partial V}\right)_T = -\frac{a}{V^2}$

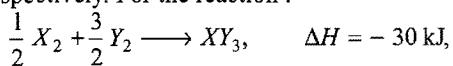
(Internal pressure in van der Waals' equation)

185. Which of the following represents total kinetic energy of one mole of gas?

[IIT (Orissa) 2008]

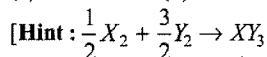
- (a) $\frac{1}{2}RT$ (b) $\frac{3}{2}RT$ (c) $(C_P - C_V)RT$ (d) $\frac{2}{3}RT$

186. Standard entropy of X_2 , Y_2 and XY_3 are 60, 40 and $50 \text{ J K}^{-1} \text{ mol}^{-1}$ respectively. For the reaction :



to be at equilibrium, the temperature will be : (AIEEE 2008)

- (a) 1000K (b) 1250K (c) 500K (d) 750K



$$\begin{aligned}\Delta S^\circ_{\text{Reaction}} &= \Delta S^\circ_{XY_3} - \frac{1}{2}\Delta S^\circ_{X_2} - \frac{3}{2}\Delta S^\circ_{Y_2} \\ &= 50 - \frac{1}{2} \times 60 - \frac{3}{2} \times 40 = -40 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

$\Delta G = \Delta H - T \Delta S = 0$ at equilibrium.

$$\therefore T = \frac{\Delta H}{\Delta S} = \frac{-30 \times 1000}{40} = 750 \text{ K}$$

187. 4.48 L of an ideal gas at S.T.P requires 12 calories to raise its temperature by 15°C at constant volume. The C_p of the gas is :

[PMT (Kerala) 2009]

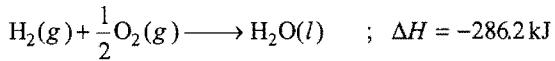
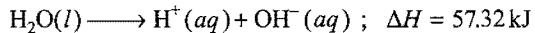
- (a) 3 cal (b) 4 cal (c) 7 cal (d) 6 cal
(e) 9 cal

[Hint : $C_V = \frac{\Delta U}{n \Delta T}$, $n = \frac{4.48}{2.24} = 0.2$
 $= \frac{12}{0.2 \times 15} = 4 \text{ cal}$

$$C_P = C_V + R = 4 + 2 = 6 \text{ cal}]$$

188. On the basis of following thermochemical data :

$[\Delta_f G^\circ \text{H}^+(aq) = 0]$

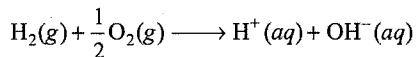


The value of enthalpy of formation of OH^- ion at 25°C is :

(AIEEE 2009)

- (a) -22.88 kJ (b) -228.88 kJ
(c) +228.88 kJ (d) -343.52 kJ

[Hint : The equation for the formation of $\text{OH}^-(aq)$ is:



It is obtained by adding the two given equations :

$$\Delta H = 57.32 + (-286.2) = -228.88 \text{ kJ}]$$

189. The values of ΔH and ΔS for the reaction,

$\text{C}(\text{graphite}) + \text{CO}_2(g) \longrightarrow 2\text{CO}(g)$ are 170 kJ and 170 J K^{-1} respectively. This reaction will be spontaneous at :

[CBSE (PMT) Pre 2009]

- (a) 510 K (b) 710 K (c) 910 K (d) 1110 K

[Hint : $\Delta G = \Delta H - T\Delta S$, ΔG should be negative for spontaneous process.]

$$\therefore \Delta H - T\Delta S < 0$$

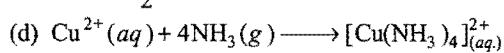
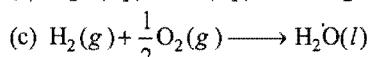
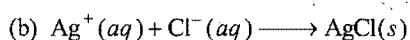
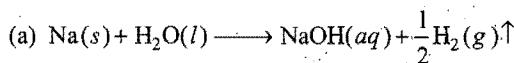
$$\Delta H < T\Delta S$$

$$\text{or } T > \frac{\Delta H}{\Delta S}, \quad T > \frac{170 \times 1000}{170}$$

$$T > 1000 \text{ K}]$$

190. In which reaction, there will be increase in entropy?

(DCE 2009)

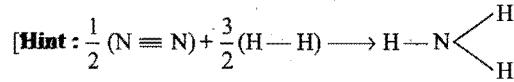


191. The species which by definition has zero standard molar enthalpy of formation at 298 K is: (IIT 2010)

- (a) $\text{Br}_2(g)$ (b) $\text{Cl}_2(g)$
(c) $\text{H}_2\text{O}(g)$ (d) $\text{CH}_4(g)$

192. The standard enthalpy of formation of NH_3 is -46 kJ mol^{-1} . If the enthalpy of formation of H_2 from its atoms is -436 kJ mol^{-1} and that of N_2 is -712 kJ mol^{-1} , the average bond enthalpy of N—H bond in NH_3 is: (AIEEE 2010)

- (a) $+1056 \text{ kJ mol}^{-1}$ (b) $-1102 \text{ kJ mol}^{-1}$
(c) -964 kJ mol^{-1} (d) $+352 \text{ kJ mol}^{-1}$



$$\Delta H = -46 \text{ kJ mol}^{-1}$$

$$\text{BE}(\text{N} \equiv \text{N}) = -712 \text{ kJ mol}^{-1}$$

$$\text{BE}(\text{H}—\text{H}) = -436 \text{ kJ mol}^{-1}$$

Let B.E. of $(\text{N}—\text{H}) = x \text{ kJ mol}^{-1}$

$$\Delta H = \sum(\text{B.E.})_{\text{Reactants}} - \sum(\text{B.E.})_{\text{Products}}$$

$$-46 = \left[\frac{1}{2}(712) + \frac{3}{2}(436) \right] - 3x$$

$$x = 352 \text{ kJ mol}^{-1}$$

193. A 1 g sample of substance A at 100°C is added to 100 mL of H_2O at 25°C . Using separate 100 mL portion of H_2O , the procedure is repeated with substance B and then with substance C . How will the final temperatures of the water compare?

Substance Specific heat

$$A \quad 0.6 \text{ J g}^{-1} \text{ °C}^{-1}$$

$$B \quad 0.4 \text{ J g}^{-1} \text{ °C}^{-1}$$

$$C \quad 0.2 \text{ J g}^{-1} \text{ °C}^{-1}$$

(DUMET 2010)

- (a) $T_C > T_B > T_A$ (b) $T_B > T_A > T_C$
(c) $T_A > T_B > T_C$ (d) $T_A = T_B = T_C$

[Hint : $q = ms\Delta T$

$$s \propto \frac{1}{\Delta T}$$

Higher is the temperature of given solution, lesser is the temperature difference, so higher is the specific heat. Order of specific heat is $A > B > C$. Hence order of temperature will be : $T_A > T_B > T_C$]

194. For vaporisation of water at 1 atmospheric pressure, the values of ΔH and ΔS are $40.63 \text{ kJ mol}^{-1}$ and $108.8 \text{ J K}^{-1} \text{ mol}^{-1}$ respectively. The temperature when Gibbs free energy change (ΔG) for transformation will be zero, is: (CBSE (PMT) 2010)

- (a) 273.4 K (b) 393.4 K
(c) 373.4 K (d) 293.4 K

[Hint : $\Delta G = \Delta H - T\Delta S$

$$0 = 40.63 \times 1000 - T \times 108.8$$

$$T = 373.4 \text{ K}$$

Set-2: The questions given below may have more than one correct answers

1. Which is intensive property?
 - (a) Mass
 - (b) Mass/volume
 - (c) Volume
 - (d) Volume/mass
2. Which is an irreversible process?
 - (a) Mixing of two gases by diffusion
 - (b) Evaporation of water at 373 K and 1 atm pressure
 - (c) Dissolution of NaCl in water
 - (d) All of the above
3. One mole of anhydrous $MgCl_2$ dissolves in water and liberates 25 cal/mol of heat. $\Delta H_{\text{hydration}}$ of $MgCl_2 \cdot H_2O$ is:
 - (a) +5 cal/mol
 - (b) -5 cal/mol
 - (c) 55 cal/mol
 - (d) -55 cal/mol
4. Following enthalpy changes are given:

| | |
|---|-------------------------------|
| α -D glucose(s) \longrightarrow α -D glucose(aq); | $\Delta H = 10.72 \text{ kJ}$ |
| β -D glucose(s) \longrightarrow β -D glucose(aq); | $\Delta H = 4.68 \text{ kJ}$ |
| α -D glucose(s) \longrightarrow β -D glucose(aq); | $\Delta H = 1.16 \text{ kJ}$ |

 Calculate the enthalpy change in,
 α -D glucose(s) \longrightarrow β -D glucose(s)
 - (a) 14.24 kJ
 - (b) 16.56 kJ
 - (c) -7.2 kJ
 - (d) 4.88 kJ
5. If x and y are arbitrary extensive variables, then:
 - (a) $(x + y)$ is an extensive variable
 - (b) x/y is an intensive variable
 - (c) dx/dy is an intensive variable
 - (d) both (b) and (c)
6. If x and y are arbitrary intensive variables, then:
 - (a) xy is an intensive variable
 - (b) x/y is an intensive variable
 - (c) $(x + y)$ is an extensive property
 - (d) dx/dy is an intensive property
7. $H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(g); \quad \Delta H = x$
 $H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l); \quad \Delta H = y$
 Heat of vaporization of water is:
 - (a) $x + y$
 - (b) $x - y$
 - (c) $y - x$
 - (d) $-(x + y)$
8. Which is correct about ΔG ?
 - (a) $\Delta G = \Delta H - T \Delta S$
 - (b) At equilibrium, $\Delta G^\circ = 0$
 - (c) At eq. $\Delta G = -RT \log K$
 - (d) $\Delta G = \Delta G^\circ + RT \log K$
9. Dissociation of sodium azide is given by,

$$NaN_3 \longrightarrow Na + 3/2N_2;$$
 ΔH for this is:
- (a) $\frac{3}{2}\Delta H_f^\circ(N_2) - \Delta H_f^\circ(NaN_3)$
- (b) $-\Delta H_f^\circ(NaN_3)$
- (c) $\Delta H_f^\circ(NaN_3) - [\Delta H_f^\circ(Na) + \frac{3}{2}\Delta H_f^\circ(N_2)]$
- (d) $\Delta H_f^\circ(Na) + \frac{3}{2}\Delta H_f^\circ(N_2) - \Delta H_f^\circ(NaN_3)$
10. The lattice energy of KCl is 202 kcal/mol. When KCl is dissolved in water 2 kcal/mol is absorbed. If the sol energies of K^+ and Cl^- are in the ratio 2 : 3; then $\Delta H_{\text{hydration}}$ of K^+ is:
 - (a) -80 kJ/mol
 - (b) -120 kJ/mol
 - (c) -150 kJ/mol
 - (d) 133.3 kJ/mol
11. Which is a correct relationship?
 - (a) $\left[\frac{dH}{dT} \right]_p - \left[\frac{dE}{dT} \right]_T = (+ve)$
 - (b) $\left[\frac{dE}{dV} \right]_T = 0$ (for ideal gas)
 - (c) $\left[\frac{dV}{dT} \right]_p = \frac{nR}{P}$ (for ideal gas)
 - (d) All of the above
12. The standard Gibbs free energy ΔG° is related to equilibrium constant K_P as:
 - (a) $K_P = -RT \log \Delta G^\circ$
 - (b) $K_P = [e/RT]^{\Delta G^\circ}$
 - (c) $K_P = -\Delta G^\circ/RT$
 - (d) $K_P = e^{-\Delta G^\circ/RT}$
13. For the two equations given below:

$$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l) + x_1 \text{ kJ}$$

$$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(g) + x_2 \text{ kJ}$$
 Select the correct answer:
 - (a) $x_1 > x_2$
 - (b) $x_2 > x_1$
 - (c) $x_1 = x_2$
 - (d) $x_1 + x_2 = 0$
14. $\Delta E = 0$, for which process?
 - (a) Cyclic process
 - (b) Isothermal expansion
 - (c) Isochoric process
 - (d) Adiabatic process
15. For a reaction to be spontaneous in neither direction, which of the following is/are correct regarding the closed system?
[BHU (Mains) 2007]
 - (1) $(\Delta G)_{T,P} = 0$
 - (2) $(\Delta G)_{T,P} < 0$
 - (3) $(\Delta S)_{U,V} = 0$
 - (4) $(\Delta S)_{U,V} > 0$

Codes:

 - (a) 1, 2 and 3 are correct
 - (b) 1 and 2 are correct
 - (c) 2 and 4 are correct
 - (d) 1 and 3 are correct

Assertion-Reason TYPE QUESTIONS

Set-1

The questions given below consist of an 'Assertion' (A) and the 'Reason' (R). Use the following keys to choose the appropriate answer:

- (a) If both (A) and (R) are correct and (R) is the correct explanation for (A).
 - (b) If both (A) and (R) are correct but (R) is not the correct explanation for (A).
 - (c) If (A) is correct but (R) is incorrect.
 - (d) If (A) is incorrect but (R) is correct.
1. (A) The endothermic reactions are favoured at lower temperature and the exothermic reactions are favoured at higher temperature.
(R) When a system in equilibrium is disturbed by changing the temperature, it will tend to adjust itself so as to overcome the effect of the change.
 2. (A) $C_P - C_V = R$ for an ideal gas.
(R) $\left[\frac{\partial E}{\partial V} \right]_T = 0$ for an ideal gas.
 3. (A) When hydrogen gas at high pressure and room temperature expands adiabatically into a region of low pressure, there is a decrease in temperature.
(R) Hydrogen gas at room temperature is above its inversion temperature.
 4. (A) The thermodynamic factor which determines the spontaneity of a process is the free energy. For a process to be spontaneous the free energy must be -ve.
(R) The change in free energy is related to the change in enthalpy and change in entropy. The change in entropy for a process must always be positive if it is spontaneous.
 5. (A) The Joules-Thomson coefficient for an ideal gas is zero.
(R) There are no intermolecular attractive forces in an ideal gas.
 6. (A) As temperature increases, heat of reaction also increases for exothermic as well as endothermic reactions.
(R) $\Delta H_{\text{reaction}}$ varies according to the relation:

$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_P$$
 7. (A) All exothermic reactions are spontaneous at room temperature.
(R) $\Delta G = -ve$ for above reactions and for spontaneous reactions $\Delta G = -ve$.
 8. (A) Efficiency of a reversible engine is 100% (maximum) when the temperature of sink is -273°C .
(R) Efficiency of engine, $\eta = \frac{T_2 - T_1}{T_2}$.

Set-2

The questions given below consist of statements 'Assertion' (A) and 'Reason' (R).

- (a) If both (A) and (R) are correct and (R) is the correct reason for (A).
 - (b) If both (A) and (R) are correct but (R) is not the correct explanation for (A).
 - (c) If (A) is true but (R) is false.
 - (d) If both (A) and (R) are false.
1. (A) Enthalpy of graphite is lower than that of diamond.
(R) Entropy of graphite is lower than that of diamond.
(AIIMS 1994)
 2. (A) The enthalpy of formation of gaseous oxygen molecules at 298 K and under a pressure of one atm is zero.
(R) The entropy of formation of gaseous oxygen molecules under the same condition is zero.
(AIIMS 1996)
 3. (A) Heat of neutralization for both HNO_3 and HCl with NaOH is 53.7 kJ per mol.
(R) NaOH is a strong electrolyte/base.
(AIIMS 1997)
 4. (A) Decrease in free energy causes spontaneous reaction.
(R) Spontaneous reactions are invariably exothermic.
(AIIMS 1997)
 5. (A) Many endothermic reactions that are not spontaneous at room temperature become spontaneous at high temperature.
(R) Entropy of the system increases with increase in temperature.
(AIIMS 1998)
 6. (A) The enthalpy of formation of $\text{H}_2\text{O}(l)$ is greater than that of $\text{H}_2\text{O}(g)$.
(R) Enthalpy change is negative for the condensation reaction

$$\text{H}_2\text{O}(g) \longrightarrow \text{H}_2\text{O}(l)$$
 7. (A) For a particular reaction, heat of combustion at constant pressure (q_P) is always greater than that at constant volume (q_V).
(R) Combustion reactions are invariably accomplished by increase in number of moles.
(AIIMS 1998)
 8. (A) The enthalpy of both graphite and diamond is taken to be zero, being elementary substances.
(R) The enthalpy of formation of an elementary substance in any state is taken as zero.
 9. (A) Heat of neutralization of perchloric acid, HClO_4 , with NaOH is same as that of HCl with NaOH .
(R) Both HCl and HClO_4 are strong acids.
 10. (A) Heat of ionization of water is equal to the heat of neutralization of a strong acid with a strong base.
(R) Water ionizes to a very small extent while H^+ ions from acid combine very rapidly with OH^- from base to form H_2O .

- 11.** (A) Enthalpy of formation of HCl is equal to the bond energy of HCl.
 (R) Enthalpy of formation and bond energy both involve formation of one mole of HCl from the elements.
- 12.** (A) Pressure, volume and temperature are all extensive properties.
 (R) Extensive properties depend upon the amount and nature of the substance.
- 13.** (A) When a gas at high pressure expands against vacuum, the work done is maximum.
 (R) Work done in expansion depends upon the pressure inside the gas and increase in volume.
- 14.** (A) When a real gas is allowed to expand adiabatically through a fine hole from a region of high pressure to a region of low pressure, the temperature of the gas falls.
 (R) Work is done at the cost of internal energy of the gas.
- 15.** (A) Internal energy change in a cyclic process is zero.
 (R) Internal energy is a state function.
- 16.** (A) An exothermic process, non-spontaneous at high temperature, may become spontaneous at low temperature.
 (R) With decrease in temperature, randomness (entropy) decrease.
- 17.** (A) There is no reaction known for which ΔG is positive, yet it is spontaneous.
 (R) For photochemical reaction, ΔG is negative.
- 18.** (A) A reaction which is spontaneous and accompanied by decrease of randomness must be exothermic.
 (R) All exothermic reactions are accompanied by decrease of randomness.
- 19.** (A) Molar entropy of vaporization of water is different from ethanol.
 (R) Water is more polar than methanol.
- 20.** (A) Heat of neutralization for both HNO_3 and HCl with NaOH is 53.7 kJ/mol.
 (R) NaOH is a strong electrolyte/base.
- 21.** (A) In the following reaction:

$$\text{C}(s) + \text{O}_2(g) \longrightarrow \text{CO}_2(g); \quad \Delta H = \Delta U - RT$$
 (R) ΔH is related to ΔU by the equation,

$$\Delta H = \Delta U - \Delta n_g RT$$
- 22.** (A) Enthalpy of graphite is lower than that of diamond.
 (R) Entropy of graphite is greater than that of diamond.
- 23.** (A) For a reaction

$$2\text{NH}_3(g) \longrightarrow \text{N}_2(g) + 3\text{H}_2(g); \quad \Delta H > \Delta E$$
 (R) Enthalpy change is always greater than internal energy change.

(AIIMS 2008)

Answers - COMPREHENSIVE QUESTIONS**Set-1**

- | | | | | | | | |
|----------|----------|----------|----------|----------|----------|----------|----------|
| 1. (b) | 2. (c) | 3. (d) | 4. (a) | 5. (c) | 6. (a) | 7. (b) | 8. (d) |
| 9. (a) | 10. (d) | 11. (c) | 12. (d) | 13. (c) | 14. (d) | 15. (a) | 16. (a) |
| 17. (c) | 18. (a) | 19. (a) | 20. (a) | 21. (b) | 22. (d) | 23. (b) | 24. (a) |
| 25. (c) | 26. (d) | 27. (d) | 28. (b) | 29. (d) | 30. (b) | 31. (c) | 32. (a) |
| 33. (c) | 34. (b) | 35. (a) | 36. (a) | 37. (d) | 38. (b) | 39. (d) | 40. (c) |
| 41. (d) | 42. (d) | 43. (c) | 44. (b) | 45. (b) | 46. (c) | 47. (a) | 48. (a) |
| 49. (a) | 50. (d) | 51. (b) | 52. (c) | 53. (d) | 54. (d) | 55. (b) | 56. (c) |
| 57. (a) | 58. (c) | 59. (b) | 60. (d) | 61. (b) | 62. (c) | 63. (a) | 64. (b) |
| 65. (c) | 66. (d) | 67. (b) | 68. (a) | 69. (d) | 70. (a) | 71. (d) | 72. (a) |
| 73. (b) | 74. (b) | 75. (c) | 76. (d) | 77. (d) | 78. (c) | 79. (c) | 80. (b) |
| 81. (a) | 82. (c) | 83. (a) | 84. (d) | 85. (b) | 86. (c) | 87. (d) | 88. (a) |
| 89. (d) | 90. (c) | 91. (a) | 92. (b) | 93. (a) | 94. (a) | 95. (c) | 96. (c) |
| 97. (a) | 98. (b) | 99. (c) | 100. (d) | 101. (c) | 102. (b) | 103. (d) | 104. (a) |
| 105. (c) | 106. (a) | 107. (b) | 108. (a) | 109. (c) | 110. (a) | 111. (a) | 112. (a) |
| 113. (c) | 114. (a) | 115. (c) | 116. (b) | 117. (c) | 118. (a) | 119. (d) | 120. (d) |
| 121. (a) | 122. (b) | 123. (d) | 124. (c) | 125. (a) | 126. (d) | 127. (b) | 128. (a) |
| 129. (d) | 130. (c) | 131. (c) | 132. (a) | 133. (a) | 134. (a) | 135. (b) | 136. (c) |
| 137. (b) | 138. (a) | 139. (d) | 140. (a) | 141. (c) | 142. (a) | 143. (b) | 144. (a) |
| 145. (a) | 146. (a) | 147. (d) | 148. (c) | 149. (b) | 150. (c) | 151. (b) | 152. (a) |
| 153. (b) | 154. (a) | 155. (a) | 156. (c) | 157. (b) | 158. (b) | 159. (a) | 160. (d) |
| 161. (b) | 162. (d) | 163. (c) | 164. (a) | 165. (c) | 166. (c) | 167. (d) | 168. (b) |
| 169. (b) | 170. (d) | 171. (a) | 172. (b) | 173. (a) | 174. (c) | 175. (b) | 176. (a) |
| 177. (a) | 178. (d) | 179. (a) | 180. (a) | 181. (c) | 182. (a) | 183. (d) | 184. (c) |
| 185. (b) | 186. (d) | 187. (d) | 188. (b) | 189. (d) | 190. (a) | 191. (b) | 192. (d) |
| 193. (c) | 194. (c) | | | | | | |

Set-2

- | | | | | | | | |
|-----------|-----------|---------|---------|--------------|--------------|---------|-----------|
| 1. (b, d) | 2. (a, c) | 3. (a) | 4. (d) | 5. (a, b, c) | 6. (a, b, d) | 7. (b) | 8. (a, d) |
| 9. (b) | 10. (a) | 11. (d) | 12. (d) | 13. (a) | 14. (a, b) | 15. (d) | |

Answers - ASSERTION-REASON TYPE QUESTIONS**Set-1**

- | | | | | | | | |
|--------|--------|--------|--------|--------|--------|--------|--------|
| 1. (d) | 2. (b) | 3. (d) | 4. (c) | 5. (a) | 6. (d) | 7. (a) | 8. (a) |
|--------|--------|--------|--------|--------|--------|--------|--------|

Set-2

- | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (b) | 2. (c) | 3. (b) | 4. (c) | 5. (b) | 6. (a) | 7. (d) | 8. (d) |
| 9. (a) | 10. (b) | 11. (d) | 12. (d) | 13. (d) | 14. (a) | 15. (a) | 16. (b) |
| 17. (d) | 18. (c) | 19. (b) | 20. (a) | 21. (d) | 22. (b) | 23. (c) | |

BRAIN STORMING PROBLEMS

OBJECTIVE QUESTIONS for IIT ASPIRANTS

The following questions contain single correct option :

1. In which of the following pairs, both properties are intensive?
 (a) Pressure, temperature (b) Density, volume
 (c) Temperature, density (d) Pressure, volume
2. Although the dissolution of ammonium chloride (NH_4Cl) in water is an endothermic reaction, even then it is spontaneous because:
 (a) $\Delta S = -ve$ (b) $\Delta S = zero$
 (c) $T \Delta S < \Delta H$ (d) $\Delta S = +ve$ and $\Delta H < T \Delta S$
3. The S—S bond energy is if $\Delta H_f^\circ(E_t - S - E_t) = -147 \text{ kJ/mol}$;
 $\Delta H_f^\circ(E_t - S - S - E_t) = -202 \text{ kJ/mol}$ and $\Delta H_f^\circ S(g) = +223 \text{ kJ/mol}$:
 (a) 168 kJ (b) 126 kJ (c) 278 kJ (d) 572 kJ

[Hint:



$$\Delta H_{\text{reaction}} = \Sigma \Delta H_f^\circ(\text{products}) - \Sigma \Delta H_f^\circ(\text{reactants}) \\ = (-202) - (-147) = -55 \text{ kJ}$$

$$\Delta H_{\text{reaction}} = \Sigma (\text{BE})_{\text{reactants}} - \Sigma (\text{BE})_{\text{products}} \\ -55 = \text{Heat of sublimation or enthalpy of atomisation of sulphur} - \text{BE(S—S)}$$

$$-55 = 223 - \text{BE(S—S)}$$

$$\text{BE(S—S)} = 223 + 55 = 278 \text{ kJ}$$

(Common bonds of reactants and products are rejected.)]

4. Standard enthalpies of formation of O_3 , CO_2 , NH_3 and HI are 142.2 , -393.2 , -46.2 and $+25.9 \text{ kJ mol}^{-1}$ respectively. The order of their increasing stabilities will be:
 (a) O_3 , CO_2 , NH_3 , HI (b) CO_2 , NH_3 , HI , O_3
 (c) O_3 , HI , NH_3 , CO_2 (d) NH_3 , HI , CO_2 , O_3

[Hint: (i) Exothermic compounds are more stable than endothermic compounds.

(ii) Greater is the amount of heat evolved in the formation of a compound, more will be its stability.]

5. Combustion of octane takes place in an automobile engine. The homogeneous equation of combustion is:



The signs of ΔH , ΔS and ΔG for the reaction will be:

- (a) +ve, -ve, +ve (b) -ve, +ve, -ve
 (c) -ve, +ve, +ve (d) +ve, +ve, -ve

6. Which among the following represents the reaction of formation of the product?

- (a) $\text{C}_{(\text{diamond})} + \text{O}_2(g) \longrightarrow \text{CO}_2(g)$
 (b) $\text{S}_{(\text{monoclinic})} + \text{O}_2(g) \longrightarrow \text{SO}_2(g)$
 (c) $2\text{N}_2(g) + \text{O}_2(g) \longrightarrow 2\text{N}_2\text{O}(g)$
 (d) None of the above

7. How much energy must be supplied to change 36 g of ice at 0°C to water at room temperature 25°C ?

Data for water

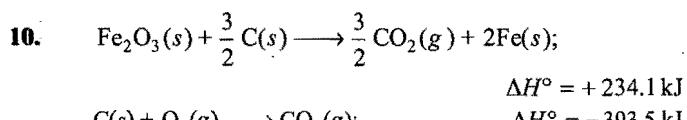
| | |
|--------------------|--|
| ΔH_f° | 6.01 kJ/mol |
| C_p liquid | $4.18 \text{ J K}^{-1} \text{ g}^{-1}$ |

- (a) 12 kJ (b) 16 kJ (c) 19 kJ (d) 22 kJ

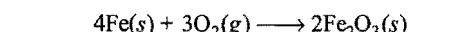
[Hint: $\Delta H = \Delta H_{\text{fusion}}$ of two moles + $ms \Delta T$
 $= 6.01 \times 2 + 36 \times 4.18 \times 25 \times 10^{-3}$
 $\approx 16 \text{ kJ}]$

8. A large positive value of ΔG° corresponds to which of these?
 (a) Small positive K (b) Small negative K
 (c) Large positive K (d) Large negative K
9. Consider the values for ΔH° (in kJ mol^{-1}) and for ΔS° (in $\text{J mol}^{-1} \text{ K}^{-1}$) given for four different reactions. For which reaction will ΔG° increase the most (becoming more positive) when the temperature is increased from 0°C to 25°C ?
 (a) $\Delta H^\circ = 50$, $\Delta S^\circ = 50$ (b) $\Delta H^\circ = 90$, $\Delta S^\circ = 20$
 (c) $\Delta H^\circ = -20$, $\Delta S^\circ = -50$ (d) $\Delta H^\circ = -90$, $\Delta S^\circ = -20$

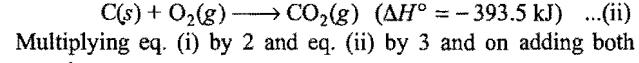
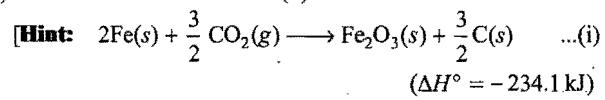
[Hint: Use the relation, $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ]$



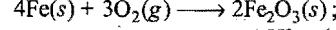
Use these equations and ΔH° values to calculate ΔH° for this reaction:



- (a) -1648.7 kJ (b) -1255.3 kJ
 (c) -1021.2 kJ (d) -129.4 kJ



Multiplying eq. (i) by 2 and eq. (ii) by 3 and on adding both equations, we get:



$$\Delta H^\circ = (-234.1 \times 2) + (-3 \times 393.5) \\ = -1648.7 \text{ kJ}]$$

11. Consider this equation and the associated value for ΔH° :



Which statement about this information is incorrect?

- (a) If the equation is reversed, the ΔH° value equals +92.3 kJ
 (b) The four HCl bonds are stronger than four bonds in H_2 and Cl_2
 (c) The ΔH° value will be -92.3 kJ if HCl is produced as a liquid
 (d) 23.1 kJ of heat will be evolved when 1 mole of $\text{HCl}(g)$ is produced

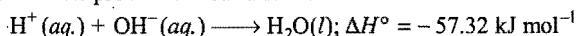
12. If the internal energy of an ideal gas decreases by the same amount as the work done by the system, the process is:

- (a) cyclic (b) isothermal (c) adiabatic (d) isolated

13. The enthalpy of neutralization of a strong acid by a strong base is $-57.32 \text{ kJ mol}^{-1}$. The enthalpy of formation of water is $-285.84 \text{ kJ mol}^{-1}$. The enthalpy of formation of hydroxyl ion is:

- (a) +228.52 kJ mol $^{-1}$ (b) -114.26 kJ mol $^{-1}$
 (c) -228.52 kJ mol $^{-1}$ (d) +114.2 kJ mol $^{-1}$

[Hint: The process of neutralization is:



$\Delta H_{\text{reaction}} = \Sigma \text{Heat of formation of products}$

$- \Sigma \text{Heat of formation of reactants}$

$$= \Delta H_f^\circ \text{H}_2\text{O}(l) - [\Delta H_f^\circ \text{H}^+(\text{aq}) + \Delta H_f^\circ \text{OH}^-(\text{aq})]$$

$$-57.32 = -285.84 - (0 + x)$$

$$x = -285.84 + 57.32$$

$$= -228.52 \text{ kJ}$$

14. For which process will ΔH° and ΔG° be expected to be most similar?

- (a) $2\text{Al}(s) + \text{Fe}_2\text{O}_3(s) \longrightarrow 2\text{Fe}(s) + \text{Al}_2\text{O}_3(s)$
- (b) $2\text{Na}(s) + 2\text{H}_2\text{O}(l) \longrightarrow 2\text{NaOH(aq)} + \text{H}_2(g)$
- (c) $2\text{NO}_2(g) \longrightarrow \text{N}_2\text{O}_4(g)$
- (d) $2\text{H}_2(g) + \text{O}_2(g) \longrightarrow 2\text{H}_2\text{O}(g)$

[Hint: (a) In this reaction, $\Delta S^\circ = 0$

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

$$\Delta G^\circ = \Delta H^\circ]$$

15. For a particular reaction, $\Delta H^\circ = -38.3 \text{ kJ}$ and $\Delta S^\circ = -113 \text{ J K}^{-1} \text{ mol}^{-1}$. This reaction is:

- (a) spontaneous at all temperatures
- (b) non-spontaneous at all temperatures
- (c) spontaneous at temperatures below 66°C
- (d) spontaneous at temperatures above 66°C

[Hint: $\Delta G = \Delta H - T \Delta S$

For spontaneous process, $\Delta G < 0$.

$$\therefore \Delta H - T \Delta S < 0$$

$$\frac{\Delta H}{\Delta S} < T$$

$$\frac{-38.3 \times 1000}{-113} < T$$

$$\text{i.e., } T > 338.93 \text{ K, i.e., } 66^\circ\text{C}]$$

16. Which halogen in its standard state has the greatest absolute entropy per mole?

- (a) $\text{F}_2(g)$
- (b) $\text{Cl}_2(g)$
- (c) $\text{Br}_2(l)$
- (d) $\text{I}_2(s)$

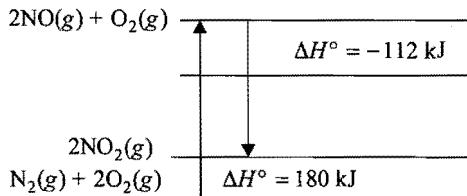
17. For which of these processes is the value of ΔS negative?

- I. Sugar is dissolved in water.
- II. Steam condenses on a surface.
- III. CaCO_3 is decomposed into CaO and CO_2 .
- (a) I only
- (b) II only
- (c) I and III only
- (d) II and III only

18. When solid NH_4NO_3 is dissolved in water at 25°C , the temperature of the solution decreases. What is true about the signs of ΔH and ΔS for this process?

| | ΔH | ΔS |
|-----|------------|------------|
| (a) | — | + |
| (b) | — | — |
| (c) | + | + |
| (d) | + | — |

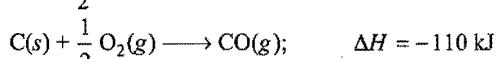
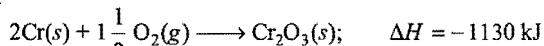
19. The diagram below shows the heat of reaction between N_2 , O_2 , NO and NO_2 :



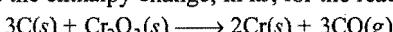
Which of the following statements pertaining to the formation of NO and NO_2 are correct?

1. The standard heat of formation of NO_2 is 68 kJ mol^{-1} .
 2. NO_2 is formed faster than NO at higher temperature.
 3. The oxidation reaction of nitrogen to NO_2 is endothermic.
 4. These two reactions often take place in troposphere and causes green house effect.
 5. These two reactions often take place and are responsible for city smog.
- (a) 1 and 2
 - (b) 1 and 3
 - (c) 1 and 4
 - (d) 3 and 4
 - (e) 3 and 5

20. The enthalpy changes for two reactions are given by the equations:

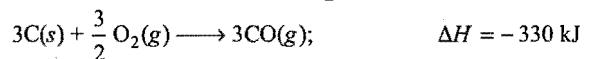
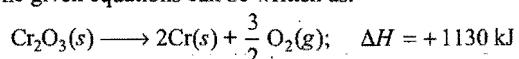


What is the enthalpy change, in kJ, for the reaction?

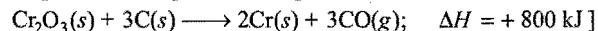


- (a) -1460 kJ
- (b) -800 kJ
- (c) $+800 \text{ kJ}$
- (d) $+1020 \text{ kJ}$
- (e) $+1460 \text{ kJ}$

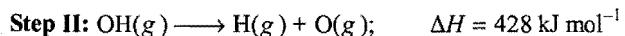
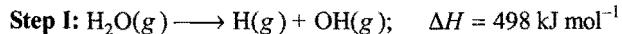
[Hint: The given equations can be written as:



Adding the above equations, we get:



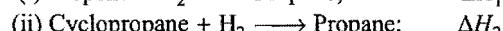
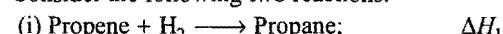
21. The enthalpy change at 298 K for decomposition is given in the following two steps:



The bond enthalpy of the $\text{O}-\text{H}$ bond is:

- (a) 498 kJ mol^{-1}
- (b) 463 kJ mol^{-1}
- (c) 428 kJ mol^{-1}
- (d) 70 kJ mol^{-1}

22. Consider the following two reactions:



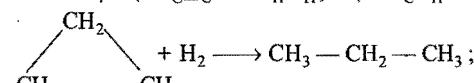
Then, $\Delta H_2 - \Delta H_1$ will be:

$$(a) 0 \quad (b) 2\text{BE}_{\text{C}-\text{C}} - \text{BE}_{\text{C}=\text{C}}$$

$$(c) \text{BE}_{\text{C}=\text{C}} \quad (d) 2\text{BE}_{\text{C}=\text{C}} - \text{BE}_{\text{C}-\text{C}}$$

[Hint: $\text{CH}_3-\text{CH}=\text{CH}_2 + \text{H}_2 \longrightarrow \text{CH}_3-\text{CH}_2-\text{CH}_3$;

$$\Delta H_1 = (\text{BE}_{\text{C}=\text{C}} + \text{BE}_{\text{H}-\text{H}}) - (2\text{BE}_{\text{C}-\text{H}} + \text{BE}_{\text{C}-\text{C}})$$



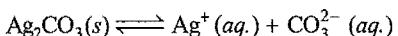
$$\Delta H_2 = (\text{BE}_{\text{C}-\text{C}} + \text{BE}_{\text{H}-\text{H}}) - (2 \times \text{BE}_{\text{C}-\text{H}})$$

$$\Delta H_2 - \Delta H_1 = 2\text{BE}_{\text{C}-\text{C}} - \text{BE}_{\text{C}=\text{C}}$$

23. Under which circumstances would the free energy change for a reaction be relatively temperature independent?

- (a) ΔH° is negative
- (b) ΔH° is positive
- (c) ΔS° has a large positive value
- (d) ΔS° has a small magnitude

24. Use the free energy change, $\Delta G^\circ = +63.3 \text{ kJ}$, for this reaction, to calculate the K_{sp} of $\text{Ag}_2\text{CO}_3(s)$ in water at 25°C :



- (a) 3.2×10^{-26}
- (b) 8×10^{-12}
- (c) 2.9×10^{-3}
- (d) 7.9×10^{-2}

25. Which statement(s) is/are true?

- 1. S° values for all elements in their states are positive.
- 2. S° values for all aqueous ions are positive.
- 3. ΔS° values for all spontaneous reactions are positive.
- (a) 1 only
- (b) 1 and 2 only
- (c) 2 and 3 only
- (d) All of these

26. The enthalpy of a reaction does not depend upon:

- (a) the intermediate reaction steps
- (b) the temperature of initial and final state of the reaction
- (c) the physical states of reactants and products
- (d) use of different reactants for the formation of the same product

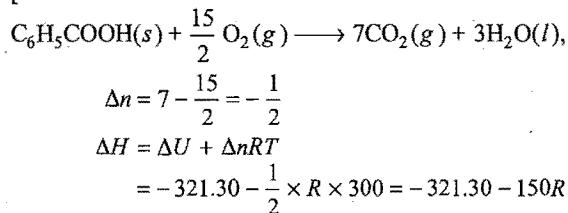
27. When a solution of 500 mL of 2 M KOH is added to 500 mL of 2 M HCl, then the rise in temperature T_1 is noted. When the same experiment is repeated by mixing 250 mL of each solution, the rise in temperature T_2 is noted:

- (a) $T_1 = T_2$
- (b) $T_1 = 2T_2$
- (c) $T_2 = 2T_1$
- (d) $T_1 = 4T_2$

28. The heat of combustion of solid benzoic acid at constant volume is -321.30 kJ at 27°C . The heat of combustion at constant pressure is:

- (a) $-321.30 - 300R$
- (b) $-321.30 + 300R$
- (c) $-321.30 - 150R$
- (d) $-321.30 + 900R$

[Hint:



29. $A \longrightarrow B; \quad \Delta U = 40 \text{ kJ mol}^{-1}$

If the system goes from A to B by a reversible path and returns to state A by an irreversible path, what would be the net change in internal energy?

- (a) More than 40 kJ
- (b) Zero
- (c) Less than 40 kJ
- (d) 40 kJ

30. For the process, $\text{NH}_3(g) + \text{HCl}(g) \longrightarrow \text{NH}_4\text{Cl}(s)$:

- (a) $\Delta H = +\text{ve}$, $\Delta S = +\text{ve}$
- (b) $\Delta H = -\text{ve}$, $\Delta S = +\text{ve}$
- (c) $\Delta H = +\text{ve}$, $\Delta U = -\text{ve}$
- (d) $\Delta H = -\text{ve}$, $\Delta S = -\text{ve}$

31. Match the thermodynamic properties (List-I) with their relation (List-II):

List-I **List-II**

- | | |
|--|-------------------|
| A. Free energy change (ΔG°) | (i) $RT \log_e K$ |
| B. Entropy change ΔS° | (ii) $-nFE$ |

- C. ΔH° enthalpy change of a reaction in standard state

$$(iii) RT^2 \left(\frac{d \ln K}{dT} \right)_P$$

- D. Standard free energy change (ΔG°)

$$(iv) - \left\{ \frac{d \Delta G}{dT} \right\}_P$$

Select the correct answer:

| Codes: | A | B | C | D |
|--------|------|------|-------|-------|
| (a) | (i) | (ii) | (iii) | (iv) |
| (b) | (ii) | (iv) | (iii) | (i) |
| (c) | (iv) | (ii) | (iii) | (i) |
| (d) | (i) | (ii) | (iv) | (iii) |

32. An ideal gas is allowed to expand under adiabatic conditions. The zero value is of:

- (a) ΔT
- (b) ΔS
- (c) ΔG
- (d) none of these

33. Match the physical changes in List-I with their relations given in List-II:

| List-I | List-II |
|---------------------|---|
| A. ΔG | (i) $\Delta U + P\Delta V$ |
| B. ΔH | (ii) $-nFE$ |
| C. ΔS° | (iii) $-RT \log_e K$ |
| D. ΔG° | (iv) $nR \log_e \left(\frac{V_2}{V_1} \right)$ |

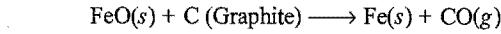
Select the correct answer from the given codes:

| Codes: | A | B | C | D |
|--------|------|-------|-------|-------|
| (a) | (ii) | (i) | (iv) | (iii) |
| (b) | (i) | (ii) | (iii) | (iv) |
| (c) | (iv) | (iii) | (ii) | (i) |
| (d) | (i) | (ii) | (iv) | (iii) |

34. Given the following data:

| Substance | $\Delta H^\circ(\text{kJ/mol})$ | $S^\circ(\text{J/mol K})$ | $\Delta G^\circ(\text{kJ/mol})$ |
|--------------|---------------------------------|---------------------------|---------------------------------|
| FeO(s) | -266.3 | 57.49 | -245.12 |
| C (Graphite) | 0 | 5.74 | 0 |
| Fe(s) | 0 | 27.28 | 0 |
| CO(g) | -110.5 | 197.6 | -137.15 |

Determine at what temperature the following reaction is spontaneous?



- (a) 298 K

- (b) 668 K

- (c) 966 K

- (d) ΔG° is +ve, hence the reaction will never be spontaneous.

$$[\text{Hint: } \Delta H_{\text{reaction}} = \Sigma \{\Delta H_f^\circ \text{Fe}(s) + \Delta H_f^\circ \text{CO}(g)\}$$

$$- \{\Delta H_f^\circ \text{FeO}(s) + \Delta H_f^\circ \text{C(graphite)}\}$$

$$= (0 - 110.5) - (-266.3 + 0) = 155.8 \text{ kJ mol}^{-1}$$

$$\Delta S_{\text{reaction}} = \Sigma [S_{\text{Fe}(s)}^\circ + S_{\text{CO}(g)}^\circ] - [S_{\text{FeO}(s)}^\circ + S_{\text{C(graphite)}}^\circ]$$

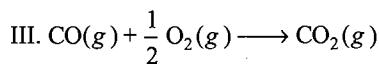
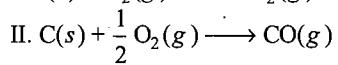
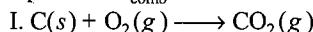
$$= (27.28 + 197.6) - (57.49 + 5.74)$$

$$= 161.65 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$\text{For spontaneous reaction, } T > \frac{\Delta H}{\Delta S}; T > \frac{155.8 \times 1000}{161.65}$$

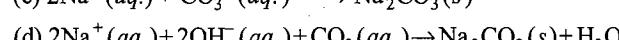
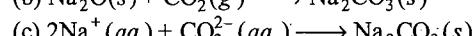
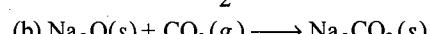
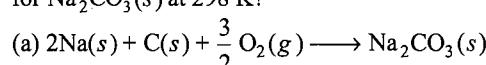
$$\therefore T > 966 \text{ K}$$

35. Which of the following equations has/have enthalpy changes equal to ΔH_{comb} C?



- (a) I and II (b) I, II and III
(c) I and III (d) I only

36. The enthalpy change of which reaction corresponds to ΔH_f° for $Na_2CO_3(s)$ at 298 K?



37. Enthalpy is equal to: (VITEEE 2007)

(a) $T^2 \left[\frac{\partial(G/T)}{\partial T} \right]_P$ (b) $-T^2 \left[\frac{\partial(G/T)}{\partial T} \right]_P$

(c) $T^2 \left[\frac{\partial(G/T)}{\partial T} \right]_V$ (d) $-T^2 \left[\frac{\partial(G/T)}{\partial T} \right]_V$

[Hint: $G = H - TS$... (i)

$$G = U + PV - TS$$

$$\Delta G = \Delta U + P\Delta V + V\Delta P - T\Delta S - S\Delta T$$

From the first and second laws,

$$T\Delta S = \Delta U + P\Delta V$$

$$\Delta G = V\Delta P - S\Delta T$$

At constant pressure, $\Delta P = 0$

$$\frac{\Delta G}{\Delta T} = -S \quad \dots \text{(ii)}$$

From eqs. (i) and (ii),

$$G = H + T \frac{\Delta G}{\Delta T}$$

OR

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

$$-\frac{H}{T^2} = -\frac{G}{T^2} + \frac{1}{T} \left(\frac{\partial G}{\partial T} \right)_P$$

$$= \left[\frac{\partial(G/T)}{\partial T} \right]_P$$

$$H = -T^2 \left[\frac{\partial(G/T)}{\partial T} \right]_P$$

38. When a bomb calorimeter is used to determine the heat of reaction, which property of the system under investigation is most likely to remain constant?

- (a) Number of molecules (b) Pressure
(c) Temperature (d) Volume

39. For the reaction shown, which is closest to the value of ΔH° ?



$$\Delta H_f^\circ \quad (\text{kJ mol}^{-1})$$

$$Cr^{3+}(aq.) \quad -143$$

$$Ni^{2+}(aq.) \quad -54$$

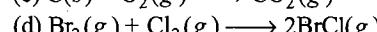
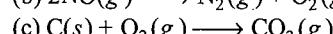
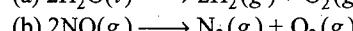
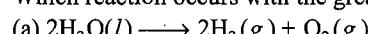
- (a) 124 kJ (b) 89 kJ
(c) -89 kJ (d) -124 kJ

40. An ice cube at 0.00°C is placed in 200 g of distilled water at 25°C. The final temperature after the ice is completely melted is 5°C. What is the mass of the ice cube?

$$(\Delta H_{\text{fus}} = 340 \text{ J g}^{-1}, C_p = 4.18 \text{ J g}^{-1} \text{ C}^{-1})$$

- (a) 23.6 g (b) 46.3 g
(c) 50.0 g (d) 800 g

41. Which reaction occurs with the greatest increase in entropy?



42. The bond dissociation energies for single covalent bonds formed between carbon and A, B, C, D and E atoms are:

| Bond | Bond energy (kcal mol ⁻¹) |
|------|---------------------------------------|
|------|---------------------------------------|

(i) C—A 240

(ii) C—B 382

(iii) C—D 276

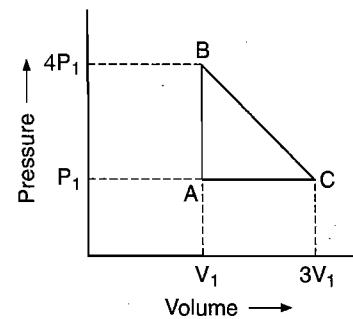
(iv) C—E 486

This indicates that the smallest atom is:

- (a) A (b) B (c) C (d) E

[Hint: C—E bond has highest bond energy; it means that the covalent bond C—E will be strongest. Smaller is the size of atom, stronger is the covalent bond.]

43. An ideal gas is taken around the cycle ABCA as:



- (a) $12P_1V_1$ (b) $6P_1V_1$ (c) $3P_1V_1$ (d) P_1V_1

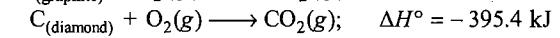
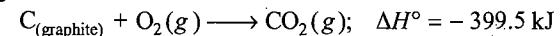
[Hint: Work done in the cyclic process

= Area bounded (ABCA)

$$= \frac{1}{2} \times AC \times AB$$

$$= \frac{1}{2} \times 2V_1 \times 3P_1 = 3P_1V_1]$$

44. One gram mole of graphite and diamond were burnt to form CO_2 gas.



- (a) graphite is more stable than diamond
 (b) diamond is more stable than graphite
 (c) graphite has greater affinity with oxygen
 (d) diamond has greater affinity with oxygen

[Hint: Thermal stability of one isotope is directly proportional to the heat of combustion.]

45. Which among the following is not an exact differential?
 (a) Q (dQ = heat absorbed)
 (b) U (dU = change in internal energy)
 (c) S (dS = entropy change)
 (d) G (dG = Gibbs free energy change)

[Hint: Heat ' Q ' is a path dependent function, hence its exact differentiation is not possible; however, internal energy, entropy and Gibbs free energy are state functions, hence can be differentiated exactly.]

46. A gas expands adiabatically at constant pressure such that:

$$T \propto \frac{1}{\sqrt{V}}$$

The value of γ , i.e., (C_p / C_v) of the gas will be:

- (a) 1.30 (b) 1.50 (c) 1.70 (d) 2

[Hint: $T \propto \frac{1}{\sqrt{V}}$

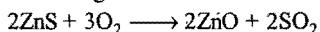
$$TV^{1/2} = \text{constant}$$

For adiabatic process, $TV^{1/2} = TV^{\gamma-1} = \text{constant}$

$$\therefore \gamma - 1 = \frac{1}{2}, \quad \gamma = \frac{3}{2}$$

47. $2\text{Zn} + \text{O}_2 \longrightarrow 2\text{ZnO}; \quad \Delta G^\circ = -616 \text{ J} \quad \dots (\text{i})$
 $2\text{Zn} + \text{S} \longrightarrow 2\text{ZnS}; \quad \Delta G^\circ = -293 \text{ J} \quad \dots (\text{ii})$
 $2\text{S} + 2\text{O}_2 \longrightarrow 2\text{SO}_2(\text{g}); \quad \Delta G^\circ = -408 \text{ J} \quad \dots (\text{iii})$

ΔG° for the following reaction:



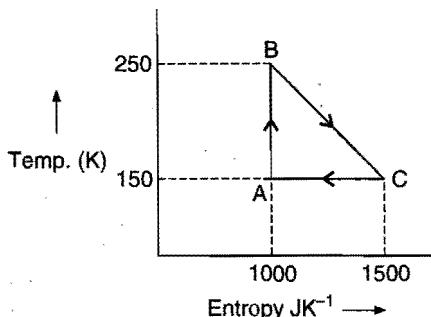
would be:

- (a) -731 J (b) -1317 J (c) +731 J (d) +1317 J

[Hint: $\Delta G^\circ = 2\Delta G_{\text{ZnO}}^\circ + 2\Delta G_{\text{SO}_2}^\circ - 2\Delta G_{\text{ZnS}}^\circ$
 $= [-616 - 408] - [-293]$
 $= -1024 + 293$
 $= -731 \text{ J}]$

48. The efficiency of the reversible cycle shown in the figure will be:

- (a) 33.33% (b) 56% (c) 66% (d) 25%



[Hint: Efficiency of cycle = $\frac{\text{Area of closed cycle}}{\text{Area under the curve}} \times 100$

$$\begin{aligned}
 &= \frac{\frac{1}{2} \times (1500 - 1000) \times (250 - 150)}{\frac{1}{2} \times (1500 - 1000) \times (250 - 150) + (1500 - 1000) \times (150 - 0)} \times 100 \\
 &= \frac{\frac{1}{2} \times 500 \times 100}{\frac{1}{2} \times 500 \times 100 + 500 \times 150} \times 100 \\
 &= \frac{500 \times 50 \times 100}{500 \times 50 + 500 \times 150} = 25]
 \end{aligned}$$

49. In Haber's process of ammonia manufacture:

| | | | |
|---|-----------------|-----------------|------------------|
| Molecules | $\text{N}_2(g)$ | $\text{H}_2(g)$ | $\text{NH}_3(g)$ |
| $C_P \text{ J K}^{-1} \text{ mol}^{-1}$ | 29.1 | 28.8 | 35.1 |

If C_P is independent of temperature, then reaction at 100°C as compared to that of 25°C will be:

- (a) more endothermic (b) less endothermic
 (c) more exothermic (d) less exothermic

[Hint: Use: $\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_P$]

50. Consider the following statements:

- I. Change in enthalpy is always smaller than change in internal energy.
 II. The variation in enthalpy of a reaction with temperature is given by Kirchhoff's equation.
 III. The entropy change in reversible adiabatic process is equal to zero.

Select the correct answer:

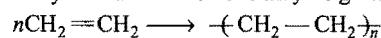
- (a) I and II (b) II and III
 (c) III and I (d) all are correct

51. In C_2H_4 , energy of formation of ($\text{C}=\text{C}$) and ($\text{C}-\text{C}$) are -145 kJ/mol and -80 kJ/mol respectively. What is the enthalpy change when ethylene polymerises to form polythene?

[JEE (Orissa) 2006]

- (a) +650 kJ/mol (b) +65 kJ/mol
 (c) -650 kJ mol⁻¹ (d) -65 kJ mol⁻¹

[Hint: Polymerisation of ethene may be given as:



$$\Delta H = \Sigma(\text{BE})_{\text{reactants}} - \Sigma(\text{BE})_{\text{products}}$$

$$= (+145) - (+80) = +65 \text{ kJ/mol}]$$

[Note: C—H bonds are common in both reactants and products.]

52. If 150 kJ of energy is needed for muscular work to walk a distance of 1 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 kJ mol⁻¹: [PMT (Kerala) 2007]

- (a) 75 g (b) 30 g (c) 180 g (d) 150 g
 (e) 45 g

53. The value of $\log_{10} K$ for a reaction $A \rightleftharpoons B$ is:

(Given, $\Delta_r H_{298\text{K}}^\circ = -54.07 \text{ kJ mol}^{-1}$,
 $\Delta_r S_{298\text{K}}^\circ = 10 \text{ JK}^{-1} \text{ mol}^{-1}$ and $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$;
 $2.303 \times 8.314 \times 298 = 5705$) [IIT 2007]

- (a) 5 (b) 10 (c) 95 (d) 100

$$[\text{Hint: } \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ]$$

$$= -54.07 \times 1000 - 298 \times 10 \\ = -57050 \text{ J}$$

$$\Delta G^\circ = -2.303 RT \log_{10} K$$

$$-57050 = -5705 \log_{10} K \\ \log_{10} K = 10]$$

54. The lattice enthalpy and hydration enthalpy of four compounds are given below :

| Compound | Lattice enthalpy (kJ/mol) | Hydration enthalpy (kJ/mol) |
|----------|------------------------------|--------------------------------|
| P | + 780 | - 920 |
| Q | + 1012 | - 812 |
| R | + 828 | - 878 |
| S | + 632 | - 600 |

The pair of compounds which is soluble in water is :

[PET (Kerala) 2008]

- (a) P and Q (b) Q and R (c) R and S (d) Q and S
 (e) P and R

[Hint : For solubility of ionic compounds, hydration energy must be greater than lattice energy.]

Following questions may have more than one correct options :

1. Which of the following are correct about irreversible isothermal expansion of ideal gas ?

$$(a) W = -q \quad (b) \Delta U = 0 \\ (c) \Delta T = 0 \quad (d) W = -nRT \ln \frac{P_1}{P_2}$$

2. The work done during adiabatic expansion or compression of an ideal gas is given by :

$$(a) n C_V \Delta T \quad (b) \frac{nR}{(\gamma - 1)} (T_2 - T_1) \\ (c) -nR P_{\text{ext}} \left[\frac{T_2 P_1 - T_1 P_2}{P_1 P_2} \right] \quad (d) -2.303 RT \log \frac{V_2}{V_1}$$

3. For an ideal gas $\left(\frac{C_{Pm}}{C_{Vm}} = \gamma \right)$; of molar mass M, its specific heat capacity at constant volume is :

$$(a) \frac{\gamma R}{(\gamma - 1)M} \quad (b) \frac{\gamma}{M(\gamma - 1)} \quad (c) \frac{M}{R(\gamma - 1)} \quad (d) \frac{\gamma RM}{\gamma - 1}$$

[Hint : $\frac{C_{Pm}}{C_{Vm}} = \gamma$, $C_{Pm} - C_{Vm} = R$

$$C_{Vm} = \frac{R}{\gamma - 1} \text{ and } C_{Pm} = \frac{R\gamma}{\gamma - 1}$$

$$\frac{\gamma}{\gamma - 1} = C_{Vm} \times M$$

$$C_{Vm} = \frac{x}{M(\gamma - 1)}$$

Answers

• Single correct option

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

• One or more than one correct options

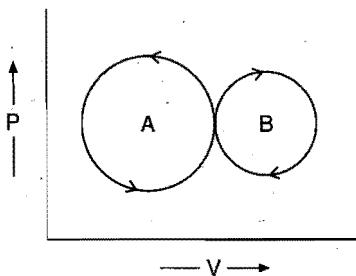
1. (a,b,c,d) 2. (a,b,c) 3. (b)

Integer Answer TYPE QUESTIONS

| X | Y | Z | W |
|---|---|---|---|
| ① | ② | ③ | ④ |
| ① | ② | ③ | ⑤ |
| ② | ③ | ④ | ⑥ |
| ③ | ④ | ⑤ | ⑦ |
| ④ | ⑤ | ⑥ | ⑧ |
| ⑤ | ⑥ | ⑦ | ⑨ |
| ⑥ | ⑦ | ⑧ | |
| ⑦ | ⑧ | ⑨ | |
| ⑧ | ⑨ | | |
| ⑨ | | | |

This section contains 11 questions. The answer to each of the questions is a single digit integer, ranging from 0 to 9. If the correct answers to question numbers X, Y, Z and W (say) are 6, 0, 9 and 2 respectively, then the correct darkening of bubbles will look like the given figure :

- A bubble of 8 moles of helium is submerged at certain depth in water. The temperature of water increases by 30°C . How much heat is added approximately to helium (in kJ) during expansion?
- For a liquid, enthalpy of fusion is $1.435 \text{ kcal mol}^{-1}$ and molar entropy change is $5.26 \text{ cal mol}^{-1} \text{ K}^{-1}$. The freezing point of liquid in celcius will be :
- For the reaction, $\text{Ag}_2\text{O}(s) \rightleftharpoons 2\text{Ag}(s) + \frac{1}{2}\text{O}_2(g)$
 ΔH , ΔS and T are $40.63 \text{ kJ mol}^{-1}$, $108.8 \text{ J K}^{-1} \text{ mol}^{-1}$ and 373.4 K respectively. Free energy change ΔG of the reaction will be:
- Standard Gibbs Free energy change ΔG° for a reaction is zero. The value of equilibrium constant of the reaction will be:
- ΔG° for the reaction $x + y \rightleftharpoons z$ is -4.606 kcal . The value of equilibrium constant of the reaction at 227°C is $(x \times 10^2)$. The value of 'x' is :
- 4.48 L of an ideal gas at STP requires 12 cal to raise the temperature by 15°C at constant volume. The C_p of the gas is cal.
- .



(IIT 2010)

[Hint : w_d = work done along dotted line

$$= \sum P \Delta V$$

$$= 4 \times 1.5 + 1 \times 1 + 2.5 \times \frac{2}{3} = 8.65 \text{ L atm}$$

w_s = It is reversible isothermal process

$$= 2.303 nRT \log \left(\frac{V_2}{V_1} \right)$$

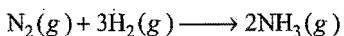
$$= 2.303 \times (PV) \log \left(\frac{V_2}{V_1} \right)$$

$$= 2.303 \times 2 \log \frac{5.5}{0.5} = 4.79 \text{ L atm}$$

$$\frac{w_d}{w_s} = \frac{8.65}{4.79} \approx 2]$$

In the present graph, the area of circle A and B are 25 unit and 20 unit respectively. Work done will be unit.

- For the reaction,



Heat of reaction at constant volume exceeds the heat of reaction at constant pressure by the value of xRT . The value of x is :

1. (3)

2. (0)

3. (0)

4. (1)

5. (1)

6. (6)

7. (5)

8. (2)

9. (1)

10. (9)

11. (2)

LINKED COMPREHENSION TYPE QUESTIONS

● Passage 1

Chemical reactions are invariably associated with the transfer of energy either in the form of heat or light. In the laboratory, heat changes in physical and chemical processes are measured with an instrument called calorimeter. Heat change in the process is calculated as:

$$q = ms \Delta T; \quad s = \text{Specific heat} \\ = c\Delta T; \quad c = \text{Heat capacity}$$

Heat of reaction at constant volume is measured using bomb calorimeter.

$$q_v = \Delta U = \text{Internal energy change}$$

Heat of reaction at constant pressure is measured using simple or water calorimeter:

$$q_p = \Delta H \\ q_p = q_v + P \Delta V \\ \Delta H = \Delta U + \Delta nRT$$

The amount of energy released during a chemical change depends on the physical state of reactants and products, the condition of pressure, temperature and volume at which the reaction is carried out. The variation of heat of reaction with temperature and pressure is given by Kirchhoff's equation:

$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_p; \quad \frac{\Delta U_2 - \Delta U_1}{T_2 - T_1} = \Delta C_v$$

(At constant pressure) (At constant volume)

Answer the following questions:

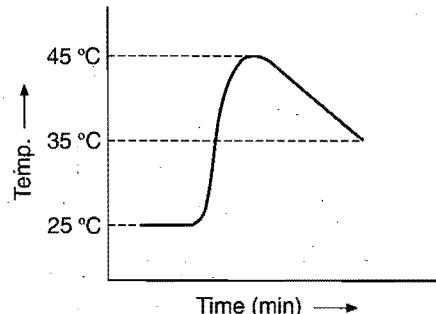
1. Match the List-I with List-II and select the answer from the given codes:

| List-I | | List-II | | |
|--|--|--------------------------------|--|--|
| A. $C(s) + O_2(g) \rightarrow CO_2(g)$ | | 1. $\Delta H = \Delta U + RT$ | | |
| B. $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ | | 2. $\Delta H = \Delta U$ | | |
| C. $NH_4HS(s) \rightarrow NH_3(g) + H_2S(g)$ | | 3. $\Delta H = \Delta U - 2RT$ | | |
| D. $PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$ | | 4. $\Delta H = \Delta U + 2RT$ | | |
| E. $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$ | | 5. $\Delta H = \Delta U - RT$ | | |

| Codes: A B C D E | | | | |
|--------------------------------------|---|---|---|---|
| (a) 1 | 2 | 3 | 4 | 5 |
| (b) 5 | 2 | 3 | 4 | 1 |
| (c) 1 | 3 | 4 | 2 | 5 |
| (d) 2 | 3 | 4 | 1 | 5 |

2. The heat capacity of a bomb calorimeter is 500 J/K. When 0.1 g of methane was burnt in this calorimeter, the temperature rose by 2°C. The value of ΔU per mole will be:
 (a) +1 kJ (b) -1 kJ (c) +160 kJ (d) -160 kJ
3. For which reaction will $\Delta H = \Delta U$? Assume each reaction is carried out in an open container:
 (a) $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$
 (b) $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$
 (c) $C(s) + 2H_2O(g) \rightarrow 2H_2(g) + CO_2(g)$
 (d) $PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$

4. What value of ΔT should be used for the calorimetry experiment that gives the following graphical results?



- (a) 10°C (b) 25°C (c) 20°C (d) 35°C

5. The enthalpy of fusion of ice is 6.02 kJ mol⁻¹. The heat capacity of water is $4.18 \text{ J g}^{-1} \text{ C}^{-1}$. What is the smallest number of ice cubes at 0°C, each containing one mole of water, that are needed to cool 500 g of liquid water from 20°C to 0°C?

