CHEMISTRY

A Textbook for Grade 11

C11TB

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Foreword

Liberia, having gone through a period of utmost turmoil till 2003, due to the civil wars, is still reeling under its effect and the added trauma of Ebola in 2014 and effects of the COVID-19 outbreak in 2020. The Liberian government, in the past decade, has made valiant efforts to bring order to the lives of its people. In one such effort, the Ministry of Education (MoE) brought changes to the National Curriculum Framework which are relevant to the present generation, and which would prepare them to meet the challenges of the changing trends of the world. The National Curriculum Framework (NCF) 2018 recommends a change in basic assumptions in the teaching learning process from behaviorist to constructivist approach — moving from hardcore print material to the digital world. Keeping in consideration the sociocultural context and varied experiences of learners as laid down in the Framework, our Teaching Learning Materials are expected to be competent to use multiple methods and techniques like e-learning resources, energized textbooks, and readily available reference material to engage the learners.

As a first initiative, the MoE, through its World Bank-funded Improving Results in Secondary Education (IRISE) project, has adapted textbooks for Grades 10 to 12 in five subjects — English Language and Literature, Mathematics, Biology, Physics and Chemistry.

The National Curriculum Framework, 2018, recommends that children's learning at school is a reflection of their life outside the school and shows them the path to become a responsible citizen who makes knowledge-based choices.This principle marks a departure from the legacy of teacher centered learning to student centered learning. The syllabi and textbooks developed on the basis of the NCF indicate a serious attempt to implement the idea of Activity Base Learning (ABL). We hope these measures will take us ahead in the direction of building a system of education as outlined in the NCF.

Combined with the efforts by the school principals and teachers this will encourage children to reflect on their own learning and to pursue imaginative activities and questions.With this in mind, perhaps for the first time in our country, we are able to provide separate subject specific textbooks accompanied with guides for teachers for 10–12 grades. Not only have these been developed, adapted and modified to the Liberian context, each of the eight Minimum Learning Competencies (MLCs) have been included in each textbook. So as to reach every high school student, for the first time in the country's history we have included the digitized form of the textbook accessible by a Quick Response (QR) code given in each book. Not only does it have the digitized textbook, but it provides additional learning materials for use by students, teachers and interested persons. The links to these e-resources and digitized material is being made available on the MoE's website.

The Textbooks and Teacher Guides have reached the hands of the students after a rigorous quality evaluation by carefully handpicked subject specialists by the MoE, to whom the Ministry expresses gratitude. For the success of this project, I acknowledge the contributions of the IRISE Project Team in the World Bank, and in particular, the Task-Team Leaders; the Project Implementation Team in Liberia headed by its Coordinator Abraham A. Kiazolu II, supported by the Executive Director of the Center of Excellence for Curriculum Development and Textbooks Research, Mrs. Julia K. Sandiman-Gbeyai and her technical working group (TWG), and the International Textbook Consultant and Advisor, Dr Shveta Uppal engaged by the MoE. These notwithstanding would not have been possible without the guidance of the Senior Management Team (SMT) of the Ministry of Education, and in particular, the Deputy Ministers for Instructions, Administration, and Planning, Research and Development, respectively.

Professor Dao Ansu Sonii, Sr.
Minister of Education
Republic of Liberia

Monrovia, Republic of Liberia
January 24, 2023

Acknowledgments

The development of textbooks contributes to the quality of teaching and learning that go on in the classroom.

The Ministry of Education (MoE) has aligned its Curriculum for Grades 10–12 to the National Curriculum Framework (NCF) of 2018. To ensure the provision of Teaching Learning Materials (TLMs) that support the revised curriculum, the Ministry has sought, reviewed and adapted a new set of textbooks and teacher guides along with digitized contents and e-learning resources for the five core subjects taught at the Senior Secondary education level, namely English Language and Literature, Mathematics, Biology, Chemistry and Physics, through an internationally competitive bidding process from the market supported by the World Bank funded Improving Results in Secondary Education (IRISE) Project.

With profound gratitude and honor, we recognize the Senior Management Team of the Ministry, headed by the Coach, Professor D. Ansu Sonii, Sr., for the strategic decision to make teaching learning materials available and accessible to all in the Liberian Senior Secondary School System, and for providing directions through the process of securing these textbooks and other teaching learning materials for our students and teachers. Our special thanks and appreciation to the World Bank for the financial support towards this policy intervention, and its education task-team including Alonso Sanchez, Oni Lusk-Stover and Binta B. Massaquoi for all their technical inputs offered throughout the process to ensure the kind of quality TLMs the Liberian students deserve are made available for improved learning outcomes.

We would like to specifically recognize the invaluable contributions of the 15 subject experts selected by the MoE from across the various education systems and the West African Examinations Council (WAEC) to evaluate, review and sign off on these teaching learning materials. They didn’t just deliver according to our expectations, but also ensured the contextual relevance of the materials

to the Liberian Secondary Education Curriculum and its minimum learning competencies (MLCs). These subject experts include Professor Isaac Saye-Lakpoh Zawolo – *Superintendent* of the Monrovia Consolidated School System (MCSS), Mr. Matthew V.Z. Darblo, Sr. – *Mathematics Instructor* at the University of Liberia (UL), Mr. Charles Tieh Bropleh – *Mathematics Specialist* (MoE), Mrs. Linda Y. Dean – *English Specialist*, Mr. Hassan M. Bangura – *English Language and Literature Expert*, Mr. J. Emmanuel Milton – *English Specialist* (MoE), Mr. Moses K.M. Togbah – *Physics Specialist*, Mr. Prince A. Dossen – *Physics Specialist*, Mr. Benjamin Koryah – *Physics Instructor* at the University of Liberia (UL), Mr. Dominic Dugbe Doe – *Chemistry Specialist*, Mr. Patrick A. Anderson, Sr. – *Director* of the Division of Technical and Vocational Education (MoE), Mr. Kandakai Massaquoi – *Chemistry Specialist*, Ms. Patricia N. Doe – *Head* of Biology Department, African Methodist Episcopal University (AMEU), Mr. Job Carpenter – *Biology Specialist* and Mr. Prince Philip K.A. Aderibigbe – *Biology Specialist*.

The MoE is sincerely grateful to Dr Shveta Uppal, the *International Textbook Consultant* engaged by the IRISE Project to provide technical guidance and quality assurance support to the revising of the Textbooks Management Guidelines (TMG) and the procurement process leading to the provision of textbooks, teacher guides, digital contents and e-learning resources for the Senior Secondary School System in Liberia in accordance with the revised TMG. Heartfelt thanks and appreciations also to the *Executive Director* for the Center of Excellence for Curriculum Development and Textbooks Research, Mrs. Julia K. Sandiman-Gbeyai, and members of her Technical Working Group (TWG) for taking up the responsibility to lead the process of making textbooks and other TLMs available to Liberian students and teachers.

Lastly, we acknowledge the IRISE Project Delivery Team led by Mr. Abraham A. Kiazolu, II – *Project Coordinator*, Mr. Fuseini A. Abu – *International Procurement Specialist* and Mr. Lawrence S. Taylor – *Project Control Specialist* who coordinated the entire process.

We remain grateful to you all!

Hon. Alexander N. Duopu, Sr.,
Deputy Minister for Instruction
Ministry of Education, Republic of Liberia
#The Teacher

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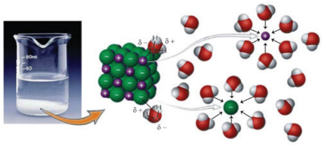

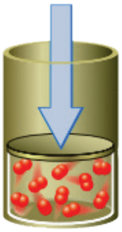

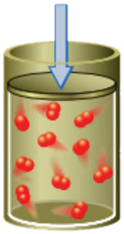

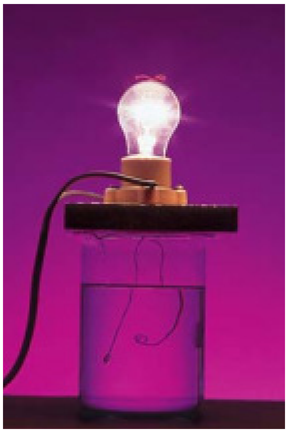

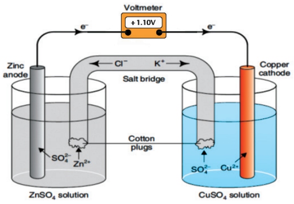
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e⁻
Zinc anode
Cl⁻
K⁺
Salt bridge
Copper cathode
Cotton plugs
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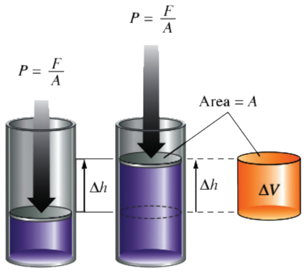

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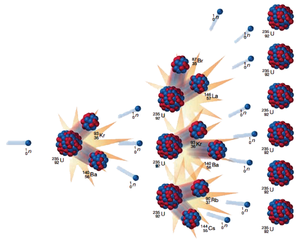

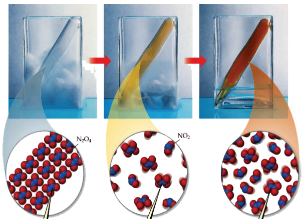

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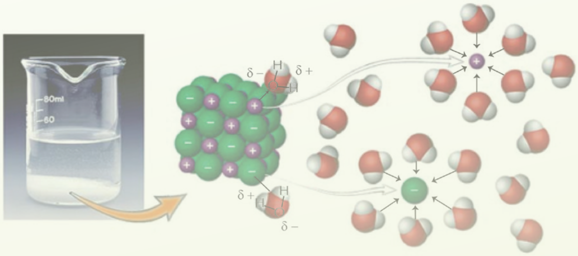
CHAPTER 1

SOLUTIONS AND SOLUBILITY

Chapter Contents



Chapter Outcomes

By the end of this chapter, you will be able to:

- elaborate the properties of solutions, develop mathematical skills as well as laboratory techniques.
- aquire a sound knowledge of solubility as well as demonstrate its practical applications.

Most substances we encounter in our daily lives are mixtures. Often they are homogeneous mixtures, which are called solutions. Some solutions we commonly encounter are salt solution, soft drinks, or antifreeze.

What are the necessary components of a solution? Why do some substances dissolve, while others do not? What effect does a dissolved substance have on the properties of the solution? Answering these questions is the first step in understanding the solutions we encounter in our daily lives.

1.1 SOLUTIONS

Upon completion of this topic, learners will be able to:

- classify mixtures as homogeneous or heterogeneous based on their appearance.
- identify the solute and solvent in a given solution.

All samples of matter are either pure substances or mixtures. A mixture is made up of two or more kinds of matter, each of which retains its own identity and properties. The parts, or components, of a mixture are simply mixed together physically and can usually be separated. In contrast to a pure substance, which by definition has a fixed composition, irrespective of the composition of a mixture.

Mixtures are of two types: homogeneous and heterogeneous.

A. Homogeneous mixtures

A homogeneous mixture is a mixture in which the components that make up the mixture are uniformly distributed throughout the mixture. The composition of the mixture is same throughout. There is only one phase of matter observed in a homogeneous mixture at a time.

There are several examples of homogeneous mixtures encountered in everyday life; these include air, aqueous solution of NaCl, vinegar, dishwashing detergent, and steel.

B. Heterogeneous mixtures

A heterogeneous mixture is a mixture in which the component parts of the mixture are not uniform. Different samples from the mixture are not identical to each other. There are always two or more phases in a heterogeneous mixture, where you can identify a region with properties that are distinct from those of another region.

Where do solutions fit in this classification scheme?

A solution is a homogeneous mixture of two or more substances with each substance retaining its own chemical identity.

A simple binary solution has two components: a solute and a solvent.

Solute is the component that is dissolved or is the less abundant component in the solution. It is the component of the solution that changes physical state.

Solvent is the dissolving agent. In all solutions, whether gaseous, liquid, or solid, the substance present in the greater amount is the solvent, and the physical state of the solvent determines the state of the solution.

Examples

1. A solution of sugar in water is a solid-liquid solution. In this solution, sugar is the solute and water is the solvent.
2. Aerated drinks like soda water, are gas-liquid solutions. These contain carbon(IV) oxide (gas) as solute and water (liquid) as solvent.
3. Air is a gas-gas homogeneous mixture. Its two main constituents are: oxygen (21%) and nitrogen (78%). The other gases are present in very small quantities.

How can you separate components of a mixture?

ACTIVITY 1

Separation of a mixture using simple distillation

The use of distillation to separate the components in a mixture is based on the principle that the liquid in the boiling flask and the vapor have different compositions. Simple distillation involves a single vaporization–condensation cycle. It is used to purify liquids that contain either non-volatile impurities, such as salts, or very small amounts of higher- or lower-boiling liquids.

Procedure

1. In this experiment a salt-water mixture will be separated by distillation. The purity of the collected distilled water will be demonstrated by chemical tests specific for sodium ions (Na^+) and chloride ions (Cl^-).
2. Assemble an apparatus as illustrated in Figure 1. Before fitting the pieces together, apply a light coating of silicone grease to each joint to prevent the joints from sticking.
3. Take a 100 mL round-bottom flask for the distillation flask and a receiving flask. Fill the distillation flask with 50 mL of the prepared salt-water mixture. Add two boiling chips to the distillation flask to ensure smooth boiling of the mixture and to prevent bumping. Be sure that the rubber tubing to the condenser enters the lower

opening and leaves the upper opening. Turn on the water faucet and allow the water to fill the jacket of the condenser slowly, so as not to trap air. Adjust the bulb of the thermometer to below the junction of the condenser and the distillation column.

4. Gently heat the distillation flask with a Bunsen burner. Eventually the liquid will boil, vapors will rise and enter the condenser, and liquid will recondense and be collected in the receiving flask.

Figure 1. Simple distillation setup

5. Discard the first 1 mL of water collected. Record the temperature of the vapors as soon as the 1 mL of water has been collected. Continue collection of the distilled water until approximately one-half of the mixture has been distilled. Record the temperature of the vapors at this point.
6. Turn off the Bunsen burner and allow the glassware to cool before dismantling the distillation apparatus.
7. The distilled water and the liquid in the distillation flask will be tested.
8. Place in separate clean, dry test tubes 2 mL of distilled water and 2 mL of the residue liquid from the distillation flask. Add to each sample 5 drops of silver nitrate solution. Watch the appearance of a white precipitate. Record your observations.
9. Place in separate clean, dry test tubes 2 mL of distilled water and 2 mL of the residue liquid from the flask. Obtain a clean nickel wire from your instructor. In the hood, dip the wire into concentrated nitric acid and hold the wire in a Bunsen burner flame until the yellow color in the flame disappears. Dip the wire into the distilled water sample. Put the wire into the Bunsen burner flame. Record the color of the flame. Repeat the above procedure, cleaning the wire, dipping the wire into the liquid from the boiling flask, and observing the color of the Bunsen burner flame. Record your observations. Sodium ions produce a bright yellow flame in a Bunsen burner flame.

10. Make sure you wipe the grease from the joints before washing the glassware used in the distillation.

Result and analysis

1. Boiling point of water at measured pressure ______________
2. Temperature of vapor after collecting 1 mL ______________
3. Temperature of vapor at the end of distillation ______________

Solution	Observation with 0.5 M $AgNO_3$	Color in Flame test
Distilled water		
Liquid in distillation flask		

1.2 TYPES OF SOLUTIONS

Upon completion of this topic, learners will be able to:

- identify the types of solution.
- define solubility and describe how to determine whether a solution is saturated, unsaturated, or supersaturated.
- describe the role of equilibrium in the solution process and its relationship to the solubility of a solute.

A solution does not always involve water. Solutions may exist as gases, liquids, or solids. Some possible solute-solvent combinations of gases, liquids, and solids in solutions are summarized in Table 1.

Table 1 Examples of solutions

State of solute	State of solvent	Types of solution	State of solution	Example
Gas	Gas	Gas-gas	Gas	Air (O_2 in N_2), natural gas
Gas	Liquid	Gas-liquid	Liquid	Carbon(IV) oxide in water
Liquid	Liquid	Liquid-liquid	Liquid	Ethanol in water
Liquid	Solid	Liquid-solid	Solid	Dental amalgam (Hg in Ag and other metals)
Solid	Liquid	Solid-liquid	Liquid	Brine solution
Solid	Solid	Solid-solid	Solid	Alloys

Exercises

1. Identify the solute (s) and solvent (s) in the following solutions.
   (a) Aerated drinks
   (b) 88% g of Cu and 12% of Sn

(c) Steel

(d) 5 g of $MgCl_2$ dissolved in 1000 g of H_2O

(e) Air which consists of 21% O_2 in N_2

(f) Give an example of a solid solution prepared from a liquid and a solid.

2. What are aqueous solutions?

Depending on the amount of solute present, solutions can be categorized into saturated solutions, unsaturated solutions and supersaturated solutions.

Saturated solutions

When a small amount of solute is added to a solvent, the solute dissolves very easily in the solvent. If the addition of solute continued stage is reached when the solvent cannot dissolve any more solute. At this stage, further added solute remains undissolved and it settles down at the bottom of the container.

A solution containing maximum amount of solute at a given temperature is called a saturated solution. A saturated solution is one in which undissolved solute is in equilibrium with dissolved solute.

The amount of solute needed to form a saturated solution in a given quantity of solvent is known as the solubility of that solute. That is, the solubility of a solute in a given solvent is the maximum amount of the solute that can dissolve in a given amount of the solvent at a specified temperature. For example, the solubility of NaCl in water at 0°C is 35.7 g per 100 g of water. This is the maximum amount of NaCl that can be dissolved in water to give a stable equilibrium solution at that temperature.

Unsaturated solutions

If a solution contains less solute than the amount needed to form a saturated solution, the solution is known as unsaturated. Such solutions have the capacity to dissolve more solute to become a saturated solution without altering any other conditions. Thus, a solution containing 10.0 g of NaCl per 100 mL of water at 0°C is unsaturated because it has the capacity to dissolve more solute.

What happens if a solute is added to an unsaturated solution?

Supersaturated solutions

When saturated solutions are heated, they develop further capacity to dissolve more solute. Such solutions contain higher amount of solute than is required to form a saturated solution. A solution that contains more solute than a saturated solution is known as supersaturated solution. Because the solute in a supersaturated solution is present in an amount higher than the equilibrium concentration, supersaturated solutions are unstable. Therefore, an easy way to get a supersaturated solution is to prepare a saturated solution at high temperature. It is then cooled to a temperature where excess solute crystallizes out and leaves behind a saturated solution. The addition of a small crystal of the solute (a seed crystal) provides a template for crystallization of the excess solute, leading to a saturated solution in contact with excess solid.

Figure 2. Addition of a crystal causes precipitation from a supersaturated solution.

Exercises

1. Given a solution of $MnSO_4.H_2O$, what experiment could you perform to determine whether the given solution is unsaturated, saturated or supersaturated?

1.3 DILUTE AND CONCENTRATED SOLUTIONS

Upon completion of this topic, learners will be able to:

- distinguish between dilute and concentrated solutions.

Concentration of a solution expresses the amount of solute dissolved in a given quantity of solvent or solution. The concentration of a solution can be expressed either qualitatively or quantitatively. The terms dilute and concentrated are used to describe a solution qualitatively. Dilute solutions are those which contain a relatively smaller amount of dissolved solute in the solution.

Concentrated solutions are those which contain a relatively larger amount of dissolved solute in the solution. For example, brine is a concentrated solution of common salt in water.

1.4 SOLUTION CONCENTRATION UNITS

Upon completion of this topic, learners will be able to:

- express the concentration of a solution using different units.
- convert between the different concentration units.
- describe how to prepare solutions of specific concentration using pure solutes and solvent, or using solutions of higher concentration than the one desired.

Chemists use various ways to express concentration quantitatively. Let us examine the most common units of concentration: %w/w, %v/v, ppm, ppb, mole fraction, molarity, normality, and molality.

Percentage

Percentage unit of concentration refers to the percentage of solute present in a solution. The percentage of solute can be expressed by mass or by volume.

Mass percentage :- mass/mass (%w/w)

It is the number of grams of solute in 100 grams of solution. Calculation of this ratio is carried out by using the following formula:

$$\%\ \text{w/w} = \frac{\text{Mass of solute (g)}}{\text{Mass of solute (g)} + \text{Mass of solvent (g)}} \times 100$$

$$= \frac{\text{Mass of solute (g)}}{\text{Mass of solution (g)}} \times 100$$

Example: A solution of hydrochloric acid that is 36 % HCl by mass contains 36 g of HCl in 100 g of solution.

We often express the concentration of very dilute solutions in parts per million (ppm) or parts per billion (ppb). These quantities are similar to mass percentage but use 10^6 (a million) or 10^9 (a billion), respectively, in place of 100 as a multiplier for the ratio of the mass of solute to the mass of solution.

Parts per million (ppm) is defined as parts of solute present in (10^6 part) of solution. Thus, parts per million is defined as:

$$\text{ppm of component} = \frac{\text{Mass of solute (g)}}{\text{Total mass of solution (g)}} \times 10^6$$

A solution whose solute concentration is 1 ppm contains 1 g of solute in one million grams of solution.

The acceptable maximum concentrations of toxic or carcinogenic substances in the environment are often expressed in ppm or ppb.

Parts per billion (ppb) is defined as:

$$\text{ppm of component} = \frac{\text{Mass of solute (g)}}{\text{Total mass of solution (g)}} \times 10^9$$

Volume Percentage: volume /volume (% v/v)

The volume percent is the volume of a liquid in 100 mL of solution. The label on a bottle of ordinary rubbing alcohol reads "isopropyl alcohol, 70% by volume."

Such a solution can be made by mixing 70 mL of alcohol with water to make a total volume of 100 mL.

$$\% \text{ v/v} = \frac{\text{Volume of liquid}}{\text{Total volume of solution}} \times 100$$

Mole fraction

It is the ratio of number of moles of a particular component to the total number of moles of all the components in the solution. If substance 'A' dissolves in substance 'B' and their number of moles are n_A and n_B respectively; then the mole fractions of A and B are given as

$$\text{Mole fraction of A} = \frac{\text{Number of moles of A}}{\text{Number of moles of solution}} = \frac{n_A}{n_A + n_B}$$

$$\text{Mole fraction of B} = \frac{\text{Number of moles of B}}{\text{Number of moles of solution}} = \frac{n_B}{n_A + n_B}$$

The symbol χ is commonly used for mole fraction, with a subscript to indicate the component of interest. Thus, if a solution contains 1.00 mol of HCl (36.5 g) and 8.00 mol of water (144 g), the mole fraction of HCl is

$$\chi_{\text{HCl}} = \frac{\text{moles of solute}}{\text{moles of solute} + \text{moles of solution}} = \frac{1.00 \text{ mol}}{1.00 \text{ mol} + 8.00 \text{ mol}} = 0.111$$

Mole fractions have no units. The sum of the mole fractions of all components of a solution must be equal to 1. Thus, in the aqueous HCl solution

$$\chi_{H_2O} = 1.000 - 0.111 = 0.899$$

For a solution containing *i* number of components, we have:

$$\chi_i = \frac{n_i}{n_1 + n_2 + \ldots + n_i} = \frac{n_i}{\sum_1^i n_i}$$

It can be shown that in a given solution the sum of all the mole fractions is unity, i.e.

$$\chi_1 + \chi_2 + \ldots + \chi_i = 1$$

Examples

Calculate the mole fraction of HCl in a solution of hydrochloric acid in water, containing 36 percent HCl by weight?

Solution

The solution contains 36 g of HCl and 64 g of H_2O

$$\text{Number of moles of HCl} = (36 \text{ g HCl})\left(\frac{1 \text{ mol HCl}}{36.5 \text{ g HCl}}\right) = 0.99 \text{ mol}$$

$$\text{Number of moles of } H_2O = (64 \text{ g } H_2O)\left(\frac{1 \text{ mol } H_2O}{18 \text{ g } H_2O}\right) = 3.55 \text{ mol}$$

$$\chi_{HCl} = \frac{\text{Moles of HCl}}{\text{Moles of HCl} + \text{Moles of } H_2O} = \frac{0.99}{0.99 + 3.55} = \frac{0.99}{4.54} = 0.22$$

Exercises

1. Calculate the χ_{H_2O} in example and check to see that the mole fractions of each substance sum to 1.
2. Calculate the mole fractions of toluene and benzene in the solution that contains 35.6 g of toluene and 125 g of benzene?

Molarity

Molarity is the most common concentration measure for aqueous solutions. It is a concentration unit defined as 'number of moles of solute dissolved in one liter of solution.'

One mole of NaOH has a mass of 40.0 g. If this quantity of NaOH is dissolved in enough water to make exactly 1.00 L of solution, the solution is a 1 M solution. This relationship between molarity, moles, and volume is expressed in the following way.

$$\text{Molarity (M)} = \frac{\text{Number of mole of solute (mol)}}{\text{Volume of solution (L)}}$$

Examples

You have 3.50 L of solution that contains 90.0 g of sodium chloride, NaCl. What is the molarity of that solution?

Solution

Given: Mass of solute = 90.0 g NaCl

Volume of solution = 3.50 L

Unknown: Molarity of NaCl solution

Molarity is the number of moles of solute per liter of solution. The solute in the problem is described by mass, not in moles. You need one conversion (grams to moles of solute) using the inverted molar mass of NaCl to arrive at your answer.

$$\text{grams of solute} \longrightarrow \text{number of moles of solute} \longrightarrow \text{molarity}$$

$$\text{g NaCl} \times \frac{\text{1 mol NaCl}}{\text{g NaCl}} = \text{mol NaCl}$$

$$\frac{\text{Number of moles of solute}}{\text{V solution L}} = \text{Molarity of solution (M)}$$

You need the molar mass of NaCl (58.44 g/mol).

$$\text{90.0 g NaCl} \times \frac{\text{1 mol NaCl}}{\text{58.44 g NaCl}} = \text{1.54 mol NaCl}$$

$$\frac{\text{1.54 mol NaCl}}{\text{3.50 L of solution}} = \text{0.440 M NaCl}$$

The units cancel to give the desired moles of solute per liter of solution, which is molarity.

Exercises

1. What is the molarity of a solution containing of 5.85 g of potassium iodide, KI, dissolved in enough water to make 0.125 L of solution?
2. How many moles of H_2SO_4 are present in 0.500 L of a 0.150 M H_2SO_4 solution?

Molarity is not a convenient concentration measure when the temperature of the solution changes. This is because a solution expands as it is heated. Consequently, the total volume of solution changes with temperature, causing molarity to vary.

ACTIVITY 2

Preparation of a standard solution of sodium carbonate

A standard solution is one whose concentration is accurately known. A primary standard is a substance that can be used to prepare a standard solution directly. A primary standard (such as anhydrous sodium carbonate) is available in a pure state, is stable and is water-soluble.

Anhydrous sodium carbonate (Na_2CO_3) has a molar mass of 106 g mol^{-1}. A 0.1 M solution is made, using a 250 cm^3 volumetric flask. For 250 cm^3 of 0.1 M sodium carbonate solution, the mass required is: (106 × 0.1 × 250) / 1000 = 2.65 g

Procedure

1. Using a balance, measure accurately 2.65 g of pure anhydrous sodium carbonate on a watch glass.

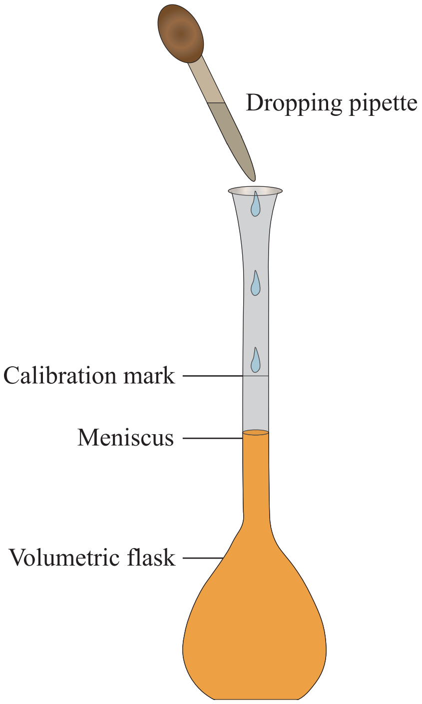


Figure 3.

2. Slowly transfer the sodium carbonate with stirring, to about 50 cm^3 of deionised water in a clean 250 cm^3 beaker. To ensure that all the sodium carbonate is transferred, use a wash bottle to rinse the watch glass with deionised water, and add rinsings to the beaker.

3. Continue stirring the mixture with a stirring rod until the sodium carbonate has fully dissolved. Using a wash bottle, wash off the solution on the stirring rod with deionised water into the beaker.
4. Pour the solution using a clean funnel into the 250 cm^3 volumetric flask. Using a wash bottle, rinse out the beaker several times with deionised water, and add the rinsings to the solution in the flask. Rinse the funnel with deionised water, allowing the water to run into the flask.
5. Fill the flask to within about 1 cm of the calibration mark, and then add the water dropwise, using a dropping pipette, until the bottom of the meniscus just rests on the calibration mark.
6. Stopper the flask and invert it several times to ensure a homogeneous (evenly mixed) solution. Label the flask.

Discussion questions

1. Why is it possible to make a standard solution of sodium carbonate directly?
2. Why is it necessary to slowly add the solid sodium carbonate, with stirring, to the water in the beaker?
3. What precaution is taken to ensure that all of the sodium carbonate is transferred from the watch glass to the beaker?
4. Why is it necessary to be careful when adding the last few drops of water to the volumetric flask?

Molality

For applications where the solution temperature changes, chemists prefer to use molality (m, units of mol/kg).

Molality is the concentration of a solution expressed in moles of solute per kilogram of solvent. A solution that contains 1 mol of solute, (sodium hydroxide, NaOH, for example), dissolved in exactly 1 kg of solvent is a “one molal” solution. The symbol for molality is m, and the concentration of this solution is written as 1 m NaOH.

The molality of any solution can be found by dividing the number of moles of solute by the mass in kilograms of the solvent in which it is dissolved.

$$\text{Molality} = \frac{\text{Moles of solute}}{\text{Mass of solvent (kg)}}$$

Examples

Hydrogen peroxide as a disinfectant typically contains 3.0% H_2O_2 by mass. Assuming that the rest of the content is water, what is the molality of this disinfectant?

Solution

To calculate molality, we need moles of solute and mass of solvent in kilograms. To find these quantities, it is convenient to consider 100 g of solution, for which the mass percentage of one component is given.

In 100 g of disinfectant, there are 3.0 g of hydrogen peroxide and 97 g of water. We need to convert the mass of solute into moles and the mass of solvent into kilograms:

$$\text{Molar mass of } H_2O_2 = 34.02 \text{ g/mol}$$

$$nH_2O_2 = \frac{\text{Mass of solute}}{\text{Molar mass}} = \frac{3.0 \text{ g}}{34.02 \text{ g/mol}} = 0.0882 \text{ mol}$$

$$\text{Mass of water} = (97 \text{ g}) \frac{1 \text{ kg}}{1000 \text{ g}} = 0.0970 \text{ kg}$$

$$m = \frac{n}{\text{Mass of solvent in kg}} = \frac{0.0882 \text{ mol}}{0.0970 \text{ kg}} = 0.909 \text{ m}$$

The unit mole of solute per kg of solvent is correct for molality.

Exercises

1. How much iodine must be added to prepare 0.480 m solution of iodine in CCl_4 if 100.0 g of CCl_4 is used?
2. What is the molality of acetone in a solution containing 255 g of acetone, $(CH_3)_2CO$ dissolved in 200 g of water?
3. What quantity, in grams, of methanol, (CH_3OH), is required to prepare 0.244 m solution in 400 g of water?

Normality

Normality is defined as 'the number of gram equivalents (or simply equivalents) per liter of solution', where the definition of an equivalent depends on the reaction taking place in the solution.

Mathematically,

$$\text{Normality (N)} = \frac{\text{Number of equivalent of solute}}{\text{Volume of solution in liter}}$$

$$\text{Number of equivalent of solute} = \frac{\text{Mass of solute (g)}}{\text{Equivalent mass of solute (g)}}$$

$$\text{or, } N = \frac{\text{Mass of solute (g)}}{\text{Equivalent mass of solute (g)} \times \text{Volume of solution (L)}}$$

A solution containing one gram-equivalent of solute per liter of solution is called one normal solution or 1N solution.

Equivalent masses are determined as follows:

1. The equivalent mass of an acid is defined as 'mass of the acid which can furnish one mole of H^+. In other words, the equivalent mass is the molar mass divided by the number of H^+ furnished per molecule.

   Example The equivalent masses of HCl and CH_3COOH are the same as their molar masses, since each contains one acidic hydrogen per molecule.

2. The equivalent mass of a base is that fraction of the molar mass which contains or can supply one mole of OH^-, or can react with one mole of H^+.

   Example The equivalent mass of $Ba(OH)_2$ is ½ of its molar mass.

3. The equivalent mass of an oxidizing or reducing agent for a particular reaction is equal to its molar mass divided by the total number of moles of electrons gained or lost when the reaction of one mole occurs.

   For example: MnO_4^- reacting in an acidic solution accepts five electrons to produce Mn^{2+}:

   $$MnO_4^- + 5e^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O$$

   Since the MnO_4^- ion present in 1 mole of $KMnO_4$ consumes 5 moles of electrons, the equivalent mass is the molar mass divided by 5:

   $$\text{Equivalent mass of KMnO}_4 = \frac{\text{Molar mass}}{5} = \frac{158\text{ g}}{5} = 31.6\text{ g}$$

4. Equivalent mass of a salt is the ratio of

   $$\text{Equivalent mass of a salt} = \frac{\text{Molar mass of the salt}}{\text{Total positive valency}}$$

Activity 3

Preparation of 0.1N oxalic acid solution

Procedure

Calculate the amount of oxalic acid required to prepare 1 liter of 0.1N solution. Weigh out accurately pure oxalic acid in a clean dry beaker, dissolve in about 200 mL of distilled water and transfer it to a 1 liter volumetric flask. Make at least three washings to the beaker with distilled water and transfer to the volumetric flask. Make up the volume to the 1 liter mark with distilled water. This is 0.1 N solution of oxalic acid. Transfer to a reagent bottle and label it.

The standard solution of oxalic acid (Primary standard) is used to find the strength of solutions of alkalies like NaOH, KOH (Secondary standards) whose standard solutions cannot be made by direct weighing.

Secondary standard substances

Those substances or reagents which cannot be obtained in a sufficient pure state, e.g. NaOH, KOH, HCl, H_2SO_4 are called secondary standard substances. What analytical method can be used for the standardization of secondary standard solution?

Converting concentration units

Sometimes it is desirable to convert one concentration unit of a solution to another. Mole fraction, molarity, and molality all are mole-based for the solute, but the denominators of these concentration measures are quite different. Mole fraction uses total number of moles, molarity uses total volume, and molality uses mass of solvent.

To interconvert molality and molarity, we need to know the density of the solution. The mass of the solution is the sum of masses of the solvent and solute. The volume of the solution can be calculated from its mass and density.

Example outlines the calculation of the molality of a solution from the mass of solute and the mass of solvent.

Examples

The density of a 2.45 M aqueous solution of methanol (CH_3OH) is 0.976 g/mL. What is the molality of the solution? The molar mass of methanol is 32.04 g.

Solution

To calculate the molality, we need to know the number of moles of methanol and the mass of solvent in kilograms. We assume 1 L of solution, so the number of moles of methanol is 2.45 mol.

$$m = \frac{\text{Mole of solute}}{\text{Mass of solvent kg}}$$

Our first step is to calculate the mass of water in one liter of the solution, using density as a conversion factor. The total mass of 1 L of a 2.45 M solution of methanol is

$$1\text{L soln} \times \frac{1000\text{ mL soln}}{1\text{L soln}} \times \frac{0.976\text{ g}}{1\text{ mL soln}} = 976\text{ g}$$

Because this solution contains 2.45 moles of methanol, the amount of water (solvent) in the solution is mass of H_2O = Mass of solution – Mass of solute

$$= 976\text{ g} - \left(2.45\text{ mol }CH_3OH \times \frac{32.04\text{ g }CH_3OH}{1\text{ mol }CH_3OH}\right)$$

$$= 898\text{ g}$$

The molality of the solution can be calculated by converting 898 g to 0.898 kg:

$$\text{molality} = \frac{2.45\text{ mol }CH_3OH}{0.898\text{ kg }H_2O}$$

$$= 2.73\text{ m}$$

Exercises

1. A solution containing equal masses of glycerol ($C_3H_8O_3$) and water has a density of 1.10 g/mL. Calculate (a) the molality of glycerol, (b) the molarity of glycerol in the solution.
2. Determine the molality and mole fraction of concentrated aqueous HCl, which is 12.0 M and has a density of 1.19 g/mL.

Diluting solutions

Commercially available aqueous ammonia (28.0% NH_3) is 14.8 M NH_3. Suppose you want a solution that is 1.00 M NH_3. You need to dilute the concentrated solution with a definite quantity of water. For this purpose, you must know the relationship between the molarity of the solution before dilution (the initial molarity) and that after dilution (the final molarity).

To obtain this relationship, first recall the equation defining molarity:

$$\text{Molarity (M)} = \frac{\text{Number of mole of solute (mol)}}{\text{Volume of solution (L)}}$$

You can rearrange this to give

$$\text{Moles of solute} = \text{Molarity} \times \text{liters of solution}$$

The product of molarity and the volume (in liters) gives the moles of solute in the solution. Writing for the initial molar concentration and for the initial volume of solution, you get

$$\text{Moles of solute} = M_i \times V_i$$

When the solution is diluted by adding water, the concentration and volume change to M_f (the final molar concentration) and V_f (the final volume), and the moles of solute equals

$$\text{Moles of solute} = M_f \times V_f$$

Because the moles of solute has not changed during the dilution

$$M_i \times V_i = M_f \times V_f$$

Examples

You are given a solution of 14.8 M NH_3. How many milliliters of this solution do you require to give 100.0 mL of 1.00 M NH_3 when diluted?

Solution

You know the final volume (100.0 mL), final concentration (1.00 M), and initial concentration (14.8 M). You write the dilution formula and rearrange it to give the initial volume.

$$M_i \times V_i = M_f \times V_f$$

$$V_i = \frac{M_f \times V_f}{M_i}$$

Now you substitute the known values into the right side of the equation.

$$V_i = \frac{1.00\ \text{M} \times 100.0\ \text{mL}}{14.8\ \text{M}} = 6.76\ \text{mL}$$

Exercises

1. You have a solution that is 1.5 M H_2SO_4 (sulfuric acid). How many milliliters of this acid do you need to prepare 100.0 mL of 0.18 M H_2SO_4?

ACTIVITY 4

Dilution of concentrated solutions

A solution of desired concentration can be prepared by diluting a small volume of a more concentrated solution with additional solvent. A stock solution is a commercially prepared solution of known concentration and is often used for this purpose. Diluting a stock solution is preferred because the alternative method, weighing out tiny amounts of solute, is difficult to carry out with a high degree of accuracy. Dilution is also used to prepare solutions from substances that are sold as concentrated aqueous solutions, such as strong acids.

It requires calculating the number of moles of solute desired in the final volume of the more dilute solution and then calculating the volume of the stock solution that contains this amount of solute.

The procedure for preparing a solution of known concentration from a stock solution is shown in the following figure:

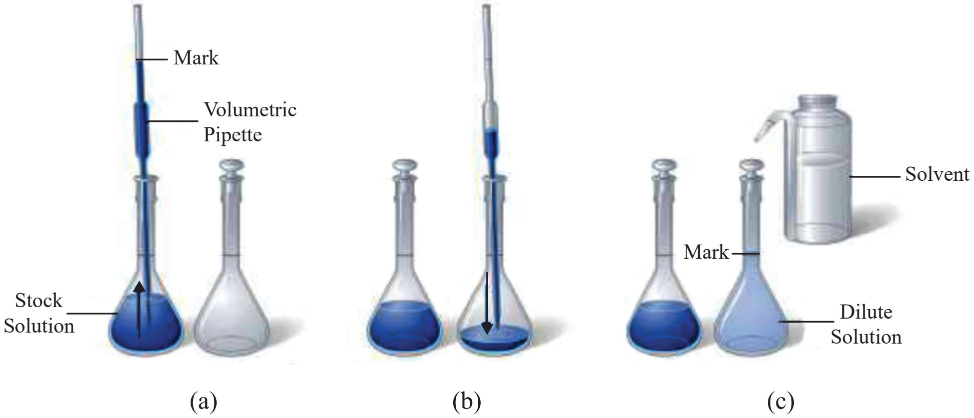


Figure 4. Preparation of a Solution of Known Concentration by Diluting a Stock Solution (a) A volume (V_i) containing the desired moles of solute (M_i) is measured from a stock solution of known concentration. (b) The measured volume of stock solution is transferred to a second volumetric flask. (c) The measured volume in the second flask is then diluted with solvent up to the volumetric mark [$V_iM_i=V_fM_f$].

Remember that diluting a given quantity of stock solution with solvent does *not* change the number of moles of solute present. The relationship between the volume and concentration of the stock solution and the volume and concentration of the desired diluted solution is therefore

Moles of solute before dilution = Moles of solute after dilution

$$V_i M_i = V_f M_f$$

where the subscripts *i* and *f* indicate the initial and final states of solutions, respectively.

Procedure

1. Calculate the volume of stock solution of H_2SO_4 for preparing the required concentration of H_2SO_4.
2. Carefully add the concentrated acid into the burette.
3. With the help of a measuring cylinder, take a measured volume of distilled water that is slightly less than the volume of water which will be required.
4. Slowly add with stirring 10.0 mL of the acid into a beaker containing 50 mL of distilled water.
5. After all the acid has been added, transfer the new solution into a volumetric flask (1 L) and add water up to the mark.

Observations and analysis

(a) Why are acid added to the water not the water to the acid?

(b) Explain whether volume, mass or number of moles of the solute is changed or not in the process.

(c) What is the new concentration of the H_2SO_4? Show your steps?

Conclusion

Summarize and explain what happened in your experiment. Look back at the purpose of your experiment and assess whether or not you met your goal in performing the experiment.

Write a laboratory report in groups and present your report to the rest of the class.

1.5 COLLIGATIVE PROPERTIES

Upon completion of this topic, learners will be able to:

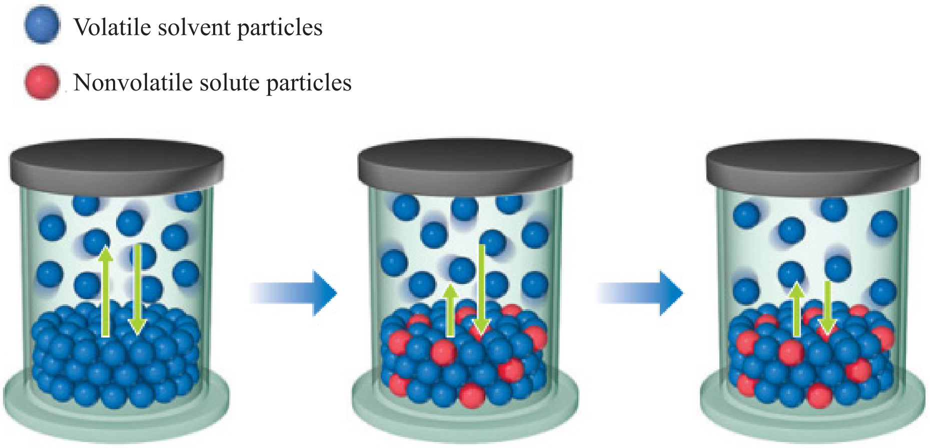
- describe the colligative properties of solutions.
- carry out calculations based on the colligative properties of solutions like vapour pressure, boiling point, freezing point, and osmotic pressure.
- explain why colligative properties of ionic solutions vary from the predicted properties.
- calculate the colligative properties for solutions of electrolytes.
- predict the ideal van't Hoff factor of ionic solutes.

A solution formed by the addition of a non-volatile solute to a solvent has a lower freezing point, a higher boiling point, and a lower vapor pressure than that of the pure solvent. These effects are related and are known as colligative properties. Colligative properties are properties that depend only on the number of solute particles in a solution, not on the nature of particles. These colligative properties include vapor pressure lowering, boiling point elevation, freezing point depression, and osmotic pressure. This small set of properties is of central importance to many natural phenomena and technological applications. As we examine each one, notice how solute concentration quantitatively affects the properties.

Vapor pressure lowering

A liquid in a closed container establishes equilibrium with its vapor. The vapor pressure is the pressure exerted by the vapor when it is in equilibrium with the liquid. A substance that has no measurable vapor pressure is non-volatile, whereas one that exhibits a vapor pressure is volatile.

If a solute is non-volatile, the vapor pressure of its solution is always less than that of the pure solvent. This lowering of vapor pressure is a direct consequence of some of the solute molecules or ions occupying positions on the surface of the liquid. Their presence decreases the probability of solvent molecules escaping; that is, the number of surface-occupying solvent molecules has been decreased, as illustrated in Figure 5.



Equilibrium

Rate of vaporization reduced by the presence of non-volatile solute

Equilibrium reestablished with fewer molecules in gas phase

Figure 5. Vapor-pressure lowering. The presence of a non-volatile solute particles in a liquid solvent results in reduction of the vapor pressure above the liquid.

The vapor pressure of a volatile solvent above a solution containing a non-volatile solute is proportional to the solvent's concentration in the solution. This relationship is expressed by Raoult's law, which states that the vapor pressure of a solvent over a solution, $P_{solvent}$, is given by the vapor pressure of the pure solvent, $P^{\circ}_{solvent}$, times the mole fraction of the solvent in the solution, $\chi_{solvent}$:

$$P_{solvent} = \chi_{solvent} P^{\circ}_{solvent}$$

where, $P_{solvent}$ is the vapour pressure of the solvent in the solution

$P^{\circ}_{solvent}$ is the vapour pressure of the pure solvent

For example, the vapor pressure of pure water at 20°C is $P^{\circ}_{H_2O} = 17.5$ torr. Imagine holding the temperature constant while adding glucose ($C_6H_{12}O_6$) to the water so that the mole fractions in the resulting solution are $\chi_{H_2O} = 0.800$ and $\chi_{C_6H_{12}O_6}$

= 0.200. The vapor pressure of the water above this solution is 80.0 % of that of pure water:

$$P_{H_2O} = \chi_{H_2O} P^\circ_{H_2O} = (0.800)(17.5\ \text{torr}) = 14.0\ \text{torr}$$

The presence of the non-volatile solute lowers the vapor pressure of the volatile solvent by $\Delta P = P^\circ_{\text{solvent}} - P_{\text{solvent}}$.

$$\Delta P = P^\circ_{H_2O} - P_{H_2O}$$

$$\Delta P = 17.5\ \text{torr} - 14.0\ \text{torr}$$
$$\Delta P = 3.5\ \text{torr}$$

In a solution containing only one solute, $\chi_{\text{solvent}} = 1 - \chi_{\text{solute}}$, Raoult's law equation can be written as:

$$P_{\text{solvent}} = (1 - \chi_{\text{solute}})\, P^\circ_{\text{solvent}}$$
$$P_{\text{solvent}} = P^\circ_{\text{solvent}} - P^\circ_{\text{solvent}}\chi_{\text{solute}}$$
$$P^\circ_{\text{solvent}} - P_{\text{solvent}} = P^\circ_{\text{solvent}}\chi_{\text{solute}}$$
$$\Delta P = P^\circ_{\text{solvent}}\chi_{\text{solute}}$$

Thus, the decrease in vapour pressure, ΔP, is directly proportional to the solute concentration (measured in mole fraction).

Thus, for the example of the solution of glucose in water, we have

$$\Delta P = \chi_{C_6H_{12}O_6} P^\circ_{H_2O} = (0.200)(17.5\ \text{torr}) = 3.50\ \text{torr}$$

Exercises

1. Why does seawater evaporate more slowly than fresh water at the same temperature?
2. Glycerin ($C_3H_8O_3$) is a non-volatile non-electrolyte with a density of 1.26 g/mL at 25°C. Calculate the vapor pressure at 25°C of a solution made by adding 50.0 mL of glycerin to 500.0 mL of water. The vapor pressure of pure water 25°C is 23.8 torr, and its density is 1.00 g/mL.
3. The vapor pressure of pure water at 110°C is 1070 torr. A solution of ethylene glycol and water has a vapor pressure of 1.00 atm at 110°C. Assuming that Raoult's law is obeyed, what is the mole fraction of ethylene glycol in the solution?

Solutions sometimes have two or more volatile components. Gasoline, for example, is a solution of several volatile liquids. To gain some understanding of such mixtures, consider an ideal solution of two volatile liquids, A and B. The partial pressures above the solution are given by Raoult's law:

$$P_A = \chi_A P_A^\circ \quad \text{and} \quad P_B = \chi_B P_B^\circ$$

and the total vapor pressure above the solution is given by Dalton's law of partial pressure

$$P_{total} = P_A + P_B = \chi_A P_A^\circ + \chi_B P_B^\circ$$

Boiling point elevation

The boiling point of a solution is the temperature at which its vapor pressure equals the external atmospheric pressure.

Adding a non-volatile solute to a solvent raises the boiling point of the resulting solution above that of the pure solvent. This is logical when we consider that the vapor pressure of the solution is lower than that of the pure solvent and that the boiling point depends on vapor pressure. A higher temperature will be needed to raise the depressed vapor pressure of the solution to atmospheric pressure. As a result, the boiling point of the solution is higher than that of the pure solvent.

The boiling point elevation (ΔT_b) is defined as the boiling point of the solution (T_b) minus the boiling point of the pure solvent (T_b°):

$$\Delta T_b = T_b - T_b^\circ$$

Because $T_b > T_b^\circ$, ΔT_b is a positive quantity.

The value of ΔT_b is directly proportional to the solution molality:

$$\Delta T_b = K_b m$$

When K_b is expressed in°C/m and m is expressed in mol of solute/kg of solvent, ΔT_b is the boiling-point elevation in°C.

The magnitude of K_b, which is called the molal boiling-point-elevation constant, depends only on the solvent. The molal boiling-point constant (K_b) is the boiling-point elevation of the solvent in a 1-molal solution of a non-volatile, non-electrolyte solute. The boiling-point elevation of a 1-molal solution of any non-electrolyte solute in water has been found by experiment to be 0.51°C. Thus, the molal boiling-point constant for water is 0.51°C/m.

For different solvents, the molal boiling-point constants have different values. Some other values for K_b are included in Table 2. Like the freezing-point constants, these values are most accurate for dilute solutions.

Table 2 **Molal boiling point elevation constants (K_b) and freezing point depression constants (K_f) for several solvents**

Solvent	Boiling point (°C)	K_b (°C · kg/mol)	Freezing Point (°C)	K_f (°C · kg/mol)
Water (H_2O)	100.0	0.51	0	1.86
Carbon tetrachloride (CCl_4)	76.5	5.03	-22.99	30.
Chloroform ($CHCl_3$)	61.2	3.63	-63.5	4.70
Benzene (C_6H_6)	80.1	2.53	5.5	5.12
Carbon disulfide (CS_2)	46.2	2.34	-111.5	3.83
Ethyl Ether ($C_4H_{10}O$)	34.5	2.02	-116.2	1.79
Camphor ($C_{10}H_{16}O$)	208.0	5.95	179.8	40.

Examples

What is the boiling point elevation of a solution made from 20.1 g of a non-electrolyte solute and 400.0 g of water? The molar mass of the solute is 62.0 g.

Solution

Given: Solute mass = 20.1 g

Solute molar mass = 62.0 g

Solvent mass and identity = 400.0 g of water

Unknown: Boiling point elevation

Find the molal boiling point constant, K_b, from table 2. To use the equation for boiling-point elevation, $\Delta T_b = K_b m$, you need to determine the molality of the solution.

$$\text{Mass of solute}(\text{g}) \times \frac{1 \text{ mol solute}}{\text{Molar mass solute}(\text{g})} = \text{Amount of solute } (\text{mol})$$

$$20.1 \text{ g of solute} \times \frac{1 \text{ mol solute}}{62.0 \text{ g of solute}} = 0.324 \text{ mol off solute}$$

$$\frac{\text{Amount of solute}(\text{mol})}{\text{Mass of solvent}(\text{g})} \times \frac{1000 \text{ g Water}}{1 \text{ kg Water}} = \text{Molality}$$

$$\frac{0.324\ \text{mol of solute}}{400.0\ \text{g Water}} \times \frac{1000\ \text{g Water}}{1\ \text{kg Water}} = 0.810\frac{\text{mol solute}}{\text{kg Water}}$$

$$\text{m} = 0.810\ \text{m}$$

$$\Delta T_b = 0.51\frac{°\text{C}}{\text{m}} \times 0.810\ \text{m} = 0.41°\text{C}/\text{m}$$

A common application of the phenomenon of boiling point elevation involves automobiles. The coolant ethylene glycol (a non-volatile solute) is added to car radiators to prevent boil over in hot weather. The engine may not run any coolant, but the coolant–water mixture will not boil until it reaches a temperature well above the normal boiling point of water.

Exercises

1. A solution contains 450.0 g of sucrose, $C_{12}H_{22}O_{11}$, a non-electrolyte dissolved in 250.0 g of water. What is the boiling point of the solution?
2. If the boiling-point elevation of an aqueous solution containing a non-volatile electrolyte is 1.02°C, what is the molality of the solution?
3. The boiling point of an aqueous solution containing a non-volatile electrolyte is 100.75°C.
    (a) What is the boiling point elevation?
    (b) What is the molality of the solution?

ACTIVITY 5

Elevation in boiling point

In this investigation, the boiling points of water, a sugar-water solution, and a salt-water solution will be determined.

Procedure

1. Turn on the hot plate.
2. Measure 125 mL of water and pour it into a 250 mL beaker.
3. Record the initial temperature of the water and record it for the 0 min. reading in the Data Table.
4. Begin heating and record the time and temprature readings at 30 second intervals. Record temprature to the nearest 0.1°C. Continue until boiling (the temp. remains constant for 2 or 3 readings).
5. Empty and set aside the beaker to cool. Fill a different 250 mL beaker with 125 mL of water and add approximately 20 g of NaCl. Record the exact mass added. Stir until the NaCl dissolves.
6. Repeat steps 3-4 for the NaCl solution.

7. Measure and record the mass of 6 sugar cubes. Using a different 250 mL beaker add the sugar cubes to 125 mL of water. Stir until the sugar dissolves.
8. Repeat steps 3-4 for the sugar solution.

Observations

Mass of NaCl added .... g

Mass of sugar ($C_{12}H_{22}O_{11}$) added .... g

Draw your own Data Table.

Calculations

1. Calculate the molality of the NaCl solution.
2. Calculate the molality of the sugar ($C_{12}H_{22}O_{11}$) solution.
3. Predict the new boiling point for the NaCl solution. (b.p. of water is 100^{o}C)
4. For the m value here, use molality of total ions. 1 mol NaCl = 2 mol ions
5. Predict the new boiling point for the sugar solution.
6. Construct a graph using the data collected (Use an entire page). Plot temp. *vs*. time. Plot the data for all the three samples. Use different colors or symbols to differentiate the three samples.
7. Calculate the % error for the boiling point of the NaCl solution and the sugar solution using your data in number 3 and 4 answers (the theoretical values) and your measured values.
8. Based on your results, which of the ionic solid or non-dissociating solid, has a greater effect on the boiling point of water?
9. With regard to vapor pressure, explain why the boiling points of the solutions are higher than the boiling point of water.

Freezing point depression

The freezing point of a solution is the temperature at which the first crystals of the pure solvent form in equilibrium with the solution.

The freezing point of a 1 m solution of any non-electrolyte solute in water is found by experiment to be 1.86°C lower than the freezing point of water. That is, when 1 mol of a non-electrolyte solute is dissolved in 1 kg of water, the freezing point of the solution is –1.86°C instead of 0.00°C. When 2 mol of a non-electrolyte solute is dissolved in 1 kg of water, the freezing point of the solution is –3.72°C. This is 2 × (–1.86°C).

In fact, for any concentration of a non-electrolyte solute in water, the decrease in freezing point can be estimated by using the value of –1.86°C/m. This value, called the molal freezing point constant (K_f) is the freezing point depression of the solvent in a 1 molal solution of a non-volatile, non-electrolyte solute. Each solvent has its own characteristic molal freezing point constant. The values of for some common solvents are given in Table 2.

The freezing-point depression, ΔT_f, is the difference between the freezing points of the pure solvent and a solution of a non-electrolyte in that solvent, and it is directly proportional to the molal concentration of the solution.

Freezing point depression can be calculated using the following equation.

$$\Delta T_f = K_f m$$

K_f is expressed as°C/m, m is expressed in mol (solute)/kg (solvent) i.e., (molality), and ΔT_f is expressed in°C.

Examples

What mass of ethylene glycol ($C_2H_6O_2$, molar mass = 62.1 g/mol), the main component of antifreeze, must be added to 10.0 L of water to produce a solution for use in a car's radiator that freezes at –10.0°F (–23.3°C)? Assume the density of water is exactly 1 g/mL.

Solution

The freezing point lowered from 0°C to –23.3°C. To determine the molality of ethylene glycol needed to accomplish this, we can use the equation:

$$\Delta T_f = K_f m$$

where ΔT_f = 23°C and K_f = 1.86°Ckg/mol (from, table 1.2). Solving for the molality gives:

$$m_{solute} = \frac{\Delta T_f}{K_f} = \frac{23.3°C}{1.86°C.kg/mol} = 12.5 \text{ mol/kg}$$

This means that 12.5 mol ethylene glycol must be added per kilogram of water. We have 10.0 L, or 10.0 kg, of water. Therefore, the total number of moles of ethylene glycol needed is

$$\frac{12.5 \text{ mol}}{\text{kg}} \times 10.0 \text{ kg} = 1.25 \times 10^3 \text{ mol}$$

The mass of ethylene glycol needed is:

$$1.25 \times 10^3 \text{ mol} \times \frac{62.1 \text{ g}}{\text{mol}} = 7.76 \times 10^3 \text{ g or } 7.76 \text{ kg}$$

Exercises

1. If 0.500 mol of a non-electrolyte solute are dissolved in 500.0 g of diethyl ether, what is the freezing point of the solution?

2. The freezing point of an aqueous solution that contains a non-electrolyte is –9.0°C.
   (a) What is the freezing-point depression of the solution?
   (b) What is the molal concentration of the solution?
3. Calculate the freezing point and boiling point of an antifreeze solution that is 50.0% by mass of ethylene glycol ($HOCH_2CH_2OH$) in water. Ethylene glycol is a non-electrolyte.

Osmotic pressure

The process of osmosis and the colligative property of osmotic pressure are extremely important phenomena when we consider biochemical solutions.

Osmosis

Osmosis is the movement of solvent through a semi-permeable membrane from the side of lower solute concentration to the side of higher solute concentration. Osmosis occurs whenever two solutions of different concentrations are separated by a semi-permeable membrane.

In Figure 6, A solution is separated from the pure solvent by a semi-permeable membrane. The semi-permeable membrane allows solvent molecules, but not solute molecules, to pass through. As time passes, the volume of the solution increases and that of the solvent decreases. This causes the level of the solution to rise. Eventually the liquid levels stop changing, indicating that the system has reached equilibrium. Because the liquid levels are different at this point, there is a greater hydrostatic pressure on the solution than on the pure solvent. This excess pressure is called the osmotic pressure.