- (a) 1 (b) 7 (c) 14 (d) 125

[Hint: Heat released to cool 500 g water from 20°C to 0°C,

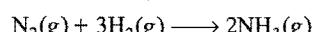
$$q = ms \Delta T \\ = 500 \times 4.18 \times 20 = 41800 \text{ J} = 41.8 \text{ kJ}$$

Number of moles of water (ice) that will melt to absorb 41.8 kJ

$$= \frac{41.8}{6.02} \approx 7$$

∴ Number of cubes of ice that will melt = 7]

6. The enthalpy change (ΔH) for the reaction,



is -92.38 kJ at 298 K. The internal energy change ΔU at 298 K is:

(AIIMS 2006)

- (a) -92.38 kJ (b) -87.42 kJ (c) -97.34 kJ (d) -89.9 kJ

[Hint: $\Delta n_g = 2 - 4 = -2$

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

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

$$= -92.38 \times 1000 - (-2) \times 8.314 \times 298$$

$$= -87424 \text{ J} = -87.424 \text{ kJ}]$$

7. The specific heat of I_2 in vapour and solid state are 0.031 and 0.055 cal/g respectively. The heat of sublimation of iodine at 200°C is 6.096 kcal mol⁻¹. The heat of sublimation of iodine at 250°C will be:

- (a) 3.8 kcal mol⁻¹ (b) 4.8 kcal mol⁻¹
 (c) 2.28 kcal mol⁻¹ (d) 5.8 kcal mol⁻¹

[Hint: $I_2(s) \rightleftharpoons I_2(g)$

$$\Delta C_P = (0.031 - 0.055) \times 10^{-3} \times 254$$

$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_P$$

$$\frac{\Delta H_2 - 6.096}{50} = (0.031 - 0.055) \times 10^{-3} \times 254$$

$$\Delta H_2 = 5.79 \text{ kcal mol}^{-1}]$$

● Passage 2

In a chemical reaction, the bonds of reactants are decomposed and new bonds of products are formed. The amount of energy required to break a particular bond in a gaseous molecule under standard conditions homolytically is called the standard bond dissociation enthalpy of that bond (ΔH_{A-B}°).

Bond energies can be used to obtain an approximate value for a reaction enthalpy of a gas phase reaction if the appropriate enthalpies of formation are not available.

$$\Delta H_{\text{reaction}}^{\circ} = \Sigma \text{Bond energy of bonds, broken in the reactants}$$

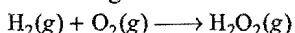
$$- \Sigma \text{Bond energy of bonds, formed in the products}$$

Bond energy depends on three factors:

- (a) Greater is the bond length, lesser is the bond energy.
- (b) Bond energy increases with the bond multiplicity.
- (c) Bond energy increases with the electronegativity difference between the bonding atoms.

Answer the following questions:

1. Arrange N—H, O—H and F—H bonds in the decreasing order of bond energy:
 (a) F—H > O—H > N—H (b) O—H > N—H > F—H
 (c) N—H > O—H > F—H (d) F—H > N—H > O—H
2. X_2 represents halogen molecule. Bond energy of different halogen molecules will lie in following sequences:
 (a) $F_2 > Cl_2 > Br_2 > I_2$ (b) $Cl_2 > Br_2 > F_2 > I_2$
 (c) $I_2 > Cl_2 > Br_2 > I_2$ (d) $Br_2 > F_2 > I_2 > Cl_2$
 [Hint: Bond energy of F_2 is surprisingly low due to strong repulsion between the lone pairs of two fluorine atoms.]
3. Which among the following sequences is correct about the bond energy of C—C, C=C and C≡C bonds?
 (a) $C \equiv C > C = C > C - C$ (b) $C \equiv C < C = C < C - C$
 (c) $C = C > C \equiv C > C - C$ (d) $C \equiv C > C - C > C = C$
4. In CH_4 molecule, which of the following statements is correct about the C—H bond energy?
 (a) All C—H bonds of methane have same energy
 (b) Average of all C—H bond energies is considered
 (c) Fourth C—H bond requires highest energy to break
 (d) None of the above
5. Use the bond energies to estimate ΔH for this reaction:



| Bond | Bond energy |
|------|--------------------------|
| H—H | 436 kJ mol ⁻¹ |
| O—O | 142 kJ mol ⁻¹ |
| O=O | 499 kJ mol ⁻¹ |
| H—O | 460 kJ mol ⁻¹ |

- (a) -127 kJ (b) -209 kJ (c) -484 kJ (d) -841 kJ

6. The heat of formation of NO from its elements is +90 kJ mol⁻¹. What is the approximate bond dissociation energy of the bond in NO?

$$BE_{N \equiv N} = 941 \text{ kJ mol}^{-1} \quad BE_{O=O} = 499 \text{ kJ mol}^{-1}$$

- (a) 630 kJ mol⁻¹ (b) 720 kJ mol⁻¹
 (c) 760 kJ mol⁻¹ (d) 810 kJ mol⁻¹

● Passage 3

The change in Gibbs free energy (ΔG) of the system alone provides a criterion for the spontaneity of a process at constant temperature and pressure. A change in the free energy of a system at constant temperature and pressure will be:

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

At constant temperature and pressure:

$$\Delta G_{\text{system}} < 0 \text{ (spontaneous)}$$

$$\Delta G_{\text{system}} = 0 \text{ (equilibrium)}$$

$$\Delta G_{\text{system}} > 0 \text{ (non-spontaneous)}$$

Free energy is related to the equilibrium constant, as:

$$\Delta G^{\circ} = 2.303RT \log_{10} K_e$$

Answer the following questions:

1. The free energy for a reaction having $\Delta H = 31400$ cal, $\Delta S = 32 \text{ cal K}^{-1} \text{ mol}^{-1}$ at 1000°C is: [JEE (Orissa) 2005]
 (a) -9336 cal (b) -7386 cal (c) -1936 cal (d) +9336 cal
2. For a spontaneous reaction ΔG , equilibrium ' K ' and E_{cell}° will be respectively: (AIEEE 2005)
 (a) -ve, > 1 , +ve (b) +ve, > 1 , -ve
 (c) -ve, < 1 , -ve (d) -ve, > 1 , -ve
3. For a system in equilibrium, $\Delta G = 0$, under conditions of constant..... : (KCET 2005)
 (a) temperature and pressure (b) temperature and volume
 (c) pressure and volume (d) energy and volume
4. If both ΔH and ΔS are negative, the reaction will be spontaneous:
 (a) at high temperature (b) at low temperature
 (c) at all temperatures (d) at absolute zero
5. A reaction has positive values of ΔH and ΔS . From this you can deduce that the reaction:
 (a) must be spontaneous at any temperature
 (b) cannot be spontaneous at any temperature
 (c) will be spontaneous only at low temperature
 (d) will be spontaneous only at high temperature
6. For a reaction to be spontaneous at all temperatures:
 (a) $\Delta G - ve, \Delta H + ve$ and $\Delta S + ve$
 (b) $\Delta G + ve, \Delta H - ve$ and $\Delta S + ve$
 (c) $\Delta G - ve, \Delta H - ve$ and $\Delta S - ve$
 (d) $\Delta G - ve, \Delta H - ve$ and $\Delta S + ve$

3 moles of CO_2 gas expands isothermally against external pressure of 1 bar. Volume increases from 10 L to 30 L respectively. The system is in thermal contact of surroundings at temperature 15°C. Entropy change in isothermal process is:

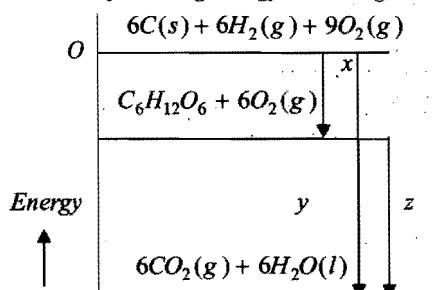
$$\Delta S = 2.303 nR \log \left(\frac{V_2}{V_1} \right)$$

Answer the following questions:

7. If CO_2 behaves like an ideal gas, then entropy change of system (ΔS_{system}) will be:
 (a) +27.4 J K⁻¹ (b) 9.1 J K⁻¹
 (c) -27.4 J K⁻¹ (d) -9.1 J K⁻¹
8. Select the correct relation:
 (a) $\Delta S_{\text{system}} > 0, \Delta S_{\text{surr.}} = 0$ (b) $\Delta S_{\text{surr.}} < 0, \Delta S_{\text{system}} > 0$
 (c) $\Delta S_{\text{system}} = 0, \Delta S_{\text{surr.}} = 0$ (d) $\Delta S_{\text{surr.}} > 0, \Delta S_{\text{system}} < 0$

● Passage 4

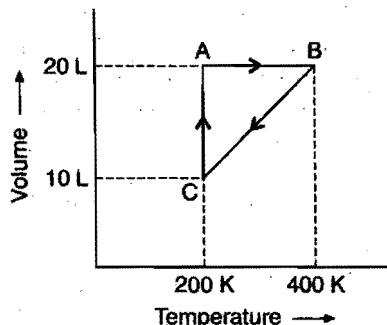
Consider the following energy level diagram:



Answer the following questions on the basis of the given diagram:

- The heat of formation of glucose is:
(a) $-x$ (b) $-y$ (c) $x - y$ (d) $-x + z$
- In the given diagram z refers to:
(a) $6 \times \Delta H_f^\circ \text{CO}_2$ (b) $\Delta H_f^\circ \text{C}_6\text{H}_{12}\text{O}_6$
(c) $\Delta H_{\text{combustion}}^\circ \text{C}_6\text{H}_{12}\text{O}_6$ (d) $\Delta H_{\text{combustion}}^\circ \text{C(s)} + \Delta H_f^\circ \text{H}_2\text{O(l)}$
- The quantity y is equal to:
(a) $\Delta H_{\text{combustion}} \text{C(s)} + \Delta H_{\text{combustion}} \text{H}_2\text{(g)}$
(b) $x + z$
(c) $x - z$
(d) $\Delta H_f \text{CO}_2 + \Delta H_{\text{H}_2\text{O}}$
- Select the incorrect statement(s):
(a) combustion of glucose is exothermic process
(b) standard state of glucose is $\text{C}_6\text{H}_{12}\text{O}_6(s)$
(c) heat of formation of glucose = Heat of combustion of glucose
(d) $x + y = z$

● Passage 5



Graph for one mole gas

Answer the following questions based on the above diagram:

- Process, $A \rightarrow B$ represents:
(a) isobaric (b) isochoric (c) isothermal (d) adiabatic
- The pressure at C is:
(a) 3.284 atm (b) 1.642 atm (c) 0.0821 atm (d) 0.821 atm
- Work done in the process $C \rightarrow A$ is:
(a) zero (b) 8.21 L atm (c) 16.2 L atm (d) unpredictable

- The process which occurs in going from, $B \rightarrow C$ is:
(a) isothermal (b) adiabatic (c) isobaric (d) isochoric
- The pressures at A and B in the atmosphere are respectively:
(a) 0.821 and 1.642 (b) 1.642 and 0.821
(c) 1 and 2 (d) 0.082 and 0.164

● Passage 6

The thermodynamic property that measures the extent of molecular disorder is called entropy. The direction of a spontaneous process for which the energy is constant is always the one that increases the molecular disorder. Entropy change of phase transformation can be calculated using Trouton's formula $(\Delta S = \frac{\Delta H}{T})$. In the reversible adiabatic process, however, ΔS will

be zero. The rise in temperature in isobaric and isochoric conditions is found to increase the randomness or entropy of the system.

$$\Delta S = 2.303C \log(T_1/T_2)$$

$$C = C_P \text{ or } C_V$$

Answer the following questions:

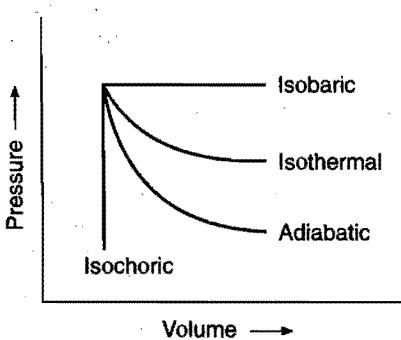
- The entropy change in an adiabatic process is:
(a) zero
(b) always positive
(c) always negative
(d) sometimes positive and sometimes negative
- If, water in an insulated vessel at -10°C , suddenly freezes, the entropy change of the system will be:
(a) $+10 \text{ J K}^{-1} \text{ mol}^{-1}$
(b) $-10 \text{ J K}^{-1} \text{ mol}^{-1}$
(c) zero
(d) equal to that of surroundings
- The melting point of a solid is 300 K and its latent heat of fusion is 600 cal mol^{-1} . The entropy change for the fusion of 1 mole of the solid (in cal K^{-1}) at the same temperature would be:
(a) 200 (b) 2 (c) 0.2 (d) 20
- For which of the following cases $\Delta S = \frac{\Delta H}{T}$?
(a) A process for which $\Delta C_P = 0$ but $\Delta C_V \neq 0$
(b) An adiabatic process
(c) An isobaric or isothermal process
(d) An isothermal reversible phase transition process
- When 1 mol of an ideal gas is compressed to half of its volume, its temperature becomes double; then the change in entropy (ΔS) would be:
(a) $C_V \ln 2$ (b) $C_P \ln 2$
(c) $C_V R \ln 2$ (d) $(C_V - R) \ln 2 \times C_P$

$$[\text{Hint: } \Delta S = 2.303C_P \log_{10}\left(\frac{V_1}{V_2}\right)]$$

$$= C_P \ln\left(\frac{V_1}{V_2}\right) = C_P \ln_e\left(\frac{1}{1/2}\right) \\ = C_P \ln_e 2]$$

● Passage 7

The pressure-volume behaviour of various thermodynamic processes is shown in graphs:



Work is the mode of transference of energy. If the system involves gaseous substance and there is difference of pressure between system and surroundings, such a work is referred to as pressure-volume work ($w_{PV} = -P_{ext} \Delta V$). It has been observed that reversible work done by the system is the maximum obtainable work.

$$w_{rev} > w_{irr}$$

The works of isothermal and adiabatic processes are different from each other.

$$w_{isothermal\ reversible} = 2.303nRT \log_{10}\left(\frac{V_2}{V_1}\right) = 2.303nRT \log_{10}\left(\frac{P_1}{P_2}\right)$$

$$w_{adiabatic\ reversible} = C_V(T_1 - T_2)$$

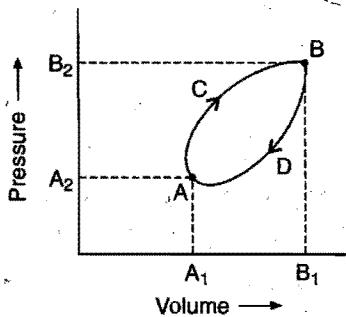
Answer the following questions:

1. If w_1, w_2, w_3 and w_4 are work done in isothermal, adiabatic, isobaric and isochoric reversible processes, then the correct sequence (for expansion) would be:

- (a) $w_1 > w_2 > w_3 > w_4$ (b) $w_3 > w_2 > w_1 > w_4$
 (c) $w_3 > w_2 > w_4 > w_1$ (d) $w_3 > w_1 > w_2 > w_4$

[Hint: w = Work done = Area under curve.]

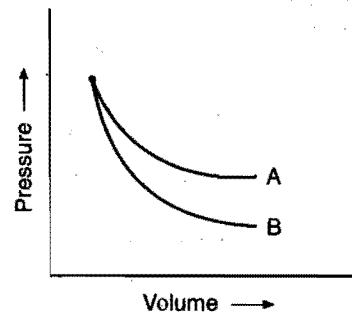
2. A thermodynamic system goes in acyclic process as represented in the following P-V diagram:



The net work done during the complete cycle is given by the area:

- (a) cycle ACBDA
 (b) AA₁B₁BDA
 (c) AA₂B₂B
 (d) half of area bounded by curve

3. P-V plots for two gases during adiabatic processes are given in the given figure:



Plot A and plot B should correspond to:

- (a) He and O₂ (b) He and Ar (c) O₂ and He (d) O₂ and F₂

[Hint: Slope of the adiabatic curve $\propto \gamma$

Slope of B > Slope of A

He ($\gamma = 1.66$); O₂ ($\gamma = 1.44$)

Thus, correct answer will be (c).]

4. The q value and work done in isothermal reversible expansion of one mole of an ideal gas from initial pressure of 1 bar to final pressure of 0.1 bar at constant temperature 273 K are:

- (a) 5.22 kJ, -5.22 kJ (b) -5.22 kJ, 5.22 kJ
 (c) 5.22 kJ, 5.22 kJ (d) -5.22 kJ, -5.22 kJ

[Hint: $w = -2.303nRT \log\left(\frac{P_1}{P_2}\right)$

$$= -2.303 \times 1 \times 8.314 \times 273 \log\left(\frac{1}{0.1}\right)$$

$$= -5.227 \text{ kJ}$$

$q = -w = +5.227 \text{ kJ}$ for isothermal process]

5. Calculate work done when 1 mole of an ideal gas is expanded reversibly from 20 L to 40 L at a constant temperature of 300 K.

- (a) 7.78 kJ (b) -1.73 kJ (c) 11.73 kJ (d) -4.78 kJ

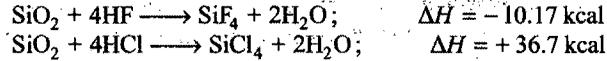
Answers

- | | | | | | | | |
|-------------------|--------|--------|--------|-----------|--------|--------|--------|
| Passage 1. | 1. (d) | 2. (d) | 3. (b) | 4. (c) | 5. (b) | 6. (b) | 7. (d) |
| Passage 2. | 1. (a) | 2. (b) | 3. (a) | 4. (b) | 5. (a) | 6. (a) | |
| Passage 3. | 1. (a) | 2. (a) | 3. (a) | 4. (c) | 5. (d) | 6. (d) | 7. (a) |
| Passage 4. | 1. (a) | 2. (c) | 3. (b) | 4. (c, d) | | | |
| Passage 5. | 1. (b) | 2. (b) | 3. (b) | 4. (c) | 5. (a) | | |
| Passage 6. | 1. (a) | 2. (c) | 3. (b) | 4. (d) | 5. (b) | | |
| Passage 7. | 1. (d) | 2. (a) | 3. (c) | 4. (a) | 5. (b) | | |

SELF ASSESSMENT**ASSIGNMENT NO. 7****SECTION-I****Straight Objective Type Questions**

This section contains 10 multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which only one is correct.

1. Reaction of silica with mineral acids may be given as:



which among the following is correct?

- (a) HF and HCl both will react with silica
- (b) Only HF will react with silica
- (c) Only HCl will react with silica
- (d) Neither HF nor HCl will react with silica

[Hint: Exothermic reactions are spontaneous]

2. In Mayer's relation,

$$C_P - C_V = R$$

'R' stands for:

- (a) translational kinetic energy of 1 mol gas
- (b) rotational kinetic energy of 1 mol gas
- (c) vibrational kinetic energy of 1 mol gas
- (d) work done to increase the temperature of 1 mol gas by one degree

[Hint: $PV = RT$ (For 1 mol gas) ... (i)

$$P(V + \Delta V) = R(T + 1) \quad \dots \text{(ii)}$$

From eqs. (i) and (ii)

$$P\Delta V = R$$

i.e.,

$$W = R \text{ (work done)}$$

3. For an ideal gas, the Joule-Thomson coefficient is:

- (a) zero
- (b) positive
- (c) negative
- (d) depends on atomicity of gas

4. Entropy change in reversible adiabatic process is:

- (a) infinite
- (b) zero
- (c) equal to $C_V \Delta T$
- (d) equal to $nR \ln \left(\frac{V_2}{V_1} \right)$

5. For a process to be in equilibrium, it is necessary that:

- (a) $\Delta S_{\text{system}} = \Delta S_{\text{surr.}}$
- (b) $\Delta S_{\text{system}} = -\Delta S_{\text{surr.}}$
- (c) $\Delta S_{\text{system}} = 0$
- (d) $\Delta S_{\text{surr.}} = 0$

6. Predict the sign of ΔS for each of the following processes, which occur at constant temperature:

I. The volume of 2 mol of $\text{O}_2(\text{g})$ increases from 44L to 54L

II. The pressure of 2 mol of $\text{O}_2(\text{g})$ increases from 1 atm to 1.2 atm.

I II

- (a) $\Delta S = -\text{ve}$
- (b) $\Delta S = -\text{ve}$
- (c) $\Delta S = +\text{ve}$
- (d) $\Delta S = +\text{ve}$
- $\Delta S = -\text{ve}$
- $\Delta S = +\text{ve}$
- $\Delta S = -\text{ve}$
- $\Delta S = +\text{ve}$

7. Which of the following statements must be true for the entropy of a pure solid to be zero?

I. The temperature must be zero kelvin

II. The solid must be perfectly crystalline

III. The solid must be an element

IV. The solid must be ionic

- (a) I
- (b) I and II
- (c) I, II and III
- (d) All are correct

8. Which of the following statements is correct?

- (a) Slope of adiabatic $P-V$ curve is smaller than that in isothermal one
- (b) Slope of adiabatic $P-V$ curve will be same as that in isothermal one
- (c) Slope of adiabatic $P-V$ curve will be larger than in isothermal one
- (d) Slope of adiabatic $P-V$ curve will be zero

9. $\left(\frac{\partial H}{\partial P} \right)_T$ for an ideal gas is equal to:

- (a) zero
- (b) $\frac{\Delta VRT}{P}$
- (c) $\frac{P\Delta V}{T}$
- (d) $nR\Delta T$

10. A refrigerator is used to remove heat from enclosure at 0°C at the rate of 600 watt. If the surroundings temperature is 30°C , calculate the power needed:

(a) 303 watt (b) 11000 watt
 (c) 65.9 watt (d) 110 watt

SECTION-II

Multiple Answers Type Objective Questions

11. ΔU will be zero for which processes?
- (a) Cyclic process (b) Isothermal expansion
 - (c) Isochoric process (d) Adiabatic process
12. If x and y are two intensive variables then:
- (a) xy is an intensive variable
 - (b) $\frac{x}{y}$ is an intensive variable
 - (c) $(x + y)$ is an intensive variable
 - (d) $\frac{dx}{dy}$ is an extensive property
13. Which of the following expressions is/are correct for an adiabatic process?
- (a) $\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$
 - (b) $\frac{P_2}{P_1} = \left(\frac{T_1}{T_2}\right)^{\gamma-1/\gamma}$
 - (c) $P_2 V_2^\gamma = P_1 V_1^\gamma$
 - (d) $P_1 V_1^{\gamma-1} = P_2 V_2^{\gamma-1}$
14. Select the state functions among the following:
- (a) temperature (b) entropy
 - (c) work (d) enthalpy
15. Select the correct expressions among the following:
- (a) $\frac{\Delta G - \Delta H}{T} = \left(\frac{\partial \Delta G}{\partial T}\right)_P$
 - (b) $\frac{\Delta G - \Delta H}{T} = \left[\frac{\partial (\Delta G)}{\partial T}\right]_V$
 - (c) $\frac{\Delta S}{nF} = \left(\frac{\partial E_{cell}}{\partial T}\right)_P$
 - (d) $\left(\frac{\partial T}{\partial P}\right)_H = -\left(\frac{\partial H}{\partial P}\right)_{T/C_P}$
16. Which of the following are correct for an ideal gas?
- (a) $\left(\frac{\partial U}{\partial V}\right)_T = 0$
 - (b) $\left(\frac{\partial H}{\partial P}\right)_T = 0$
 - (c) $\left(\frac{\partial T}{\partial P}\right)_H = 0$
 - (d) $\left(\frac{\partial P}{\partial T}\right)_V = 0$
17. The Clausius-Clapeyron equation may be given as:
- (a) $\log_{10} \left(\frac{P_2}{P_1}\right) = \frac{\Delta H_{vap}}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$
 - (b) $\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$
 - (c) $\frac{dP}{dT} = \frac{q}{T\Delta V}$
 - (d) $\frac{dP}{dT} = \frac{\Delta V}{\Delta S}$
18. Which of the following is/are not state function?
- (a) q (b) $q - w$
 - (c) $\frac{q}{w}$ (d) $q + w$

SECTION-III

Assertion-Reason Type Questions

This section contains 5 questions. Each question contains Statement-1 (Assertion) and Statement-2 (Reason). Each question has following 4 choices (a), (b), (c) and (d), out of which only one is correct.

- (a) Statement-1 is true; statement-2 is true; statement-2 is a correct explanation for statement-1.
 (b) Statement-1 is true; statement-2 is true; statement-2 is not a correct explanation for statement-1.
 (c) Statement-1 is true; statement-2 is false.
 (d) Statement-1 is false; statement-2 is true.
19. Statement-1: Most of the combustion reactions are exothermic.

Because

Statement-2: Products are more stable than reactants in exothermic process.

20. Statement-1: There is no exchange in internal energy in a cyclic process.

Because

Statement-2: In a cyclic process, the system returns to original state in a number of steps.

21. Statement-1: The value of enthalpy of neutralization of weak acid and strong base is always numerically less than 57.1 kJ.

Because

Statement-2: All the OH^- ions furnished by 1 gram equivalent of strong base are not completely neutralized.

22. Statement-1: Heat of solution is positive when $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ is dissolved in water but it is negative when anhydrous CuSO_4 is dissolved in water.

Because

Statement-2: Molar masses of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and CuSO_4 are different.

23. Statement-1: The extensive property of a single pure substance depends upon the number of moles of the substance present.

Because

Statement-2: Any extensive property expressed per mole becomes intensive.

SECTION-IV

Matrix-Matching Type Questions

This section contains 3 questions. Each question contains statement given in two columns which have to be matched. Statements (a, b, c and d) in Column-I have to be matched with statements (p, q, r and s) in Column-II. The answers to these questions have to be appropriately bubbled as illustrated in the following examples:

If the correct matches are (a-p,s); (b-q,r); (c-p,q) and (d-s); then correct bubbled 4×4 matrix should be as follows:

| | p | q | r | s |
|---|-----|-----|-----|-----|
| a | (p) | (q) | (r) | (s) |
| b | (p) | (q) | (r) | (s) |
| c | (p) | (q) | (r) | (s) |
| d | (p) | (q) | (r) | (s) |

24. Match the List-I with List-II:

| List-I | List-II |
|--|----------------|
| (a) $\left(\frac{\partial T}{\partial P}\right)_H$ | (p) V |
| (b) $\left(\frac{\partial G}{\partial P}\right)_T$ | (q) T |
| (c) $\left(\frac{\partial H}{\partial S}\right)_P$ | (r) $-S$ |
| (d) $\left(\frac{\partial G}{\partial T}\right)_P$ | (s) μ_{jT} |

25. Match the List-I with List-II and select the correct answer from the given codes:

| List-I (Thermodynamic properties) | List-II (Expression) |
|--------------------------------------|--|
| (I) ΔG | (A) $-RT \log_e K$ |
| (II) ΔH° | (B) $RT^2 \left(\frac{d \ln K}{dT} \right)_P$ |
| (III) ΔS | (C) nFE |
| (IV) ΔG° | (D) $-\left[\frac{\partial \Delta G}{\partial T} \right]_P$ |

Codes:

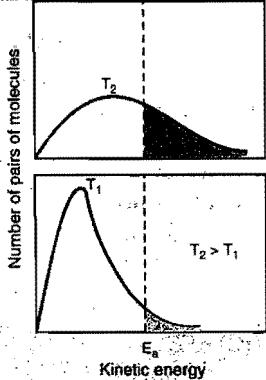
- (a) I-C, II-B, III-D, IV-A
 (b) I-B, II-C, III-D, IV-A
 (c) I-A, II-B, III-C, IV-D
 (d) I-D, II-A, III-B, IV-C

26. Match the List-I with List-II:

| List-I | List-II |
|---|---|
| (a) Perfectly crystalline solid | (p) $\Delta U = 0$ |
| (b) Reversible reaction at equilibrium | (q) $T = \text{constant}$ |
| (c) Isothermal process | (r) $\lim_{T \rightarrow 0K} S \rightarrow 0$ |
| (d) $\left(\frac{\partial G}{\partial P}\right) = -S$ | (s) $\Delta S_{\text{universe}} = 0$ |

Answers

- | | | | | | | | |
|-----------------------------|---------------|--------------------------------|---------------|------------|---------------|---------------|---------------|
| 1. (b) | 2. (d) | 3. (a) | 4. (b) | 5. (b) | 6. (c) | 7. (b) | 8. (c) |
| 9. (a) | 10. (c) | 11. (a, b) | 12. (a, b, d) | 13. (a, c) | 14. (a, b, d) | 15. (a, c, d) | 16. (a, b, c) |
| 17. (a, b, c) | 18. (a, b, c) | 19. (a) | 20. (a) | 21. (c) | 22. (c) | 23. (b) | |
| 24. (a-s) (b-p) (c-q) (d-r) | 25. (a) | 26. (a-r) (b-s) (c-p, q) (d-q) | | | | | |



CHAPTER 8

CHEMICAL KINETICS

8.1 INTRODUCTION

Thermodynamics deals with the feasibility of a chemical change. The free energy change, ΔG , of a reaction helps us to understand whether the reaction will occur or not. Even though there may be decrease in free energy but reactants do not always form the products instantaneously and actual rate of the reaction may vary from extremely slow to very fast. Thermodynamics is concerned only with initial and final states of reacting systems but offers no explanation about the various stages through which the reactants pass to reach the final state. This leads to following questions concerning chemical changes.

(i) How fast do the chemical reactions go?

(ii) How can the speed of the reaction change?

(iii) What intermediate steps, the reactants follow to reach the final state of products, i.e., the mechanism of the reaction.

The branch of physical chemistry which deals with the rate at which the chemical reactions occur, the mechanism by which the chemical reactions take place and the influence of various factors such as concentration, temperature, pressure, catalyst, etc., on the reaction rates, is called the **chemical kinetics**.

Different chemical reactions occur at different rates. On the basis of rates, the chemical reactions are broadly divided into three categories:

(a) Very fast or instantaneous reactions: These reactions are so fast that they occur as soon as the reactants are brought together. Generally, these reactions involve ionic species and thus known as ionic reactions. These reactions take about 10^{-14} to 10^{-16} seconds for completion. It is almost impossible to determine the rates of these reactions. Some such examples are:

(i) Precipitation of AgCl when solutions of silver nitrate and sodium chloride are mixed.



(ii) Precipitation of BaSO₄ when solutions of barium chloride and sulphuric acid are mixed.



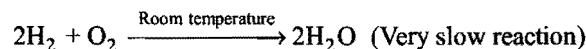
(iii) Neutralisation of an acid with a base when their aqueous solutions are mixed.



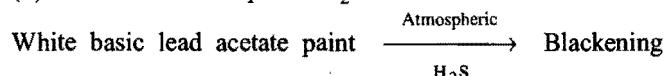
(b) Very slow reactions: There are certain reactions which are extremely slow. They may take months together to show any measurable change at room temperature. It is also difficult to study the kinetics of such reactions.

Some examples are:

(i) Reaction between hydrogen and oxygen at room temperature.

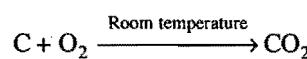


(ii) Reaction of atmospheric H₂S on basic lead acetate.



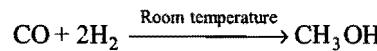
of paint occurs very slowly
(due to formation of PbS.)

(iii) Reaction between carbon and oxygen.



Carbon and oxygen are thermodynamically less stable than CO₂ at 298 K, yet coke does not spontaneously catch fire in air and remains unreacted even for years.

(iv) Reaction between carbon monoxide and hydrogen.



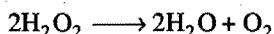
The reaction is thermodynamically feasible at 298 K but in actual practice the reaction proceeds infinitesimally slowly.

(v) Rusting of iron occurs very slowly.

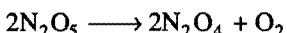
(c) Moderate reactions: Between the above two extremes, there are a number of reactions which take place at moderate and measurable rates at room temperature and it is these reactions which are studied in chemical kinetics. Mostly these reactions are

molecular in nature. Some common examples of such type are given below:

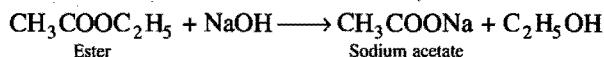
(i) Decomposition of hydrogen peroxide.



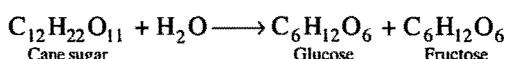
(ii) Decomposition of nitrogen pentoxide.



(iii) Hydrolysis of an ester.



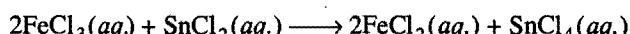
(iv) Inversion of cane sugar in aqueous solution.



(v) Reaction between nitrogen dioxide and carbon monoxide.



(vi) Reaction between ferric chloride and stannous chloride.



(vii) Decolourisation of acidified potassium permanganate with sodium oxalate.

(viii) Reaction between nitric oxide and chlorine.



The chemical reactions can be slowed down or speeded up by changing conditions under which they occur. For example, very slow reaction, $\text{CO} + 2\text{H}_2 \longrightarrow \text{CH}_3\text{OH}$, can be speeded up by maintaining temperature around 400°C , pressure about 300 atmospheres and using a catalyst containing ZnO and Cr_2O_3 . The decay of food articles can be slowed down by preserving them in refrigerators. There are two principal reasons for studying chemical kinetics.

(i) To predict the rate of a particular reaction under specified conditions: The conditions can be adjusted to make the reaction to go at a desired rate, either rapidly or slowly or moderately. The field of chemical kinetics is useful in industry as the conditions for maximum yields of industrial products can be ascertained.

(ii) To predict the mechanism of the reaction: The intelligent guess regarding various elementary processes responsible for the formation of products can be made which should be consistent with experimental data.

8.2 RATE OF REACTION (Average and Instantaneous Rate)

We are all familiar with processes in which something changes with time. Rate is usually expressed as the ratio of the amount of change in some quantity to the time required to produce that change.

$$\text{Rate} = \frac{\text{Change in some quantity}}{\text{Time taken for the change}} = \frac{\Delta X}{\Delta t}$$

The term ΔX means $X_{\text{final}} - X_{\text{initial}}$ and Δt is the amount of time elapsed. For example, a car driver starts his journey at 9.0 a.m. with odometer reading x miles. At 11.0 a.m. he reaches his

destination. The odometer reading at destination is y miles. The rate of his travel can be calculated as:

$$\begin{aligned} \text{Rate} &= \frac{\Delta(\text{distance})}{\Delta(\text{time})} = \frac{\text{distance}(f) - \text{distance}(in)}{\text{time}(f) - \text{time}(in)} \\ &= \frac{y - x}{11.0 - 9.0} = \frac{y - x}{2} \text{ miles hr}^{-1} \end{aligned}$$

The above example indicates that the car has been driven with uniform rate but actually it has been driven sometimes faster and sometimes slower depending upon the conditions of the road. Thus, the overall rate is an average rate and the rate at which the car was moving at any instant, i.e., instantaneous rate was changeable.

The rate measured over a long time interval is called average rate and the rate measured for an infinitesimally small time interval is called instantaneous rate.

In a chemical change, reactants and products are involved. As the chemical reaction proceeds, the concentration of the reactants decreases, i.e., reactants are consumed and the concentration of products increases, i.e., products are produced. The rate of reaction (average rate) is defined as the change of concentration of any one of its reactants (or products) per unit time.

Average rate of reaction,

$$r_{av} = \frac{\text{Change of concentration of one of the reactants or products}}{\text{Time taken for the change}}$$

Consider a common hypothetical reaction,



The average rate of reaction may be expressed either in terms of decrease in concentration of A (reactants) or in terms of increase in concentration of B (product).

$$\text{Average rate of reaction} = \frac{\text{Decrease in concentration of } A}{\text{Time taken}}$$

$$\text{or } \text{Average rate of reaction} = \frac{\text{Increase in concentration of } B}{\text{Time taken}}$$

The concentrations of reactants or products are expressed as number of moles per litre. The symbol for the molar concentration consists of the formula of the substance enclosed in bracket. The symbol $[A]$ stands for the molar concentration of A . The symbol $\Delta[A]$, therefore, stands for the change in molar concentration of A .

The rate of decrease or increase in the concentration of reactants or products may also be expressed in terms of change in their concentration during the time interval, Δt , as:

$$\text{Average rate of reaction} = - \frac{\Delta[A]}{\Delta t}$$

$$\text{or } \text{Average rate of reaction} = + \frac{\Delta[B]}{\Delta t}$$

(A negative sign placed before a reaction rate symbol signifies a decrease in concentration of the reactant with increase of time and a positive sign before the rate symbol signifies that the concentration of the product increases with increase in time. The

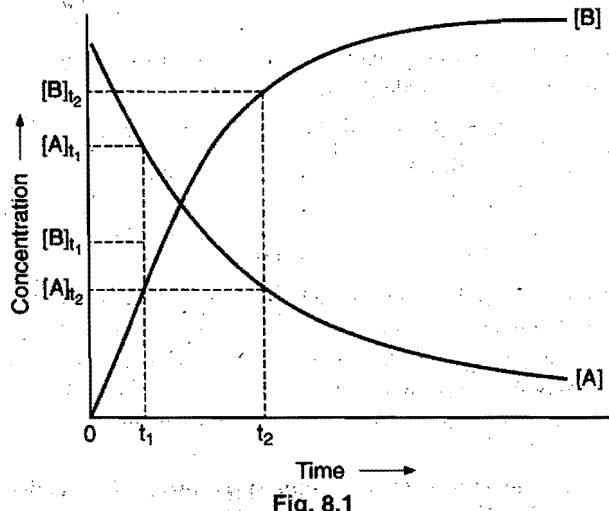


Fig. 8.1

concentration change may be positive or negative but the rate of reaction is always positive. The minus sign is always written when required, but the plus sign is usually not mentioned.)

Figure 8.1 shows the change of concentrations of reactant (A) and product (B) as the chemical reaction $A \rightarrow B$ progresses with time. Let $[A]_{t_1}$ and $[A]_{t_2}$ be the concentrations of A at time t_1 and t_2 , respectively.

$$\Delta[A] = [A]_{t_2} - [A]_{t_1}$$

and

$$\Delta t = t_2 - t_1$$

$$r_{av} = -\frac{\Delta[A]}{\Delta t} = -\frac{[A]_{t_2} - [A]_{t_1}}{t_2 - t_1}$$

Over the same time interval t_1 to t_2 , the concentration of B changes from $[B]_{t_1}$ to $[B]_{t_2}$.

$$r'_{av} = \frac{\Delta[B]}{\Delta t} = \frac{[B]_{t_2} - [B]_{t_1}}{t_2 - t_1}$$

Since, one mole of A produces one mole of B , the rate of decrease in concentration of A should be equal to the rate of increase in concentration of B . Thus,

$$r_{av} = r'_{av}$$

$$-\frac{\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t}$$

Reaction rate has the units of concentration or molarity divided by time. Therefore, the units of rate of reaction may be expressed as:

mole/litre sec ($\text{mol L}^{-1} \text{s}^{-1}$)

or mole/litre min ($\text{mol L}^{-1} \text{min}^{-1}$)

or mole/litre hour ($\text{mol L}^{-1} \text{h}^{-1}$)

or mole/litre day ($\text{mol L}^{-1} \text{d}^{-1}$)

or mole/litre year ($\text{mol L}^{-1} \text{y}^{-1}$)

Note : In case of gaseous reaction, pressure may be taken in place of concentration. Thus, rate will have the unit of atm sec^{-1} or atm min^{-1} .

$$PV = nRT \quad \text{or} \quad P = \left[\frac{n}{V} \right] RT \quad \text{or} \quad P = CRT$$

$$\frac{\Delta[P]}{\Delta t} = \frac{\Delta[C]}{\Delta t} \cdot RT \quad \text{or} \quad \text{Rate in } [\text{atm/sec}] = \text{Rate in } [\text{molarity/sec}] \times RT$$

SOME SOLVED EXAMPLES

Example 1. In a reaction, the concentration of a reactant (A) changes from $0.200 \text{ mol litre}^{-1}$ to $0.150 \text{ mol litre}^{-1}$ in 10 minutes. What is the average rate of reaction during this interval?

$$\begin{aligned} \text{Solution:} \quad \Delta[A] &= [A]_{\text{final}} - [A]_{\text{initial}} \\ &= [0.150 - 0.200] = -0.050 \text{ mol litre}^{-1} \end{aligned}$$

$$\Delta t = 10 \text{ minutes}$$

$$\begin{aligned} \text{Average rate of reaction} &= \frac{-\Delta[A]}{\Delta t} = \frac{-[-0.050]}{10} \\ &= \frac{0.050}{10} = 0.005 \text{ mol litre}^{-1} \text{ min}^{-1} \end{aligned}$$

Expression of Rate

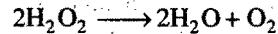
Consider the following reaction between CO and NO_2 :



The equation shows that when one mole of CO reacts with one mole of NO_2 , one mole each of CO_2 and NO are formed. The average rate of reaction can be expressed either by decrease of concentration of any one of the reactants (CO or NO_2) or by the increase in concentration of any one of the products (CO_2 or NO).

$$\text{Thus, } -\frac{\Delta[\text{CO}]}{\Delta t} = -\frac{\Delta[\text{NO}_2]}{\Delta t} = \frac{\Delta[\text{CO}_2]}{\Delta t} = \frac{\Delta[\text{NO}]}{\Delta t}$$

However, for the reaction,



it is observed that when 2 moles of H_2O_2 decompose, one mole of O_2 is formed in the same time interval. The rate of increase in the concentration of O_2 , therefore, is half that of the disappearance of the concentration of H_2O_2 in the same time interval;

$$\text{So, } \frac{\Delta[\text{O}_2]}{\Delta t} = -\frac{1}{2} \frac{\Delta[\text{H}_2\text{O}_2]}{\Delta t}$$

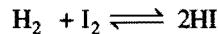
In general, for a reaction,



the rate expression may be expressed as:

$$-\frac{1}{n_1} \frac{\Delta[\text{A}]}{\Delta t} = -\frac{1}{n_2} \frac{\Delta[\text{B}]}{\Delta t} = \frac{1}{m_1} \frac{\Delta[\text{C}]}{\Delta t} = \frac{1}{m_2} \frac{\Delta[\text{D}]}{\Delta t}$$

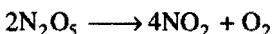
Thus, for the reaction,



the rate may be expressed as:

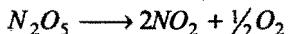
$$-\frac{\Delta[\text{H}_2]}{\Delta t} = -\frac{\Delta[\text{I}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{HI}]}{\Delta t}$$

Similarly, for the decomposition of N_2O_5 in CCl_4 medium, the rate may be expressed as:



$$-\frac{1}{2} \frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{4} \frac{\Delta[NO_2]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$$

Example 2. Decomposition of N_2O_5 is expressed by the equation,



If during a certain time interval, the rate of decomposition of N_2O_5 is 1.8×10^{-3} mol litre $^{-1}$ min $^{-1}$, what will be the rates of formation of NO_2 and O_2 during the same interval?

Solution: The rate expression for the decomposition of N_2O_5 is:

$$-\frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{2} \frac{\Delta[NO_2]}{\Delta t} = 2 \cdot \frac{\Delta[O_2]}{\Delta t}$$

$$\text{So, } \frac{\Delta[NO_2]}{\Delta t} = 2 \frac{\Delta[N_2O_5]}{\Delta t} = 2 \times 1.8 \times 10^{-3}$$

$$= 3.6 \times 10^{-3} \text{ mol litre}^{-1} \text{ min}^{-1}$$

$$\text{and } \frac{\Delta[O_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{2} \times 1.8 \times 10^{-3}$$

$$= 0.9 \times 10^{-3} \text{ mol litre}^{-1} \text{ min}^{-1}$$

(Rate is always positive and hence $-\frac{\Delta[N_2O_5]}{\Delta t}$ is taken positive.)

Instantaneous Rate

In chemical kinetics, the rate at any particular instant, i.e., instantaneous rate rather than the average rate over a time interval has much more practical application and importance. It is defined as the rate of change of concentration of any one of the reactants or products over a very small interval of time.

If we take infinitesimal small interval of time dt , it may be assumed that the rate is uniform through this interval; then if dx is amount of substance A transformed to B during this interval, the rate of reaction at that instant is given as $-\frac{dx}{dt}$.

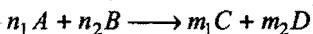
[In differential calculus, when Δt becomes very small and approaches zero, the ratio $\frac{\Delta[A]}{\Delta t}$ may be replaced by the

derivative, $\frac{d[A]}{dt}$, i.e.,

$$r_{\text{inst}} = \lim_{\Delta t \rightarrow 0} -\frac{\Delta[A]}{\Delta t} = -\frac{d[A]}{dt}$$

On the other hand, if the rate of reaction is expressed in terms of the concentration of any of the products which goes on increasing, then rate of reaction at particular instant = $\frac{dx}{dt}$.

In general, for a reaction,



The instantaneous rate may be expressed as:

$$r_{\text{inst}} = -\frac{1}{n_1} \frac{d[A]}{dt} = -\frac{1}{n_2} \frac{d[B]}{dt} = \frac{1}{m_1} \frac{d[C]}{dt} = \frac{1}{m_2} \frac{d[D]}{dt}$$

Experimental Determination of Instantaneous Rate of Reaction

In order to determine changes in concentration of reactants or products, it is customary to take small portions of the reaction mixture at suitable intervals of time and freeze them rapidly to about 0°C as to stop the reaction. The concentration is then measured with the help of a suitable method. In several cases, concentration changes are measured by observing changes in certain physical properties which are proportional to it such as optical densities, electrical conductivity, optical rotation, etc. A curve is plotted between concentration and time. A tangent is drawn to the curve at the point corresponding to time interval 't'. The slope of this tangent gives the instantaneous rate of reaction. This is shown in Fig. 8.2 (a).

Instantaneous rate of reaction = Slope of curve

$$= \frac{\text{Intercept along ordinate}}{\text{Intercept along abscissa}} = \frac{\Delta x}{\Delta t}$$

Since, the concentrations of the reactants keep on decreasing with time, the rate of reaction correspondingly decreases with time. Thus, the rate of reaction will depend on the stage considered during progress of the reaction. The rate of reaction is maximum at the initial stage and decreases with time. Theoretically, infinite time would be required for a reaction to complete. But the reaction rate becomes so slow after a certain time that for all practical purposes, the reaction can be considered to be completed. It is evident from Fig. 8.2 (b) that the rate of reaction is varying from moment to moment.

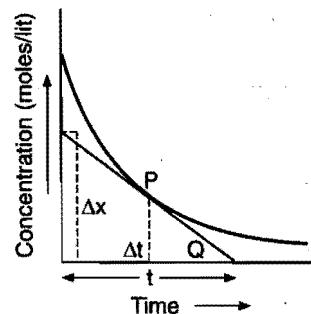


Fig. 8.2(a) Determination of rate of reaction

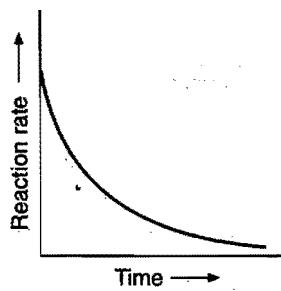
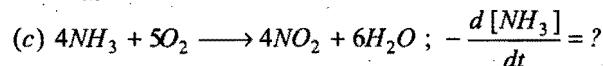
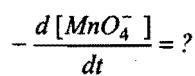
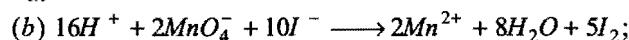
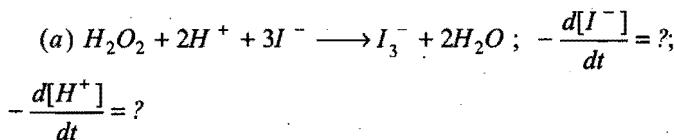


Fig. 8.2(b) Variation of rate of reaction

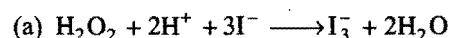
Reaction Life Time

It is defined as the time taken by a reaction to proceed to 98% of completion. The shorter the life time, the faster the reaction. Reaction life times are used to compare the various reactions. Reactions are also compared with half life periods. The half life period is defined as the time during which the concentration of a reactant is reduced to one-half of its initial value or the time in which half of the reaction is completed. It is generally denoted by $t_{1/2}$. The shorter the half life period, the faster is the reaction.

Example 3. For each of the following reactions express the given rate of change of concentration of the reactant or product in terms of the rate of change of concentration of other reactants or products in that reaction :



Solution: We have,

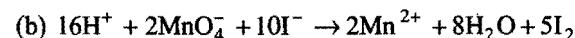


The equality in this case is:

$$-\frac{d[H_2O_2]}{dt} = -\frac{1}{2} \frac{d[H^+]}{dt} = -\frac{1}{3} \frac{d[I^-]}{dt} = \frac{d[I_3^-]}{dt} = \frac{1}{2} \frac{d[H_2O]}{dt}$$

$$\text{So, } -\frac{d[I^-]}{dt} = -3 \frac{d[H_2O_2]}{dt} = -\frac{3}{2} \frac{d[H^+]}{dt} = 3 \frac{d[I_3^-]}{dt} = \frac{3}{2} \frac{d[H_2O]}{dt}$$

$$\text{and } -\frac{d[H^+]}{dt} = -2 \frac{d[H_2O_2]}{dt} = -\frac{2}{3} \frac{d[I^-]}{dt} = 2 \frac{d[I_3^-]}{dt} = \frac{d[H_2O]}{dt}$$



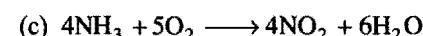
The equality in this case is:

$$-\frac{1}{16} \frac{d[H^+]}{dt} = -\frac{1}{2} \frac{d[MnO_4^-]}{dt} = -\frac{1}{10} \frac{d[I^-]}{dt}$$

$$= \frac{1}{2} \frac{d[Mn^{2+}]}{dt} = \frac{1}{8} \frac{d[H_2O]}{dt} = \frac{1}{5} \frac{d[I_2]}{dt}$$

$$\text{So, } -\frac{d[MnO_4^-]}{dt} = -\frac{1}{8} \frac{d[H^+]}{dt} = -\frac{1}{5} \frac{d[I^-]}{dt}$$

$$= \frac{d[Mn^{2+}]}{dt} = \frac{1}{4} \frac{d[H_2O]}{dt} = \frac{2}{5} \frac{d[I_2]}{dt}$$

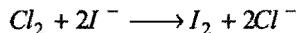


The equality in this case is:

$$-\frac{1}{4} \frac{d[NH_3]}{dt} = -\frac{1}{5} \frac{d[O_2]}{dt} = \frac{1}{4} \frac{d[NO_2]}{dt} = \frac{1}{6} \frac{d[H_2O]}{dt}$$

$$\text{So, } -\frac{d[NH_3]}{dt} = -\frac{4}{5} \frac{d[O_2]}{dt} = \frac{d[NO_2]}{dt} = \frac{2}{3} \frac{d[H_2O]}{dt}$$

Example 4. The following reaction was carried out in water:



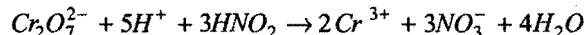
The initial concentration of I^- was 0.25 mol L^{-1} and the concentration after 10 minutes 0.23 mol L^{-1} . Calculate the rate of disappearance of I^- and appearance of I_2 .

Solution: $\Delta[I^-] = [I^-]_{\text{final}} - [I^-]_{\text{initial}}$
 $= 0.23 - 0.25 = -0.02 \text{ mol L}^{-1}$
 $\Delta t = 10 - 0 = 10 \text{ min}$
 $-\frac{\Delta[I^-]}{\Delta t} = -\frac{(-0.02)}{10} = 0.002 \text{ mol L}^{-1} \text{ min}^{-1}$

$$\text{Rate of appearance of } I_2 = -\frac{1}{2} \frac{\Delta[I^-]}{\Delta t} = \frac{0.002}{2} = 0.001 \text{ mol L}^{-1} \text{ min}^{-1}$$

$$= 1 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1}$$

Example 5. The reaction between $Cr_2O_7^{2-}$ and HNO_2 in an acidic medium is:



The rate of disappearance of $Cr_2O_7^{2-}$ is found to be $2.4 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$ during a measured time interval. Find the rate of disappearance of HNO_2 and the rate of appearance of Cr^{3+} during this time interval.

Solution: The equality in this case is:

$$-\frac{\Delta[Cr_2O_7^{2-}]}{\Delta t} = -\frac{1}{3} \frac{\Delta[HNO_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[Cr^{3+}]}{\Delta t}$$

It is given that,

$$-\frac{\Delta[Cr_2O_7^{2-}]}{\Delta t} = 2.4 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

$$\text{So, } -\frac{\Delta[HNO_2]}{\Delta t} = 3 \times 2.4 \times 10^{-4} = 7.2 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

$$\text{and } \frac{\Delta[Cr^{3+}]}{\Delta t} = 2 \times 2.4 \times 10^{-4} = 4.8 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

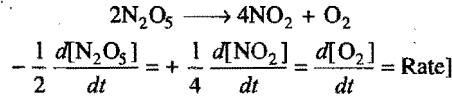
ILLUSTRATIONS OF OBJECTIVE QUESTIONS

1. For the reaction, $2N_2O_5 \rightarrow 4NO_2 + O_2$ rate of reaction is: (AIIMS 2006)

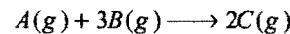
- (a) $\frac{1}{2} \frac{d}{dt}[N_2O_5]$ (b) $2 \frac{d}{dt}[N_2O_5]$
(c) $\frac{1}{4} \frac{d}{dt}[NO_2]$ (d) $4 \frac{d}{dt}[NO_2]$

[Ans. (c)]

[Hint: For the reaction:



2. Observe the following reaction:



The rate of this reaction $\left\{ \frac{-d[A]}{dt} \right\}$ is $3 \times 10^{-3} \text{ mol litre}^{-1} \text{ min}^{-1}$

What is the value of $\frac{-d[B]}{dt}$ in $\text{mol litre}^{-1} \text{ min}^{-1}$?

(EAMCET 2006)

- (a) 3×10^{-3} (b) 9×10^{-3} (c) 10^{-3} (d) 1.5×10^{-3}

[Ans. (b)]

[Hint: $\frac{-d[A]}{dt} = -\frac{1}{3} \frac{d[B]}{dt}$

$$\therefore \frac{-d[B]}{dt} = 3 \left\{ \frac{-d[A]}{dt} \right\} = 3 \times 3 \times 10^{-3}$$

$$= 9 \times 10^{-3} \text{ mol litre}^{-1} \text{ min}^{-1}$$

3. For the reaction, $2A + B \longrightarrow 3C + D$, which of the following does not express the reaction rate?

[CBSE (Med.) 2006]

(a) $\frac{-d[C]}{3dt}$ (b) $\frac{-d[B]}{dt}$ (c) $\frac{d[D]}{dt}$ (d) $\frac{-d[A]}{2dt}$

[Ans. (a)]

[Hint: $-\frac{1}{2} \frac{d[A]}{dt} = \frac{-d[B]}{dt} = +\frac{1}{3} \frac{d[C]}{dt} = +\frac{d[D]}{dt}$ = Rate]

4. Consider the reaction, $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$. The equality relationship between $\frac{d[NH_3]}{dt}$ and $-\frac{d[H_2]}{dt}$ is:

[CBSE (Med.) 2006]

(a) $\frac{d[NH_3]}{dt} = -\frac{1}{3} \frac{d[H_2]}{dt}$ (b) $\frac{d[NH_3]}{dt} = -\frac{2}{3} \frac{d[H_2]}{dt}$
 (c) $\frac{d[NH_3]}{dt} = -\frac{3}{2} \frac{d[H_2]}{dt}$ (d) $\frac{d[NH_3]}{dt} = -\frac{d[H_2]}{dt}$

[Ans. (b)]

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

5. For a reaction $\frac{1}{2}A \longrightarrow 2B$ rate of disappearance of A is related to the rate of appearance of B by the expression:

(AIEEE 2008)

(a) $\frac{-d[A]}{dt} = 4 \frac{d[B]}{dt}$ (b) $\frac{-d[A]}{dt} = \frac{1}{2} \frac{d[B]}{dt}$
 (c) $\frac{-d[A]}{dt} = \frac{1}{4} \frac{d[B]}{dt}$ (d) $\frac{-d[A]}{dt} = +\frac{d[B]}{dt}$

[Ans. (c)]

[Hint: The reaction may be given as

$$A \longrightarrow 4B$$

$$\frac{-d[A]}{dt} = +\frac{1}{4} \frac{d[B]}{dt} = \text{Rate of reaction.}$$

6. In a reaction of acidified hydrogen peroxide with potassium iodide, the concentration of iodine formed rises from 0 to 10^{-5} mol dm $^{-3}$ in 10 seconds. What is the rate of reaction?

[PET (Raj.) 2008]

(a) 10^{-6} mol dm $^{-3}$ s $^{-1}$ (b) 10^6 mol dm $^{-3}$ s $^{-1}$
 (c) 10^{-5} mol dm $^{-3}$ s $^{-1}$ (d) 10^4 mol dm $^{-3}$ s $^{-1}$

[Ans. (a)]

[Hint: The reaction is



$$\text{Rate} = +\frac{d[I_2]}{dt} = \frac{10^{-5}}{10} = 10^{-6} \text{ mol dm}^{-3}\text{s}^{-1}$$

8.3 LAW OF MASS ACTION (Guldberg and Waage, 1864)

This law relates rate of reaction with active mass or molar concentration of reactants.

"At a given temperature, the rate of a reaction at a particular instant is proportional to the product of the active masses of the reactants at that instant raised to powers which are numerically equal to the numbers of their respective molecules in the stoichiometric equation describing the reaction."

$$\begin{aligned} \text{Active mass} &= \text{molar concentration of the substance} \\ &= \frac{\text{number of gram moles of the substance}}{\text{volume in litres}} \\ &= \frac{w/M}{V} = \frac{n}{V} \end{aligned}$$

where, w = mass of substance and ' M ' is the molecular mass in gram, ' n ' is the number of gram moles and V is volume in litre.

Example 6. 4 g of hydrogen and 128 g of hydrogen iodide are present in a 2 litre flask. What are their active masses?

Solution: Mass of hydrogen = 4 g

Mol. mass of hydrogen = 2

Volume of the flask = 2 litre

$$\text{Active mass of hydrogen} = \frac{4}{2 \times 2} = 1 \text{ mol L}^{-1}$$

Mass of HI = 128 g

Mol. mass of HI = 128

Volume of the flask = 2 litre

$$\text{Active mass of hydrogen iodide} = \frac{128}{128 \times 2} = 0.5 \text{ mol L}^{-1}$$

8.4 RATE CONSTANT

Consider a simple reaction $A \rightarrow B$.

If C_A is the molar concentration or active mass of A at a particular instant, then

$$\frac{dx}{dt} \propto C_A \text{ or } \frac{dx}{dt} = k C_A$$

where, k is a proportionality constant, called velocity constant or rate constant or specific reaction rate.

At a fixed temperature, if $C_A = 1$, then

$$\text{Rate} = \frac{dx}{dt} = k \quad \dots (i)$$

Let us consider a general reaction.



$$\text{Rate} = \left(\frac{dx}{dt} \right) \propto [A]^a [B]^b$$

$$\text{Rate} = k [A]^a [B]^b \quad \dots (ii)$$

When $[A] = [B] = 1 \text{ mol/litre}$, then

$$\text{Rate} = k$$

Rate of a reaction at unit concentration of reactants is called rate constant.

The value of rate constant depends on:

- (i) Nature of reactant
- (ii) Temperature
- (iii) Catalyst

Unit of Rate Constant

Rate constant has different units for reactions of different order. General rule for rate of reaction may be given as:

$$\begin{aligned}\text{Unit of rate constant} &= \left[\frac{1}{\text{unit of concentration}} \right]^{n-1} \times \text{time}^{-1} \\ &= \left[\frac{1}{\text{mol/litre}} \right]^{n-1} \times \text{sec}^{-1} \\ &= \left[\frac{\text{litre}}{\text{mol}} \right]^{n-1} \times \text{sec}^{-1}\end{aligned}$$

where, n = order of reaction.

| S. No. | Rate of reaction | Reaction rate constant |
|--------|--|--|
| 1. | It is the speed with which reactants are converted into products. | It is proportionality constant. |
| 2. | It is measured as the rate of decrease of concentration of reactants or the rate of increase of concentration of products with time. | It is equal to the rate of reaction when the concentration of each of the reactants is unity. |
| 3. | It depends upon the initial concentration of reactants. | It is independent of the initial concentration of the reactants. It has a constant value at fixed temperature. |

8.5 COLLISION THEORY OF REACTION RATE (Arrhenius Theory of Reaction Rate)

(1) A chemical reaction takes place due to collision among reactant molecules. The number of collisions taking place per second per unit volume of the reaction mixture is known as **collision frequency (Z)**. The value of collision frequency is very high, of the order of 10^{25} to 10^{28} in case of binary collisions.

(2) Every collision does not bring a chemical change. The collisions that actually produce the products are **effective collisions**. The effective collisions which bring chemical change are few in comparison to the total number of collisions. The collisions that do not form a product are **ineffective elastic collisions**, i.e., molecules just collide and disperse in different directions with different velocities. For a collision to be effective, the following two barriers are to be cleared:

Energy Barrier

The minimum amount of energy which the colliding molecules must possess as to make the chemical reaction to occur, is known as **threshold energy**.

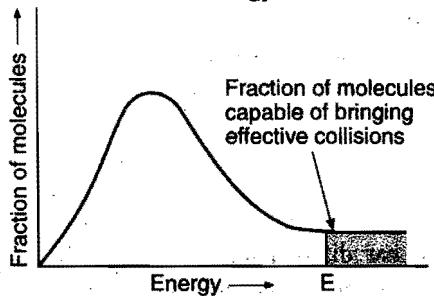


Fig. 8.3

In the graph (Fig. 8.3), ' E ' corresponds to minimum or threshold energy for effective collision in a hypothetical reaction.

There is an energy barrier for each reaction. The reacting species must be provided with sufficient energy as to cross the energy barrier.

The minimum amount of energy required by reactant molecules to participate in a reaction is called activation energy.

Activation energy = threshold energy – average kinetic energy of reacting molecules

Threshold energy = initial potential energy of reactant molecules + activation energy.

A collision between high energy molecules overcomes the forces of repulsion and brings the formation of an unstable molecule cluster, called the **activated complex**. The life span of an activated complex is very small. Thus, the activated complex breaks either into reactants again or new substances, i.e., products. The activation energy (E_a) depends upon the nature of chemical bonds undergoing rupture and is independent of enthalpies of reactants and products. The energy changes during exothermic and endothermic reactions *versus* the progress of the reaction are shown in Fig. 8.4.

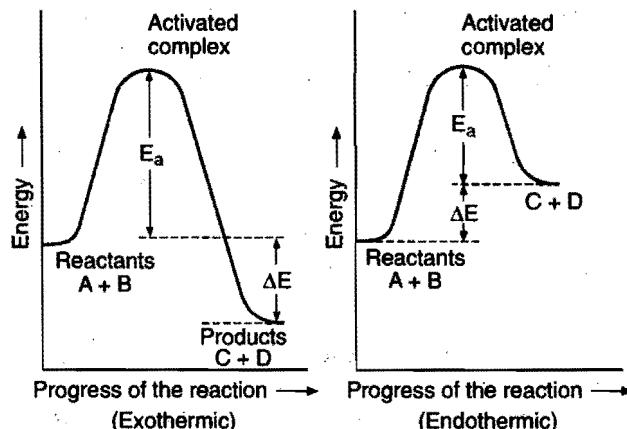


Fig. 8.4 Activation energy of exothermic and endothermic reaction

Thus, every chemical reaction whether exothermic or endothermic has an energy barrier which has to be overcome before reactants can be transformed into products. If the reactant molecules have sufficient energy, they can reach the peak of the energy barrier after collision and then they can go to the right side of the slope and consequently change into products. If the activation energy for a reaction is low, the fraction of effective collisions will be large and the reaction will be fast. On the other hand, if the activation energy is high, then fraction of effective collisions will be small and the reaction will be slow. When temperature is increased, the number of active molecules increases, i.e., the number of effective collisions will increase and the rate of reaction will increase.

$$\text{Activation energy } E_a = E_{(\text{activated complex})} - E_{(\text{ground state})}$$

$$\Delta H = \text{activation energy of forward reaction}$$

$$- \text{activation energy of backward reaction.}$$

Orientation Barrier

Energy alone does not determine the effectiveness of the collision. The reacting molecules must collide in proper manner if the reaction is to occur. This has been shown in Fig. 8.5.