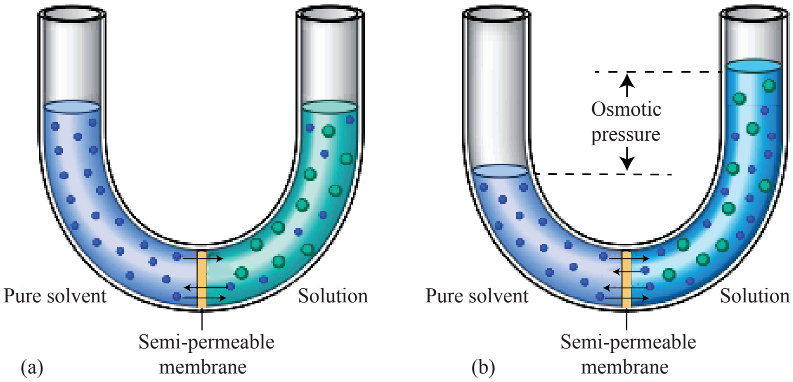


Figure 6. Osmotic Pressure

(a) A pure solvent and its solution (containing a non-volatile solute) are separated by a semi-permeable membrane through which solvent molecules (blue) can pass but solute molecules (green) cannot. The rate of solvent transfer is higher from solvent to solution than from solution to solvent.

(b) The system at equilibrium, where the rate of solvent transfer is the same in both directions.

The normal flow of solvent into the solution (osmosis) can be prevented by applying an external pressure to the solution. The minimum pressure required to stop the osmosis is equal to the osmotic pressure of the solution.

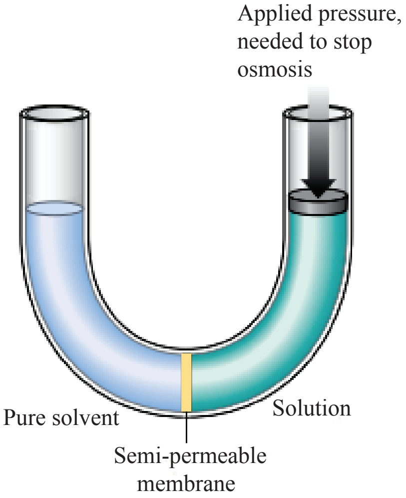


Figure 7. Osmotic pressure of the solution

Experiments show that the osmotic pressure obeys a law similar in form to the ideal-gas law,

$$\pi V = nRT$$

where π is the osmotic pressure, V is volume of the solution, n is the number of moles of solute, R is the ideal-gas constant, and T is the Kelvin temperature. From this equation, we can write

$$\pi = \frac{n}{V}RT = MRT$$

where M is the molarity of solution, R is the gas constant, and T is the Kelvin temperature. The osmotic pressure, is expressed in atm. Because the osmotic pressure for any solution depends on the solution concentration, osmotic pressure is a colligative property.

Osmotic pressure can be used to characterize solutions and determine the molar masses of biomolecules, as can the other colligative properties.

Examples

What is the osmotic pressure of a 0.0020 M sucrose ($C_{12}H_{22}O_{11}$) solution at 20°C?

Solution

Because we are given the concentration in molarity and temperature, we can solve for the osmotic pressure.

$$\pi = MRT$$

$$\pi = (0.0020\ \mathrm{M})\left(0.0821\,\frac{\mathrm{L\,.atm}}{\mathrm{mol.K}}\right)(293\ \mathrm{K}) = 0.048\ \mathrm{atm}$$

Exercises

1. A sample of 2.05 g of polystyrene of uniform polymer chain length was dissolved in enough toluene to form 0.100 L of solution. The osmotic pressure of this solution was found to be 1.21 kPa at 20°C. Calculate the molar mass of the polystyrene.

Colligative properties of electrolyte solutions

As we have seen previously, the colligative properties of solutions depend on the total concentration of solute particles. The various electrolytes ionize and yield more than one particle per formula unit in solution. Therefore, the colligative effect of an electrolyte solution is always greater than that of a non-electrolyte of the same molal concentration.

To represent the colligative properties of electrolytes by means of the same relations as for non-electrolytes, van’t Hoff (1880) suggested the use of a factor i. This is now known as van’t Hoff factor and is defined as : 'the ratio of the colligative effect produced by an electrolyte solution' to the corresponding effect for the same concentration of a non-electrolyte solution.

$$i = \frac{\text{Measured colligative property}}{\text{Expected value for a non-electrolyte}}$$

Thus, i should be 1 for all non-electrolytes. The expected value for i can be calculated for a salt by noting the number of ions per formula unit. For example, for strong electrolytes such as NaCl and KNO_3, i is 2, for strong electrolytes such as Na_2SO_4 and $CaCl_2$, i is 3, and for $Fe_3(PO_4)_2$, i is 5. These calculated values assume that when a salt dissolves, it completely dissociates into its component ions, which then move around independently. This assumption is not always true. For example, the freezing-point depression observed for 0.10 m NaCl is 1.87 times that for 0.10 m glucose rather than twice as great. That is, for a 0.10 m NaCl solution the observed value for i is 1.87 rather than 2. Why?

The colligative properties of electrolyte solutions are described by including the van't Hoff factor in the appropriate equation. Consequently, the equations for colligative properties must be modified as:

$$\Delta T_f = iK_f m$$

$$\Delta T_b = iK_b m$$

$$\pi = iMRT$$

Examples

The osmotic pressure of a 0.010 M potassium iodide (KI) solution at 25°C is 0.465 atm. Calculate the van't Hoff factor for KI at this concentration.

Solution

Note that KI is a strong electrolyte, so we expect it to dissociate completely in solution. Its osmotic pressure would be

$$\pi = iMRT = 2(0.010\,\text{m})(0.0821\,\text{L}.\frac{\text{atm}}{\text{moL.K}})(298\text{K}) = 0.489\,\text{atm}$$

However, the measured osmotic pressure is only 0.465 atm. A value smaller than the predicted osmotic pressure means that there is ion-pair formation, which reduces the number of solute particles (K^+ and I^- ions) in solution.

$$i = \frac{\pi}{MRT} = \frac{0.465\,\text{atm}}{(0.010\,\text{M})\left(0.0821\,\text{L}.\frac{\text{atm}}{\text{moL.K}}\right)(298\,\text{K})} = 1.90$$

Exercises

1. Arrange the following solutions in order of increasing osmotic pressure: 0.02 M sucrose, 0.02 M HNO_3, 0.01 M $BaCl_2$.

1.6 COLLOIDS

Upon completion of this topic, learners will be able to:

- describe the characteristics of colloids.
- explain the difference between a solution and a colloid.

A group of mixtures called colloids (or *colloidal dispersions*) exhibit properties intermediate between those of suspensions and solutions. A colloidal dispersion such as milk is a heterogeneous mixture in which the dispersed particles are intermediate in size between those of a solution and a suspension. The particles are spread evenly throughout the dispersion medium, which can be a solid, liquid, or gas.

The particles dispersed in a colloidal dispersion are called the dispersed phase, and the substance in which they are dispersed is called the dispersing medium. Particles of the dispersed phase in a colloidal dispersion are so small that (1) they are not usually visible by the naked eye, (2) they do not settle out under the influence of gravity, and (3) they cannot be filtered out using filter paper that has relatively large pores.

ACTIVITY 6

Activity to demonstrate the concept of colloids

Chemicals and apparatus required

Video recorded about simple colloids, computers, internet access, milk, food colors (red, yellow, and blue), liquid detergent.

Have a look at the video recorded about simple colloids and reflect your view about the colloids, and then perform the following two (A and B) lab activities.

Procedure

A. The Currents of Color

The purpose of this experiment is to prove that a detergent can cause the movement of the other molecules. The materials to be used are milk, food colors (red, yellow, and blue) as well as liquid detergent.

1. In the experimental process, initially, enough milk is placed on a dish to cover its base.
2. Afterwards, two drops of each food color are added with a distance between them. From the detergent bottle, which must be placed above the center of the dish, only one drop is used.
3. Notice the movement of colors.

Why do the colors move outwards? The addition of the detergent results the movement of the liquid. What is the reason for this?

B. Coagulated Milk and Whey

The purpose of the experiment is the separation of the two parts of the milk, the solid from the liquid. The materials to be used to carry out this specific experiment are milk and vinegar.

In the experimental process, first, fill the conical flask with fresh milk. Afterwards, add 2 tablespoons (30 mL) of vinegar and shake very well. Allow the conical flask to rest for two to three minutes.

The milk is separated into two parts, consisting of a white solid and a clear liquid (Figure 8).

Figure 8. The milk is separated into two parts

Why this result occurs? What do you think about the role of vinegar in the formation of the solid part called coagulated milk?

1.7 FACTORS AFFECTING SOLUBILITY

Upon completion of this topic, learners will be able to:

- discuss factors affecting solubility.
- describe the relationship between intermolecular forces and solubility, including use of the "like dissolves like" rule.
- state the effects of pressure and temperature on solubility.

Solubility is a physical property referring to the ability a given substance, called solute, to dissolve in a solvent. It is measured in terms of the maximum amount of solute dissolved in a solvent at equilibrium. The resulting solution is called a saturated solution.

Solubility ranges widely from infinitely soluble such as ethanol in water, to poorly soluble compounds, such as silver chloride in water.

The extent to which one substance dissolves in another depends on the nature of the intermolecular forces between the solute and solvent. It also depends on temperature and, for gases, on pressure.

Solute–solvent interactions

Any of the various intermolecular forces can operate between solute and solvent particles in a solution. Dispersion forces, for example, dominate when one non-polar substance, such as C_7H_{16}, dissolves in another, such as C_5H_{12}, and ion-dipole forces dominate in solutions of ionic substances in water.

Three kinds of intermolecular interactions are involved in solution formation:

1. Solute-solute interactions between solute particles must be overcome in order to disperse the solute particles in the solvent.
2. Solvent-solvent interactions between solvent particles must be overcome to make room for the solute particles in the solvent.

3. Solvent-solute interactions between solvent and solute particles occur as the particles mix.

The extent to which one substance is able to dissolve in another depends on the relative magnitudes of these three types of interactions. If the interaction between the solute and solvent is greater than the other two (solute-solute, and solvent-solvent interactions), then the solute becomes readily soluble in the solvent. For example, ethanol and water are completely miscible in each other in all proportions.

What can you say about the solubility of C_6H_6 and CCl_4?

What happens if octane, a typical hydrocarbon, is added to water?

Effects of pressure on solubility

Changes in pressure have very little effect on the solubilities of liquids or solids in liquid solvents. However, the solubility of a gas in any solvent is increased as the partial pressure of the gas above the solvent increases. We can understand the effect of pressure on gas solubility by considering Figure 9, which shows carbon dioxide gas distributed between the gas and solution phases.

When equilibrium is established, the rate at which gas molecules enter the solution equals the rate at which solute molecules escape from the solution to enter the gas phase. The equal number of up and down arrows in the left container in Figure 9 represent these opposing processes.

Now suppose we exert a higher pressure on the piston and compress the gas above the solution, as shown in the middle container in Figure 9.

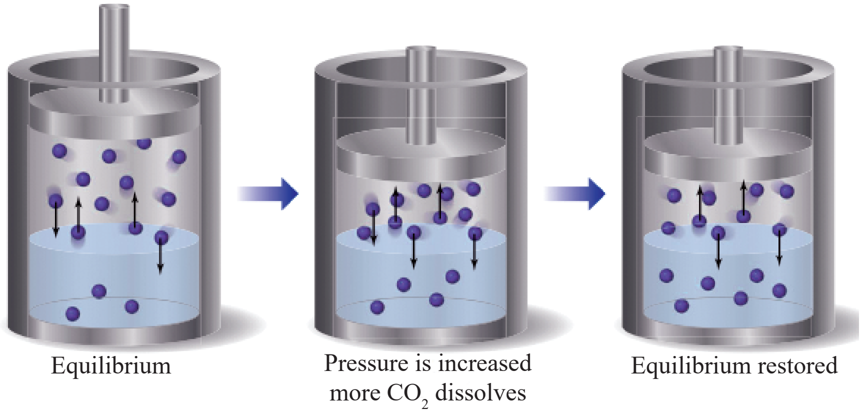


Figure 9. Effect of pressure on gas solubility

If we reduce the gas volume to half its original value, the pressure of the gas increases to about twice its original value. As a result of this pressure increase, the rate at which gas molecules strike the liquid surface and enter the solution phase increases. Thus, the solubility of a gas in a liquid solvent increases in direct proportion to the partial pressure of the gas above the solution.

The relationship between pressure and gas solubility is expressed by Henry's law:

$$S_g = kP_g$$

Here, S_g is the solubility of the gas in the solvent (usually expressed as molarity), P_g is the partial pressure of the gas above the solution, and k is a proportionality constant known as the Henry's law constant. The value of this constant depends on the solute, and temperature.

Bottlers use the effect of pressure on solubility in producing carbonated beverages, which are bottled under a carbon dioxide pressure greater than 1 atm. When the bottles are opened, the partial pressure of CO_2 above the solution decreases. Hence, the solubility of CO_2 decreases, and CO_2(g) escapes from the solution as bubbles.

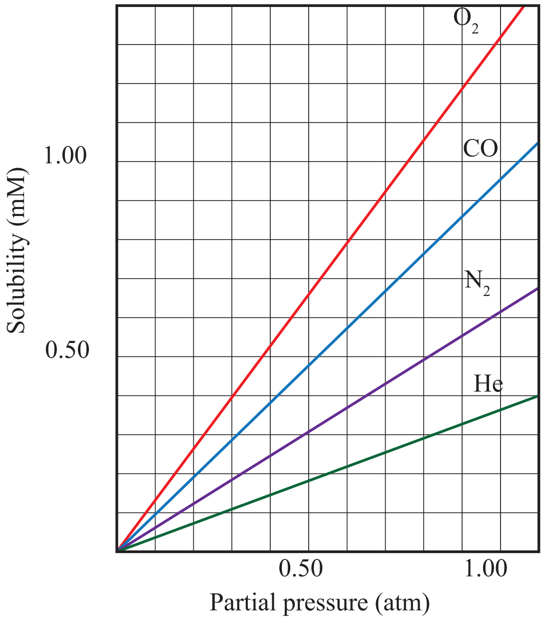


Figure 10. The solubility of a gas in water is directly proportional to the partial pressure of the gas. The solubilities are in millimoles per liter of solution.

Examples

The solubility of nitrogen gas at 25°C and 1 atm is 6.8×10^{-4} mol/L. What is the concentration (in molarity) of nitrogen dissolved in water under atmospheric conditions?

The partial pressure of nitrogen gas in the atmosphere is 0.78 atm.

Solution

The first step is to calculate the quantity k

$$S_{N_2} = kP_{N_2}$$

$$6.8 \times 10^{-4} \text{mol} / \text{L} = \text{k} \ (1 \text{ atm})$$

$$\text{k} = 6.8 \times 10^{-4} \text{ mol/L atm}$$

Therefore, the solubility of nitrogen gas in water is

$$S_{N_2} = (6.8 \times 10^{-4} \text{mol} / \text{L atm}) \ 0.78 \text{ atm}$$

$$= (5.3 \times 10^{-4} \text{ mol/L})$$

$$= 5.3 \times 10^{-4} \text{ mol/L}$$

Exercises

1. Calculate the molar concentration of oxygen in water at 25°C for a partial pressure of 0.22 atm. The Henry's law constant for oxygen is $1.3 \times 10^{-3} \left(\frac{\text{mol}}{\text{L atm}} \right)$.

The effect of temperature on solubility

Recall that solubility is defined as the maximum amount of a solute that will dissolve in a given quantity of solvent at a specific temperature. Temperature affects the solubility of most substances. In this section we will consider the effects of temperature on the solubility of solids and gases.

First, let's consider gas solubility. Increasing the temperature usually decreases gas solubility. As the temperature increases, the average kinetic energy of the molecules in solution increases. A greater number of solute molecules are able to escape from the attraction of solvent molecules and return to the gas phase. At higher temperatures, therefore, equilibrium is reached with fewer gas molecules in solution, and gases are generally less soluble, as shown in Figure 11.

You know that heating decreases the solubility of a gas, so dissolution of gases is exothermic. How do the values for the enthalpies of solution support this idea of exothermic solution processes for gaseous solutes?

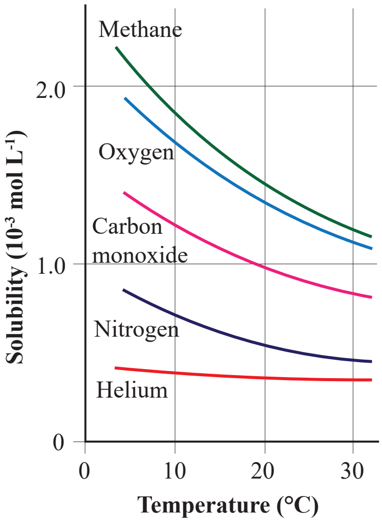


Figure 11. The solubilities of gases in water as a function of temperature at a constant pressure of 1 atm of gas above the solution.

For most solids dissolved in a liquid, an increase in temperature results in increased solubility (see Figure 12). However, no single rule governs the solubility of solids in liquids with change in temperature. Compare the effect of temperature on the solubility of NaCl with the effect of temperature on the solubility of potassium nitrate, KNO_3 . Sometimes, solubility of a solid decreases with an increase in temperature. For example, between 0°C and 60°C the solubility of cerium sulfate, $Ce_2(SO_4)_3$, decreases by about 17 g/100 g.

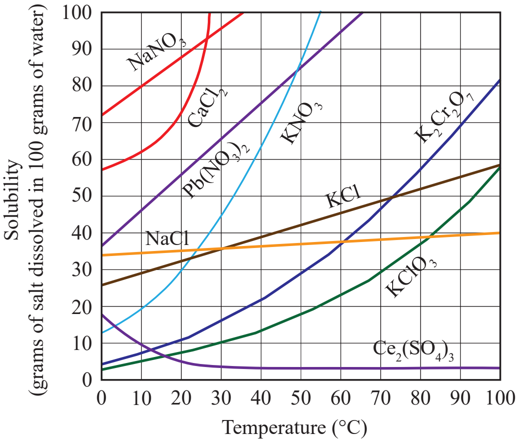


Figure 12. Effect of temperature on solubility of different salts in water.

1.8 GENERAL PRINCIPLES OF SOLUBILITY

Upon completion of this topic, learners will be able to:

- discuss the general principles of solubility.
- predict in a general way the solubilities of solutes in solvents on the basis of molecular polarity.

The natural tendency of substances to mix and the various interactions among solute and solvent particles are all involved in determining solubilities. Nevertheless, insight into variations in solubility can often be gained by simply focusing on the interaction between the solute and solvent.

Substances with similar intermolecular attractive forces tend to be soluble in one another. This generalization is often stated as “like dissolves like.” It is a useful rule for predicting solubility. The “like” referred to is the type of bonding, polar or non-polar and the intermolecular forces between the solute and solvent molecules.

Liquid solutes and solvents

Pairs of liquids that mix in all proportions, such as ethanol and water, are miscible, whereas those that do not dissolve in one another are immiscible. Gasoline, which is a mixture of hydrocarbons, is immiscible with water. The attraction between the polar water molecules and the non-polar hydrocarbon molecules is not sufficiently strong to allow the formation of a solution. Non-polar liquids tend to be insoluble in polar liquids.

Many organic compounds have polar groups attached to a non-polar framework of carbon and hydrogen atoms. For example, alcohols contain the polar -OH group. For example, ethanol (CH_3CH_2OH) molecules can form hydrogen bonds with water molecules as well as with each other.

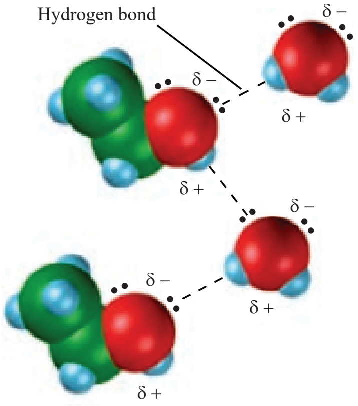


Figure 13. Hydrogen bonding involving OH groups.

As a result, the solute-solute, solvent-solvent, and solute-solvent forces are not widely different in a mixture of CH_3CH_2OH and H_2O. Thus, ethanol is completely miscible with water.

Dissolving ionic compounds in aqueous solution

Let us consider what happens at the microscopic level when we add solid NaCl to water. Ion-dipole forces attract the positive (hydrogen) end of the polar water molecules to the negative chloride ions at the surface of the solid, and they attract the negative (oxygen) ends to the positive sodium ions. The water molecules penetrate between individual Na^+ and Cl^- ions and surround them, reducing the strong interionic forces that bind the ions together and letting them enter into solution as solvated ions, as shown in figure 14.

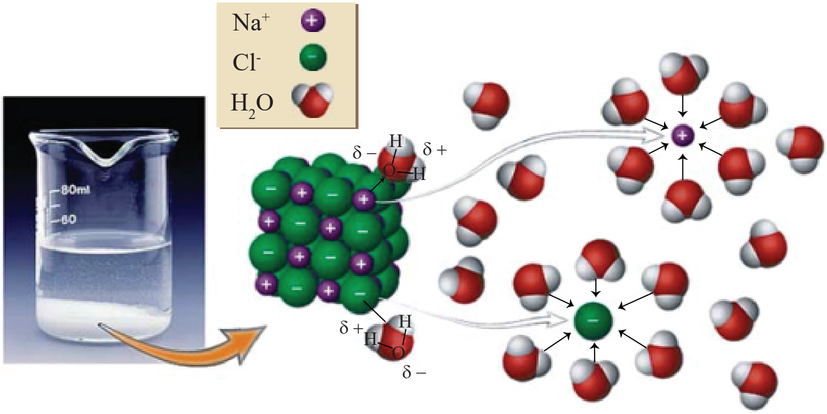


Figure 14. How sodium chloride dissolves in water

In general, we predict that ionic compounds should be much more soluble in polar solvents, such as water, liquid ammonia, and liquid hydrogen fluoride, than in non-polar solvents, such as benzene and carbon tetrachloride. Because the molecules of non-polar solvents lack a dipole moment, they cannot effectively solvate the Na^+ and Cl^- ions. Solvation is the process in which an ion or a molecule is surrounded by solvent molecules arranged in a specific manner. The process is called hydration when the solvent is water.

The predominant intermolecular interaction between ions and non-polar compounds is ion-induced dipole interaction, which is much weaker than ion-dipole interaction. Consequently, ionic compounds usually have extremely low solubility in non-polar solvents.

Exercises

1. Predict whether each of the following substances is more likely to dissolve in the non-polar solvent carbon tetrachloride (CCl_4) or in water: C_7H_{16}, Na_2SO_4, HCl, and I_2.

A. Saturated solution as an equilibrium system

There are two opposing processes that occur in a solution in contact with undissolved solute. These are

(a) Dissolution – the particles of the solute leaving the solid and entering into solution.

(b) Recrystallisation – the particles of the solute returning from the solution and precipitating on the solid.

To start with the rate at which the particles leave the solid is much greater than the rate at which they return to it. As the number of particles of the solute in solution increases, the rate at which they return to the solid also increases. Eventually, if there is some excess solid present the rate of dissolution and the rate of recrystallisation become equal. At this stage, a state of equilibrium between the molecules of the solute in solution and the solid solute is said to have been reached. Thus,

$$\text{Solute solid} \rightleftharpoons \text{Solute dissolved}$$

The competition between the two processes and the eventual equality of the rates of the two processes, shows an important phenomenon in chemistry called dynamic equilibrium. The term dynamic refers to the fact that both processes occur continuously but due to the equality of the two rates (equilibrium) no net change in the amount of the solute in solution phase occurs with time.

B. Solubility expressed in concentration terms: mol dm^{-3} and g dm^{-3}

The concentration of a solution is the amount of solute dissolved in a solvent to make 1 dm^3 (one cubic decimetre) of solution. There are 1000 cm^3 in a cubic decimetre. When 1 mole of a compound is dissolved to make 1 dm^3 of solution the concentration is 1 mol dm^{-3}. This is equivalent to 1 mol/L.

$$\text{Concentration}\left(\text{mol dm}^{-3}\right)=\frac{\text{Number of moles of solute }(\text{mol})}{\text{Volume of solution }\left(\text{dm}^{3}\right)}$$

When performing calculations involving concentrations in mol dm^{-3} you need to change:

- mass in grams to moles
- cm^3 to dm^3 (by dividing the number of cm^3 by 1000).

Examples

Calculate the concentration in mol dm^{-3} of sodium hydroxide, NaOH, if 250 cm^3 of a solution contains 2.0 g of sodium hydroxide.

Solution

(i) Change grams to moles

$$\frac{2.0}{40.0} = 0.050 \text{ mol NaOH}$$

(ii) Change cm^3 to dm^3

$$250 \text{ cm}^3 = 0.25 \text{ dm}^3$$

(iii) Calculate concentration.

$$\frac{0.050 \text{ mol}}{0.25 \text{ mol}^3} = 0.20 \text{ mol dm}^{-3}$$

Exercises

1.

(a) Calculate the concentration, in mol dm^{-3}, of the following solutions:

  (i) Solution of sodium hydroxide, NaOH, containing 2.0 g of sodium hydroxide in 50 cm^3 of solution

  (ii) Solution of ethanoic acid, CH_3CO_2H, containing 12.0 g of ethanoic acid in 250 cm^3 of solution

(b) Calculate the number of moles of solute dissolved in each of the following:

  (i) 40 cm^3 of aqueous nitric acid of concentration 0.2 mol dm^{-3}

  (ii) 50 cm^3 of calcium hydroxide solution of concentration 0.01 mol dm^{-3}

C. Relationship between solubility and crystallization

Recrystallization is a technique that chemists use to purify solid compounds. It is based on the principles of solubility: compounds (solutes) tend to be more soluble in hot liquids (solvents) than they are in cold liquids. If a saturated hot solution is allowed to cool, the solute is no longer soluble in the solvent and forms crystals of the pure compound. Impurities are excluded from the growing crystals and the pure solid crystals can be separated from the dissolved impurities by filtration.

Solubility is a key factor in the development of a crystallization process. As mentioned earlier, solubility allows us to determine how much solute can dissolve in the solvent initially, how much solute will remain in the solvent at the end of crystallization, and how much of each of the impurities, if their solubilities are available, can be rejected.

For example, if the solubility of a compound is 100 mg/mL (100 g/L) at 50ºC and 10 mg/mL (10 g/L) at 0ºC, it is feasible to design a crystallization process which dissolves 100 g of compound at 50ºC and crystallizes 90 g of it at 0ºC per liter of solvent. The yield of this crystallization process is 90 gm/100 gm = 90%.

D. Crystallization/recrystallization as method of purification

The purification of solids by crystallization is based upon differences in their solubility in a given solvent or mixture of solvents.

In its simplest form, the crystallization process consists of the following:

1. Dissolving the impure substance in some suitable solvent at or near the boiling point.
2. Filtering the hot solution from particles of insoluble material and dust.
3. Allowing the hot solution to cool thus causing the dissolved substance to crystallize out, and
4. Separating the crystals from supernatant solution or mother-liquor.

The resulting solid, after drying, is tested for purity and if found impure, it is recrystallized from fresh solvent. The process is repeated until the pure compound is obtained.

1.9 SOLUBILITY CURVES AND THEIR USES

Upon completion of this topic, learners will be able to:

- analyze and interpret solubility curves.

A graphical relationship between the solubility and temperature is termed as the solubility curve. A *solubility curve* gives the deviation in the solubility of a substance with the change of temperature. It helps to determine the quantity of solute that will dissolve in the given quantity of solvent at diverse temperatures.

Solubility curve can be used to determine the amount of substance deposited when the solution is cooled. The importance of solubility curve is listed on next page.

- The solubility of a substance at a particular temperature can be determined.
- The solubility curve helps us to predict which substance will crystallize out first from a solution containing two or more solutes.
- The solubility curve helps us to compare the solubilities of different substances at the same temperature.
- It gives a clear idea that solubility of substance changes with the temperature.
- It is used to differentiate the material that will crystallize or concentrate from a solution with two or more solutes.

How to interpret solubility curves?

Work on the following activity.

ACTIVITY 7

4. **Directions:** Use the solubility curve below to answer the following questions. All questions assume the amount of water is 100 g.

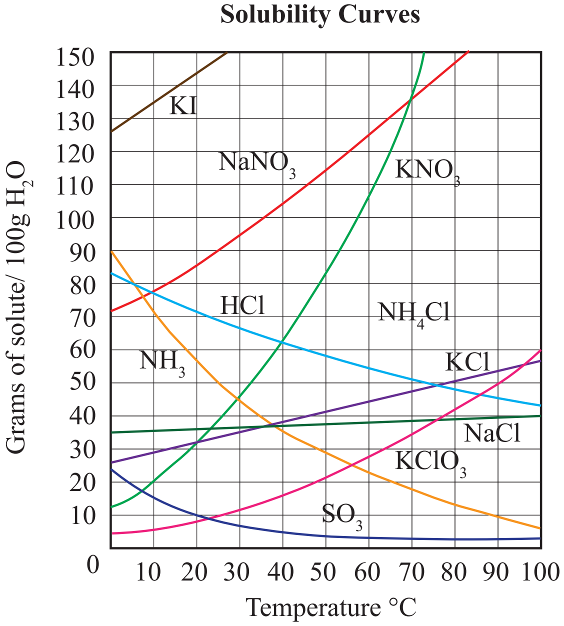


Figure 15.