Rate of reaction is directly proportional to the number of effective collisions.

$$\text{Rate} = -\frac{dx}{dt} = \text{collision frequency} \times \text{fraction of effective collisions}$$

$$= Z \times f$$

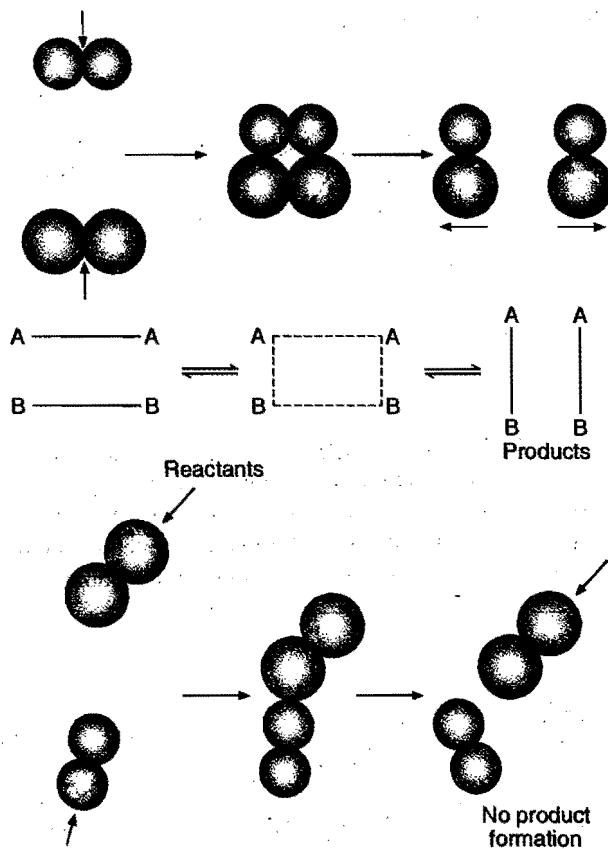


Fig. 8.5 Orientation of collisions

Factors Affecting Rate of Reaction

(i) Nature of the reactants

(a) Physical state of reactants: This has considerable effect over rate of reaction.

Gaseous state > Liquid state > Solid state

Decreasing rate of reaction

Similarly, in a heterogeneous system, collision is not so effective as in homogeneous system. Thus, reactions in liquid phase or solution phase will be faster in comparison to heterogeneous conditions when same concentrations of the reactants are taken.

(b) Physical size of the reactants: Among the solids, rate increases with decrease in particle size. In powdered state rate of

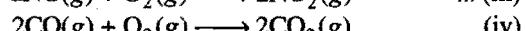
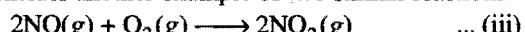
reaction is maximum because in powdered state, surface area is maximum.

(c) Chemical nature of reactants: Consider the following two reactions:



The first reaction is faster than the second because in the first reaction only N≡O bond is to be broken whereas in the second reaction four (C—H) bonds are to be broken.

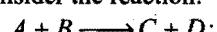
Similarly, consider another example of two similar reactions:



NO bond is weaker than CO bond, hence broken easily. Thus, reaction (iii) is faster than (iv).

(ii) Concentration of reactants

Let us consider the reaction:



$$\text{Rate} = k [A][B]$$

Rate of the above reaction decreases with the passage of time because the concentration of reactants A and B will decrease as time passes on.

Let us consider the following reversible reaction:



$$\text{Rate of forward reaction} = k_f [A][B]$$

$$\text{Rate of backward reaction} = k_b [C][D]$$

Rate of forward reaction decreases and that of backward reaction increases with passage of time. At equilibrium both the rates become equal.

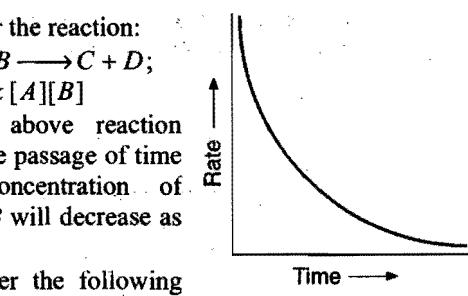


Fig. 8.6

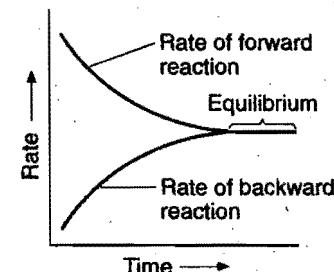


Fig. 8.7

(iii) Effect of temperature

The rate of reaction increases considerably with an increase in temperature. The rates of many reactions are approximately doubled or tripled for every 10°C rise in temperature. The temperature coefficient of a chemical reaction is defined as the ratio of the specific reaction rates of a reaction at two temperatures differing by 10°C.

$$\mu = \text{Temperature coefficient} = \frac{k_{t+10}}{k_t}$$

Let temperature coefficient of a reaction be ' μ ' when temperature is raised from T_1 to T_2 ; then the ratio of rate constants or rate may be calculated as:

$$\frac{k_{T_2}}{k_{T_1}} = (\mu)^{(T_2 - T_1)/10} = \mu^{\Delta T/10}$$

$$\log_{10} \left(\frac{k_{T_2}}{k_{T_1}} \right) = \frac{\Delta T}{10} \log_{10} \mu$$

$$\frac{k_{T_2}}{k_{T_1}} = \text{antilog} \left[\frac{\Delta T}{10} \log_{10} \mu \right]$$

Its value lies generally between 2 and 3.

When the temperature is increased, heat energy is supplied which increases the kinetic energy of the reacting molecules. This will increase the number of collisions and ultimately the rate of reaction will be enhanced. Arrhenius suggested an equation which describes k as a function of temperature, i.e.,

$$k = A e^{-E_a/RT}$$

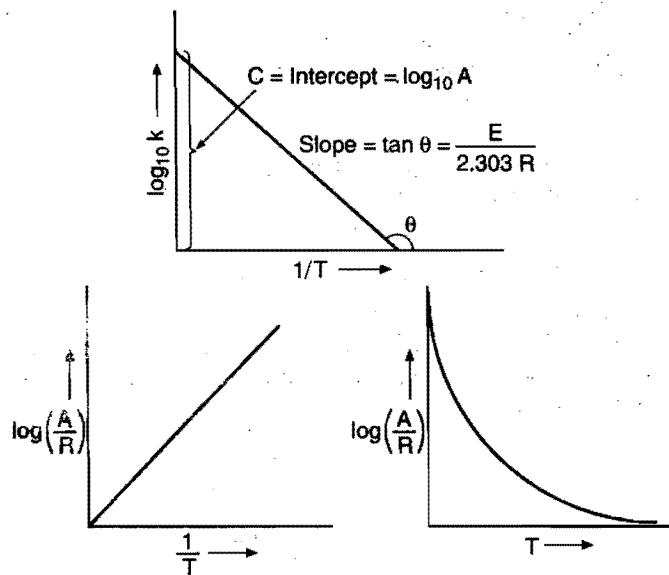


Fig. 8.8

where, $k \rightarrow$ rate constant

$A \rightarrow$ a constant (frequency factor)

$E_a \rightarrow$ energy of activation

At two temperatures T_1 and T_2 , taking log of Arrhenius equation, we get

$$\log_e k_1 = \log A - \frac{E_a}{RT_1} \log_e e \quad \dots (i)$$

$$\text{and} \quad \log_e k_2 = \log A - \frac{E_a}{RT_2} \log_e e \quad \dots (ii)$$

Subtracting eq. (ii) from eq. (i) and converting the log to the base 10, we get

$$\log_{10} \frac{k_1}{k_2} = -\frac{E_a}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right] \text{ or } \log_{10} \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

This equation can be used for calculation of energy of activation.

Logarithmic Arrhenius equation is:

$$\log_{10} k = \log_{10} A - \frac{E_a}{2.303R} \left[\frac{1}{T} \right]$$

$$Y = C + M X$$

It is the equation of straight line with negative slope. On plotting $\log_{10} k$ against $[1/T]$ we get a straight line as shown in Fig. 8.8. The graph gives two kinetic parameters.

The slope gives **activation energy** and intercept gives **frequency factor**.

The dependence of rate constant on temperature for two reactions is shown in the Fig. 8.9.

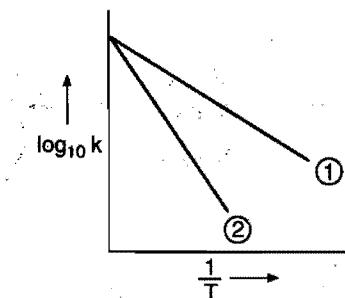


Fig. 8.9

In the reaction (2), the modulus of slope is greater than that of reaction (1), hence reaction (2) has higher activation energy. The reaction (2) will be more sensitive to temperature change.

Reactions on the basis of influence of temperature are classified into five types. These are shown in the graphs.

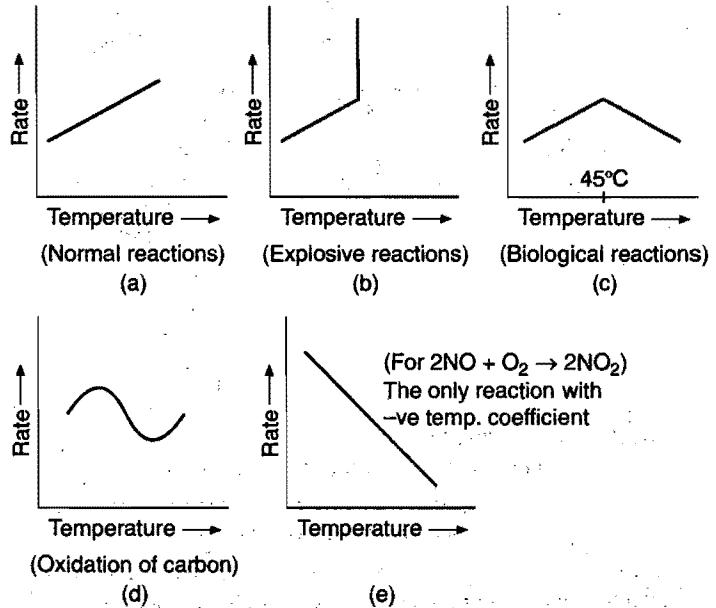


Fig. 8.10

(iv) Presence of a positive catalyst

The function of a positive catalyst is to lower down the activation energy. The greater the decrease in the activation energy caused by the catalyst, higher will be the reaction rate. In

In the presence of a catalyst, the reaction follows a path of lower activation energy. Under this condition, a large number of reacting molecules are able to cross over the energy barrier and thus the rate of reaction increases. Fig. 8.11 shows how the activation energy is lowered in presence of a catalyst.

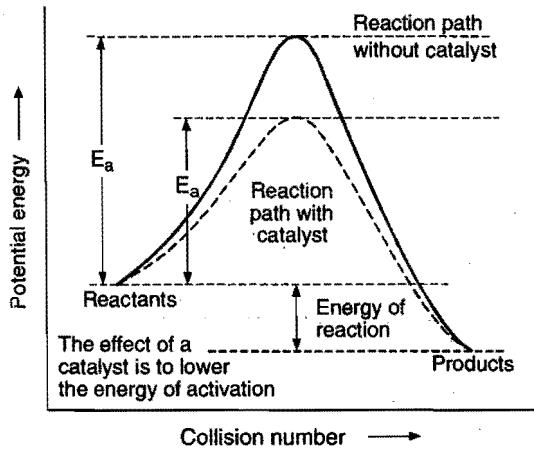


Fig. 8.11 A catalyst changes the reaction path (Positive catalyst)

(v) Presence of negative catalyst

A negative catalyst increases the activation energy of reaction by forming a new intermediate of high energy, i.e., by changing the reaction mechanism.

Due to increased activation energy, some active molecules become inactive, therefore, rate of reaction decreases.

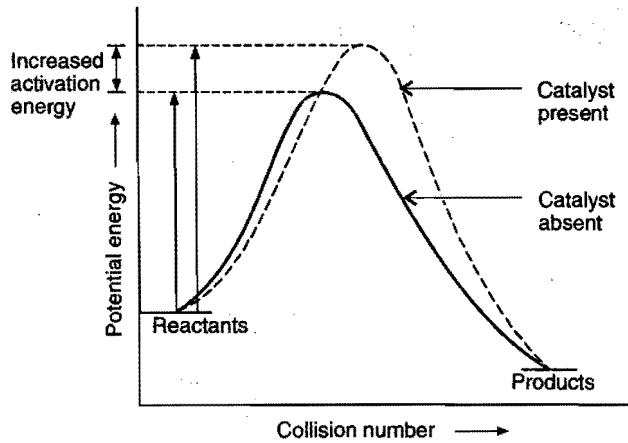


Fig. 8.12 Negative catalyst

Let 'p' denote presence of catalyst and 'a' denote absence of catalyst.

$$k_p = Ae^{-E_p/RT} \quad \dots (i)$$

$$k_a = Ae^{-E_a/RT} \quad \dots (ii)$$

Dividing eq. (i) by eq. (ii), we get

$$\frac{k_p}{k_a} = e^{(E_a - E_p)/RT} = e^{\Delta E/RT}$$

$$\frac{k_p}{k_a} = \text{antilog} \left[\frac{\Delta E}{2.303RT} \right]$$

SOME SOLVED EXAMPLES

Example 7. The rate of a reaction triples when temperature changes from 20°C to 50°C. Calculate energy of activation for the reaction. ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)

Solution: The Arrhenius equation is,

$$\log_{10} \frac{k_2}{k_1} = \frac{E_a}{R \times 2.303} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\text{Given: } \frac{k_2}{k_1} = 3; R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}; T_1 = 20 + 273 = 293 \text{ K}$$

$$\text{and } T_2 = 50 + 273 = 323 \text{ K}$$

Substituting the given values in the Arrhenius equation,

$$\log_{10} 3 = \frac{E_a}{8.314 \times 2.303} \left[\frac{323 - 293}{323 \times 293} \right]$$

$$E_a = \frac{2.303 \times 8.314 \times 323 \times 293 \times 0.477}{30}$$

$$= 28811.8 \text{ J mol}^{-1}$$

$$= 28.8118 \text{ kJ mol}^{-1}$$

Example 8. In Arrhenius equation for a certain reaction, the value of A and E_a (activation energy) are $4 \times 10^{13} \text{ sec}^{-1}$ and 98.6 kJ mol^{-1} respectively. At what temperature, the reaction will have specific rate constant $1.1 \times 10^{-3} \text{ sec}^{-1}$?

Solution: According to Arrhenius equation,

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

$$\text{or } \log_e k = \log_e A - \frac{E_a}{RT} \log_e e$$

$$\text{or } 2.303 \log_{10} k = 2.303 \log_{10} A - \frac{E_a}{RT}$$

$$\text{or } 2.303 \log (1.1 \times 10^{-3}) = 2.303 \log (4 \times 10^{13}) - \frac{98.6 \times 10^3}{8.314 \times T}$$

$$T = \frac{98.6 \times 10^3}{8.314 \times 2.303 \times 16.56} \text{ K}$$

$$= 310.96 \text{ K}$$

Example 9. The rate constant is given by Arrhenius equation,

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

Calculate the ratio of the catalysed and uncatalysed rate constants at 25°C if the energy of activation of a catalysed reaction is 162 kJ and for the uncatalysed reaction the value is 350 kJ.

Solution: Let k_{ca} and k_{un} be the rate constants for catalysed and uncatalysed reactions.

$$2.303 \log_{10} k_{ca} = 2.303 \log_{10} A - \frac{162 \times 10^3}{RT} \quad \dots (i)$$

$$\text{and } 2.303 \log_{10} k_{\text{un}} = 2.303 \log_{10} A - \frac{350 \times 10^3}{RT} \quad \dots (\text{i})$$

Subtracting eq. (ii) from eq. (i)

$$\begin{aligned} \log_{10} \frac{k_{\text{ca}}}{k_{\text{un}}} &= \frac{10^3}{2.303RT} (350 - 162) \\ &= \frac{188 \times 10^3}{2.303 \times 8.314 \times 298} = 32.95 \\ \frac{k_{\text{ca}}}{k_{\text{un}}} &= 8.88 \times 10^{32} \end{aligned}$$

Example 10. Calculate the rate constant of a reaction at 293 K when the energy of activation is 103 kJ mol⁻¹ and the rate constant at 273 K is $7.87 \times 10^{-7} \text{ s}^{-1}$.
($R = 8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$)

Solution: The Arrhenius equation is,

$$\log_{10} \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

Given: $k_1 = 7.87 \times 10^{-7} \text{ s}^{-1}$; $E_a = 103 \text{ kJ mol}^{-1}$;
 $R = 8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$;

$T_1 = 273 \text{ K}$ and $T_2 = 293 \text{ K}$

Substituting the values in Arrhenius equation,

$$\begin{aligned} \log_{10} \frac{k_2}{7.87 \times 10^{-7}} &= \frac{103 \times 20}{2.303 \times 8.314 \times 10^{-3} \times 293 \times 273} \\ &= 1.345 \\ k_2 &= 1.74 \times 10^{-5} \text{ s}^{-1} \end{aligned}$$

Example 11. At 407 K, the rate constant of a chemical reaction is $9.5 \times 10^{-5} \text{ s}^{-1}$ and at 420 K, the rate constant is $1.9 \times 10^{-4} \text{ s}^{-1}$. Calculate the frequency factor of the reaction.

Solution: The Arrhenius equation is,

$$\log_{10} \frac{k_2}{k_1} = \frac{E_a}{2.303 \times R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

Given: $k_1 = 9.5 \times 10^{-5} \text{ s}^{-1}$; $k_2 = 1.9 \times 10^{-4} \text{ s}^{-1}$;

$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$;

$T_1 = 407 \text{ K}$ and $T_2 = 420 \text{ K}$

Substituting the values in Arrhenius equation

$$\begin{aligned} \log_{10} \frac{1.9 \times 10^{-4}}{9.5 \times 10^{-5}} &= \frac{E_a}{2.303 \times 8.314} \left[\frac{420 - 407}{420 \times 407} \right] \\ E_a &= 75782.3 \text{ J mol}^{-1} \end{aligned}$$

Applying now $\log k_1 = \log A - \frac{E_a}{2.303RT_1}$

$$\log 9.5 \times 10^{-5} = \log A - \frac{75782.3}{2.303 \times 8.314 \times 407}$$

$$\begin{aligned} \text{or } \log \frac{A}{9.5 \times 10^{-5}} &= \frac{75782.3}{2.303 \times 8.314 \times 407} = 9.7246 \\ A &= 5.04 \times 10^5 \text{ s}^{-1} \end{aligned}$$

Example 12. The energy of activation for a reaction is 100 kJ mol⁻¹. Presence of a catalyst lowers the energy of activation by 75%. What will be effect on rate of reaction at 20°C, other things being equal?

Solution: The Arrhenius equation is,

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

In absence of catalyst, $k_1 = Ae^{-100/RT}$

In presence of catalyst, $k_2 = Ae^{-25/RT}$

$$\text{So, } \frac{k_2}{k_1} = e^{75/RT} \text{ or } 2.303 \log \frac{k_2}{k_1} = \frac{75}{RT}$$

$$\text{or } 2.303 \log \frac{k_2}{k_1} = \frac{75}{8.314 \times 10^{-3} \times 293}$$

$$\text{or } \log \frac{k_2}{k_1} = \frac{75}{8.314 \times 10^{-3} \times 293 \times 2.303}$$

$$\text{or } \frac{k_2}{k_1} = 2.34 \times 10^{13}$$

As the things being equal in presence or absence of a catalyst,

$$\frac{k_2}{k_1} \text{ must be} = \frac{\text{rate in presence of catalyst}}{\text{rate in absence of catalyst}}$$

$$\text{i.e., } \frac{r_2}{r_1} = \frac{k_2}{k_1} = 2.34 \times 10^{13}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

7. For a reaction $E_a = 0$ and $k = 3.2 \times 10^4 \text{ s}^{-1}$ at 300 K. The value of k at 310 K would be:

- (a) $6.4 \times 10^4 \text{ s}^{-1}$ (b) $3.2 \times 10^4 \text{ s}^{-1}$
(c) $3.2 \times 10^8 \text{ s}^{-1}$ (d) $3.2 \times 10^5 \text{ s}^{-1}$

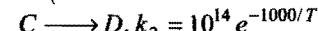
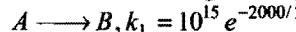
[Ans. (b)]

[Hint: $k = Ae^{-E_a/RT}$

When $E_a = 0$, $k = A = \text{constant}$

$$\therefore k_{310} = k_{300} = 3.2 \times 10^4 \text{ s}^{-1}]$$

8. For a gaseous reaction, following data is given:



The temperature at which $k_1 = k_2$ is:

- (a) 1000 K (b) 2000 K (c) 868.82 K (d) 434.2 K

[Ans. (d)]

[Hint: When $k_1 = k_2$,

$$10^{15} e^{-2000/T} = 10^{14} e^{-1000/T}$$

$$10 = e^{1000/T}$$

$$2.303 \log 10 = \frac{1000}{T}$$

$$T = 434.2 \text{ K}]$$

9. For $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ + 22 kcal, E_a for the reaction is 70 kcal. Hence, the activation energy for $2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$ is:
 (a) 92 kcal (b) 70 kcal (c) 48 kcal (d) 22 kcal

[Ans. (a)]

[Hint: $\Delta H = E_f - E_b$
 $-22 = 70 - E_b$
 $E_b = 92 \text{ kcal}$]

10. On introducing a catalyst at 500 K, the rate of a first order reaction increases by 1.718 times. The activation energy in the presence of a catalyst is 6.05 kJ mol^{-1} . The slope of the plot of $\ln k (\text{sec}^{-1})$ against $1/T$ in the absence of catalyst is:

- (a) +1 (b) -1 (c) +1000 (d) -1000

[Ans. (d)]

[Hint: $\frac{\text{Rate in presence of catalyst}}{\text{Rate in absence of catalyst}} = \text{Antilog} \left[\frac{+ΔE}{2.303RT} \right]$
 $1.718 = \text{Antilog} \frac{E_a - E_p}{2.303 \times 8.314 \times 500}$

$$\begin{aligned} E_a - E_p &= 2.25 \text{ kJ} \\ E_a &= E_p + 2.25 = 6.05 + 2.25 = 8.30 \text{ kJ mol}^{-1} \\ &= 8.3 \text{ kJ mol}^{-1} \\ \ln k &= \ln A - \frac{E_a}{R} \times \frac{1}{T} \\ \text{Slope} &= \frac{-E_a}{R} = \frac{-8.3 \times 1000}{8.3} = -1000 \end{aligned}$$

11. For which of the following reactions k_{310}/k_{300} would be maximum?

- (a) $A + B \rightarrow C$; $E_a = 50 \text{ kJ}$
 (b) $X + Y \rightarrow Z$; $E_a = 40 \text{ kJ}$
 (c) $P + Q \rightarrow R$; $E_a = 60 \text{ kJ}$
 (d) $E + F \rightarrow G$; $E_a = 100 \text{ kJ}$

[Ans. (d)]

[Hint: Increase in rate constant is maximum for the reaction having maximum activation energy.]

12. The activation energy of exothermic reaction $A \rightarrow B$ is 80 kJ mol^{-1} . The heat of reaction is 200 kJ mol^{-1} . The activation energy for the reaction $B \rightarrow A$ (in kJ/mol) will be:
 [PET (Kerala) 2007]

- (a) 80 (b) 120 (c) 40 (d) 200

(e) 280

[Ans. (e)]

[Hint: $\Delta H = E_f - E_b$
 $-200 = 80 - E_b$
 $E_b = 280 \text{ kJ/mol}$]

13. Which equation is true to calculate the energy of activation, if the rate of reaction is doubled by increasing temperature from $T_1 \text{ K}$ to $T_2 \text{ K}$?
 [CET (Gujarat) 2008]

- (a) $\log_{10} \left(\frac{k_1}{k_2} \right) = \frac{E_a}{2.303 R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$
 (b) $\log_{10} \left(\frac{k_2}{k_1} \right) = \frac{E_a}{2.303 R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$

(c) $\log_{10} \frac{1}{2} = \frac{E_a}{2.303} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$

(d) $\log_{10} 2 = \frac{E_a}{2.303 R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$

[Ans. (d)]

[Hint: We know, $\log \left(\frac{k_2}{k_1} \right) = \frac{E_a}{2.303 R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$]

When reaction rate becomes double then $\frac{k_2}{k_1}$ will be equal to 2.

Then, $\log_{10} 2 = \frac{E_a}{2.303 R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$

8.6 MOLECULARITY OF REACTION

In general, **molecularity of simple reactions is equal to the sum of the number of molecules of reactants involved in the balanced stoichiometric equation.**

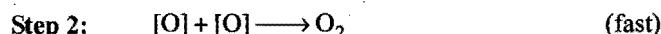
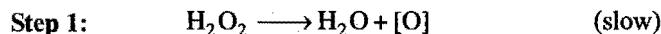
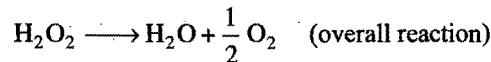
OR

The molecularity of a reaction is the number of reactant molecules taking part in a single step of the reaction.

| | |
|-------|--|
| e.g., | $\text{PCl}_5 \rightarrow \text{PCl}_3 + \text{Cl}_2$ (Unimolecular) |
| | $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$ (Bimolecular) |
| | $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$ (Trimolecular) |
| | $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$ (Bimolecular) |
| | $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$ (Trimolecular) |
| | $2\text{FeCl}_3 + \text{SnCl}_2 \rightarrow \text{SnCl}_4 + 2\text{FeCl}_2$ (Trimolecular) |

The minimum number of reacting particles (molecules, atoms or ions) that come together or collide in a rate determining step to form product or products is called the molecularity of a reaction.

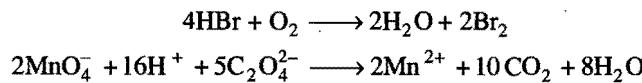
For example, decomposition of H_2O_2 takes place in the following two steps:



The slowest step is rate-determining. Thus, from step 1, reaction appears to be unimolecular.

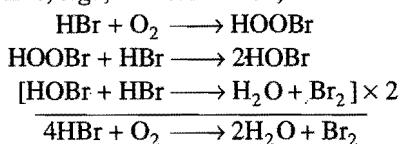
- Note: (i) Molecularity is a theoretical concept.
 (ii) Molecularity cannot be zero, -ve, fractional, infinite and imaginary.
 (iii) Molecularity cannot be greater than three because more than three molecules may not mutually collide with each other.

There are some chemical reactions whose molecularity appears to be more than three from stoichiometric equations, e.g., in



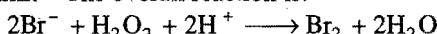
In the first reaction, molecularity seems to be '5' and in the second reaction molecularity seems to be '23'. Such reactions

involve two or more steps; each step has its own molecularity not greater than three, e.g., in first reaction,

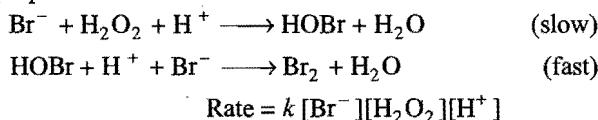


Molecularity of each of the above steps is 2.

(a) Reaction between Br^- and H_2O_2 in acidic medium: The overall reaction is:



The proposed mechanism is:

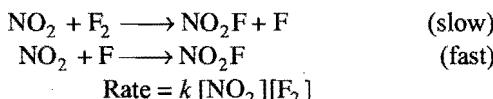


The reaction is trimolecular.

(b) Reaction between NO_2 and F_2 : The overall reaction is:

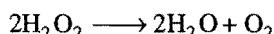


The proposed mechanism is:

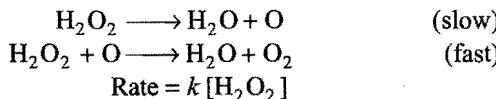


The reaction is bimolecular.

(c) Decomposition of H_2O_2 : The overall reaction is:



The proposed mechanism is:



The reaction is unimolecular.

8.7 ORDER OF REACTION

Let us consider a general reaction:



Let active moles of 'A', 'B' and 'C' be ' α ', ' β ' and ' γ ' respectively. Then, rate of reaction may be given as:

$$\text{Rate} = k[A]^\alpha[B]^\beta[C]^\gamma$$

Sum of powers of concentration terms involved in rate law expression is called order of reaction.

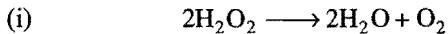
$$\alpha + \beta + \gamma = \text{order}$$

When $\alpha + \beta + \gamma = m_1 + m_2 + m_3$, then

Order of reaction = molecularity of reaction.

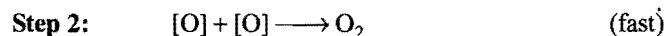
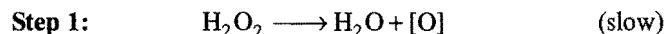
Order is an experimentally determined quantity. It may be equal to zero, positive, negative, fractional and greater than three. Infinite and imaginary values are not possible.

Examples:



$$-\frac{dx}{dt} = k[\text{H}_2\text{O}_2]^2$$

(observed from law of mass action)



$$\text{Actual rate} \quad -\frac{dx}{dt} = k[\text{H}_2\text{O}_2]$$

Thus, order of reaction is unity.



Rate law from law of mass action:

$$-\frac{dx}{dt} = k[\text{NO}_2]^2[\text{F}_2]$$

Experimentally observed rate law:

$$-\frac{dx}{dt} = k[\text{NO}_2][\text{F}_2]$$

Slowest step is $\text{NO}_2 + \text{F}_2 \longrightarrow \text{NO}_2\text{F} + [\text{F}]$

Thus, order of reaction = $1 + 1 = 2$



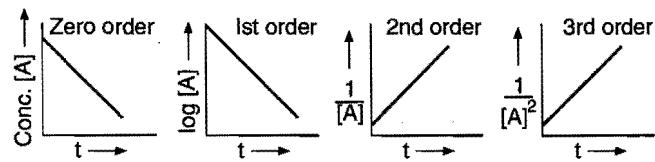
The rate equation derived from experimental data is found to be

$$-\frac{dx}{dt} = k[\text{CH}_3\text{CHO}]^{1.5}$$

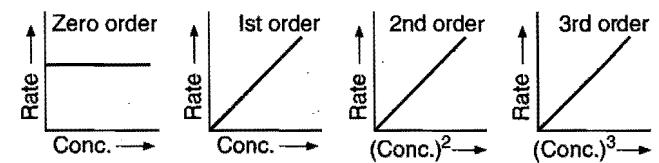
The order of reaction is 1.5.

Some typical linear plots for the reactions of different orders:

(a) Plots of rate vs concentrations [Rate = $k(\text{conc.})^n$]

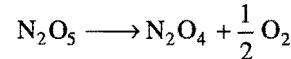


(b) Plots from integrated rate equations:



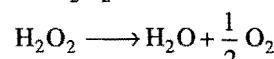
From the study of the kinetics of many simple reactions, it is observed that for a large number of reactions, the molecularity and order are the same. Some examples are given below to justify this point.

1. Dissociation of N_2O_5 ,



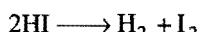
Order = 1, Molecularity = 1

2. Dissociation of H_2O_2 ,



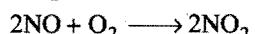
Order = 1, Molecularity = 1

3. Dissociation of HI,



Order = 2, Molecularity = 2

4. Formation of NO₂,



Order = 3, Molecularity = 3

8.8 PSEUDO-ORDER REACTION

Reactions whose actual order is different from that expected using rate law expression are called **pseudo-order reactions**, e.g.,



Expected rate law:

$$\text{Rate} = k[\text{RCl}][\text{H}_2\text{O}]$$

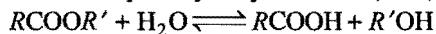
$$\text{Expected order} = 1+1=2$$

Actual rate law:

$$\text{Rate} = k'[\text{RCl}];$$

$$\text{Actual order} = 1$$

Water is taken in excess; therefore, its concentration may be taken constant. The reaction is, therefore, **pseudo first order**. Similarly, the acid catalysed hydrolysis of ester, viz.,



follow first order kinetics:

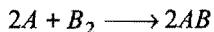
$$\text{Rate} = k[\text{RCOOR}']$$

It is also a pseudo first order reaction.

The main differences between molecularity and order of reaction are given below:

| Molecularity | Order of reaction |
|--|---|
| 1. It is the total number of reacting species (molecules, atoms or ions) which bring the chemical change. | It is the sum of powers of molar concentrations of the reacting species in the rate equation of the reaction. |
| 2. It is always a whole number. | It may be a whole number, zero, fractional, positive or negative. |
| 3. It is a theoretical concept. | It is experimentally determined. |
| 4. It is meaningful only for simple reactions or individual steps of a complex reaction. It is meaningless for overall complex reaction. | It is meant for the reaction and not for its individual steps. |

Example 13. The experimental data for the reaction,



is as follows:

| Expt. No. | [A] (mol L ⁻¹) | [B ₂] (mol L ⁻¹) | Rate (mol L ⁻¹ s ⁻¹) |
|-----------|----------------------------|--|---|
| 1. | 0.50 | 0.50 | 1.6×10^{-4} |
| 2. | 0.50 | 1.00 | 3.2×10^{-4} |
| 3. | 1.00 | 1.00 | 3.2×10^{-4} |

Write the most probable equation for the rate of reaction giving reason for your answer.

Solution: From an examination of above data, it is clear that when the concentration of B₂ is doubled, the rate is doubled. Hence, the order of reaction with respect to B₂ is one.

Further, when concentration of A is doubled, the rate remains unaltered. So, order of reaction with respect to A is zero.

The probable rate law for the reaction will be

$$-\frac{dx}{dt} = k[B_2][A]^0 = k[B_2]$$

$$\text{Alternatively, } \text{Rate} = k[B_2]^\alpha$$

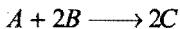
$$1.6 \times 10^{-4} = k[0.5]^\alpha$$

$$3.2 \times 10^{-4} = k[1]^\alpha$$

On dividing we get, $\alpha = 1$

$$\text{Rate} = k[A]^0[B_2]^1 = k[B_2]$$

Example 14. For the reaction,



the following data were obtained:

| Expt. No. | Initial concentrations (mol L ⁻¹) | Initial reaction rates (mol L ⁻¹ min ⁻¹) | |
|-----------|---|---|------|
| | [A] | [B] | |
| 1. | 1.0 | 1.0 | 0.15 |
| 2. | 2.0 | 1.0 | 0.30 |
| 3. | 3.0 | 1.0 | 0.45 |
| 4. | 1.0 | 2.0 | 0.15 |
| 5. | 1.0 | 3.0 | 0.15 |

Write down the rate law for the reaction.

Solution: Let the rate law be

$$-\frac{dx}{dt} = k[A]^x[B]^y$$

By keeping the concentration of B constant in experiments (1), (2) and (3) and increasing the concentration uniformly, the rate also increases uniformly. Thus,

$$\text{Rate} \propto [A], \text{ i.e., } x = 1$$

By keeping the concentration of A constant in experiments (1), (4) and (5) and increasing the concentration of B, the rate remains the same.

Hence,

$$y = 0$$

$$\text{The rate law is } -\frac{dx}{dt} = k[A]$$

Alternative method:

$$\text{From expt. (1), } k[1.0]^x[1.0]^y = 0.15 \quad \dots (\text{i})$$

$$\text{From expt. (2), } k[2.0]^x[1.0]^y = 0.30 \quad \dots (\text{ii})$$

Dividing eq. (ii) by eq. (i),

$$\frac{[2.0]^x}{[1.0]^x} = \frac{0.30}{0.15} = 2$$

$$\text{So, } x = 1$$

$$\text{From expt. (1), } k[1.0]^x[1.0]^y = 0.15 \quad \dots (\text{i})$$

From expt. (4), $k[1.0]^x[2.0]^y = 0.15$... (iii)

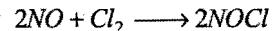
Dividing eq. (iii) by eq. (i),

$$\frac{[2.0]^y}{[1.0]^y} = 1$$

So, $y = 0$

Hence, the rate law is $-\frac{dx}{dt} = k[A]$

Example 15. For the reaction,



at 300 K, following data are obtained:

| Expt. No. | Initial Concentration | | Initial rate |
|-----------|-----------------------|--------------------|----------------------|
| | [NO] | [Cl ₂] | |
| 1. | 0.010 | 0.010 | 1.2×10^{-4} |
| 2. | 0.010 | 0.020 | 2.4×10^{-4} |
| 3. | 0.020 | 0.020 | 9.6×10^{-4} |

Write rate law for the reaction. What is the order of the reaction? Also calculate the specific rate constant.

Solution: Let the rate law for the reaction be

$$\text{Rate} = k[\text{NO}]^x[\text{Cl}_2]^y$$

From expt. (1), $1.2 \times 10^{-4} = k[0.010]^x[0.010]^y$... (i)

From expt. (2), $2.4 \times 10^{-4} = k[0.010]^x[0.020]^y$... (ii)

Dividing eq. (ii) by eq. (i),

$$\frac{2.4 \times 10^{-4}}{1.2 \times 10^{-4}} = \frac{[0.020]^y}{[0.010]^y}$$

or

$$2 = (2)^y$$

$$y = 1$$

From expt. (2), $2.4 \times 10^{-4} = k[0.010]^x[0.020]^y$... (ii)

From expt. (3), $9.6 \times 10^{-4} = k[0.020]^x[0.020]^y$... (iii)

Dividing eq. (iii) by eq. (ii),

$$\frac{9.6 \times 10^{-4}}{2.4 \times 10^{-4}} = \frac{[0.020]^x}{[0.010]^x}$$

or

$$4 = 2^x$$

$$x = 2$$

Order of reaction = $x + y = 2 + 1 = 3$

Rate law for the reaction is

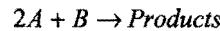
$$\text{Rate} = k[\text{NO}]^2[\text{Cl}_2]$$

Considering eq. (i) again,

$$1.2 \times 10^{-4} = k[0.010]^2[0.010]$$

$$k = \frac{1.2 \times 10^{-4}}{[0.010]^3} = 1.2 \times 10^2 \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}$$

Example 16. For the hypothetical reaction



the following data are obtained:

| Expt. No. | Initial conc. of (A) (mol L ⁻¹) | Initial conc. of (B) (mol L ⁻¹) | Initial rate mol L ⁻¹ s ⁻¹ |
|-----------|--|--|---|
| 1. | 0.10 | 0.20 | 3×10^2 |
| 2. | 0.30 | 0.40 | 3.6×10^3 |
| 3. | 0.30 | 0.80 | 1.44×10^4 |
| 4. | 0.10 | 0.40 | ... |
| 5. | 0.20 | 0.60 | ... |
| 6. | 0.30 | 1.20 | ... |

Find out how the rate of the reaction depends upon the concentration of A and B and fill in the blanks.

Solution: From expt. (2) and (3), it is clear that when concentration of A is kept constant and that of B is doubled, the rate increases four times. This shows that the reaction is of second order with respect to B.

Similarly, from expt. (1) and (2), it is observed that when concentration of A is increased three times and that of B two times, the rate becomes twelve times. Hence, the reaction is first order with respect to A.

Thus, the rate law for the reaction is:

$$\text{Rate} = k[A][B]^2$$

Fill in the blanks: Substituting the values of expt. (1) in the rate equation,

$$3 \times 10^2 = k[0.10][0.20]^2$$

or $k = \frac{3 \times 10^2}{[0.10][0.20]^2} = 7.5 \times 10^4 \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}$

Expt. (4): Rate = $k[0.10][0.40]^2$

$$= 7.5 \times 10^4 \times 0.10 \times 0.40 \times 0.40$$

$$= 1.2 \times 10^3 \text{ mol L}^{-1} \text{ s}^{-1}$$

Expt. (5): Rate = $k[0.20][0.60]^2$

$$= 7.5 \times 10^4 \times 0.20 \times 0.60 \times 0.60$$

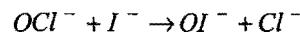
$$= 5.4 \times 10^3 \text{ mol L}^{-1} \text{ s}^{-1}$$

Expt. (6): Rate = $k[0.30][1.20]^2$

$$= 7.5 \times 10^4 \times 0.30 \times 1.20 \times 1.20$$

$$= 3.24 \times 10^4 \text{ mol L}^{-1} \text{ s}^{-1}$$

Example 17. The table given below gives kinetic data for the following reaction at 298 K:



| Expt. No. | [OCl ⁻] mol dm ⁻³ | [I ⁻] mol dm ⁻³ | [OH ⁻] mol dm ⁻³ | $10^{-4} \times d[IO^-]/dt$ mol dm ⁻³ s ⁻¹ |
|--------------|---|---|--|---|
| 1. | 0.0017 | 0.0017 | 1.0 | 1.75 |
| 2. | 0.0034 | 0.0017 | 1.0 | 3.50 |
| 3. | 0.0017 | 0.0034 | 1.0 | 3.50 |
| 4. | 0.0017 | 0.0017 | 0.5 | 3.50 |

What is the rate law and what is the value of rate constant?

Solution: Let the rate law be $r = k[\text{OCl}^-]^x[\text{I}^-]^y[\text{OH}^-]^z$

$$\text{From expt. (1), } 1.75 \times 10^{-4} = k[0.0017]^x[0.0017]^y[1.0]^z \dots (\text{i})$$

$$\text{From expt. (2), } 3.50 \times 10^{-4} = k[0.0034]^x[0.0017]^y[1.0]^z \dots (\text{ii})$$

Dividing eq. (ii) by eq. (i),

$$\frac{3.50 \times 10^{-4}}{1.75 \times 10^{-4}} = \frac{[0.0034]^x}{[0.0017]^x}$$

$$\text{or } 2 = 2^x$$

$$\text{or } x = 1, \text{ i.e., first order w.r.t. OCl}^-$$

$$\text{From expt. (1), } 1.75 \times 10^{-4} = k[0.0017]^x[0.0017]^y[1.0]^z \dots (\text{i})$$

From expt. (3),

$$3.50 \times 10^{-4} = k[0.0017]^x[0.0034]^y[1.0]^z \dots (\text{iii})$$

Dividing eq. (iii) by eq. (i),

$$\frac{3.50 \times 10^{-4}}{1.75 \times 10^{-4}} = \frac{[0.0034]^y}{[0.0017]^y}$$

$$\text{or } 2 = 2^y$$

$$\text{or } y = 1, \text{ i.e., first order w.r.t. I}^-$$

$$\text{From expt. (1), } 1.75 \times 10^{-4} = k[0.0017]^x[0.0017]^y[1.0]^z \dots (\text{i})$$

From expt. (4),

$$3.50 \times 10^{-4} = k[0.0017]^x[0.0017]^y[0.5]^z \dots (\text{iv})$$

Dividing eq. (i) by eq. (iv),

$$\frac{1.75 \times 10^{-4}}{3.50 \times 10^{-4}} = \frac{[1.0]^z}{[0.5]^z}$$

$$\text{or } \frac{1}{2} = 2^z$$

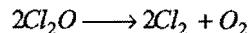
$$\text{or } 2^{-1} = 2^z$$

$$z = -1, \text{ i.e., order w.r.t. OH}^- \text{ is } -1.$$

$$\text{Rate law} = \frac{k[\text{OCl}^-][\text{I}^-]}{[\text{OH}^-]}$$

$$\text{From expt. (1)} \quad k = \frac{1.75 \times 10^{-4} [\text{OH}^-]}{[\text{OCl}^-][\text{I}^-]} = \frac{1.75 \times 10^{-4} \times 1.0}{0.0017 \times 0.0017} \\ = 60.55 \text{ s}^{-1}$$

Example 18. The rate law for the reaction,



at 200°C is found to be: $\text{rate} = k[\text{Cl}_2\text{O}]^2$.

(a) How would the rate change if [Cl₂O] is reduced to one-third of its original value?

(b) How should the [Cl₂O] be changed in order to double the rate?

(c) How would the rate change if [Cl₂O] is raised to threefold of its original value?

Solution: (a) Rate equation for the reaction,

$$r = k[\text{Cl}_2\text{O}]^2$$

$$\text{Let the new rate be } r'; \text{ so, } r' = k \left[\frac{\text{Cl}_2\text{O}}{3} \right]^2 = \frac{1}{9} r$$

(b) In order to have the rate = 2r, let the concentration of Cl₂O be x.

$$\text{So, } 2r = kx^2 \dots (\text{i})$$

$$\text{We know that, } r = k[\text{Cl}_2\text{O}]^2 \dots (\text{ii})$$

Dividing eq. (i) by eq. (ii),

$$\frac{2r}{r} = \frac{kx^2}{k[\text{Cl}_2\text{O}]^2}$$

$$\text{or } 2 = \frac{x^2}{[\text{Cl}_2\text{O}]^2}$$

$$\text{or } x^2 = 2[\text{Cl}_2\text{O}]^2$$

$$\text{or } x = \sqrt{2}[\text{Cl}_2\text{O}]$$

$$\text{(c) New rate} = k[3\text{Cl}_2\text{O}]^2 = 9k[\text{Cl}_2\text{O}]^2 = 9r$$

i.e., nine times of the original rate.

Example 19. For a reaction in which A and B form C, the following data were obtained from three experiments:

| Expt. No. | Initial conc. (mol L ⁻¹) | | Initial rate (mol L ⁻¹ s ⁻¹) |
|--------------|--------------------------------------|------|--|
| | [A] | [B] | |
| 1. | 0.03 | 0.03 | 0.3×10^{-4} |
| 2. | 0.06 | 0.06 | 1.2×10^{-4} |
| 3. | 0.06 | 0.09 | 2.7×10^{-4} |

What is the rate equation of the reaction and what is the value of rate constant?

Solution: Let the rate equation be $r = k[A]^x[B]^y$.

$$\text{From expt. (1), } 0.3 \times 10^{-4} = k[0.03]^x[0.03]^y \dots (\text{i})$$

$$\text{From expt. (2), } 1.2 \times 10^{-4} = k[0.06]^x[0.06]^y \dots (\text{ii})$$

$$\frac{1.2 \times 10^{-4}}{0.3 \times 10^{-4}} = \frac{[0.06]^x[0.06]^y}{[0.03]^x[0.03]^y}$$

$$= 2^x \times 2^y = 4 \dots (\text{iii})$$

Similarly, from expt. (1) and expt. (3),

$$2^x \times 3^y = 9 \quad \dots \text{(iv)}$$

Solving eqs. (iii) and (iv),

$$x = 0, y = 2$$

Rate equation, $\text{Rate} = k[B]^2$

Considering eq. (i) again,

$$k = \frac{0.3 \times 10^{-4}}{[0.03]^2} = 3.33 \times 10^{-2} \text{ mol}^{-1} \text{ L s}^{-1}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

14. For the decomposition of HI at 1000 K ($2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$), the following data were obtained:

| $[\text{HI}], M$ | Rate of decomposition of HI ($\text{mol L}^{-1} \text{s}^{-1}$) |
|------------------|---|
| 0.1 | 2.75×10^{-8} |
| 0.2 | 11×10^{-8} |
| 0.3 | 24.75×10^{-8} |

The order of reaction is:

- (a) 1 (b) 2 (c) 0 (d) 1.5
[Ans. (b)]

[Hint: $\text{Rate} = k[\text{HI}]^n$

$$11 \times 10^{-8} = k[0.2]^n \quad \dots \text{(i)}$$

$$2.75 \times 10^{-8} = k[0.1]^n \quad \dots \text{(ii)}$$

Dividing eq. (i) by eq. (ii),

$$4 = 2^n, n = 2$$

15. Consider a reaction, $A \rightarrow B + C$. If the initial concentration of A was reduced from 2 M to 1 M in 1 hour and from 1 M to 0.25 M in 2 hours, the order of the reaction is:

- (a) 1 (b) 0 (c) 2 (d) 3

[Ans. (a)]

[Hint: Half life of the given reaction is independent of initial concentration, hence, it is a first order reaction.

$$t_{1/2} \propto \frac{1}{a^{n-1}}$$

16. The rate of a gaseous reaction is given by the expression $k[A]^2[B]^3$. The volume of the reaction vessel is suddenly reduced to one half of the initial volume. The reaction rate relative to the original rate will be:

- (a) 1/24 (b) 1/32 (c) 32 (d) 24

[Ans. (c)]

[Hint: $\text{Rate} = k[A]^2[B]^3$... (i)

When volume is halved, the concentration will become double.

$$\therefore \text{Rate} = k[2A]^2[2B]^3$$

$$= 32k[A]^2[B]^3$$

$$= 32 \times \text{Original rate from (i)}$$

17. For a chemical reaction, $A \rightarrow B$, the rate of reaction increases by a factor of 1.837 when the concentration of A is

increased by 1.5 times. The order of reaction with respect to A is:

- (a) 1 (b) 1.5 (c) 2 (d) -1
[Ans. (b)]

[Hint: $\text{Rate} = k[A]^n$... (i)

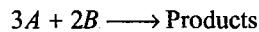
$$1.837 \times \text{Rate} = k[1.5A]^n \quad \dots \text{(ii)}$$

Dividing eq. (ii) by eq. (i),

$$1.837 = 1.5^n$$

$$\therefore n = 3/2 \text{ (solving by logarithmic method)}$$

18. The rate of the reaction,



is given by the rate expression:

$$\text{Rate} = k[A][B]^2$$

If A is taken in excess, the order of the reaction would be:

- (a) 3 (b) 2 (c) 1 (d) 5

[Ans. (b)]

[Hint: When A is taken in excess, its concentration will become constant; the rate law may, therefore, be given as:

$$\text{Rate} = k'[B]^2 \text{ Order} = 2$$

19. For a reaction $A + B \rightarrow C + D$, if the concentration of A is doubled without altering the concentration of B, the rate gets doubled. If the concentration of B is increased by nine times without altering the concentration of A, the rate gets tripled. The order of the reaction is: (KCET 2006)

- (a) 2 (b) 1 (c) 3/2 (d) 4/3

[Ans. (c)]

[Hint: $\text{Rate} = k[A]^\alpha[B]^\beta$... (i)

$$2 \times \text{rate} = k[2A]^\alpha[B]^\beta \quad \dots \text{(ii)}$$

$$3 \times \text{rate} = k[A]^\alpha[9B]^\beta \quad \dots \text{(iii)}$$

$$\text{From eqs. (i) and (ii), } \alpha = 1$$

$$\text{From eqs. (i) and (iii), } \beta = 1/2$$

$$\text{Order} = \alpha + \beta = 1 + \frac{1}{2} = \frac{3}{2}$$

20. Inversion of cane sugar in dilute acid is: [CET (J&K) 2007]

- (a) bimolecular reaction
(b) pseudo-unimolecular reaction
(c) unimolecular reaction
(d) trimolecular reaction
[Ans. (b)]

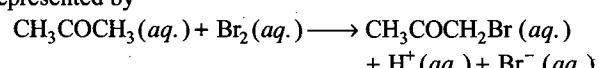
[Hint: $\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{C}_6\text{H}_{12}\text{O}_6 + \text{C}_6\text{H}_{12}\text{O}_6$
 $\text{Rate} = k[\text{C}_{12}\text{H}_{22}\text{O}_{11}][\text{H}_2\text{O}]$

When water is in excess, its concentration will be constant.

$$\therefore \text{Rate} = k'[\text{C}_{12}\text{H}_{22}\text{O}_{11}]$$

The reaction is, therefore, pseudo first order or pseudo unimolecular reaction.]

21. The bromination of acetone that occurs in acid solution is represented by



These kinetic data were obtained for given reaction concentrations:

| Initial concentrations (M) | | | Initial rate of disappearance of $\text{Br}_2, M \text{ s}^{-1}$ |
|--------------------------------|-----------------|----------------|--|
| $[\text{CH}_3\text{COCH}_3]$ | $[\text{Br}_2]$ | $[\text{H}^+]$ | |
| 0.30 | 0.05 | 0.05 | 5.7×10^{-5} |
| 0.30 | 0.10 | 0.05 | 5.7×10^{-5} |
| 0.30 | 0.10 | 0.10 | 1.2×10^{-4} |
| 0.40 | 0.05 | 0.20 | 3.1×10^{-4} |

[CBSE (PMT) 2008]

Based on these data, rate equation is :

(a) Rate = $k [\text{CH}_3\text{COCH}_3][\text{Br}_2][\text{H}^+]^2$

(b) Rate = $k [\text{CH}_3\text{COCH}_3][\text{Br}_2][\text{H}^+]$

(c) Rate = $k [\text{CH}_3\text{COCH}_3][\text{H}^+]$

(d) Rate = $k [\text{CH}_3\text{COCH}_3][\text{Br}_2]$

[Ans. (c)]

[Hint : Rate = $k [\text{CH}_3\text{COCH}_3]^\alpha [\text{Br}_2]^\beta [\text{H}^+]^\gamma$

$5.7 \times 10^{-5} = k [0.30]^\alpha [0.05]^\beta [0.05]^\gamma \quad \dots(i)$

$5.7 \times 10^{-5} = k [0.30]^\alpha [0.10]^\beta [0.05]^\gamma \quad \dots(ii)$

$1.2 \times 10^{-4} = k [0.30]^\alpha [0.10]^\beta [0.10]^\gamma \quad \dots(iii)$

$3.1 \times 10^{-4} = k [0.40]^\alpha [0.05]^\beta [0.20]^\gamma \quad \dots(iv)$

Dividing eq. (i) by eq. (ii),

$1 = \left[\frac{1}{2} \right]^\beta, \text{ i.e., } \beta = 0$

Dividing eq. (ii) by eq. (iii),

$\frac{1}{2} = \left[\frac{1}{2} \right]^\gamma, \text{ i.e., } \gamma = 1$

Dividing eq. (i) by eq. (iv),

$\frac{5.7 \times 10^{-5}}{3.1 \times 10^{-4}} = \left[\frac{3}{4} \right]^\alpha \times \left[\frac{1}{4} \right]^\beta$

$\alpha \approx 1$

Thus, rate law will be

rate = $k [\text{CH}_3\text{COCH}_3]^1 [\text{H}^+]^1$

8.9 REACTION MECHANISM

Knowledge about involved steps in a reaction, and to determine which step is slowest or rate determining, is called mechanism.

The intelligent guess depending on the observed rates of reactions about the series of steps (known as elementary processes) leading to the formation of products is called the reaction mechanism.

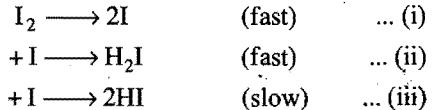
For illustration a few examples of reaction mechanisms are given below:

1. The reaction between H_2 and I_2 to form hydrogen iodide was originally postulated as a simple one step reaction.

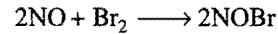


Rate = $k[\text{H}_2][\text{I}_2]$

But, the formation of HI has been explained on the basis of the following mechanism:

Overall reaction: $\text{H}_2 + \text{I}_2 \longrightarrow 2\text{HI}$

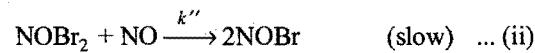
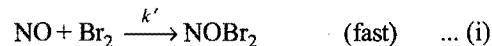
2. The reaction of NO and Br_2 is known to be of second order in NO and first order in Br_2 .



Rate = $k [\text{NO}]^2 [\text{Br}_2]$

The likelihood of three molecules (2 molecules of NO and 1 molecule of Br_2) colliding simultaneously is far less than the likelihood that two molecules will collide.

The mechanism is believed to be as under:

Overall reaction: $2\text{NO} + \text{Br}_2 \xrightarrow{k} 2\text{NOBr}$

The rate determining step involves 1 molecule of NO and 1 molecule of NOBr_2 . Thus, the expected rate expression should be

Rate = $k'' [\text{NOBr}_2][\text{NO}]$

However, NOBr_2 is a reaction intermediate and its concentration at the beginning of second step cannot be directly measured.

Concentration of NOBr_2 will be equal to

[NOBr_2] = $k' [\text{NO}][\text{Br}_2]$

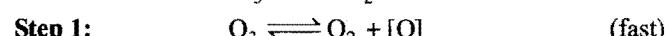
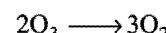
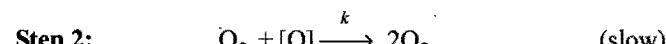
If this is substituted in the above equation, we get

Rate = $k' k'' [\text{NO}]^2 [\text{Br}_2]$

= $k [\text{NO}]^2 [\text{Br}_2]$

3. Depletion of ozone takes place in the following steps:

Overall reaction:

(Equilibrium constant K_c)

Rate = $k[\text{O}_3][\text{O}] \quad \dots(\text{i})$

Nascent oxygen $[\text{O}]$ is not present in overall reaction; thus it should be eliminated.

$$K_c = \frac{[\text{O}_2][\text{O}]}{[\text{O}_3]}, [\text{O}] = K_c \frac{[\text{O}_3]}{[\text{O}_2]} \quad \dots(\text{ii})$$

From eqs. (i) and (ii),

Rate = $k[\text{O}_3] \cdot K_c \frac{[\text{O}_3]}{[\text{O}_2]}$

= $k K_c [\text{O}_3]^2 [\text{O}_2]^{-1}$

= $K [\text{O}_3]^2 [\text{O}_2]^{-1}$

$K = k \times K_c$

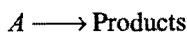
Order = $2 - 1 = 1$

3.10 REACTIONS OF VARIOUS ORDERS

(i) Zero order reactions

A reaction is said to be of zero order if its rate is independent of the concentration of the reactants, i.e., the rate is proportional to the zeroth power of the concentration of the reactants.

For the reaction



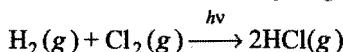
to be of zero order,

$$-\frac{dx}{dt} = k[A]^0 = k$$

Some photochemical reactions and a few heterogeneous reactions are zero order reactions. Such reactions are not common.

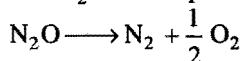
Examples:

- Photochemical reaction between hydrogen and chlorine:



This photochemical reaction is zero order reaction. The reaction is studied by placing H_2 and Cl_2 gases over water. The rate of reaction is studied by noting the rate at which water rises in the vessel due to dissolution of HCl formed. The rate of rise of water is the same as the rate of disappearance of H_2 and Cl_2 , i.e., the concentration of the gases per unit volume in the gaseous phase will not change with time, although the quantities will change.

- Decomposition of N_2O on hot platinum surface:

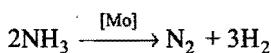


$$\text{Rate} \propto [\text{N}_2\text{O}]^0 = k[\text{N}_2\text{O}]^0 = k$$

or

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

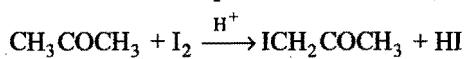
- Decomposition of NH_3 in presence of molybdenum or tungsten is a zero order reaction.



The surface of the catalyst is almost completely covered by NH_3 molecules. The adsorption of gas on the surface cannot change by increasing the pressure or concentration of NH_3 . Thus, the concentration of gas phase remains constant although the product is formed. Therefore, this reaction shows zero order kinetics.

Other examples of zero order are:

- Decomposition of HI on the gold surface.
- Iodation of acetone in presence of H^+ ions,



The rate equation of this reaction does not include $[\text{I}_2]$ factor, i.e.,

$$-\frac{dx}{dt} = k[\text{CH}_3\text{COCH}_3][\text{H}^+]$$

Characteristics of zero order reaction

- The concentration of reactant decreases linearly with time.

$$[A]_t = [A]_0 - kt$$

- The time required for the reaction to be complete, i.e., time at which $[A]$ is zero.

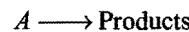
$$t_{\text{Completion}} = \frac{[A]_0}{k} = \frac{\text{Initial concentration}}{\text{Rate constant}}$$

- The units of k are $\text{mol L}^{-1} \text{time}^{-1}$.

(ii) First order reactions

A reaction is said to be of first order if its rate is determined by the change of one concentration term only.

Consider the reaction,



Let a be the concentration of A at the start and after time t , the concentration becomes $(a-x)$, i.e., x has been changed into products. The rate of reaction after time 't' is given by the expression

$$\frac{dx}{dt} = k(a-x)$$

or

$$\frac{dx}{(a-x)} = k dt$$

upon integration of above equation,

$$\int \frac{dx}{(a-x)} = k \int dt$$

or

$$-\log_e (a-x) = kt + c$$

where c is integration constant.

When $t = 0$, $x = 0$,

$$c = -\log_e a$$

Putting the value of 'c',

$$-\log_e (a-x) = kt - \log_e a$$

$$\text{or } \log_e a - \log_e (a-x) = kt$$

$$\log_e \frac{a}{(a-x)} = kt$$

$$\text{or } k = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)}$$

This is known as the kinetic equation for a reaction of the first order. The following two important conclusions are drawn from this equation:

- A change in concentration unit will not change the numerical value of k . Let the new unit be n times the first one.

$$\text{So, } k = \frac{2.303}{t} \log_{10} \frac{na}{n(a-x)}$$

$$\text{or } k = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)}$$

Thus, for first order reactions, any quantity which is proportional to concentration can be used in place of concentration for evaluation of ' k '.

- The time taken for the completion of same fraction of change is independent of initial concentration. For example, for half change,

$$x = 0.5a \text{ and } t = t_{1/2}$$

$$\text{So, } k = \frac{2.303}{t_{1/2}} \log_{10} \frac{a}{0.5a} = \frac{2.303}{t_{1/2}} \log_{10} 2$$

$$\frac{0.693}{t_{1/2}} = \frac{0.693}{k}$$

or

$$t_{1/2} = \frac{0.693}{k}$$

Thus, $t_{1/2}$ is independent of initial concentration 'a'.

This time 't' in which the initial concentration becomes half is termed as **half life period**. Half life period of a first order reaction is independent of the initial concentration of the reactant.

Since, the velocity constant is independent of concentration and depends inversely on the time, the unit of k will be time⁻¹, i.e., sec⁻¹ or min⁻¹ or hour⁻¹. The equation of the first order can also be written in the following form when initial concentration is not known:

$$k = \frac{2.303}{(t_2 - t_1)} \log_{10} \frac{(a - x_1)}{(a - x_2)}$$

$(a - x_1)$ is the concentration after time t_1 and $(a - x_2)$ the concentration after time t_2 when $t_2 > t_1$.

When the log of the concentration of the reactant at various intervals of time is plotted against the time intervals, a straight line is obtained (Fig. 8.13). The slope of this line gives the value $2.303/k$, from which k can be evaluated.

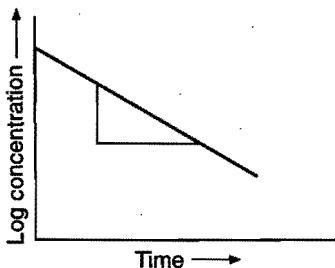
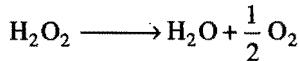


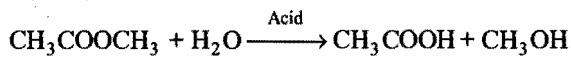
Fig. 8.13

Examples of first order reactions

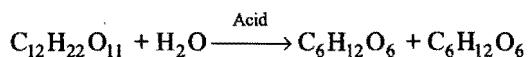
- Decomposition of H₂O₂ in aqueous solution.



- Hydrolysis of methyl acetate in presence of mineral acids.



- Inversion of cane sugar in presence of mineral acids.



- Decomposition of ammonium nitrite in aqueous solution.



- Hydrolysis of diazo derivatives.



Note: In case of gases, pressure can be used in place of concentration.

First order growth kinetics

It is used for population growth and bacteria multiplication, e.g.,

| Time | Population |
|------|------------|
| 0 | a |

Growth rate is directly proportional to present population.

$$\begin{aligned} \frac{dx}{dt} &\propto (a + x) \\ &= k(a + x) \\ \frac{dx}{(a + x)} &= k dt \end{aligned} \quad \dots (i)$$

It is a differential equation of first order and first degree in variable separable form. It may be solved on integration.

$$\int \frac{dx}{(a + x)} = k \int dt + c \quad \dots (ii)$$

Here,

At $t = 0$,

$$\therefore x = 0$$

$$x = 0$$

$$\log_e a = k \times 0 + c$$

$$c = \log_e a$$

... (iii)

Substituting the value of 'c' in eq. (ii), we get

$$\begin{aligned} \log_e (a + x) &= kt + \log_e a \\ kt &= -\log_e \frac{a}{a + x} \\ k &= -\frac{2.303}{t} \log_{10} \left(\frac{a}{a + x} \right) \end{aligned}$$

This is the kinetics for first order growth kinetics.

Note: (1) If volumes of reagents are given in volumetric analysis then we use the following equation to determine rate constant:

$$k = \frac{2.303}{t} \log_{10} \frac{V_\infty - V_0}{V_\infty - V_t}$$

where, V_0 = volume used at zero time,

V_t = volume used at time 't',

V_∞ = volume used at infinite time

Case I: When V_0 is not given, we use

$$k = \frac{2.303}{t} \log_{10} \frac{V_\infty}{V_\infty - V_t}$$

Case II: When V_∞ is not given, then

$$k = \frac{2.303}{t} \log_{10} \left(\frac{V_0}{V_t} \right)$$

(2) If information is given in terms of angle of rotation of optically active compounds, measured by polarimeter with respect to time, then

$$k = \frac{2.303}{t} \log_{10} \left\{ \frac{r_\infty - r_t}{r_\infty - r_0} \right\}$$

where, r_0 = angle of rotation at zero time,

r_t = angle of rotation at time 't',

r_∞ = angle of rotation at infinite time

Case I: If r_i is not given, then

$$k = \frac{2.303}{t} \log_{10} \left\{ \frac{r_\infty}{r_\infty - r_i} \right\}$$

Case II: If r_∞ is not given, then

$$k = \frac{2.303}{t} \log_{10} \left\{ \frac{r_i}{r_t} \right\}$$

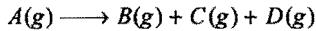
(3) If pressure is given in gaseous reactions, then we use the following kinetic equation:

$$k = \frac{2.303}{t} \log_{10} \left\{ \frac{p_0}{p_0 - x} \right\}$$

where, p_0 = pressure of reactant at initial stage,

$(p_0 - x)$ = pressure of such a reactant at 't' time.

Values of ' p_0 ' and 'x' can be calculated using the following examples:



At $t = 0$ p_0 0 0 0

Pressure after time 't' $(p_0 - x)$ x x x

Pressure after a long time or infinite time 0 p_0 p_0 p_0

Case I: If total pressure of reaction mixture is given in place of pressure of reactant, then

$$p_t = (p_0 - x + x + x + x)$$

where, p_t = pressure of vessel at time 't'.

Case II: If pressure of vessel after a long time or infinite time is given, then

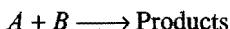
$$p_\infty = p_0 + p_0 + p_0$$

(iii) Second order reactions

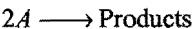
A reaction is said to be of second order if its reaction rate is determined by the variation of two concentration terms.

The kinetics of second order reactions are given as follows:

(a) When concentrations of both reactants are equal or two molecules of the same reactant are involved in the change, i.e.,



or



$$\frac{dx}{dt} = k(a - x)^2$$

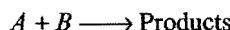
On solving this equation,

$$k = \frac{1}{t} \cdot \frac{x}{a(a - x)}$$

where, a = initial concentration of the reactant or reactants and

x = concentration of the reactant changed in time t .

(b) When the initial concentrations of the two reactants are different, i.e.,



Initial conc.

$$a \quad b$$

$$\frac{dx}{dt} = k(a - x)(b - x)$$

$$k = \frac{2.303}{t(a - b)} \log_{10} \frac{b(a - x)}{a(b - x)}$$

$(a - x)$ and $(b - x)$ are the concentrations of A and B after time interval, t .

Characteristics of the second order reactions

(i) The value of k (velocity constant) depends on the unit of concentration. The unit of k is expressed as $(\text{mol/litre})^{-1} \text{time}^{-1}$ or litre mol $^{-1}$ time $^{-1}$.

$$(ii) \text{ Half life period } (t_{1/2}) = \frac{1}{k} \cdot \frac{0.5a}{a \times 0.5a} = \frac{1}{ka}$$

Thus, half life is inversely proportional to initial concentration.

(iii) Second order reaction conforms to the first order when one of the reactants is present in large excess.

$$\text{Taking, } k = \frac{2.303}{t(a - b)} \log_{10} \frac{b(a - x)}{a(b - x)}, \text{ if } a \ggg b \text{ then}$$

$$(a - x) \approx a \text{ and } (a - b) \approx a$$

$$\text{Hence, } k = \frac{2.303}{ta} \log_{10} \frac{ba}{a(b - x)}$$

$$\text{or } ka = k' = \frac{2.303}{t} \log_{10} \frac{b}{(b - x)}$$

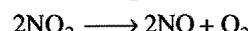
(since, 'a' being very large, may be treated as constant after the change). Thus, the reaction follows first order kinetics with respect to the reactant taken relatively in small amount.

Examples of second order reactions

1. Hydrolysis of ester by an alkali (saponification).



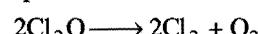
2. The decomposition of NO_2 into NO and O_2 .



3. Conversion of ozone into oxygen at 100°C .



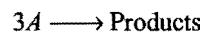
4. Thermal decomposition of chlorine monoxide.



(iv) Third order reactions

A reaction is said to be of third order if its rate is determined by the variation of three concentration terms.

When the concentration of all the three reactants is same or three molecules of the same reactant are involved, the rate expression is given as:



$$\frac{dx}{dt} = k(a - x)^3$$

On solving this equation,

$$k = \frac{1}{t} \cdot \frac{x(2a - x)}{2a^2(a - x)^2}$$

Characteristics of third order reactions

1. Half life period

$$= \frac{1}{k} \cdot \frac{0.5a(2a - 0.5a)}{2a^2(0.5a)^2} = \frac{1}{k} \cdot \frac{0.5a \times 1.5a}{2a^2 \times 0.5a \times 0.5a}$$

$$= \frac{3}{2a^2 k}$$

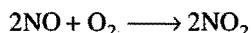
Thus, half life is inversely proportional to the square of initial concentration.

2. The change in the unit of concentration changes the numerical value of k .

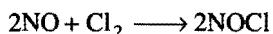
3. The unit of k is expressed as $(\text{mol/litre})^{-2} \text{ time}^{-1}$ or $\text{litre}^2 \text{ mol}^{-2} \text{ time}^{-1}$.

Examples of third order reactions

1. Reaction between nitric oxide and oxygen.



2. Reaction between nitric oxide and chlorine.



3. Reduction of FeCl_3 by SnCl_2 .



Expressions for rate constant for reactions of different orders:

Reaction Order Rate law eqn. Expression for rate const.

$$A \rightarrow \text{Products} \quad 0 \quad \text{Rate} = k \quad k = \frac{1}{t} [A]_0 - [A]$$

$$A \rightarrow \text{Products} \quad 1 \quad \text{Rate} = k[A] \quad k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

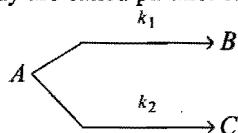
$$2A \rightarrow \text{Products} \quad 2 \quad \text{Rate} = k[A]^2 \quad k = \frac{1}{t} \left[\frac{1}{[A]} - \frac{1}{[A]_0} \right]$$

$$A + B \rightarrow \text{Products} \quad 2 \quad \text{Rate} = k[A][B] \quad k = \frac{2.303}{t([A]_0 - [B]_0)} \log \frac{[B]_0[A]}{[A]_0[B]}$$

$$3A \rightarrow \text{Products} \quad 3 \quad \text{Rate} = k[A]^3 \quad k = \frac{1}{2t} \left[\frac{1}{[A]^2} - \frac{1}{[A]_0^2} \right]$$

Parallel or Competing reaction

The reaction in which a substance reacts or decomposes in more than one way are called parallel or side reactions,



$$\frac{-d[A]}{dt} = (k_1 + k_2)[A] = k_{av}[A]$$

k_1 = fractional yield of $B \times k_{av}$

k_2 = fractional yield of $C \times k_{av}$

If $k_1 \gg k_2$ then,

$A \longrightarrow B$ main and

$A \longrightarrow C$ is side reaction

Let after a definite interval x mol/litre of B and y mol/litre of C are formed.

$$\frac{x}{y} = \frac{k_1}{k_2}$$

$$\text{i.e., } \frac{d[B]}{dt} / \frac{d[C]}{dt} = \frac{k_1}{k_2}$$

Variation of concentration A , B and C with time may be graphically represented as,

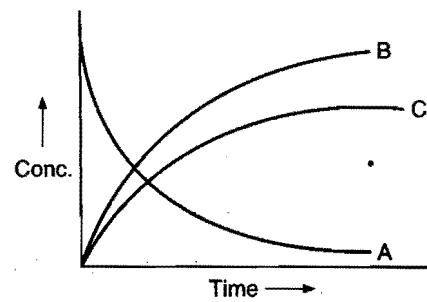
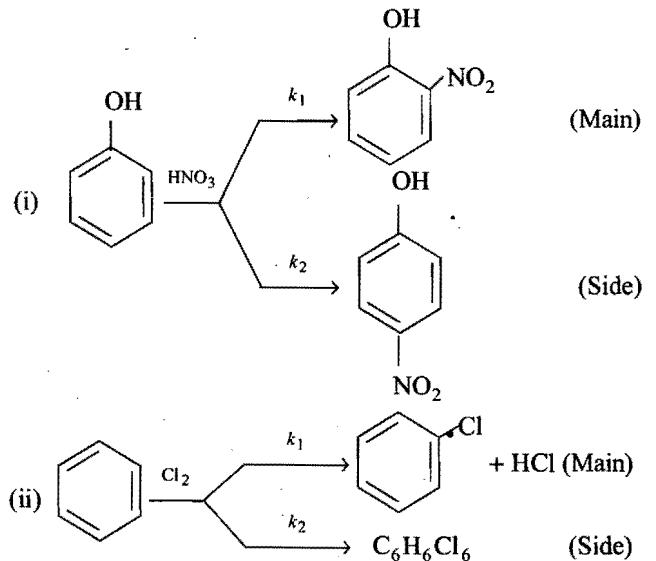


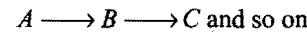
Fig. 8.14

Examples:

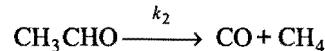
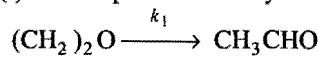


Consecutive reaction

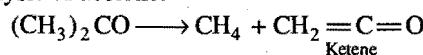
This reaction is defined as that reaction which proceeds from reactants to final products through one or more intermediate stages. The overall reaction is a result of several successive or consecutive steps.



Examples: (i) Decomposition of ethylene oxide:



(ii) The pyrolysis of acetone:



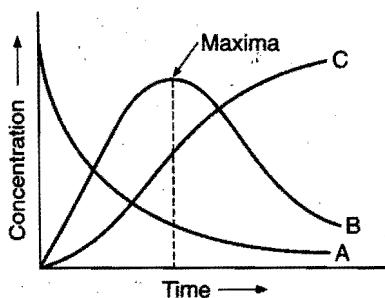
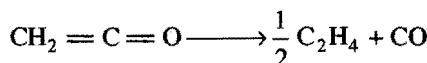
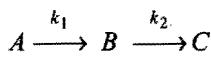


Fig. 8.15

Variation of concentration of various substances during the progress of reaction ($A \rightarrow B \rightarrow C$)



Let initially ($t = 0$), $[B] = 0$ and $k_1 < k_2$ then maximum concentration of $[B]$ may be calculated as,

$$[B]_{\max} = [A]_0 \left[\frac{k_1}{k_2} \right]^{k_2/k_1 - k_2}$$

where, $[A]_0$ = initial concentration of A

Time in which B attains maximum concentration may be given as,

$$t_{\max} = \frac{2.303}{k_2 - k_1} \log \left(\frac{k_2}{k_1} \right)$$

Concentration of $[B]$ after time ' t ' may be calculated as,

$$[B]_t = \frac{k_1 [A]_0}{k_2 - k_1} [e^{-k_1 t} - e^{-k_2 t}]$$

Activation energy diagram of a composite reaction involves more than one peaks and number of peaks indicate the number of different types of activated complexes involved. The number of valleys in the activation energy diagram indicates the number of different types of reactive intermediates involved.

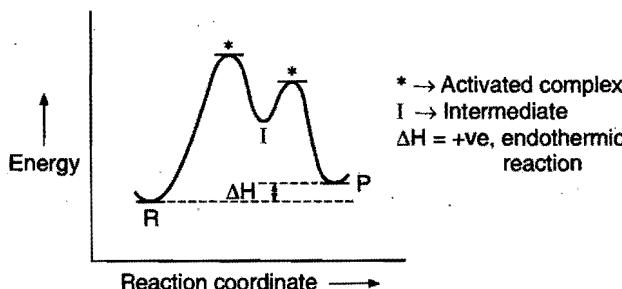
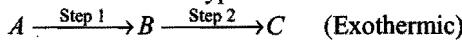


Fig. 8.16 Activation energy diagram of a two steps composite reaction

Energy Diagram of two Steps Reaction

Let us consider a reaction of the type :



These are two possibilities in this reaction

First possibility :

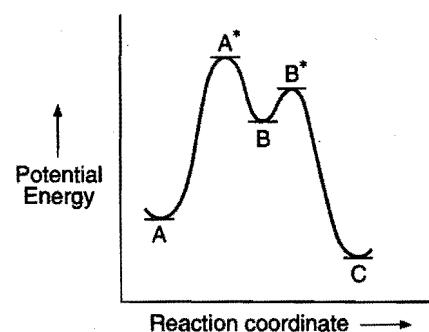
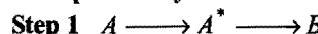


Fig. 8.17

Activation energy of step 1 is greater than that of step 2 thus step 1 will be slow and rate determining.

Second possibility :

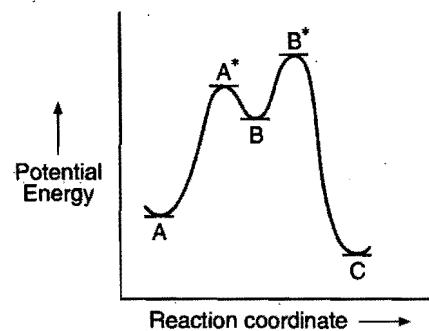


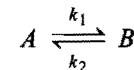
Fig. 8.18

Activation energy of step 2 is greater than that of step 1 hence step 2 will be slow and rate determining

Reversible Reactions

The reactions in which the products of chemical change react together to form the original reactants, are called reversible reactions. These are also called opposing or counter reactions.

Let us consider a reversible reaction in which both forward and backward reactions are of first order.



Initial state ($t = 0$) a 0

Conc. at time (t) $a - x$ x

Equilibrium conc. $(a - x_e)$ x_e

$$k_1 + k_2 = \frac{2.303}{t} \log_{10} \left\{ \frac{x_e}{x_e - x} \right\}$$

8.11 METHODS FOR DETERMINATION OF ORDER OF A REACTION

The important methods used are the following:

1. Method of integration (Hit and trial method)

The most simple method is the one in which the quantities a , x and t are determined and substituted in the kinetic equations of various orders. The equation which gives the most constant value for the specific rate constant (k) for a series of time intervals is the one corresponding to the order of reaction. If all the reactants are at the same molar concentrations, the kinetic equations are:

$$k = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)}, \text{ for first order reactions;}$$

$$k = \frac{1}{t} \left[\frac{1}{(a-x)} - \frac{1}{a} \right], \text{ for second order reactions;}$$

$$k = \frac{1}{2t} \left[\frac{1}{(a-x)^2} - \frac{1}{a^2} \right], \text{ for third order reactions.}$$

2. Graphical method

A graphical method based on the respective rate laws can also be used.

If the plot of $\log(a-x)$ versus 't' is a straight line, the reaction follows first order.

If the plot of $\frac{1}{(a-x)}$ versus 't' is a straight line, the reaction follows second order.

If the plot of $\frac{1}{(a-x)^2}$ versus 't' is a straight line, the reaction follows third order.

In general, for a reaction of n th order, a graph of $\frac{1}{(a-x)^{n-1}}$ versus 't' must be a straight line.

3. Half life method

A general expression for the half life, ($t_{1/2}$), is given by

$$t_{1/2} \propto \frac{1}{a^{n-1}}$$

where, 'n' is the order of the reaction.

Starting with two different initial concentrations a_1 and a_2 for the same reaction, the half lives are $(t_{1/2})_1$ and $(t_{1/2})_2$ respectively are determined. As we know that,

$$(t_{1/2})_1 \propto \frac{1}{a_1^{n-1}} \quad \dots (i)$$

$$\text{and} \quad (t_{1/2})_2 \propto \frac{1}{a_2^{n-1}} \quad \dots (ii)$$

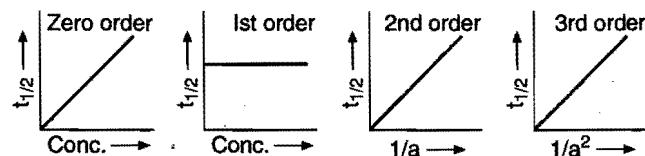
Dividing eq. (i) by eq. (ii),

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a_2}{a_1} \right)^{n-1} \quad \dots (iii)$$

Taking logarithms on both sides,

$$\begin{aligned} \log_{10} (t_{1/2})_1 - \log_{10} (t_{1/2})_2 &= (n-1)[\log_{10} a_2 - \log_{10} a_1] \\ (n-1) &= \frac{\log_{10} (t_{1/2})_1 - \log_{10} (t_{1/2})_2}{\log_{10} a_2 - \log_{10} a_1} \\ \text{or} \quad n &= 1 + \frac{\log_{10} (t_{1/2})_1 - \log_{10} (t_{1/2})_2}{\log_{10} a_2 - \log_{10} a_1} \quad \dots (iv) \end{aligned}$$

Plots of half lives vs. concentration ($t_{1/2} \propto a^{1-n}$):



This relation can be used to determine order of reaction 'n'.

4. van't Hoff differential method

As we know that, the rate of a reaction varies as the n th power of the concentration of the reactant where 'n' is the order of the reaction. Thus, for two different initial concentrations C_1 and C_2 , equations can be written in the form

$$-\frac{dC_1}{dt} = kC_1^n \text{ and } -\frac{dC_2}{dt} = kC_2^n$$

Taking logarithms,

$$\log_{10} \left(-\frac{dC_1}{dt} \right) = \log_{10} k + n \log_{10} C_1 \quad \dots (i)$$

$$\text{and} \quad \log_{10} \left(-\frac{dC_2}{dt} \right) = \log_{10} k + n \log_{10} C_2 \quad \dots (ii)$$

Subtracting eq. (ii) from eq. (i),

$$\log_{10} \left(-\frac{dC_1}{dt} \right) - \log_{10} \left(-\frac{dC_2}{dt} \right) = n (\log_{10} C_1 - \log_{10} C_2)$$

$$\text{or} \quad n = \frac{\log_{10} \left(-\frac{dC_1}{dt} \right) - \log_{10} \left(-\frac{dC_2}{dt} \right)}{\log_{10} C_1 - \log_{10} C_2} \quad \dots (iii)$$

$-\frac{dC_1}{dt}$ and $-\frac{dC_2}{dt}$ are determined from concentration vs. time graphs and the value of 'n' can be determined.

::: SOME SOLVED EXAMPLES :::

Example 20. Rate of a reaction $A + B \rightarrow \text{product}$, is given as a function of different initial concentrations of A and B.

| [A] (mol L ⁻¹) | [B] (mol L ⁻¹) | Initial rate (mol L ⁻¹ min ⁻¹) |
|-------------------------------|-------------------------------|--|
| 0.01 | 0.01 | 0.005 |
| 0.02 | 0.01 | 0.010 |
| 0.01 | 0.02 | 0.005 |

Determine the order of the reaction with respect to A and w.r.t.

B. What is the half life of A in the reaction?

Solution: Let the rate of reaction be

$$\text{Rate} = k[A]^x[B]^y$$

From the data given, it is clear that by doubling the concentration of A, the rate also becomes double when B is kept constant. Thus, the rate is directly proportional to concentration of A.

$$\text{Rate} \propto [A], \text{ i.e., } x = 1$$

Or the order of reaction w.r.t. A is 1.

When the concentration of A is kept constant and the concentration of B is doubled, the rate does not change, i.e., $y = 0$; or the order of reaction w.r.t. B is zero.

$$\text{Thus, reaction rate, } -\frac{dx}{dt} = k[A]$$

$$\text{Again } k = \frac{0.005}{0.01} = 0.5 \text{ min}^{-1}$$

$$\text{Half life of } A = \frac{0.693}{k} = \frac{0.693}{0.5} = 1.386 \text{ min}$$

Example 21. Thermal decomposition of a compound is of the first order. If 50% of a sample of the compound is decomposed in 120 minutes, how long will it take for 90% of the compound to decompose?

Solution: Half life of reaction = 120 min

We know that,

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{120} = 5.77 \times 10^{-3} \text{ min}^{-1}$$

Applying first order reaction equation,

$$t = \frac{2.303}{k} \log_{10} \frac{a}{a-x}$$

If $a = 100$, $x = 90$ or $(a-x) = 10$,

$$\text{So, } t = \frac{2.303}{5.77 \times 10^{-3}} \cdot \log_{10} 10 = \frac{2.303}{5.77 \times 10^{-3}} = 399 \text{ min}$$

Example 22. The decomposition of Cl_2O_7 at 400 K in the gas phase to Cl_2 and O_2 is a first order reaction.

(i) After 55 seconds at 400 K, the pressure of Cl_2O_7 falls from 0.062 to 0.044 atm. Calculate the rate constant.

(ii) Calculate the pressure of Cl_2O_7 after 100 seconds of decomposition at this temperature.

Solution: (i) As pressure \propto concentration,

$$\begin{aligned} k &= \frac{2.303}{t} \log_{10} \frac{P_i \text{ (initial pressure)}}{P_t \text{ (pressure after time } t)} \\ &= \frac{2.303}{55} \log_{10} \frac{0.062}{0.044} = 6.2 \times 10^{-3} \text{ s}^{-1} \end{aligned}$$

(ii) Again applying the first order kinetic equation,

$$k = \frac{2.303}{t} \log_{10} \frac{P_i \text{ (initial pressure)}}{P_t \text{ (pressure after time } t)}$$

$$6.2 \times 10^{-3} = \frac{2.303}{100} \log_{10} \frac{0.062}{P_t}$$

$$\text{or } \frac{6.2 \times 10^{-3} \times 100}{2.303} = \log_{10} 0.062 - \log_{10} (P_t)$$

$$\text{or } 0.2692 = \log_{10} 0.062 - \log_{10} (P_t)$$

$$\text{or } \log_{10} (P_t) = \log_{10} 0.062 - 0.2692 \\ = (\bar{2}.7924 - 0.2692)$$

$$P_t = 0.033 \text{ atmosphere}$$

$$\text{Pressure after 100 sec} = 0.033 \text{ atm}$$

Example 23. The half life of a first order reaction is 60 min. How long will it take to consume 90% of the reactant?

Solution: For the first order reaction

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{60} = 11.55 \times 10^{-3} \text{ min}^{-1}$$

Applying first order kinetic equation,

$$t = \frac{2.303}{k} \log_{10} \frac{a}{(a-x)}$$

$$\text{Given: } a = 100, x = 90, \text{ i.e., } (a-x) = (100-90) = 10$$

$$\begin{aligned} \text{Hence, } t &= \frac{2.303}{11.55 \times 10^{-3}} \cdot \log_{10} 10 \\ &= 199 \text{ min} \end{aligned}$$

Example 24. A first order reaction has a rate constant of $15 \times 10^{-3} \text{ s}^{-1}$. How long will 5.0 g of this reactant take to reduce to 3.0 g?

Solution: Applying first order kinetic equation,

$$t = \frac{2.303}{k} \log_{10} \frac{a}{(a-x)}$$

$$\text{Given: } k = 15 \times 10^{-3} \text{ sec}^{-1}, a = 5 \text{ g}, (a-x) = 3 \text{ g}$$

$$\text{So, } t = \frac{2.303}{15 \times 10^{-3}} \log_{10} \frac{5}{3} = 34.07 \text{ sec}$$

Example 25. Catalytic decomposition of nitrous oxide by gold at 900°C at an initial pressure of 200 mm was 50% in 53 minutes and 73% in 100 minutes.

(a) What is the order of reaction?

(b) How much it will decompose in 100 minutes at the same temperature but at an initial pressure of 600 mm? (IIT 1990)

Solution: (a) Using first order kinetic equation and substituting given values,

$$\text{In first case: } k = \frac{2.303}{53} \log_{10} \frac{200}{200-100} = 0.0131 \text{ min}^{-1}$$

$$\text{In second case: } k = \frac{2.303}{100} \log_{10} \frac{200}{200-146} = 0.0131 \text{ min}^{-1}$$

As the values of k come out to be the same in both cases, the reaction is of first order.

(b) As in the first order reaction, the time required for the completion of same fraction is independent of initial concentration; the percentage decomposition in 100 minutes when the initial pressure is 600 mm will also be 73%.

Example 26. A substance reacts according to the first order rate law and the specific reaction rate for the reaction is $1 \times 10^{-2} \text{ s}^{-1}$. If the initial concentration is 1.0 M.

(a) What is the initial rate?

(b) What is the reaction rate after 1 minute?

Solution: (a) Initial rate of a first order reaction = kC

$$= 1 \times 10^{-2} \times 1.0 = 1 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$$

(b) Concentration after 60 seconds is calculated by applying first order kinetic equation,

$$k = \frac{2.303}{60} \log_{10} \frac{1}{(1-x)}$$

$$\text{or } 1 \times 10^{-2} = \frac{2.303}{60} [-\log(1-x)]$$

$$\text{or } \frac{60 \times 10^{-2}}{2.303} = -\log(1-x) = 0.2605$$

$$\begin{aligned} \log(1-x) &= -0.2605 \\ &= 1.7395 \end{aligned}$$

$$(1-x) = \text{antilog of } (1.7395) = 0.5489 \text{ mol L}^{-1}$$

Rate of reaction after 1 minute = $k \times C$

$$\begin{aligned} &= 1 \times 10^{-2} \times 0.5489 \\ &= 5.489 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1} \end{aligned}$$

Example 27. A first order reaction is 50% completed in 30 minutes at 27°C and in 10 minutes at 47°C. Calculate the reaction rate constant at 27°C and the energy of activation of the reaction in kJ mol⁻¹.

Solution: For first order reaction $k = \frac{0.693}{t_{1/2}}$

$$\text{At } 27^\circ\text{C}, \quad k_{27^\circ\text{C}} = \frac{0.693}{30} = 0.0231 \text{ min}^{-1}$$

$$\text{At } 47^\circ\text{C}, \quad k_{47^\circ\text{C}} = \frac{0.693}{10} = 0.0693 \text{ min}^{-1}$$

Now applying the following equation:

$$\log_{10} \frac{k_1}{k_2} = \frac{-E_a}{2.303 \times R} \cdot \left(\frac{T_2 - T_1}{T_2 \cdot T_1} \right)$$

$$\text{or } \log_{10} \frac{0.0231}{0.0693} = \frac{-E_a}{2.303 \times 8.314} \cdot \left(\frac{320 - 300}{320 \times 300} \right)$$

$$\begin{aligned} \text{or } -\log_{10} 0.3333 &= \frac{E_a}{19.1471} \times \frac{20}{96000} \\ E_a &= -\frac{19.1471 \times 96000}{20} \times \log 0.3333 \\ &= -91906 \times (-0.4772) \\ &= 43857 \text{ J mol}^{-1} = 43.857 \text{ kJ mol}^{-1} \end{aligned}$$

Example 28. In Arrhenius equation for a certain reaction, the values of A and E_a (activation energy) are $4 \times 10^{13} \text{ sec}^{-1}$ and 98.6 kJ mol^{-1} respectively. If the reaction is of first order, at what temperature will its half life period be 10 minutes?

(IIT 1990)

Solution: According to Arrhenius equation,

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

$$\text{or } \log_e k = \log_e A - \frac{E_a}{RT}$$

$$\text{or } 2.303 \log_{10} k = 2.303 \log_{10} A - \frac{E_a}{RT}$$

$$\text{For a first order reaction } t_{1/2} = \frac{0.693}{k}$$

$$\text{So, } k = \frac{0.693}{600} \text{ sec}^{-1} \quad (t_{1/2} = 10 \text{ min} = 600 \text{ sec}) \\ = 1.1 \times 10^{-3} \text{ sec}^{-1}$$

$$\text{Hence, } \log(1.1 \times 10^{-3}) = \log(4 \times 10^{13}) - \frac{98.6 \times 10^3}{2.303 \times 8.314 \times T} \\ T = 310.95 \text{ K}$$

Example 29. A second order reaction, in which both the reactants have same concentration, is 20% completed in 500 seconds. How much time it will take for 60% completion?

Solution: The second order equation when both the reactants have same concentration is

$$k = \frac{1}{t} \cdot \frac{x}{a(a-x)}$$

If $a = 100$, $x = 20$, $t = 500$ seconds.

$$\text{So, } k = \frac{1}{500} \times \frac{20}{100 \times (100-20)}$$

When $a = 100$, $x = 60$, $t = ?$

$$t = \frac{1}{k} \cdot \frac{60}{100 \times 40}$$

Substituting the value of k ,

$$t = \frac{500 \times 100 \times 80}{20} \times \frac{60}{100 \times 40}$$

or $t = 3000$ seconds

Example 30. A first order reaction is 20% complete in 10 minutes. Calculate the time taken for the reaction to go to 80% completion.

Solution: Applying first order equation,

$$\begin{aligned} k &= \frac{2.303}{t} \log_{10} \frac{100}{(100-20)} \\ &= \frac{2.303}{10} \log_{10} \frac{100}{80} = 0.0223 \text{ min}^{-1} \end{aligned}$$

Again applying first order equation,

$$\begin{aligned} t &= \frac{2.303}{k} \log_{10} \frac{100}{(100 - 80)} \\ &= \frac{2.303}{0.0223} \log_{10} \frac{100}{20} \\ &= 72.18 \text{ min} \end{aligned}$$

Example 31. The decomposition of dinitrogen pentoxide (N_2O_5) follows first order rate law. Calculate the rate constant from the given data:

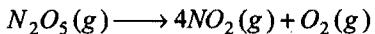
$$t = 800 \text{ sec} \quad [N_2O_5] = 1.45 \text{ mol L}^{-1} = [A_1]$$

$$t = 1600 \text{ sec} \quad [N_2O_5] = 0.88 \text{ mol L}^{-1} = [A_2]$$

Solution: Applying the formula,

$$\begin{aligned} k &= \frac{2.303}{(t_2 - t_1)} \log_{10} \frac{[A_1]}{[A_2]} \\ &= \frac{2.303}{(1600 - 800)} \log_{10} \frac{1.45}{0.88} \\ &= \frac{2.303}{800} \times 0.2169 = 6.24 \times 10^{-4} \text{ sec}^{-1} \end{aligned}$$

Example 32. The decomposition of N_2O_5 according to the equation,



is a first order reaction. After 30 minutes from the start of the decomposition in a closed vessel, the total pressure developed is found to be 284.4 mm Hg and on completion, the total pressure is 584.5 mm Hg. Calculate the rate constant of the reaction.

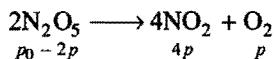
(IIT 1991)

Solution: $2N_2O_5 \longrightarrow 4NO_2 + O_2$

On decomposition of 2 moles of N_2O_5 , 4 moles of NO_2 and 1 mole of O_2 are produced. Thus, the total pressure after completion corresponds to 5 moles and initial pressure to 2 moles.

$$\text{Initial pressure of } N_2O_5, p_0 = \frac{2}{5} \times 584.5 = 233.8 \text{ mm Hg}$$

After 30 minutes, the total pressure = 284.5 mm Hg



$$\text{or} \qquad p_0 + 3p = 284.5$$

$$\text{or} \qquad 3p = 284.5 - 233.8 = 50.7 \text{ mm Hg}$$

$$\text{or} \qquad p = \frac{50.7}{3} = 16.9 \text{ mm Hg}$$

Pressure of N_2O_5 after 30 minutes = $233.8 - (2 \times 16.9)$

$$= 200 \text{ mm Hg}$$

$$k = \frac{2.303}{30} \log_{10} \frac{233.8}{200.0} = 5.2 \times 10^{-3} \text{ min}^{-1}$$

Example 33. The gas phase decomposition of dimethyl ether follows first order kinetics.



The reaction is carried out in a constant volume container at 500°C and has a half life of 14.5 minutes. Initially only dimethyl ether is present at a pressure of 0.40 atm. What is the total pressure after 12 minutes? Assume ideal gas behaviour.

(IIT 1993)

$$\text{Solution: } k = \frac{0.693}{t_{1/2}} = \frac{0.693}{14.5} = 0.047793 \text{ min}^{-1}$$

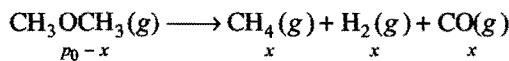
Let the pressure of dimethyl ether after 12 minutes be p atm. Applying first order equation,

$$\begin{aligned} k &= \frac{2.303}{t} \log_{10} \frac{p_0}{p} \\ \log_{10} \frac{0.4}{p} &= \frac{0.047793 \times 12}{2.303} = 0.2490 \end{aligned}$$

$$\text{or} \qquad \frac{0.4}{p} = 1.7743$$

$$\text{or} \qquad p = \frac{0.4}{1.7743} = 0.2254 \text{ atm}$$

Decrease in pressure, $x = 0.4 - 0.2254 = 0.1746 \text{ atm}$

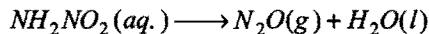


$$\text{Total pressure} = p_0 + 2x$$

$$= 0.4 + 2 \times 0.1746$$

$$= 0.7492 \text{ atm}$$

Example 34. The half life of first order decomposition of nitramide is 2.1 hours at 15°C .



If 6.2 g of NH_2NO_2 is allowed to decompose calculate (i) time taken for NH_2NO_2 to decompose 99% and (ii) the volume of dry N_2O produced at this point, measured at STP.

(IIT 1994)

$$\text{Solution: (i)} \qquad k = \frac{0.693}{t_{1/2}} = \frac{0.693}{2.1} = 0.33 \text{ hr}^{-1}$$

Applying kinetic equation of first order reaction,

$$k = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)}$$

$$\text{or} \qquad t = \frac{2.303}{0.33} \log_{10} \frac{100}{(100-99)}$$

$$= 13.96 \text{ hrs}$$

(ii) No. of moles of NH_2NO_2 decomposed

$$= 0.99 \times \frac{6.2}{62}$$

$$= 0.099$$

No. of moles of N_2O formed = 0.099

$$\text{Volume of } N_2O \text{ at STP} = 0.099 \times 22400 \text{ mL}$$

$$= 2217.6 \text{ mL}$$

Example 35. From the following data for the reaction between A and B:

| Expt. No. | [A] (mol L ⁻¹) | [B] (mol L ⁻¹) | Initial rate (mol L ⁻¹ s ⁻¹) | |
|--------------|-------------------------------|-------------------------------|---|------------------------|
| | | | 300 K | 320 K |
| (1) | 2.5 × 10 ⁻⁴ | 3.0 × 10 ⁻⁵ | 5.0 × 10 ⁻⁴ | 2.0 × 10 ⁻³ |
| (2) | 5.0 × 10 ⁻⁴ | 6.0 × 10 ⁻⁵ | 4.0 × 10 ⁻³ | ... |
| (3) | 1.0 × 10 ⁻³ | 6.0 × 10 ⁻⁵ | 1.6 × 10 ⁻² | ... |

Calculate the following:

- (i) The order of the reaction with respect to A and with respect to B,
 - (ii) The rate constant at 300 K,
 - (iii) The energy of activation and
 - (iv) The pre-exponential factor.
- (IIT 1994)

Solution: (i) Let the rate law be:

$$\text{Rate} = k[A]^x[B]^y$$

$$\text{From expt. (1), } 5.0 \times 10^{-4} = k[2.5 \times 10^{-4}]^x[3.0 \times 10^{-5}]^y \quad \dots (\text{i})$$

$$\text{From expt. (2), } 4.0 \times 10^{-3} = k[5.0 \times 10^{-4}]^x[6.0 \times 10^{-5}]^y \quad \dots (\text{ii})$$

$$\text{Dividing eq. (ii) by eq. (i), } \frac{4.0 \times 10^{-3}}{5.0 \times 10^{-4}} = 2^x \cdot 2^y = 8$$

$$\text{From expt. (3), } 1.6 \times 10^{-2} = k[1.0 \times 10^{-3}]^x[6.0 \times 10^{-5}]^y \quad \dots (\text{iii})$$

$$\text{Dividing eq. (iii) by eq. (ii), } \frac{1.6 \times 10^{-2}}{4.0 \times 10^{-3}} = 2^x = 4$$

$$\text{or } x = 2 \text{ and } y = 1$$

Hence, order w.r.t. A is 2nd and order w.r.t. B is 1st.

$$(ii) \quad \text{Rate} = k \cdot [A]^2[B]$$

$$\text{From expt. (1), } 5 \times 10^{-4} = k[2.5 \times 10^{-4}]^2[3.0 \times 10^{-5}]$$

$$\text{or } k = \frac{5 \times 10^{-4}}{[2.5 \times 10^{-4}]^2[3.0 \times 10^{-5}]} = 2.67 \times 10^8 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$$

(iii) From Arrhenius equation,

$$\log_{10} \frac{2.0 \times 10^{-3}}{5.0 \times 10^{-4}} = \frac{E_a}{2.303 \times 8.314} \times \frac{20}{300 \times 320}$$

$$E_a = \frac{2.303 \times 8.314 \times 300 \times 320}{20} \times \log_{10} 4$$

$$= 55.333 \text{ kJ mol}^{-1}$$

(iv) Applying $\log_{10} k = \log_{10} A - \frac{E_a}{2.303RT}$

$$\log_{10} \frac{A}{k} = \frac{55.333}{2.303 \times 8.314 \times 300} = 9.633$$

$$\text{or } \frac{A}{k} = 4.29 \times 10^9$$

$$\text{or } A = 4.29 \times 10^9 \times 2.67 \times 10^8$$

$$= 1.145 \times 10^{18}$$

Example 36. At a certain temperature, the half change period for the catalytic decomposition of ammonia were found as follows:

Pressure (Pascals): 6667 13333 26666

Half life period in hours: 3.52 1.92 1.0

Calculate the order of reaction.

$$\text{Solution: } \frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a_2}{a_1} \right)^{n-1} \text{ where, } n \text{ is order of reaction}$$

From the given data,

$$\frac{3.52}{1.92} = \left(\frac{13333}{6667} \right)^{n-1} \quad (a \propto \text{initial pressure})$$

$$= (2)^{n-1}$$

$$\log \frac{3.52}{1.92} = (n-1) \log 2$$

$$= 0.3010 \times (n-1)$$

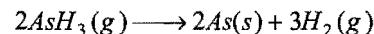
$$0.2632 = 0.3010 \times (n-1)$$

$$n = 1.87 \approx 2$$

Similar calculations are made between first and third observations. n comes equal to 1.908 (≈ 2).

Thus, the reaction is of second order.

Example 37. On heating, arsine (AsH_3) decomposes as:



The total pressure measured at constant temperature and constant volume varies with time as follows:

| | | | | |
|---------|-----|-----|-------|-------|
| t (min) | 0 | 5 | 7.5 | 10 |
| p/mm Hg | 760 | 836 | 866.4 | 896.8 |

Calculate the rate constant assuming the reaction to follow the first order rate law.

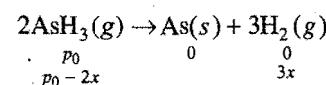
Solution: For first order, the rate equation is

Initially after time t

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]} = \frac{2.303}{t} \log \frac{p_0}{p}$$

given, $p_0 = 760 \text{ mm Hg}$.

The decomposition reaction is:



Total pressure, $p_t = p_0 - 2x + 3x = p_0 + x$

$$x = p_t - p_0$$

$$p_{\text{AsH}_3} = (p_0 - 2x) = p_0 - 2p_t + 2p_0 = 3p_0 - 2p_t$$

After 5 minutes, $p_{\text{AsH}_3} = (3 \times 760) - (2 \times 836)$
 $= 608 \text{ mm Hg}$
 $k = \frac{2.303}{5} \log_{10} \frac{760}{608} = 0.0446 \text{ min}^{-1}$

After 7.5 minutes, $p_{\text{AsH}_3} = (3 \times 760) - (2 \times 866.4)$
 $= 547.2 \text{ mm Hg}$
 $k = \frac{2.303}{7.5} \log_{10} \frac{760}{547.2} = 0.0438 \text{ min}^{-1}$

After 10 minutes, $p_{\text{AsH}_3} = (3 \times 760) - (2 \times 896.8)$
 $= 486.4 \text{ mm Hg}$
 $k = \frac{2.303}{10} \log_{10} \frac{760}{486.4} = 0.0446 \text{ min}^{-1}$

Example 38. Cane sugar is gradually converted into dextrose and laevulose by dilute acid. The rate of inversion is observed by measuring the polarisation angle, at various times, when the following results are obtained:

| Time (min) | 0 | 10 | 20 | 30 | 40 | 100 | ∞ |
|------------|------|------|------|------|------|------|----------|
| Angle | 32.4 | 28.8 | 25.5 | 22.4 | 19.6 | -6.1 | -14.1 |

Show that the reaction is of first order. Calculate the value of k , when the solution is optically inactive.

Solution: In case, the inversion of cane sugar is a first order change, then

$$k = \frac{2.303}{t} \log_{10} \frac{[A]_0}{[A]} = \frac{2.303}{t} \log_{10} \frac{r_0 - r_\infty}{r_t - r_\infty}$$

When, $t = 10$, $r_0 = 32.4$, $r_t = 28.8$, $r_\infty = -14.1$

$$k = \frac{2.303}{10} \log_{10} \frac{32.4 - (-14.1)}{28.8 - (-14.1)} = \frac{2.303}{10} \log_{10} \frac{46.5}{42.9} = 0.008 \text{ min}^{-1}$$

When, $t = 20$, $r_0 = 32.4$, $r_t = 25.5$, $r_\infty = -14.1$

$$k = \frac{2.303}{20} \log_{10} \frac{32.4 - (-14.1)}{25.5 - (-14.1)} = \frac{2.303}{20} \log_{10} \frac{46.5}{39.6} = 0.008 \text{ min}^{-1}$$

When, $t = 30$, $r_0 = 32.4$, $r_t = 22.4$, $r_\infty = -14.1$

$$k = \frac{2.303}{30} \log_{10} \frac{32.4 - (-14.1)}{22.4 - (-14.1)} = \frac{2.303}{30} \log_{10} \frac{46.5}{36.5} = 0.008 \text{ min}^{-1}$$

Thus, the reaction is of first order as the value of k is constant.

The solution will be optically inactive when half of the cane sugar is inverted.

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.008} = 86.6 \text{ min}$$

Example 39. 1 mL of methyl acetate was added to a flask containing 20 mL of N/20 HCl maintained at 25°C. 2 mL of the reaction mixture were withdrawn at different intervals and

titrated with a standard alkali solution. The following results were obtained:

| Time (min) | 0 | 75 | 119 | 183 | ∞ |
|------------------|-------|-------|-------|-------|----------|
| Alkali used (mL) | 19.24 | 24.20 | 26.60 | 29.32 | 42.03 |

Show that the reaction follows first order kinetics.

Solution: In case the hydrolysis follows first order kinetics, then

$$k = \frac{2.303}{t} \log_{10} \frac{[A]_0}{[A]} = \frac{2.303}{t} \log_{10} \frac{V_\infty - V_t}{V_\infty - V_0}$$

When, $t = 75 \text{ min}$, $V_\infty = 42.03$, $V_0 = 19.24$, $V_t = 24.20$

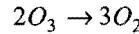
$$k = \frac{2.303}{75} \log_{10} \frac{(42.03 - 19.24)}{(42.03 - 24.20)} = \frac{2.303}{75} \log_{10} \frac{22.79}{17.83} = 0.00327 \text{ min}^{-1}$$

$t = 119 \text{ min}$, $V_\infty = 42.03$, $V_0 = 19.24$, $V_t = 26.60$

$$k = \frac{2.303}{119} \log_{10} \frac{(42.03 - 19.24)}{(42.03 - 26.60)} = \frac{2.303}{119} \log_{10} \frac{22.79}{15.43} = 0.00327 \text{ min}^{-1}$$

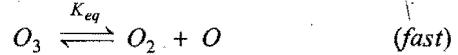
Since, the values of k are constant, hence, it follows first order kinetics.

Example 40. The gaseous decomposition of ozone



obeys the rate law $r = -\frac{d[O_3]}{dt} = \frac{k[O_3]^2}{[O_2]}$

Show that the following mechanism is consistent with the above rate law:



Solution: From the slow rate determining step

$$r = -\frac{d[O_3]}{dt} = k$$

From the fast reaction,

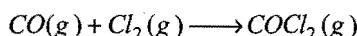
$$K_{eq} = \frac{[O_2][O]}{[O_3]}$$

or $[O] = \frac{K_{eq}[O_3]}{[O_2]}$

Substituting the value of $[O]$ in the above expression

$$r = -\frac{d[O_3]}{dt} = \frac{k_1 K_{eq} [O_3]^2}{[O_2]} = \frac{k [O_3]^2}{[O_2]}$$

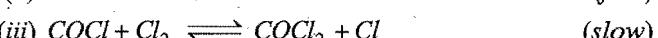
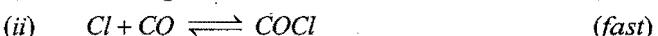
Example 41. For the formation of phosgene from $CO(g)$ and chlorine,



the experimentally determined rate equation is,

$$\frac{d[COCl_2]}{dt} = k[CO][Cl_2]^{3/2}$$

Is the following mechanism consistent with the rate equation?



Solution: Multiplying equation (ii) by 2 and adding (i), we get:



$$K = \frac{[\text{COCl}]^2}{[\text{Cl}_2][\text{CO}]^2}$$

$$[\text{COCl}] = (K)^{1/2} [\text{Cl}_2]^{1/2} [\text{CO}] \quad \dots(\text{i})$$

Slowest step is rate determining, hence,

$$\text{Rate} = k[\text{COCl}][\text{Cl}_2] \quad \dots(\text{ii})$$

From eqs. (i) and (ii), we get

$$\text{Rate} = kK^{1/2} [\text{Cl}_2]^{1/2} [\text{Cl}_2][\text{CO}]$$

$$\text{Rate} = k'[\text{Cl}_2]^{3/2} [\text{CO}]$$

Thus, rate law is in accordance with the mechanism.

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

22. A first order reaction has half life of 14.5 hrs. What percentage of the reactant will remain after 24 hrs?
 (a) 18.3% (b) 31.8% (c) 45.5% (d) 68.2%

[Ans. (b)]

[Hint: $k = \frac{2.303}{t} \log \left(\frac{a}{a-x} \right)$

$$\frac{0.693}{14.5} = \frac{2.303}{24} \log \frac{100}{(a-x)}$$

On solving, $(a-x) = 31.8\%$

23. Half life of a first order reaction is 10 min. What % of reaction will be completed in 100 min?

- (a) 25% (b) 99.9% (c) 75% (d) 80%

[Ans. (b)]

[Hint: $\frac{0.693}{t_{1/2}} = \frac{2.303}{t} \log_{10} \left(\frac{a}{a-x} \right)$

$$\frac{0.693}{10} = \frac{2.303}{100} \log \left(\frac{100}{100-x} \right)$$

$x = 99.9\%$

24. A certain zero order reaction has $k = 0.025 \text{ M s}^{-1}$ for the disappearance of A. What will be the concentration of A after 15 seconds if the initial concentration is 0.5 M ?

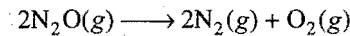
- (a) 0.5 M (b) 0.32 M (c) 0.12 M (d) 0.06 M

[Ans. (c)]

[Hint: $x = kt = 0.025 \times 15 = 0.375 \text{ M}$

Remaining conc. $= 0.5 - 0.375 = 0.125 \text{ M}$

25. A first order reaction:



has a rate constant of $1.3 \times 10^{-11} \text{ s}^{-1}$ at 270°C and $4.5 \times 10^{-10} \text{ s}^{-1}$ at 350°C . What is the activation energy for this reaction?

- (a) 15 kJ (b) 30 kJ (c) 68 kJ (d) 120 kJ

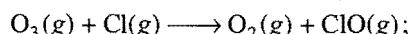
[Ans. (d)]

[Hint: $\log \left(\frac{k_2}{k_1} \right) = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$

$$\log \left(\frac{4.5 \times 10^{-10}}{1.3 \times 10^{-11}} \right) = \frac{E_a}{2.303 \times 8.314 \times 10^{-3}} \left[\frac{1}{543} - \frac{1}{623} \right]$$

$$E_a = 120 \text{ kJ}$$

26. The reaction of O_3 with chlorine atom is given as:

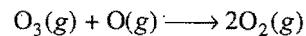


$$k_1 = 5.2 \times 10^9 \text{ L mol}^{-1} \text{ sec}^{-1}$$



$$k_2 = 2.6 \times 10^{10} \text{ L mol}^{-1} \text{ sec}^{-1}$$

Which of these values is closest to the rate constant of the overall reaction?



$$(a) 5.2 \times 10^9 \quad (b) 2.6 \times 10^{10}$$

$$(c) 3.1 \times 10^{10}$$

$$(d) 1.4 \times 10^{20}$$

[Ans. (a)]

[Hint: Lowest value of k shows that the step is rate determining.]

27. If a first order reaction takes 32 minutes for 75% completion, then time required for 50% completion is:

[AMU (Medical)]

$$(a) 32 \text{ min} \quad (b) 16 \text{ min} \quad (c) 8 \text{ min} \quad (d) 4 \text{ min}$$

[Ans. (b)]

[Hint: $k = \frac{2.303}{t} \log \left(\frac{a}{a-x} \right)$

When, $a = 100$, $x = 75$, $t = 32$

$$k = \frac{2.303}{32} \log_{10} \left(\frac{100}{25} \right) = 0.0433 \text{ min}^{-1}$$

$$\text{Time for } 50\% \text{ completion } (t_{1/2}) = \frac{0.693}{k} = \frac{0.693}{0.0433} \approx 16 \text{ min}$$

28. Rate constant of a reaction is $175 \text{ litre}^{-2} \text{ mol}^{-2} \text{ sec}^{-1}$. What is the order of reaction?

[CET (Gujarat) 2005]

- (a) First (b) Second (c) Third (d) Zero

[Ans. (c)]

[Hint: Unit of $k = \left[\frac{\text{litre}}{\text{mol}} \right]^{n-1} \times \text{sec}^{-1}$]

Given unit of $k = \text{litre}^2 \text{ mol}^{-2} \text{ sec}^{-1}$

Comparing the unit of litre,

$$n-1 = 2$$

$$n = 3$$

29. The half life of a first order reaction having rate constant $k = 1.7 \times 10^{-5} \text{ sec}^{-1}$ is:

[JIPMER 2006]

- (a) 12.1 hrs (b) 9.7 hrs (c) 11.3 hrs (d) 1.8 hrs

[Ans. (c)]

[Hint: $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{1.7 \times 10^{-5}} = 40764 \text{ sec} = 11.3 \text{ hrs}$]

30. At 500 K, the half life period of a gaseous reaction at an initial pressure of 80 kPa is 350 sec. When the pressure is 40 kPa, the half life period is 175 sec; the order of the reaction is:

[PET (Kerala) 2007]

- (a) zero (b) one (c) two (d) three
 (e) half

[Ans. (a)]

$$\text{Hint: } \frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{p_2}{p_1}\right)^{n-1}$$

$$\frac{350}{175} = \left(\frac{40}{80}\right)^{n-1}$$

$$2 = \left(\frac{1}{2}\right)^{n-1}$$

$$n-1 = -1$$

$n = 0$ (zero order reaction)]

31. 90% of the first order reaction is completed in 70 minutes. The velocity constant of the reaction is: [Comed (Karnataka) 2008]

(a) 0.0329 (b) 0.329 (c) 3.29 (d) 0.0293

[Ans. (a)]

$$\begin{aligned}\text{Hint: } k &= \frac{2.303}{t} \log \frac{a}{a-x} \\ &= \frac{2.303}{70} \log \frac{100}{100-90} \\ &= 0.0329 \text{ min}^{-1}\end{aligned}$$

32. The half life period of a first order reaction is 1 min 40 seconds. Calculate its rate constant. (VITEEE 2008)

(a) $6.93 \times 10^{-3} \text{ min}^{-1}$ (b) $6.93 \times 10^{-3} \text{ sec}^{-1}$
 (c) $6.93 \times 10^{-3} \text{ sec}$ (d) $6.93 \times 10^3 \text{ sec}$

[Ans. (b)]

$$\text{Hint: } k = \frac{0.693}{t_{1/2}} = \frac{0.693}{100} = 6.93 \times 10^{-3} \text{ sec}^{-1}$$

MISCELLANEOUS NUMERICAL EXAMPLES

Example 1. Ammonia and oxygen react at higher temperature as,



in an experiment, the concentration of NO increases by $1.08 \times 10^{-2} \text{ mol litre}^{-1}$ in 3 seconds. Calculate:

- (i) rate of reaction, (ii) rate of disappearance of ammonia,
 (iii) rate of formation of water.

Solution:

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

$$\text{Rate} = \frac{1}{4} \times \frac{1.08 \times 10^{-2}}{3} = 9 \times 10^{-4} \text{ mol litre}^{-1} \text{ sec}^{-1}$$

$$(ii) \frac{-d[\text{NH}_3]}{dt} = 4 \times \text{rate} = 4 \times 9 \times 10^{-4}$$

$$= 36 \times 10^{-4} \text{ mol litre}^{-1} \text{ sec}^{-1}$$

$$(iii) \frac{d[\text{H}_2\text{O}]}{dt} = 6 \times \text{rate} = 6 \times 9 \times 10^{-4}$$

$$= 54 \times 10^{-4} \text{ mol litre}^{-1} \text{ sec}^{-1}$$

Example 2. Decomposition of $\text{N}_2\text{O}_5(g)$ into $\text{NO}_2(g)$ and $\text{O}_2(g)$ is a first order reaction. If initial concentration of $\text{N}_2\text{O}_5(g)$, i.e., $[\text{N}_2\text{O}_5]_0$ is $0.03 \text{ mol litre}^{-1}$, what will be its concentration after 30 minutes? Rate constant of the reaction is $1.35 \times 10^{-4} \text{ s}^{-1}$.

$$\text{Solution: } k = \frac{2.303}{t} \log_{10} \frac{[A_0]}{[A]}$$

$$1.35 \times 10^{-4} = \frac{2.303}{30 \times 60} \log_{10} \frac{0.03}{[A]}$$

$$[A] = 0.0235 \text{ mol litre}^{-1}$$

Example 3. Rate constant for the decomposition of ethylene oxide into CH_4 and CO may be described by the equation, $\log k (\text{s}^{-1}) = 14.34 - \frac{1.25 \times 10^4}{T}$.

(a) What is the energy of activation of this reaction?

(b) What is the value of k at 670 K ?

Solution: (a) We know that,

$$\log_{10} k = \log_{10} A - \frac{E}{2.303RT} \quad \dots (i)$$

$$\log_{10} k (\text{s}^{-1}) = 14.34 - \frac{1.25 \times 10^4}{T} \quad \dots (ii)$$

Comparing eq. (i) and eq. (ii), we get

$$\frac{E}{2.303R} = 1.25 \times 10^4$$

$$E = 1.25 \times 10^4 \times 2.303 \times 8.314 \times 10^{-3}$$

$$E = 239.339 \text{ kJ/mol}$$

(b) Substituting the value of T , i.e., at 670 K , in equation (ii), we get,

$$\begin{aligned}\log k (\text{s}^{-1}) &= 14.34 - \frac{1.25 \times 10^4}{670} = -4.3167 \\ k &= 4.82 \times 10^{-5} \text{ s}^{-1}\end{aligned}$$

Example 4. A drug becomes ineffective after 30% decomposition. The original concentration of a sample was 5 mg/mL , which becomes 4.2 mg/mL during 20 months. Assuming the decomposition of first order, calculate the expiry time of the drug in months. What is the half life of the product?

$$\begin{aligned}\text{Solution: } k &= \frac{2.303}{t} \log_{10} \left(\frac{a}{a-x} \right) = \frac{2.303}{20} \log_{10} \left(\frac{5}{4.2} \right) \\ &= 0.00872 \text{ month}^{-1}\end{aligned}$$

Expiry time ' t ' may be calculated as:

$$k = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$$

$$0.00872 = \frac{2.303}{t} \log_{10} \frac{100}{70}$$

$$t = 40.9 \approx 41 \text{ month}$$

$$t_{1/2} = \frac{0.693}{0.00872} = 79.4 \text{ month}$$

Example 5. Two reactions of the same order have equal exponential factors but their activation energies differ by 24.9 kJ/mol. Calculate the ratio between the rate constants of these reactions at 27°C. ($R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$) (Dhanbad 1990)

Solution: We know that,

$$\log_{10} k = \log_{10} A - \frac{E}{2.303RT}$$

$$\text{So, } \log_{10} k_2 = \log_{10} A - \frac{E_2}{2.303RT}$$

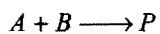
$$\text{and } \log_{10} k_1 = \log_{10} A - \frac{E_1}{2.303RT}$$

$$\log_{10} \left(\frac{k_2}{k_1} \right) = \frac{(E_1 - E_2)}{2.303RT}$$

$$\log_{10} \left(\frac{k_2}{k_1} \right) = \frac{24.9 \times 1000}{2.303 \times 8.314 \times 300}$$

$$\frac{k_2}{k_1} = 2.199 \times 10^4$$

Example 6. Pseudo first order rate for the reaction,

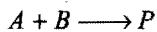


when studied in 0.1 M of B is given by

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

where, $k = 1.85 \times 10^4 \text{ sec}^{-1}$. Calculate the value of second order rate constant.

Solution:



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

$$-\frac{d[A]}{dt} = 1.85 \times 10^4 \times [A] \quad \dots (\text{i})$$

Assuming the reaction to be of second order,

$$-\frac{d[A]}{dt} = k'[A][B]$$

$$-\frac{d[A]}{dt} = k'[A][0.1] \quad \dots (\text{ii})$$

Dividing eq. (i) by eq. (ii), we get

$$1 = \frac{1.85 \times 10^4}{k'[0.1]}$$

$$k' = 1.85 \times 10^5 \text{ litre mol}^{-1} \text{ sec}^{-1}$$

Example 7. The time required for 10% completion of a first order reaction at 298 K is equal to that required for its 25% completion at 308 K. If the pre-exponential factor for the reaction is $3.56 \times 10^9 \text{ sec}^{-1}$, calculate its rate constant at 318 K and also the energy of activation. (IIT 1997)

Solution: We know that,

$$k = \frac{2.303}{t} \log_{10} \left(\frac{a}{a-x} \right)$$

$$\text{At 298 K, } x = 10, a = 100,$$

$$k_{298} = \frac{2.303}{t_1} \log_{10} \frac{100}{90} \quad \dots (\text{i})$$

$$\text{At 308 K, } a = 100, x = 25, (a-x) = 75$$

$$k_{308} = \frac{2.303}{t_2} \log_{10} \left(\frac{100}{75} \right) \quad \dots (\text{ii})$$

$t_1 = t_2$, dividing eq. (ii) by eq. (i)

$$\frac{k_{308}}{k_{298}} = 2.73$$

$$\log \frac{k_{308}}{k_{298}} = \frac{E}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\log 2.73 = \frac{E}{2.303 \times 8.314} \left(\frac{1}{308} - \frac{1}{298} \right)$$

$$E = 76.622 \text{ kJ/mol}$$

Similarly, we can solve for k_{318} which is equal to $9.22 \times 10^{-4} \text{ s}^{-1}$.

Example 8. The rate constant of a reaction is $1.5 \times 10^7 \text{ s}^{-1}$ at 50°C and $4.5 \times 10^7 \text{ s}^{-1}$ at 100°C. Calculate the Arrhenius parameter A and E_a . (IIT 1998)

$$\text{Solution: } \log_{10} \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\log_{10} \frac{4.5 \times 10^7}{1.5 \times 10^7} = \frac{E_a}{2.303 \times 8.314} \left(\frac{1}{323} - \frac{1}{373} \right)$$

$$E_a = 2.2 \times 10^4 \text{ J/mol}$$

We know that,

$$\log_{10} k = \log_{10} A - \frac{E_a}{2.303RT}$$

$$\log_{10} (1.5 \times 10^7) = \log_{10} A - \frac{2.2 \times 10^4}{2.303 \times 8.314 \times 323}$$

$$A = 5.42 \times 10^{10} \text{ s}^{-1}$$

Example 9. In hydrogenation reaction at 25°C, it is observed that hydrogen gas pressure falls from 2 atm to 1.2 atm in 50 min. Calculate the rate of reaction in molarity per sec. ($R = 0.0821 \text{ litre-atm degree}^{-1} \text{ mol}^{-1}$)

$$\text{Solution: Rate} = \frac{dP}{dt} = \frac{2 - 1.2}{50 \times 60}$$

$$= 2.666 \times 10^{-4} \text{ atm s}^{-1}$$

$$PV = nRT$$

$$\frac{P}{\text{sec}} = \left(\frac{n}{V} \right) \frac{RT}{\text{sec}}$$

$$\left[\frac{n}{V} \right] \frac{1}{\text{sec}} = \left[\frac{P}{\text{sec}} \right] \frac{1}{RT}$$

$$\text{Rate (molarity/sec)} = \frac{2.666 \times 10^{-4}}{0.0821 \times 298}$$

$$= 1.09 \times 10^{-5} \text{ mol litre}^{-1} \text{ s}^{-1}$$

Example 10. A drop of solution (volume 0.05 mL) contains 3×10^{-6} mole H^+ ions. If the rate of disappearance of the H^+ ions is 1×10^{-7} mol litre $^{-1}$ sec $^{-1}$, how long would it take for H^+ ions in the drop to disappear?

Solution:

$$\text{Concentration of drop} = \frac{\text{mole}}{\text{volume in mL}} \times 1000$$

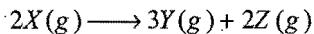
$$= \frac{3 \times 10^{-6}}{0.05} \times 1000 = 0.06 \text{ mol litre}^{-1}$$

$$\text{Rate of disappearance} = \frac{\text{conc. change}}{\text{time}}$$

$$1 \times 10^{-7} = \frac{0.06}{\text{time}}$$

$$\text{Time} = 6 \times 10^{-9} \text{ sec}$$

Example 11. A constant temperature and volume X decomposes as,



P_X is the partial pressure of X .

| Observation No. | Time (min) | P_X (in mm Hg) |
|-----------------|------------|------------------|
| 1 | 0 | 800 |
| 2 | 100 | 400 |
| 3 | 200 | 200 |

- (i) What is the order of the reaction with respect to X ?
- (ii) Find the rate constant.
- (iii) Find the time for 75% completion of the reaction.
- (iv) Find the total pressure when pressure of X is 700 mm Hg.

Solution: (i) Data shows that half life of the reaction is constant, i.e., 100 min; hence, it is a first order reaction.

$$(ii) k = \frac{0.693}{t_{1/2}} = \frac{0.693}{100} = 6.93 \times 10^{-3} \text{ min}^{-1}$$

$$(iii) t_{75\%}, \text{ i.e., } t_{3/4} = 2 \times t_{1/2} = 2 \times 100 = 200 \text{ min}$$

$$(iv) 2X(g) \longrightarrow 3Y(g) + 2Z(g)$$

$$t = 0 \quad 800 \quad 0 \quad 0$$

$$dt \quad 800 - 2X \quad 3X \quad 2X$$

$$\text{Total pressure} = 800 - 2X + 3X + 2X = 800 + 3X \dots (i)$$

$$800 - 2X = 700$$

$$X = 50$$

$$\therefore \text{Total pressure} = 800 + 3 \times 50 = 950 \text{ mm Hg}$$

Example 12. Suppose 50 bacteria are placed in a flask containing nutrients for the bacteria so that they can multiply.

A study at 35°C gave the following results:

| Time (minute) | 0 | 15 | 30 | 45 | 60 |
|--------------------|----|-----|-----|-----|-----|
| Number of bacteria | 50 | 100 | 200 | 400 | 800 |

Show that the rate of production of bacteria is of first order. How many bacteria will be there after 3 hours?

Solution: For bacterial growth,

$$k = -\frac{2.303}{t} \log_{10} \left(\frac{a}{a+x} \right)$$

$$\text{At 15 minutes: } k = -\frac{2.303}{15} \log_{10} \left(\frac{50}{100} \right)$$

$$= 0.0462 \text{ min}^{-1}$$

$$\text{At 30 minutes: } k = -\frac{2.303}{30} \log_{10} \left(\frac{50}{200} \right)$$

$$= 0.0462 \text{ min}^{-1}$$

$$\text{At 45 minutes: } k = -\frac{2.303}{45} \log_{10} \left(\frac{50}{400} \right) = 0.0462 \text{ min}^{-1}$$

Same values of rate constants show that the process corresponds to first order.

Let there be ' n ' bacteria after 3 hrs.

$$k = -\frac{2.303}{t} \log_{10} \left(\frac{a}{a+x} \right)$$

$$0.0462 = -\frac{2.303}{180} \log_{10} \frac{50}{n}$$

$$n = 2.04 \times 10^5$$

Example 13. A viral preparation was inactivated in a chemical bath. The inactivation process was found to be of first order in virus concentration, and at the beginning of the experiment 2.0% of the virus was found to be inactivated per minute. Evaluate ' k ' for the inactivation process.

Solution: $a = 100, a - x = 98, t = 60 \text{ sec}$

$$k = \frac{2.303}{t} \log_{10} \left(\frac{a}{a-x} \right)$$

$$= \frac{2.303}{60} \log_{10} \left(\frac{100}{98} \right) = 3.3 \times 10^{-4} \text{ sec}^{-1}$$

Example 14. Trans-1,2-dideuteriocyclopropane (A) undergoes a first order decomposition. The observed rate constant at a certain temperature, measured in terms of disappearance of ' A ', was $1.52 \times 10^{-4} \text{ sec}^{-1}$. Analysis of products showed that the reaction followed two parallel paths, one leading to dideuteropropane (B) and the other to cis-1,2-dideuteriocyclopropane (C). (B) was found to constitute 11.2% of the reaction product, independently of extent of reaction. What is the order of reaction for each path and what is the value of the rate constant for the formation of each of the products?

Solution:

In case of parallel path reaction,

$$k_B = k_A \times \text{fractional yield of } B \\ = 1.52 \times 10^{-4} \times 0.112 = 1.7 \times 10^{-5} \text{ sec}^{-1}$$

$$k_C = k_A \times \text{fractional yield of } C \\ = 1.52 \times 10^{-4} \times 0.888 = 1.35 \times 10^{-4} \text{ sec}^{-1}$$

The reaction will be first order for each individual path.