1. What is the solvent in this solubility curve?
2. Per solvent how many saturation points given?

3. What is the saturation point of $NaNO_3$ at 10°C, 40°C, and 80°C?
4. How much NH_3 can you dissolve in water at 10°C, 30°C, and 90°C?
5. What is the maximum amount of KCl that can be dissolved in water at 20°C, 50°C, and 90°C?
6. If you want to make a saturated solution of NaCl how many grams would you dissolve in 100 grams of water at 80°C?
7. What conclusions can you draw about the effects of temperature on the solubility for gases compared to that of solids?
8. What substance has a saturation point that is least affected by changes in temperature?
9. Suppose 40 g of $KClO_3$ is dissolved in water at 95°C. The water is then cooled. At what temperature will the $KClO_3$ precipitate out of the solution?
10. 90 g of KNO_3 is placed in 100 g of water at 40°C…
    - (a) Will the solution be saturated? If the answer is yes, how much (if any) KNO_3 will remain undissolved? If the answer is no, how much more KNO_3 could be dissolved?
    - (b) If the solution is heated to 70°C will it be saturated? If the answer is yes, how much (if any) KNO_3 will be undissolved? If the answer is no, how much more KNO_3 could be dissolved?
    - (c) If the solution is cooled to 20°C will it be saturated? If the answer is yes, how much (if any) KNO_3 will be undissolved? If the answer is no, how much more KNO_3 could be dissolved?

1.10 SOLUBILITY OF IONIC SUBSTANCES

Upon completion of this topic, learners will be able to:

- discuss the solubility of ionic substances.

In this section, we will present some rules for qualitatively predicting solubility of solutes. These rules are based on polarity considerations—specifically, on the magnitude of the difference between the polarity of the solute and solvent. In general, it is found that the greater the difference in solute-solvent polarity, the less soluble is the solute. This means that substances of like polarity tend to be more soluble in each other than substances that differ in polarity.

The generalization "like dissolves like" is a useful tool for predicting solubility behavior in many, but not in all, solute-solvent situations.

Some guidelines concerning the solubility of ionic compounds in water, which should be used in place of "like dissolves like," are given in Table 4.

Table 3 **Solubility guidelines for ionic compounds in water**

Soluble Compounds	**Important Exceptions**
Compounds containing the following ions are soluble with exceptions as noted.	
Group IA (Li^+, Na^+, K^+, etc)	None
Ammonium (NH_4^+)	None
Acetate (CH_3COO^-)	None
Nitrate (NO_3^-)	None
Chloride (Cl^-), bromide (Br^-), and iodide (I^-)	Ag^+, Pb^{2+}, Hg_2^{2+}
Sulfate (SO_4^{2-})	Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+}
Insoluble Compounds*	**Important Exceptions**
Compounds containing the following ions are insoluble with exceptions as noted.	
Carbonate (CO_3^{2-})	Group IA and NH_4^+
Phosphate (PO_4^{3-})	Group IA and NH_4^+
Sulfide (S^{2-})	Group IA and IIA and NH_4^+
Hydroxide (OH^-)	Group IA, Ca^{2+}, Sr^{2+}, Ba^{2+}
*All ionic compounds, even the least soluble ones, dissolve to a slight extent in water. Thus the "insoluble" classification really means ionic compounds that have limited solubility in water.	

Exercises

1. With the help of Table 4, classify these ionic compounds as soluble or insoluble in water:
   (a) Sodium carbonate, Na_2CO_3,
   (b) Lead sulfate, $PbSO_4$.
   (c) Cobalt(II) hydroxide,
   (d) Barium nitrate,
   (e) Ammonium phosphate

Ionic equations

In writing equations for reactions in aqueous solution, it is often useful to indicate whether the dissolved substances are present predominantly as ions or as molecules. Let's consider the precipitation reaction between $Pb(NO_3)_2$ and KI:

$$Pb(NO_3)_2(aq) + 2KI(aq) \longrightarrow PbI_2(s) + 2KNO_3(aq)$$

An equation written in this form, showing the complete chemical formulas of reactants and products, is called a molecular equation because it shows chemical formulas without indicating ionic character. Because, $Pb(NO_3)_2$, KI, and KNO_3 are all water soluble ionic compounds and therefore strong electrolytes, we can write the equation in a form that indicates which species exist as ions in the solution:

$$Pb^{2+}(aq) + 2NO_3^-(aq) + 2K^+(aq) + 2I^-(aq) \longrightarrow PbI_2(s) + 2K^+(aq) + 2NO_3^-(aq)$$

An equation written in this form, with all soluble strong electrolytes shown as ions, is called a complete ionic equation.

Notice that K^+ (aq) and NO_3^- (aq) appear on both sides. Ions that appear in identical forms on both sides of a complete ionic equation, called spectator ions, play no direct role in the reaction. When spectator ions are omitted from the equation (they cancel out like algebraic quantities), we are left with the net ionic equation, which includes only the ions and molecules directly involved in the reaction:

$$Pb^{2+}(aq) + 2I^-(aq) \longrightarrow PbI_2(s)$$

Because charge is conserved in reactions, the sum of the ionic charges must be the same on both sides of a balanced net ionic equation.

Exercise

1. Write the net ionic equation for the precipitation reaction that occurs when aqueous solutions of silver nitrate and potassium phosphate are mixed.

1.11 PRECIPITATION AND QUANTITATIVE ANALYSIS

Upon completion of this topic, learners will be able to:

- apply the solubility table to determine the quantitative analysis of a solution.

ACTIVITY 8

Precipitation reactions

What observations indicate that a chemical reaction has occurred? Some indications include: the formation of an insoluble solid (precipitate), color change, the evolution of a gas, or a temperature change. In this experiment, you will predict what will happen when two aqueous solutions are mixed, and then test your predictions in the laboratory.

Precipitation results in the formation of an insoluble solid called a precipitate. Example

$$Pb(NO_3)_2\ (aq) + \ KI\ (aq) \longrightarrow KNO_3\ (aq) + \underset{\text{Precipitate}}{PbI_2\ (s)}$$

write the balanced molecular equation, an ionic equation with spectator ions crossed out, and the balanced net ionic equation for the reaction of each pair of aqueous solutions. (Be sure to include all states, aq, l, s or g. Use the solubility rules as a guide.)

Tabulate your expected results in the chart below based on the solubility rules.

Place PPT in the box if you expect a precipitate to form and NR if you do not think a reaction will occur. Write SS if any of the reactions generate a slightly soluble product.

Predicted results

	NH_4NO_3	$AgNO_3$	$Ba(NO_3)_2$
NaCl			
Na_2SO_4			
NaOH			
Na_2CO_3			

Procedure

In this part of the experiment, you will compare you predictions of reactions in aqueous solutions against your observed results obtained when aqueous solutions are mixed in the laboratory.

1. Test tubes that you use do not need to be completely dry. However, rinse them with deionized water before use.
2. Select three small test tubes. Using a graduated cylinder, measure 5 mL of deionized water and transfer it to a test tube.
3. Add 1 mL of 1 M NaCl to each of the three test tubes. Then, in order, add 1 mL of NH_4NO_3, $AgNO_3$ and $Ba(NO_3)_2$ into the three separate test tubes. For example, the first test tube should contain NaCl and NH_4NO_3, the second should contain NaCl and $AgNO_3$, and the third should contain NaCl and $Ba(NO_3)_2$.
4. Record your observations. Dispose of the silver and barium solutions in the appropriate waste container.
5. Repeat step 3 for all solution combinations in the Table. Again, dispose of all solutions containing silver and barium in the appropriate waste container.

Results

Tabulate your observations in the chart below. Compare your results to your predictions. Explain any observations that do not agree with your predictions.

	NH_4NO_3	$AgNO_3$	$Ba(NO_3)_2$
NaCl			
Na_2SO_4			
NaOH			
Na_2CO_3			

Write a word equations, balanced chemical equations, and balanced net ionic equations for the precipitation reactions that actually occurred.

Most ionic compounds dissolve in water. Some ionic compounds, however, are insoluble or only slightly soluble in water. But even ‘insoluble’ ionic compounds may dissolve to a very small extent in water.

- Sodium chloride is regarded as a soluble salt: a saturated solution contains 36 g per 100 g of water.
- Lead(II) chloride is regarded as an insoluble salt: a saturated solution of it contains 0.99 g per 100 g of water.

Solubility product

An equilibrium is established when an undissolved ionic compound is in contact with a saturated solution of its ions. The ions move from the solid to the saturated solution at the same rate as they move from the solution to the solid (Figure 16).

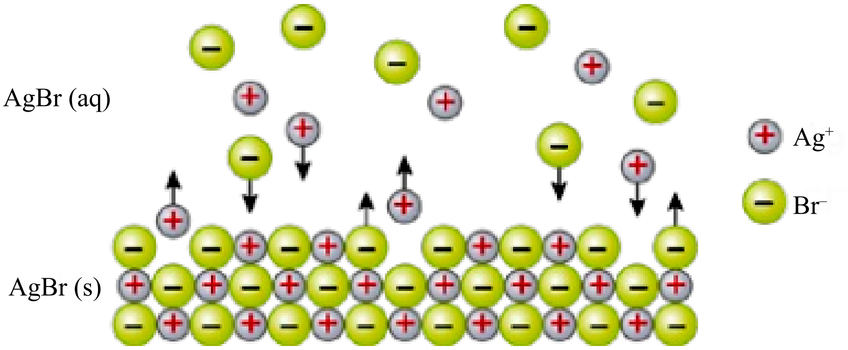


Figure 16. An equilibrium is established between solid silver chloride and its saturated solution. Water molecules are not shown.

When solid silver bromide dissolves, it is in contact with a saturated silver bromide solution and the following equilibrium is set up:

$$\mathrm{AgCl}(s) \rightleftharpoons \mathrm{Ag}^{+}(aq) + \mathrm{Br}^{-}(aq)$$

The equilibrium expression for this equation is:

$$K_c = \frac{[\mathrm{Ag}^{+}(aq)][\mathrm{Br}^{-}(aq)]}{[\mathrm{AgBr}(s)]}$$

For any solid, the concentration of the solid phase remains constant and can be combined with the value of K_c.

So we can write this equilibrium expression as:

$$K_{sp} = \left[Ag^{+}(aq)\right]\left[Br^{-}(aq)\right]$$

K_{sp} is called the solubility product. Values are quoted at 298 K.

$$K_{sp} = \left[C^{y+}(aq)\right]^{a}\left[A^{x-}(aq)\right]^{b}$$

where **a** is the number of cations in one formula unit of the compound and **b** is the number of anions in one formula unit of the compound.

So for Fe_2S_3 (which contains Fe^{3+} ions and S^{2-} ions) the equilibrium is:

$$Fe_2S_3(s) \rightleftharpoons 2Fe^{3+}(aq) + 3S^{2-}(aq)$$

and the equilibrium expression is:

$$K_{sp} = \left[Fe^{3+}(aq)\right]^{2}\left[S^{2-}(aq)\right]^{3}$$

The idea of solubility product only applies to ionic compounds that are slightly soluble. The units of solubility product depend on the number of each type of ion present in solution.

The idea of solubility product is only useful for sparingly soluble salts. The smaller the value of K_{sp} the lower is the solubility of the salt. Some values of K_{sp} are given in Table 5.

Table 4 **Some values of solubility product at 298 K**

Compound	**K_{sp} / (mol dm^{-3})$^{a+b}$**
AgCl	1.8×10^{-10}
$Al(OH)_3$	1.0×10^{-32}
$BaCO_3$	5.5×10^{-10}
$BaSO_4$	1.0×10^{-10}
$CaCO_3$	5.0×10^{-9}
CuS	6.3×10^{-36}
$Fe(OH)_2$	7.9×10^{-16}

FeS_3	1.0×10^{-88}
$PbCl_2$	1.6×10^{-5}
$Zn(OH)_2$	2.0×10^{-17}
ZnS	1.6×10^{-23}

Solubility product calculations

You may be asked to calculate the solubility product of a compound from its solubility, or you may be asked to calculate the solubility of a compound from its solubility product.

Examples

Calculate the solubility of copper (II) sulfide in mol dm^{-3}.

(K_{sp} for CuS = 6.3×10^{-36} $mol^2\ dm^{-6}$)

Solution

Step 1: Write down the equilibrium equation.

$$CuS(s) \rightleftharpoons Cu^{2+}(aq) + S^{2-}(aq)$$

Step 2: Write the equilibrium expression in terms of one ion only. From the equilibrium equation

$$[Cu^{2+}] = [S^{2-}]$$

So $K_{sp} = [Cu^{2+}][S^{2-}]$ becomes $K_{sp} = [Cu^{2+}]^2$.

Step 3: Substitute the value of K_{sp}.

$$(6.3 \times 10^{-36}) = [Cu^{2+}]^2$$

Step 4: Calculate the concentration. In this case we take the square root of K_{sp}.

$$[Cu^{2+}] = \sqrt{K_{sp}}$$

$$[Cu^{2+}] = \sqrt{K_{sp}} = \sqrt{(6.3 \times 10^{-36})} \times 2.5 \times 10^{-18}\ \text{mol. dm}^{-3}$$

Predicting precipitation

We can use the knowledge of K_{sp} values to predict whether or not a precipitate will form when two solutions are mixed together. For example, will we get a precipitate when we mix a solution of barium chloride with a solution of sodium sulfate. Barium sulfate is mostly insoluble compound, and so could potentially precipitate from the mixture. However, it is first necessary to calculate the ion product, $[Ba^{2+})][SO_4^{2-}]$, for the solution. If the value of the ion product is less than the value of the K_{sp}, then no precipitate will form. If the value of the ion product is greater than the value of the K_{sp}, then a precipitate will form.

Activity 9

Generalizations about solubility of salts and their applications to quantitative analysis

In this experiment, you will quantify the solubility of "insoluble" salts.

Determination of K_{sp}

In order to quantify the "insolubility" of salts such as AgCl, we cannot directly measure how much can be dissolved (as it is such a small amount) we must take a round about route. The easiest method, for us, is to use the idea of dynamic equilibrium.

For example, let us consider taking a saturated solution of the "insoluble" salt $PbCl_2$, in contact with the solid. The following equilibrium will take place:

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^{-}(aq)$$

As this is an equilibrium condition, we can set up the mass action expression, which, in this special case refers to the solubility product equilibrium constant, the K_{sp}.

$$K_{sp} = [Pb^{2+}][Cl^{-}]^2$$

As K_{sp} is constant at a given temperature, we can define the solubility of an "insoluble salt" using the value of K_{sp} and we may derive the value of K_{sp}, by measuring the concentrations of K_{sp} the ions present in a saturated solution. (You should note, that, as all ions come from the same source, all you have to do is determine the concentration of one of the ions).

In the first part of the experiment, you are going to calculate the K_{sp}, value of an "insoluble" hydroxide-$Ca(OH)_2$ in solution, this dissociates into calcium ions and hydroxide ions, thus providing us with a providing simple easy way of determining the concentrations by way of acid-base titration.

Procedure

Determination of K_{sp},

1. Rinse the Burette with 0.02 M HCl solution. Record the exact concentration of the HCl on the data sheet (1). Fill the Burette with the HCl solution
2. Decant some (about 55 mL) of the saturated $Ca(OH)_2$ solution into your beaker. Be sure that you do not get any of the solid.
3. Pipette about 25 mL. $Ca(OH)_2$ solution from your beaker into an Erlenmeyer flask. Record the exact volume on the data sheet (2). Add of drops of methyl orange indicator (methyl orange is yellow in basic solution one or two red in acidic).
4. Record the initial volume of the HCl in the burette (3) and titrate the $Ca(OH)_2$ until you see the color change. Record the final volume (4).

5. Repeat steps 3 and 4.
6. Do appropriate calculations to determine your K_{sp}, (5-10)
7. Using the data, calculate the class mean and standard deviation.

DATA SHEET

Slightly soluble salts

(a) Determination of K*sp*

Determination of K_{sp}	Trial 1	Trial 2
Concentration of HCl solution (mol/L)		
Volume of $Ca(OH)_2$ (mL)		
Initial burette reading (mL)		
Final burette reading (mL)		
Volume of HCl used (mL)		
Moles of HCl added		
Moles of OH present		
$[OH^-]$ (M)		
K_{sp}		
Average K_{sp}		
Class Data		
K_{sp}		
Class mean		
Standard deviation		

Conclusion

(a) How do your results for the compare to the class average?

(b) Identify any sources of error in the K_{sp} experiment.

Exercises

1. Calculate the solubility product of the following solutions:
   (a) A saturated aqueous solution of cadmium sulfide, CdS (solubility = 1.46 × 10^{-11} mol dm^{-3})
   (b) A saturated aqueous solution of calcium fluoride, CaF_2, containing 0.0168 g dm^{-3} CaF_2
2. Calculate the solubility in mol dm^{-3} of zinc sulfide, ZnS. (K_{sp} = 1.6 × 10^{-23} mol^2 dm^{-6})

KEY TERMS

- Homogeneous solution
- Dilution
- Heterogeneous solution
- Colligative properties
- Solution
- Vapor pressure lowering
- Solute
- Boiling point elevation
- Solvent
- Freezing point depression
- Saturated solution
- Osmotic pressure
- Unsaturated solution
- Van’t Hoff factor
- Supersaturated solution
- Colloids
- Mass percentage
- Henry’s law
- Parts per million
- Like dissolves like principle
- Parts per billion
- Solubility
- Mole fraction
- Miscible
- Molarity
- Immiscible
- Normality
- Crystallization
- Molality
- Solubility curve

SUMMARY

Solutions are homogeneous mixtures of two or more substances, which may be solids, liquids, or gases. The component of a solution that is present in the greater amount is the solvent. A solute is a component of a solution that is present in a smaller or amount relative to the solvent.

The equilibrium between a saturated solution and undissolved solute is dynamic; the process and the reverse process, **crystallization**, occur simultaneously. In a solution in equilibrium with undissolved solute, the two processes occur at equal rates, giving a **saturated** solution. If there is less solute present than is needed to saturate the solution, the solution is **unsaturated**. When solute concentration is greater than the equilibrium concentration value, the solution is **supersaturated**. This is an unstable condition, and separation of some solute from the solution will occur if the process is initiated with a solute seed crystal.

The solubility of a solute is the maximum amount of solute that will dissolve in a given amount of solvent. The extent to which a solute dissolves in a solvent depends on the solute and solvent interaction, temperature, and pressure. Polar and ionic solutes tend to dissolve in polar solvents, and non-polar solutes tend to dissolve in non-polar solvents (“like dissolves like”). Liquids that mix in all proportions are **miscible**; those that do not dissolve significantly in one another are **immiscible**. Hydrogen-bonding interactions between solute and solvent often play an important role in determining solubility; for example, ethanol and water, whose molecules form hydrogen bonds with each other, are miscible. The solubilities of gases in a liquid are generally proportional to the pressure of the gas over the solution, as expressed by **Henry's law**: $S_g = kP_g$. The solubilities of most solid solutes in water increase as the temperature of the solution increases. In contrast, the solubilities of gases in water generally decrease with increasing temperature.

The concentration of a solution is the amount of solute present in a specified amount of solution. Percent solute and molarity are commonly used concentration units. Percent concentration units include percent by mass, and percent by volume.

Dilution involves adding solvent to an existing solution. Although the amount of solvent increases, the amount of solute remains the same. The net effect of dilution is a decrease in the concentration of the solution.

Properties of a solution that depend on the number of solute particles in solution, not on their identity, are called **colligative properties**. Vapor-pressure lowering, boiling-point elevation, freezing-point depression, and osmotic pressure are all colligative properties.

The solution process is complex and depends on the strengths of solute-solute, solvent-solvent, and solute-solvent attractive forces, as well as the change in disorder that occurs on mixing. Whereas the solution process can be either endothermic or exothermic, dissolution requires that the strengths of the solute-solvent interactions be close to those of the solute-solute and solvent-solvent interactions. Although these enthalpy considerations make it possible to formulate qualitative predictions about the relative solubility of a substance in two different solvents, the dissolution process is too complex to predict the solubility of any given solute. The interaction of dipolar water molecules with ions in aqueous solution is called hydration. The hydration of ions is an exothermic process, comparable with the energy of attraction between oppositely charged ions in an ionic solid.

Particles that are large on the molecular scale but still small enough to remain suspended indefinitely in a solvent system form **colloids**, or **colloidal dispersions**. Colloids are intermediate between solutions and heterogeneous mixtures, have many practical applications. One useful physical property of colloids, the scattering of visible light, which is referred to as the **Tyndall effect**.

Exercises

1. Indicate whether each of the following statements about the general properties of solutions is true or false.
   (a) For solution formation to occur, the solute and solvent must chemically react with each other.
   (b) All solutions are homogeneous mixtures.

   (c) Every part of a solution has exactly the same properties as every other part.
   (d) The solutes present in a solution will “settle out” with time if the solution is left undisturbed.
   (e) Solutes are present as individual particles (molecules, atoms, or ions) in a solution

2. Identify the solute and the solvent in solutions composed of the following:
   (a) 5.00 g of NaBr and 200.0 g of water
   (b) 50.0 g of $AgNO_3$ and 1000 g of water
   (c) 50.0 mL of water and 100.0 mL of methyl alcohol
   (d) 50.0 mL of isopropyl alcohol and 20.0 mL of ethyl alcohol
3. Classify each of the following solutions as saturated, unsaturated, or supersaturated based on the following observations.
   (a) The added solute rapidly dissolves.
   (b) Heating the solution causes excess undissolved solute present to dissolve.
   (c) The added solute falls to the bottom of the container remaining without any decrease in size
   (d) The added solute causes the formation of a large amount of solid white crystals.
   (e) The amount of solute dissolved is less than the maximum amount that could dissolve under the conditions at which the solution exists.
4. A solution is made containing 14.6 g of CH_3OH in 184 g H_2O. Calculate:
   (a) Mole fraction of CH_3OH,
   (b) Mass percent of CH_3OH,
   (c) Molality of CH_3OH.
5. Calculate the mass, in grams, of K_2SO_4 needed to prepare 32.00 g of 2.0% (m/m) K_2SO_4 solution.
6. Calculate the normality of a solution that contains 16g of $Fe_2(SO_4)_3$ in 200 mL of solution?
7. Calculate the volume percent of solute in each of the following solutions.
   (a) 20.0 mL of methyl alcohol in enough water to give 475 mL of solution.
   (b) 4.00 mL of bromine in enough carbon tetrachloride to give 87.0 mL of solution.
8. Ascorbic acid (vitamin C, $C_6H_8O_6$) is a water-soluble vitamin. A solution containing 80.5 g of ascorbic acid dissolved in 210 g of water has a density of 1.25 g/mL at 55°C. Calculate:
   (a) Mass percentage
   (b) Mole fraction

(c) Molality
(d) Molarity of ascorbic acid in this solution.

9.
(a) How much water must be added to concentrated sulfuric acid (17.8 M) to prepare 8.4 L of 1.5 M sulfuric acid solution?
(b) How many moles are there in one milliliter of the original concentrated solution?
(c) How many moles are there in one milliliter of the diluted solution?

10. How many grams of sucrose ($C_{12}H_{22}O_{11}$) must be added to 552 g of water to give a solution with a vapor pressure 2.0 mmHg less than that of pure water at 20°C? (The vapor pressure of water at 20°C is 17.5 mmHg.)

11. What are the boiling point and freezing point of a 2.47 m solution of naphthalene in benzene? (The boiling point and freezing point of benzene are 80.1°C and 5.5°C, respectively.)

12. Lysozyme is an enzyme that breaks bacterial cell walls. A solution containing 0.150 g of this enzyme in 210 mL of solution has an osmotic pressure of 0.953 torr at 25°C. What is the molar mass of lysozyme?

13.
(a) Why does a 0.10 m aqueous solution of NaCl have a higher boiling point than a 0.10 m aqueous solution of $C_6H_{12}O_6$?
(b) Calculate the boiling point of each solution.
(c) The experimental boiling point of NaCl solution is lower than that calculated, assuming that NaCl is completely dissociated in solution. Why is this the case?

14. List the following aqueous solutions in order of increasing boiling point and decreasing freezing point: 0.120 m glucose, 0.050 m LiBr, 0.050 m $Zn(NO_3)_2$.

15. Indicate whether each of the following characterizations applies to a true solution, a colloidal dispersion, or a suspension. There may be more than one correct answer for a given characterization.
(a) Dispersed phase can be trapped by filter paper
(b) Dispersed phase can often be seen with the naked eye
(c) Appearance is that of a homogeneous mixture
(d) Dispersed phase scatters light
(e) Dispersed phase rapidly settles out under the influence of gravity

16.
(a) Explain why carbonated beverages must be stored in sealed containers.
(b) Once the beverage has been opened, why does it maintain more carbonation when refrigerated than at room temperature?

17. The solubility of acetylene (C_2H_2) in water at 20°C and 0.200 atm pressure is 9.38×10^{-3} molal.
    (a) Calculate the Henry's law constant for this gas in units of molal/torr.
    (b) How many grams of acetylene are dissolved in 1.00 kg water at 20°C if the pressure of the gas is 300 torr?
18. Indicate the type of solute-solvent interaction that are most important in each of the following solutions:
    (a) CCl_4 in benzene (C_6H_6)
    (b) Methanol (CH_3OH) in water
    (c) KBr in water
    (d) HCl in acetonitrile (CH_3CN).
19. Basing your answer on intermolecular force considerations, explain what "like dissolves like" means.
20. Water and glycerol, $CH_2(OH)CH(OH)CH_2OH$, are miscible in all proportions. What does this mean? How do the -OH groups of the alcohol molecule contribute to this miscibility?
21. The solubility of potassium chloride in water increases from 34.7 g/100 g at 20°C to 56.7 g/100 g at 100°C. Is the enthalpy of solution for this compound endothermic or exothermic? Explain your answer.
22. In each of the following sets of ionic compounds, identify the compounds that are soluble in water.
    (a) NaCl, Na_2SO_4, $NaNO_3$, Na_2CO_3
    (b) $AgNO_3$, KNO_3, $Ca(NO_3)_2$, $Cu(NO_3)_2$
    (c) NaCl, AgCl, $BeCl_2$, $CuCl_2$
    (d) $Ba(OH)_2$, $BaSO_4$, $BaCO_3$, $Ba(NO_3)_2$.
23. Write the formula equation, the overall ionic equation, and the net ionic equation for the precipitation reaction that occurs when solutions of zinc chloride, $ZnCl_2$, and sodium sulfide, Na_2S, are mixed.
24. A saturated solution of copper (I) sulfide, Cu_2S, contains 1.91×10^{-12} g of Cu_2S dissolved in 1 dm³ of water. (Cu = 63.5, S = 32.1)
    (a) Write an equilibrium expression for the solubility product of copper(I) sulfide.
    (b) Calculate the value of the solubility product of copper(I) sulfide.

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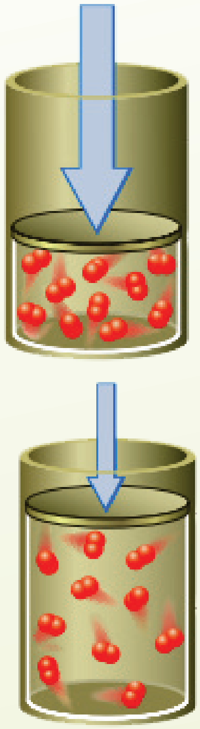
CHAPTER 2

KINETIC THEORY OF GASES

Chapter Contents



Chapter Outcomes

By the end of this chapter, you will be able to:

- define pressure and its units.
- learn the ideal gas law equation.
- solve both composition and reaction stoichiometry problems.
- calculate the partial pressure and mole fractions of a gas in a mixture.
- list the five postulates of the kinetic theory of gases.
- describe how the root-mean-square (rms) molecular speed of gas molecules varies with temperature.
- describe how individual gas molecules move undergoing diffusion and effusion.
- understand atmospheric chemistry.

Gases play an important roles in industry and in our everyday lives. It is important to know how they behave when their conditions, such as temperature or pressure, are modified. Gases have similar physical behaviors, which allow us to develop models to predict their properties. We present a model that explains the behavior of gases on the molecular level.

2.1 PRESSURE

Upon completion of this topic, learners will be able to:

- describe the concept of pressure.
- define the pressure of a gas and know the units in which it is measured.
- define and convert among the units of pressure measurements.

Pressure is defined as 'the force exerted on a surface divided by the area of the surface'. The mathematical equation for pressure is

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}}$$

$$P = \frac{F}{A}$$

For a gas, the force that creates pressure is exerted by the gas molecules or atoms as they constantly collide with the walls of their container. When a rubber balloon is inflated with air, it stretches and maintains its larger size because the pressure on the inside is greater than that on the outside. Pressure results from the collisions of gas molecules with the walls of the balloon.

The effects of pressure are also observed in the mixture of gases in the atmosphere, which is composed of about 78% nitrogen, 21% oxygen, 1% argon, and other minor constituents by volume. Atmospheric pressure is the sum of the individual pressures of the various gases in the atmosphere.

How is atmospheric pressure measured?

Units of pressure

A number of different units are used to measure pressure. Because instruments used for measuring pressure, such as the barometer and manometer, often contain mercury, the most commonly used units for pressure are based on the height of the mercury column (in millimeters) that the gas pressure can support. A related unit for pressure is the standard atmosphere (abbreviated atm).

Standard atmospheric pressure (1 atm) is equal to the pressure that supports a column of mercury exactly 760 mm (or 76 cm) high at 0°C at sea level. In other words, the standard atmosphere equals a pressure of 760 mmHg, where mmHg represents the pressure exerted by a column of mercury 1 mm high. The mmHg unit is also called the torr, after the Italian scientist Evangelista Torricelli, who invented the barometer. Thus,

$$1 \text{ torr} = 1 \text{ mmHg} \quad \text{and} \quad 1 \text{ atm} = 760 \text{ mmHg}.$$

The SI unit of pressure is the pascal (Pa), named after French scientist Blaise Pascal.

$$1 \text{ Pa} = 1\frac{\text{N}}{\text{m}^2} = \frac{1 \text{ kg}}{\text{m.s}^2}$$

Where N is newton, m is meter, and s is second.

The relationship between atmosphere and pascal is

$$1 \text{ atm} = 101,325 \text{ Pa} = 1.01325 \times 10^5 \text{ Pa}$$

We will usually express gas pressure in atmosphere, pascal, kilopascal, or torr, so you should be familiar in converting pressures from one unit to another.

Exercise

1. Convert 749 mmHg to atmosphere.
2. Convert a pressure of 0.975 atm into Pa and kPa.

ACTIVITY 1

Observing atmospheric pressure in action

In this Lab, you will see how powerful atmospheric pressure can be.

Safety precautions

Use safety goggles during this activity. Handle the heated can carefully using beaker tongs.

Procedure

1. Pour 5 mL of water into a soft drink can.
2. Heat the can on the hot plate until steam begins rising from the opening of the can.
3. Using the beaker tongs, quickly invert the can into the large beaker of ice water so that the opening of the can is just under the surface of the water. Observe carefully.

Observation and analysis

1. What happened to the air and water molecules inside the can when it was heated?
2. Explain what happened to the can when it was placed in the ice water.
3. Calculate the surface area of the outside of the can exposed to the atmosphere. Assuming an atmospheric pressure of 100.0 kPa, how much force was applied to the can by the atmosphere?

Conclusion

Summarize and explain what happened in your experiment.

Your conclusion should be based solely on your results. Look back at the purpose of your experiment and assess whether or not you met your goal in performing the experiment. What can you conclude from the experiment? Write a short report of your observation.

2.2 THE IDEAL GAS LAWS

Upon completion of this topic, learners will be able to:

- explain and apply Boyle's Law, Charles' Law, Gay Lussac's Law, Avogadro's Law to observe gas behavior.
- perform calculations using the Ideal Gas Laws.

In this section we will consider several mathematical laws that relate the properties of gases. The gas laws are simple mathematical relationships between the volume, temperature, pressure, and amount of a gas. These laws are derived from experiments involving careful measurements of the relevant gas properties. From these experimental results, the mathematical relationships among the properties can be discovered. These relationships are often represented pictorially by means of graphs.

A. Boyle's Law

Robert Boyle discovered that doubling the pressure on a sample of gas at constant temperature reduces its volume by one-half. Reducing the pressure on a gas by one-half allows the volume of the gas to double. From such experiments, he formulated the law now known by his name.

Boyle's law states that 'the volume of a fixed mass of gas varies inversely with the pressure at constant temperature.'

Mathematically, Boyle's law can be expressed as follows:

$$V \propto 1/P \text{ ,}$$

where V is the volume, P is the pressure, and $\propto$ means "is proportional to."

$$PV = \text{constant} \quad \text{(for a given amount of gas at fixed temperature)}$$

Since P and V vary inversely, their product remains the same. Because two quantities that are equal to the same thing are equal to each other, the relationship between changes of pressure and volume can be expressed as shown below.

$$P_1V_1 = P_2V_2$$

P_1 and V_1 represent initial conditions. P_2 and V_2 represent a different set of conditions.

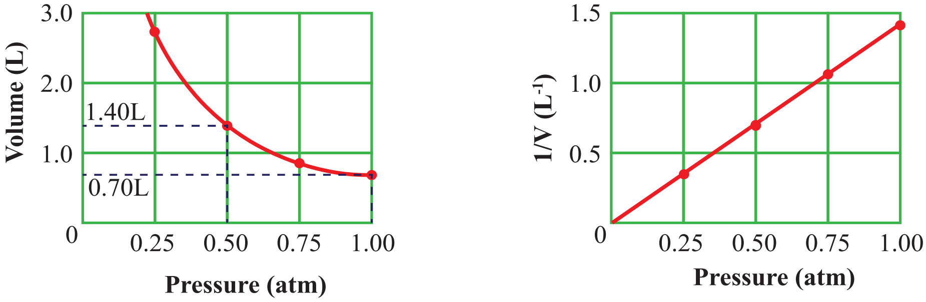
Given three of the four values P_1, V_1, P_2, and V_2, you can use this equation to calculate the fourth value for a system at constant temperature.

Figure 1 presents a molecular view of the pressure–volume relationship for two data points.

(a) (b)

Figure 1. Model of gas pressure–volume relationship at a constant temperature
(a) When a 1.000-g sample of O_2 gas at 0°C is placed in a container at a pressure of 0.50 atm, it occupies a volume of 1.40 L.
(b) When the pressure on the O_2 sample is doubled to 1.0 atm, the volume is reduced to 0.70 L, which is half the original volume.

Note that the product of the pressure and volume for each data pair is nearly constant. By plotting the volume of the oxygen gas at different pressures (as shown in Figure 2), you obtain a graph showing the inverse relationship between P and V.



(a) (b)

Figure 2. Gas pressure–volume relationship
(a) Plot of volume vs. pressure for a sample of oxygen gas. The volume (of 1.000 g O_2 at 0°C) decreases with increasing pressure. When the pressure is doubled (from 0.50 atm to 1.00 atm), the volume is halved (from 1.40 L to 0.70 L).
(b) Plot of 1/V vs. pressure (at constant temperature) for the same sample. The straight line indicates that volume varies inversely with pressure.

ACTIVITY 2

Pressure vs. Volume and Boyle's Law

Objectives

1. To show the validity of Boyle's Law.
2. To measure the volume of a fixed quantity of air as the pressure changes at constant temperature.

Procedure

1. Set up the apparatus as shown in Figure 3.

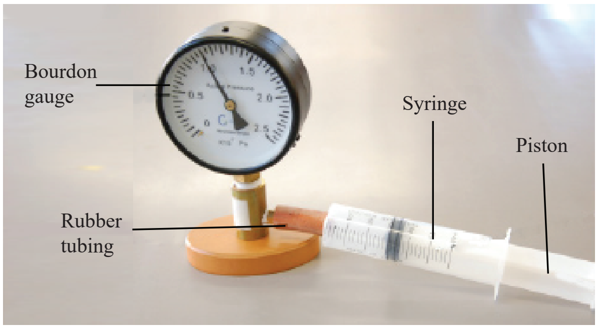


Figure 3. Arrangement of the apparatus

2. The piston of the syringe is adjusted until the volume of air, V, in the syringe is 100 cm^3 at atmospheric pressure.
3. The syringe is connected to a bourdon gauge and the pressure of the air, P, in the syringe is observed and recorded.
   Precaution: The rubber tube must be fixed tightly to prevent leakage.
4. The piston is then pushed in so that the volume of air trapped is 90 cm^3. The pressure is again recorded, this procedure is repeated for enclosed volumes of 80 cm^3, 70 cm^3, 60 cm^3.
5. The value of the volume of air, V, the pressure of air, P, and 1/V are recorded.
6. The graph of pressure of the air, P against 1/V is plotted.

Tabulation of Data

Table 1

Volume, V in cm^3	1/V in cm^{-3}	Pressure P in N/m^2
100		
90		
80		
70		
60		

Result and Discussion

1. Plot a graph of pressure (y-axis) versus volume of the gas (x-axis).
2. Determine the gradient of the graph of pressure, P against 1/V.
3. Based on your graph, determine the pressure, P, when the volume, V is 75 cm^3?
4. The above experiment can be explained by a Boyle's law.

Conclusion

Summarize and explain what happened in your experiment.

Exercise

1. A balloon filled with helium gas has a volume of 500 mL at a pressure of 1 atm. The balloon is released and reaches an altitude of 6.5 km, where the pressure is 0.5 atm. If the temperature has remained the same, what volume does the gas occupy at this height?

B. Charles's Law

Boyle's law depends on the temperature of the system remaining constant. But suppose the temperature changes: How does a change in temperature affect the volume and pressure of a gas?

One of the first quantitative observations of gases at different temperatures was made by Jacques Alexandre Charles in 1787. He studied the volume behavior of gas samples kept at constant pressure as they were heated. He found that a sample of gas at a fixed pressure increases in volume linearly with temperature. By linearly, we mean that if we plot the volume occupied by a given sample of gas at various temperatures, we get a straight line.

In terms of the Kelvin scale, Charles's law states: The volume of a fixed amount of gas maintained at constant pressure is directly proportional to its absolute temperature. Thus, doubling the absolute temperature causes the gas volume to double. Mathematically, Charles's law takes the form

$$V = \text{Constant} \times T \text{ or } \frac{V}{T} = \text{Constant}$$

with the value of the constant depending on the pressure and on the amount of gas.

Consider a sample of gas at a fixed pressure, and suppose the temperature changes from its initial value T_i to a final value T_f. How does the volume changes? Because the volume divided by absolute temperature is constant, you can write

$$\frac{V_f}{T_f} = \frac{V_i}{T_i}$$

Or, rearranging slightly,

$$V_f = V_i \times \frac{T_f}{T_i}$$

Note that to obtain the final volume, the initial volume is multiplied by a ratio of absolute temperatures.

Examples

A sample of gas at 15°C and 1 atm has a volume of 2.58 L. What volume will this gas occupy at 38°C and 1 atm?

Solution

Charles's law, which describes the dependence of the volume of a gas on temperature at constant pressure, can be used to solve this problem.

Charles's law in the form V = kT can be rearranged to:

$$\frac{V}{T} = k(\text{constant})$$

An equivalent statement is:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} = k$$

where the subscripts 1 and 2 represent two states for a given sample of gas at constant pressure. In this case, we are given the following (note that the temperature values must be changed to the Kelvin scale):

$T_1 = 15°C + 273 = 288$ K

$V_1 = 2.58$ L

$T_2 = 38°C + 273 = 311$ K

$V_2 = ?$

Solving for V_2 gives

$$V_2 = V_1 \times \frac{T_2}{T_1} = 2.58\text{ L} \times \frac{311\text{ K}}{288\text{ K}} = 2.79\text{ L}$$

The new volume is greater than the initial volume, which makes physical sense because the gas will expand as it is heated.

ACTIVITY 3

Charles's Law: The Volume–Temperature Relationship of a Gas

The objective of this activity is to measure the volume of a fixed quantity of air as the temperature changes at constant pressure.

Procedure

Charles' law can be demonstrated with the help of apparatus shown below. A 30-mL syringe and a thermometer are inserted through a rubber stopper into a flask that has been cooled to 0°C. The ice bath is then removed and the flask is immersed in a warm-water bath. The gas in the flask expands as it warms, slowly pushing the piston out of the syringe. The total volume of the gas in the system is equal to the volume of the flask plus the volume of the syringe.

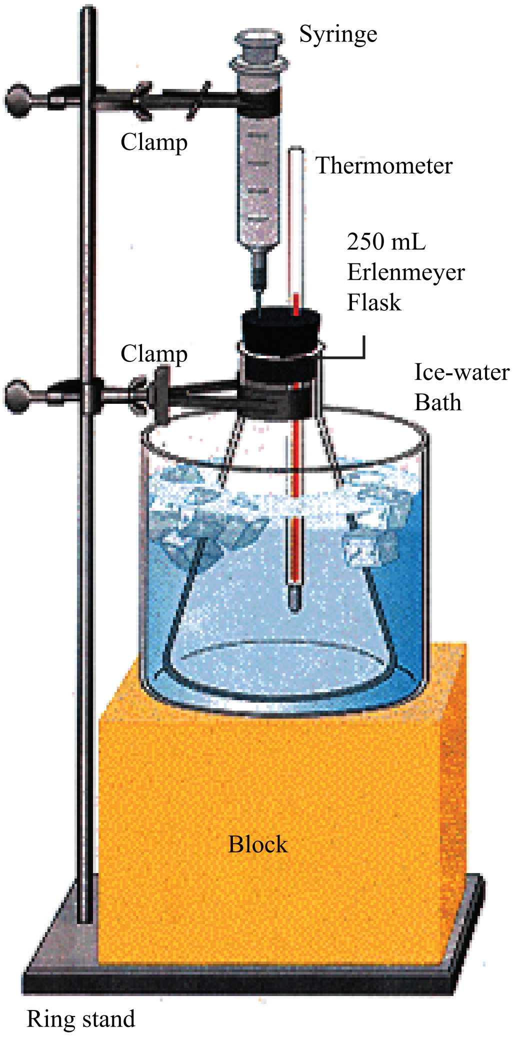


Figure 4. Experiment set up

Record the data obtained with this apparatus using the table below:

The dependence of the volume of a gas on its temperature

Temperature (°C)	Volume (mL)

Plot a graph of the data recorded and interpret it.

What happens to the piston of the syringe when the flask is removed from the ice bath and placed in a warm-water bath?

To what value the volume of the gas approaches when data obtained with the Charles' law are extrapolated?

Conclusion

Look back at the purpose of your experiment and assess whether or not you met your goal in performing the experiment?

Exercise

1. Does the volume of a fixed quantity of gas decreases to half its original value when the temperature is lowered from 100°C to 50°C?

C. Gay-Lussac's Law

You have just learned about the quantitative relationship between volume and temperature at constant pressure. What would you predict about the relationship between pressure and temperature at constant volume?

When the temperature of a sample of gas in a rigid container is increased, the pressure of the gas increases as well. The increase in kinetic energy results in the molecules of gas striking the walls of the container with more force, resulting in a greater pressure. The French chemist Joseph Gay-Lussac (1778-1850) discovered the relationship between the pressure of a gas and its absolute temperature.

Gay-Lussac's Law states that the pressure of a given mass of gas varies directly with the absolute temperature of the gas, when the volume is kept constant.

Mathematically, Gay-Lussac's law is expressed as follows:

$$P = k\,T \quad \text{or} \quad \frac{P}{T} = k$$

The value of T is the temperature in kelvins, and k is a constant that depends on the quantity of gas and the volume. For a given mass of gas at constant volume, the ratio P/T is the same for any set of pressure-temperature values. Unknown values can be found using the following formula:

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} = k$$

P_1 and T_1 represent initial conditions, and P_2 and T_2 represent a different set of conditions. When values are known for three of the four quantities, the fourth value can be calculated for a system at constant volume.

Example

A certain light bulb containing argon at 1.20 atm and 18°C is heated to 85°C at constant volume. Calculate its final pressure (in atm).

Solution

Initial Conditions

$P_1 = 1.20$ atm

$T_1 = 18°\text{C} + 273 = 291$ K

Final Conditions

$T_2 = 85°\text{C} + 273 = 358$ K

Unknown: P_2 of gas in atm

The final pressure is given by

$$P_2 = P_1 \times \frac{T_2}{T_1}$$

$$= 1.20 \text{ atm} \times \frac{358 \text{ K}}{291 \text{ K}}$$

$$= 1.48 \text{ atm}$$

At constant volume, the pressure of a given amount of gas is directly proportional to its absolute temperature. Therefore the increase in pressure is reasonable.

Exercise

1. The data plotted in Figure 5 illustrate Gay-Lussac's law

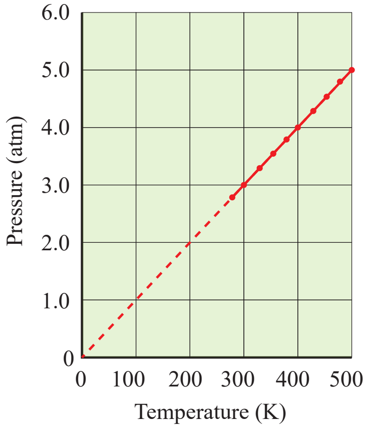


Figure 5. Pressure vs. Temperature for a Gas at Constant Volume

What happens to the pressure of the gas as the temperature increases?

2. A sample of helium gas has a pressure of 1.20 atm at 22°C. At what Celsius temperature will the helium reach a pressure of 2.00 atm, assuming constant volume?

D. Avogadro's Law

Let us take a balloon containing a certain mass of gas. If we add to it more mass of gas, holding the temperature (T) and pressure (P) constant, the volume of gas (V) will increase. It was found experimentally that the amount of gas in moles is proportional to the volume. That is,

$V \propto n$ (T and P constant) or V = k n where k is constant of proportionality.

Avogadro's Law in the form V = k n can be rearranged to

$$\frac{V}{n} = k$$

For any two gases with volumes V_1, V_2 and moles n_1, n_2 at constant T and P,

$$\frac{V_1}{n_1} = \frac{V_2}{n_2} = k$$

$$\text{If } V_1 = V_2,\ n_1 = n_2.$$

Thus for equal volumes of the two gases at fixed T and P, number of moles is also equal. This is the basis of Avogadro's Law which may be stated as: equal volumes of gases at the same temperature and pressure contain equal number of moles or molecules. If the molar amount is doubled, the volume is doubled.

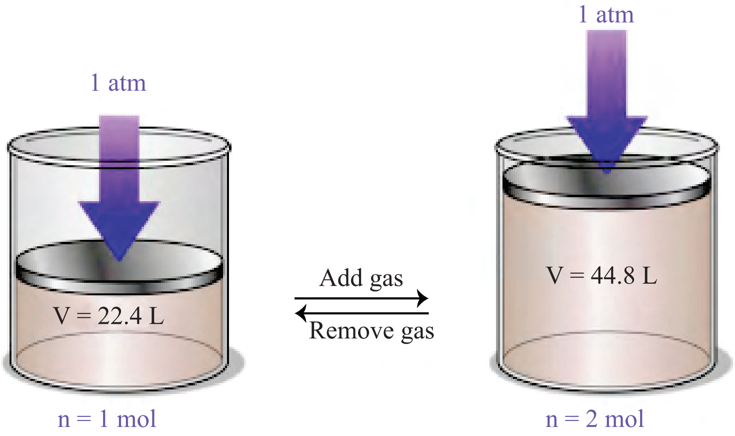


Figure 6. Avogadro's law states that under equal conditions of temperature and pressure equal volumes of gases contain equal number of molecules.

Molar gas volume

It follows as a corollary of Avogadro's Law that one mole of any gas at a given temperature (T) and pressure (P) has the same fixed volume. It is called the molar gas volume or molar volume.

In order to compare the molar volumes of gases, chemists use a fixed reference temperature and pressure. This is called standard temperature and pressure (abbreviated, STP). The standard temperature used is 273 K (0°C) and the standard pressure is 1 atm (760 mm Hg). At STP we find experimentally that one mole of any gas occupies a volume of 22.4 litres. To put it in the form of an equation, we have

1 mole of a gas at STP = 22.4 litres

Example

Calculate the volume in dm^3 of 0.40 mol of nitrogen at STP.

Solution

$$\text{Volume}\left(\text{in dm}^3\right) = 22.4\ \text{dm}^3/\text{mol} \times \text{number of moles of gas}$$

$$= 22.4\ \text{dm}^3/\text{mol} \times 0.40\ \text{mol} = 8.96\,\text{dm}^3$$

Exercises

1. State Avogadro's law, and explain its significance.
2. Calculate the volume, in dm^3, occupied by 26.4 g of carbon dioxide at STP.

3. An 11.2 L sample of gas is determined to contain 0.50 mol of N_2. At the same temperature and pressure, how many moles of gas would there be in a 20 L sample?

2.3 THE IDEAL GAS EQUATION

Upon completion of this topic, learners will be able to:

- perform calculations using the Ideal Gas Equation.

Let us summarize the gas laws we have discussed so far:

Boyle's law	$V \propto \frac{1}{P}$	(constant n, T)
Charles's law	$V \propto T$	(constant n, P)
Avogadro's law	$V \propto n$	(T and P constant)

We can combine these relationships into a general gas law:

$$V \propto \frac{nT}{P}$$

and if we call the proportionality constant R, we obtain an equality:

$$V = R\left(\frac{nT}{P}\right)$$

which we can rearrange to

$$PV = nRT$$

which is the ideal-gas equation. This equation describes the relationship among the four variables P, V, T, and n.

The term R in the ideal-gas equation is the gas constant. The value for T in the ideal-gas equation must always be the absolute temperature (in kelvins instead of degrees Celsius). The quantity of gas, n, is normally expressed in moles.

The value and units of R depend on the units of P, V, n, and T. For most calculations, we will round off the value of R to three significant figures

$$(0.0821\,\frac{\text{L.atm}}{\text{K.mol}} \text{ or } 8.31\,\frac{\text{J}}{\text{K.mol}}).$$

Example

Calculate the volume (in liters) occupied by 7.4 g of CO_2 at STP?

Solution

The ideal gas equation is given as:

$$PV = nRT$$

$$V = \frac{nRT}{P} = \frac{mRT}{MP}, \qquad n = \frac{m}{M}$$

$$V = \frac{7.4\,g \times 0.0821\frac{L.atm}{K.mol} \times 273\,K}{44\frac{g}{mol} \times 1\,atm} = 3.77\,L$$

Exercise

1. How many molecules are in 22.41 L of an ideal gas at STP?
2. Calculate the volume, in liters, occupied by 3.25 moles of Cl_2 gas at 1.54 atm pressure and a temperature of 213°C.

2.4 GAS STOICHIOMETRY

Upon completion of this topic, learners will be able to:

- apply the concept of the gas laws to gas phase reactions and perform stoichiometric calculations.

In this section, we use the ideal-gas equation first to define the relationship between the density of a gas and its molar mass, and then to calculate the volumes of gases formed or consumed in chemical reactions.

Molar mass of a gas

Recall that density of a gas was measured to determine the molar mass of the gas molecules.

Example

What is the molecular mass of a substance weighing 0.970 g whose vapor occupies 200.0 mL (0.2000 L) at 99°C (372 K) and 733 mmHg (0.964 atm)?

Solution

The density of the vapor is 0.970 g/0.2000 L = 4.85 g/L.

We can calculate the molar mass of a gas if we know its density, temperature, and pressure.

$$M = \frac{dRT}{P} = \frac{4.85\frac{g}{L} \times 0.0821\frac{L.atm}{K.mol} \times 372\,K}{0.964\,atm} = 154\,g/mol$$

Exercise

1. The density of a gas at a pressure of 1.34 atm and a temperature of 303 K is found to be 1.77 g/L. What is the molar mass of this gas?

Stoichiometric problems involving gas volumes

Consider the following reaction, which is often used to generate small quantities of oxygen gas:

$$2KClO_3(s) \xrightarrow{\Delta} 2KCl(s) + 3O_2(g)$$

Suppose you heat 0.0100 mol of potassium chlorate, $KClO_3$, in a test tube. How many liters of oxygen can you produce at 298 K and 1.02 atm?

You solve such a problem by breaking it into two problems, one involving stoichiometry and the other involving the ideal gas law. Note that 2 mol $KClO_3$ yields 3 mol O_2. Therefore,

$$0.0100\,mol\,KClO_3 \times \frac{3\,mol\,O_2}{2\,mol\,KClO_3} = 0.0150\,mol\,O_2$$

Now that you have the moles of oxygen produced, you can use the ideal gas law to calculate the volume of oxygen under the conditions given. Rearrange the ideal gas law, $PV = nRT$, and solve for the volume:

$$V = \frac{nRT}{P}$$

Substitute for n, T, and P. Because the pressure is given in units of atmospheres, you choose the value of R in units of L·atm/(K·mol). The answer comes out in liters.

$$V = \frac{nRT}{P} = \frac{0.0150\,mol \times 0.0821\frac{L.atm}{K.mol} \times 298\,K}{1.02\,atm} = 0.360\,L$$

Exercise

In the first step in the industrial process for making nitric acid, ammonia reacts with oxygen in the presence of a suitable catalyst to form nitric oxide and water vapor:

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

How many liters of $NH_3(g)$ at 850°C and 5.00 atm are required to react with 1.00 mol of $O_2(g)$ in this reaction?

2.5 DALTON'S LAW OF PARTIAL PRESSURES

Upon completion of this topic, learners will be able to:

- describe the relationship between partial pressure and the total pressure as described in Dalton's Law of partial pressure.

Thus far we have considered mainly pure gases—those that consist of only one substance in the gaseous state. How do we deal with mixtures of two or more different gases? While studying the properties of air, John Dalton made an important observation: The total pressure of a mixture of gases equals the sum of the pressures that each would exert if it were present alone. The pressure exerted by a particular component of a mixture of gases is called the partial pressure of that component. Dalton's observation is known as Dalton's law of partial pressures.

Let P_t be the total pressure of a mixture of gases and P_1, P_2, P_3 and so forth be the partial pressures of the individual gases, we can write Dalton's law of partial pressures as:

$$P_t = P_1 + P_2 + P_3 + \ldots.$$

This equation implies that each gas behaves independently of the others, as we can see by the following analysis. Let n_1, n_2, n_3 and so forth be the number of moles of each of the gases in the mixture and n_t be the total number of moles of gas. If each gas obeys the ideal-gas equation, we can write

$$P_t = (n_1 + n_2 + n_3 + \ldots)\left(\frac{RT}{V}\right) = n_t\left(\frac{RT}{V}\right)$$

That is, at constant temperature and constant volume, the total pressure of a gas sample is determined by the total number of moles of gas present, whether that total represents just one gas or a mixture of gases.

Collecting a gas over water

A useful application of the law of partial pressures arises when you collect gases over water (a method used for gases that do not dissolve appreciably in water). Figure 7 shows how a gas, produced by chemical reaction in the flask, is collected by leading it to an inverted tube, where it displaces water. As gas bubbles through the water, the gas picks up molecules of water vapor that mix with it. The partial pressure of water vapor in the gas mixture in the collection tube depends only on the temperature. This partial pressure of water vapor is called the vapor pressure of water.

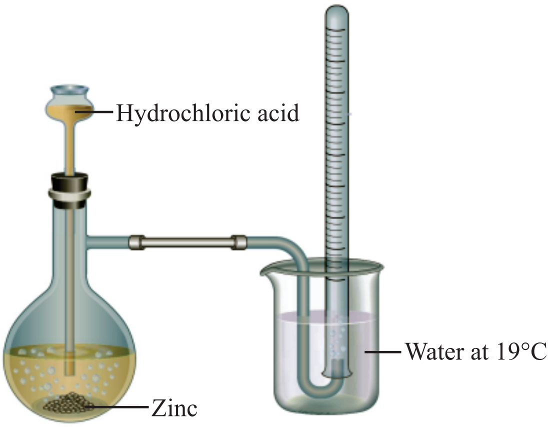


Figure 7. Collection of gas over water

The following example shows how to find the partial pressure and then the mass of the collected gas.

Example

Hydrogen gas is produced by the reaction of hydrochloric acid, HCl, on zinc metal.

$$2HCl(aq) + Zn(s) \longrightarrow ZnCl_2(aq) + H_2(g)$$

The gas is collected over water. If 156 mL of gas is collected at 19°C and 769 mmHg total pressure, what is the mass of hydrogen collected?

Solution

The vapor pressure of water at 19°C is 16.5 mmHg.

From Dalton's law of partial pressures, you know that the total gas pressure equals the partial pressure of hydrogen, P_{H_2}, plus the partial pressure of water, P_{H_2O}.

$$P = P_{H_2} + P_{H_2O}$$

Substituting and solving for the partial pressure of hydrogen, we get

$$P_{H_2} = P - P_{H_2O} = (769 - 16.5)\text{mm Hg} = 752 \text{ mm Hg}$$

Now use the ideal gas law to find the moles of hydrogen collected:

$$P = 752 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} = 0.989 \text{ atm}$$

$$V = 156\ \text{mL} = 0.156\ \text{L}$$

$$T = (19 + 273)\text{K} = 292\ \text{K}$$

$$n = ?$$

From the ideal gas law, PV = nRT, you have

$$n = \frac{PV}{RT} = \frac{0.989\ \text{atm} \times 0.156\ \text{L}}{0.0821\ \text{L.atm.K}^{-1}\text{mol}^{-1} \times 293\ \text{K}} = 0.00641\ \text{mol}$$

After converting moles of H_2 to grams of H_2

$$0.00641\ \text{mol} \times \frac{2.02\ \text{g H}_2}{1\ \text{mol H}_2} = 0.0130\ \text{g H}_2$$

Exercise

1. Oxygen can be prepared by heating potassium chlorate, $KClO_3$, with manganese dioxide as a catalyst. The reaction is:

$$2KClO_3(s) \xrightarrow{\Delta} 2KCl(s) + 3O_2(g)$$

How many moles of O_2 would be obtained from 1.300 g $KClO_3$? If this amount of O_2 were collected over water at 23°C and at a total pressure of 745 mmHg, what volume would it occupy?

2.6 THE KINETIC MOLECULAR THEORY OF GASES

Upon completion of this topic, Learners will be able to:

- state the postulates of the kinetic-molecular theory.
- use these postulates to explain the gas laws.
- apply the ideas of Kinetic Molecular Theory to various gas phenomena.

To understand the physical properties of gases, we need a model that helps us picture what happens to gas particles when conditions such as pressure or temperature change. Such a model is known as the Kinetic-Molecular Theory of gases.

Postulates of Kinetic theory

The Kinetic Molecular Theory (KMT) is a simple microscopic model that effectively explains the gas laws. This theory is based on the following five postulates described here.

1. Gases are composed of molecules whose size is negligible compared with the average distance between them.

2. Molecules move randomly in straight lines in all directions and at various speeds.
3. The forces of attraction or repulsion between two molecules (intermolecular forces) in a gas are very weak or negligible, except when they collide.
4. When molecules collide with one another, the collisions are elastic. In an elastic collision, the total kinetic energy remains constant; no kinetic energy is lost.
5. The average kinetic energy of a molecule is proportional to the absolute temperature.

Application of kinetic-molecular theory to gas laws

On a qualitative basis, it is possible to use the kinetic theory of gases to account for the general properties of substances in the gaseous state.