Example 15. In milk, at 37°C , *lactobacillus acidophilus* has a generation time of about 75 minutes. Calculate the population relative to the initial value at 30, 60, 75, 90 and 150 minutes.

Solution: For growth kinetics,

$$k = -\frac{2.303}{t} \log_{10} \left(\frac{a}{a+x} \right)$$

$$k = -\frac{2.303}{t} \log_{10} \left(\frac{N_0}{N} \right)$$

Generation time = 75 minutes; $a = 1$, $a + x = 2$

$$k = -\frac{2.303}{75} \log_{10} \left(\frac{1}{1+1} \right) = 0.00924 \text{ min}^{-1}$$

After 30 minutes,

$$k = -\frac{2.303}{t} \log_{10} \left(\frac{N_0}{N} \right)$$

$$0.00924 = -\frac{2.303}{30} \log_{10} \left(\frac{N_0}{N} \right)$$

$$\frac{N}{N_0} = 1.319 \approx 1.32$$

Similarly, we may calculate after 60, 75, 90 and 150 minutes.

Example 16. Rate law for ozone layer depletion is,

$$\frac{d[O_3]}{dt} = \frac{K[O_3]^2}{[O_2]}$$

Give the probable mechanism of reaction?

Solution: $O_3 \rightleftharpoons O_2 + O$ (fast reaction)

(equilibrium constant K_c)

$O_3 + O \longrightarrow 2O_2$ (slow reaction, rate constant k)

$$\text{Rate} = k[O_3][O] \quad \dots (i)$$

$$K_c = \frac{[O_2][O]}{[O_3]} \text{ or } [O] = K_c \frac{[O_3]}{[O_2]},$$

putting the value in eq. (i)

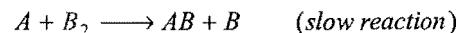
From eq. (i),

$$\text{Rate} = k \cdot [O_3] \cdot K_c \frac{[O_3]}{[O_2]} = k \cdot K_c \cdot \frac{[O_3]^2}{[O_2]} = K \cdot \frac{[O_3]^2}{[O_2]}$$

Here,

$$K = k \times K_c$$

Example 17. In hypothetical reaction $A_2 \rightarrow 2AB$, follows the mechanism as given below:



Give the rate law and order of reaction.

Solution: Slowest step is rate determining.

$$\text{Rate} = k[A][B_2] \quad \dots (i)$$

Here, $[A]$ should be eliminated.

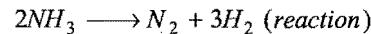
$$K_c = \frac{[A][A]}{[A_2]} = \frac{[A]^2}{[A_2]}$$

$$[A] = K_c^{1/2} [A_2]^{1/2}$$

$$\text{From eq. (i), Rate} = k K_c^{1/2} [A_2]^{1/2} [B_2] \\ = K [A_2]^{1/2} [B_2]; \quad [K = k \cdot K_c]$$

$$\text{Order} = 1 + 1/2 = 3/2$$

Example 18. Calculate order of reaction from the following data:



| | | | |
|------------------|------|------|------|
| Pressure (mm Hg) | 50 | 100 | 200 |
| Half lives (min) | 3.52 | 1.82 | 0.93 |

Solution: We know that,

$$n = 1 + \frac{\log_{10} (t_{1/2})_1 - \log_{10} (t_{1/2})_2}{\log_{10} p_2 - \log_{10} p_1} \\ = 1 + \frac{\log_{10} 3.52 - \log_{10} 1.82}{\log_{10} 100 - \log_{10} 50} \\ = 1.95 \approx 2$$

Similarly, we may calculate for other set of conditions.

Example 19. The chemical reaction between mercuric chloride and potassium oxalate proceeds as under:



the mass of Hg_2Cl_2 precipitated from different solutions in a given time, at 100°C was as follows:

| Expt. No. | $HgCl_2$ (mol L^{-1}) | $K_2C_2O_4$ (mol L^{-1}) | Time (minutes) | Hg_2Cl_2 precipitated (mole) |
|-----------|----------------------------------|-------------------------------------|----------------|--------------------------------|
| (1) | 0.0836 | 0.404 | 65 | 0.0068 |
| (2) | 0.0836 | 0.202 | 120 | 0.0031 |
| (3) | 0.0418 | 0.404 | 60 | 0.0032 |

From these data calculate order of the reaction.

Solution: $\text{Rate} = k[HgCl_2]^\alpha [K_2C_2O_4]^\beta$;

$$\frac{0.0068}{65} = k[0.0836]^\alpha [0.404]^\beta; \quad \dots (i)$$

$$\frac{0.0031}{120} = k[0.0836]^\alpha [0.202]^\beta, \dots \text{(ii)}$$

$$\frac{0.0032}{60} = k[0.0418]^\alpha [0.404]^\beta \dots \text{(iii)}$$

Dividing eq. (i) by eq. (ii), we get $4 = 2^\beta; \beta = 2$

Dividing eq. (i) by eq. (iii), we get $2 = 2^\alpha; \alpha = 1$

Thus, overall order $= \alpha + \beta = 3$

Example 20. The rate constant of the reaction $A \rightarrow B$ is $k = 0.5$; the initial concentration of A being 1 mol/litre . Calculate the degree of conversion of substance 'A' within 1 hour if the reaction is of zeroth, first and second order. How does the degree of conversion depend on the order of reaction?

Solution: Zero order:

$$x = kt$$

$$x = 0.5 \times 1 = 0.5$$

First order: $k = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$

$$k = 0.5; t = 1 \text{ hr}; a = 1 \text{ M}$$

$$0.5 = \frac{2.303}{1} \log_{10} \frac{1}{(1-x)}$$

$$x = 0.39$$

Second order: $k = \frac{1}{t} \frac{x}{a(a-x)}$

$$0.5 = \frac{1}{1} \frac{x}{1(1-x)}$$

$$x = 0.33$$

Example 21. Two first order reactions proceed at 25°C at the same rate. The temperature coefficient of the rate of the first reaction is 2 and that of second reaction is 3. Find the ratio of the rates of these reactions at 75°C .

Solution: For first order reaction, $r_1 = k[A]^1$

$$\therefore r_1/r_2 = k_1/k_2 = \text{temperature coefficient}$$

Let the rate of reaction for Ist at 25°C be R_1 and the rate of reaction for IInd at 25°C be R_2 .

Also,

$$R_1 = R_2$$

Rates of reaction

| At 25°C | R_1 | R_2 |
|------------------------|-------------|-------------|
| 35°C | $2R_1$ | $3R_2$ |
| 45°C | $(2)^2 R_1$ | $(3)^2 R_2$ |
| 55°C | $(2)^3 R_1$ | $(3)^3 R_2$ |
| 65°C | $(2)^4 R_1$ | $(3)^4 R_2$ |
| 75°C | $(2)^5 R_1$ | $(3)^5 R_2$ |

$$\therefore \text{Temperature coefficient for 1st reaction} = \frac{k_{35}}{k_{25}} = \frac{R_{35}}{R_{25}} = 2$$

i.e., for each 10°C rise in temperature, rate becomes 2 times.

Similarly, for 2nd reaction it becomes 3 times,

\therefore At 75°C

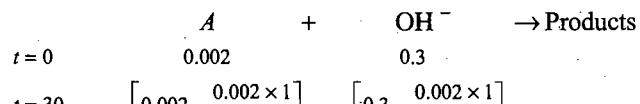
$$\frac{\text{rate of reaction for 2nd}}{\text{rate of reaction for 1st}} = \frac{(3)^5 R_2}{(2)^5 R_1} = 7.5937 (\because R_1 = R_2)$$

Example 22. The reaction, $A + OH^- \rightarrow \text{Products}$, obeys rate law expression as:

$$\frac{-d[A]}{dt} = k[A][OH^-]$$

If initial concentrations of $[A]$ and $[OH^-]$ are 0.002 M and 0.3 M respectively and if it takes 30 sec for 1% A to react at 25°C , calculate the rate constant for the reaction.

Solution:



$$\text{Using } k = \frac{2.303}{t(a-b)} \log_{10} \frac{b(a-x)}{a(b-x)},$$

$$k = \frac{2.303}{30 \times (0.002 - 0.3)} \log_{10} \frac{0.3 \left[0.002 - \frac{0.002 \times 1}{100}\right]}{0.002 \left[0.3 - \frac{0.002 \times 1}{100}\right]}$$

$$k = 1.12 \times 10^{-3} \text{ litre mol}^{-1} \text{ s}^{-1}$$

Example 23. A hydrogenation reaction is carried out at 500 K . If the same reaction is carried out in presence of a catalyst at the same rate, the temperature required is 400 K . Calculate the activation energy of the reaction if the catalyst lowers the activation barrier by 20 kJ mol^{-1} . (IIT 2000)

Solution: Arrhenius equation may be given as,

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

Let k_{500} and k_{400} be the rate constants at temperatures 500 K and 400 K (in presence of catalyst) respectively. E_{500} and E_{400} be the activation energies at temperatures 500 K and 400 K respectively.

$$k_{500} = Ae^{-E_{500}/R \times 500} \dots \text{(i)}$$

$$k_{400} = Ae^{-E_{400}/R \times 400} \dots \text{(ii)}$$

Given, $k_{500} = k_{400}$ (same rates in presence and absence of a catalyst).

On comparing eq. (i) with eq. (ii),

$$\frac{E_{500}}{R \times 500} = \frac{E_{400}}{R \times 400}$$

or

$$\frac{E_{500}}{5} = \frac{E_{400}}{4}$$

or

$$E_{500} = \frac{E_{400}}{4} \times 5 \dots \text{(iii)}$$

Given,

$$E_{500} = E_{400} + 20$$

Substituting in eq. (iii),

$$E_{400} + 20 = E_{400} \times 1.25$$

$$\text{or } E_{400} = \frac{20}{0.25} = 80 \text{ kJ mol}^{-1}$$

$$\text{So, } E_{500} = 80 + 20 = 100 \text{ kJ mol}^{-1}$$

Example 24. Some $\text{PH}_3(g)$ is introduced into a flask at 600°C containing an inert gas. PH_3 proceeds to decompose into $\text{P}_4(g)$ and $\text{H}_2(g)$ and the reaction goes to completion. Total pressure is given below as a function of time. Find the order of the reaction and calculate the rate constant,

| Time (sec) | 0 | 60 | 120 | ∞ |
|------------------|--------|--------|--------|----------|
| Pressure (mm Hg) | 262.40 | 272.90 | 275.51 | 276.40 |

(IIT 2001)

Solution: $4\text{PH}_3(g) + \text{Inert gas} \rightarrow \text{P}_4(g) + 6\text{H}_2(g) + \text{Inert gas}$

| | | | | | |
|--------------|-----------|-------|-------|--------|-------|
| $t = 0$ | P | P_i | 0 | 0 | 0 |
| $t = t$ | $(P - x)$ | P_i | $x/4$ | $6x/4$ | P_i |
| $t = \infty$ | 0 | P_i | $P/4$ | $6P/4$ | P_i |

$$\text{At } t = 0, \quad 262.40 = P + P_i \quad \dots \text{(i)}$$

$$\text{At } 60 \text{ sec}, \quad 272.90 = P_{\text{PH}_3(\text{left})} + P_{\text{P}_4(\text{g})} + P_{\text{H}_2(\text{g})} + P_i$$

$$\text{At } 120 \text{ sec}, \quad 275.51 = P_{\text{PH}_3(\text{left})} + P_{\text{P}_4(\text{g})} + P_{\text{H}_2(\text{g})} + P_i$$

$$\text{At } \infty, \quad 276.40 = P_{\text{P}_4(\text{g})} + P_{\text{H}_2(\text{g})} + P_i$$

$$276.40 = \frac{P}{4} + \frac{6P}{4} + P_i$$

$$276.40 \times 4 = 7P + 4P_i \quad \dots \text{(ii)}$$

$$\text{At } t = 0, \quad 262.40 = P + P_i \quad \dots \text{(iii)}$$

On solving eqs. (ii) and (iii), we get

$$P = 18.66 \text{ mm}, P_i = 243.74 \text{ mm}$$

$$\text{At } 60^\circ\text{C}: \quad 272.90 = (P - x) + P_i + \frac{x}{4} + \frac{6x}{4}$$

$$272.90 = 18.66 - x + 243.74 + \frac{7x}{4}$$

$$x = 14 \text{ mm}$$

$$k = \frac{2.303}{t} \log \left(\frac{a}{a-x} \right) = \frac{2.303}{60} \log \frac{18.66}{18.66 - 14}$$

$$k = 2.32 \times 10^{-2} \text{ sec}^{-1}$$

Similarly, at 120 sec $k = 2.30 \times 10^{-2} \text{ sec}^{-1}$ (do yourself)

Since, values of 'k' are same, hence the reaction belongs to first order.

Example 25. For the given reaction, $A + B \rightarrow \text{Products}$ following data were obtained:

| | $[A_0]$ | $[B_0]$ | $R_0 \text{ mol litre}^{-1} \text{ sec}^{-1}$ |
|----|---------|---------|---|
| 1. | 0.1 M | 0.2 M | 0.05 |
| 2. | 0.2 M | 0.2 M | 0.10 |
| 3. | 0.1 M | 0.1 M | 0.05 |

(i) Write the rate law expression.

(ii) Find the rate constant. [IIT 2004 (Memory based)]

Solution: Let order with respect to A and B are α and β respectively. Rate law expression may be given as,

$$\text{Rate} = k[A]^\alpha [B]^\beta$$

$$0.05 = k[0.1]^\alpha [0.2]^\beta \quad \dots \text{(i)}$$

$$0.10 = k[0.2]^\alpha [0.2]^\beta \quad \dots \text{(ii)}$$

$$0.05 = k[0.1]^\alpha [0.1]^\beta \quad \dots \text{(iii)}$$

Dividing eq. (i) by eq. (ii), we get

$$\frac{1}{2} = \left[\frac{1}{2} \right]^\alpha, \text{ i.e., } \alpha = 1$$

Dividing eq. (i) by eq. (iii), we get

$$1 = [2]^\beta, \text{ i.e., } \beta = 0$$

$$\text{Rate} = k[A]^1 [B]^0$$

Substituting the value of α and β in eq. (i), we get

$$0.05 = k[0.1]^1 [0.2]^0$$

$$k = 0.5 \text{ sec}^{-1}$$

Example 26. $A + 2B \rightarrow 3C + 2D$

The rate of disappearance of B is $1 \times 10^{-2} \text{ mol litre}^{-1} \text{ sec}^{-1}$. What will be the (i) rate of the reaction and (ii) rate of change in concentration of A and C ? [CBSE (Mains) 2005]

$$\begin{aligned} \text{Solution: (i)} \quad \text{Rate} &= -\frac{1}{2} \frac{d[B]}{dt} \\ &= -\frac{1}{2} [-1 \times 10^{-2}] \\ &= 0.5 \times 10^{-2} \text{ mol litre}^{-1} \text{ sec}^{-1} \end{aligned}$$

$$\begin{aligned} \text{(ii)} \quad -\frac{d[A]}{dt} &= -\frac{1}{2} \left[\frac{d[B]}{dt} \right] = 0.5 \times 10^{-2} \text{ mol litre}^{-1} \text{ sec}^{-1} \\ \frac{1}{3} \frac{d[C]}{dt} &= -\frac{1}{2} \frac{d[B]}{dt} \\ \frac{d[C]}{dt} &= -\frac{3}{2} \times (-1 \times 10^{-2}) \end{aligned}$$

$$= 1.5 \times 10^{-2} \text{ mol litre}^{-1} \text{ sec}^{-1}$$

Example 27. For the reaction, $A + B \rightarrow \text{Products}$, rate is given as, rate = $k[A][B]^2$.

How will the rate change if volume of the reaction mixture is reduced to 1/3rd of its original volume? (BCECE 2006)

Solution: When volume is reduced to 1/3rd, then concentration will increase three times.

$$r_1 = k[A][B]^2 \quad \dots \text{(i)}$$

$$r_2 = k[3A][3B]^2 \quad \dots \text{(ii)}$$

From eqs. (i) and (ii),

$$\frac{r_1}{r_2} = \frac{1}{27}$$

$$r_2 = 27r_1$$

∴ Rate will increase 27 times.

Example 28. For first order reaction, if rate constant at 17°C is $2.8 \times 10^{-5} \text{ s}^{-1}$ and at 27°C is $2.8 \times 10^{-4} \text{ s}^{-1}$.

(i) Write the equation for calculation of activation energy.

(ii) Calculate the activation energy.

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

[AIPMT (Mains) 2008]

Solution. We know,

$$\log \left(\frac{k_2}{k_1} \right) = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\begin{aligned} \log \frac{2.8 \times 10^{-4}}{2.8 \times 10^{-5}} &= \frac{E_a}{2.303 \times 8.3} \left[\frac{1}{290} - \frac{1}{300} \right] \\ E_a &= \frac{2.303 \times 8.3 \times 290 \times 300}{10} \\ &= 166299.6 \text{ J mol}^{-1} \\ &= 166.3 \text{ kJ mol}^{-1} \end{aligned}$$

SUMMARY AND IMPORTANT POINTS TO REMEMBER

1. Chemical kinetics: It is the branch of chemistry which deals with the rates of reactions, the factors which influence it and the mechanism by which the reactions occur.

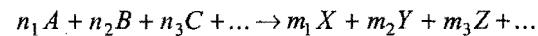
2. Rate of reaction: It is the speed with which the reactants are converted into products. It may be expressed in terms of rate of disappearance of any of the reactants or rate of appearance of any of the products.

The rate measured over a long time interval is called the average rate.

$$\begin{aligned} \text{Average rate of reaction} &= \frac{\text{Decrease in conc. of reactant}}{\text{Time taken}} \\ &= + \frac{\text{Increase in conc. of product}}{\text{Time taken}} \end{aligned}$$

A -ve sign signifies a decrease in concentration of the reactant and +ve sign indicates an increase in concentration of the product.

In general, for a reaction,



$$-\frac{1}{n_1} \frac{\Delta A}{\Delta t} = -\frac{1}{n_2} \frac{\Delta B}{\Delta t} = -\frac{1}{n_3} \frac{\Delta C}{\Delta t} = \dots$$

$$\frac{1}{m_1} \frac{\Delta X}{\Delta t} = \frac{1}{m_2} \frac{\Delta Y}{\Delta t} = \frac{1}{m_3} \frac{\Delta Z}{\Delta t} = \dots$$

Average rate is not very useful as it does not remain constant throughout its life span. It is more appropriate to express instantaneous rate.

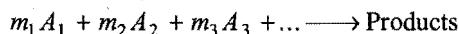
Rate of reaction with reference to a particular instant of time is called instantaneous rate of reaction. It is defined as the rate of change of concentration of any one of the reactant or product species over a small interval of time.

$$\text{Rate of reaction} = -\frac{dx}{dt} \text{ or } +\frac{dx}{dt}$$

Units of rate of reaction are conc. time⁻¹, e.g., mol L⁻¹ s⁻¹ or mol L⁻¹ hr⁻¹, etc.

3. Law of mass action: It was presented by Guldberg and Waage in 1864. At a given temperature, the rate of a reaction at a particular instant is proportional to the product of the active

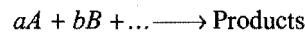
masses of the reactants at that instant raised to powers which are numerically equal to the numbers of their respective molecules in the stoichiometric equation describing the reaction. Consider the following general reaction,



$$\text{Rate of reaction} \propto [A_1]^{m_1} [A_2]^{m_2} [A_3]^{m_3} \dots$$

4. Rate constant: It is equal to rate of reaction when concentration of each reactant is unity, i.e., one mole litre⁻¹. It is a constant for a particular reaction at a given temperature and also known as specific rate constant or specific reaction rate.

Consider a general reaction,



$$\frac{dx}{dt} = k[A]^a [B]^b \dots$$

If $C_A = C_B = 1$ or $[A] = [B] = 1$

$$\text{Then, } \frac{dx}{dt} = k$$

5. Collision theory of reaction rate: A chemical reaction occurs when the existing bonds of the reactants are broken down and new bonds come into existence in the molecules of products. The basic requirement for a reaction to occur is that there should be physical contact between reacting species, i.e., they must collide with one another. Effective collisions which bring chemical change are few inspite of large number of actual collisions. For a collision to be effective, the following two conditions must be satisfied:

(i) Reacting species must possess adequate energy to overcome the energy barrier.

(ii) Reacting molecules must be properly oriented at the time of collision.

The minimum amount of energy which the colliding particles must possess as to make the chemical reaction to occur is called threshold energy. The excess energy (over and above the average energy of the reacting species) required by the reacting species to undergo chemical reaction is called activation energy (E_a).

Activation energy = Threshold energy – Average kinetic energy of the reacting molecules

Every chemical reaction whether exothermic or endothermic has an energy barrier which has to be overcome before the reactants can be transformed into products. The reacting molecules must have sufficient energy as to cross this energy barrier. The effective collisions increase with increase of temperature, i.e., rate of reaction increases with increase of temperature.

6. Factors influencing the reaction rate: The chief factors which influence the rates of reactions are:

(i) **Nature of reactants:** The reactants with weak bonds react quickly whereas the reactions involving reactants with strong bonds are slow. The molecular reactions are generally slow while ionic reactions are fast.

(ii) **Concentration of reactants:** The rate of reaction increases with increase in concentration of reactants as the number of collisions increases.

(iii) **Catalyst:** Positive catalysts increase the reaction rate by providing an alternative path involving lesser amount of activation energy.

(iv) **Temperature:** The rate of reaction increases with an increase in temperature. The number of effective collisions increases with increase of temperature. The rates of many reactions are approximately doubled or tripled for every 10°C rise in temperature. The temperature coefficient is defined as the ratio of specific reaction rates of a reaction at two temperatures differing by 10°C .

$$\text{Temp. coefficient} = \frac{k_{t+10}}{k_t} \quad (\text{value lies generally between 2 and 3})$$

Arrhenius suggested an equation which describes k as a function of temperature, i.e.,

$$k = A e^{-E_a/RT}$$

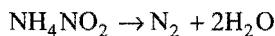
where, k = rate constant, A = a frequency factor (constant), E_a = energy of activation, R = gas constant and T = temperature.

At two temperatures T_1 and T_2 ,

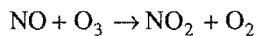
$$\log_{10} \left(\frac{k_2}{k_1} \right) = \frac{E_a}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

7. Molecularity and order of reaction:

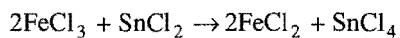
(i) **Molecularity of reaction:** The minimum number of reacting particles (molecules, atoms or ions) that come together or collide in a rate determining step to form product or products is called the molecularity of the reaction. The reactions are termed as unimolecular, bimolecular or trimolecular, etc., depending upon the number of reacting particles as 1, 2, 3, etc., in the rate determining step. Simultaneous collisions involving more than three molecules are very rare and hence reactions with molecularity more than three are also rare.



(Unimolecular)



(Bimolecular)



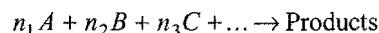
(Trimolecular)

In simple reactions involving one step only, the molecularity is equal to the sum of number of molecules of the reactants

involved in the balanced equation. There are number of reactions which are complex in nature and occur in several steps; the molecularity of such reactions is determined by the slowest step. Thus, molecularity depends upon the mechanism of the reaction.

(ii) **Order of reaction:** Rate equation or rate law is an experimentally determined mathematical expression relating the molar concentrations of the reactants to the actual reaction rate.

Consider a general reaction,



The rate law or rate equation is

$$\text{Rate} = -\frac{dx}{dt} = k[\text{A}]^x [\text{B}]^y [\text{C}]^z \dots$$

Order of reaction is the sum of the exponents (powers) to which molar concentration terms are raised in the rate law.

$$\text{Order of reaction} = (x + y + z + \dots)$$

The value of $(x + y + z + \dots)$ usually ranges between 0 and 2 and even 3. It may have positive, negative, zero and fractional values. It is termed overall order. The reactions are classified as zero, first, second, third order according as $(x + y + z + \dots)$ is zero, one, two or three respectively. The order can be expressed either in terms of the order of the specific reactant or in terms of overall order of the reaction.

The reactions which obey a first order rate equation, although they are not unimolecular, are said to be pseudo first order.

8. Reactions of various orders: In such reactions, the concentrations of various reactants except one remain practically constant during the course of reaction.

(i) **Zero order reactions:** A reaction in which the rate is independent of the concentration of the reactant molecules, i.e., the rate is proportional to the zeroth power of the concentration of the reactants.

$$-\frac{dx}{dt} = k[\text{A}]_0 = k$$

i.e., the reaction velocity remains constant throughout the progress of the reaction. The concentration decreases linearly with time.

$$[\text{A}]_t = [\text{A}]_0 - kt$$

$$t_{\text{completion}} = \frac{[\text{A}]_0}{k} = \frac{\text{Initial concentration}}{\text{Rate constant}}$$

The units of k are mol L⁻¹ time⁻¹.

(ii) **First order reactions:** The rate depends upon the concentration of one reactant only.

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

$$k = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)} = \frac{2.303}{t} \log_{10} \frac{[\text{A}]_0}{[\text{A}]_t}$$

t = time, a = initial concentration and $(a-x)$ = concentration at time t .

A change in concentration unit does not affect the numerical value of k . Thus, for first order reactions, any quantity which is

proportional to concentration can be used in place of concentration in the integrated equation.

The time taken for the completion of same fraction of change is independent of initial concentration. When $x = 0.5a$ and $t = t_{1/2}$,

$$k = \frac{2.303}{t_{1/2}} \log_{10} \frac{a}{0.5a} = \frac{2.303}{t_{1/2}} \log_{10} 2 = \frac{0.693}{t_{1/2}}$$

$$t_{1/2} = \frac{0.693}{k}$$

Thus, $t_{1/2}$ is independent of initial concentration.

The equation of the first order can also be written in the following form when initial concentration is not known.

$$k = \frac{2.303}{(t_2 - t_1)} \log_{10} \frac{(a - x_1)}{(a - x_2)} = \frac{2.303}{(t_2 - t_1)} \log_{10} \frac{[A]_{t_1}}{[A]_{t_2}}$$

The unit of k is time⁻¹.

(iii) Second order reactions: Reaction rate depends upon the concentration of two reactants.

$$\frac{dx}{dt} = k[A][B] = k[A]^2$$

$$k = \frac{2.303}{t(a-b)} \log_{10} \frac{b(a-x)}{a(b-x)}$$

$(a-x)$ and $(b-x)$ are the concentrations of A and B after time interval t .

When concentrations of both the reactants are same,

$$k = \frac{1}{t} \cdot \frac{x}{a(a-x)}$$

(x is the concentration changed in time interval t)

Half life period, $t_{1/2} = \frac{1}{ka}$, i.e., inversely proportional to initial concentration. The units of k are litre mol⁻¹ time⁻¹.

(iv) Third order reactions: Expression for third order reactions of the type



$$\frac{dx}{dt} = k[A]^3$$

$$k = \frac{1}{t} \cdot \frac{x(2a-x)}{2a^2(a-x)^2}$$

The units of k are L² mol⁻² time⁻¹.

9. Methods for the determination of order of a reaction:

(i) Initial rate method: A number of experiments are carried out by varying concentration of a reactant w.r.t. which the order is to be determined keeping the concentrations of all other reactants constant. The initial rate of the reaction at each concentration is determined by concentration-time curves. The order of the reactant is then calculated from the rates at various

concentrations. The experiments are repeated with other reactants in a similar way. Likewise, the orders w.r.t. all reactants are determined. The overall order is the sum of the orders of all the reactants.

(ii) Integration method: The quantities a, x and t are determined and substituted in the kinetic equations of various orders. The equation which gives the most consistent values for the specific rate constant (k) for a series of time intervals is the one corresponding to order of reaction.

$$k = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)} \quad \text{for first order reactions}$$

$$k = \frac{1}{t} \cdot \left[\frac{a}{a(a-x)} \right] \quad \text{for second order reactions}$$

$$\text{Rate} = k \quad \text{for zero order reactions}$$

(iii) Graphical method: If the plot of $\log(a-x)$ versus ' t ' is a straight line, the reaction follows first order.

If a plot of $\frac{1}{(a-x)}$ versus ' t ' is a straight line, the reaction follows second order.

If a plot of $\frac{1}{(a-x)^2}$ versus ' t ' is a straight line, the reaction follows third order.

(iv) Half life method: Starting with two different concentrations a_1 and a_2 for the same reaction, the half lives ($t_{1/2}$)₁ and ($t_{1/2}$)₂ are determined.

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a_2}{a_1} \right)^{\frac{n-1}{n}} \quad \text{or} \quad n = 1 + \frac{\log(t_{1/2})_1 - \log(t_{1/2})_2}{\log a_2 - \log a_1}$$

n is the order of reaction.

(v) van't Hoff differential method: For two different initial concentrations C_1 and C_2 equations can be written in the form

$$-\frac{dC_1}{dt} = kC_1^n \quad \text{and} \quad -\frac{dC_2}{dt} = kC_2^n$$

Taking logarithms of two equations and then subtracting

$$n = \frac{\log \left(-\frac{dC_1}{dt} \right) - \log \left(-\frac{dC_2}{dt} \right)}{\log C_1 - \log C_2}$$

10. Mechanism: An intelligent guess depending upon the observed rates of reactions about the series of steps (known as elementary processes) leading to the formation of products is called the reaction mechanism. The overall reaction is the summation of all elementary steps. The slowest step is taken as the rate determining step.

Questions

1. Matrix Matching Problems:

(According to the new pattern of IIT Screening)

[A] Match the reactions of List-I with their orders in List-II:

| List-I | List-II |
|---|--|
| (a) $C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+}$ | (p) Pseudo first order |
| $C_6H_{12}O_6 + C_6H_{12}O_6$ | |
| (b) $CH_3COOC_2H_5 \xrightarrow[H^+ \text{ or } OH^-]{HOH}$ | (q) Zero order ↓ $CH_3COOH + C_2H_5OH$ |
| (c) $H_2 + Cl_2 \xrightarrow{hv}$ | (r) Second order |
| (d) $CH_3Cl + OH^- \xrightarrow{} CH_3OH + Cl^-$ | (s) First order |

[B] Match the reactions in Column-I with the units of their rate constant in Column-II:

| Column-I (Reactions) | Column-II (Unit of k) |
|--|-----------------------------|
| (a) $SO_2Cl_2 \longrightarrow SO_2 + Cl_2$ | (p) sec^{-1} |
| (b) $CH_3COOC_2H_5 + NaOH \xrightarrow{} CH_3COONa + C_2H_5OH$ | (q) min^{-1} |
| (c) $2H_2O_2 \longrightarrow 2H_2O + O_2$ | (r) $L mol^{-1} min^{-1}$ |
| (d) $H_2O_2 + 2I^- + 2H^+ \longrightarrow 2H_2O + I_2$ | (s) $L mol^{-1} s^{-1}$ |

[C] Match the kinetic equations of Column-I with the units of their rate constant in Column-II:

| Column-I (Kinetic equations) | Column-II (Units of rate constant) |
|--|---------------------------------------|
| (a) $x = kt$ | (p) sec^{-1} |
| (b) $k = \frac{2.303}{t} \log_{10} \left(\frac{a}{a-x} \right)$ | (q) $L mol^{-1} sec^{-1}$ |
| (c) $k = \frac{1}{t} \left[\frac{1}{(a-x)} - \frac{1}{a} \right]$ | (r) $mol L^{-1} sec^{-1}$ |
| (d) $k = \frac{2.303}{t(a-b)} \log \left[\frac{b(a-x)}{a(b-x)} \right]$ | (s) $atm^{-1} sec^{-1}$ |

[D] Match the half lives in Column-I with the orders in Column-II:

| Column-I (Half life) | Column-II (Order) |
|-----------------------------------|------------------------|
| (a) $t_{1/2} = \text{constant}$ | (p) First order |
| (b) $t_{1/2} \propto a$ | (q) Pseudo first order |
| (c) $t_{1/2} \propto \frac{1}{a}$ | (r) Second order |
| (d) $t_{1/2} \propto p^{-1}$ | (s) Zero order |

where, a = Initial concentration of the reactant

p = Initial pressure of the reactant

[E] Match the reactions of List-I with the increase in rate when concentration is raised two times in List-II:

| List-I (Reactions) | List-II (Increase in rate when conc. of reactant is doubled) |
|-----------------------|---|
|-----------------------|---|

| | |
|---|---------------------------------|
| (a) $CH_3CHO \longrightarrow CH_4 + CO$ | (p) 2 times |
| (b) $SO_2Cl_2 \longrightarrow SO_2 + Cl_2$ | (q) $2^{1.5}$ times |
| (c) $2H_2O_2 \longrightarrow 2H_2O + O_2$ | (r) 2 times in acid medium |
| (d) $CH_3COOC_2H_5 \xrightarrow{HOH} CH_3COOH + C_2H_5OH$ | (s) 2^2 times in basic medium |

[F] Match the List-I with List-II and List-III:

| List-I | List-II | List-III |
|--------|---------|----------|
|--------|---------|----------|

| | | |
|--|------------------------|-------------------------------|
| (a) x is plotted against 't' in zero order reaction | (p) Slope = $-k/2.303$ | (u) Intercept = 0 |
| (b) $\log(a-x)$ is plotted against 't' in first order reaction | (q) Slope = $2k$ | (v) Intercept = $1/a$ |
| (c) $(a-x)^{-1}$ is plotted against 't' in second order reaction | (r) Slope = $-k$ | (w) Intercept = $1/a^2$ |
| (d) $(a-x)^2$ is plotted against 't' in second order reaction | (s) Slope = k | (x) Intercept = $\log_{10} a$ |

where, a = Initial concentration of reactant
 x = Extent of reaction in time 't' sec

[G] Match the List-I with List-II:

| List-I | List-II |
|--------|---------|
|--------|---------|

| | |
|---|--------------------|
| (a) Molecularity | (p) 0 |
| (b) Order | (q) $1/2$ |
| (c) Temperature coefficient | (r) Between 2 to 3 |
| (d) Activation energy for participation of all reactant molecules | (s) 2 |

[H] Match the Column-I with Column-II:

| Column-I (Rate law) | Column-II (Order) |
|------------------------|----------------------|
|------------------------|----------------------|

| | |
|--|-------------------------------------|
| (a) Rate = $k \times$ Intensity of light | (p) Second order |
| (b) Rate = $k[A]^1[B]^1$ | (q) Zero order |
| (c) Rate = $k[A]^{3/2}[B]^{1/2}$ | (r) First order when A is excess |
| (d) Rate = $k[A]^2[B]^1$ | (s) Second order when B is excess |

[I] Match the Column-I with Column-II:

| Column-I | Column-II |
|---------------------------------|--|
| (a) $t_{1/2} = \frac{0.693}{k}$ | (p) Zero order |
| (b) $t_{1/2} = \frac{a}{2k}$ | (q) First order |
| (c) $\tau = \frac{1}{k}$ | (r) Average life |
| (d) $t_{3/4} = 2t_{1/2}$ | (s) 75% completion (t) 25% completion |

[J] Match the Column-I with Column-II:

| Column-I | Column-II |
|--|--------------------|
| (a) $t_{3/4} = \frac{3}{2} \times t_{1/2}$ | (p) 99% completion |
| (b) $t_{3/4} = 2 \times t_{1/2}$ | (q) Zero order |
| (c) $6.909/k$ | (r) First order |
| (d) $2.303/k$ | (s) 90% completion |

Here, $t_{1/2}$ = half life

$t_{3/4}$ = 3/4th life

k = rate constant

[K] Match the Column-I with Column-II:

| Column-I | Column-II |
|--|---|
| (a) First order reaction | (p) $C_0 = 0.1 M; t_{1/2} = 25 \text{ min}$ $C_0 = 0.05 M; t_{1/2} = 12.5 \text{ min}$ |
| (b) Second order reaction | (q) $C_0 = 0.1 M; t_{1/2} = 12 \text{ min}$ $C_0 = 0.05 M; t_{1/2} = 24 \text{ min}$ |
| (c) Zero order reaction | (r) Radioactive decay |
| (d) $t_{1/2}$ varies inversely to the concentration of the reactants | (s) $C_0 = 0.1 M; t_{1/2} = 8 \text{ min}$ $C_0 = 0.05 M; t_{1/2} = 8 \text{ min}$ |

Answers

- [A] (a-p), (b-r, s), (c-q), (d-r)
- [B] (a-p, q), (b-r, s), (c-p, q), (d-r, s)
- [C] (a-r), (b-p), (c-q, s), (d-q, s)
- [D] (a-p, q), (b-s), (c-r, s), (d-r, s)
- [E] (a-q), (b-p), (c-p), (d-r, s)
- [F] (a-s-u), (b-p, r-x), (c-s-v), (d-q-w)

[G] (a-s), (b-p, q, s), (c-r), (d-p)

[H] (a-q), (b-p), (c-p), (d-r, s)

[I] (a-q), (b-p), (c-q, r), (d-q, s)

[J] (a-q), (b-r), (c-p, r), (d-r, s)

[K] (a-r, s), (b-q), (c-p), (d-q)

● PRACTICE PROBLEMS ●

1. For the reaction $A \rightarrow B$, it was found that the concentration of B increased by 0.3 mol L^{-1} in 2 hours. What is the average rate of reaction?

[Ans. $0.15 \text{ mol L}^{-1} \text{ hr}^{-1}$]

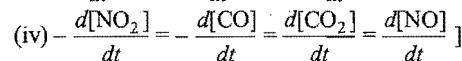
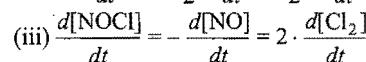
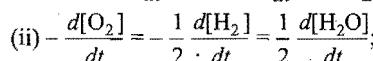
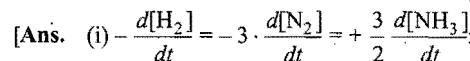
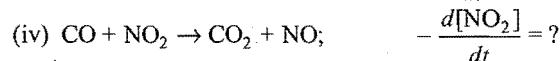
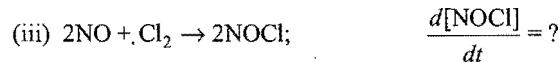
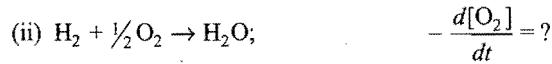
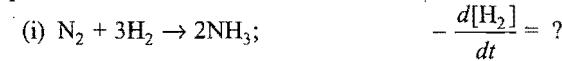
2. In the reaction $X \rightarrow Y$, the initial concentration of X is 2.5 mol L^{-1} and its concentration after 3 hours is 0.7 mol L^{-1} . What is the average rate of the reaction?

[Ans. $6.0 \times 10^{-1} \text{ mol L}^{-1} \text{ hr}^{-1}$]

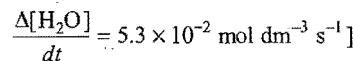
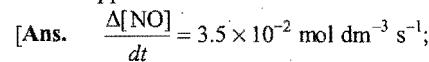
3. For the reaction $2A + B \rightarrow C$, the rate of formation of C is $0.25 \text{ mol L}^{-1} \text{ hr}^{-1}$. What is the rate of disappearance of A and B ?

[Ans. $0.5 \text{ mol L}^{-1} \text{ hr}^{-1}$; $0.25 \text{ mol L}^{-1} \text{ hr}^{-1}$]

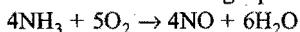
4. For each of the following reactions express the given rate of change of the concentration of the reactant or product in terms of the rate of change of concentration of the other reactants or products in that reaction.



5. When ammonia is treated with O_2 at elevated temperatures, the rate of disappearance of ammonia is found to be $3.5 \times 10^{-2} \text{ mol dm}^{-3} \text{ s}^{-1}$ during a measured time interval. Calculate the rate of appearance of nitric oxide and water.



[Hint: Consider the following equation:



The equality in this case is

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

6. In a reaction, $\text{N}_2\text{O}_5 \rightarrow 2\text{NO}_2 + \frac{1}{2}\text{O}_2$,

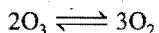
the rate of disappearance of N_2O_5 is $6.5 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$.

Compute the rates of formation of NO_2 and O_2 .

[Ans. $\frac{d[\text{NO}_2]}{dt} = 1.25 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$;

$$\frac{d[\text{O}_2]}{dt} = 3.125 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$$

7. For the reaction,

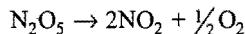


$-\frac{\Delta[\text{O}_3]}{dt}$ was found to be $4.0 \times 10^{-4} \text{ atm s}^{-1}$.

Determine the value of $\frac{\Delta[\text{O}_2]}{\Delta t}$ in atm s^{-1} during this period of time.

[Ans. $6.0 \times 10^{-4} \text{ atm s}^{-1}$]

8. The following reaction was carried out at 44°C :



The concentration of NO_2 is $6.0 \times 10^{-3} M$ after 10 minutes of the start of the reaction. Calculate the rate of production of NO_2 over the first ten minutes of the reaction.

[Ans. $6.0 \times 10^{-4} \text{ mol L}^{-1} \text{ min}^{-1}$]

9. The rate of a particular reaction doubles when temperature changes from 27°C to 37°C . Calculate the energy of activation for such reaction. ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)

[Ans. $53.59 \text{ kJ mol}^{-1}$]

10. The rate constant of a reaction is $2 \times 10^{-2} \text{ s}^{-1}$ at 300 K and $8 \times 10^{-2} \text{ s}^{-1}$ at 340 K . Calculate the energy of activation of the reaction.

[Ans. $29.39 \text{ kJ mol}^{-1}$]

11. For a chemical reaction the energy of activation is 85 kJ mol^{-1} . If the frequency factor is $4.0 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$, what is the rate constant at 400 K ?

[Ans. $k = 3.19 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$]

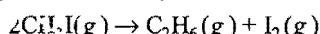
12. The energy of activation of a reaction is 140 kJ mol^{-1} . If its rate constant at 400 K is $2.0 \times 10^{-6} \text{ s}^{-1}$, what is the value at 500 K ?

[Ans. $9.06 \times 10^{-3} \text{ s}^{-1}$]

13. Calculate the ratio of the catalysed and uncatalysed rate constant at 20°C if the energy of activation of a catalysed reaction is 20 kJ mol^{-1} and for the uncatalysed reaction is 75 kJ mol^{-1} .

[Ans. 6.4×10^9]

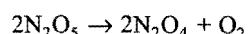
14. The decomposition of methyl iodide,



at 273°C has a rate constant of $2.418 \times 10^{-5} \text{ s}^{-1}$. If activation energy for the reaction is $+179.9 \text{ kJ mol}^{-1}$, what is the value of collision factor 'A' at 273°C ?

[Ans. $3.9 \times 10^{12} \text{ s}^{-1}$]

15. The reaction,

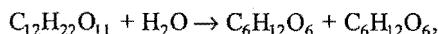


occurs in carbon tetrachloride. The rate constant is $2.35 \times 10^{-4} \text{ sec}^{-1}$ at 20°C and $9.15 \times 10^{-4} \text{ sec}^{-1}$ at 30°C .

Calculate the activation energy of the reaction.

[Ans. $100.343 \text{ kJ mol}^{-1}$]

16. For the inversion of cane sugar,



the rate constant is $2.12 \times 10^{-4} \text{ L mol}^{-1} \text{ sec}^{-1}$ at 27°C . The activation energy of the reaction is $1.07 \times 10^5 \text{ J mol}^{-1}$. What is the rate constant of the reaction at 37°C ?

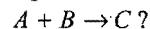
[Ans. $8.46 \text{ L mol}^{-1} \text{ sec}^{-1}$]

17. From the data given below for the reaction $2A + B \rightarrow 3C$ at 298 K , find out the rate law expression for the reaction.

| Expt. No. | [A] (mol L ⁻¹) | [B] (mol L ⁻¹) | Rate of formation of C |
|-----------|----------------------------|----------------------------|------------------------|
| 1. | 0.10 | 0.10 | 4.0×10^{-4} |
| 2. | 0.30 | 0.30 | 1.2×10^{-3} |
| 3. | 0.10 | 0.30 | 4.0×10^{-4} |
| 4. | 0.20 | 0.40 | 8.0×10^{-4} |

[Ans. Rate = $k[A][B]$]

18. What is the rate law expression for the reaction,

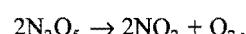


The following data were collected from the experiments:

| Expt. No. | Initial [A] (mol L ⁻¹) | Initial [B] (mol L ⁻¹) | Rate of formation of C |
|-----------|------------------------------------|------------------------------------|------------------------|
| 1. | 0.10 | 0.10 | 4.0×10^{-4} |
| 2. | 0.20 | 0.20 | 3.2×10^{-3} |
| 3. | 0.10 | 0.20 | 1.6×10^{-3} |

[Ans. Rate = $k[A][B]^2$]

19. The reaction,



was studied and the following data were collected:

| Expt. No. | [N ₂ O ₅] (mol L ⁻¹) | Rate of disappearance of N ₂ O ₅ (mol L ⁻¹ min ⁻¹) |
|-----------|---|---|
| 1. | 1.13×10^{-2} | 34×10^{-5} |
| 2. | 0.84×10^{-2} | 25×10^{-5} |
| 3. | 0.62×10^{-2} | 18×10^{-5} |

Determine (i) order the reaction (ii) the rate law and (iii) rate constant for the reaction.

[Hint: Let the rate law for the reaction be

Rate = $k[\text{N}_2\text{O}_5]^x$

$34 \times 10^{-5} = k[1.13 \times 10^{-2}]^x$

$$25 \times 10^{-5} = k[0.84 \times 10^{-2}]^x$$

$$\text{or } \frac{34 \times 10^{-5}}{25 \times 10^{-5}} = \frac{[1.13 \times 10^{-2}]^x}{[0.84 \times 10^{-2}]^x}$$

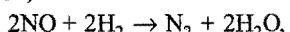
$$1.36 = [1.345]^x$$

$$x = 1$$

Order of the reaction is 1. Rate law = $k[N_2O_5]$

$$k = \frac{\text{Rate}}{[N_2O_5]} = \frac{34 \times 10^{-5}}{1.13 \times 10^{-2}} = 30.08 \times 10^{-3} \text{ min}^{-1}$$

20. For the reaction,



the following kinetic data were obtained:

| Expt. No. | [H ₂] (mol L ⁻¹) | [NO] (mol L ⁻¹) | Rate of reaction (mol L ⁻¹ s ⁻¹) |
|-----------|--|-----------------------------|---|
| 1. | 0.12 | 0.12 | 0.25×10^{-4} |
| 2. | 0.12 | 0.24 | 1.0×10^{-4} |
| 3. | 0.24 | 0.24 | 2.0×10^{-4} |

Determine the rate law and the rate constant.

$$[\text{Ans. Rate} = k[H_2][\text{NO}]^2; k = 1.45 \times 10^{-2} \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}]$$

21. Fill in the blanks in the following table which treats reaction of a compound A with a compound B, that is of the first order with respect to A and zero order with respect to B:

| Expt. No. | [A] (mol L ⁻¹) | [B] (mol L ⁻¹) | Initial rate (mol L ⁻¹ s ⁻¹) |
|-----------|----------------------------|----------------------------|---|
| 1. | 0.1 | 0.1 | 2.0×10^{-2} |
| 2. | ... | 0.2 | 4.0×10^{-2} |
| 3. | 0.4 | 0.4 | ... |
| 4. | ... | 0.2 | 2.0×10^{-2} |

$$[\text{Ans. (2)} [A] = 0.2 \text{ mol L}^{-1}$$

$$(3) \text{ Rate} = 8.0 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$$

$$(4) [A] = 0.1 \text{ mol L}^{-1}$$

22. The reaction $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$, follows the rate law = $k[\text{NO}]^2[\text{O}_2]$. What is the order of the reaction? If $k = 2.0 \times 10^{-6} \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}$, what is the rate of the reaction when $[\text{NO}] = 0.04 \text{ mol L}^{-1}$ and $[\text{O}_2] = 0.2 \text{ mol L}^{-1}$?

$$[\text{Ans. Order of the reaction} = 3;$$

$$\text{Rate} = 6.4 \times 10^{-10} \text{ mol L}^{-1} \text{ s}^{-1}]$$

23. From the following data of initial concentrations and rates, calculate the order of reaction $aA \rightarrow \text{Products}$; and its rate constant.

$$[A] \text{ mol L}^{-1} \quad 0.1 \quad 0.2 \quad 0.4$$

$$\text{Rate mol L}^{-1} \text{ s}^{-1} \quad 9 \times 10^{-5} \quad 36 \times 10^{-5} \quad 144 \times 10^{-5}$$

$$[\text{Ans. Order of reaction} = 2;$$

$$\text{Rate constant} = 9.0 \times 10^{-3} \text{ mol}^{-1} \text{ L s}^{-1}]$$

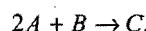
24. For a reaction $aA + bB \rightarrow mM + nN$, the rate of reaction is given as $k[A]^x[B]^y$.

Calculate the order of the reaction and the rate constant from the given initial concentrations and the corresponding rates.

| | | | |
|--|--------------------|---------------------|--------------------|
| [A] mol L ⁻¹ | 0.1 | 0.1 | 0.2 |
| [B] mol L ⁻¹ | 0.2 | 0.4 | 0.2 |
| Rate mol L ⁻¹ s ⁻¹ | 4×10^{-4} | 16×10^{-4} | 8×10^{-4} |

$$[\text{Ans. Order of the reaction} = 3, k = 1.0 \times 10^7 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}]$$

25. The data given in the following table pertain to the reaction,

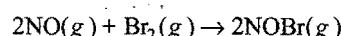


Determine the form of the rate equation and the value of the rate constant.

| Expt. No. | Initial concentration (mol L ⁻¹) | | Initial rate (mol L ⁻¹ s ⁻¹) |
|-----------|--|--------------------|---|
| | [A] | [B] | |
| 1. | 1×10^{-3} | 1×10^{-3} | 7×10^{-6} |
| 2. | 1×10^{-3} | 2×10^{-3} | 14×10^{-6} |
| 3. | 1×10^{-3} | 3×10^{-3} | 21×10^{-6} |
| 4. | 2×10^{-3} | 3×10^{-3} | 84×10^{-6} |

$$[\text{Ans. Rate} = k[A]^2[B]; k = 7 \times 10^3]$$

26. The following initial rate data were obtained for the reaction:



| Run | [NO]/M | [Br ₂]/M | Rate/M min ⁻¹ |
|-----|--------|----------------------|--------------------------|
| 1. | 1.0 | 1.0 | 1.30×10^{-3} |
| 2. | 2.0 | 1.0 | 5.20×10^{-3} |
| 3. | 4.0 | 2.0 | 4.16×10^{-2} |

Determine the reaction rate law and the value of the rate constant. (Dhanbad 1992)

$$[\text{Ans. } -\frac{dx}{dt} = k[\text{NO}]^2[\text{Br}_2]; K = 1.30 \times 10^{-3} \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}]$$

27. The data below are for the reaction of NO and Cl₂ to form NOCl at 295 K.

| Expt. No. | [Cl ₂] (mol L ⁻¹) | [NO] (mol L ⁻¹) | Initial rate (mol L ⁻¹ s ⁻¹) |
|-----------|---|-----------------------------|---|
| 1. | 0.05 | 0.05 | 1.0×10^{-3} |
| 2. | 0.15 | 0.05 | 3.0×10^{-3} |
| 3. | 0.05 | 0.15 | 9.0×10^{-3} |

- (a) What is the order w.r.t. NO and Cl₂ in the reaction?
(b) Write the rate expression.
(c) Calculate the rate constant.
(d) Determine the reaction rate when concentrations of Cl₂ and NO are 0.2 M and 0.4 M respectively. (IIT 1993)

- [Ans. (a) Order w.r.t. NO = 2; order w.r.t. Cl₂ = 1

$$(b) \text{Rate expression, } r = k[\text{NO}]^2[\text{Cl}_2]$$

$$(c) k = 8.0 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$$

$$(d) \text{Rate} = 0.256 \text{ mol L}^{-1} \text{ s}^{-1}]$$

28. In the hydrolysis of propyl acetate in presence of dilute HCl in aqueous solution, the following data were recorded:

| | | |
|-----------------------------|-------|-------|
| Time from start (in minute) | 60 | 350 |
| % of ester decomposed | 18.17 | 69.12 |

Calculate the rate constant of decomposition and time in which half of the ester was decomposed.

[Ans. $3.34 \times 10^{-3} \text{ min}^{-1}$; 207.6 min]

29. In a first order reaction the concentration of the reactant is reduced to one-fourth of its initial value in 50 seconds. Calculate the rate constant of the reaction.

[Ans. $2.77 \times 10^{-2} \text{ s}^{-1}$]

30. For a first order reaction, the rate constant is 0.1 s^{-1} . How much time will it take to reduce the concentration from initial value of 0.6 mol L^{-1} to 0.06 mol L^{-1} ?

[Ans. 23.0 second]

31. A substance decomposes following first order reaction. If the half life period of the reaction is 35 minutes, what is the rate constant of this reaction?

[Ans. $1.98 \times 10^{-2} \text{ min}^{-1}$]

32. For a certain first order reaction, it takes 5 minutes for the initial concentration of 0.6 mol L^{-1} to become 0.2 mol L^{-1} . What is the rate constant for this reaction? [$\log 3 = 0.4771$].

[Ans. 0.2197 min^{-1}]

33. Find the two-thirds life ($t_{2/3}$) of a first order reaction in which $k = 5.48 \times 10^{-1} \text{ sec}^{-1}$ ($\log 3 = 0.4771$; $\log 2 = 0.3010$).

[Ans. 2.005 s]

[Hint: $t_{2/3} = \frac{2.303}{k} \log_{10} \frac{a}{a - \frac{2}{3}a}$]

34. A first order reaction has a specific rate of 10^{-3} sec^{-1} . How much time will it take from 10 g of the reactant to reduce to 7.5 g ($\log 2 = 0.3010$; $\log 4 = 0.6020$ and $\log 6 = 0.7782$)?

[Ans. 287.7 s]

35. In a reaction 5 g ethyl acetate is hydrolysed per litre in presence of dilute HCl in 300 min. If the reaction is of first order and initial concentration is 22 g per litre, calculate the rate constant for the reaction.

[Ans. $k = 8.59 \times 10^{-4} \text{ min}^{-1}$]

36. Calculate the half life of the reaction $A \rightarrow B$, when the initial concentration of A is 0.01 mol L^{-1} and initial rate is $0.00352 \text{ mol L}^{-1} \text{ min}^{-1}$. The reaction is of the first order.

[Ans. 1.969 min]

[Hint: Evaluate k from $\frac{dx}{dt} = k[A]$]

37. In a reaction, $A \rightarrow B + C$, the following data were obtained:

| | | | |
|----------------------|------|------|------|
| t in seconds | 0 | 900 | 1800 |
| Concentration of A | 50.8 | 19.7 | 7.62 |

Prove that it is a first order reaction.

[Hint: Calculate the value of k in both cases by using first order equation.]

38. The first order reaction has $k = 1.5 \times 10^{-6}$ per second at 200°C . If the reaction is allowed to run for 10 hours at the same temperature, what percentage of the initial concentration

would have changed into the product? What is the half life period of this reaction?

[Ans. $t_{1/2} = 128.3 \text{ hours}; 5.27\%$]

39. A first order reaction is 20% completed in 10 minutes. Calculate (i) the specific rate constant of the reaction and (ii) the time taken for the reaction to go to 75% completion.

[Ans. $k = 2.232 \times 10^{-2} \text{ min}^{-1}$; $t = 62.12 \text{ min}$]

40. The rate constant of a reaction with respect to reactant A is 6 min^{-1} . If we start with $[A] = 0.8 \text{ mol L}^{-1}$, when would $[A]$ reach the value of 0.08 mol L^{-1} ?

[Ans. 0.3838 min]

41. What will be the initial rate of a reaction if the rate constant is 10^{-3} min^{-1} and the concentration is 0.2 mol dm^{-3} ? How much of the reactant will be converted into the product in 200 minutes?

[Ans. Initial rate = $2 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$; 0.036 mol]

42. A substance A decomposes by the first order reaction. Starting initially with $[A] = 2.00 M$, after 200 minutes $[A] = 0.25 M$. For this reaction what is $t_{1/2}$ and k ?

[Ans. $t_{1/2} = 66.66 \text{ min}$, $k = 0.01039 \text{ min}^{-1}$]

43. The specific rate constant for the concentration of H_2 and I_2 to form HI is $0.0234 \text{ mol}^{-1} \text{ L s}^{-1}$ at 400°C and $750 \text{ mol}^{-1} \text{ L s}^{-1}$ at 500°C . Calculate the activation energy of the reaction.

[CBSE (Sihar) 1993]

[Ans. 107.9 kcal]

44. For a certain reaction it takes 10 minutes for the initial concentration of 2.0 mol L^{-1} to become 1.0 mol L^{-1} and another 10 minutes to become 0.5 mol L^{-1} . Calculate the rate constant of the reaction.

[Ans. 0.0693 min^{-1}]

45. The catalytic decomposition of H_2O_2 was studied by titrating it at different intervals with KMnO_4 and the following data were obtained:

| | | | |
|-----------------------------|------|------|------|
| t (seconds) | 0 | 600 | 1200 |
| V of KMnO_4 (mL) | 22.8 | 13.8 | 8.3 |

Calculate the velocity constant for the reaction assuming it to be a first order reaction.

[Ans. $8.4 \times 10^{-3} \text{ s}^{-1}$]

[Hint: Volume of KMnO_4 used \propto concentration of H_2O_2

Hence, $k = \frac{2.303}{t} \log_{10} \frac{V_0}{V_t}$

46. The half life of a first order reaction is 10 seconds. Calculate the time for completion of 99.9% of the reaction.

[Ans. $99.7 \text{ sec} \approx 100 \text{ sec}$]

47. A first order reaction is 40% complete after 8 min. How long will it take before it is 90% complete? What is the value of the rate constant?

[Ans. $k = 0.06386 \text{ min}^{-1}$; $t = 36.06 \text{ min}$]

48. The reaction $\text{SO}_2\text{Cl}_2 \rightarrow \text{SO}_2 + \text{Cl}_2$, is a first order gas reaction with $k = 2.2 \times 10^{-5} \text{ s}^{-1}$ at 573 K . What per cent of SO_2Cl_2 is decomposed on heating at 573 K for 90 min?

[Ans. 11.2]

49. The decomposition of $AB(g) \rightarrow A(g) + B(g)$, is first order reaction with a rate constant $k = 4 \times 10^{-4} \text{ s}^{-1}$ at 318 K. If AB has 26664.5 Pa pressure at the initial stage, what will be the partial pressure of AB after half an hour?

[Ans. 12981.7 Pa]

50. In the first order reaction $A(g) \rightarrow B(g) + C(g)$, the initial pressure of A is 11200 Pa and the total pressure at the end of 16 minutes is 14667 Pa. Calculate the half life period of reaction.

[Ans. 30 min]

51. It was found that a solution of cane sugar was hydrolysed to the extent of 25% in 1 hr. Calculate the time taken for the sugar to be 50% hydrolysed assuming that the reaction is of first order.

[Ans. 2.408 hours]

52. A reaction is 20% complete in 20 minutes. How long will it take for 80% completion if the order of reaction is (a) zero and (b) one?

[Ans. (a) 80 minutes (b) 144.27 minutes]

53. A second order reaction where $a = b$ is 20% completed in 500 seconds. How long will the reaction take to be 60% complete?

[Hint: Apply

$$k = \frac{x}{ta(x-x)} = \frac{20}{500[100 \times (100-20)]} = \frac{1}{200000} \text{ mol}^{-1} \text{ L s}^{-1}$$

$$t = \frac{60}{k \times 100 \times 40} = \frac{60 \times 200000}{100 \times 40} = 3000 \text{ seconds}$$

54. At a certain temperature, the half life periods of a reaction at different initial pressures were as follows:

| | | | |
|-----------|-----|-------|-------|
| p (kPa) | 100 | 66.67 | 33.33 |
| t (min) | 105 | 235 | 950 |

Find out the order of the reaction.

[Ans. 3]

55. The time for half change for a gaseous reaction was measured for various initial pressures and the following data were obtained:

| | | | |
|-----------|------|------|------|
| p (kPa) | 26.6 | 40 | 53.3 |
| t (min) | 150 | 99.8 | 75.3 |

Find out the order of the reaction.

[Ans. 2]

56. Show that for a first order reaction the time required for 99% completion is twice the time required for the completion of 90% of the reaction.

57. Show that for a first order reaction the time required to complete 99.9% of the reaction is 10 times that required for half the reaction.

58. Show that for a first order reaction, the time required for a 50% reaction is half that for 75% reaction.

59. The decomposition of an aqueous solution of ammonium nitrite was studied. The volume of nitrogen gas collected at different intervals of time was as follows:

| | | | | |
|--------------------|------|------|-------|----------|
| Time (minutes) | 10 | 15 | 20 | ∞ |
| Vol. of N_2 (mL) | 6.25 | 9.00 | 11.40 | 35.05 |

From the above data prove that the reaction is of the first order.

[Hint: $[A]_0 = \text{volume of nitrogen at } \infty = 35.05$

$$[A]_t = V_\infty - V_t$$

$$\text{when } t = 10, \quad k = \frac{2.303}{10} \log \frac{35.05}{(35.05 - 6.25)} = 0.0196$$

when $t = 15, \quad k = 0.0198$

when $t = 20, \quad k = 0.0196$]

60. Optical rotation of sucrose in 1 N HCl at various times was found as shown below:

| | | | | | |
|----------------|---------|--------|--------|--------|----------|
| Time (sec) | 0 | 7.18 | 18.0 | 27.05 | ∞ |
| Rotation (deg) | + 24.09 | + 21.7 | + 17.7 | + 15.0 | - 10.74 |

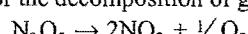
Show that the inversion of sucrose is a first order reaction.

[Hint: Initial concentration, $[A]_0 = r_0 - r_\infty$

$$\text{At time } t, \quad [A]_t = r_t - r_\infty$$

$$k = 11.8 \times 10^{-3} \text{ s}^{-1}]$$

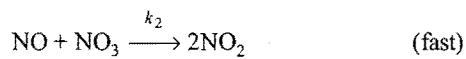
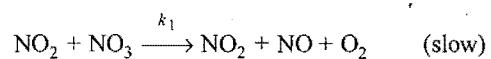
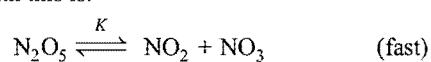
61. The rate law for the decomposition of gaseous N_2O_5



is observed to be:

$$-\frac{d[N_2O_5]}{dt} = k[N_2O_5]$$

A reaction mechanism which has been suggested to be consistent with this is:



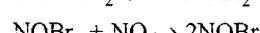
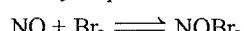
Show that the mechanism is consistent with the observed law.

[Hint: $r = k_1[N_2O_2][NO_3]$,

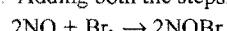
$$K = \frac{[NO_2][NO_3]}{[N_2O_5]} \quad \text{or} \quad [NO_3] = \frac{K[N_2O_5]}{[NO_2]}$$

$$r = k_1 K [N_2O_5] = k[N_2O_5]]$$

62. Write the overall reaction and the rate law equation from the following elementary steps:



[Hint: Adding both the steps, we get overall reaction,



The second step is slow and, therefore, a rate determining step.

$$r = k'[NOBr_2][NO]$$

$$K = \frac{[NOBr_2]}{[NO][Br_2]} \quad \text{or} \quad [NOBr_2] = K[NO][Br_2]$$

$$r = k'K[NO]^2[Br_2]]$$

63. The reaction, $2NO + O_2 \rightarrow 2NO_2$ proceeds in two steps. If one elementary reaction is $NO + O_2 \rightarrow NO_3$, write the second elementary reaction. Write the rate law of the reaction.

[Ans. $NO + NO_3 \rightarrow 2NO_2$, rate = $k[NO]^2[O_2]$]

64. At 380°C, the half life period for the first order decomposition of H_2O_2 is 360 min. The energy of activation of the reaction is 200 kJ mol⁻¹. Calculate the time required for 75% decomposition at 450°C. (IIT 1995)

[Ans. 20.39 min]

65. Calculate the average rate of decomposition of N_2O_5 by the reaction,



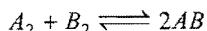
During the time interval from $t = 600$ s to $t = 1200$ s using the following data:

| Time | [N ₂ O ₅] |
|--------|----------------------------------|
| 600 s | 1.24 × 10 ⁻² M |
| 1200 s | 0.93 × 10 ⁻² M |

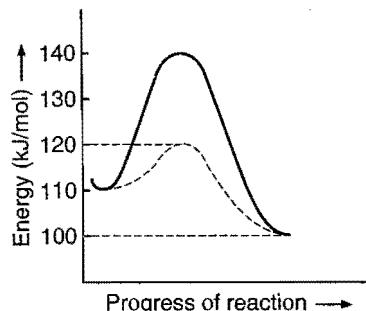
[CED (Bharat) 1995]

[Ans. 5.166 × 10⁻⁶ M s⁻¹]

66. Consider the diagram for reaction:



- (a) Calculate the ΔH of the reaction.
- (b) Calculate the energy of activation for forward and backward reaction.
- (c) The dotted line curve is the path in the presence of a catalyst. What is the energy of activation for the forward and backward reactions in the presence of the catalyst?



What is the lowering in activation energy in the presence of the catalyst?

- (d) Will the catalyst change the extent of the reaction?

[Ans. (a) $\Delta H = -10$ kJ/mol;
 (b) $E_f = 30$ kJ/mol; $E_b = 40$ kJ/mol;
 (c) $E_f = 10$ kJ/mol; $E_b = 20$ kJ/mol; 20 kJ/mol;
 (d) no]

67. Temperature coefficient, $\mu = \frac{k_{35^\circ\text{C}}}{k_{25^\circ\text{C}}}$ of a reaction is

1.82. Calculate the energy of activation in calories. ($R = 1.987$ cal degree⁻¹ mol⁻¹).

[Ans. 10.924 kcal/mol]

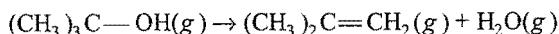
68. For first order gaseous reaction, $\log k$ when plotted against $\frac{1}{T}$ gives a straight line with a slope of -8000 . Calculate the activation energy of the reaction.

[Ans. 36.6 kcal]

69. The rate at 27°C of a chemical reaction increases 1000 times when a suitable catalyst is introduced. Calculate the change in the energy of activation that the catalyst has brought in.

[Ans. 4118 cal]

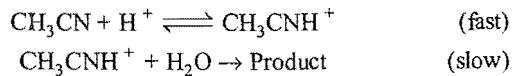
70. Dehydration of tertiary butyl alcohol follows a first order reaction,



the rate constant at 300°C is 2.27×10^{-8} s⁻¹. Calculate the rate constant at 400°C if the energy of activation for the reaction is 58 kcal.

[Ans. 4.392×10^{-5} s⁻¹]

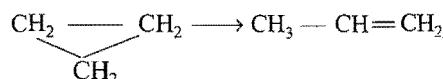
71. Let us consider the following mechanism:



What would be the rate law?

[Ans. Rate = $k[\text{CH}_3\text{CN}][\text{H}_2\text{O}][\text{H}^+]$]

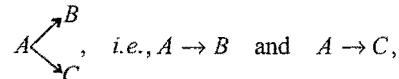
72. The thermal isomerization of cyclopropane occurs according to the equation:



The specific reaction rate constant for this reaction at 499°C was 5.95×10^{-4} sec⁻¹. What is the half life of the reaction? What fraction of the cyclopropane will remain after 1 hour at 499.5°C ?

[Ans. 1165 s; 11.7%]

73. A substance 'A' was found to undergo two parallel first order reactions,



with rate constants 1.26×10^{-4} s⁻¹ and 3.8×10^{-5} s⁻¹ respectively. What were the percentage distributions of B and C?

[Ans. 76.83% of B and 23.17% of C]

74. Two reactions proceed at 25°C at the same rate; the temperature coefficient of the rate of the first reaction is 2 and that of the second reaction is 2.5. Find the ratio of rates of these reactions at 95°C .

[Ans. 5 times]

75. The population of India in the year 1988 was 800 million. Growth rate is 25 per thousand per year. What will be the population in the year 2000 if the growth follows first order kinetics?

[Ans. 1075 million]

76. Half lives against initial pressure are given below. Calculate the order of the reaction.

| | | | |
|---------|-----|-----|-----|
| p (mm) | 750 | 500 | 250 |
| t (min) | 105 | 235 | 950 |

Find out the order of the reaction.

[Ans. 3]

77. For a given reaction at temperature T , the velocity constant k , is expressed as:

$$k = Ae^{-E_a/RT} \quad (k' = \text{Boltzmann constant})$$

Given, $R = 2$ cal K⁻¹ mol⁻¹. Calculate the value of energy of activation. Comment on the results.

[Ans. $E = 18 \times 10^{20}$ cal]

[Hint: Compare the equation with Arrhenius equation

$$k = Ae^{-E_a/RT} \quad \dots (i)$$

$$k = Ae^{-27000k'/T} \quad \dots (ii)$$

$$\frac{E_a}{RT} = \frac{27000k'}{T}$$

$$E_a = 27000Rk'$$

$$= 27000 R \times \frac{R}{N} = \frac{27000 \times (2)^2}{6.023 \times 10^{23}}$$

$$= 18 \times 10^{-20} \text{ cal}$$

Activation energy is low, therefore reaction will be fast.]

78. If the activation energy of a reaction is 80.9 kJ mol^{-1} , calculate the fraction of molecules at 400°C which have enough energy to react to form the products.

[Ans. 5.257×10^{-7}]

[Hint: Fraction of total molecules which are active at a temperature is given as,

$$\begin{aligned} \frac{k}{A} &= e^{-E_a / RT} \\ \log \frac{k}{A} &= \frac{-E_a}{2.303 RT} \\ \frac{k}{A} &= \text{antilog} \left(\frac{-E_a}{2.303 RT} \right) \end{aligned}$$

Substituting the values of E and T we can solve the problem.]

79. The following data were obtained for a given reaction at 300 K :

| Reaction | Energy of activation (kJ/mol) |
|----------------|-------------------------------|
| 1. Uncatalysed | 76 |
| 2. Catalysed | 57 |

Calculate by what factor the rate of catalysed reaction is increased?

[Ans. 2000]

[Hint: Use: $\frac{k_p}{k_a} = \text{antilog} \left(\frac{\Delta E}{2.303 RT} \right)$

k_p = rate constant in presence of catalyst

k_a = rate constant in absence of catalyst

$\Delta E = 76 - 57 = 19 \text{ kJ/mol}$]

80. The Arrhenius equations for *cis-trans* isomerization of but-2-ene ($\text{CH}_3 - \text{CH}=\text{CH}-\text{CH}_3$) and but-2-ene, 1-nitrile ($\text{CH}_3 - \text{CH}=\text{CH}-\text{CN}$) are,

$$k(\text{s}^{-1}) = 10^{13.8} \exp(-263.5 \text{ kJ mol}^{-1} / RT)$$

$$k^{-1}(\text{s}^{-1}) = 10^{11} \exp(-214.5 \text{ kJ mol}^{-1} / RT)$$

Calculate the temperature at which $k = k^{-1}$.

[Ans. 914 K]

81. The half life for a reaction between fixed concentration of reactants varies with temperature as follows:

| $t^\circ\text{C}$ | 520 | 533 | 555 | 574 |
|-----------------------|------|-----|-----|-----|
| $t_{1/2} \text{ sec}$ | 1288 | 813 | 562 | 477 |

Calculate the activation energy of this reaction.

[Ans. $86.47 \text{ kJ mol}^{-1}$]

[Hint: Use: $\log \left(\frac{k_2}{k_1} \right) = \frac{E}{2.303 R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$

$$k_2 = 0.693 / t_2$$

$$k_1 = 0.693 / t_1$$

$$\log \left(\frac{t_1}{t_2} \right) = \frac{E}{2.303 R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

82. What percentage of reactant molecules will crossover the energy barrier at 325 K ? Heat of reaction is 0.12 kcal and activation energy of backward reaction is 0.02 kcal .

[Hint: Activation energy of forward reaction = $0.12 - 0.02$
 $= 0.10 \text{ kcal}$

Fraction of molecules which are active

or which crossover the energy barrier $\left(\frac{k}{A} \right) = e^{-E/RT}$

$$\log_e \left(\frac{k}{A} \right) = - \frac{E}{RT}$$

$$\frac{k}{A} = \text{antilog} \left[\frac{-E}{2.303 RT} \right]$$

$$= \text{antilog} \left[\frac{-0.10 \times 1000}{2.303 \times 2 \times 325} \right]$$

$$= \text{antilog} [-0.06680] = 0.8574$$

∴ Percentage of reactant molecules crossing over the barrier
 $= 0.8574 \times 100 = 85.74\%$

83. In a milk at 37°C Lactobacillus acidophilus has a generation time of about 75 minutes. Calculate the population relative to the initial value at 30, 60, 75, 90 and 150 minutes.

[Ans. t_{\min} 30 60 75 90
 N/N_0 1.32 1.74 2 2.30]

[Hint: In the case of population growth we have to use growth kinetics.

$$-k = \frac{2.303}{t} \log \left(\frac{a}{a+x} \right)$$

a = initial population

x = growth in population in time ' t '

Here, $N_0 = a$; $N = a + x$

84. Two reactions of same order have equal pre-exponential factors but their activation energies differ by 41.9 J/mol . Calculate the ratios between rate constants of these reactions at 600 K .

[Ans. 0.002]

[Hint: Use the relation,

$$\log_{10} k = \log_{10} A - \frac{E}{2.303 RT} \quad \dots (i)$$

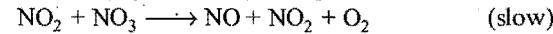
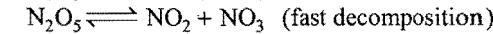
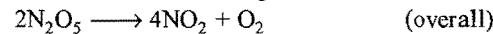
$$\log_{10} k_1 = \log_{10} A - \frac{E_1}{2.303 \times 8.314 \times 600} \quad \dots (ii)$$

$$\log_{10} k_2 = \log_{10} A - \frac{E_2}{2.303 \times 8.314 \times 600} \quad \dots (iii)$$

$$E_1 - E_2 = 41.95 / \text{mol} \quad \dots (iv)$$

Subtract eq. (iii) from eq. (ii) to determine the ratio.]

85. A decomposition reaction has following mechanism



Determine rate law, is the mechanism corresponds to first order reaction.

$$[\text{Ans. } \frac{-d[\text{N}_2\text{O}_5]}{dt} = \frac{2k_1 k_3}{k_1 + k_3} [\text{N}_2\text{O}_5]]$$

86. Rate constant of a reaction changes by 2% by 0.1°C rise in temperature at 25°C . The standard heat of reaction is $121.6 \text{ kJ mol}^{-1}$. Calculate E_a of reverse reaction.

[Ans. 24.7 kJ/mol]

[Hint: $\log\left(\frac{k_2}{k_1}\right) = \frac{E_a}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

$$\log \frac{102}{100} = \frac{E}{2.303 \times 8.314} \left(\frac{1}{298} - \frac{1}{298.1} \right)$$

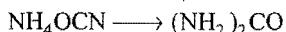
$$E = 1.463 \times 10^5 \text{ J/mol} = 146.3 \text{ kJ/mol}$$

$$\Delta H = E_f - E_b$$

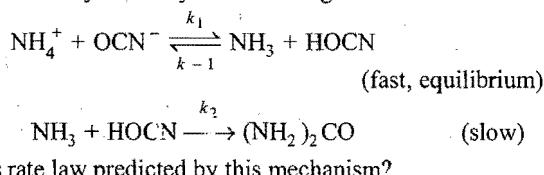
$$121.6 = 146.3 - E_b$$

$$E_b = 24.7 \text{ kJ/mol}$$

87. Urea $(\text{NH}_2)_2\text{CO}$ can be prepared by heating ammonium cyanate NH_4OCN .



The reaction may occur by the following mechanism:



What is rate law predicted by this mechanism?

[Ans. Rate = $\frac{k_2 k_1}{k-1} [\text{NH}_4^+] [\text{OCN}^-] = k[\text{NH}_4^+] [\text{OCN}^-]$]

88. For the reaction $\text{N}_2(g) + 3\text{H}_2(g) \longrightarrow 2\text{NH}_3(g)$, under certain conditions of pressure and temperature of the reactants, the rate of formation of NH_3 is 0.001 kg hr^{-1} . Calculate the rate of reaction for N_2 and H_2 .

[Ans. $1.76 \times 10^{-4} \text{ kg hr}^{-1}$]

[Hint: $-\frac{d[\text{N}_2]}{dt} = -\frac{1}{3} \frac{d[\text{H}_2]}{dt} = +\frac{1}{2} \frac{d[\text{NH}_3]}{dt}$

$$\frac{d[\text{NH}_3]}{dt} = 0.001 \text{ kg hr}^{-1} = \frac{0.001 \times 1000}{17} \text{ mol hr}^{-1}$$

$$= 0.058 \text{ mol hr}^{-1}$$

$$-\frac{d[\text{N}_2]}{dt} = \frac{1}{2} \times 0.058 \text{ mol hr}^{-1}$$

$$= 0.029 \text{ mol hr}^{-1}$$

$$= 0.029 \times 28 \times 10^{-3} \text{ kg hr}^{-1}$$

$$= 8.12 \times 10^{-4} \text{ kg hr}^{-1}$$

Similarly, $-\frac{d[\text{H}_2]}{dt} = 1.76 \times 10^{-4} \text{ kg hr}^{-1}$]

OBJECTIVE QUESTIONS

Set-1: Questions with single correct answer

1. Chemical kinetics, a branch of physical chemistry, deals with:

- (a) heat changes in a reaction
- (b) physical changes in a reaction
- (c) rates of reactions
- (d) structure of molecules

2. The rate at which a substance reacts depends upon its:

- (a) atomic mass
- (b) equivalent mass
- (c) molecular mass
- (d) active mass

3. The rate of a chemical reaction:

- (a) increases as the reaction proceeds
- (b) decreases as the reaction proceeds
- (c) may increase or decrease during the reaction
- (d) remains constant as the reaction proceeds

4. For the reaction, $\text{N}_2 + 3\text{H}_2 \longrightarrow 2\text{NH}_3$, rate is expressed as:

- (a) $-3 \frac{d[\text{N}_2]}{dt} = -\frac{d[\text{H}_2]}{dt} = \frac{3}{2} \frac{d[\text{NH}_3]}{dt}$
- (b) $-\frac{d[\text{N}_2]}{dt} = -\frac{1}{3} \frac{d[\text{H}_2]}{dt} = \frac{1}{2} \frac{d[\text{NH}_3]}{dt}$
- (c) $-\frac{d[\text{N}_2]}{dt} = -\frac{3d[\text{H}_2]}{dt} = \frac{2d[\text{NH}_3]}{dt}$
- (d) $-\frac{d[\text{N}_2]}{dt} = -\frac{d[\text{H}_2]}{dt} = \frac{d[\text{NH}_3]}{dt}$

5. For the reaction, $2\text{NO}_2 \longrightarrow 2\text{NO} + \text{O}_2$, rate is expressed as:

- (a) $-\frac{1}{2} \frac{d[\text{NO}_2]}{dt} = \frac{1}{2} \frac{d[\text{NO}]}{dt} = \frac{d[\text{O}_2]}{dt}$
- (b) $-\frac{1}{2} \frac{d[\text{NO}_2]}{dt} = -\frac{1}{2} \frac{d[\text{NO}]}{dt} = \frac{d[\text{O}_2]}{dt}$

(c) $-\frac{2d[\text{NO}_2]}{dt} = \frac{2d[\text{NO}]}{dt} = \frac{d[\text{O}_2]}{dt}$

(d) $-\frac{d[\text{NO}_2]}{dt} = \frac{d[\text{NO}]}{dt} = \frac{d[\text{O}_2]}{dt}$

6. The rate of reaction that does not involve gases, is not dependent on:

- (a) pressure
- (b) temperature
- (c) concentration
- (d) catalyst

7. For the reaction, $A + B \longrightarrow 2C + D$, which one is the incorrect statement?

- (a) Rate of disappearance of A = Rate of disappearance of B
- (b) Rate of disappearance of A = Rate of appearance of D
- (c) Rate of disappearance of B = $2 \times$ rate of appearance of C
- (d) Rate of disappearance of B = $\frac{1}{2} \times$ rate of appearance of C

8. In a reaction, $2A_2 + B_2 \longrightarrow 2A_2B$, the reactant A will disappear at:

- (a) half the rate that B will decrease
- (b) the same rate that B will decrease
- (c) double the rate that A_2B will form
- (d) twice the rate that B will decrease

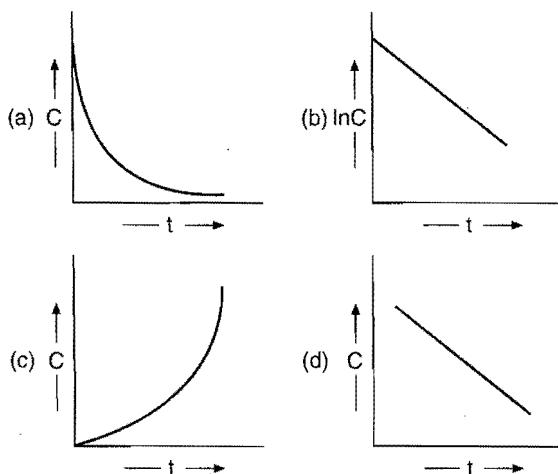
9. In the reaction $3A \rightarrow 2B$, rate of reaction $+ \frac{d[B]}{dt}$ is equal to:

[JEE (WB) 2008]

- (a) $-\frac{1}{3} \frac{d[A]}{dt}$
- (b) $-\frac{2}{3} \frac{d[A]}{dt}$
- (c) $+2 \frac{d[A]}{dt}$
- (d) $-\frac{3}{2} \frac{d[A]}{dt}$

10. For the reaction, $2\text{NO} \longrightarrow \text{N}_2 + \text{O}_2$, the expression $-\frac{1}{2} \frac{d[\text{NO}]}{dt}$ represents:

- (a) the rate of formation of NO
 (b) the average rate of the reaction
 (c) the instantaneous rate of the reaction
 (d) all of the above
11. The term $-\frac{dx}{dt}$ in the rate expression refers to the:
 (a) instantaneous rate of reaction
 (b) average rate of reaction
 (c) increase in the concentration of reactants
 (d) concentration of reactants
12. According to collision theory of reaction rates:
 (a) every collision between reactant molecules leads to a chemical reaction
 (b) rate of reaction is proportional to the velocity of the molecules
 (c) rate of reaction is proportional to the average energy of the molecules
 (d) rate of reaction is proportional to the number of collisions per second
13. According to collision theory:
 (a) all collisions are sufficiently violent
 (b) all collisions are responsible for product formation
 (c) all collisions are effective
 (d) only a fraction of collisions are effective which have enough energy to form products
14. Which of the following has been used to explain the subject of chemical kinetics?
 (a) Collision theory of bimolecular reactions
 (b) The activated complex theory
 (c) Arrhenius equation
 (d) All of the above
15. The activation energy for a chemical reaction depends upon:
 (a) temperature
 (b) nature of reacting species
 (c) concentration of the reacting species
 (d) collision frequency
16. In a reaction, the threshold energy is equal to:
 (a) activation energy + normal energy of reactants
 (b) activation energy - normal energy of reactants
 (c) normal energy of reactants - activation energy
 (d) average kinetic energy of molecules of reactants
17. The influence of temperature on the rate of reaction is determined by:
 (a) Nernst's equation (b) Gibbs-Helmholtz equation
 (c) Arrhenius equation (d) van't Hoff equation
18. According to the collision theory of reaction rates, the rate of reaction increases with temperature due to:
 (a) greater number of collisions
 (b) higher velocity of reacting molecules
 (c) greater number of molecules having the activation energy
 (d) decrease in the activation energy
19. The temperature coefficient of a reaction is:
 (a) ratio of rate constants at two temperatures differing by 1°C
 (b) ratio of rate constants at temperature 35°C and 25°C
 (c) ratio of rate constants at temperature 30°C and 25°C
 (d) specific reaction rate at 25°
20. In general, with every 10°C rise in temperature, the rate of reaction becomes approximately
 (a) ten times (b) double
 (c) half (d) one tenth
21. Activation energy of the reaction is:
 (a) the energy released during the reaction
 (b) the energy evolved when activated complex is formed
 (c) minimum amount of energy needed to overcome the potential barrier
 (d) the energy needed to form one mole of the product
22. The temperature coefficient of most of the reactions lies between:
 (a) 2 and 3 (b) 1 and 2
 (c) 2 and 4 (d) 3 and 4
23. According to Arrhenius equation, rate constant of a chemical reaction is equal to:
 (a) $Ae^{-E_a/RT}$ (b) $Ae^{E_a/RT}$
 (c) Ae^{RT/E_a} (d) Ae^{-RT/E_a}
24. The correct expression for Arrhenius equation showing the effect of temperature on the rate constant is ($T_2 > T_1$):
 (DCE 2004)
 (a) $\log_{10} \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{T_1 T_2}{T_2 - T_1} \right]$
 (b) $\log_{10} \frac{k_2}{k_1} = \frac{R}{2.303E_a} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$
 (c) $\log_{10} \frac{k_2}{k_1} = \frac{E_a}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$
 (d) $\log_{10} \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{T_2 - T_1}{T_2 T_1} \right]$
25. In order to react, a molecule, at the time of collision, must possess a certain amount of energy known as:
 (a) free energy (b) kinetic energy
 (c) threshold energy (d) internal energy
26. The activation energy of a reaction is zero. The rate constant of the reaction:
 (C.E.T.(Ph.) 1991)
 (a) increases with increase of temperature
 (b) decreases with decrease of temperature
 (c) decreases with increase of temperature
 (d) is nearly independent of temperature
27. The activation energy of a reaction can be lowered by:
 (a) using a positive catalyst
 (b) increasing temperature
 (c) decreasing temperature
 (d) increasing concentration of the reactants
28. The activation energy for a hypothetical reaction $A \longrightarrow$ Product is 12.49 kcal/mol. If temperature is raised from 295 to 305, the rate of reaction increases by:
 (a) 60% (b) 100%
 (c) 50% (d) 20%
29. The plot between concentration versus time for a zero order reaction is represented by:
 (AMU (Phys.) 2004)



30. The rate of reaction increases with rise in temperature because of : **[Comed (Karnataka) 2008]**
- increase in the number of activated molecules
 - increase in the activation energy
 - decrease in the activation energy
 - increase in the number of molecular collisions
31. Which of the following is a first order reaction?
- $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$
 - $2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2$
 - $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$
 - $\text{NH}_4\text{NO}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$
32. Which one of the following is not a first order reaction?
- $\text{CH}_3\text{COOCH}_3 + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{CH}_3\text{COOH} + \text{CH}_3\text{OH}$
 - $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + \text{C}_2\text{H}_5\text{OH}$
 - $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$
 - $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$
33. Rate expression of a chemical change is $-\frac{dx}{dt} = k[\text{A}]^2[\text{B}][\text{C}]^0$. The order of reaction is:
- 3
 - 2
 - 1
 - zero
34. For a reaction, $2\text{A} + \text{B} \rightarrow \text{C} + \text{D}$, the concentration of B is kept constant and that of A is tripled the new rate of reaction will be:
- nine times
 - three times
 - same
 - zero
35. The rate of the reaction, $\text{A} + \text{B} + \text{C} \rightarrow \text{Products}$, is given by
- $$-\frac{d[\text{A}]}{dt} = k[\text{A}]^{1/2}[\text{B}]^{1/3}[\text{C}]^{1/4}$$
- The order of the reaction is:
- 1/2
 - 13/12
 - 1
 - 2
36. Which of the following rate laws has an overall order of 0.5 for the reaction involving substances x , y and z ?
- Rate = $k[\text{C}_x][\text{C}_y][\text{C}_z]$
 - Rate = $k[\text{C}_x]^{0.5}[\text{C}_y]^{0.5}[\text{C}_z]^{0.5}$
 - Rate = $k[\text{C}_x]^{1.5}[\text{C}_y]^{-1}[\text{C}_z]^0$
 - Rate = $k[\text{C}_x][\text{C}_y]^{-2}[\text{C}_z]^0$
37. If the rate of reaction between A and B is given by rate = $k[\text{A}][\text{B}]^2$, then the reaction is:

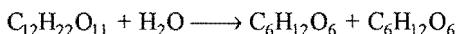
- (a) first order in A (b) second order in B
 (c) third order overall (d) all are correct
38. For the reaction $\text{A} \rightarrow \text{B}$, the rate of reaction is quadrupled when the concentration of A is doubled; the rate of the reaction is $r = k[\text{A}]^n$; the value of n is:
- 1
 - zero
 - 3
 - 2
39. Select the rate law that corresponds to the data shown for the following reaction: $\text{A} + \text{B} \rightarrow \text{C}$ **(CBSE 1994)**
- | Expt. No. | $[\text{A}]_0$ | $[\text{B}]_0$ | Initial rate |
|-----------|----------------|----------------|--------------|
| 1. | 0.012 | 0.035 | 0.10 |
| 2. | 0.024 | 0.070 | 0.80 |
| 3. | 0.024 | 0.035 | 0.10 |
| 4. | 0.012 | 0.070 | 0.80 |
- rate = $k[\text{B}]^3$
 - rate = $k[\text{B}]^4$
 - rate = $k[\text{A}][\text{B}]^3$
 - rate = $k[\text{A}]^2[\text{B}]^2$
40. For a chemical reaction, $\text{A} \rightarrow \text{E}$, it is found that rate of reaction is doubled when the concentration of A is increased four times. The order of the reaction is:
- 1
 - 2
 - 1/2
 - zero
41. The rate of reaction, $\text{A} + \text{B} \rightarrow \text{Products}$, is given by the equation, $r = k[\text{A}][\text{B}]$. If B is taken in large excess, the order of reaction would be: **(BIT 1992)**
- 2
 - 1
 - zero
 - unpredictable
42. The rate of reaction between A and B increases by a factor of 100, when the concentration of A is increased 10 folds. The order of reaction with respect to A is:
- 10
 - 2
 - 1
 - 20
43. The rate law for the reaction,
- $$\text{RCI} + \text{NaOH}(\text{aq.}) \rightarrow \text{ROH} + \text{NaCl}$$
- is given by, Rate = $k[\text{RCI}]$. The rate of reaction will be:
- unaffected by increasing temperature of the reaction
 - doubled on doubling the concentration of NaOH
 - halved on reducing the concentration of NaOH to one half
 - halved on reducing the concentration of RCI to one half
44. A zero order reaction is one:
- in which reactants do not react
 - in which one of the reactants is in large excess
 - whose rate is uniform and not affected by time
 - whose rate increases with time
45. The rates of a certain reaction at different time intervals are as follows:
- | Time (second) | 0 | 10 | 20 |
|---------------|----------------------|-----------------------|---|
| Rate | 1.8×10^{-2} | 1.82×10^{-2} | 1.79×10^{-2} mol L ⁻¹ s ⁻¹ |
- The reaction is of:
- zero order
 - first order
 - second order
 - third order
46. For which of the following, the units of rate and rate constant of the reaction are identical?
- First order reaction
 - Zero order reaction
 - Second order reaction
 - Fractional order reaction

47. The unit of rate constant for a zero order reaction is:
 (a) mol time⁻¹ (b) L time⁻¹
 (c) mol L⁻¹ time⁻¹ (d) L mol⁻¹ time⁻¹
48. For a zero order reaction: (EAMCET 1990)
 (a) $t_{1/2} \propto a$ (b) $t_{1/2} \propto \frac{1}{a}$ (c) $t_{1/2} \propto a^2$ (d) $t_{1/2} \propto \frac{1}{a^2}$
49. The rate of the first order reaction, $A \rightarrow \text{Products}$, is $7.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$, when the concentration of A is 0.2 mol L⁻¹. The rate constant of the reaction is:
 (a) $2.5 \times 10^{-5} \text{ s}^{-1}$ (b) $8.0 \times 10^{-4} \text{ s}^{-1}$
 (c) $6.0 \times 10^{-4} \text{ s}^{-1}$ (d) $3.75 \times 10^{-3} \text{ s}^{-1}$
50. If the concentration is expressed in mole per litre and time in second, the units of rate constant for a first order reaction is:
 (a) mol L⁻¹ sec⁻¹ (b) sec⁻¹
 (c) mol L⁻¹ (d) mol⁻¹
51. Which one of the following formula represents a first order reaction?
 (a) $k = \frac{2.303}{t} \log \frac{[A]_t}{[A]_0}$ (b) $k = \frac{1}{t} \cdot \frac{x}{a(a-x)}$
 (c) $k = \frac{2.303}{t} \log \frac{a}{a-x}$ (d) $k = \frac{2.303}{t} \log \frac{a}{x}$
52. 75% of a first order reaction was completed in 32 minute; when was 50% of the reaction completed?
 (a) 4 min (b) 8 min (c) 24 min (d) 16 min
53. The first order rate constant for the decomposition of N_2O_5 is $6.2 \times 10^{-4} \text{ s}^{-1}$. The half life period for this decomposition is: (MLNR 1991)
 (a) 1117.7 s (b) 1117 s (c) 223.4 s (d) 160.9 s
54. The half life period of a first order reaction is:
 (a) $\frac{0.693}{a}$ (b) $\frac{0.693}{k}$ (c) $\frac{0.693}{t}$ (d) $\frac{0.693}{ak}$
55. The specific rate constant of a first order reaction depends on:
 (a) concentration of the reactants
 (b) concentration of the products
 (c) time
 (d) temperature
56. For a given reaction of first order, it takes 20 minutes for the concentration to drop from 1.0 M to 0.6 M . The time required for the concentration to drop from 0.6 M to 0.36 M will be:
 (a) more than 20 minutes (b) less than 20 minutes
 (c) equal to 20 minutes (d) infinity
57. For the first order reaction $A \rightarrow \text{Product}$, the half life is 200 seconds. The rate constant of the reaction is:
 (a) $3.46 \times 10^{-2} \text{ s}^{-1}$ (b) $3.46 \times 10^{-3} \text{ s}^{-1}$
 (c) $3.46 \times 10^{-4} \text{ s}^{-1}$ (d) $3.46 \times 10^{-5} \text{ s}^{-1}$
58. The following data were obtained for the thermal decomposition of nitrous oxide on finely divided gold:
 t (minutes) 0 20 40 60 80
 Concentration of N_2O (mol L⁻¹) 0.10 0.08 0.06 0.04 0.02
- The order of reaction is:
 (a) zero (b) 1 (c) 2 (d) 3
59. The following data are for the decomposition of ammonium nitrite in aqueous solution:
 Vol. of N_2 in cm³ 6.25 9.0 11.42 13.65 35.02
 Time (min) 10 15 20 25 ∞
 The order of reaction is:
 (a) 3 (b) 2 (c) 1 (d) zero
 [Hint: $a = 35.02$, $(a - x) = 35.02 - V_t$
 Apply, $k = \frac{2.303}{t} \log \frac{35.02}{(35.02 - V_t)}$]
60. In the first order reaction, the concentration of reactant decreases from 1.0 M to 0.25 M in 20 minutes. The value of specific rate is:
 (a) 69.32 (b) 6.932 (c) 0.6932 (d) 0.06932
61. The half life period of a first order reaction is 10 minutes. The time required for the concentration of the reactant to change from 0.08 M to 0.02 M is: (IIT 1990)
 (a) 10 min (b) 20 min (c) 30 min (d) 40 min
62. The rate constant for the hydrolysis reaction of an ester by dilute acid is $0.6931 \times 10^{-3} \text{ s}^{-1}$. The time required to change the concentration of ester from 0.04 M to 0.01 M is:
 (a) 6931 sec (b) 4000 sec
 (c) 2000 sec (d) 1000 sec
63. The rate of a gaseous reaction is given by the expression $k[A][B]$. If the volume of reaction vessel is suddenly reduced to one-fourth of the initial volume, the reaction rate relative to the original rate will be: (IIT 1992)
 (a) 1/16 (b) 1/8 (c) 8 (d) 16
64. The velocity of a reaction is doubled for every 10°C rise in temperature. If the temperature is raised to 50°C , the reaction velocity increases by about:
 (a) 12 times (b) 16 times (c) 32 times (d) 50 times
65. If the rate expression for a reaction is $\frac{dx}{dt} = k[A]^{1/2}[B]^{3/2}$, the overall order of the reaction is: (CEE (Bihar) 1992)
 (a) 2 (b) 1/2 (c) 3/2 (d) 1
66. The rates of a certain reaction at different times are as follows:
 Time (second) 0 10 20 30
 Rate 2.8×10^{-2} 2.78×10^{-2} 2.81×10^{-2} 2.79×10^{-2}
 ($\text{mol L}^{-1} \text{ s}^{-1}$)
- The reaction is of:
 (a) third order (b) second order
 (c) first order (d) zero order
67. The second order rate constant is usually expressed as:
 (a) mol L⁻¹ s⁻¹ (b) mol⁻¹ L⁻¹ s⁻¹
 (c) mol⁻¹ L s⁻¹ (d) mol L s⁻¹
68. The hydrolysis of ethyl acetate is a reaction of:

$$\text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH}$$

 (a) zero order (b) first order
 (c) second order (d) third order

69. The inversion of cane sugar is represented by,



It is a reaction of:

[PMT (MP) 1993]

- (a) second order
 - (b) unimolecular
 - (c) pseudo-unimolecular
 - (d) zero order
70. In a second order reaction, the time needed for the initial concentration of the reactant to reduce to half that value is:
- (a) independent of the initial concentration
 - (b) proportional to the initial concentration
 - (c) inversely proportional to initial concentration
 - (d) proportional to the square of the initial concentration
71. Which of the following statements regarding molecularity of the reaction is wrong?
- (a) It may be either whole number or fractional
 - (b) It is calculated from the reaction mechanism
 - (c) It depends on the rate determining step
 - (d) It is number of molecules of reactants taking part in a single step chemical reaction

72. For the reaction, $\text{H}_2(g) + \text{Br}_2(g) \rightarrow 2\text{HBr}(g)$, the reaction rate is:

$$\text{rate} = k[\text{H}_2][\text{Br}_2]^{1/2}$$

Which one of the following statements is true for this reaction?

- (a) The reaction is of second order
- (b) The molecularity of the reaction is 3/2
- (c) The unit of k is sec^{-1}
- (d) The molecularity of the reaction is two

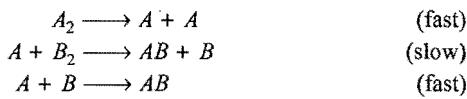
73. Molecularity of the reaction:

- (a) is always a whole number
- (b) is never a whole number
- (c) can have a fractional value
- (d) can be zero

74. For a single step reaction, $A + 2B \longrightarrow \text{Products}$, the molecularity is:

- (a) zero
- (b) three
- (c) two
- (d) one

75. The hypothetical reaction, $A_2 + B_2 \longrightarrow 2AB$, follows the following mechanism:



The order of the overall reaction is:

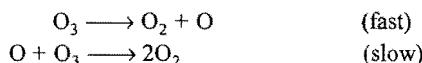
[PMT (Pb.) 1991]

- (a) zero
- (b) 1
- (c) 2
- (d) 3/2

76. The molecularity of a reaction is:

- (a) same as its order
- (b) different from order
- (c) may be same or different as compared to order
- (d) always zero

77. The chemical reaction, $2\text{O}_3 \longrightarrow 3\text{O}_2$ proceeds as follows:



The rate law expression should be:

- (a) $r = k[\text{O}_3]^2$
- (b) $r = k[\text{O}_3]^2[\text{O}_2]^{-1}$
- (c) $r = k[\text{O}_3][\text{O}_2]$
- (d) $r = [\text{O}_3][\text{O}_2]^2$

[Hint: $r = k'[\text{O}_3][\text{O}] = \frac{k'k''[\text{O}_3][\text{O}_2]}{[\text{O}_2]} = k[\text{O}_3]^2[\text{O}_2]^{-1}$]

78. Time required to decompose half of the substance for n th order reaction is inversely proportional to:

- (a) a^{n+1}
- (b) a^{n-1}
- (c) a^{n-2}
- (d) a^n

79. What is the order of the reaction which obeys the expression $t_{1/2} = \frac{1}{ka}$?

- (a) Zero
- (b) Third
- (c) First
- (d) Second

80. The order of reaction can be deduced from:

- (a) experiment
- (b) chemical equation
- (c) rate constant
- (d) thermochemical equations

81. The order of a reaction may be determined by:

- (a) differential method
- (b) initial rate method
- (c) graphical method
- (d) all of these

82. A graph between time (t) and the substance consumed at any time is found to be a straight line passing through the origin. This indicates that the reaction is of:

- (a) second order
- (b) first order
- (c) zero order
- (d) fractional order

83. A plot of $\log(a - x)$ against time ' t ' is a straight line. This indicates that the reaction is of:

- (a) zero order
- (b) first order
- (c) second order
- (d) third order

84. For the reaction $\text{N}_2\text{O}_5(g) \longrightarrow 2\text{NO}_2(g) + \frac{1}{2}\text{O}_2(g)$, the value of rate of disappearance of N_2O_5 is given as 6.25×10^{-3} $\text{mol L}^{-1}\text{s}^{-1}$. The rate of formation of NO_2 and O_2 is given respectively as:

- (a) 6.25×10^{-3} $\text{mol L}^{-1}\text{s}^{-1}$ and 6.25×10^{-3} $\text{mol L}^{-1}\text{s}^{-1}$
- (b) 1.25×10^{-2} $\text{mol L}^{-1}\text{s}^{-1}$ and 3.125×10^{-3} $\text{mol L}^{-1}\text{s}^{-1}$
- (c) 6.25×10^{-3} $\text{mol L}^{-1}\text{s}^{-1}$ and 3.125×10^{-3} $\text{mol L}^{-1}\text{s}^{-1}$
- (d) 1.25×10^{-2} $\text{mol L}^{-1}\text{s}^{-1}$ and 6.25×10^{-3} $\text{mol L}^{-1}\text{s}^{-1}$

[Hint: $\frac{-d[\text{N}_2\text{O}_5]}{dt} = +\frac{1}{2} \frac{d[\text{N}_2\text{O}_5]}{dt} = +2 \frac{d[\text{O}_2]}{dt}$
 $\therefore \frac{d[\text{N}_2\text{O}_5]}{dt} = 2 \left\{ \frac{-d[\text{N}_2\text{O}_5]}{dt} \right\} = 2 \times 6.25 \times 10^{-3}$
 $= 1.25 \times 10^{-2} \text{ mol L}^{-1}\text{s}^{-1}$
 $\frac{d[\text{O}_2]}{dt} = \frac{1}{2} \left\{ \frac{-d[\text{N}_2\text{O}_5]}{dt} \right\} = \frac{1}{2} \times 6.25 \times 10^{-3}$
 $= 3.125 \times 10^{-3} \text{ mol L}^{-1}\text{s}^{-1}$]

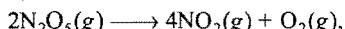
85. The ratio of the time required for $\frac{3}{4}$ th of the reaction of first order to complete to that required for half of the reaction:

- (a) 4 : 3
- (b) 3 : 2
- (c) 2 : 1
- (d) 1 : 2

86. In pseudo-unimolecular reactions:

- (a) one of the reactants is present in large excess
- (b) both the reactants have same concentration
- (c) both the reactants are present in low concentration
- (d) one of the reactants is less reactive

87. The reaction,



is first order with respect to N_2O_5 . Which of the following graph, would yield a straight line?

- (a) $\log(p_{\text{N}_2\text{O}_5})$ versus time with -ve slope
- (b) $(p_{\text{N}_2\text{O}_5})^{-1}$ versus time
- (c) $(p_{\text{N}_2\text{O}_5})$ versus time
- (d) $\log(p_{\text{N}_2\text{O}_5})$ versus time with +ve slope

88. Consider the following statements :

- (i) increase in concentration of reactant increases the rate of a zero order reaction
- (ii) rate constant k is equal to collision frequency ' A' if $E_a = 0$
- (iii) rate constant k is equal to collision frequency A if $E_a = \infty$
- (iv) $\log_e k$ vs T is a straight line
- (v) $\log_e k$ vs $1/T$ is a straight line

Correct statement are :

[PMT (Kerala) 2010]

- (a) (i) and (iv)
- (b) (ii) and (v)
- (c) (iii) and (iv)
- (d) (ii) and (iii)
- (e) (i) and (v)

89. If we plot a graph between $\log k$ and $\frac{1}{T}$ by Arrhenius equation, the slope is:

[EAMCET (Engg.) 2010]

- (a) $-E_a/R$
- (b) $+E_a/R$
- (c) $-\frac{E_a}{2.303R}$
- (d) $+\frac{E_a}{2.303R}$

90. The rate of the reaction,



is given by the equation, rate = $k[\text{CCl}_3\text{CHO}][\text{NO}]$. If concentration is expressed in mol / litre, the units of k are:

[PMT (MP) 1993]

- (a) $\text{mol}^{-2} \text{L}^2 \text{s}^{-1}$
- (b) $\text{mol L}^{-1} \text{s}^{-1}$
- (c) $\text{L mol}^{-1} \text{s}^{-1}$
- (d) s^{-1}

91. In a reaction, $2A + B \longrightarrow A_2B$, the reactant A will disappear at:

[PMT (MP) 1993]

- (a) half the rate that B will decrease
- (b) twice the rate that B will decrease
- (c) the same rate that B will decrease
- (d) the same rate that A_2B will form

92. The rate of the reaction, $2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2$, at 25°C is $0.028 \text{ mol L}^{-1} \text{s}^{-1}$. The experimental rate is given by

$$r = k[\text{NO}]^2[\text{O}_2]$$

If the initial concentrations of the reactants are $\text{O}_2 = 0.040 \text{ mol L}^{-1}$ and $\text{NO} = 0.01 \text{ mol L}^{-1}$, the rate constant of the reaction is:

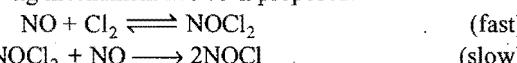
- (a) $7.0 \times 10^{-2} \text{ L mol}^{-1} \text{s}^{-1}$
- (b) $7.0 \times 10^{-4} \text{ L}^2 \text{ mol}^{-2} \text{s}^{-1}$
- (c) $7.0 \times 10^2 \text{ L}^2 \text{ mol}^{-2} \text{s}^{-1}$
- (d) $7.0 \times 10^3 \text{ L}^2 \text{ mol}^{-2} \text{s}^{-1}$

[Hint: $0.028 = k[0.01]^2[0.040]$]

93. For the reaction,



the following mechanism has been proposed.



The rate law for the reaction is:

$$(a) \text{rate} = k[\text{NO}]^2[\text{Cl}_2] \quad (b) \text{rate} = k[\text{NO}][\text{Cl}_2]^2$$

$$(c) \text{rate} = k[\text{NOCl}_2] \quad (d) \text{rate} = k[\text{NOCl}]^2$$

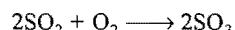
[Hint:

$$\text{rate} = k'[\text{NO}][\text{NOCl}_2] = k'K[\text{NO}][\text{NO}][\text{Cl}_2] = k[\text{NO}]^2[\text{Cl}_2]$$

94. The rate of a reaction can be increased in general by all the following factors except:

- (a) by increasing the temperature
- (b) using a suitable catalyst
- (c) by increasing the concentration of reactants
- (d) by an increase in activation energy

95. How will the rate $r = k[\text{SO}_2][\text{O}_2]$ of reaction,



change if the volume of the reaction vessel is tripled?

- (a) It will be $\frac{1}{3}$ rd of its initial value
- (b) It will be 3 times of its initial value
- (c) It will be 9 times of its initial value
- (d) It will be $\frac{1}{9}$ th of its initial value

96. Radioactive disintegration is an example of:

- (a) zero order reaction
- (b) first order reaction
- (c) second order reaction
- (d) third order reaction

97. In the formation of sulphur trioxide by the contact process, $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$, the rate of reaction was measured as

$$\frac{d[\text{O}_2]}{dt} = 3.0 \times 10^{-4} \text{ mol L}^{-1} \text{s}^{-1}.$$

The rate of reaction expressed in terms of SO_3 will be:

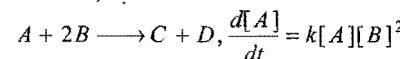
- (a) $3.0 \times 10^{-4} \text{ mol L}^{-1} \text{s}^{-1}$
- (b) $6.0 \times 10^{-4} \text{ mol L}^{-1} \text{s}^{-1}$
- (c) $1.5 \times 10^{-4} \text{ mol L}^{-1} \text{s}^{-1}$
- (d) $4.5 \times 10^{-4} \text{ mol L}^{-1} \text{s}^{-1}$

98. The rate constant for a first order reaction is 6.909 min^{-1} . Therefore, the time required in minutes for the participation of 75% of the initial reactant is:

[PET (J&K) 2009]

- (a) $\frac{2}{3} \log 2$
- (b) $\frac{2}{3} \log 4$
- (c) $\frac{3}{2} \log 2$
- (d) $\frac{3}{2} \log 4$

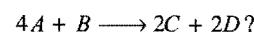
99. For the reaction,



the expression for $\frac{d[B]}{dt}$ will be:

- (a) $2k[A][B]^2$
- (b) $\frac{1}{2}k[A][B]^2$
- (c) $k[A][B]^2$
- (d) $k[A][B/2]^2$

100. Which of the following statements is not correct for the reaction,



- (a) The rate of appearance of C is one-half the rate of disappearance of B
- (b) The rate of disappearance of B is one-fourth of the rate of disappearance of A
- (c) The rate of formation of D is one-half of the rate of consumption of A
- (d) The rates of formation of C and D are equal

- 101.** The overall rate of a reaction is governed by:
 (a) the rate of the fastest intermediate step
 (b) the sum total of the rates of all the intermediate steps
 (c) the average of the rates of all the intermediate steps
 (d) the rate of the slowest intermediate step
- 102.** The rate constant of a reaction does not depend upon:
 (a) temperature
 (b) activation energy
 (c) catalyst
 (d) concentration of reactants and products
- 103.** The half-life period of a first order chemical reaction is 6.93 minutes. The time required for the completion of 99% of the chemical reaction will be : ($\log 2 = 0.301$) (AIEEE 2009)
 (a) 230.3 minutes (b) 23.03 minutes
 (c) 46.06 minutes (d) 460.6 minutes
- 104.** For the chemical reaction $x \rightarrow y$, it is found that the rate of reaction increases 2.25 times when the concentration of x is increased 1.5 times. What is the order of reaction?
 (a) One (b) Two (c) Three (d) Zero
[Hint: $r = k[x]^a$ and $2.25r = k[1.5x]^a$
 So, $2.25 = (1.5)^a$ or $a = 2$]
- 105.** The half life period of a reaction is constant for:
 (a) zero order (b) first order
 (c) second order (d) none of these
- 106.** From different sets of data of $t_{1/2}$ at different initial concentrations say ' a ' for a given reaction, the $[t_{1/2} \propto a]$ is found to be constant. The order of reaction is:
 (a) zero (b) 1 (c) 2 (d) 3
- 107.** Diazonium salt decomposes as
 $C_6H_5N_2^+Cl^- \rightarrow C_6H_5Cl + N_2$.
 At 0°C, the evolution of N_2 becomes two times faster when the initial concentration of the salt is doubled. Therefore, it is: (MLNR 1994)
 (a) a first order reaction
 (b) a second order reaction
 (c) independent of the initial concentration of the salt
 (d) a zero order reaction
- 108.** For the reaction, $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$, under certain conditions of temperature and pressure of the reactants, the rate of formation of ammonia is 0.001 kg hr^{-1} . The rate of consumption of hydrogen under the same conditions is kg hr^{-1} .
 (a) 0.001 (b) 0.003 (c) 0.002 (d) 0.0015
- 109.** The rate constant, the activation energy and the Arrhenius parameter of a chemical reaction at 25°C are $3.0 \times 10^{-4} \text{ s}^{-1}$, $104.4 \text{ kJ mol}^{-1}$ and $6.0 \times 10^{14} \text{ s}^{-1}$ respectively. The value of rate constant at $T \rightarrow \infty$ is: (IIT 1996)
 (a) $2.0 \times 10^{18} \text{ s}^{-1}$ (b) $6.0 \times 10^{14} \text{ s}^{-1}$
 (c) infinity (d) $3.6 \times 10^{30} \text{ s}^{-1}$
- 110.** In the reaction
 $BrO_3(aq.) + 5Br^-(aq.) + 6H^+ \rightarrow 3Br_2(l) + 3H_2O(l)$

The rate of appearance of bromine (Br_2) is related to rate of disappearance of bromide ions as following:

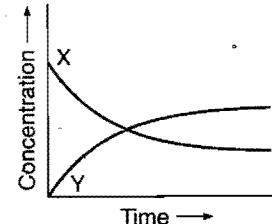
[CBSE (PMT) 2009]

$$(a) \frac{d[Br_2]}{dt} = \frac{3}{5} \frac{d[Br^-]}{dt} \quad (b) \frac{d[Br_2]}{dt} = -\frac{3}{5} \frac{d[Br^-]}{dt}$$

$$(c) \frac{d[Br_2]}{dt} = -\frac{5}{3} \frac{d[Br^-]}{dt} \quad (d) \frac{d[Br_2]}{dt} = +\frac{5}{3} \frac{d[Br^-]}{dt}$$

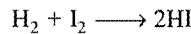
- 111.** Given that k is the rate constant for some order of any reaction at temp. T , then the value of $\lim_{T \rightarrow \infty} \log k$, (where, A is the Arrhenius constant) is:
 (a) $A / 2.303$ (b) A (c) $2.303A$ (d) $\log A$

- 112.** The curve depicts the change in concentration of species X and Y as a function of time. The point of intersection of the two curves represents:
 (a) $t_{1/2}$
 (b) $t_{3/4}$
 (c) $t_{2/3}$
 (d) data insufficient to predict



- 113.** In gaseous reactions, important for the understanding of the upper atmosphere H_2O and O react bimolecularly to form two OH radicals. ΔH for this reaction is 72 kJ at 500 K and E_a is 77 kJ mol^{-1} ; then E_a for the bimolecular recombination of two OH radicals to form H_2O and O is:
 (a) 3 kJ mol^{-1} (b) 4 kJ mol^{-1}
 (c) 5 kJ mol^{-1} (d) 7 kJ mol^{-1}

- 114.** From the following data, the activation energy for the reaction (cal/mol) is:



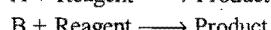
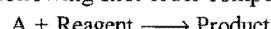
| T (K) | 1/T (K⁻¹) | log K |
|--------------|-----------------------------|--------------|
| 769 | 1.3×10^{-3} | 2.9 |
| 667 | 1.5×10^{-3} | 1.1 |

- (a) 4×10^4 (b) 2×10^4
 (c) 8×10^4 (d) 3×10^4

- 115.** The hydrolysis of an ester was carried out separately with 0.05 $NHCl$ and 0.05 NH_2SO_4 . Which of the following will be true?
 (a) $k_{HCl} > k_{H_2SO_4}$ (b) $k_{H_2SO_4} > k_{HCl}$
 (c) $k_{H_2SO_4} = 2k_{HCl}$ (d) $k_{H_2SO_4} = k_{HCl}$

- 116.** For an endothermic reaction, where, ΔH represents the enthalpy of the reaction in kJ/mol, the minimum value for the energy of activation will be:
 (a) less than ΔH (b) zero
 (c) more than ΔH (d) equal to ΔH

- 117.** In the following first order competing reactions;

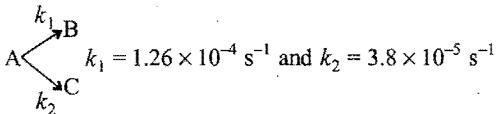


- The ratio of k_1/k_2 if only 50% of B will have been reacted when 94% of A has been reacted is:

- (a) 4.06 (b) 3.06
 (c) 2.06 (d) 0.06

- 118.** Two reactions $A \rightarrow \text{Products}$ and $B \rightarrow \text{Products}$, have rate constants k_A and k_B at temperature T and activation energies E_A and E_B respectively. If $k_A > k_B$ and $E_A < E_B$ and assuming that A for both the reactions is same, then:

- (a) at higher temperatures k_A will be greater than k_B
 (b) at lower temperatures k_A and k_B will be close to each other in magnitude
 (c) as temperature rises, k_A and k_B will be close to each other in magnitude
 (d) at lower temperature $k_B > k_A$
119. A substance undergoes first order decomposition. The decomposition follows two parallel first order reactions as:



The percentage distributions of B and C are:

- (a) 80% B and 20% C (b) 76.83% B and 23.17% C
 (c) 90% B and 10% C (d) 60% B and 40% C
120. Inversion of a sugar follows first order rate equation which can be followed by noting the change in rotation of the plane of polarisation of light in a polarimeter. If r_∞ , r_t and r_0 are the rotations at $t = \infty$, $t = t$ and $t = 0$, then first order reaction can be written as:

$$\begin{array}{ll} (a) k = \frac{1}{t} \log_e \frac{r_t - r_\infty}{r_0 - r_\infty} & (b) k = \frac{1}{t} \log_e \frac{r_0 - r_\infty}{r_t - r_0} \\ (c) k = \frac{1}{t} \log_e \frac{r_\infty - r_0}{r_\infty - r_t} & (d) k = \frac{1}{t} \log_e \frac{r_\infty - r_t}{r_\infty - r_0} \end{array}$$

121. Rate of a chemical reaction can be kept constant by: (BHU 1993)

- (a) stirring the compounds
 (b) keeping the temperature constant
 (c) both (a) and (b)
 (d) none of the above

122. The number of molecules of the reactants taking part in a single step of the reaction tells about: (AMU 1992)
 (a) molecularity of the reaction
 (b) mechanism of the reaction
 (c) order of reaction
 (d) all of the above

123. Number of moles of a substance present in 1 litre volume is known as: [PMT (MP) 1993]
 (a) activity (b) molar concentration
 (c) active mass (d) none of these

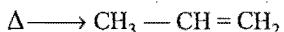
124. The inversion of cane sugar into glucose and fructose is:
 (a) I order (b) II order (c) III order (d) zero order
125. The unit of rate constant obeying the rate expression $r = k[A][B]^{2/3}$ is:
 (a) $\text{mol}^{-2/3} \text{ litre}^{2/3} \text{ time}^{-1}$ (b) $\text{mol}^{2/3} \text{ litre}^{-2/3} \text{ time}^{-1}$
 (c) $\text{mol}^{-5/3} \text{ litre}^{5/3} \text{ time}^{-1}$ (d) none of these

126. For the reaction,
- $$\text{N}_2\text{O}_5 \longrightarrow 2\text{NO}_2 + 1/2\text{O}_2,$$
- $$-\frac{d[\text{N}_2\text{O}_5]}{dt} = k_1[\text{N}_2\text{O}_5]$$
- $$\frac{d[\text{NO}_2]}{dt} = k_2[\text{N}_2\text{O}_5]$$
- $$\frac{d[\text{O}_2]}{dt} = k_3[\text{N}_2\text{O}_5]$$

The relation in between k_1 , k_2 and k_3 is:

- (a) $2k_1 = k_2 = 4k_3$ (b) $k_1 = k_2 = k_3$
 (c) $2k_1 = 4k_2 = k_3$ (d) none of these
127. The rate constant is numerically the same for three reactions of first, second and third order respectively. Which one is true for the rates of the three reactions if the concentration of the reactant is greater than $1 M$?
 (a) $r_1 = r_2 = r_3$ (b) $r_1 > r_2 > r_3$
 (c) $r_1 < r_2 < r_3$ (d) All of these
128. In the Q.No. 127, if the concentration of the reactant is less than $1 M$, then:
 (a) $r_1 = r_2 = r_3$ (b) $r_1 > r_2 > r_3$
 (c) $r_1 < r_2 < r_3$ (d) all of these
129. In the Q.No. 127, if the concentration of the reactant is $1 M$, then:
 (a) $r_1 = r_2 = r_3$ (b) $r_1 > r_2 > r_3$
 (c) $r_1 < r_2 < r_3$ (d) all of these
130. For a first order reaction, $A \longrightarrow \text{Product}$, the rate of reaction at $[A] = 0.2 \text{ mol L}^{-1}$ is $1.0 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1}$. The half life period for the reaction is: (IIT 1999)
 (a) 832 s (b) 440 s (c) 416 s (d) 14 s
131. The rate constant of a first order reaction, $A \longrightarrow \text{Products}$, is $60 \times 10^{-4} \text{ min}^{-1}$. Its rate at $[A] = 0.01 \text{ mol L}^{-1}$ would be: (IIT 1997)
 (a) $60 \times 10^{-6} \text{ mol L}^{-1} \text{ min}^{-1}$ (b) $36 \times 10^{-4} \text{ mol L}^{-1} \text{ min}^{-1}$
 (c) $60 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1}$ (d) $36 \times 10^{-1} \text{ mol L}^{-1} \text{ min}^{-1}$
132. For a first order reaction, the half life is independent of: (CBSE 1999)
 (a) initial concentration
 (b) cube root of initial concentration
 (c) first power of final concentration
 (d) square root of final concentration
133. Activation energy of a chemical reaction can be determined by: (CBSE 1998)
 (a) changing concentration of reactants
 (b) evaluating rate constant at standard temperature
 (c) evaluating rate constants at two different temperatures
 (d) evaluating velocities of reaction at two different temperatures
134. The experimental data for the reaction $2A + B_2 \rightarrow 2AB$, is:
- | Expt. No. | [A] | [B ₂] | Rate (mol s ⁻¹) |
|-----------|------|-------------------|-----------------------------|
| 1. | 0.50 | 0.50 | 1.6×10^{-4} |
| 2. | 0.50 | 1.00 | 3.2×10^{-4} |
| 3. | 1.0 | 1.00 | 3.2×10^{-4} |
- The rate equation for the above data is: (CBSE 1997)
 (a) rate = $k[B_2]^2$ (b) rate = $k[B_2]$
 (c) rate = $k[A]^2[B]^2$ (d) rate = $k[A]^2[B]$
135. For the reaction $A \rightarrow B$, the rate law is: rate = $k[A]$. Which of the following statements is incorrect? [PMT (Pb.) 1998]
 (a) The reaction follows first order kinetics
 (b) The $t_{1/2}$ of the reaction depends on initial concentration
 (c) k is constant for the reaction at a constant temperature
 (d) The rate law provides a simple way of predicting the concentration of reactants at any time after the start of the reaction

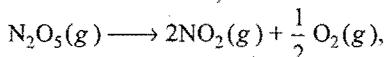
136. Cyclopropane rearranges to form propene:



This follows first order kinetics. The rate constant is $2.714 \times 10^{-3} \text{ sec}^{-1}$. The initial concentration of cyclopropane is 0.29 M. What will be the concentration of cyclopropane after 100 sec? [JEE (Orissa) 2009]

- (a) 0.035 M (b) 0.22 M
 (c) 0.145 M (d) 0.0018 M

137. The rate constant for the reaction,



is $2.3 \times 10^{-2} \text{ sec}^{-1}$. Which equation given below describes the change of $[\text{N}_2\text{O}_5]$ with time $[\text{N}_2\text{O}_5]_0$ and $[\text{N}_2\text{O}_5]_t$ correspond to concentration of N_2O_5 initially and time 't'? (AIIMS 2004)

- (a) $[\text{N}_2\text{O}_5]_0 = [\text{N}_2\text{O}_5]_t e^{kt}$
 (b) $\log_e \frac{[\text{N}_2\text{O}_5]_0}{[\text{N}_2\text{O}_5]_t} = kt$
 (c) $\log_{10} [\text{N}_2\text{O}_5]_t = \log_{10} [\text{N}_2\text{O}_5]_0 - kt$
 (d) $[\text{N}_2\text{O}_5]_t = [\text{N}_2\text{O}_5]_0 + kt$

138. The reaction, $X \longrightarrow Y$ (Product) follows first order kinetics.

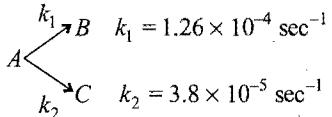
In 40 minutes, the concentration of X changes from 0.1 M to 0.025 M, then the rate of reaction when concentration of X is 0.01 M is: [IIT (S) 2004]

- (a) $1.73 \times 10^{-4} \text{ M/min}$ (b) $3.47 \times 10^{-5} \text{ M/min}$
 (c) $3.47 \times 10^{-4} \text{ M/min}$ (d) $1.73 \times 10^{-5} \text{ M/min}$

139. In a first order reaction, the concentration of the reactant, decreases from 0.8 M to 0.4 M in 15 minutes. The time taken for the concentration to change from 0.1 M to 0.025 M is:

- (a) 30 min (b) 15 min (c) 7.5 min (d) 60 min

140. A substance undergoes first order decomposition. The decomposition follows two parallel first order reactions as;



The percentage distribution of B and C are:

[PMT (Kerala) 2004]

- (a) 75% B and 25% C (b) 80% B and 20% C
 (c) 60% B and 40% C (d) 90% B and 10% C
 (e) 76.83% B and 23.17% C

141. For a reaction $2\text{NH}_3 \longrightarrow \text{N}_2 + 3\text{H}_2$, it is observed that $\frac{-d(\text{NH}_3)}{dt} = k_1(\text{NH}_3)$, $\frac{d(\text{N}_2)}{dt} = k_2(\text{NH}_3)$, $\frac{d(\text{H}_2)}{dt} = k_3(\text{NH}_3)$.

What is the relation between k_1 , k_2 and k_3 ?

- (a) $k_1 = k_2 = k_3$ (b) $3k_1 = 6k_2 = 2k_3$
 (c) $2k_1 = 3k_2 = 6k_3$ (d) $6k_1 = 3k_2 = 2k_3$

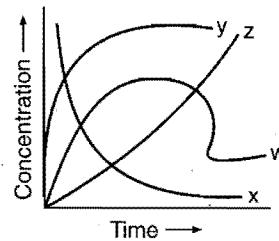
142. In Arrhenius equation $k = Ae^{-E_a/RT}$, factor $e^{-E_a/RT}$ is known as:

- (a) frequency factor (b) activation factor
 (c) pre-exponential factor (d) Boltzmann factor

143. Unit of frequency factor (A) is:

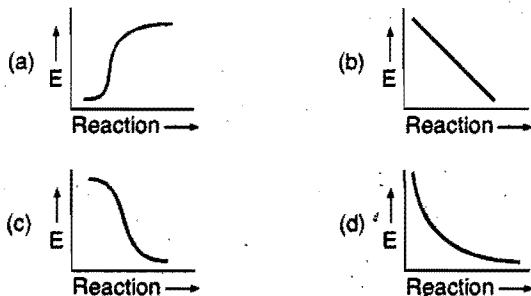
- (a) moles/lit (b) moles/lit/sec
 (c) depends upon order (d) no unit

144. For the reaction $A + B \longrightarrow C + D$, the variation of the concentration of the products is given by the curve:



- (a) x (b) y (c) z (d) w

145. Which graph shows zero activation energy?



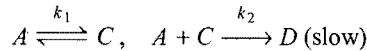
146. $E_{\text{Threshold}}$ can never be:

- (a) $> E_R$ (b) $> E_P$
 (c) $< E_P$ (d) $> E_R$ as well as $> E_P$

147. A reaction takes place in three steps; the rate constants are k_1 , k_2 and k_3 . The overall rate constant $k = \frac{k_1 k_2}{k_2}$. If energies of activation are 40, 30 and 20 kJ, the overall energy of activation is:

- (a) 10 (b) 15 (c) 30 (d) 60

148. For hypothetical reaction $A \rightarrow B$ takes place according to



Rate law will be:

- (a) $k_2[A][C]$ (b) $k_1 k_2[A]$ (c) $k_1 k_2[A]^2$ (d) $k_1 k_2[A][C]$

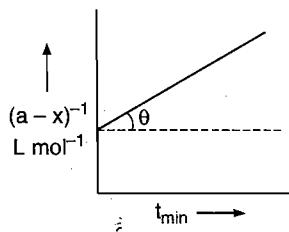
149. If concentration of reactant is increased by ' m '; then k becomes:

- (a) e^{km} (b) k (c) k/m (d) mk

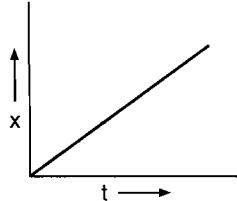
150. $aA + bB \longrightarrow P$; $\frac{dx}{dt} = k[A]^a[B]^b$. If conc. of A is doubled, rate is doubled. If B is doubled, rate becomes four times. Which is correct?