A. Pressure and volume (Boyle's law)

The pressure exerted by a gas results from the impact of its molecules on the walls of the container. The rate of collision, or the number of molecular collisions with the walls per second, is proportional to the number density (that is, number of molecules per unit volume) of the gas. Decreasing the volume of a given amount of gas increases its number density and hence its rate of collision. For this reason, the pressure of a gas is inversely proportional to the volume it occupies; as volume decreases, pressure increases and vice versa.

B. Pressure and temperature (Gay-Lussac's law)

If the temperature is increased, the average speed and kinetic energy of the gas molecules increase. If the volume is held constant, the increased speed of the gas molecules results in more frequent and more forceful collisions with the walls of the container, therefore increasing the pressure.

C. Volume and temperature (Charles's law)

If the temperature of a gas is increased, a constant pressure may be maintained only if the volume occupied by the gas increases. This will result in greater average distances travelled by the molecules to reach the container walls, as well as increased wall surface area. These conditions will decrease both the frequency of molecule-wall collisions and the number of collisions per unit area, the combined effects of which outweigh those of increased collision forces due to the greater kinetic energy at the higher temperature. The net result is a decrease in gas pressure.

D. Volume and number of moles (Avogadro's law)

We have shown that the pressure of a gas is directly proportional to both the density and the temperature of the gas. Because the mass of the gas is directly proportional to the number of moles (n) of the gas, we can represent density by n/V. Therefore

$$P \propto \frac{n}{V}T$$

For two gases, 1 and 2, we write

$$P_1 \propto \frac{n_1 T_1}{V_1} = k\frac{n_1 T_1}{V_1}$$

$$P_2 \propto \frac{n_2 T_2}{V_2} = k\frac{n_2 T_2}{V_2}$$

where k is the proportionality constant. Thus, for two gases under the same conditions of pressure, volume, and temperature (that is, when $P_1 = P_2$, $T_1 = T_2$, and $V_1 = V_2$), it follows that $n_1 = n_2$, which is a mathematical expression of Avogadro's law.

E. Mixture of gases (Dalton's law)

If molecules do not attract or repel one another (postulate 3), then the pressure exerted by one type of molecule is unaffected by the presence of another gas. Consequently, the total pressure is given by the sum of individual gas pressures.

F. Deriving the ideal gas law

One of the most important features of kinetic theory is its explanation of the ideal gas law. To show how you can get the ideal gas law from the kinetic theory, we will first find an expression for the pressure of a gas.

According to the kinetic theory, the pressure of a gas, P, will be proportional to the frequency of molecular collisions with a surface and to the average force exerted by a molecule in collision.

$$P \propto \text{Frequency of collisions} \times \text{Average force}$$

The average force exerted by a molecule during a collision depends on its mass m and its average speed v—that is, on its average momentum mu. In other words, greater the mass of the molecule and faster it is moving, and greater would be the force exerted during collision. The frequency of collisions is also proportional to the average speed u, because faster a molecule is moving, the more often it strikes the container walls. Frequency of collisions is inversely proportional to the gas volume

V, because larger the volume, the less often a given molecule strikes the walls of the container. Finally, the frequency of collisions is proportional to the number of molecules N in the gas volume. Putting these factors together gives:

$$P \propto \left(u \times \frac{1}{V} \times N \right) \times mu$$

Bringing the volume to the left side, you get

$$PV \propto Nmu^2$$

Because the average kinetic energy of a molecule of mass m and average speed u is ½ mu^2, PV is proportional to the average kinetic energy of a molecule. Moreover, the average kinetic energy is proportional to the absolute temperature. Noting that the number of molecules, N, is proportional to the moles of molecules, n, you have

$$PV \propto nT$$

You can write this as an equation by inserting a constant of proportionality, R, which you can identify as the molar gas constant.

$$PV = nRT$$

G. The Meaning of temperature

Kinetic-molecular theory explains both pressure and temperature at the molecular level.

The absolute temperature of a gas is a measure of the average kinetic energy of its molecules. If two gases are at the same temperature, their molecules have the same average kinetic energy (postulate 5 of the Kinetic-Molecular Theory). If the absolute temperature of a gas is doubled, the average kinetic energy of its molecules doubles. Thus, molecular motion increases with increasing temperature.

2.7 ROOT MEAN SQUARE VELOCITY

Upon completion of this topic, learners will be able to:

- apply the ideas of Kinetic Molecular Theory to various gas phenomena.
- discuss the Root Mean Square Velocity as it relates to gas particles.

Root-mean-square velocity

How fast does a molecule move, on the average, at any temperature T? One way to estimate molecular speed is to calculate the root-mean-square (rms) speed

(u_{rms}), which is an average molecular speed. One of the results of the kinetic theory of gases is that the total kinetic energy of a mole of any gas equals (3/2) RT.

Earlier we saw that the average kinetic energy of one molecule is ½ mu^2 and so we can write:

$$k^2 = 3RT / M$$

Taking the square root of both sides we get:

$$\sqrt{K^2} = u_{rms} = \sqrt{3RT / M}$$

This equation shows that the root-mean-square speed of a gas increases with the square root of its temperature (in kelvins). Because M appears in the denominator, it follows that heavier the gas, the more slowly its molecules move. If we substitute 8.314 J/K.mol for R and convert the molar mass to kg/mol, then u_{rms} will be calculated in meters per second (m/s).

Example

Calculate the root-mean-square velocity for a nitrogen molecule at 30°C.

Solution

Convert the temperature into Kelvin: 30°C + 273 = 303 K

Determine the mass of a nitrogen molecule in kilograms:

$$\frac{28.0\ \text{g}}{1\ \text{mol}} \times \frac{1\ \text{kg}}{1000\ \text{g}} = 0.028\ \text{kg/mol}$$

Replace the variables and constants in the root-mean-square velocity equation, replacing Joules with the equivalent kg m^2 s^{-2}:

$$u_{rms} = \sqrt{\frac{3RT}{M}}$$

$$u_{rms} = \sqrt{\frac{3(8.314\ \text{J/mol K})(303\ \text{K})}{(0.028\ \text{kg/mol})}} = \sqrt{2.70 \times 10^5\ \text{m}^2\text{s}^{-2}} = 519\ \text{m/s}$$

Exercise

1. Calculate the root-mean-square velocity for an oxygen molecule at –23°C.
2. Calculate the root-mean-square speed of molecular chlorine in m/s at 20°C.

2.8 EFFUSION AND DIFFUSION

Upon completion of this topic, learners will be able to:

- discuss effusion and diffusion in relation to Graham's Law.

ACTIVITY 4

Determination of diffusion of gases

In this experiment hydrogen chloride gas, HCl(g), will react with ammonia gas, $NH_3(g)$, to form the white solid ammonium chloride. Hydrogen chloride gas is released from concentrated hydrochloric acid.

$$\text{Ammonia} + \text{Hydrogen chloride} \longrightarrow \text{Ammonium chloride}$$

$$NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$$

This is a teacher demonstration and it is recommended that it is performed in a fume cupboard. It is also recommended that a sheet of black paper be placed behind the demonstration so that the formation of the white solid ammonium chloride can be observed clearly.

Procedure

Throughout, the teacher/demonstrator must wear eye protection and safety gloves.

1. While working in a fume cupboard, clamp the glass tubing at both ends. Ensure that the glass tubing lies horizontally.
2. Put the end of one of the cotton buds into the concentrated ammonia solution. Quickly repeat this procedure with the second cotton bud into the concentrated hydrochloric acid. Push the buds into opposite ends of the tube and start a stopwatch. Replace the tops on the bottles of the ammonia and hydrochloric acid solutions.

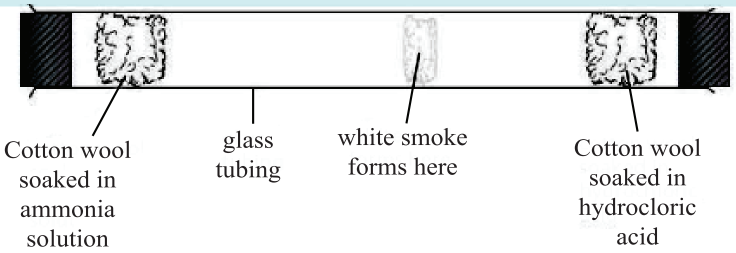


Figure 8. Diagram of the apparatus to determine diffusion of gases.

3. Watch the ring of white solid forming in the tube, and stop the stopwatch when it is initially observed.
4. Measure the distance each gas has travelled from one end of the tube to where the white solid formed.

Discussion questions

5. Why is it important that the glass tube is clamped horizontally before experiment begins?
6. Why is it important that the experiment takes place in a fume cupboard?

Results and calculations

Time taken for the white solid to form: ....

Distance travelled by ammonia gas: ....

Distance travelled by hydrogen chloride gas: ....

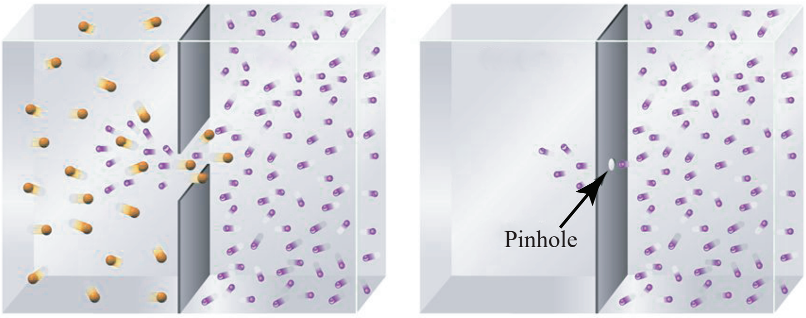
Rate of diffusion of the ammonia gas: ....

Rate of diffusion of the hydrogen chloride gas: ....

Conclusions

1. Which gas has moved the shorter distance to the white ring?
2. How will the length of the tube affect the time of formation of the white solid?
3. Does the ring form closer to the ammonia or hydrogen chloride end of the tube?
4. Why do you think that the white solid forms closer to this end of the tube?
5. How do you compare the rate of diffusion of the two gases?
6. Which gas diffuses faster? HCl or NH_3?
7. Write your conclusions about the experiment.

The dependence of molecular speed on mass has two interesting consequences. The first is **effusion**, which is the escape of gas molecules through a tiny hole. The second is **diffusion**, which is the spread of one substance throughout a space or throughout a second substance. For example, the molecules of a perfume diffuse throughout a room.



(a) Diffusion (b) Effusion

Figure 9. (a) Diffusion is mixing of gas molecules by random motion under conditions where molecular collisions occur. (b) Effusion is escape of a gas through a pinhole without molecular collisions.

Gas diffusion

In 1832 the Scottish chemist Thomas Graham found that under the same conditions of temperature and pressure, rates of diffusion for gases are inversely proportional to the square roots of their molar masses. This statement, now known as Graham's law of diffusion. Mathematically, it may be expressed as:

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} \quad \text{(P, T constant)}$$

where r_1 and r_2 are the rates of diffusion of gases 1 and 2, while M_1 and M_2 are their molecular masses.

Gas effusion

Effusion is the process by which a gas under pressure escapes from one compartment of a container to another by passing through a small opening. Although effusion differs from diffusion in nature, the rate of effusion of a gas has the same form as Graham's law of diffusion. The rate of effusion of a gas also depends, on the molecular mass of the gas.

Dalton's law when applied to effusion of a gas is called Dalton's Law of Effusion. Mathematically, it may be expressed as:

$$\frac{\text{Effusion rate of Gas 1}}{\text{Effusion rate of Gas 2}} = \sqrt{\frac{M_2}{M_1}} \quad \text{(P, T constant)}$$

The determination of rate of effusion is much easier compared to the rate of diffusion. Therefore, Dalton's law of effusion is often used to find the molecular mass of a given gas.

Example

If a gas diffuses at a rate of one-half as fast as O_2, find the molecular mass of the gas.

Solution

Applying Graham's law of diffusion

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

$$\frac{\frac{1}{2}}{1} = \sqrt{\frac{32}{M_1}}$$

Squaring both sides of the equation

$$\left(\frac{1}{2}\right)^2 = \frac{32}{M_1} \text{ or } \frac{1}{4} = \frac{32}{M_1}$$

$$M_1 = 128$$

Thus the molecular mass of the unknown gas is 128.

Example

A flammable gas made up only of carbon and hydrogen is found to effuse through a porous barrier in 1.50 min. Under the same conditions of temperature and pressure, it takes an equal volume of bromine vapor 4.73 minutes to effuse through the same barrier. Calculate the molar mass of the unknown gas, and suggest what this gas might be.

Solution

The rate of diffusion is the number of molecules passing through a porous barrier in a given time. The longer the time it takes, the slower is the rate. Therefore, the rate is inversely proportional to the time required for diffusion. This can be expressed as:

$$\frac{r_1}{r_2} = \frac{t_2}{t_1} = \sqrt{\frac{M_2}{M_1}}$$

where t_1 and t_2 are the times for effusion for gases 1 and 2, respectively.

From the molar mass of Br_2, we write

$$\frac{1.50 \text{ min}}{4.73 \text{ min}} = \sqrt{\frac{M}{159.8 \text{ g/mol}}}$$

where M is the molar mass of the unknown gas. Solving for M, we obtain

$$M = \left(\frac{150 \text{ min}}{4.73 \text{ min}}\right)^2 \times 159.8\frac{\text{g}}{\text{mol}} = 16.1 \text{ g/mol}$$

Because the molar mass of carbon is 12.01 g and that of hydrogen is 1.008 g, the gas is methane (CH_4).

Exercise

1. It takes 192 s for an unknown gas to effuse through a porous wall and 84 s for the same volume of N_2 gas to effuse at the same temperature and pressure. What is the molar mass of the unknown gas?

2.9 REAL GASES

Upon completion of this topic, learners will be able to:

- explain the general principles of the Van der Waal's Model of gas.

Although we can assume that real gases behave like an ideal gas, we cannot expect them to do so under all conditions. To study real gases accurately, then, we need to modify the ideal gas equation, taking into account intermolecular forces and finite molecular volumes.

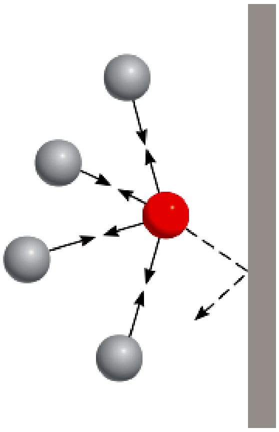


Figure 10. A molecule approching the walls of a container

Consider a particular molecule approching the wall of a container (Figure 10). The intermolecular attractions exerted by its neighbors tend to soften the impact made by this molecule against the wall. The overall effect is a lower gas pressure than we would expect for an ideal gas. Van der Waals suggested that the pressure exerted by an ideal gas, P_{ideal}, is related to the experimentally measured pressure, P_{ideal}, by the equation

$$P_{ideal} = P_{real} + \frac{an^2}{V^2}$$

where a is a constant and n and V are the number of moles and volume of the container, respectively. The correction term for pressure (an^2/V^2) can be understood as follows. The intermolecular interaction that gives rise to non-ideal behavior depends on how frequently any two molecules approach each other closely. The frequency of such “encounters” increases with the square of the number of molecules per unit volume (n^2/V^2), because the probability of finding each of the two molecules in a particular region is proportional to n/V. Thus, a is just a proportionality constant.

Another correction concerns the volume occupied by the gas molecules. In the ideal gas equation, V represents the volume of the container. However, each molecule does occupy a finite, although small, intrinsic volume, so the effective volume of the gas becomes (V - nb), where n is the number of moles of the gas and b is a constant. The term nb represents the volume occupied by n moles of the gas.

Having taken into account the corrections for pressure and volume, we can rewrite the ideal gas equation as follows:

$$\underbrace{\left(P+\frac{an^2}{V^2}\right)}_{\text{Corrected Pressure}}\underbrace{\left(V-nb\right)}_{\text{Corrected Volume}}=nRT$$

This equation, relating P, V, T, and n for a non-ideal gas, is known as the Van der Waals equation.

Table 2 **Lists the values of a and b for a number of gases. The value of a indicates how strongly molecules of a given type of gas attract one another.**

Van der waals Constants of Some Common Gases		
Gases	**a** $\left(\frac{\text{atm L}^2}{\text{mol}^2}\right)$	**b** $\left(\frac{\text{L}}{\text{mol}}\right)$
He	0.034	0.0237
Ne	0.211	0.0171
Ar	1.34	0.0322
Kr	2.32	0.0398
Xe	4.19	0.0266
H_2	0.244	0.0266
N_2	1.39	0.0391
O_2	1.36	0.0318
Cl_2	6.49	0.0562
CO_2	3.59	0.0427
CH_4	2.25	0.0428
CCl_4	20.4	0.138
NH_3	4.17	0.0317
H_2O	5.46	0.0305

Characteristics of several real gases

We can understand gas behavior more completely if we examine the characteristics of several common gases.

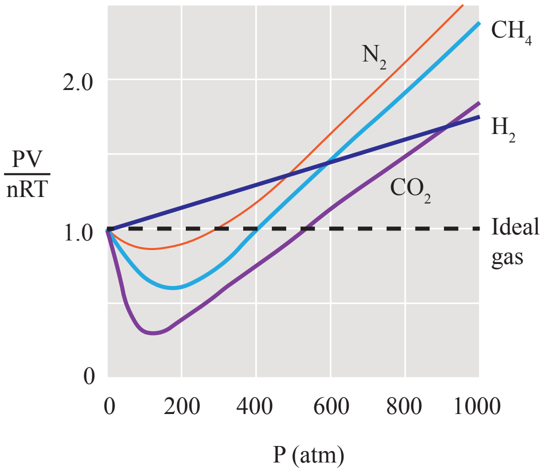


Figure 11. Plots of PV/nRT versus P for several gases (200 K). Note the significant deviations from ideal behavior (PV/nRT = 1). The behavior is close to ideal gas only at low pressures (less than 1 atm).

Note from Figure 11 that the gases H_2, N_2, CH_4, and CO_2 show different behavior when the compressibility PV/nRT is plotted versus P. For example, notice that the plot for $H_2(g)$ never drops below the ideal value (1.0) in contrast to all the other gases. What is special about H_2 compared to other gases? Remember that the value reflects how much of a correction must be made to adjust the observed pressure up to the expected ideal pressure:

$$P_{ideal} = P_{obs} + a\left(\frac{n}{V}\right)^2$$

A low value reflects weak intermolecular forces among the gas molecules. Also notice that although the compressibility for N_2 dips below 1.0, it does not show as much deviation as that for CH_4, which in turn does not show as much deviation as the compressibility for CO_2. Based on this behavior, we can summise that the importance of intermolecular interactions increases in this order:

$$H_2 < N_2 < CH_4 < CO_2$$

The main point to be made here is that real gas behavior can tell us about the relative importance of intermolecular attractions among gas molecules.

Example

Given that 3.50 moles of NH_3 occupy 5.20 L at 47°C, calculate the pressure of the gas (in atm) using the ideal gas equation and the Van der Waals equation.

Solution

We have the following data:

$$V = 5.20\ \text{L}$$

$$T = (47 + 273)\text{K} = 320\text{K}$$

$$n = 3.50\ \text{mol}$$

$$R = 0.0821 \frac{\text{L.atm}}{\text{K.mol}}$$

Substituting these values in the ideal gas equation, we write

$$PV = \frac{nRT}{V} = \frac{(3.50\ \text{mol})\left(0.0821 \frac{\text{L.atm}}{\text{K.mol}}\right)(320\ \text{K})}{5.20\ \text{L}}$$

$$P = 17.7\ \text{atm}$$

From Table 2, we have

$$a = 4.17\ \text{atm.}\frac{\text{L}^2}{\text{mol}^2}$$

$$b = 0.0371\ \text{L/mol}$$

so that the correction terms for pressure and volume are:

$$\frac{an^2}{V^2} = \frac{\left(4.17\ \text{atm.}\frac{\text{L}^2}{\text{mol}^2}\right)(3.50\ \text{mol})^2}{5.20\ \text{L}^2}$$

$$nb = (3.50\ \text{mol})\left(0.0371 \frac{\text{L}}{\text{mol}}\right) = 0.130\ \text{L}$$

Finally, substituting these values in the Van der Waals equation, we have

$$(P + 1.89\ \text{atm})(5.20\ \text{L - }0.130\ \text{L}) = (3.50\ \text{mol})\left(0.0821 \frac{\text{L.atm}}{\text{K.mol}}\right)(320\ \text{K}) = 16.2\ \text{atm}$$

Based on your understanding of non-ideal gas behavior, is it reasonable that the pressure calculated using the Van der Waals equation should be smaller than that using the ideal gas equation. Why?

Exercise

1. Using the data shown in Table 2, calculate the pressure exerted by 4.37 moles of molecular chlorine confined in a volume of 2.45 L at 38°C. Compare the pressure with that calculated using the ideal gas equation.

2.10 CHEMISTRY IN THE ATMOSPHERE

Upon completion of this topic, learners will be able to:

- discuss the concept of chemistry in the atmosphere.

The gases that are most important to us are found in the atmosphere that surrounds the earth's surface. The principal components are N_2 and O_2, but many other important gases, such as H_2O and CO_2, are also present.

The composition of the atmosphere varies as a function of distance from the earth's surface. Heavier molecules tend to be near the surface due to gravity.

Upper atmosphere chemistry is largely affected by ultraviolet, x-ray, and cosmic radiation coming from space. In fact, the upper atmosphere serves as an important shield to prevent this high energy radiation from reaching the earth, where it would damage the relatively fragile molecules sustaining life. In particular, the ozone in the upper atmosphere helps prevent high-energy ultraviolet radiation from penetrating to the earth.

Manufacturing and other processes of our modern society affect the chemistry of our atmosphere. Air pollution is a direct result of such processes. The combustion of petroleum in vehicles produces CO, CO_2, NO, and NO_2, along with unburned molecules from petroleum. When this mixture is trapped close to the ground in stagnant air, reactions occur producing chemicals that are potentially irritating and harmful to living systems.

The complex chemistry of polluted air appears to center around the nitrogen oxides (NO_x). At high temperatures found in the gasoline and diesel engines of cars and trucks, N_2 and O_2 react to form a small quantity of NO that is emitted into the air with the exhaust gases. This NO is immediately oxidized in air to NO_2, which, in turn, absorbs energy from sunlight and breaks up into nitric oxide and free oxygen atoms. Oxygen atoms are very reactive and can combine with O_2 to form ozone. Ozone is also very reactive and can react directly with other pollutants, or the ozone can absorb light and break up to form an energetically excited O_2 molecule (O_2^*) and an energetically excited oxygen atom (O^*). The latter species readily reacts with a water molecule to form two hydroxyl radicals (•OH). The hydroxyl radical is a very reactive oxidizing agent. For example, •OH can react with NO_2 to form nitric acid.

The •OH radical also can react with the unburned hydrocarbons in the polluted air to produce chemicals that cause the eyes to water and burn and are harmful to the respiratory system.

The end product of this whole process is often referred to as photochemical smog, so called because light is required to initiate some of the reactions. The production of photochemical smog can be understood more clearly by examining as a group the reactions discussed above:

$$\begin{array}{lrl}
 & NO_2(g) & \longrightarrow NO(g) + O(g) \\
 & O(g) + O_2(g) & \longrightarrow O_3(g) \\
 & NO(g) + \frac{1}{2}O_2(g) & \longrightarrow NO_2(g) \\
\hline
\text{Net reaction:} & O_2(g) + \frac{1}{2}O_2(g) & \longrightarrow O_3(g)
\end{array}$$

Note that the NO_2 molecules assist in the formation of ozone without being themselves used up.

The other major source of pollution results from burning coal to produce electricity. Much of the coal found in the midwest contains significant quantities of sulfur, which, when burned, produces sulfur dioxide:

$$S(\text{in coal}) + O_2(g) \longrightarrow SO_2(g)$$

A further oxidation reaction occurs when sulfur dioxide is changed to sulfur trioxide in the air

$$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$$

The production of sulfur trioxide is significant because it can combine with droplets of water in the air to form sulfuric acid:

$$SO_3(g) + H_2O(g) \longrightarrow H_2SO_4(aq)$$

Sulfuric acid is very corrosive to both living things and building materials. Another result of this type of pollution is acid rain.

Exercise

1. Write reactions to show how nitric and sulfuric acids are produced in the atomosphere.
2. What methods do you recommend to reduce air pollution? Write a report about your findings.

Key Terms

- Pressure
- Boyle's Law
- Charles's Law
- Absolute zero
- Gay-Lussac's Law
- Avogadro's Law
- Standard temperature and pressure
- Molar Gas Volume
- Ideal-gas equation
- Dalton's law of partial pressure
- Kinetic-Molecular Theory of gases
- Root-mean-square velocity
- Effusion
- Diffusion
- Graham's law of diffusion
- Real Gases
- Pollutants

Summary

Substances that are gases at room temperature are usually molecular substances with low molar masses. Air, a mixture composed mainly of N_2 and O_2, is the most common gas we encounter.

To describe the state or condition of a gas, we must specify four variables: pressure (P), volume (V), temperature (T), and quantity (n). Volume is usually measured in liters, temperature in kelvins, and quantity of gas in moles.

Pressure is the force per unit area. It is expressed in SI units as pascals, Pa. A related unit, the bar, equals Pa. In chemistry, **standard atmospheric pressure** is used to define the atmosphere (atm) and the torr (also called the millimeter of mercury). One atmosphere of pressure equals 101.325 kPa, or 760 torr. A barometer is often used to measure atmospheric pressure. A manometer can be used to measure the pressure of enclosed gases.

Studies have revealed several simple gas laws: For a constant quantity of gas at constant temperature, the volume of the gas is inversely proportional to the pressure (**Boyle's law**).

For a fixed quantity of gas at constant pressure, the volume is directly proportional to its absolute temperature (**Charles's law**).

Equal volumes of gases at the same temperature and pressure contain equal numbers of molecules (**Avogadro's hypothesis**). For a gas at constant temperature and pressure, the volume of the gas is directly proportional to the number of moles of gas (**Avogadro's law**). Each of these gas laws is a special case of the **ideal-gas equation**.

The ideal-gas equation, $PV = nRT$, is the equation of state for **an ideal gas**. The term R in this equation is the gas constant. We can use the ideal-gas equation to calculate variations in one variable when one or more of the others are changed. Most gases at pressures less than 10 atm and temperatures near 273 K and above obey the ideal-gas equation reasonably well.

The conditions of 273 K and 1 atm are known as the **standard temperature and pressure** (STP). In all applications of the ideal-gas equation we must remember to convert temperatures to the absolute-temperature scale (the Kelvin scale).

Using the ideal-gas equation, we can relate the density of a gas to its molar mass: $M = dRT/P$. We can also use the ideal-gas equation to solve problems involving gases as reactants or products in chemical reactions.

In gas mixtures the total pressure is the sum of the partial pressures that each gas would exert if it were present alone under the same conditions (**Dalton's law of partial pressures**). The partial pressure of a component of a mixture is equal to its mole fraction times the total pressure: $P_1 = xP_t$. In calculating the quantity of a gas collected over water, correction must be made for the partial pressure of water vapor in the gas mixture.

The **kinetic-molecular theory of gases** accounts for the properties of an ideal gas in terms of a set of statements about the nature of gases. Briefly, these statements are as follows:

Molecules are in continuous random motion. The volume of gas molecules is negligible compared to the volume of their container. The gas molecules neither attract nor repel each other. The average kinetic energy of the gas molecules is proportional to the absolute temperature and does not change if the temperature remains constant.

The individual molecules of a gas do not all have the same kinetic energy at a given instant. Their speeds are distributed over a wide range; the distribution varies with the molar mass of the gas and with temperature. The **root-mean-square (rms) speed**, varies in proportion to the square root of the absolute temperature and inversely with the square root of the molar mass: $u_{rms} = \sqrt{3RT / M}$.

It follows from the kinetic-molecular theory that the rate at which a gas undergoes **effusion** (escapes through a tiny hole) is inversely proportional to the square root of its molar mass (**Graham's law**).

The **diffusion** of one gas through the space occupied by a second gas is another phenomenon related to the speeds at which molecules move.

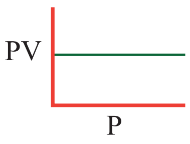
Departures from ideal behavior increase in magnitude as pressure increases and as temperature decreases. Real gases depart from ideal behavior because the molecules possess finite volume and because the molecules experience attractive forces for one another.

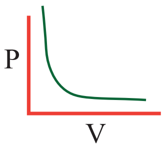
The **Van der Waals** equation is an equation of state for gases that modifies the ideal-gas equation to account for intrinsic molecular volume and intermolecular forces.

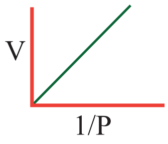
Ozone in our upper atmosphere protects us from harmful ultraviolet radiation. The ozone layer is being destroyed by **pollutants**. These molecules produce free radicals, which interact with ozone to convert it to oxygen. In the lower atmosphere ozone causes damage to plants, cracking of rubber, and irritations to humans. Other air pollutants such as nitrogen oxides and sulfur oxides are found in urban areas, creating smog, which can impact our daily lives.

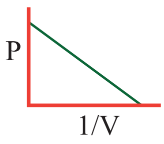
Exercises

1. Define pressure and give the common units for pressure.
2. Why is mercury a more suitable substance to use in a barometer than water?
3. State the following gas laws in words and also in the form of an equation: Boyle's law, Charles's law, Avogadro's law. In each case, indicate the conditions under which the law is applicable, and give the units for each quantity in the equation.
4. Boyle's law can be represented graphically in several ways. Which of the following plots does not correctly represent Boyle's law (assuming constant T and n)? Explain.