- (a) $\frac{-d[A]}{dt} = \frac{-d[B]}{dt}$ (b) $\frac{-d[A]}{dt} = \frac{-2d[B]}{dt}$
 (c) $\frac{-2d[A]}{dt} = \frac{-d[B]}{dt}$ (d) None of these

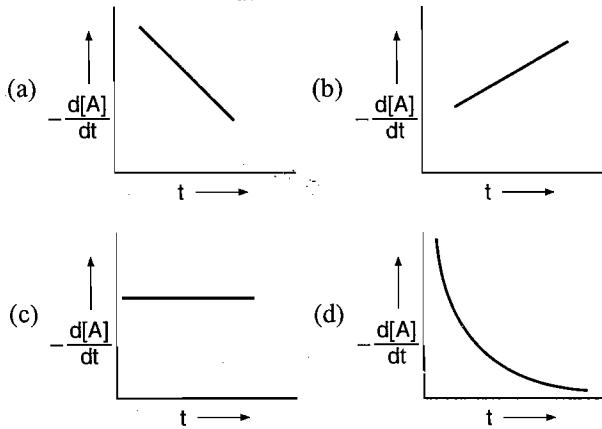
151. A drop of solution (volume 0.05 mL) contains 3×10^{-6} mole of H^+ . If the rate constant of disappearance of H^+ is $10^7 \text{ mol litre}^{-1} \text{ sec}^{-1}$, how long would it take for H^+ in the drop to disappear?
 (a) $6 \times 10^{-8} \text{ sec}$ (b) $6 \times 10^{-9} \text{ sec}$
 (c) $6 \times 10^{-10} \text{ sec}$ (d) $6 \times 10^{-12} \text{ sec}$
152. For the reaction, $\text{H}_2 + \text{I}_2 \xrightleftharpoons[k_2]{k_1} 2\text{HI}$. The rate law expression is:
 (a) $\left[-\frac{1}{2} \frac{d[\text{HI}]}{dt} \right] = k_1 [\text{H}_2][\text{I}_2]$
 (b) $\left[-\frac{1}{2} \frac{d[\text{HI}]}{dt} \right] = \frac{k_1 [\text{HI}]^2}{k_2 [\text{H}_2][\text{I}_2]}$
 (c) $\left[-\frac{1}{2} \frac{d[\text{HI}]}{dt} \right] = k_1 [\text{H}_2][\text{I}_2] - k_2 [\text{HI}]^2$
 (d) $\left[-\frac{1}{2} \frac{d[\text{HI}]}{dt} \right] = k_1 k_2 [\text{H}_2][\text{I}_2]$
153. The chemical reaction, $2\text{O}_3 \rightarrow 3\text{O}_2$ proceeds as;
 $\text{O}_3 \rightleftharpoons \text{O}_2 + \text{O}$ (fast), $\text{O} + \text{O}_3 \rightarrow 2\text{O}_2$ (slow)
 The rate law expression will be:
 (a) rate = $k[\text{O}][\text{O}_3]$ (b) rate = $k[\text{O}_3]^2$
 (c) rate = $k[\text{O}_3]^2[\text{O}_2]^{-1}$ (d) can't be determined
154. For the reaction $\text{NH}_4^+ + \text{OCN}^- \rightarrow \text{NH}_2\text{CONH}_2$, the probable mechanism is,
 $\text{NH}_4^+ + \text{OCN}^- \rightleftharpoons \text{NH}_4\text{OCN}$ (fast)
 and $\text{NH}_4\text{OCN} \rightarrow \text{NH}_2\text{CONH}_2$ (slow)
 The rate law will be:
 (a) rate = $k[\text{NH}_2\text{CONH}_2]$ (b) rate = $k[\text{NH}_4^+][\text{OCN}^-]$
 (c) rate = $k[\text{NH}_4\text{OCN}]$ (d) none of these
155. For a 1st order decomposition,
- $$\begin{array}{ccccc} & & A & & \\ & \swarrow k_n & \downarrow k_1 & \searrow k_2 & \\ A_1 & & & & A_2 \end{array}$$
- overall k will be given by:
 (a) $k = k_1 + k_2 + \dots + k_n$ (b) $k = (k_1 + k_2 + \dots + k_n)/n$
 (c) $k = k_1 \times k_2 \times \dots \times k_n$ (d) none of these
156. For a reaction $A + 3B \rightarrow P$, Rate = $\frac{-d[A]}{dt}$, the expression for the rate of reaction in terms of change in the concentration of B , $\frac{-d[B]}{dt}$ will be:
 (a) $k[A]^2[B]$ (b) $k[A]^2[3B]$
 (c) $3k[A]^2[B]$ (d) $(\frac{1}{3})k[A]^2[B]$
157. Which of the following statements is correct?
 (a) Rate of reaction $\propto \frac{1}{E_a}$
 (b) At lower temp., increase in temp. causes more change in the value of k
 (c) Both (a) and (b) are correct
 (d) None is correct
158. For $X \rightarrow Y$; $k = 10^{10} e^{-500/T}$, and for $W \rightarrow Z$; $k = 10^{12} e^{-1000/T}$ at what temperature 'T' both reactions will have same value of k ?
 (a) 500 K (b) 1500 K
 (c) $\frac{4.606}{500}$ K (d) $\frac{2.303}{5000}$ K
159. For a reversible reaction where the forward reaction is exothermic, which of the following statements is correct?
 [JEE (WB) 2010]
 (a) The backward reaction has higher activation energy than the forward reaction
 (b) The backward and the forward processes have same activation energy
 (c) The backward reaction has lower activation energy
 (d) No activation energy is required at all since energy is liberated in the process
160. For the reaction, $A + 3B \rightarrow 2C + D$ which one of the following is not correct?
 [EAMCET (Med.) 2010]
 (a) Rate of disappearance of A = Rate of formation of D
 (b) Rate of formation of $C = \frac{2}{3} \times$ Rate of disappearance of B .
 (c) Rate of formation of $D = \frac{1}{3} \times$ Rate of disappearance of B
 (d) Rate of disappearance of $A = 2 \times$ Rate of formation of C
161. $2A \rightarrow B + C$, would be a zero order reaction when:
 [CBSE (PMT) 2002]
 (a) the rate of reaction is proportional to square of concentration of 'A'
 (b) the rate of reaction is same at any concentration of 'A'
 (c) the rate remains unchanged at any concentration of 'B' and 'C'
 (d) the rate of reaction doubles if concentration of 'B' is increased to double
162. Units of rate constants for first and zero order reactions in terms of molarity M unit are respectively: (AIEEE 2002)
 (a) $\text{sec}^{-1}, M \text{ sec}^{-1}$ (b) sec^{-1}, M
 (c) $M \text{ sec}^{-1}, \text{sec}^{-1}$ (d) M, sec^{-1}
163. Following is the graph between $\log t_{1/2}$ and $\log a$ (a = initial concentration) for a given reaction at 27°C. Hence, order is:
-
164. Following is the graph between $(a-x)^{-1}$ and time t for second order reaction. $\theta = \tan^{-1}(1/2)$; $OA = 2 \text{ L mol}^{-1}$, hence rate at the start of reaction will be:
 (a) 0 (b) 1 (c) 2 (d) 3



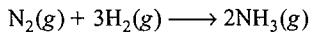
164. (a) $1.25 \text{ L mol}^{-1} \text{ min}^{-1}$ (b) $0.5 \text{ mol L}^{-1} \text{ min}^{-1}$
 (c) $0.125 \text{ mol L}^{-1} \text{ min}^{-1}$ (d) $1.25 \text{ mol L}^{-1} \text{ min}^{-1}$
165. Graph between concentration of the product 'x' and time 't' for $A \rightarrow B$ is given ahead:



The graph between $-\frac{d[A]}{dt}$ and time will be of the type:



166. Consider the chemical reaction,

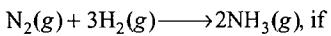


The rate of reaction can be expressed in terms of time derivative of concentration of $\text{N}_2(g)$, $\text{H}_2(g)$ or $\text{NH}_3(g)$. Identify the correct relationship amongst the rate expressions:

(IIT 2002)

- (a) rate = $-\frac{d[\text{N}_2]}{dt} = -\frac{1}{3} \frac{d[\text{H}_2]}{dt} = +\frac{1}{2} \frac{d[\text{NH}_3]}{dt}$
 (b) rate = $-\frac{d[\text{N}_2]}{dt} = -3 \frac{d[\text{H}_2]}{dt} = +2 \frac{d[\text{NH}_3]}{dt}$
 (c) rate = $\frac{d[\text{N}_2]}{dt} = \frac{1}{3} \frac{d[\text{H}_2]}{dt} = \frac{1}{2} \frac{d[\text{NH}_3]}{dt}$
 (d) rate = $-\frac{d[\text{N}_2]}{dt} = -\frac{d[\text{H}_2]}{dt} = \frac{d[\text{NH}_3]}{dt}$

167. For the reaction,



$\frac{d[\text{NH}_3]}{dt} = 2 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$, the value of $\frac{-d[\text{H}_2]}{dt}$ would be:

(CBSE (PMT) 2009)

- (a) $1 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$ (b) $3 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
 (c) $4 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$ (d) $6 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$

168. Temperature dependent equation can be written as:

[JEE (Orissa) 2005]

- (a) $\ln k = \ln A - e^{E_a/RT}$ (b) $\ln k = \ln A + e^{E_a/RT}$
 (c) $\ln k = \ln A - e^{RT/E_a}$ (d) all of these

169. If the rate of reaction $A \longrightarrow B$ doubles on increasing the concentration of A by 4 times, the order of reaction is:

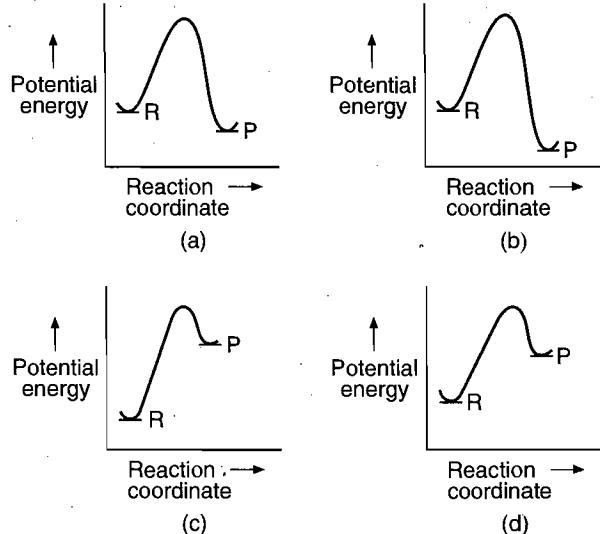
[CET (J&K) 2005]

- (a) 2 (b) 1 (c) 1/2 (d) 4
 170. For the reaction: $2\text{N}_2\text{O}_5(g) \longrightarrow 4\text{NO}_2(g) + \text{O}_2(g)$ if the concentration of NO_2 increases by $5.2 \times 10^{-3} \text{ M}$ in 100 sec, then the rate of reaction is: [PET (Kerala) 2005]
 (a) $1.3 \times 10^{-5} \text{ M s}^{-1}$ (b) $5 \times 10^{-4} \text{ M s}^{-1}$
 (c) $7.6 \times 10^{-4} \text{ M s}^{-1}$ (d) $2 \times 10^{-3} \text{ M s}^{-1}$
 (e) $2.5 \times 10^{-5} \text{ M s}^{-1}$

171. A first order reaction is 10% complete in 20 min. The time taken for 19% completion is: [PET (Kerala) 2005]

- (a) 30 min (b) 40 min (c) 50 min (d) 38 min
 (e) 45 min

172. An endothermic reaction with high activation energy for the forward reaction is given by the diagram: (AIIMS 2005)



173. For reaction $aA \longrightarrow xP$, when $[A] = 2.2 \text{ m-M}$, the rate was found to be 2.4 m M s^{-1} . On reducing concentration of A to half, the rate changes to 0.6 m M s^{-1} . The order of reaction with respect to A is: (AIIMS 2005)

- (a) 1.5 (b) 2.0 (c) 2.5 (d) 3.0

[Hint: Rate = $k [A]^a$]

$$2.4 = k [2.2]^a \quad \dots \text{(i)}$$

$$0.6 = k [1.1]^a \quad \dots \text{(ii)}$$

Dividing eq. (i) by eq. (ii), $a = 2 \therefore \text{order} = 2$

174. According to the law of mass action, rate of a chemical reaction is proportional to: (AFMC 2005)

- (a) concentration of reactants
 (b) molar concentration of reactants
 (c) concentration of products
 (d) molar concentration of products
175. Consider the endothermic reaction $X \rightarrow Y$ with the activation energies E_b and E_f for backward and forward reactions, respectively. In general: (AIEEE 2005)
- (a) $E_b < E_f$
 (b) $E_b > E_f$
 (c) $E_b = E_f$
 (d) there is no definite relation between E_f and E_b
176. Which one of the following statements for order of reaction is not correct? [IIT (S) 2005]
- (a) Order can be determined experimentally
 (b) Order of reaction is equal to sum of powers of concentration terms in differential rate law
 (c) It is not affected by the stoichiometric coefficient of the reactants
 (d) Order cannot be fractional
177. The rate constant of a reaction is found to be 3×10^{-3} mol L⁻¹ min⁻¹. The order of the reaction is: [CET (J&K) 2006]
- (a) zero (b) 1 (c) 2 (d) 1.5
- [Hint: Unit of rate and rate constants are same for zero order reaction.]
178. In the first order reaction, the concentration of the reactants is reduced to 25% in one hour. The half life period of the reaction is: [UGET (Manipal) 2005]
- (a) 2 hrs (b) 4 hrs (c) 1/2 hr (d) 1/4 hr
- [Hint: $k = \frac{2.303}{t} \log\left(\frac{a}{a-x}\right)$
- $$k = \frac{2.303}{1} \log\left(\frac{100}{25}\right) = 2 \times 0.693$$
- $$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{2 \times 0.693} = \frac{1}{2} \text{ hr}]$$
179. A substance reacts with initial concentration of a mol dm⁻³ according to zero order kinetics. The time it takes for the completion of the reaction is: (k = rate constant) [AIEE 2006; CET (Karnataka) 2009]
- (a) $\frac{k}{a}$ (b) $\frac{a}{2k}$ (c) $\frac{a}{k}$ (d) $\frac{2k}{a}$
 (e) ka
- [Hint: $x = k \times t$
- $$t = \frac{x}{k}$$
- Time for completion of reaction (when
- $x = a$
-), i.e.,
- $t = \frac{a}{k}$
-]
180. Rate of a reaction can be expressed by Arrhenius equation as, $k = Ae^{-E_a/RT}$. In this equation, E represents: (AIEEE 2006)
- (a) the energy above which all the colliding molecules will react
 (b) the energy below which colliding molecules will not react
 (c) the total energy of the reacting molecules at a temperature T
 (d) the fraction of molecules with energy greater than the activation energy of the reaction
181. The rate constant of a first order reaction at 27°C is 10^{-3} min⁻¹. The temperature coefficient of this reaction is 2. What is the rate constant (in min⁻¹) at 17°C for this reaction? [VITEEE 2006]
- (a) 10^{-3} (b) 5×10^{-4} (c) 2×10^{-3} (d) 10^{-2}
- [Hint: $\frac{k_{T_2}}{k_{T_1}} = (\mu)^{\Delta T/10}$
- $$\frac{10^{-3}}{k_{T_1}} = (\mu)^{10/10} = 2$$
- $$k_{T_1} = \frac{10^{-3}}{2} = 0.5 \times 10^{-3}$$
- $$= 5 \times 10^{-4} \text{ min}^{-1}]$$
182. In a chemical reaction, two reactants take part. The rate of reaction is directly proportional to the concentration of one of them and inversely proportional to the concentration of the other. The order of the reaction is: [PMT (Raj.) 2006]
- (a) zero (b) 1 (c) 2 (d) 4
183. According to Arrhenius equation, the rate constant (k) is related to temperature (T) as: (VITEEE 2007)
- (a) $\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$
 (b) $\ln\left(\frac{k_2}{k_1}\right) = -\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$
 (c) $\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} + \frac{1}{T_2}\right)$
 (d) $\ln\left(\frac{k_2}{k_1}\right) = -\frac{E_a}{R}\left(\frac{1}{T_1} + \frac{1}{T_2}\right)$
184. Consider a reaction $aG + bH \rightarrow \text{Products}$. When concentration of both the reactants G and H are doubled, the rate increases by eight times. However, when the concentration of G is doubled keeping the concentration of H fixed, the rate is doubled. The overall order of reaction is: [IIT 2007]
- (a) 0 (b) 1 (c) 2 (d) 3
- [Hint: Order with respect to ' G ' will be two and with respect to ' H ' the order will be one.
- $$\text{Rate} = k [G]^2 [H]^1$$
- When concentration of both
- G
- and
- H
- are doubled, the rate will increase eight times.]
185. The temperature dependence of rate constant (k) of a chemical reaction is written in terms of Arrhenius equation $k = Ae^{-E_a/RT}$. Activation energy (E_a) of the reaction can be calculated by plotting: [MS 2007]
- (a) $\log k$ vs T (b) $\log k$ vs $\frac{1}{T}$ (c) k vs T (d) k vs $\frac{1}{\log T}$
186. Consider the reaction, $2A + B \rightarrow \text{Products}$. When concentration of B alone was doubled, the half life did not change. When the concentration of A alone was doubled, the rate increased by two times. The unit of rate constant for this reaction is: (AIEEE 2007)
- (a) s⁻¹ (b) L mol⁻¹s⁻¹ (c) unitless (d) mol L⁻¹s⁻¹

[Hint: Concentration change in 'B' does not change half life, it means the reaction is first order with respect to B. When concentration of only 'A' is doubled, the rate of reaction becomes double, thus order with respect to A will also be one.]

Overall order of reaction = 2

unit of rate constant = L mol⁻¹s⁻¹]

187. In a first order reaction $A \rightarrow B$, if k is rate constant and initial concentration of the reactant A is 0.5 M then half life is:

[CBSE (Med) 2007]

- (a) $\frac{\log 2}{k}$ (b) $\frac{\log 2}{k\sqrt{0.5}}$ (c) $\frac{\ln 2}{k}$ (d) $\frac{0.693}{0.5k}$

188. For the first order reaction, half life is 14 sec, the time required for the initial concentration to reduce to $1/8$ of its value is:

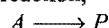
[CET (J&K) 2007]

- (a) $(14)^3\text{ sec}$ (b) 28 sec (c) 42 sec (d) $(14)^2\text{ sec}$

189. 75% of a first order reaction was completed in 32 min, when was 50% of the reaction completed? [BHU (Mains) 2007]

- (a) 24 min (b) 16 min (c) 8 min (d) 48 min

190. For a zero order reaction,



$t_{1/2}$ is: (k is rate constant)

- (a) $\frac{[A]_0}{2k}$ (b) $\frac{\ln 2}{k}$ (c) $\frac{1}{k[A]_0}$ (d) $\frac{\ln 2}{[A]_0 k}$

191. The rate constants k_1 and k_2 for two different reactions are $10^{16} e^{-2000/T}$ and $10^{15} e^{-1000/T}$, respectively. The temperature at which $k_1 = k_2$ is:

[CBSE (PMT) 2008]

- (a) 2000 K (b) $\frac{1000}{2.303}$ K (c) 1000 K (d) $\frac{2000}{2.303}$ K

[Hint : $10^{15} e^{-1000/T} = 10^{16} e^{-2000/T}$

$$\frac{e^{-2000/T}}{e^{-1000/T}} = \frac{10^{15}}{10^{16}}$$

$$e^{-1000/T} = 10^{-1}$$

$$\log_e e^{-1000/T} = \log_e 10^{-1}$$

$$-\frac{1000}{T} = 2.303 \log_{10} 10^{-1}$$

$$= -2.303$$

$$T = \frac{1000}{2.303} \text{ K}$$

192. Under the same reaction conditions, initial concentration of 1.386 mol dm^{-3} of a substance becomes half in 40 seconds and 20 seconds through first order and zero order kinetics respectively. Ratio $\left(\frac{k_1}{k_0}\right)$ of the rate constant for first order (k_1)

and zero order (k_0) of the reaction is:

(IIT 2008)

- (a) $0.5\text{ mol}^{-1}\text{ dm}^3$ (b) 1 mol dm^{-3}
(c) 1.5 mol dm^{-3} (d) $2\text{ mol}^{-1}\text{ dm}^3$

[Hint : $t_{1/2} = \frac{0.693}{k_1}$,

$$t_{1/2} = \frac{a_0}{2k_0}$$

$$40 = \frac{0.693}{k_1},$$

$$20 = \frac{1.386}{2k_0} = \frac{0.693}{k_0}$$

$$\frac{20}{40} = \frac{0.693/k_0}{0.693/k_1} = \frac{k_1}{k_0}$$

$$\frac{k_1}{k_0} = 0.5 \frac{\text{sec}^{-1}}{\text{mol dm}^{-3} \text{sec}^{-1}} = 0.5 \text{ mol}^{-1} \text{dm}^3$$

193. The decomposition of HI on the surface of gold is :

[Comed (Karnataka) 2008]

- (a) Pseudofirst order (b) zero order
(c) first order (d) second order

194. Consider following two reactions



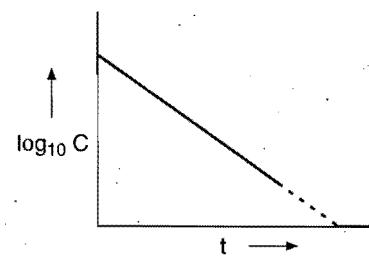
k_1 and k_2 are expressed in terms of molarity (mol L^{-1}) and time (s^{-1}) as:

- (a) $\text{s}^{-1}, \text{M s}^{-1} \text{L}^{-1}$ (b) $\text{M s}^{-1}, \text{M s}^{-1}$
(c) $\text{s}^{-1}, \text{M}^{-1} \text{s}^{-1}$ (d) $\text{M s}^{-1}, \text{s}^{-1}$

195. If a plot of $\log_{10} C$ versus t gives a straight line for a given reaction, then the reaction is:

- (a) zero order (b) first order (c) second order (d) third order

[Hint:



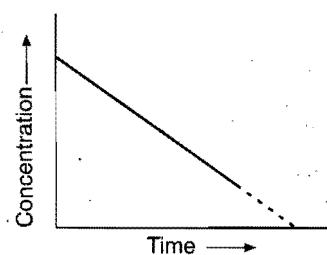
In first order reaction, $\log_{10} C$ when plotted against time 't' then we get straight line. Slope of the line $\left(\frac{2.303}{k}\right)$ gives the value of rate constant.]

196. For a zero order reaction the plot of concentration of reactant versus time is: (intercept refers to concentration axis)

[PET (Kerala) 2008]

- (a) linear with +ve slope and zero intercept
(b) linear with -ve slope and zero intercept
(c) linear with -ve slope and non zero intercept
(d) linear with +ve slope and non zero intercept
(e) a curve asymptotic to concentration axis

[Hint :



Linear with negative slope and non zero intercept.]

197. T_{50} of first order reaction is 10 min. Starting with 10 mol L^{-1} , rate after 20 min is:

(AIIMS 2008)

- (a) $0.0693\text{ mol L}^{-1} \text{min}^{-1}$
(b) $0.0693 \times 2.5\text{ mol L}^{-1} \text{min}^{-1}$

- (c) $0.0693 \times 5 \text{ mol L}^{-1} \text{ min}^{-1}$
 (d) $0.0693 \times 10 \text{ mol L}^{-1} \text{ min}^{-1}$

[Hint : Remaining concentration of reactant after 20 min

$$= \frac{1}{4} \times 10 = 2.5 \text{ mol L}^{-1}$$

Rate = $k \times [\text{Reactant}]$

$$= \frac{0.693}{t_{1/2}} \times [\text{Reactant}]$$

$$= \frac{0.693}{10} \times 2.5 = 0.0693 \times 2.5 \text{ mol L}^{-1} \text{ min}^{-1}$$

198. For the decomposition of AB at 600 K, the following data were obtained

| [AB] mol dm⁻³ | Rate of decomposition of AB in mol dm⁻³s⁻¹ |
|---------------------------------|---|
| 0.20 | 2.75×10^{-8} |
| 0.40 | 11×10^{-8} |
| 0.60 | 24.75×10^{-8} |

The order of the decomposition of AB is :

[CET (Karnataka) 2009]

- (a) 0 (b) 1 (c) 2 (d) 1.5
199. For a reaction between A and B , the initial rate of reaction is measured for various initial concentrations of A and B . The data provided are:

(DCE 2009)

| Exp. No. | [A] | [B] | Initial reaction rate (mol L⁻¹s⁻¹) |
|-----------------|------------|------------|---|
| 1. | 0.2 M | 0.3 M | 5×10^{-5} |
| 2. | 0.2 M | 0.1 M | 5×10^{-5} |
| 3. | 0.4 M | 0.05 M | 7.5×10^{-5} |

The overall order of the reaction is: (DCE 2009)

- (a) one (1) (b) two (2)
 (c) two and a half (2.5) (d) between 1 and 2
200. For a first order reaction $A \rightarrow P$, the temperature (T) dependent rate constant (k) was found to follow the equation:

$$\log k = -(2000) \frac{1}{T} + 6.0$$

The pre exponential factor A and the activation energy E_a respectively, are : (IIT 2009)

$$(a) 1 \times 10^6 \text{ s}^{-1} \text{ and } 9.2 \text{ kJ mol}^{-1}$$

$$(b) 6 \text{ s}^{-1} \text{ and } 16.6 \text{ kJ mol}^{-1}$$

$$(c) 1 \times 10^6 \text{ s}^{-1} \text{ and } 16.6 \text{ kJ mol}^{-1}$$

$$(d) 1 \times 10^6 \text{ s}^{-1} \text{ and } 38.3 \text{ kJ mol}^{-1}$$

$$[\text{Hint : } \log k = \log_{10} A - \frac{E_a}{2.303} \times \frac{1}{T}]$$

Comparing this equation with the given equation we get,

$$A = 10^6 \text{ s}^{-1}, E_a = 38.3 \text{ kJ mol}^{-1}]$$

201. The time for half-life period of a certain reaction,

$A \rightarrow \text{Product}$ is 1 hour. When the initial concentration of the reactant ' A ' is 2 mol L^{-1} . How much time does it take for its concentration to come from 0.50 to 0.25 mol L^{-1} if it is a zero order reaction? (AIEEE 2010)

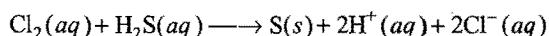
- (a) 0.25 h (b) 1 h (c) 4 h (d) 0.5 h

$$[\text{Hint : } \frac{t_1}{t_2} = \left(\frac{a_2}{a_1} \right)^{n-1}]$$

$$\frac{1}{t_2} = \left(\frac{0.5}{2} \right)^{0-1}$$

$$t_2 = 0.25 \text{ h}]$$

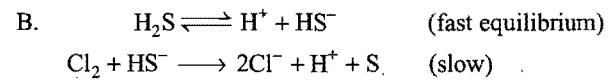
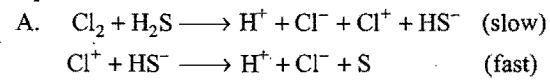
202. Consider the reaction :



The rate equation for this reaction is :

$$\text{Rate} = k [\text{Cl}_2][\text{H}_2\text{S}]$$

Which of these mechanisms is/are consistent with this rate equation?



(AIEEE 2010)

- (a) neither A nor B (b) A only
 (c) B only (d) both A and B

Assertion-Reason TYPE QUESTIONS

The questions given below consist of two statements each printed as 'Assertion' (A) and 'Reason' (R). While answering these questions you are required to choose any one of the following four options:

- (a) If both (A) and (R) are correct and (R) is the correct explanation for (A).
 - (b) If both (A) and (R) are correct but (R) is not the correct explanation for (A).
 - (c) If (A) is correct but (R) is incorrect.
 - (d) If (A) is incorrect but (R) is correct.
1. (A) The rate of reaction sometimes does not depend on concentration.
(R) The order of reaction can be negative.
 2. (A) The rate of reaction increases generally by 2 to 3 times for every 10°C rise in temperature.
(R) Increase in temperature increases the collision frequency.
 3. (A) Hydrolysis of ethyl acetate in presence of acid is a reaction of first order whereas in presence of alkali, it is a reaction of second order.
(R) Acid acts as catalyst only whereas alkali acts as one of the reactant.
 4. (A) The molecularity of the reaction, $\text{H}_2 + \text{Br}_2 \longrightarrow 2\text{HBr}$ is 2.
(R) The order of this reaction is 3/2.
 5. (A) Positive catalysts lower the activation energy of the reaction whereas heat of reaction remains same.
(R) Heat of reaction is equal to the difference between activation energies for forward and the backward reactions.
 6. (A) Positive catalysts increase the rate of reaction.
(R) Catalysts decrease the value of ΔG° .

7. (A) $k = Ae^{-E_a/RT}$, the Arrhenius equation represents the dependence of rate constant with temperature.
(R) Plot of $\log k$ against $1/T$ is linear and the activation energy can be calculated with this plot.
8. (A) If the activation energy of a reaction is zero, temperature will have no effect on the rate constant.
(R) Lower the activation energy, faster is the reaction.
9. (A) Order with respect to any reactant or product can be zero, positive, negative and fractional.
(R) Rate cannot decrease with increase in concentration of a reactant or product.
10. (A) Formation of HI is a bimolecular reaction.
(R) Two molecules of reactants are involved in this reaction.
11. (A) The order of the reaction,

$$\text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH}$$
is 2.
(R) The molecularity of this reaction is 2.
12. (A) For: $aA + bB \longrightarrow \text{Product}$. The order of the reaction is equal to $(a+b)$.
(R) Rate of reaction = $k [A]^a [B]^b$.
13. (A) The hydrolysis of methyl acetate by dil HCl is a pseudo first order reaction.
(R) HCl acts as a catalyst for the hydrolysis. (AIIMS 2007)
14. (A) The order of a reaction can have fractional value.
(R) The order of a reaction cannot be written from balanced equation of a reaction. (AIIMS 2008)

Answers : OBJECTIVE QUESTIONS

- | | | | | | | | |
|----------|----------|----------|----------|----------|-------------|----------|----------|
| 1. (c) | 2. (d) | 3. (b) | 4. (b) | 5. (a) | 6. (a) | 7. (c) | 8. (d) |
| 9. (b) | 10. (c) | 11. (a) | 12. (d) | 13. (d) | 14. (d) | 15. (b) | 16. (a) |
| 17. (c) | 18. (c) | 19. (b) | 20. (b) | 21. (c) | 22. (a) | 23. (a) | 24. (d) |
| 25. (c) | 26. (d) | 27. (a) | 28. (b) | 29. (d) | 30. (d) | 31. (d) | 32. (b) |
| 33. (a) | 34. (a) | 35. (b) | 36. (c) | 37. (d) | 38. (d) | 39. (a) | 40. (c) |
| 41. (b) | 42. (b) | 43. (d) | 44. (c) | 45. (a) | 46. (b) | 47. (c) | 48. (a) |
| 49. (d) | 50. (b) | 51. (c) | 52. (d) | 53. (a) | 54. (b) | 55. (d) | 56. (c) |
| 57. (b) | 58. (a) | 59. (c) | 60. (d) | 61. (b) | 62. (c) | 63. (d) | 64. (c) |
| 65. (a) | 66. (d) | 67. (c) | 68. (b) | 69. (c) | 70. (c) | 71. (a) | 72. (d) |
| 73. (a) | 74. (b) | 75. (d) | 76. (c) | 77. (b) | 78. (b) | 79. (d) | 80. (a) |
| 81. (d) | 82. (c) | 83. (b) | 84. (b) | 85. (c) | 86. (a) | 87. (a) | 88. (b) |
| 89. (c) | 90. (c) | 91. (b) | 92. (d) | 93. (a) | 94. (d) | 95. (d) | 96. (b) |
| 97. (b) | 98. (a) | 99. (a) | 100. (a) | 101. (d) | 102. (d) | 103. (c) | 104. (b) |
| 105. (b) | 106. (c) | 107. (a) | 108. (d) | 109. (b) | 110. (b) | 111. (d) | 112. (a) |
| 113. (c) | 114. (a) | 115. (a) | 116. (c) | 117. (a) | 118. (a, c) | 119. (b) | 120. (b) |
| 121. (b) | 122. (a) | 123. (c) | 124. (a) | 125. (a) | 126. (a) | 127. (c) | 128. (b) |
| 129. (a) | 130. (a) | 131. (a) | 132. (a) | 133. (c) | 134. (b) | 135. (b) | 136. (b) |
| 137. (b) | 138. (c) | 139. (a) | 140. (e) | 141. (c) | 142. (d) | 143. (b) | 144. (b) |
| 145. (c) | 146. (c) | 147. (c) | 148. (c) | 149. (b) | 150. (c) | 151. (b) | 152. (c) |
| 153. (c) | 154. (b) | 155. (a) | 156. (c) | 157. (c) | 158. (c) | 159. (a) | 160. (d) |
| 161. (b) | 162. (a) | 163. (a) | 164. (c) | 165. (c) | 166. (a) | 167. (b) | 168. (a) |
| 169. (c) | 170. (a) | 171. (b) | 172. (c) | 173. (b) | 174. (b) | 175. (a) | 176. (d) |
| 177. (a) | 178. (c) | 179. (c) | 180. (b) | 181. (b) | 182. (a) | 183. (a) | 184. (d) |
| 185. (b) | 186. (b) | 187. (c) | 188. (c) | 189. (b) | 190. (a) | 191. (b) | 192. (a) |
| 193. (b) | 194. (d) | 195. (b) | 196. (c) | 197. (b) | 198. (c) | 199. (d) | 200. (d) |
| 201. (a) | 202. (b) | | | | | | |

Answers : ASSERTION-REASON TYPE QUESTIONS

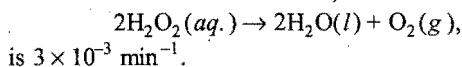
- | | | | | | | | |
|--------|---------|---------|---------|---------|---------|--------|--------|
| 1. (b) | 2. (b) | 3. (a) | 4. (b) | 5. (b) | 6. (c) | 7. (a) | 8. (b) |
| 9. (c) | 10. (a) | 11. (d) | 12. (b) | 13. (b) | 14. (b) | | |

BRAIN STORMING PROBLEMS

OBJECTIVE QUESTIONS for IIT ASPIRANTS

- Which of the following is correct?
 - Molecularity of a reaction can be fractional
 - Zero order reaction never stops
 - A first order reaction must be homogeneous
 - The frequency factor 'A' in Arrhenius equation ($k = Ae^{-E_a/RT}$) increases with increase in temperature

- The rate constant of the reaction,



At what concentration of H_2O_2 , the rate of the reaction will be $2 \times 10^{-4} \text{ M s}^{-1}$?

- $6.67 \times 10^{-3} \text{ M}$
- 2 M
- 4 M
- 0.08 M

[Hint: Rate = $k [\text{H}_2\text{O}_2]^1$

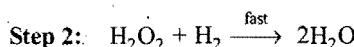
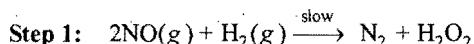
$$2 \times 10^{-4} = \frac{3 \times 10^{-3}}{60} \times [\text{H}_2\text{O}_2]$$

$$[\text{H}_2\text{O}_2] = 4 \text{ M}$$

- The mechanism of the reaction,



is:



- rate = $k [\text{NO}]^2 [\text{H}_2]^2$
- rate = $k [\text{H}_2\text{O}_2][\text{H}_2]$
- on doubling the concentration of H_2 , keeping the concentration of NO constant, the rate will become double
- if the initial concentration of H_2 and NO is C_0 and after time 't' the concentration of N_2 is x , then

$$\text{Rate} = k(C_0 - 2x)^x$$

[Hint: Slowest step is rate determining

$$\therefore \text{Rate} = k [\text{NO}]^2 [\text{H}_2]$$

∴ On doubling the concentration of H_2 without changing the concentration of NO, the rate will become double.]

- The rate law for a reaction between A and B is given by:

$$\text{Rate} = k [A]^n [B]^m$$

On doubling the concentration of A and halving the concentration of B , the ratio of new rate to the earlier rate of the reaction will be as:

- $n - m$
- 2^{n-m}
- $2^{1/(n+m)}$
- 2^{m-n}

- The reaction $A \xrightarrow{k}$ Product, is zero order while the reaction $B \xrightarrow{k}$ Product, is first order reaction. For what initial concentration of A , are the half lives of the two reactions equal?
 - $(\log_e 4) M$
 - $2 M$
 - $2 \log 2 M$
 - $\ln 2 M$

[Hint: For zero order reaction,

$$x = kt$$

$$\therefore \frac{a}{2} = k \times t_{1/2}, \text{ i.e., } t_{1/2} = \frac{a}{2k} \quad \dots (i)$$

For first order reaction,

$$t_{1/2} = \frac{\log_e 2}{k} \quad \dots (ii)$$

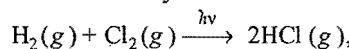
$$\text{From eqs. (i) and (ii), } \frac{a}{2k} = \frac{\log_e 2}{k}$$

$$a = \log_e 4 M]$$

- Which of the following is pseudo-unimolecular reaction?

- $2\text{H}_2\text{O}_2 \longrightarrow 2\text{H}_2\text{O} + \text{O}_2$
- $\text{C}_6\text{H}_5\text{N}_2\text{Cl} + \text{HOH} \longrightarrow \text{C}_6\text{H}_5\text{OH} + \text{N}_2 + \text{HCl}$
- $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{NaOH} \longrightarrow \text{CH}_3\text{COONa} + \text{C}_2\text{H}_5\text{OH}$
- $2\text{O}_3 \longrightarrow 3\text{O}_2$

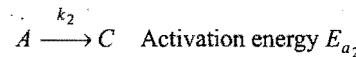
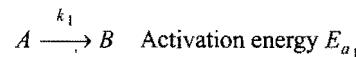
- The order and molecularity of the chain reaction,



are:

- 2, 0
- 0, 2
- 1, 1
- 3, 0

- A reactant (A) forms two products:



If $E_{a_2} = 2E_{a_1}$, then k_1 and k_2 will be related as:

- $k_2 = k_1 e^{\frac{E_{a_1}}{RT}}$
- $k_2 = k_1 e^{\frac{E_{a_2}}{RT}}$
- $k_1 = A k_2 e^{\frac{E_{a_1}}{RT}}$
- $k_1 = 2k_2 e^{\frac{E_{a_2}}{RT}}$

[Hint: $k_2 = A e^{-E_{a_2}/RT}$

$$k_1 = A e^{-E_{a_1}/RT}$$

$$\frac{k_2}{k_1} = e^{(-E_{a_2} + E_{a_1})/RT}$$

$$\frac{k_2}{k_1} = e^{\frac{E_{a_1}}{RT}}$$

Since, $E_{a_2} = 2E_{a_1}$

$$k_2 = k_1 e^{\frac{E_{a_1}}{RT}}$$

- Collision theory is satisfactory for:

- first order reactions
- second order reactions
- bimolecular reactions
- zeroth order reactions

- Initial concentration of reactant for n th order reaction is ' a '. Which of the following relations is correct about $t_{1/2}$ of the reaction?

- $\ln t_{1/2} = \ln (\text{constant}) - (n-1) \log_e a$
- $\ln t_{1/2} = \ln n + \ln (\text{constant}) - \ln a$
- $t_{1/2} \ln n = \ln (\text{constant}) + \ln a_0$
- $\ln t_{1/2} = n \ln a_0$

[Hint: $t_{1/2} \propto \frac{1}{a^{n-1}}$
 $t_{1/2} = k \frac{1}{a^{n-1}}$

$\ln t_{1/2} = \ln k - (n-1) \log_e a$

11. Half life of a reaction becomes half when initial concentrations of reactants are made double. The order of the reaction will be:
 (a) 1 (b) 2 (c) 0 (d) 3

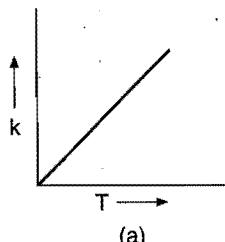
[Hint: $t_{1/2} \propto \frac{1}{a^{n-1}}$
 $t_{1/2} \propto \frac{1}{a}$

where, n = order of reaction for second order reaction.]

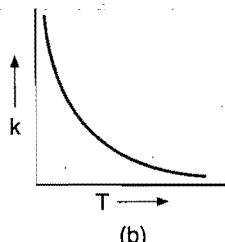
12. Arrhenius equation is:

$$k = Ae^{-E/RT}$$

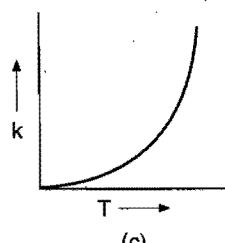
Which of the following graphs represents the variation of rate constant k against temperature T ? (IIT 2010)



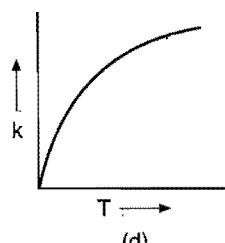
(a)



(b)

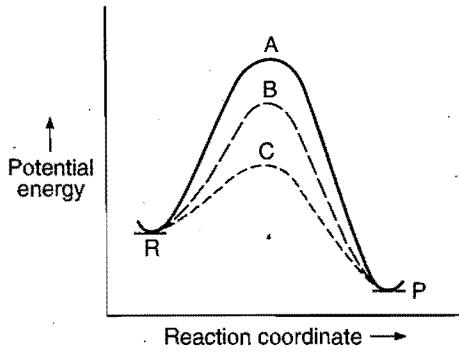


(c)



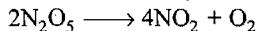
(d)

13. If a homogeneous catalytic reaction follows three alternative paths A, B and C, then which of the following indicates the relative ease with which the reaction moves?



- (a) $A > B > C$ (b) $C > B > A$ (c) $A > C > B$ (d) $A = B = C$

14. The rate constant for the reaction,



is $3 \times 10^{-5} \text{ sec}^{-1}$. If the rate is $2.4 \times 10^{-5} \text{ mol litre}^{-1} \text{ sec}^{-1}$, then the concentration of N_2O_5 in mol litre^{-1} will be:

- (a) 1.4 (b) 2.1 (c) 1.27 (d) 0.8

[Hint: Rate = $k [\text{N}_2\text{O}_5]$

$$2.4 \times 10^{-5} = 3 \times 10^{-5} [\text{N}_2\text{O}_5]$$

$$[\text{N}_2\text{O}_5] = 0.8 \text{ M}$$

15. Consider the following statements:

1. The rate of reaction is always proportional to the concentrations of reactants.
2. The order of an elementary chemical reaction step can be determined by examining its stoichiometry.
3. The first order reactions follow an exponential time course.

Of these statements:

- (a) 1, 2 and 3 are correct (b) 1 and 2 are correct
- (c) 2 and 3 are correct (d) 1 and 3 are correct

[Hint: Statement (1) cannot be correct because the rate of zero order reactions does not depend on concentration of reactant.]

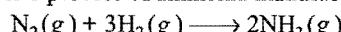
16. Two different first order reactions have rate constants k_1 and k_2 at T_1 ($k_1 > k_2$). If temperature is increased from T_1 to T_2 , then new constants become k_3 and k_4 respectively. Which among the following relations is correct?

- (a) $k_1 > k_2 = k_3 = k_4$ (b) $k_1 < k_3$ and $k_2 < k_4$
- (c) $k_1 = k_3 = k_4$ (d) $k_1 > k_2 > k_3 > k_4$

17. In the reaction, $A + B \longrightarrow C + D$, the rate $\left(\frac{dx}{dt}\right)$ when plotted against time 't' gives a straight line parallel to time axis. The order and rate of reaction will be:

- (a) 1, $k+1$ (b) 0, k (c) 1, $k+1$ (d) $k, k+1$

18. In the Haber's process of ammonia manufacture,



the rate of appearance of NH_3 is:

$$\frac{d[\text{NH}_3]}{dt} = 2 \times 10^{-4} \text{ mol L}^{-1} \text{ sec}^{-1}$$

The rates of the reaction expressed in terms of N_2 and H_2 will be:

Rates in terms of H_2
 $(\text{mol L}^{-1} \text{ sec}^{-1})$

- | | | |
|-----|--------------------|--------------------|
| (a) | 3×10^{-4} | 2×10^{-4} |
| (b) | 3×10^{-4} | 1×10^{-4} |
| (c) | 1×10^{-4} | 3×10^{-4} |
| (d) | 2×10^{-4} | 2×10^{-4} |

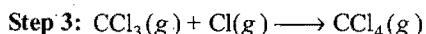
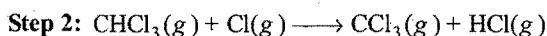
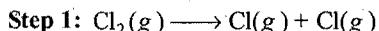
[Hint: Rate = $\frac{1}{2} \frac{d[\text{NH}_3]}{dt} = \frac{-d[\text{N}_2]}{dt} = \frac{1}{3} \frac{d[\text{N}_2]}{dt}$
 $\frac{-d[\text{H}_2]}{dt} = \frac{3}{2} \times \frac{d[\text{NH}_3]}{dt}$
 $= \frac{3}{2} \times 2 \times 10^{-4} = 3 \times 10^{-4} \text{ mol L}^{-1} \text{ sec}^{-1}$
 $\frac{-d[\text{N}_2]}{dt} = \frac{1}{2} \frac{d[\text{NH}_3]}{dt} = \frac{1}{2} \times 2 \times 10^{-4}$
 $= 1 \times 10^{-4} \text{ mol L}^{-1} \text{ sec}^{-1}$]

19. A reaction $A \longrightarrow B$, involves following mechanism:

Step 1: $A \xrightarrow{k_1} B$ (fast)

Step 2: $B \xrightarrow{k_2} C$ (slow)

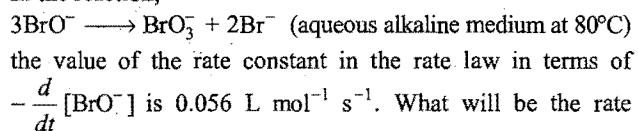
Step 3: $C \xrightarrow{k_3} D$ (fast)



If this reaction is first order in CHCl_3 and half order in Cl_2 , which statement about the relative rates of steps 1, 2 and 3 is correct?

- (a) Step 1 is the slowest
- (b) Steps 1 and 2 must both be slow
- (c) Step 2 must be slower than step 1
- (d) Step 3 must be the slowest

31. In the reaction,



- (a) 18.7×10^{-3} L mol⁻¹ s⁻¹ (b) 37.4×10^{-3} L mol⁻¹ s⁻¹
 (c) 0.0187 L mol⁻¹ s⁻¹ (d) 18.7×10^{-2} L mol⁻¹ s⁻¹

[Hint] $-\frac{1}{3} \frac{d[\text{BrO}^-]}{dt} = \frac{d[\text{BrO}_3^-]}{dt} = +\frac{1}{2} \frac{d[\text{Br}^-]}{dt}$

Required rate constant = $\frac{1}{3} \times 0.056 \text{ L mol}^{-1} \text{ s}^{-1}$
 $= 0.0187 \text{ L mol}^{-1} \text{ s}^{-1}$

32. The dependence of the rate constant for a reaction on temperature is given by the equation $k = Ae^{-E_a/RT}$.

Under what conditions is the rate constant k the smallest?

- (a) High T and large E_a (b) High T and small E_a
 (c) Low T and large E_a (d) Low T and small E_a

33. The activation energy of a certain reaction is 87 kJ mol⁻¹. What is the ratio of the rate constants for this reaction when the temperature is decreased from 37°C to 15°C?

- (a) 5/1 (b) 8.3/1 (c) 13/1 (d) 24/1

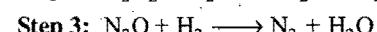
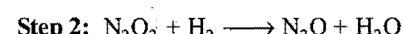
34. Consider this reaction,



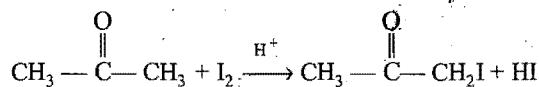
The rate law for this reaction is:

$$\text{Rate} = k [\text{H}_2][\text{NO}]^2$$

Under what conditions could these steps represent the mechanism?



- (a) These steps cannot be the mechanism under any circumstances
 - (b) These steps could be the mechanism if step 1 is the slow step
 - (c) These steps could be the mechanism if step 2 is the slow step
 - (d) These steps could be the mechanism if step 3 is the slow step
35. Propanone reacts with iodine in acid medium according to the following equation:



These data were obtained when the reaction was studied:

| $[\text{CH}_3 - \overset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{CH}_3], M$ | $[\text{I}_2], M$ | $[\text{H}^+], M$ | Relative rate |
|---|-------------------|-------------------|---------------|
| 0.010 | 0.010 | 0.010 | 1 |
| 0.020 | 0.010 | 0.010 | 2 |
| 0.020 | 0.020 | 0.010 | 2 |
| 0.020 | 0.010 | 0.020 | 4 |

What is the rate equation for the reaction?

(a) Rate = $k [\text{CH}_3 - \overset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{CH}_3][\text{I}_2]$

(b) Rate = $k [\text{CH}_3 - \overset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{CH}_3]^2$

(c) Rate = $k [\text{CH}_3 - \overset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{CH}_3][\text{I}_2][\text{H}^+]$

(d) Rate = $k [\text{CH}_3 - \overset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{CH}_3][\text{H}^+]$

36. Arrhenius equation $k = Ae^{-E_a/RT}$

If the activation energy of the reaction is found to be equal to RT , then:

- (a) the rate of reaction does not depend upon initial concentration
- (b) the rate constant becomes about 37% of the Arrhenius constant A
- (c) the rate constant becomes equal to 73% of the Arrhenius constant A
- (d) the rate of the reaction becomes infinite or zero

37. At 25°C, the values of rate constant, activation energy and Arrhenius constant of a reaction are $3 \times 10^{-4} \text{ sec}^{-1}$, 129 kJ/mol and $2 \times 10^5 \text{ sec}^{-1}$ respectively.

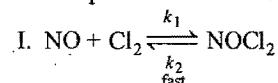
The value of rate constant as $T \rightarrow \infty$ is:

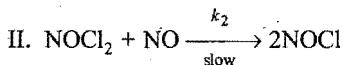
- (a) zero (b) 2×10^5 (c) 3×10^{-4} (d) 6×10^{11}

38. The observed rate of a chemical reaction is substantially lower than the collision frequency. One or more of the following statements is/are true to account for this fact.

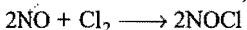
- A. the reactants do not have the required energy.
 - B. the partners do not collide in the proper orientation
 - C. collision complex exists for a very short time.
 - D. collision frequency over estimates the number of effective collisions
- (ISAT 2010)
- (a) A, B and C (b) A, B and D
 (c) B, C and D (d) A, C and D

39. The reaction between NO and Cl_2 takes place in the following two steps:





The rate law of overall reaction,



can be given by:

- (a) rate = $k [\text{NO}]^2 [\text{Cl}_2]$ (b) rate = $k [\text{NO}][\text{Cl}_2]$
 (c) rate = $k [\text{NOCl}_2][\text{NO}]$ (d) rate = $k [\text{NO}][\text{Cl}_2]^2$

40. Which of the following reactions will have fractional order for A_2 or B_2 ?

- (a) $A_2 \rightleftharpoons A + A$ (fast) (b) $A_2 \rightleftharpoons C$ (slow)
 $A + B_2 \rightleftharpoons AB + B$ (slow) $C + B_2 \rightleftharpoons D$ (fast)
 $A + B \rightleftharpoons AB$ (fast) $D + A_2 \rightleftharpoons \text{Products}$
 (c) $B_2 \rightleftharpoons B + B$ (fast) (d) All have fractional order
 $A_2 + B \rightleftharpoons AB + A$ (slow)
 $AB \longrightarrow \text{Products}$ (fast)

41. In which of the following, E_a for backward reaction is greater than E_a for forward reaction?

- $E_a = 50 \text{ kcal}$
 (a) $A \xrightarrow[E_a = 50 \text{ kcal}]{ } B; \Delta H = -10 \text{ kcal}$
 (b) $A \xrightarrow[E_a = 60 \text{ kcal}]{ } B; \Delta H = +10 \text{ kcal}$
 (c) $A \xrightarrow[E_a = 60 \text{ kcal}]{ } B; \Delta H = +20 \text{ kcal}$
 (d) All of the above

[Hint: $\Delta H = (E_a)_f - (E_a)_b$
 $(E_a)_b = (E_a)_f - \Delta H = 50 + 10 = 60 \text{ kcal}$]

42. For n th order reaction $\frac{t_{1/2}}{t_{3/4}}$ depends on ($n \neq 1$):

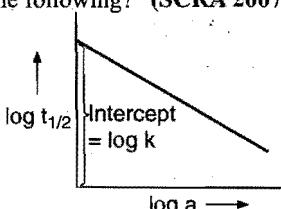
- (a) initial concentration only
 (b) ' n ' only
 (c) initial concentration and ' n ' both
 (d) sometimes ' n ' and sometimes initial concentration

[Hint: Time for fractional change $\propto \frac{1}{a^{n-1}}$]

43. For a second order reaction, $2A \longrightarrow \text{Products}$, a plot of $\log t_{1/2}$ vs $\log a$ (where, a is initial concentration) will give an intercept equal to which one of the following? (SCRA 2007)

- (a) $\frac{1}{k}$ (b) $\log\left(\frac{1}{2k}\right)$
 (c) $\log\left(\frac{1}{k}\right)$ (d) $\log k$

[Hint: Kinetic equation for second order reaction is:



$$k = \frac{1}{t} \left[\frac{1}{(a-x)} - \frac{1}{a} \right]$$

$$\text{when } x = \frac{a}{2}, t = t_{1/2}$$

$$\therefore t_{1/2} = \frac{1}{k} \times \frac{1}{a}$$

$$\log t_{1/2} = -\log k - \log a$$

44. For a reaction taking place in three steps, the rate constants are k_1 , k_2 and k_3 . The overall rate constant $k = \frac{k_1 k_2}{k_3}$. If the energy of activation values for the first, second and third stages are

respectively 40, 50 and 60 kJ mol^{-1} , then the overall energy of activation in kJ mol^{-1} is: [PMT (Kerala) 2008]

- (a) 30 (b) 40 (c) 60 (d) 50
 (e) 150

[Hint: $k = \frac{k_1 k_2}{k_3}$

$$Ae^{-E_1/RT} = \frac{Ae^{-E_1/RT} \times Ae^{-E_2/RT}}{Ae^{-E_3/RT}}$$

$$e^{-E/RT} = e^{(-E_1 - E_2 + E_3)/RT}$$

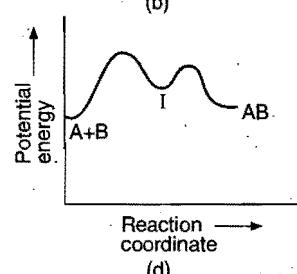
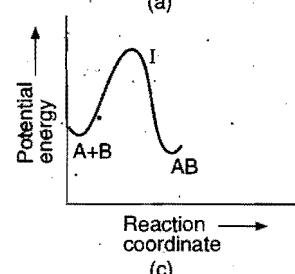
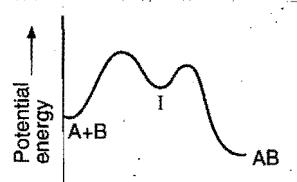
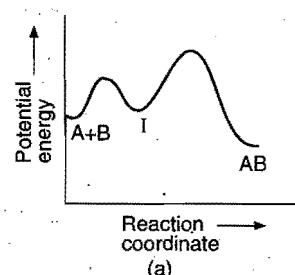
$$E = E_1 + E_2 - E_3$$

$$= 40 + 50 - 60 = 30 \text{ kJ mol}^{-1}$$

45. For an exothermic reaction, following two steps are involved.

- Step 1. $A + B \longrightarrow I$ (slow)
 Step 2. $I \longrightarrow AB$ (fast)

Which of the following graphs correctly represent this reaction?



46. A reaction takes place in three steps with individual rate constant and activation energy

| | Rate constant | Activation energy |
|--------|---------------|-------------------------------|
| Step 1 | k_1 | $E_{a1} = 180 \text{ kJ/mol}$ |
| Step 2 | k_2 | $E_{a2} = 80 \text{ kJ/mol}$ |
| Step 3 | k_3 | $E_{a3} = 50 \text{ kJ/mol}$ |

$$\text{overall rate constant, } k = \left(\frac{k_1 k_2}{k_3} \right)^{2/3}$$

overall activation energy of the reaction will be :

- (a) 140 kJ/mol (b) 150 kJ/mol
 (c) 130 kJ/mol (d) 120 kJ/mol

[Hint: $Ae^{-E_a/RT} = \left[\frac{Ae^{-E_{a1}/RT} Ae^{-E_{a2}/RT}}{Ae^{-E_{a3}/RT}} \right]^{2/3}$

$$= [Ae^{(-E_{a1} - E_{a2} + E_{a3})/RT}]^{2/3}$$

$$E_a = \frac{2}{3} [E_{a1} + E_{a2} - E_{a3}]$$

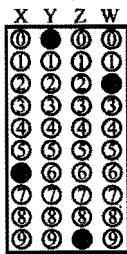
$$= \frac{2}{3} [180 + 80 - 50] = 140 \text{ kJ/mol}$$

Answers

- | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|------------|
| 1. (d) | 2. (c) | 3. (c) | 4. (b) | 5. (a) | 6. (b) | 7. (b) | 8. (a) |
| 9. (c) | 10. (a) | 11. (b) | 12. (c) | 13. (b) | 14. (d) | 15. (c) | 16. (b) |
| 17. (b) | 18. (b) | 19. (b) | 20. (b) | 21. (b) | 22. (b) | 23. (c) | 24. (d) |
| 25. (b) | 26. (b) | 27. (d) | 28. (a) | 29. (b) | 30. (c) | 31. (c) | 32. (c) |
| 33. (c) | 34. (c) | 35. (d) | 36. (b) | 37. (b) | 38. (a) | 39. (a) | 40. (a, c) |
| 41. (a) | 42. (c) | 43. (d) | 44. (a) | 45. (a) | 46. (a) | | |

Integer Answer TYPE QUESTIONS

This section contains 10 questions. The answer to each of the questions is a single digit integer, ranging from 0 to 9. If the correct answers to question numbers X, Y, Z and W (say) are 6, 0, 9 and 2 respectively, then the correct darkening of bubbles will look like the given figure :



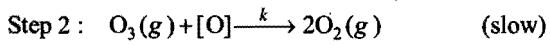
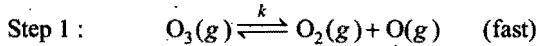
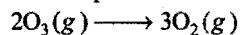
- In the reaction, $A \rightarrow B$ when the initial concentration of reactant is halved, the half-life increases by a factor of eight, what will be the order of the reaction?
- Rate of a chemical reaction increases by 1024 times by 100°C rise in temperature; the temperature coefficient of the reaction will be:
- The rate of a reaction at 10 sec intervals are as follows :

| Time (sec) | Rate (mol L ⁻¹ sec ⁻¹) |
|------------|--|
| 0 | 4.8×10^{-2} |
| 10 | 4.79×10^{-2} |
| 20 | 4.78×10^{-2} |
| 30 | 4.81×10^{-2} |

What will be the order of the reaction?

- How many times of the half-life will require to complete 75% of a reaction of first order?

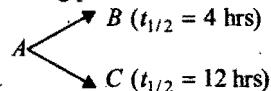
5. Ozone depletion takes place as :



order of the reaction will be :

6. If the $t_{1/2}$ for a first order reaction is 0.4 min, the time of or 99.9% completion of the reaction is min.

7. Consider following parallel first order reactions



The half-life for the decay of A is hrs.

8. The half-life period of a first order reaction is 1 hr. What is the time in hour taken for 87.5% completion of the reaction?

9. The half-life of a reaction is doubled when the initial concentration is doubled. The order of reaction is :

10. For the reaction $A_2 + 2B \rightarrow 2AB$, the following data were observed :

| Exp. No. | [A ₂] | [B] | Rate (mol L ⁻¹ s ⁻¹) |
|----------|-------------------|------|--|
| 1. | 0.1 | 0.01 | 1.5×10^{-3} |
| 2. | 0.1 | 0.04 | 6.0×10^{-3} |
| 3. | 0.2 | 0.01 | 3.0×10^{-3} |

The overall order of the reaction will be :

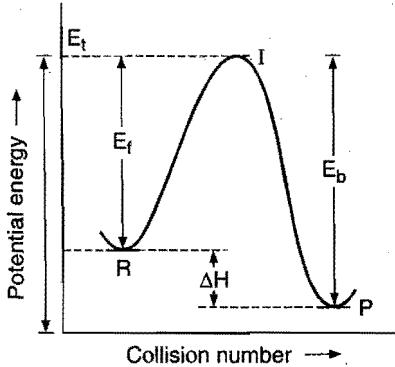
Answers

- | | | | | | | | |
|--------|---------|--------|--------|--------|--------|--------|--------|
| 1. (4) | 2. (2) | 3. (0) | 4. (2) | 5. (1) | 6. (4) | 7. (3) | 8. (3) |
| 9. (0) | 10. (2) | | | | | | |

● LINKED COMPREHENSION TYPE QUESTIONS ●

● Passage 1

A collision between reactant molecules must occur with a certain minimum energy before it is effective in yielding product molecules. This minimum energy is called activation energy E_a . Larger is the value of activation energy, smaller is the value of rate constant. Larger is the value of activation energy, greater is the effect of temperature rise on rate constant k .



E_f = Activation energy of forward reaction

E_b = Activation energy of backward reaction

$$\Delta H = E_f - E_b$$

E_t = Threshold energy

Answer the following questions:

1. If a reaction, $A + B \rightarrow C$, is exothermic to the extent of 30 kJ/mol and the forward reaction has an activation energy of 249 kJ/mol, the activation energy for reverse reaction in kJ/mol is:
(a) 324 (b) 279 (c) 40 (d) 100
2. For the following reaction at a particular temperature, according to the equations,
$$2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$$

$$2\text{NO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{N}_2\text{O}_5$$
the activation energies are E_1 and E_2 respectively. Then:
(a) $E_1 > E_2$ (b) $E_1 < E_2$ (c) $E_1 = 2E_2$ (d) $\sqrt{E_1 E_2} = 1$
3. In a hypothetical reaction, $A \rightarrow Y$, the activation energies for the forward and backward reactions are 15 and 9 kJ mol⁻¹ respectively. The potential energy of A is 10 kJ mol⁻¹. Which of the following is wrong?
(a) Threshold energy of the reaction is 25 kJ
(b) The potential energy of B is 16 kJ
(c) Heat of reaction is 6 kJ
(d) The reaction is exothermic
4. For two reactions, activation energies are E_{a_1} and E_{a_2} ; rate constants are k_1 and k_2 at the same temperature. If $k_1 > k_2$, then:
(a) $E_{a_1} > E_{a_2}$ (b) $E_{a_1} = E_{a_2}$ (c) $E_{a_1} < E_{a_2}$ (d) $E_{a_1} \geq E_{a_2}$

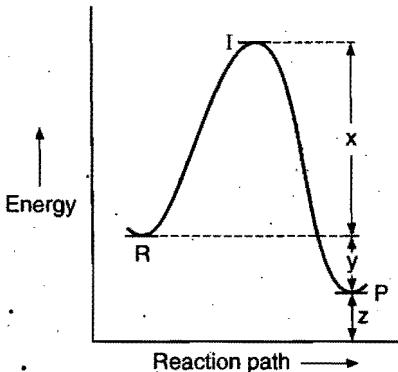
5. The rate constant of a certain reaction is given by $k = Ae^{-E_a/RT}$ (where A = Arrhenius constant). Which factor should be lowered so that the rate of reaction may increase?
(a) T (b) Z (c) A (d) E_a
6. The activation energies for forward and backward reactions in a chemical reaction are 30.5 and 45.4 kJ mol⁻¹ respectively. The reaction is:
(a) exothermic
(b) endothermic
(c) neither exothermic nor endothermic
(d) independent of temperature

● Passage 2

The energy profile diagram for the reaction:



is given below:



Answer the following questions:

1. The activation energy of the forward reaction is:
(a) x (b) y (c) $x + y$ (d) $x - y$
2. The activation energy of the backward reaction is:
(a) x (b) y (c) $x + y$ (d) $x - y$
3. The heat of the reaction is:
(a) x (b) y (c) $x + y$ (d) $x - y$
4. The threshold energy of the reaction is:
(a) $x + y - z$ (b) $x - y + z$ (c) $x + y + z$ (d) $x - y - z$

● Passage 3

Population growth of humans and bacteria follows first order growth kinetics. Suppose 50 bacteria are placed in a flask containing nutrients for the bacteria so that they can multiply. A study at 35°C gave the following results:

| | | | | | |
|--------------------|-----|-----|-----|-----|------|
| Time (minutes) | 0 | 15 | 30 | 45 | 60 |
| Number of bacteria | 100 | 200 | 400 | 800 | 1600 |

Answer the following questions:

1. The rate constant for the first order growth of bacteria can be calculated using:

$$(a) k = \frac{2.303}{t} \log_{10} \left(\frac{a}{a-x} \right) \quad (b) k = -\frac{2.303}{t} \log \left(\frac{a}{a+x} \right)$$

- (c) $k = \frac{0.693}{t}$ (d) $k = \frac{x}{t}$
2. Unit of rate constant for first order growth is:
 (a) min^{-1} (b) min^2 (c) min^{-3} (d) unitless
3. The rate constant for the reaction is:
 (a) 0.0462 min^{-1} (b) 0.462 min^{-1}
 (c) 4.62 min^{-1} (d) 46.2 min^{-1}
4. The rate of growth initially is:
 (a) 4.62 bacteria per min (b) 23.1 bacteria per min
 (c) 23.1 bacteria per sec (d) 0.231 bacteria per sec
5. At what time, there will be 6400 bacteria in the flask?
 (a) 150 min (b) 90 min (c) 160 min (d) 120 min

● Passage 4

Order of reaction is an experimentally determined quantity. It may be zero, positive, negative and fractional. The kinetic equation of nth order reaction is:

$$k \times t = \frac{1}{(n-1)} \left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}} \right]$$

Half life of nth order reaction depends on initial concentration according to the following relation:

$$t_{1/2} \propto \frac{1}{a^{n-1}}$$

Unit of the rate constant varies with the order but general relation for unit of nth order reaction is:

$$\text{Unit of } k = \left[\frac{1}{\text{conc.}} \right]^{n-1} \times \text{time}^{-1}$$

The differential rate law for nth order reaction may be given as:

$$\frac{dx}{dt} = k [A]^n$$

where, A denotes the reactant.