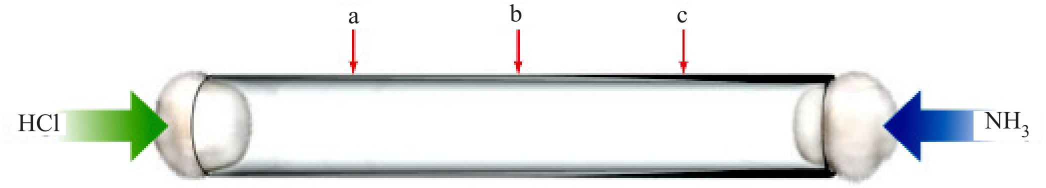




5. A gas occupying a volume of 725 mL at a pressure of 0.970 atm is allowed to expand at constant temperature until its pressure reaches 0.541 atm. What is its final volume?

6. At 46°C a sample of ammonia gas exerts a pressure of 5.3 atm. What is the pressure when the volume of the gas is reduced to one-tenth (0.10) of the original value at the same temperature?
7. What are standard temperature and pressure (STP)? What is the significance of STP in relation to the volume of 1 mole of an ideal gas?
8. A sample of nitrogen gas kept in a container of volume 2.3 L and at a temperature of 32°C exerts pressure of 4.7 atm. Calculate number of moles of gas present.
9. Calculate its volume (in liters) of 88.4 g of CO_2 at STP.
10. A gas has a density at STP of 1.78 g/L. What is its molar mass?
11. Calculate the density of hydrogen bromide (HBr) gas in grams per liter at 733 mmHg and 46°C.
12. Calculate the mass in grams of hydrogen chloride produced when 5.6 L of molecular hydrogen measured at STP reacts with an excess of molecular chlorine gas.
13. A mixture of gases contains 0.31 mol CH_4, 0.25 mol C_2H_6, and 0.29 mol C_3H_8. The total pressure is 1.50 atm. Calculate the partial pressures of the gases.
14. What are the basic assumptions of the kinetic molecular theory of gases? How does the kinetic molecular theory explain Boyle's law, Charles's law, Avogadro's law, and Dalton's law of partial pressures?
15. Indicate which of the following statements regarding the kinetic molecular theory of gases are correct. For those that are false, formulate a correct version of the statement.
    (a) Gas molecules are assumed to exert no forces on each other.
    (b) All the molecules of a gas at a given temperature have the same kinetic energy.
    (c) The volume of gas molecules is negligible in comparison to the total volume in which the gas is contained.
    (d) All gas molecules move with the same speed if they are at the same temperature.
16. The temperature in the stratosphere is -23°C. Calculate the root-mean-square speeds of N_2, O_2 , and O_3 molecules in this region.
17. Write the Van der Waals equation for a real gas. Explain the corrective terms for pressure and volume.
18. An unknown gas effuses at 0.850 times the effusion rate of nitrogen dioxide, NO_2. Estimate the molar mass of the unknown gas.

19. A thin glass tube 1 m long is filled with Ar gas at 1 atm, and the ends are stoppered with cotton plugs:



HCl gas is introduced at one end of the tube, and simultaneously NH_3 gas is introduced at the other end. When the two gases diffuse through the cotton plugs down the tube and meet, a white ring appears due to the formation of $NH_4Cl(s)$.

At which location—a, b, or c—do you expect the ring to form? Explain your choice.

20. Write reactions to show how nitric and sulfuric acids in acid rain react with marble and limestone. (Both marble and limestone are primarily calcium carbonate.)

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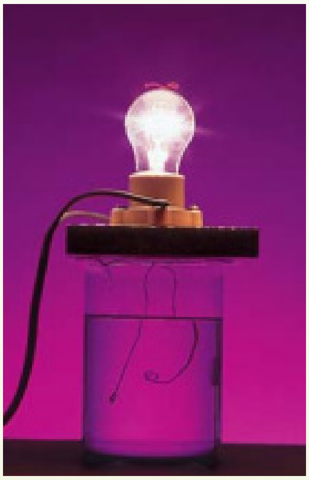
CHAPTER 3

ELECTROLYTES – ACIDS, BASES AND SALTS

Chapter Contents



Chapter Outcomes

By the end of this chapter, you will be able to:

- interpret knowledge of electrolytes – acids, bases, salts.
- understand the Arrhenius, and Bronsted-Lowry concepts of acids and bases. Know how to solve equilibrium problems involving concentration of reactants and products, k_a, k_b, *p*H and *p*OH.
- predict, in qualitative terms, whether a solution of a specific salt will be acidic, basic or netural.
- understand the Lewis concept of acids and bases.
- understand the common-ion effect, buffer solutions, acid-base indicators and acid-base titrations.
- develop the ability to perform various acid base titrations.

3.1 ELECTROLYTES AND NON-ELECTROLYTES

Upon completion of this topic, learners will be able to:

- discuss electrolytes and non-electrolytes.

Acids, bases, and soluble salts all produce ions in solution; thus they all produce solutions that conduct electricity. All these three types of compounds are said to be electrolytes. An electrolyte is a substance whose aqueous solution conducts electricity.

Some substances, such as table sugar, glucose, and *iso*-propyl alcohol, do not produce ions in solution. These substances are called non-electrolytes. A non-electrolyte is a substance whose aqueous solution does not conduct electricity.

Electrolytes can be divided into two groups: strong electrolytes and weak electrolytes. A strong electrolyte is a substance that completely (or almost completely) ionizes/dissociates into ions in aqueous solution. Strong electrolytes produce highly conducting solutions. All strong acids, strong bases and all soluble salts are strong electrolytes. A weak electrolyte is a substance that incompletely ionizes/dissociates into ions in aqueous solution. Weak electrolytes produce solutions that are intermediate between those containing strong electrolytes and those containing non-electrolytes. Weak acids and weak bases constitute weak electrolytes.

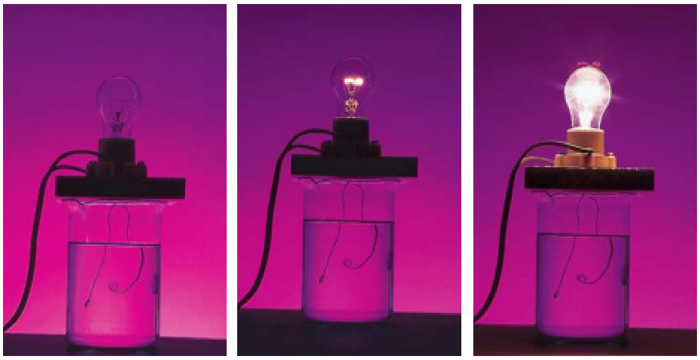


Figure 1. An arrangement for distinguishing between electrolytes and non-electrolytes (a) A non-electrolyte solution does not contain ions, and the light bulb is not lit. (b) A weak electrolyte solution contains a small number of ions, and the light bulb is dimly lit. (c) A strong electrolyte solution contains a large number of ions, and the light bulb is brightly lit.

Exercise

1. List at least five acids and bases. Then write chemical equations to show how they behave as electrolytes.

ACTIVITY 1

Experiment to demonstrate the conductivity of electrolytic solutions

Solution conductivity can be detected by a conductivity-sensing apparatus such as the one shown in Figure 2. If the electrodes are immersed in a solution containing mobile ions, the ions conduct "current," and the bulb lights. If the solution contains no ions, no current will flow, and the bulb does not light. The flow or no-flow of current is therefore a clear indication of the presence or absence of ions. The intensity of light produced (which is proportional to the magnitude of current) is a qualitative measure of the number of ions present.

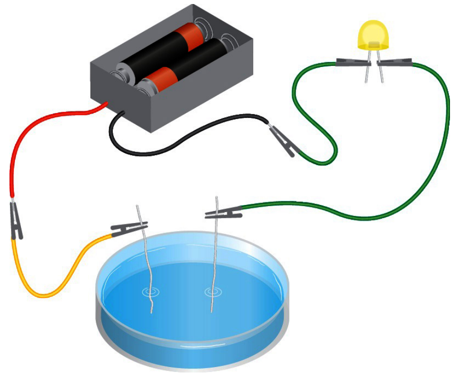


Figure 2. Conductivity-sensing apparatus

In this experiment, the conductivity of several solutions will be observed. You will be asked to make classifications, based on your experimental observations, whether the substances tested are strong electrolytes, weak electrolytes, or non-electrolytes.

Results and discussion:

Table 1

Number	Substance	Conductor (Good, poor, non-conductor)	Electrolyte		
			Strong electrolytes	Weak electrolytes	Non-electrolytes
1	Tap water				
2	Solid NaCl				
3	1.0 M NaCl				
4	1.0 M CH_3COOH				
5	1.0 M HCl				
6	1.0 M NaOH				
7	1.0 M $CH_3COO^-Na^+$				

8	1.0 M NH_4^+Cl				
9	Sugar				
10	$BaSO_4$ in water				

Conclusion

1.
   - (i) Did solid NaCl conduct current? Explain why or why not.
   - (ii) Would you predict that molten NaCl would or would not conduct current? Explain your reasoning.
   - (iii) Explain the reason for the difference in conductivities.
2. The acid having higher conductivity is --------- (1.0 M CH_3COOH or 1.0 M HCl). Give an explanation for the difference.
3. Write an equation for the disolution of sugar in water. Indicate whether the resulting solution will have mainly ions, molecules or both?

3.2 ACID-BASE THEORIES AND PROPERTIES OF ACIDS AND BASES

Upon completion of this topic, learners will be able to:

- describe acids and bases involving the Arrhenius and Bronsted-Lowry theories.
- define Bronsted-Lowry acids and bases.
- define the term conjugate acid-base pair.
- define amphiprotic species.
- understand the relationship between the strength of an acid and that of its conjugate base.

Arrhenius concept of acids and bases

We can state the Arrhenius concept of an acid as follows: An acid is a substance that, when dissolved in water, increases the concentration of hydronium ion, $H_3O^+(aq)$. For simplicity, chemists frequently use the notation $H^+(aq)$ for the $H_3O^+(aq)$ ion and call it the hydrogen ion.

A base, in the Arrhenius concept, is a substance that, when dissolved in water, increases the concentration of hydroxide ion, $OH^-(aq)$.

In Arrhenius's theory, a strong acid is a substance that completely ionizes in aqueous solution to give $H_3O^+(aq)$ and an anion.

An acid that releases few hydrogen ions in aqueous solution is a weak acid. The aqueous solution of a weak acid contains hydronium ions, anions, and dissolved acid molecules.

Table 2 Common aqueous acids

Strong acid	Weak acid
$HI + H_2O \longrightarrow H_3O^+ + I^-$	$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-$
$HClO_4 + H_2O \longrightarrow H_3O^+ + ClO_4^-$	$HF + H_2O \rightleftharpoons H_3O^+ + F^-$
$HBr + H_2O \longrightarrow H_3O^+ + Br^-$	$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$
$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$	$H_2CO_3 + H_2O \rightleftharpoons H_3O^+ + HCO_3^-$
$H_2SO_4 + H_2O \longrightarrow H_3O^+ + SO_4^{-2}$	$HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$

A strong base completely ionizes in aqueous solution to give OH^- and a cation. Sodium hydroxide is an example of a strong base.

$$NaOH(s) \xrightarrow{H_2O} Na^+(aq) + OH^-(aq)$$

The principal strong bases are the hydroxides of Group 1A elements.

Not all bases are ionic compounds. A base commonly used in household cleaners is ammonia, NH_3. Molecular Ammonia is a base because it produces hydroxide ions when it reacts with water molecules, as shown in the equation below.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Table 3 Common aqueous bases

Strong bases	Weak bases
$Ca(OH)_2 \longrightarrow Ca^{2+} + 2OH^-$	$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$
$Sr(OH)_2 \longrightarrow Sr^{2+} + 2OH^-$	$C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^-$
$Ba(OH)_2 \longrightarrow Ba^{2+} + 2OH^-$	
$KOH \longrightarrow K^+ + OH^-$	
$RbOH \longrightarrow Rb^+ + OH^-$	
$CsOH \longrightarrow Cs^+ + OH^-$	

Despite its successes, the Arrhenius concept is limited. In addition to looking at acid–base reactions only in aqueous solutions, it singles out the OH^- ion as the source of base character, when other species can play a similar role. Broader definitions of acids and bases are described in the next sections.

Brønsted-Lowry concept of acids and bases

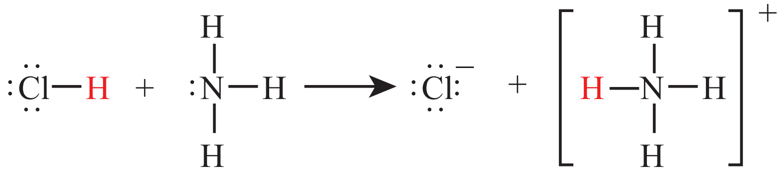
According to the Brønsted-Lowry concept, an acid is the species donating a proton in a proton-transfer reaction. A base is the species accepting the proton in a proton-transfer reaction.

In the reaction that occurs when HCl dissolves in water, the HCl molecule transfers an ion (a proton) to a water molecule.

$$HCl\,(g) + H_2O\,(l) \longrightarrow Cl^-\,(aq) + H_3O^+\,(aq)$$

Thus, when HCl dissolves in water, HCl acts as a Brønsted-Lowry acid (it donates a proton to H_2O), and H_2O acts as a Brønsted-Lowry base (it accepts a proton from HCl).

Because the emphasis in the Brønsted-Lowry concept is on proton transfer, the concept also applies to reactions that do not occur in aqueous solution. In the reaction between gas phase HCl and NH_3, for example, a proton is transferred from the acid HCl to the base NH_3:

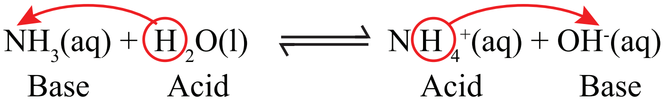


To be a Brønsted-Lowry acid, a molecule or ion must have a hydrogen atom it can lose as an H^+ ion. To be a Brønsted-Lowry base, a molecule or ion must have a non-bonding pair of electrons it can use to bind the H^+ ion.

A substance capable of acting as either an acid or a base is called amphiprotic. It is a species that can act as either an acid or a base (it can lose or gain a proton), depending on the other reactant. For example, HCO_3^- acts as an acid in the presence of OH^- but as a base in the presence of HF. Anions with ionizable hydrogens, such as HCO_3^-, and certain solvents, such as water, are amphiprotic.

Conjugate acid–base pairs

In any acid–base equilibrium, both the forward reaction and the reverse reaction involve proton transfer. Consider the reaction of NH_3 with H_2O



In the forward reaction, NH_3 accepts a proton from H_2O. Thus, NH_3 is a base and H_2O is an acid. In the reverse reaction, NH_4^+ donates a proton to OH^-. NH_4^+ ion is the acid and OH^- is the base.

Note that NH_3 and NH_4^+ differ by a proton. That is, NH_3 becomes the NH_4^+ ion by gaining a proton, whereas the NH_4^+ ion becomes the NH_3 molecule by losing a proton. The species NH_4^+ and NH_3 are a conjugate acid-base pair. A conjugate acid-base pair consists of two species in an acid-base reaction, one acid and one base, that differ by the loss or gain of a proton. Here NH_4^+ is the conjugate acid of NH_3, and NH_3 is the conjugate base of NH_4^+.

If we arrange acids in order of their ability to donate a proton, we find that the more easily a substance gives up a proton, the less easily its conjugate base accepts a proton. Similarly, the more easily a base accepts a proton, the less easily its conjugate acid gives up a proton. In other words, the stronger an acid, the weaker its conjugate base, and the stronger a base, the weaker its conjugate acid.

The inverse relationship between the strengths of acids and their conjugate bases is illustrated in Figure 3.

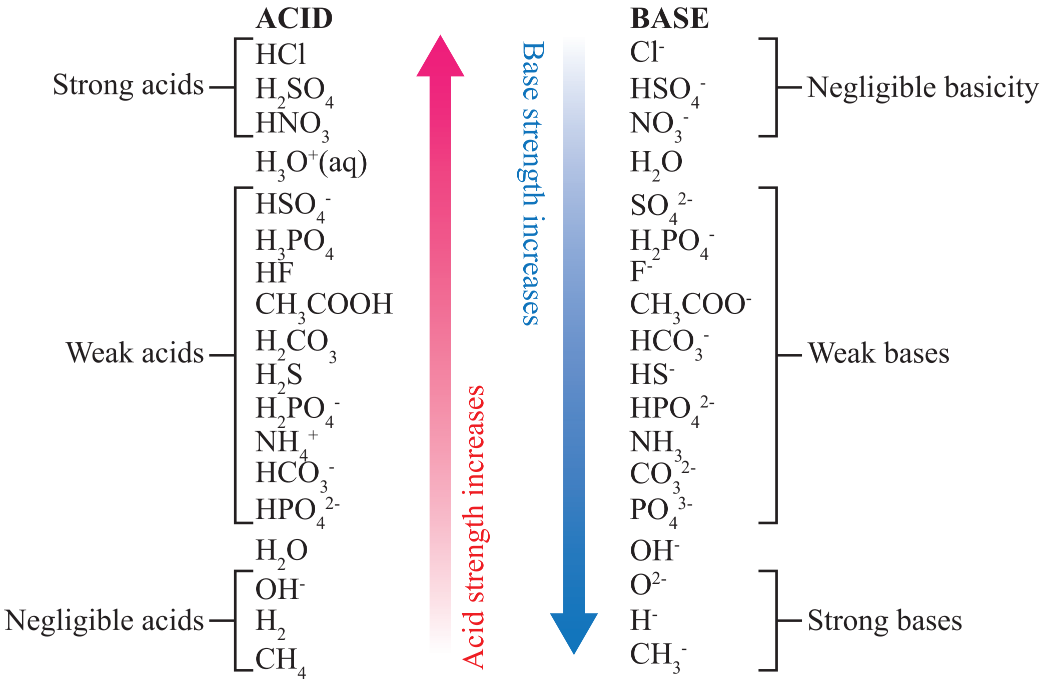


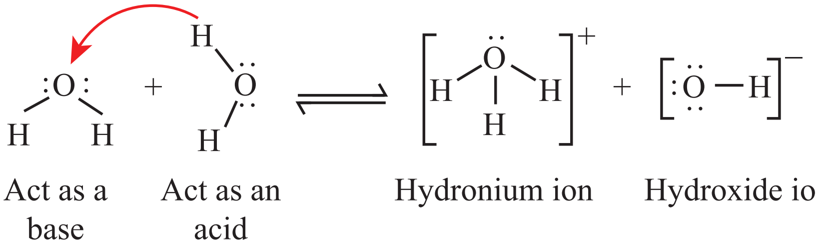
Figure 3. Relative strengths of selected conjugate acid–base pairs.

Exercise

1.
   - (a) What is the conjugate base of $HClO_4$, H_2S, HCO_3^-?
   - (b) What is the conjugate acid of CN^-, HCO_3^-, H_2O?
2. Is there any limitation to the Brønsted-Lowry definition of acids and bases? Explain if any.
3. Given that $HClO_4$ is a strong acid, how would you classify the basicity of ClO_4^- ?
4. Formic acid, HCOOH, is a stronger acid than acetic acid, $HC_2H_3O_2$. Which is the stronger base, formate ion, CHO_2^-, or acetate ion, $C_2H_3O_2^-$?

Auto-ionisation of water

The auto-ionisation (self-ionization) of a substance involves the transfer of a proton from one molecule of the substance to another molecule of the same substance. For example, water undergoes auto-ionisation as shown below:



The self-ionization of water can be represented by the following equation:

$$2H_2O\,(l) \rightleftharpoons H_3O^+(aq) + OH^-\,(aq)$$

Since this reaction is reversible, we can apply the law of mass action to write the equilibrium constant expression. The equilibrium-constant expression for the auto ionization of water is

$$K_c = \left[H_3O^+\right]\left[OH^-\right]$$

Note that K_w is the product of the molar concentrations of H_3O^+ and OH^- ions at a particular temperature. The term $[H_2O]$ is excluded from the equilibrium-constant expression because we exclude the concentrations of pure solids and liquids. Because this expression refers specifically to the autoionization of water, we use the symbol K_w to denote the equilibrium constant, which we call the ion-product constant for water.

At 25 °C, K_w equals 1.0×10^{-14}. Thus, we have

$$K_W = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \quad \text{(at 25°C)}$$

Because we use H^+ and H_3O^+ interchangeably to represent the hydrated proton, the auto ionization reaction for water can also be written as

$$H_2O\,(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

Likewise, the expression for Kw can be written in terms of either H_3O^+ or H^+, and K_w has the same value in either case:

$$K_W = [H_3O^+][OH^-] = [H^+][OH^-] = 1.0 \times 10^{-14} \quad \text{(at 25°C)}$$

In pure water at 25°C, the concentrations of H^+ and $OH^–$ ions are equal and found to be $[H^+] = 1.0 \times 10^{–7}$ M and $[OH^–] = 1.0 \times 10^{–7}$ M at 25°C,

$$K_W = [H^+][OH^-] = (1.0 \times 10^{-7})(1.0 \times 10^{-7}) = 1.0 \times 10^{-14}$$

In any aqueous solution at 25°C, no matter what it contains, the product of $[H^+]$ and $[OH^–]$ must always equal $1.0 \times 10^{–14}$.

Examples

Calculate the concentrations of hydronium ion and hydroxide ion at 25°C in:

a. 0.15 M HNO_3

b. 0.010 M $Ba(OH)_2$

Solution

a. Every mole of HNO_3 contributes one mole of H_3O^+ ion, so the H_3O^+ concentration is 0.15 M. The $OH^–$ concentration is obtained from the equation for K_w.

$$K_W = [H_3O^+][OH^-]$$

$$1.0 \times 10^{-14} = 0.15 \times [OH^-]$$

$$[OH^-] = \frac{1.0 \times 10^{-14}}{0.15} = 6.7 \times 10^{-14}$$

The concentration of OH^- in 0.15 M HNO_3 is 6.7×10^{-14}.

$$Ba(OH)_2 \xrightarrow{H_2O} Ba^{2+}(aq) + 2OH^-(aq)$$

b. Every mole of $Ba(OH)_2$ that dissolves yields two moles of OH^-. Therefore, 0.010 M $Ba(OH)_2$ contains 2 × 0.010 M OH^- = 0.020 M OH^-. The H_3O^+ concentration is obtained from

$$K_w = \left[H_3O^+\right]\left[OH^-\right]$$

$$1.0 \times 10^{-14} = 0.020 \times \left[H^+\right]$$

$$\left[H^+\right] = \frac{1.0 \times 10^{-14}}{0.020} = 5.0 \times 10^{-13}$$

The hydronium-ion concentration is 5.0×10^{-13} M.

3.3 pH AND pOH CALCULATIONS

Upon completion of this topic, learners will be able to:

- solve sample problems involving the concept of pH and pOH.
- calculate the pH of a solution given $[H^+]$ or $[OH^-]$.
- calculate the pH of a strong acid or strong base given its concentration.
- calculate K_a or K_b for a weak acid or weak base given its concentration and the pH of the solution.
- calculate the pH of a weak acid or weak base or its percent ionization given its concentration and K_a or K_b.

Because the concentrations of H^+ and OH^- ions in aqueous solutions are frequently very small numbers and therefore inconvenient to work with, Soren Sorensen in 1909 proposed a more practical measure called pH. The pH of a solution is defined as the negative logarithm of the hydrogen ion concentration (in mol/L):

$$pH = -\log\left[H_3O^+\right] \text{ or } pH = -\log\left[H^+\right]$$

A neutral solution at 25°C has a $[H^+]$ of 1.0×10^{-7} M. The logarithm of 1.0×10^{-7} is 7.0. The pH is determined as follows.

$$pH = -\log\left(1.0 \times 10^{-7}\right) = -(-7.00) = 7.00$$

The pH of a neutral solution is 7.00 at 25°C.

Because pH is simply a way to express hydrogen ion concentration, acidic and basic solutions at 25°C can be distinguished by their pH values, as follows:

Table 4 **Relationship among $[H^+]$, $[OH^-]$ and pH at 25°C**

Solution type	$[H^+]$ (M)	$[OH^-]$ (M)	pH
Acid	$> 1.0 \times 10^{-7}$	$< 1.0 \times 10^{-7}$	< 7.00
Neutral	1.0×10^{-7}	1.0×10^{-7}	7.00
Basic	$< 1.0 \times 10^{-7}$	$> 1.0 \times 10^{-7}$	> 7.00

Notice that pH increases as $[H^+]$ decreases. A change in by a factor of 10 causes the pH to change by 1. Thus, the concentration of $[H^+]$ in a solution of pH 6 is 10 times the $[H^+]$ in a solution of pH 7.

Suppose that you are given the pH of a solution. How can you determine its hydronium ion concentration?

pOH and other "p" scales

The negative logarithm is a convenient way of expressing the magnitudes of other small quantities.

Thus, we can express the concentration of pOH as:

$$pOH = -\log\left[OH^-\right]$$

Likewise, $pK_w = -\log\left[K_w\right]$.

Exercise

1. Derive the relationship. $pH + pOH = pk_w = 14$ at 25°C?
2. If the pOH for a solution is 4.00, what is the pH? Is the solution acidic or basic?

ACTIVITY 2

Determination of pH

The aim of this experiment is to learn how to measure the pH of some common solutions. The pH will be measured by universal indicator solution, and a pH-meter. The pH-scale is a convenient way to describe the acidity of solutions.

Procedure

1. Universal indicator solution

   Add 1 drop of Universal Indicator to each material in the spot plate. Compare the resulting color with the universal indicator pH color chart. Record the pH of each material and the color observed on the data sheet.

Figure 4. A digital pH Meter and Universal Indicator Paper

2. pH Meter- Demonstration by instructor
   Each solution or substance will be tested with a calibrated, standardized pH meter. Record the pH meter readings on the DATA SHEET

Determination of pH

Data sheet

Table 5

Solution or Substance	pH and color, using Universal indicator	pH meter readings
Tap water		
Deionized water		
Household vinegar		
0.1 M acetic acid		
0.1 M HCl		
Soap solution		
Detergent solution		
Household ammonia		
0.1M ammonia		
0.1M NaOH		

1. Acetic acid and hydrochloric acid had the same concentration of 0.1M. Did you also find the pH of both acids to be the same? Explain.
2. The solutions of ammonia and sodium hydroxide had the same concentration. Did you also find the pH of both solutions to be same? Explain.
3. What is the significance of pH values in everyday life such as in environmental and medical application?

Calculating the pH of strong acids

In an aqueous solution of a strong acid, the acid is normally the only significant source of H^+ ions. As a result, calculating the pH of a solution of a strong monoprotic acid is straightforward because $[H^+]$ equals the original concentration of acid. In a 0.20 M solution of $HNO_3(aq)$, for example, $[H^+] = [NO_3^-] = 0.20$ M.

Examples

What is the pH of a 0.040 M solution of $HClO_4$?

Solution

Because $HClO_4$ is a strong acid, it is completely ionized, giving $[H^+] = [ClO_4^-] = 0.040$ M.

$$pH = -\log(0.040) = 1.40.$$

Calculating the pH of strong bases

Which solution has the higher pH, a 0.001 M solution of NaOH or a 0.001 M solution of $Ba(OH)_2$?

Calculating the pH of weak acid solutions

Most acidic substances are weak acids and therefore only partially ionized in aqueous solution. We can use the equilibrium constant for the ionization reaction to express the extent to which a weak acid ionizes. If we represent a general weak acid as HA, we can write the equation for its ionization in either of the following ways, depending on whether the hydrated proton is represented as H_3O^+ or H^+

$$HA(aq) + H_2O(aq) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

or

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

Because H_2O is the solvent, it is omitted from the equilibrium-constant expression. Thus, we can write the equilibrium-constant expression as either

$$K_c = \frac{[H_3O^+][A^-]}{[HA]} \text{ or } K_c = \frac{[H^+][A^-]}{[HA]}$$

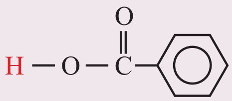
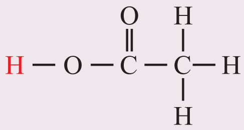
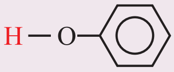
As we did for the ion-product constant for the auto ionization of water, we change the subscript on this equilibrium constant to indicate the type of equation to which it corresponds:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \quad \text{or} \quad K_a = \frac{[H^+][A^-]}{[HA]}$$

The subscript ‘a’ denotes that K_a is an equilibrium constant for the ionization of an acid, so K_a is called the acid-dissociation constant.

Table 6 shows the structural formulas, conjugate bases, and K_a values for a number of weak acids.

Table 6 Some weak acids in water at 25 °C

Acid	Structural Formula	Conjugate Base	K_a
Chlorous ($HClO_2$)	$\mathrm{H-O-Cl-O}$	ClO_2^-	1.0×10^{-2}
Hydrofluric (HF)	$\mathrm{H-F}$	F^-	6.8×10^{-4}
Nitrous (HNO_2)	$\mathrm{H-O-N=O}$	NO_2^-	4.5×10^{-4}
Benzoic (C_6H_5COOH)		$C_6H_5COO^-$	6.3×10^{-5}
Acetic (CH_3COOH)	 $\mathrm{H-O-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle H}{\vert}}{\underset{\underset{\displaystyle H}{\vert}}{C}}-H}$	CH_3COO^-	1.8×10^{-5}
Hypochlorous (HOCl)	$\mathrm{H-O-Cl}$	OCl^-	3.0×10^{-5}
Hydrocyanic (HCN)	$\mathrm{H-C\equiv N}$	CN^-	4.9×10^{-10}
Phenol (HOC_6H_5)		$C_6H_5O^-$	1.3×10^{-10}

The magnitude of K_a indicates the tendency of the acid to ionize in water:

Larger the value of K_a, stronger the acid. Chlorous acid ($HClO_2$), for example, is the strongest acid in Table 6, and phenol (HOC_6H_5) is the weakest.