Answer the following questions:

1. The unit of rate and rate constant are same for a:
 (a) zero order reaction (b) first order reaction
 (c) second order reaction (d) half order reaction

2. The rate constant for zero order reaction is:

$$(a) k = \frac{C_0}{2t} \quad (b) k = \frac{C_0 - C_t}{t}$$

$$(c) k = \ln \frac{C_0 - C_t}{2t} \quad (d) k = \frac{C_0}{C_t}$$

where C_0 and C_t are concentrations of reactants at respective times.

3. The half life for a zero order reaction equals to:

$$(a) \frac{1}{2} \frac{k}{a^2} \quad (b) \frac{a^2}{2k} \quad (c) \frac{2k}{a} \quad (d) \frac{a}{2k}$$

4. For a reaction:



in an aqueous medium, the rate of the reaction is given by

$$\frac{d[\text{IO}^-]}{dt} = k \frac{[\text{I}^-][\text{OCl}^-]}{[\text{OH}^-]}$$

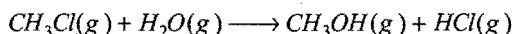
The overall order of the reaction is:

- (a) -1 (b) 1 (c) zero (d) 2

5. In a chemical reaction $A \longrightarrow B$, it is found that the rate of the reaction doubles when the concentration of A is increased four times. The order of the reaction with respect to A is:
 (a) 0 (b) 1/2 (c) 1 (d) 2

● Passage 5

Consider the reaction represented by the equation:



These kinetic data were obtained for the given reaction concentrations:

| Initial conc. (M) | Initial rate of disappearance of CH ₃ Cl M s ⁻¹ |
|----------------------|---|
| [CH ₃ Cl] | [H ₂ O] |
| 0.2 | 0.2 |
| 0.4 | 0.2 |
| 0.4 | 0.4 |

Answer the following questions based on these data:

1. The rate law for the reaction will be:
 (a) $r = k [\text{CH}_3\text{Cl}][\text{H}_2\text{O}]$ (b) $r = k [\text{CH}_3\text{Cl}]^2[\text{H}_2\text{O}]$
 (c) $r = k [\text{CH}_3\text{Cl}][\text{H}_2\text{O}]^2$ (d) $r = k [\text{CH}_3\text{Cl}]^2[\text{H}_2\text{O}]^4$
2. Order with respect to [CH₃Cl] will be:
 (a) 0 (b) 1 (c) 2 (d) 3
3. Overall order of the reaction will be:
 (a) 0 (b) 1 (c) 2 (d) 3
4. Unit of rate constant will be:
 (a) sec⁻¹ (b) litre² mol⁻² sec⁻¹
 (c) litre mol⁻¹ sec⁻¹ (d) mol litre⁻¹ sec⁻¹
5. If H₂O is taken in large excess, the order of the reaction will be:
 (a) 1 (b) 0 (c) 3 (d) 2

Answers

| | | | | | | |
|------------|--------|--------|--------|--------|--------|--------|
| Passage 1. | 1. (d) | 2. (a) | 3. (d) | 4. (c) | 5. (d) | 6. (a) |
| Passage 2. | 1. (a) | 2. (c) | 3. (b) | 4. (c) | | |
| Passage 3. | 1. (b) | 2. (a) | 3. (a) | 4. (a) | 5. (b) | |
| Passage 4. | 1. (a) | 2. (b) | 3. (d) | 4. (b) | 5. (b) | |
| Passage 5. | 1. (c) | 2. (b) | 3. (d) | 4. (b) | 5. (a) | |

SELF ASSESSMENT

ASSIGNMENT NO. 8

SECTION-I

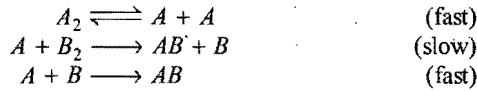
Straight Objective Type Questions

This section contains 10 multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which only one is correct.

1. What is the order of reaction,



Mechanism:



- (a) 2 (b) 1 (c) $\frac{3}{2}$ (d) $\frac{1}{2}$
2. For a gaseous reaction, $A(g) \longrightarrow$ Product, which one of the following is correct relation among $\frac{dP}{dt}$, $\frac{dn}{dt}$ and $\frac{dc}{dt}$?

$\left(\frac{dP}{dt}\right)$ = Rate of reaction in atm sec $^{-1}$; $\left(\frac{dc}{dt}\right)$ = Rate of reaction in molarity sec $^{-1}$; $\left(\frac{dn}{dt}\right)$ = Rate of reaction in mol sec $^{-1}$

- (a) $\frac{dc}{dt} = \frac{dn}{dt} = -\frac{dP}{dt}$ (b) $-\frac{dc}{dt} = -\frac{1}{V} \frac{dn}{dt} = -\frac{dP}{dt}$
 (c) $\frac{dc}{dt} = \frac{V}{RT} \frac{dn}{dt} = \frac{dP}{dt}$ (d) None of these

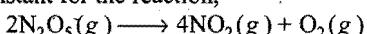
3. The rate law for a reaction between the substances A and B is given by the, rate = $k[A]^n[B]^m$. On doubling the concentration of A and halving the concentration of B , the ratio of the new rate to the earlier rate of the reaction will be as:

- (a) $\frac{1}{2^{m+n}}$ (b) $m+n$ (c) $n-m$ (d) $2^{(n-m)}$

4. A substance having initial concentration ' a ' reacts according to zero order kinetics. What will be the time for the reaction to go to completion?

- (a) $\frac{a}{k}$ (b) $\frac{k}{a}$ (c) $\frac{a}{2k}$ (d) $\frac{2k}{a}$

5. The rate constant for the reaction,



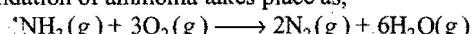
is 3×10^{-5} sec $^{-1}$. If the rate of reaction is 2.4×10^{-5} mol litre $^{-1}$ sec $^{-1}$, then the concentration of N_2O_5 in mol litre $^{-1}$ is:

- (a) 1.4 (b) 1.2 (c) 0.04 (d) 0.8

6. Half life of a reaction is inversely proportional to cube of initial concentration. The order of reaction is:

- (a) 4 (b) 3 (c) 5 (d) 2

7. The oxidation of ammonia takes place as,



if the rate of formation of N_2 is 0.7 M/s , determine the rate at which NH_3 is consumed:

- (a) $1.4\text{ mol L}^{-1}\text{s}^{-1}$ (b) $0.7\text{ mol L}^{-1}\text{s}^{-1}$
 (c) $1.5\text{ mol L}^{-1}\text{s}^{-1}$ (d) none of these

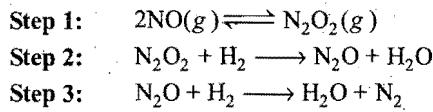
8. Consider the reaction:



The rate law for this reaction is:

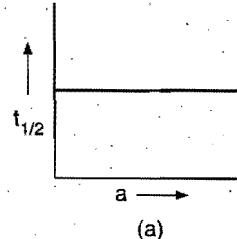
$$\text{Rate} = k[H_2][NO]^2$$

Under what conditions could these steps represent the mechanism?

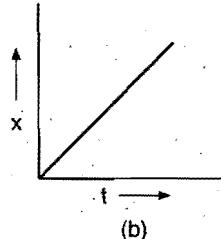


- (a) These steps can never satisfy the rate law
 (b) Step 1 should be the slowest step
 (c) Step 2 should be the slowest step
 (d) Step 3 should be the slowest step

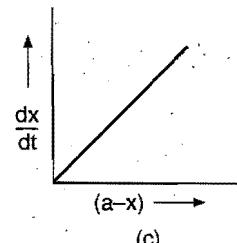
9. Which of the following is not for zero order reaction?



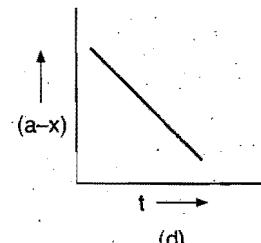
(a)



(b)



(c)



(d)

10. I. $E_a = 15\text{ kJ mol}^{-1}$, $\Delta H = -70\text{ kJ mol}^{-1}$
 II. $E_a = 30\text{ kJ mol}^{-1}$, $\Delta H = -15\text{ kJ mol}^{-1}$
 III. $E_a = 60\text{ kJ mol}^{-1}$, $\Delta H = +20\text{ kJ mol}^{-1}$

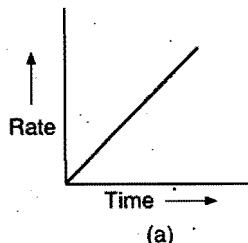
If above reactions are at same frequency factor then fastest and slowest reactions are:

- (a) III is fastest, II is slowest
 (b) I is fastest, III is slowest
 (c) II is fastest, III is slowest
 (d) III is fastest, I is slowest

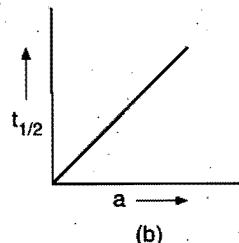
SECTION-II

Multiple Answers Type Objective Questions

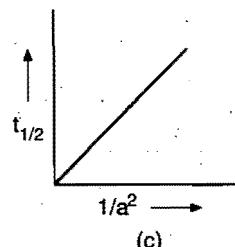
11. Which of the following graphs are correct?



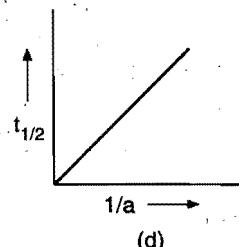
(a)



(b)



(c)



(d)

Here 'a' denotes initial concentration of reactants.

12. Arrhenius equation may be given as:

$$\begin{array}{ll} \text{(a)} \ln \frac{A}{k} = \frac{E_a}{RT} & \text{(b)} \log A = \log k + \frac{E_a}{2.303 RT} \\ \text{(c)} \log \left[\frac{-E_a}{RT} \right] = \frac{k}{a} & \text{(d)} \frac{d \ln k}{dt} = \frac{E_a}{RT} \end{array}$$

13. Which of the following is/are correct for second order reaction?

$$\begin{array}{l} \text{(a)} t_{1/2} \text{ is inversely proportional to initial concentration} \\ \text{(b)} k = \frac{1}{t} \left[\frac{1}{(a-x)} - \frac{1}{a} \right] \\ \text{(c)} k = \frac{2.303}{t} \log \left(\frac{a}{a-x} \right) \\ \text{(d)} k = \frac{1}{2t} \left[\frac{1}{(a-x)^2} - \frac{1}{a^2} \right] \end{array}$$

14. For a 1st order reaction:

$$\begin{array}{ll} A \longrightarrow B, \text{ with initial concentration} = a & \\ \text{(a)} t_{1/2} = \frac{k}{a} & \text{(b)} t_{3/4} = 2t_{1/2} \\ \text{(c)} t_{1/2} = \frac{0.693}{k} & \text{(d)} t_{1/2} = k \times 0.693 \end{array}$$

15. Select the correct statement for Arrhenius equation

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

- 'A' may be termed as the rate constant at very high temperature
- 'A' may be termed as the rate constant at zero activation energy
- E_a is the activation energy of reaction
- k is rate of reaction at zero concentration

SECTION-III

Assertion-Reason Type Questions

This section contains 3 questions. Each question of this section contains Statement-1 (Assertion) and Statement-2

(Reason). Each question has following 4 choices (a), (b), (c) and (d), out of which only one is correct.

(a) Statement-1 is true; Statement-2 is true; Statement-2 is a correct explanation for statement-1.

(b) Statement-1 is true; Statement-2 is true; Statement-2 is not a correct explanation for Statement-1.

(c) Statement-1 is true; Statement-2 is false.

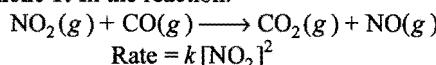
(d) Statement-1 is false; Statement-2 is true.

16. Statement-1: If temperature does not affect the rate of reaction, $E_a = 0$.

Because

Statement-2: Lesser is the activation energy, slower is the rate.

17. Statement-1: In the reaction:



The rate of reaction does not depend on the concentration of CO.

Because

Statement-2: Carbon monoxide is involved in fast step.

18. Statement-1: The reciprocal of time in which 66% of the reactant is converted to product is equal to the rate constant of first order reaction.

Because

Statement-2: The rate constant for first order reaction depends on initial concentration of reactants.

SECTION-IV

Matrix-Matching Type Questions

This section contains 3 questions. Each question contains statement given in two columns which have to be matched. Statements (a, b, c and d) in Column-I have to be matched with statements (p, q, r and s) in Column-II. The answers to these questions have to be appropriately bubbled as illustrated in the following examples:

If the correct matches are (a-p,s); (b-q,r); (c-p,q); and (d-s), then correct bubbled 4 × 4 matrix should be as follows:

| | p | q | r | s |
|---|----------------------------------|----------------------------------|-----------------------|----------------------------------|
| a | <input checked="" type="radio"/> | <input type="radio"/> | <input type="radio"/> | <input checked="" type="radio"/> |
| b | <input type="radio"/> | <input checked="" type="radio"/> | <input type="radio"/> | <input type="radio"/> |
| c | <input checked="" type="radio"/> | <input type="radio"/> | <input type="radio"/> | <input type="radio"/> |
| d | <input type="radio"/> | <input checked="" type="radio"/> | <input type="radio"/> | <input checked="" type="radio"/> |

19. Match the Column-I with Column-II:

Column-I

- Rate of reaction
- Rate constant
- Order of reaction
- Molecularity of reaction

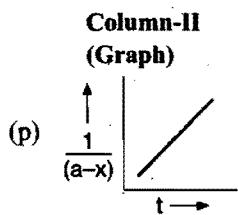
Column-II

- May be fractional
- Whole number
- Independent of temperature
- Increase with temperature

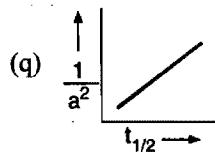
20. Match the Column-I with Column-II:

Column-I
(Order of reaction)

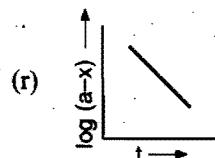
(a) First order



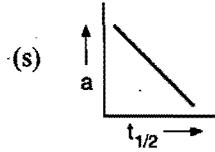
(b) Second order



(c) Third order



(d) Zero order



21. Match the Column-I with Column-II:

Column-I

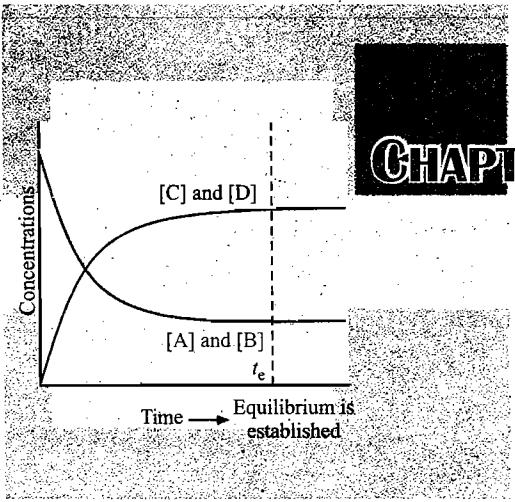
- (a) First order
(b) Pseudo first order
(c) Third order
(d) Second order

Column-II

- (p) Unit of $k = \text{sec}^{-1}$
(q) Unit of $k = \text{dm}^6 \text{mol}^{-2} \text{s}^{-1}$
(r) $t_{1/2} \propto 1/a^2$
(s) $t_{1/2} \propto \frac{1}{a}$

Answers

- | | | | | | | | |
|---------|---------|---------------------------------|-----------------------------|-----------|-------------------------------|-------------|---------|
| 1. (c) | 2. (b) | 3. (d) | 4. (a) | 5. (d) | 6. (a) | 7. (a) | 8. (c) |
| 9. (c) | 10. (b) | 11. (b,c) | 12. (a,b) | 13. (a,b) | 14. (b,c) | 15. (a,b,c) | 16. (c) |
| 17. (a) | 18. (c) | 19. (a-s) (b-s) (c-p,r) (d-q,r) | 20. (a-r) (b-p) (c-q) (d-s) | | 21. (a-p) (b-p) (c-q,r) (d-s) | | |



CHAPTER 9

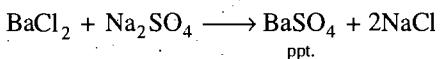
CHEMICAL EQUILIBRIUM

9.1 INTRODUCTION

It is a well established fact that many reactions do not go to completion. They proceed to some extent leaving considerable amounts of unreacted reactants, *i.e.*, the resulting mixture contains both reactants and products. When such a stage is reached in a course of reaction that no further reaction is apparent, it is said in chemical language that the reaction has attained the state of equilibrium where the composition of the system becomes fixed. At equilibrium state both the forward and backward reactions move with equal speeds, *i.e.*, the rate of disappearance of reactants is exactly equal to rate of the appearance of reactants from the products. The study of chemical equilibrium helps in the elucidation of the optimum conditions for the greater yields of the products in the case of those reactions which attain equilibrium in the course of reaction.

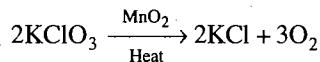
Chemical reactions can be classified as **irreversible** and **reversible** reactions.

Irreversible reactions: The chemical reactions which proceed in such a way that reactants are completely converted into products, *i.e.*, the reactions which move in one direction, *i.e.*, forward direction only are called **irreversible reactions**. In such reactions, products do not react together to produce reactants again, *i.e.*, the reaction does not move in backward direction. For example, when solutions containing equimolar concentrations of barium chloride and sodium sulphate are mixed, reaction occurs and practically whole of barium is precipitated as barium sulphate.

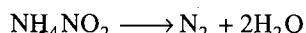


The reaction between BaSO_4 and NaCl , *i.e.*, backward reaction, is not possible under the experimental conditions. In such reactions the arrow (\rightarrow) is placed between reactants and products which indicates the direction of the chemical change. Some more examples of irreversible reactions are given below:

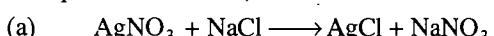
- (a) Thermal decomposition of potassium chlorate,



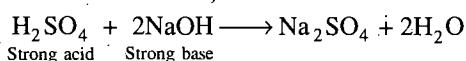
- (b) Decomposition of ammonium nitrite,



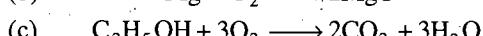
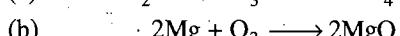
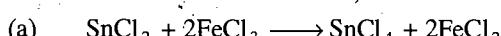
2. Precipitation reactions,



3. Neutralisation reactions,



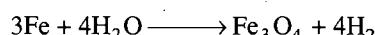
4. Redox and combustion reactions,



Reversible reactions: The chemical reactions which take place in both directions under similar conditions are called **reversible reactions**. In such reactions, the products also react with each other and produce reactants again. For example, when hydrogen is passed over heated magnetic oxide, metallic iron and water are produced.



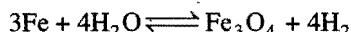
On the other hand, if steam is passed over powdered iron at the same temperature, magnetic oxide of iron and hydrogen are formed.



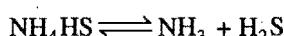
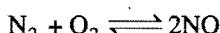
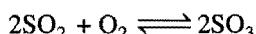
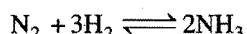
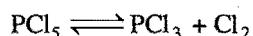
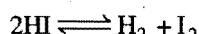
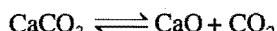
If the reaction is carried out in a closed vessel, it is found that in no case the reaction proceeds to completion. It is, thus, clear that either of the two reactions can take place independently if steam or hydrogen is allowed to escape from system by carrying out the reaction in open vessel but if a closed vessel is used and

nothing is allowed to escape both forward and backward reactions can take place in the vessel.

Reactions which thus proceed in both the directions and do not reach to completion are known as reversible reactions. The reaction proceeding from left to right is conventionally called the **forward reaction** and the opposite one proceeding from right to left is called the **reverse or backward reaction**. In such reactions the arrow (\rightarrow) or sign of equality ($=$) is replaced by two half arrows (\rightleftharpoons) pointing the reaction in both the directions. This sign (\rightleftharpoons) represents the reversibility of the reaction.

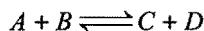


Some examples of reversible reactions are given below:



9.2 STATE OF CHEMICAL EQUILIBRIUM

The most important characteristic property of a reversible reaction is that it always attains a state of chemical equilibrium. Consider a general reversible reaction in a closed vessel.



In the initial state only A and B are present both react with each other, i.e., rate of forward reaction is maximum as only the concentrations of A and B are involved (at the beginning, the concentrations of products C and D are nil). As soon as the products C and D are produced, the backward reaction starts functioning. By the expiry of time, the rate of forward reaction decreases as the concentrations of A and B decrease while the rate of backward reaction increases as the concentrations of products C and D increase. Ultimately, a stage comes when the rate of forward reaction becomes equal to rate of backward reaction. This state is called the **equilibrium state**.

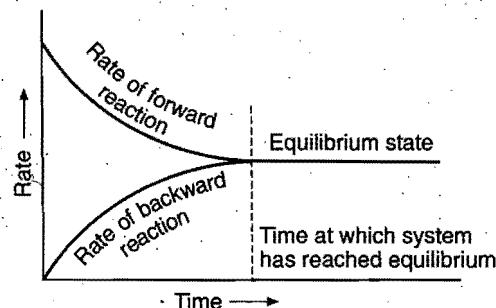


Fig. 9.1

At equilibrium state,

Rate of forward reaction = Rate of backward reaction.

It can be shown graphically as in Fig. 9.1.

Thus, chemical equilibrium in a reversible reaction is the state at which both forward and backward reactions or two opposing reactions occur at the same speed.

This state will continue indefinitely if the conditions such as temperature and concentration are not changed. At the state of equilibrium, the concentrations of reactants and products in the reaction mixture attain a constant value and the concentrations do not change with time.

When hydrogen gas and iodine vapours are heated in a closed vessel at a constant temperature 717 K, the two react to form hydrogen iodide. In the initial stage, the colour of the reaction mixture is deep violet due to the presence of large amounts of iodine. But as the reaction progresses, the intensity of the colour decreases as more and more iodine is converted into hydrogen iodide. After sometime, the intensity of the colour of the reaction mixture becomes constant. The constancy of intensity of colour indicates that concentration of both reactants and products have become constant and state of equilibrium has been attained.

The stage of the reversible reaction at which the concentrations of the reactants and products do not change with time is called the **equilibrium state**.

Or

The state in which the measurable properties of the system (such as pressure, density, colour or concentration) do not undergo any further noticeable change with time under given set of conditions is said to be a state of equilibrium.

The equilibrium state is **dynamic** and not static in nature. The reaction does not stop but both the opposing reactions are going on continuously with same speeds. At this stage, the number of moles of substances produced per second in the forward reaction is equal to the number of moles of substances which disappear per second in the backward reaction.

Characteristics of Equilibrium State

(i) Equilibrium state can only be achieved if a reversible reaction is carried out in closed space.

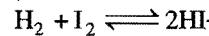
No product can leave nor any reactant from outside can enter the space. If the system is not closed, some of the products may escape and thus, the backward reaction will not occur.

(ii) Chemical equilibrium, at a given temperature, is characterised by constancy of certain properties such as pressure, concentration, density or colour.

(iii) Chemical equilibrium can be attained from either side, i.e., from the side of reactants or products.



or



At equilibrium, each reactant and each product has a fixed concentration and this is independent of the fact whether we start the reaction with the reactants or with the products.

This reaction can be graphically represented as,

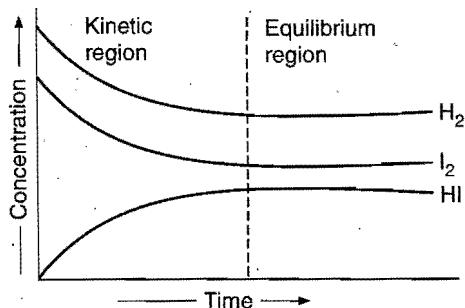


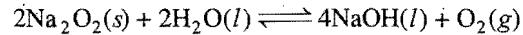
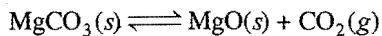
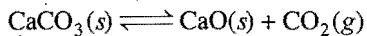
Fig. 9.2

(iv) Equilibrium state can be attained in a lesser time by the use of a positive catalyst, i.e., the relative concentrations of reactants and products remain the same irrespective of the presence or absence of a catalyst. Thus, a catalyst does not change the equilibrium state but it helps in attaining it rapidly.

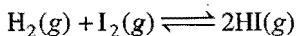
(v) It is dynamic in nature, i.e., both the reactions move with same speed. However, the reaction seems to have come to stand still because the concentrations of reactants and products do not change.

Reversible chemical reactions are classified into two types heterogeneous and homogeneous reactions.

Heterogeneous reactions: The reversible reaction in which more than one-phase is present.



Homogeneous reactions: The reversible reaction in which only one-phase is present, i.e., all the reactants and products are in the same physical state.

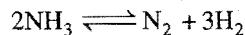
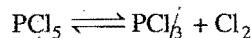


Homogeneous reversible reactions are further classified into three types:

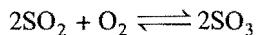
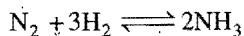
First type: When there is no change in number of molecules. Examples are:



Second type: When there is an increase in number of molecules.

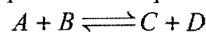


Third type: When there is a decrease in number of molecules.



9.3 THE LAW OF CHEMICAL EQUILIBRIUM (Application of Law of Mass Action)

Consider a reversible homogeneous reaction which has attained equilibrium state at a particular temperature.



Let the active masses of A, B, C and D be $[A], [B], [C]$ and $[D]$ respectively at equilibrium.

According to law of mass action,

$$\text{Rate of forward reaction} \propto [A][B]$$

$$\text{or} \quad \text{Rate of forward reaction} = k_f [A][B]$$

(where, k_f is the velocity constant for forward reaction).

Similarly,

$$\text{Rate of backward reaction} \propto [C][D]$$

$$\text{or} \quad \text{Rate of backward reaction} = k_b [C][D]$$

(where, k_b is the velocity constant for backward reaction).

At equilibrium,

$$\text{Rate of forward reaction} = \text{Rate of backward reaction},$$

$$\text{i.e.,} \quad k_f [A][B] = k_b [C][D]$$

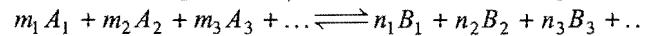
$$\text{or} \quad \frac{k_f}{k_b} = \frac{[C][D]}{[A][B]}$$

Since, k_f and k_b are both constants, the ratio k_f/k_b is also a new constant say K_c , i.e.,

$$K_c = \frac{[C][D]}{[A][B]} \quad \dots (\text{i})$$

K_c is known as equilibrium constant. K_c has a definite value for every chemical reaction at a given temperature regardless of the concentration of the reactants.

Considering a more general homogeneous reversible reaction at a particular temperature which is under chemical equilibrium,



$$\text{Rate of forward reaction} = k_f [A_1]^{m_1} [A_2]^{m_2} [A_3]^{m_3} \dots$$

$$\text{Rate of backward reaction} = k_b [B_1]^{n_1} [B_2]^{n_2} [B_3]^{n_3} \dots$$

At equilibrium,

$$k_f [A_1]^{m_1} [A_2]^{m_2} [A_3]^{m_3} \dots = k_b [B_1]^{n_1} [B_2]^{n_2} [B_3]^{n_3} \dots$$

$$\text{or} \quad \frac{k_f}{k_b} = \frac{[B_1]^{n_1} [B_2]^{n_2} [B_3]^{n_3} \dots}{[A_1]^{m_1} [A_2]^{m_2} [A_3]^{m_3} \dots} = K_c \quad \dots (\text{ii})$$

The equilibrium constant, at a given temperature, is the ratio of the rate constants of forward and backward reactions.

Or

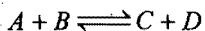
The equilibrium constant may be defined as the ratio between the product of the molar concentrations of the products to that of the product of the molar concentrations of the reactants with each concentration term raised to a power equal to stoichiometric coefficient in the balanced chemical equation.

The value of equilibrium constant is independent of the following factors:

1. Initial concentrations of the reactants involved.
2. The presence of a catalyst.
3. The direction from which the equilibrium has been attained.
4. The presence of inert materials.

The value of equilibrium constant depends on the following factors:

1. The mode of representation of the reaction: Conventionally, the concentrations of the products are put in the numerator and the concentrations of the reactants in denominator in the equilibrium law equation. Consider the reversible reaction,



The equilibrium constant for the reaction,

$$K_c = \frac{[C][D]}{[A][B]} \quad \dots \text{(i)}$$

Now, if the products are made reactants, i.e., the reaction is reversed,



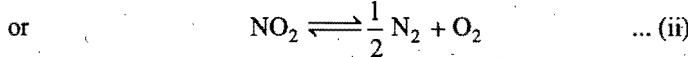
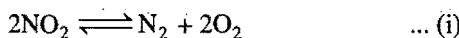
The equilibrium constant for the reaction is

$$K'_c = \frac{[A][B]}{[C][D]} \quad \dots \text{(ii)}$$

The equilibrium constant, K'_c , is actually the reciprocal of K_c , i.e.,

$$K'_c = \frac{1}{K_c}$$

2. Stoichiometric representation of the chemical equation: (a) When a reversible reaction can be written with the help of two or more stoichiometric equations, the value of equilibrium constant will be numerically different in these cases. For example, the dissociation of NO_2 can be represented as:



$$\text{For equation (i), the value of } K_c = \frac{[\text{N}_2][\text{O}_2]^2}{[\text{NO}_2]^2} \quad \dots \text{(iii)}$$

$$\text{For equation (ii), the value of } K'_c = \frac{[\text{N}_2]^{1/2}[\text{O}_2]}{[\text{NO}_2]} \quad \dots \text{(iv)}$$

Thus, the two constants are related to each other as:

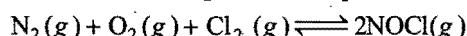
$$K'_c = \sqrt{K_c} \quad \dots \text{(v)}$$

In general, when a balanced equation having equilibrium constant K_c , is multiplied by a certain value n , the equilibrium constant for the new equation will be equal to $(K_c)^n$.

$$A + B \rightleftharpoons C + D, \quad K_c = \frac{[C][D]}{[A][B]}$$

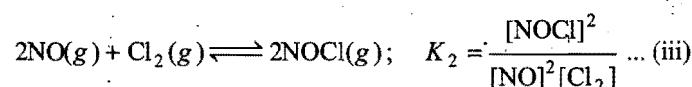
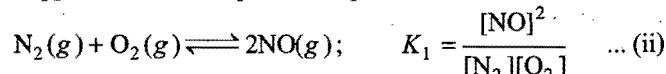
$$nA + nB \rightleftharpoons nC + nD, \quad K'_c = \frac{[C]^n[D]^n}{[A]^n[B]^n} = (K_c)^n$$

- (b) Consider the following chemical equation,



$$K_c = \frac{[\text{NOCl}]^2}{[\text{N}_2][\text{O}_2][\text{Cl}_2]} \quad \dots \text{(i)}$$

Suppose the above equation is split into two as:



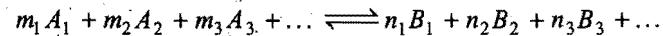
Combining above two equations,

$$K_1 \times K_2 = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} \times \frac{[\text{NOCl}]^2}{[\text{NO}]^2[\text{Cl}_2]} = \frac{[\text{NOCl}]^2}{[\text{N}_2][\text{O}_2][\text{Cl}_2]} = K_c$$

Thus, when an equation (having equilibrium constant, K_c) is written in two steps (having equilibrium constant K_1 and K_2), then $K_c = K_1 \times K_2$:

3. Use of partial pressures instead of concentrations: When the reactants and products are in gaseous state, the partial pressures can be used instead of concentrations at a definite temperature, as the partial pressure of a substance is proportional to its concentration in the gas phase.

Consider a general reversible homogeneous gaseous reaction



Let the partial pressures of various reactants and products be pA_1 , pA_2 , pA_3 , ..., and pB_1 , pB_2 , pB_3 , ... respectively at equilibrium. The equilibrium constant for the reaction,

$$K_p = \frac{(pB_1)^{n_1} (pB_2)^{n_2} (pB_3)^{n_3} \dots}{(pA_1)^{m_1} (pA_2)^{m_2} (pA_3)^{m_3} \dots} \quad \dots \text{(i)}$$

The value of K_c for the above reaction can be given as:

$$K_c = \frac{[B_1]^{n_1} [B_2]^{n_2} [B_3]^{n_3} \dots}{[A_1]^{m_1} [A_2]^{m_2} [A_3]^{m_3} \dots} \quad \dots \text{(ii)}$$

For an ideal gas,

$$pV = nRT$$

$$\text{or} \quad p = \frac{n}{V} RT \\ = \text{Active mass} \times RT$$

(where, n = number of moles and V = volume in litres. Thus, $\frac{n}{V}$ = molar concentration or active mass).

Substituting the values of partial pressures in eq. (i),

$$K_p = \frac{[B_1]^{n_1} (RT)^{n_1} \cdot [B_2]^{n_2} (RT)^{n_2} \cdot [B_3]^{n_3} (RT)^{n_3} \dots}{[A_1]^{m_1} (RT)^{m_1} \cdot [A_2]^{m_2} (RT)^{m_2} \cdot [A_3]^{m_3} (RT)^{m_3} \dots}$$

$$\text{or } K_p = \frac{([B_1]^{n_1} [B_2]^{n_2} [B_3]^{n_3} \dots)(RT)^{n_1+n_2+n_3+\dots}}{([A_1]^{m_1} [A_2]^{m_2} [A_3]^{m_3} \dots)(RT)^{m_1+m_2+m_3+\dots}}$$

$$\text{or } K_p = K_c \cdot \frac{(RT)^{\sum n}}{(RT)^{\sum m}}$$

$$= K_c (RT)^{\Sigma n - \Sigma m}$$

$$= K_c (RT)^{\Delta n} \quad \dots \text{(iii)}$$

Δn = total number of molecules of gaseous products
– total number of molecules of gaseous reactants.

Three cases may arise:

First case: When, $\Delta n = 0$,

$$K_p = K_c (RT)^0 = K_c$$

Second case: When, $\Delta n = +\text{ve}$ or $\Delta n > 0$,

$$K_p > K_c$$

Third case: When, $\Delta n = -\text{ve}$ or $\Delta n < 0$,

$$K_p < K_c$$

4. Temperature: According to Arrhenius equation,

$$k = A e^{-E/RT} \quad \dots \text{(i)}$$

where, k = rate constant, E = activation energy, R = gas constant, T = absolute temperature and e = exponential constant.

$$\log \frac{k_2}{k_1} = - \frac{E}{2.303R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right] \quad \dots \text{(ii)}$$

when, $T_2 > T_1$

for forward reaction,

$$\log \left(\frac{k_{f_2}}{k_{f_1}} \right) = - \frac{E_f}{2.303R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right] \quad \dots \text{(iii)}$$

for backward reaction,

$$\log \left(\frac{k_{b_2}}{k_{b_1}} \right) = - \frac{E_b}{2.303R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right] \quad \dots \text{(iv)}$$

Subtracting eq. (iv) from eq. (iii), we get

$$\log \left(\frac{k_{f_2}/k_{b_2}}{k_{f_1}/k_{b_1}} \right) = - \frac{(E_f - E_b)}{2.303R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

$$\text{or } \log \left(\frac{K_2}{K_1} \right) = - \frac{\Delta H}{2.303R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right] \quad \dots \text{(v)}$$

where, ΔH is the heat of reaction at constant volume and K_1 and K_2 are the equilibrium constants of a reaction at temperatures T_1 and T_2 ($T_2 > T_1$).

The effect of temperature can be studied in the following three cases:

First case: $\Delta H = 0$, i.e., neither heat is evolved, nor absorbed.

$$\text{So, } \log K_2 - \log K_1 = 0$$

$$\text{or } \log K_2 = \log K_1$$

$$\text{or } K_2 = K_1$$

Thus, equilibrium constant remains the same at all temperatures.

Second case: When, $\Delta H = +\text{ve}$, i.e., heat is absorbed, the reaction is endothermic. The temperature T_2 is higher than T_1 .

Thus, $\left(\frac{1}{T_2} - \frac{1}{T_1} \right)$ is negative.

So, $\log K_2 - \log K_1 = +\text{ve}$

$$\text{or } \log K_2 > \log K_1$$

$$\text{or } K_2 > K_1$$

The value of equilibrium constant is higher at higher temperature in the case of endothermic reactions.

Third case: When $\Delta H = -\text{ve}$, i.e., heat is evolved, the reaction is exothermic. The temperature T_2 is higher than T_1 .

Thus, $\left(\frac{1}{T_2} - \frac{1}{T_1} \right)$ is negative.

$$\text{So, } \log K_2 - \log K_1 = -\text{ve}$$

$$\text{or } \log K_1 > \log K_2$$

$$\text{or } K_1 > K_2$$

The value of equilibrium constant is lower at higher temperature in the case of exothermic reactions.

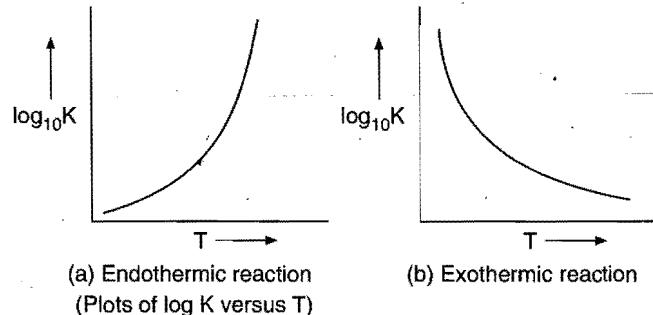
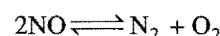


Fig. 9.3

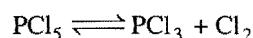
Units of Equilibrium Constant

The units of equilibrium constant vary in case of different reactions. ' K ' has no units for a reaction in which total number of moles of reactants and products are the same. For example, for dissociation of nitric oxide, K_c has no units.



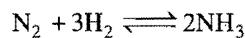
$$K_c = \frac{[\text{N}_2][\text{O}_2]}{[\text{NO}]^2}$$

K_c will have units for a reaction in which the total number of moles of reactants and products are different. For example, for decomposition of PCl_5 , the K_c has mol/litre units.



$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]}$$

In the formation of ammonia,



$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

K_c has litre² mol⁻² units.

In general; unit of $K_c = [M]^{\Delta n}$

where, $M = \text{mol litre}^{-1}$ and $\Delta n = \text{number of gaseous moles of product or products} - \text{number of gaseous moles of reactant or reactants}$.

Note: (i) The above relation can be used in homogeneous liquid system also

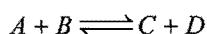
$$\Delta n = \text{number of moles of product or products} - \text{number of moles of reactant or reactants}$$

$$(ii) \text{Similarly, the unit of } K_p = [\text{atm}]^{\Delta n}$$

where, $\Delta n = \text{number of gaseous moles of product or products} - \text{number of gaseous moles of reactant or reactants}$.

9.4 REACTION QUOTIENT OR MASS ACTION RATIO

Let us consider a reaction:



$$Q = \frac{[C][D]}{[A][B]}$$

Q is denoted as Q_c or Q_p depending upon whether the concentration is taken in terms of moles per litre or partial pressures respectively. With the help of mass action ratio we can determine whether the reaction is at equilibrium or not.

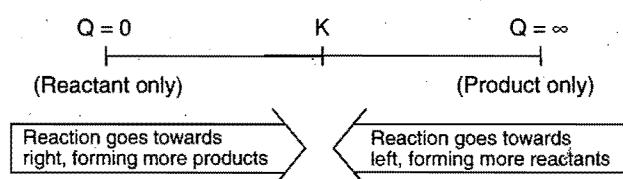
(I) When, $Q_c = K_c$ or $Q_p = K_p$, then the reversible reaction is at equilibrium, i.e., the rate of forward and backward reaction becomes equal.

(II) When, $Q_c < K_c$ or $Q_p < K_p$, then the reaction is not at equilibrium. The reaction will be fast in forward direction, i.e., reaction has a tendency to form product/products.

Rate of forward reaction > Rate of backward reaction.

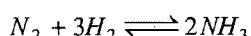
(III) When, $Q_c > K_c$ or $Q_p > K_p$, then again the reaction is not at equilibrium. The reaction will be fast in backward direction, i.e., have a tendency to form reactant/reactants.

Rate of forward reaction < Rate of backward reaction.

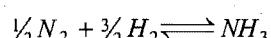


Some Solved Examples

Example 1. For the reactions,



and



write down the expression for equilibrium constant K_c and K'_c . How is K_c related to K'_c ?

Solution: For equation $N_2 + 3H_2 \rightleftharpoons 2NH_3$,

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} \quad \dots (i)$$

and for equation, $\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftharpoons NH_3$,

$$K'_c = \frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}} \quad \dots (ii)$$

Squaring equation (ii),

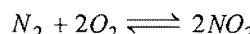
$$(K'_c)^2 = \frac{[NH_3]^2}{[N_2][H_2]^3} \quad \dots (iii)$$

Equations (i) and (iii) are same

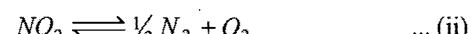
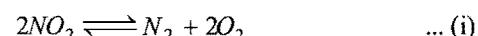
$$\text{Thus, } K_c = (K'_c)^2$$

$$\text{or } \sqrt{K_c} = K'_c$$

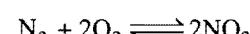
Example 2. The equilibrium constant for the reaction,



at a particular temperature is 100. Write down the equilibrium law equations for the following reactions and determine the values of equilibrium constants:



Solution: The equilibrium constant for the reaction,



$$K_c = \frac{[NO_2]^2}{[N_2][O_2]^2} = 100 \quad \dots (a)$$

The equilibrium constant equation for reaction (i),

$$K_1 = \frac{[N_2][O_2]^2}{[NO_2]^2} \quad \dots (b)$$

This equation is reciprocal of eq. (a)

$$\text{So, } K_1 = \frac{1}{K_c} = \frac{1}{100} = 1 \times 10^{-2}$$

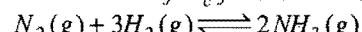
The equilibrium constant equation for reaction (ii),

$$K_2 = \frac{[N_2]^{1/2}[O_2]}{[NO_2]} \quad \dots (c)$$

Comparing eqs. (b) and (c),

$$K_2 = \sqrt{K_1} = \sqrt{10^{-2}} = 10^{-1} = 0.1$$

Example 3. The value of K_c for the reaction,



is 0.50 at 400°C. Find the value of K_p at 400°C when concentrations are expressed in mol litre⁻¹ and pressure in atmosphere.

Solution: Applying the relationship,

$$K_p = K_c (RT)^{\Delta n}$$

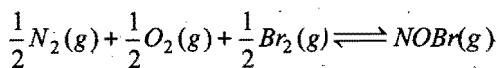
$$K_c = 0.50, \quad R = 0.082 \text{ litre-atm deg}^{-1} \text{ mol}^{-1}$$

$$T(400 + 273) = 673 \text{ K}, \quad \Delta n = (2 - 4) = -2$$

$$K_p = 0.5(0.082 \times 673)^{-2}$$

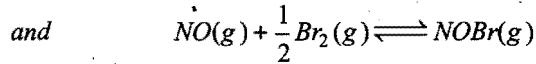
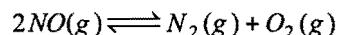
$$= 0.5(55.185)^{-2} = 1.64 \times 10^{-4}$$

Example 4. Determine K_c for the reaction,



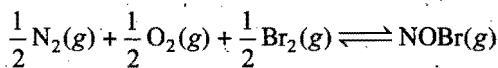
from the following data at 298 K;

The equilibrium constants for the following reactions,



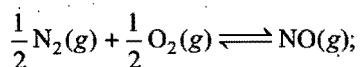
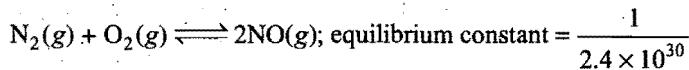
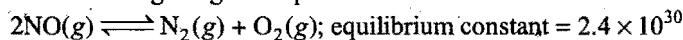
are 2.4×10^{30} and 1.4 respectively.

Solution: The net reaction is,



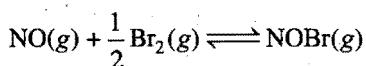
$$K_{c(\text{net})} = \frac{[NOBr]}{[N_2]^{1/2}[O_2]^{1/2}[Br_2]^{1/2}}$$

Considering the given equations:



$$\begin{aligned} \text{Equilibrium constant} &= \left(\frac{1}{2.4 \times 10^{30}} \right)^{1/2} \\ &= 0.6455 \times 10^{-15} \end{aligned}$$

$$\frac{[NO]}{[N_2]^{1/2}[O_2]^{1/2}} = K'_c = 0.6455 \times 10^{-15} \quad \dots (i)$$



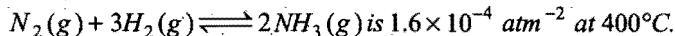
$$\frac{[NOBr]}{[NO][Br_2]^{1/2}} = K''_c = 1.4 \quad \dots (ii)$$

Multiplying both equations

$$\frac{[NO]}{[N_2]^{1/2}[O_2]^{1/2}} \times \frac{[NOBr]}{[NO][Br_2]^{1/2}} = K'_c \times K''_c = 0.6455 \times 10^{-15} \times 1.4$$

$$\begin{aligned} \text{or } \frac{[NOBr]}{[N_2]^{1/2}[O_2]^{1/2}[Br_2]^{1/2}} &= K_{c(\text{net})} = 0.9037 \times 10^{-15} \\ &= 9.037 \times 10^{-16} \end{aligned}$$

Example 5. The equilibrium constant, K_p , for the reaction



is $1.6 \times 10^{-4} \text{ atm}^{-2}$ at 400°C. What will be the equilibrium constant at 500°C if heat of reaction in this temperature range is -25.14 kcal?

Solution: Using the relation,

$$\log \frac{K_{p_2}}{K_{p_1}} = \frac{\Delta H}{2.303R} \left[\frac{T_2 - T_1}{T_2 T_1} \right]$$

Given,

$$K_{p_1} = 1.6 \times 10^{-4}; \quad \Delta H = -25.14 \text{ kcal};$$

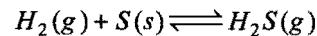
$$R = 2 \times 10^{-3} \text{ kcal deg}^{-1} \text{ mol}^{-1}$$

$$T_1 = 400 + 273 = 673 \text{ K}, \quad T_2 = 500 + 273 = 773 \text{ K}$$

$$\log \frac{K_{p_2}}{(1.6 \times 10^{-4})} = \frac{-25.14}{2.303 \times 2 \times 10^{-3}} \left[\frac{773 - 673}{773 \times 673} \right]$$

$$\begin{aligned} \log K_{p_2} &= \log (1.6 \times 10^{-4}) - \frac{25.14 \times 10^3 \times 100}{2.303 \times 2 \times 773 \times 673} \\ &= -3.7960 - 1.049 = -4.8450 \\ K_{p_2} &= 1.429 \times 10^{-5} \text{ atm}^{-2} \end{aligned}$$

Example 6. The equilibrium constant for the reaction,



is 18.5 at 925 K and 9.25 at 1000 K respectively. Calculate the enthalpy of the reaction.

Solution: Using the relation,

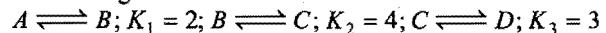
$$\log \frac{K_2}{K_1} = \frac{\Delta H}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\begin{aligned} \log \frac{9.25}{18.5} &= \frac{\Delta H}{2.303 \times 8.314} \times \frac{75}{925 \times 1000} \\ -0.301 &= \frac{\Delta H \times 75}{2.303 \times 8.314 \times 925 \times 1000} \end{aligned}$$

$$\text{or } \Delta H = -71080.57 \text{ J mol}^{-1}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

1. For the hypothetical reactions, the equilibrium constant (K) values are given:



The equilibrium constant (K) for the reaction $A \rightleftharpoons D$ is:

[PMT (Kerala) 2005]

- (a) 48 (b) 6 (c) 2.7 (d) 12

- (e) 24

[Ans. (e)]

[Hint: The reaction $A \rightleftharpoons D$ is obtained by adding the three given reactions.

$$\therefore K = K_1 \times K_2 \times K_3 = 2 \times 4 \times 3 = 24]$$

2. If, in the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, x is that part of N_2O_4 which dissociates, then the number of molecules at equilibrium will be:

[KCET 2005]

- (a) 1 (b) 3
(c) $(1+x)$ (d) $(1+x)^2$

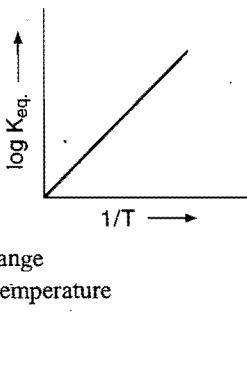
[Ans. (c)]

[Hint: $\begin{array}{ccccc} & & & & \\ & & & & \\ t=0 & N_2O_4 & \rightleftharpoons & 2NO_2 & \\ & 1 & & 0 & \\ t_{\text{eq}} & 1-x & & 2x & \end{array}$

$$\text{Total number of molecules at equilibrium} = 1 - x + 2x = (1 + x)]$$

3. A schematic plot of $\ln K_{eq}$ vs inverse of temperature for a reaction is shown in the figure. The reaction must be:

(AIEEE 2005)



- (a) exothermic
- (b) endothermic
- (c) one with negligible enthalpy change
- (d) highly spontaneous at ordinary temperature

[Ans. (a)]

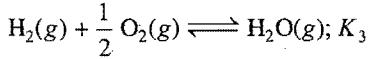
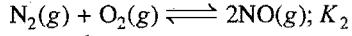
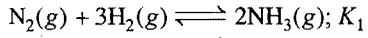
[Hint: $K_e = Ae^{-\Delta H^\circ/RT}$

$$\log K_{eq} = \log A - \frac{\Delta H^\circ}{2.303 RT}$$

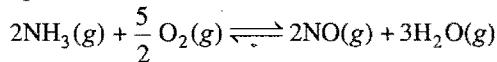
$$Y = C + MX$$

Slope of the line will be positive, when, $\Delta H^\circ = -ve$, i.e., the reaction is exothermic.]

4. Given:



The equilibrium constant for



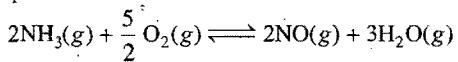
will be:

- (a) $K_1 K_2 K_3$
- (b) $\frac{K_1 K_2}{K_3}$
- (c) $\frac{K_1 K_2^2}{K_2}$
- (d) $\frac{K_2 K_3^3}{K_1}$

[Ans. (d)]

$$[Hint: K_1 = \frac{[NH_3]^2}{[N_2][H_2]^3}; K_2 = \frac{[NO]^2}{[N_2][O_2]}; K_3 = \frac{[H_2O]}{[H_2][O_2]^{1/2}}$$

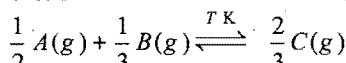
The equilibrium constant for



will be:

$$\frac{[NO]^2[H_2O]^3}{[NH_3]^2[O_2]^{5/2}} = \frac{K_2 \times K_3^3}{K_1}$$

5. What is the equation for the equilibrium constant (K_e) for the following reaction? (EAMCET 2006)



$$(a) K_e = \frac{[A]^{1/2}[B]^{1/3}}{[C]^{3/2}} \quad (b) K_e = \frac{[C]^{3/2}}{[A]^2[B]^3}$$

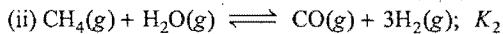
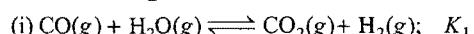
$$(c) K_e = \frac{[C]^{2/3}}{[A]^{1/2}[B]^{1/3}} \quad (d) K_e = \frac{[C]^{2/3}}{[A]^{1/2} + [B]^{1/3}}$$

[Ans. (c)]

[Hint: Coefficient goes to the power of respective active mass.

$$K_e = \frac{[C]^{2/3}}{[A]^{1/2}[B]^{1/3}}$$

6. For the following three reactions (i), (ii) and (iii), equilibrium constants are given:



Which of the following relations is correct? (AIEEE 2008)

$$(a) K_3 K_2^3 = K_1^2 \quad (b) K_1 \sqrt{K_2} = K_3$$

$$(c) K_2 K_3 = K_1 \quad (d) K_3 = K_1 K_2$$

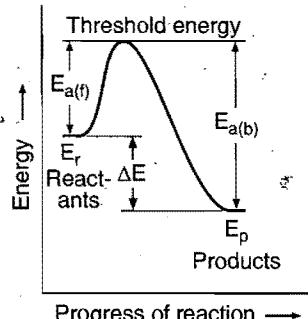
[Ans. (d)]

[Hint: Reaction (iii) is obtained by adding (i) and (ii) hence $K_3 = K_1 \times K_2$]

9.5 ACTIVATION ENERGIES FOR FORWARD AND BACKWARD REACTIONS

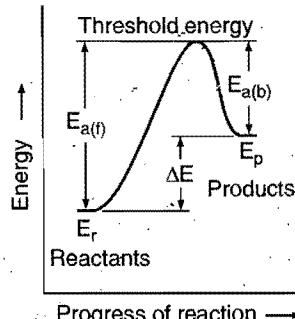
In a reversible reaction, the molecules of the reactants in the forward reaction and the molecules of the products in the backward reaction follow the same path and form the same activated complex. However, the activation energies of both forward and backward reactions are different. Fig. 9.4 (a) and (b) show the activation energies, $E_a(f)$ and $E_a(b)$ respectively, for the forward and backward reactions for exothermic and endothermic reactions. Mathematically, $E_a(f)$ and $E_a(b)$ are related to overall energy change, ΔE , in the process as:

$$\Delta E = E_a(f) - E_a(b) = \Delta H \quad (\text{At constant volume})$$



Progress of reaction →

Fig. 9.4 (a) Activation energies for the forward and backward reactions where forward reaction is exothermic



Progress of reaction →

Fig. 9.4 (b) Activation energies for the forward and backward reactions where forward reaction is endothermic

For exothermic reaction,

$$E_a(f) < E_a(b)$$

Thus, ΔE is negative.

On the other hand, for the endothermic reaction,

$$E_a(f) > E_a(b)$$

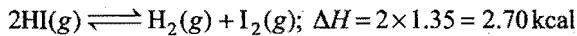
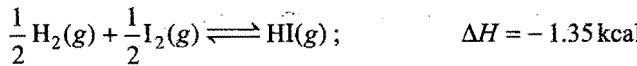
Thus, ΔE is positive

Heat of reaction $\Delta H = \text{Activation energy of forward reaction} - \text{Activation energy of backward reaction.}$

Example 7. For the dissociation of gaseous HI, the energy of activation is 44.3 kcal. Calculate the energy of activation for the reverse reaction. Given, ΔH for the formation of 1 mole of HI from H_2 and I_2 is -1.35 kcal.

Solution:

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g); E_a = 44.3 \text{ kcal}$$



$$\Delta H = E_a(f) - E_a(b)$$

$$2.70 = 44.3 - E_a(b)$$

$$E_a(b) = (44.3 - 2.70)$$

$$= 41.60 \text{ kcal}$$

or

Example 8. For a reaction $X \rightarrow Y$, heat of reaction is +83.68 kJ, energy of reactant X is 167.36 kJ and energy of activation is 209.20 kJ. Calculate (i) threshold energy (ii) energy of product Y and (iii) energy of activation for the reverse reaction ($Y \rightarrow X$).

Solution: (i) Given, $E_a(f) = 209.20 \text{ kJ}$

$$\Delta E = +83.68 \text{ kJ}$$

$$\text{Energy of reactant, } X = 167.36 \text{ kJ}$$

$$\text{Threshold energy} = \text{Energy of reactant } X + \text{Activation energy for forward reaction}$$

$$= 167.36 + 209.20 = 376.56 \text{ kJ}$$

(ii) Energy of reaction, $\Delta E = \text{Energy of product} - \text{Energy of reactant}$

$$\text{Energy of product} = 83.68 + 167.36 = 251.04 \text{ kJ}$$

(iii) Activation energy for backward reaction

$$= \text{Threshold energy} - \text{Energy of product} \\ = 376.56 - 251.04 = 125.52 \text{ kJ}$$

9.6 STANDARD FREE ENERGY CHANGE OF A REACTION AND ITS EQUILIBRIUM CONSTANT

Let ΔG° be the difference in free energy of the reaction when all the reactants and products are in the standard state (1 atmospheric pressure and 298 K) and K_c or K_p be the thermodynamic equilibrium constant of the reaction. Both are related to each other at temperature T by the following relation:

$$\Delta G^\circ = -2.303 RT \log K_c$$

and $\Delta G^\circ = -2.303 RT \log K_p$ (in case of ideal gases)
This equation represents one of the most important results of thermodynamics and relates to the equilibrium constant of a reaction to a thermochemical property. It is sometimes easier to calculate the free energy in a reaction rather than to measure the equilibrium constant.

Standard free energy change can be thermodynamically calculated as:

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

Here, ΔH° = standard enthalpy change,
 ΔS° = standard entropy change.

$$-RT \log_e K_p = \Delta H^\circ - T\Delta S^\circ$$

$$\log_e K_p = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$

$$\log_{10} K_p = \frac{\Delta S^\circ}{2.303 R} - \frac{\Delta H^\circ}{2.303 RT}$$

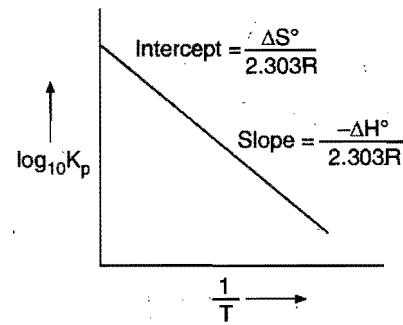


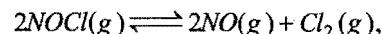
Fig. 9.5

(i) When, $\Delta G^\circ = 0$, then $K_c = 1$.

(ii) When, $\Delta G^\circ > 0$, i.e., +ve, then $K_c < 1$. In this case reverse reaction is feasible, i.e., less concentration of products at equilibrium state.

(iii) When, $\Delta G^\circ < 0$, i.e., -ve, then $K_c > 1$. In this case forward reaction is feasible showing thereby a large concentrations of products till the equilibrium is reached.

Example 9. For the reaction,



calculate the standard equilibrium constant at 298 K. Given that the values of ΔH° and ΔS° of the reaction at 298 K are 77.2 kJ mol⁻¹ and 122 JK⁻¹ mol⁻¹.

Solution: Using the relation,

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= 77200 - 298 \times 122 \\ &= 40844 \text{ J mol}^{-1} \end{aligned}$$

Let the equilibrium constant be K_c° . We know that,

$$\begin{aligned} \Delta G^\circ &= -2.303 RT \log K_c^\circ \\ \text{or } \log K_c^\circ &= -\frac{\Delta G^\circ}{2.303 \times 8.314 \times 298} = -\frac{40844}{2.303 \times 8.314 \times 298} \\ &\approx -7.158 \\ K_c^\circ &= 6.95 \times 10^{-8} \end{aligned}$$

Example 10. ΔG° for $\frac{1}{2}\text{N}_2(g) + \frac{3}{2}\text{H}_2(g) \rightleftharpoons \text{NH}_3(g)$ is -16.5 kJ mol⁻¹. Find out K_p for the reaction at 25°C. Also report K_p and ΔG° for $\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$ at 25°C.

Solution:

$$\log K_p = -\frac{\Delta G^\circ}{2.303 RT} = -\frac{(-16.5 \times 10^3)}{2.303 \times 8.314 \times 298} = 2.8917$$

$$K_p = 779.41$$

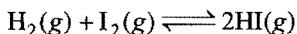
K_p for reaction $\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$ is equal to $(779.41)^2 = 6.07 \times 10^5$

$$\begin{aligned} \Delta G^\circ &= -2.303 \times 8.314 \times 298 \log 6.07 \times 10^5 \text{ joule} \\ &= -32.998 \text{ kJ mol}^{-1} \end{aligned}$$

9.7 EQUILIBRIUM CONSTANT EXPRESSIONS FOR SOME REACTIONS

Case I: Homogeneous gaseous equilibria when, $\Delta n = 0$.

Synthesis of hydrogen iodide: The formation of hydrogen iodide from hydrogen and iodine is represented by the equation:



Let a start be made with ' a ' moles of hydrogen and ' b ' moles of I_2 . These are heated in a sealed bulb having a volume V litre by keeping the bulb in a thermostat till equilibrium is established. If at equilibrium, x moles of each of H_2 and I_2 have reacted, $2x$ moles of HI will be formed.

Thus, the active masses of various reactants and products present at equilibrium are:

$$[\text{H}_2] = \frac{(a-x)}{V} \text{ mol L}^{-1}$$

$$[\text{I}_2] = \frac{(b-x)}{V} \text{ mol L}^{-1}$$

$$[\text{HI}] = \frac{2x}{V} \text{ mol L}^{-1}$$

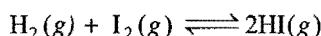
Applying law of mass action,

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)\left(\frac{b-x}{V}\right)} = \frac{4x^2}{(a-x)(b-x)}$$

When, $a = b = 1$, x becomes degree of formation of HI and

$$K_c = \frac{4x^2}{(1-x)^2}$$

The equilibrium constant, K_p , can also be calculated considering partial pressures of reactants and products at equilibrium.



| | | | |
|-----------------------------|---------|---------|------|
| Initial no. of moles | a | b | 0 |
| No. of moles at equilibrium | $(a-x)$ | $(b-x)$ | $2x$ |

Total number of moles at equilibrium

$$= (a-x) + (b-x) + 2x = (a+b)$$

Let the total pressure of the system at equilibrium be P atmosphere.

$$\text{Partial pressure of H}_2, \quad p_{\text{H}_2} = \frac{(a-x)}{(a+b)} \cdot P$$

$$\text{Partial pressure of I}_2, \quad p_{\text{I}_2} = \frac{(b-x)}{(a+b)} \cdot P$$

$$\text{Partial pressure of HI}, \quad p_{\text{HI}} = \frac{2x}{(a+b)} \cdot P$$

$$K_p = \frac{(p_{\text{HI}})^2}{(p_{\text{H}_2})(p_{\text{I}_2})} = \frac{\left(\frac{2x}{a+b}\right)^2 P^2}{\left(\frac{a-x}{a+b}\right)P \times \left(\frac{b-x}{a+b}\right)P} = \frac{4x^2}{(a-x)(b-x)}$$

Thus,

$$K_p = K_c$$

This also follows from the relationship, $K_p = K_c (RT)^{\Delta n}$.

$$\Delta n = 0, \text{ So } K_p = K_c,$$

i.e., for all gaseous reactions of first type, K_p and K_c are identical. Both K_p and K_c have no units.

(a) Effect of pressure: The equation, $K_c = \frac{4x^2}{(a-x)(b-x)}$,

does not include the volume term; hence K_c is independent of pressure. Thus, change of pressure will not alter the final state of equilibrium.

(b) Effect of adding substances (Reactants or products): On adding H_2 to the equilibrium mixture, the value of denominator of equation $K_c = 4x^2 / [(a-x)(b-x)]$ will increase. To maintain the constant value of K_c , the value of numerator must also increase. This can happen if more of HI is formed, i.e., hydrogen combines with iodine to form more of HI. Thus, the reaction moves in a direction in which the added hydrogen is used up. A similar effect is observed when iodine is added to the equilibrium mixture.

The reverse effect is observed when HI is added to the equilibrium mixture, i.e., HI decomposes into H_2 and I_2 .

(c) Effect of temperature: The formation of HI from H_2 and I_2 is an exothermic reaction, i.e., by increasing temperature, the value of equilibrium constant, K_c , decreases. Thus, the yield of HI decreases, i.e., high temperature is not favourable for greater yield of HI.

(d) Effect of adding an inert gas: Addition of an inert gas to equilibrium mixture will make no effect on equilibrium state as in the first type of reactions, volume and pressure changes have no effect on equilibrium state.

Case II: Homogeneous gaseous reaction when, $\Delta n > 0$.

Dissociation of PCl_5 : The dissociation of PCl_5 takes place according to the equation:



Let a moles of PCl_5 be taken in a closed vessel of volume V litre. It is heated and by the time equilibrium is established, x moles are dissociated into PCl_3 and Cl_2 . One molecule of PCl_5 on dissociation gives one molecule of PCl_3 and one molecule of Cl_2 . Thus, x moles of PCl_5 will give x moles of PCl_3 and x moles of Cl_2 .

At equilibrium,

$$[\text{PCl}_5] = \frac{(a-x)}{V}, [\text{PCl}_3] = \frac{x}{V}, [\text{Cl}_2] = \frac{x}{V}$$

Applying law of mass action,

$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{\frac{x}{V} \times \frac{x}{V}}{\frac{(a-x)}{V}} = \frac{x^2}{(a-x)V}$$

When, $a = 1$, x becomes degree of dissociation and

$$K_c = \frac{x^2}{(1-x)V} \quad (\text{units} = \text{mol L}^{-1})$$