Use of K_a to calculate pH of an acid

How do you calculate the pH of weak acids?

Generally, we can calculate the hydrogen-ion concentration or pH of an acid solution at equilibrium, given the initial concentration of the acid and its K_a value.

Alternatively, if we know the pH of a weak acid solution and its initial concentration, we can determine its K_a.

The following may help you to solve weak-acid dissociation problems.

- Identify the major species that can affect the pH of the solution. In most cases we can ignore the dissociation of water. Why?
- Write balanced equations for the reactions producing H_3O^+.
- List the initial concentration of the species participating in the equilibrium.
- Define the change needed to achieve equilibrium. That is, define x.
- Write the equilibrium concentration, in terms of x.
- Write the acid dissociation constant, K_a, in terms of equilibrium concentration.
- First solve for x by the approximation method. If the approximation is not valid, use the quadratic equation.
- Having solved for x, calculate the equilibrium concentrations of all species and/or the pH of the solution.

Let's calculate the pH at 25°C of a 0.30 M solution of acetic acid (CH_3COOH), the weak acid responsible for the characteristic odor and acidity of vinegar.

1. Our first step is to write the ionization equilibrium:

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

2. The second step is to write the equilibrium-constant expression and the value for the equilibrium constant. Taking $K_a = 1.8 \times 10^{-5}$ from Table 6 we write:

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = 1.8 \times 10^{-5}$$

3. Because we want to find the equilibrium value for $[H^+]$, let's call this quantity x. The concentration of acetic acid before any of it ionizes is 0.30 M. Consequently, if x moles per liter of $H^+(aq)$ form at equilibrium, x moles per liter of $CH_3COO^-(aq)$ must also form and x moles per liter of CH_3COOH must be ionized:

	$CH_3COOH(aq) \rightleftharpoons$	**$H^+(aq)$ +**	**$CH_3COO^-(aq)$**
Initial	0.30 M	0	0
Change	$-x$M	$+x$M	$+x$M
Equilibrium	$0.30 - x$M	xM	xM

4. The fourth step is to substitute the equilibrium concentrations into the equilibrium-constant expression and solve for x:

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = \frac{(x)(x)}{0.30 - x} = 1.8 \times 10^{-5}$$

This expression leads to a quadratic equation in x, which we can solve by using a quadratic equation. We can simplify the problem, however, by noting that the value of K_a is quite small. As a result, we anticipate that the equilibrium lies far to the left and that x is much smaller than the initial concentration of acetic acid. Thus, we assume that x is negligible relative to 0.30, so that is essentially equal to 0.30. We can (and should!) check the validity of this assumption when we compute the problem. By using this assumption, K_a becomes

$$K_a = \frac{x^2}{0.30} = 1.8 \times 10^{-5}$$

Solving for x, we have

$$x^2 = (0.3)\left(1.8 \times 10^{-5}\right) = 5.4 \times 10^{-6}$$

$$x = \sqrt{5.4 \times 10^{-6}} = 2.3 \times 10^{-3}$$

$$\left[H^+\right] = x = 2.3 \times 10^{-3}$$

$$pH = -\log\left(2.3 \times 10^{-3}\right) = 2.64$$

5. Now we check the validity of our simplifying assumption that $0.30 - x \simeq 0.30$. The value of x we determined is so small that, for this number of significant figures, the assumption is entirely valid. We are thus satisfied that the assumption was a reasonable one to make. Because x represents the moles per liter of acetic acid that ionize, we see that, in this particular case, less than 1% of the acetic acid molecules ionize:

$$\text{Percent ionization of } CH_3COOH = \frac{0.0023\,M}{0.30\,M} \times 100\% = 0.77\%$$

6. As a general rule, if x is more than about 5% of the initial concentration, it is better to use the quadratic formula. You should always check the validity of any simplifying assumptions after you have completed solving a problem.

3.4 PERCENT DISSOCIATION

Upon completion of this topic, learners will be able to:

- demonstrate calculations that analyze amounts of acid and base dissociated .

We have seen that the magnitude of K_a indicates the strength of an acid. Another measure of the strength of an acid is its percent ionization, which is defined as:

$$\text{Percent ionization} = \frac{\text{Ionized acid concentration at equilibrium}}{\text{Initial concentration of acid}} \times 100\%$$

The stronger the acid, the greater the percent ionization. For a monoprotic acid HA, the concentration of the acid that undergoes ionization is equal to the concentration of the H^+ ions or the concentration of the A^- ions at equilibrium. Therefore, we can write the percent ionization as:

$$\text{Percent ionization} = \frac{[H^+]}{[HA]_0} \times 100\%$$

where $[H^+]$ is the concentration at equilibrium and $[HA]_0$ is the initial concentration. For example, a 0.035 M solution of HNO_2 contains 3.7×10^{-3} M H^+ and its percent ionization is:

$$\text{Percent ionization} = \frac{[H^+]}{[HA]_0} \times 100\% = \frac{(3.7 \times 10^{-3}\,M)}{0.035\,M} \times 100\% = 11\%$$

The extent to which a weak acid ionizes depends on the initial concentration of the acid. The more dilute the solution, the greater the percentage ionization.

Exercise

1. Illustrate the dependence of percent ionization on initial concentration by using 0.50 M and 0.050 M HF?

ACTIVITY 3

Relationship between acid concentration and percent dissociation

The aim of this experiment is to determine percent dissociation of acetic acid in various concentrations and study the relationship between concentration and percent dissociation.

Procedure

Measure the pH of 5 acetic acid solutions of various concentrations, 0.10 M, 0.50 M, 1.00 M, 3.00 M, 6.00 M.

Calculations

1. Determine the % dissociation for each solution. Be sure to create initial, change and equilibrium (ICE) tables for each solution. Perform all calculations in the class and in your note book.
2. Use EXCEL to create a data table, graph (% dissociation *vs*. concentration), and one other method of illustrating your data. Print and tape into your notebook!!

Discussion Questions

1. Submit the data table and all EXCEL work
2. Submit one sample calculation
3. Write a 1 page discussion of your results

Weak bases and base ionization constants

As we did with acids, we can measure the relative strengths of bases by measuring their base-ionization constant (K_b) in aqueous solutions. In solutions of the same concentration, stronger bases ionize to a greater extent, and so yield higher hydroxide ion concentrations than do weaker bases. A stronger base has a larger ionization constant than does a weaker base.

The general reaction between a base B and water is given by:

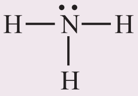
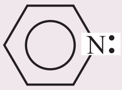
$$B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$$

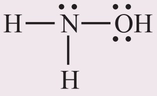
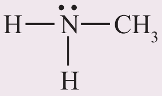
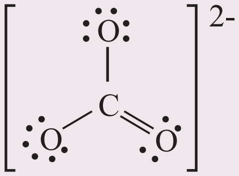
The equilibrium-constant expression for this reaction can be written as

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

Water is the acid that reacts with the base, HB^+ is the conjugate acid of the base B, and the hydroxide ion is the conjugate base of water. A weak base yields a small proportion of hydroxide ions.

Table 7 **Lewis structures, conjugate acids, and K_b values for a number of weak bases in water.**

Base	Structural Formula	Conjugate Acid	K_b
Ammonia (NH_3)	 $H-\ddot{N}-H$ with H below N	NH_4^+	1.8×10^{-5}
Pyridine (C_5H_5N)		$C_5H_5NH^+$	1.7×10^{-9}

Base	**Structural Formula**	**Conjugate Acid**	**K_b**
Hydroxylamine ($HONH_2$)	 $H-\underset{\underset{H}{\vert}}{\ddot{N}}-\ddot{\underset{\cdot\cdot}{O}}H$	$HONH_3^+$	1.1×10^{-8}
Methylamine (CH_3NH_2)	 $H-\underset{\underset{H}{\vert}}{\ddot{N}}-CH_3$	$CH_3NH_3^+$	4.4×10^{-4}
Hydrosulfide ion (HS^-)	$\left[H-\ddot{\underset{\cdot\cdot}{S}}:\right]^-$	H_2S	1.8×10^{-7}
Carbonate ion (CO_3^{2-})		HCO_3^-	1.8×10^{-4}
Hypochlorite ion (ClO^-)	$\left[:\ddot{\underset{\cdot\cdot}{Cl}}-\ddot{\underset{\cdot\cdot}{O}}:\right]^-$	$HClO^-$	3.3×10^{-7}

In solving problems involving weak bases, you should follow the same principles as you followed for weak acids. The main difference is that we calculate $[OH^-]$ first, instead of $[H^+]$.

Example

Calculate the pH of a 0.25 M solution of NH_3.

Solution

The ionization reaction and equilibrium-constant expression are:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5}$$

The equilibrium concentrations are:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Initial	0.25 M	0	0
Change	$-x$M	$+x$M	$+x$M
Equilibrium	$(0.25 - x)$M	xM	xM

Inserting these quantities into the equilibrium-constant expression gives:

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{(x)(x)}{0.25 - x} = 1.8 \times 10^{-5}$$

Because K_b is small, the amount of NH_3 that reacts with water is much smaller than the NH_3 concentration, and so we can neglect x relative to 0.25 M. Then we have:

$$\frac{x^2}{0.25 - x} = 1.8 \times 10^{-5}$$

$$x^2 = 0.25 \times 1.8 \times 10^{-5} = 4.5 \times 10^{-6}$$

$$x = [NH_4^+] = [OH^-] = \sqrt{4.5 \times 10^{-6}} = 2.1 \times 10^{-3}$$

The value obtained for x is only about 0.84% of the NH_3 concentration, 0.25 M. Therefore, neglecting x relative to 0.25 was justified.

$pOH = -\log(2.1 \times 10^{-3}) = 2.67$

$pH = 14 - pOH = 14 - 2.67 = 11.33$

Relationship between K_a and K_b

Exercise

1. Derive the relation $K_a \times K_b = K_w$ using acetic acid and its conjugate base as an example?
2. Derive the relationship, $pK_a + pK_b = pK_w = 14$ at 25°C

3.5 ACID-BASE PROPERTIES OF SALTS

Upon completion of this topic, learners will be able to:

- determine the effects of a salt on pH and pOH.
- predict whether an aqueous solution of a salt will be acidic, basic, or neutral.

A. Laboratory and industrial preparation of salts

Salts can be prepared using several methods. Any particular method chosen depends on whether the salts are soluble or not.

1. Preparation of salts by the action of an acid upon a metal

This method is used to prepare soluble salts.

$$Zn(s) + H_2SO_4(aq) \longrightarrow ZnSO_4(aq) + H_2(g)$$

The solution is filtered, leaving behind insoluble impurities, such as excess zinc and particles of carbon on the filter paper. The $ZnSO_4$ is then crystallized from the solution.

2. Preparation of salts by double decomposition

This method is used to prepare insoluble salts. It involves the reaction between two soluble compounds to produce one soluble and one insoluble products. Amongst the products, the one of importance is the insoluble salt which precipitates out of the solution.

Examples

$$Pb(NO_3)_2(aq) + Na_2SO_4(aq) \longrightarrow PbSO_4(s)\downarrow + 2NaNO_3(aq)$$
$$BaCl_2(aq) + H_2SO_4(aq) \longrightarrow BaSO_4\,(s)\downarrow + 2HCl(aq)$$
$$CaCl_2(aq) + Na_2CO_3(aq) \longrightarrow CaCO_3(s)\downarrow + 2NaCl(aq)$$

3. Preparation of salts by neutralization

Recall that neutralization is the reaction between acids and bases to form salts and water only. This method would depend on whether the base is soluble (i.e. alkali) or insoluble in water.

$$2NaOH(aq) + H_2SO_4(aq) \longrightarrow Na_2SO_4(aq) + 2H_2O(l)$$
$$2NH_3(aq) + H_2SO_4(aq) \longrightarrow (NH_4)_2SO_4(aq)$$
$$Pb(OH)_2(s) + 2HNO_3(aq) \longrightarrow Pb(NO_3)_2(aq) + 2H_2O(l)$$

B. Chemicals from sodium chloride solution

Seawater contains many salts dissolved in it. Sodium chloride is separated from these salts. Deposits of solid salt are also found in several parts of the world.

What is a rock salt? Common salt is an important raw material for various materials of daily use, such as sodium hydroxide, baking soda, washing soda, bleaching powder and many more.

The electrolysis of sodium chloride solution (brine) is an important industrial process because hydrogen, chlorine and sodium hydroxide have many uses.

When electricity is passed through an aqueous solution of sodium chloride (called brine), it decomposes to form sodium hydroxide. The process is called the chlor-alkali process.

$$2NaCl(aq) + 2H_2O(l) \longrightarrow 2NaOH(aq) + Cl_2\,(g) + H_2\,(g)$$

Chlorine gas is given off at the anode, and hydrogen gas at the cathode. Sodium hydroxide solution is formed near the cathode. Figure 5 shows the formation and different uses of these products.

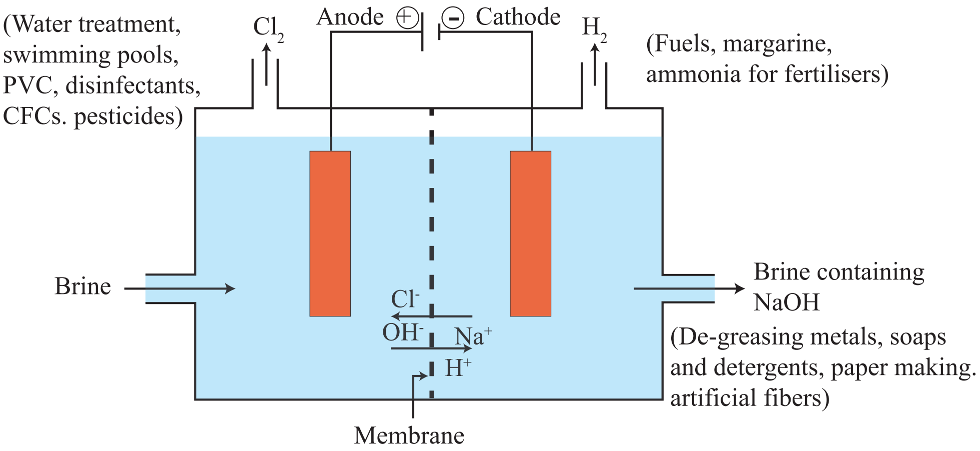


Figure 5. Electrolysis of sodium chloride solution

C. Hydrolysis of salts

What does salt hydrolysis mean?

The term salt hydrolysis describes the reaction of an anion or a cation of a salt, or both, with water. Salt hydrolysis usually affects the pH of a solution.

Hydrolysis of salts of strong acids and strong bases

Recall that the conjugate base of a strong acid has virtually no affinity for protons as compared with that of the water molecule. Thus, when anions such as Cl^- and NO_3^- are placed in water, they do not combine with H^+ and therefore have no effect on the pH. Cations such as K^+ and Na^+ from strong bases have no ability to produce H^+, so they too have no effect on the pH of an aqueous solution. Salts that consist of the cations of strong bases and the anions of strong acids have no effect on $[H^+]$ when dissolved in water. This means that aqueous solutions of salts such as KCl, NaCl, $NaNO_3$, and KNO_3 are neutral (have a pH of 7).

Hydrolysis of salts of weak acids and strong bases

The solution of a salt derived from a strong base and a weak acid is basic. For example, the dissociation of sodium acetate ($CH_3COO^-Na^+$) in water is given by:

$$CH_3COO^-Na^+(s) \xrightarrow{H_2O} Na^+(aq) + CH_3COO^-(aq)$$

The hydrated Na^+ ion has no acidic or basic properties. The acetate ion CH_3COO^-, however, is the conjugate base of the weak acid CH_3COOH and therefore has an affinity for H^+ ions. The hydrolysis reaction is given by:

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$$

Because this reaction OH^- ions are produced, the sodium acetate solution will be basic.

Hydrolysis of salts of strong acids and weak bases

When we neutralize a weak base with a strong acid, the product is a salt containing the conjugate acid of the weak base. For example, ammonium chloride, NH_4Cl, is a salt formed by the reaction of the weak base ammonia with the strong acid HCl:

$$NH_3\,(aq) + HCl(aq) \longrightarrow NH_4Cl(aq)$$

A solution of this salt contains ammonium ions and chloride ions. The chloride ion has no effect on the acidity of the solution since HCl is a strong acid. However, the ammonium ion, the conjugate acid of ammonia, reacts with water and increases the hydronium ion concentration:

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3\,(aq)$$

This dissociation produces H_3O^+ ions, the solution will be acidic.

Hydrolysis of salts of weak acids and weak bases

For salts derived from a weak acid and a weak base, both the cation and the anion hydrolyze. However, whether a solution containing such a salt is acidic, basic, or neutral depends on the relative strengths of the weak acid and the weak base.

If K_b for the anion is greater than K_a for the cation, then the solution must be basic because the anion will hydrolyze to a greater extent than the cation. Conversely, if K_b for the anion is smaller than K_a for the cation, the solution will be acidic because cation hydrolysis will be more extensive than anion hydrolysis. If K_a is approximately equal to K_b, the solution will be neutral.

Exercise

1. Calculate the pH of a 0.24 M sodium formate solution ($HCOO^-Na^+$).
2. In the following table you are given K_a and K_b values of some cations and anions, respectively.

Anion	K_b	Cation	K_a
F	1.4×10^{-11}	NH_4^+	5.6×10^{-10}

CNS^-	2.0×10^{-5}		
CH_3COO^-	5.6×10^{-10}		

Using the above table, determine whether the solutions of NH_4F, NH_4CNS and CH_3COONH_4 are acidic, basic or neutral.

3. Describe the behavior of some salts e.g. NH_4Cl, $AlCl_3$, Na_2CO_3, $CH_3COO^-Na^+$ in water?

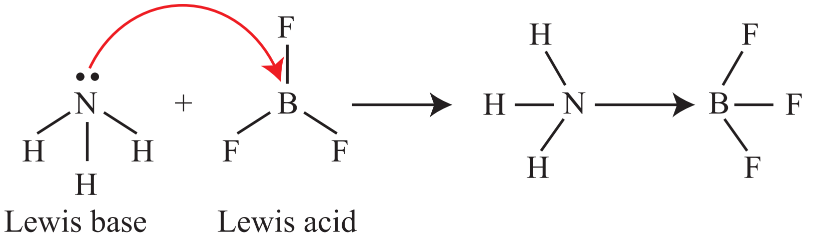
3.6 PROPERTIES OF LEWIS ACIDS AND BASES

Upon completion of this topic, learners will be able to:

- discuss the concept of Lewis acids and bases.

G. N. Lewis, who proposed the electron-pair theory of covalent bonding, realized that the concept of acids and bases could be generalized to include reactions of acidic and basic oxides and many other reactions. According to this concept, a Lewis acid is a species that can form a covalent bond by accepting an electron pair from another species; a Lewis base is a species that can form a covalent bond by donating an electron pair to another species.

The Lewis acid-base concept includes many reactions that do not involve proton-transfer reactions. For example, the reaction between NH_3 and BF_3 occurs because BF_3 has a vacant orbital in its valence shell. It therefore acts as an electron-pair acceptor (a Lewis acid) towards NH_3, which donates the electron pair:



The boron atom in boron trifluoride, BF_3, has only six electrons in its valance shell and needs two electrons to satisfy the octet rule. Consequently, BF_3 (Lewis acid) accepts a pair of electrons from NH_3 (Lewis base).

This example suggests that in a Lewis acid-base reaction, we should look for:

1. A species that has an available empty orbital to accommodate an electron pair such as the B atom in BF_3, and
2. A species that has lone-pair electrons such as NH_3.

The Lewis definition allows us to consider typical Brønsted-Lowry bases, such as OH^-, NH_3, and H_2O, as Lewis bases. They all have electron pairs available to donate for electron-deficient species.

Note that any molecule or negatively charged species having an excess of electrons can be considered as a Lewis base, and any electron-deficient molecule or positively charged species can be considered as a Lewis acid.

Exercise

1. How do Lewis acids and bases differ from Brønsted-Lowry acids and bases?
2. Are all Brønsted-Lowry acids and bases are also acids and bases according to the Lewis concept?
3. In the following reactions, identify the Lewis acid and the Lewis base.
   (a) $Al^{3+} + 6H_2O \rightleftharpoons Al(H_2O)_6^{3+}$
   (b) $H^+ + NH_3 \longrightarrow NH_4^+$

3.7 BUFFER SOLUTIONS

Upon completion of this topic, learners will be able to:

- define the common-ion effect.
- interpret the behavior of buffer solutions.
- calculate the pH of a given buffer solution.

The common ion effect

The common-ion effect is the shift in an ionic equilibrium caused by the addition of a solute that provides an ion that takes part in the equilibrium. The presence of the common ion suppresses the ionization of a weak acid or a weak base. For example, if sodium acetate and acetic acid are dissolved in the same solution, they both dissociate and ionize to produce CH_3COO^- ions.

$$CH_3COO^-Na^+(s) \longrightarrow CH_3COO^-(aq) + Na^+(aq)$$

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

Sodium acetate, $CH_3COO^-Na^+$, is a strong electrolyte, so it dissociates completely in solution, but acetic acid, CH_3COOH, is a weak acid and ionizes partially. According to Le Chatelier's principle, the addition of CH_3COO^- ions from $CH_3COO^-Na^+$ to a solution of CH_3COOH will suppress the ionization of CH_3COOH and decrease the concentration of hydrogen ions.

Therefore, a solution containing both CH_3COOH and $CH_3COO^-Na^+$ will be less acidic than a solution containing only CH_3COOH of the same concentration. The shift in equilibrium of the acetic acid ionization is caused by the acetate ions from the sodium acetate. CH_3COO^- is the common ion because it is supplied by both CH_3COOH and $CH_3COO^-Na^+$.

Exercises

1. The chemical equation for the hydrolysis of nitrous acid is:

$$HNO_2\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + NO_2^-\,(aq)$$

Which of the following, when added to a nitrous acid solution, would reduce the degree of ionization of the acid: $NaNO_3(aq)$, $KNO_2(aq)$, $HNO_3(aq)$, or $NaCl(aq)$?

2.
   (a) What would be the pH of 0.085 M HNO_2 solution if no salt were present?
   (b) Calculate the pH of solution containing 0.085 M HNO_2 and 0.10 M KNO_2.
   (c) Which solution is less acidic? Why?

Buffer Solutions

A buffer solution is a solution that resists changes in pH from the addition of a limited amount of an acid or a base.

Buffers contain either a weak acid and its conjugate base or a weak base and its conjugate acid. A buffer solution must contain a relatively large concentration of acid to react with any OH^- ions that are added to it. Similarly, it must contain a relatively large concentration of base to react with any H^+ ions.

To understand the action of buffer, consider a buffer that contains approximately equal molar amounts of a weak acid, HA, and its conjugate base, A^-. When a strong acid is added to the buffer, it supplies hydrogen ions that react with the base A^-.

$$H^+(aq) + A^-(aq) \longrightarrow HA(aq)$$

On the other hand, when a strong base is added to the buffer, it supplies hydroxide ions that react with the acid, HA.

$$OH^-(aq) + HA(aq) \longrightarrow H_2O(aq) + A^-(aq)$$

Thus, a buffer solution resists changes in pH through its ability to combine with the H^+ and OH^- ions.

Buffers are very important to chemical and biological systems.

The major buffer system used to control the pH of blood is the H_2CO_3/ HCO_3^- buffer system.

$$H_2CO_3 + H_2O \rightleftharpoons HCO_3^- + H_3O^+$$

The Henderson-Hasselbalch equation may be applied to solve buffer-system problems.

$$HA \rightleftharpoons H_3O^+ + A^-$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

From this expression

$$[H_3O^+] = K_a\frac{[HA]}{[A^-]}$$

Taking the negative logarithm of both sides of the above equation gives;

$$[H_3O^+] = K_a\frac{[HA]}{[A^-]}$$

$$-\log[H_3O^+] = -\log K_a - \log\frac{[HA]}{[A^-]}$$

$$pH = pK_a + \log\frac{[A^-]}{[HA]} \quad \text{(Henderson-Hasselbalch equation)}$$

Examples

1. Calculate the pH of a buffer system containing 1.0 M CH_3COOH and 1.0 M $CH_3COO^-Na^+$.
2. What is the pH of the buffer system in (1) after the addition of 0.10 mol of gaseous HCl to 1.0 L of the solution? Assume that the volume of the solution does not change when HCl is added.

Solution

1. In this case, you are asked to calculate the pH of the buffer system of CH_3COOH/ $CH_3COO^-Na^+$. Hence, you can apply the same method you have used to calculate a solution containing common ions:

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

Initial	1.0 M	0	1.0 M
Change	$-x$M	$+x$M	$+x$M
Equilibrium	$(1.0 - x)$M	xM	$(1.0 + x)$ M

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = 1.8 \times 10^{-5}$$

$$K_a = \frac{x(1.0 + x)}{1.0 - x} = 1.8 \times 10^{-5}$$

Assuming $1.0 + x \simeq 1.0$ and $1.0 - x \simeq 1.0$, we obtain

$$\frac{x(1.0 + x)}{1.0 - x} = \frac{x(1.0)}{1.0} = 1.8 \times 10^{-5}$$

$$x = [H^+] = 1.8 \times 10^{-5}$$

Finally, we calculate the pH from the equilibrium concentration of $[H^+]$:

$$pH = -\log\left(1.8 \times 10^{-5}\right) = 4.74$$

2. The H^+ ions provided by the strong acid, HCl, react completely with the conjugate base of the buffer, which is CH_3COO^-.

$$CH_3COO^-(aq) + H^+(aq) \longrightarrow CH_3COOH(aq)$$

The moles of H^+ ions added = 0.10 mol. The moles of acetate ions before HCl is added = 1.0 M × 1 L = 1.0 mol

0.10 mol H^+ consumes 0.10 mol CH_3COO^-. Therefore, the number of moles of CH_3COO^- that remains unreacted = 1.0 mol – 0.10 mol = 0.9 mol.

Moles of CH_3COOH formed = 0.10 mol

Total moles of CH_3COOH = 0.10 mol + 1.0 mol = 1.1 mol

$$[CH_3COO^-] = \frac{0.9\,\text{mol}}{1\,\text{L}} = 0.9\,\text{M}$$

$$[CH_3COOH] = \frac{1.1\,\text{mol}}{1\,\text{L}} = 1.1\,\text{M}$$

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

Initial	1.1 M	0	0.9 M
Change	$-x$M	$+x$M	$+x$M
Equilibrium	$(1.1 - x)$M	xM	$(0.9 + x)$ M

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = 1.8 \times 10^{-5}$$

$$K_a = \frac{x(0.9+x)}{1.1-x} = 1.8\times10^{-5}$$

Since x is very small compared to 1.1 and 0.9, $0.90 + x \approx 0.90$ and $1.1 - x \approx 1.1$, you obtain:

$$\frac{x(0.9+x)}{1.1-x} \approx \frac{x(0.9)}{1.1} = 1.8\times10^{-5}$$

$$x = \left[H^+\right] = 2.2\times10^{-5}$$

$$pH = -\log\left(2.2\times10^{-5}\right) = 4.66$$

Note that the pH of the buffer changes very little when the HCl is added.

Because CH_3COOH and CH_3COOH are a conjugate acid–base pair, we can also use the Henderson–Hasselbalch equation to solve this problem.

Exercise

1. Which of the following pairs can form a buffer system? Classify the buffers as either weak acid-salt buffer or weak base-salt buffer.
   (a) NaH_2PO_4/Na_2HPO_4
   (b) HCOOH/HCOONa
   (c) HCN/NaCN
   (d) HOCl/NaOCl
   (e) $H_2CO_3/NaHCO_3$
   (f) $CH_5NH_2/C_6H_5NH_3^+$
   (g) $H_2SO_4/NaHSO_4$
2. Calculate the pH of a buffer solution that contains 0.25 M benzoic acid ($C_6H_5CO_2H$) and 0.15 M sodium benzoate ($C_6H_5COO^-Na^+$).
3. Calculate the pH of the 0.30 M NH_3/0.36 M NH_4Cl buffer system.
   What is the pH after the addition of 20.0 mL of 0.050 M NaOH to 80.0 mL of the buffer solution?

ACTIVITY 4

The Buffer Action of Solutions

How Buffers Work

To illustrate the function of a buffer solution, consider a mixture of roughly equal amounts of acetic acid and sodium acetate. The presence of a weak conjugate acid-base pair in the solution imparts the ability to neutralize modest amounts of added strong acid or base. For example, a strong base added to this solution will neutralize hydronium ion, causing the acetic acid ionization equilibrium to shift to the right and generate additional amounts of acetate ion:

$$CH_3COOH\ (aq) + H_2O\ (l) \rightleftharpoons CH_3COO^-\ (aq) + H_3O^+\ (aq)$$

Likewise, a strong acid added to this buffer solution will shift the above ionization equilibrium to the left, which suppress dissociation of the weak acid.

Procedure:

1. Mix 5 mL of 0.10 M $CH_3COO^-Na^+$ with 5 mL of 0.10 M CH_3COOH in a 200 mL test tube. In a second test tube add 100 mL of distilled (or deionized) water. Add 5 drops of universal indicator to each sample and estimate pH.
2. Add 5 mL of 0.010 M HCl to each test tube, estimate the pH, and record each pH change. If universal indicator is not available, add 2 drops of methyl orange indicator to each and record the volume (drops) of 0.010 M HCl to reach its end-point.
3. Again prepare the solution in step 1. Test the buffering capacity of each with 5 mL of 0.010 M NaOH. If universal indicator is not available, add 2 drops of Alizarin yellow-R and record the volume (drops) of 0.010 M NaOH to reach its end-point.

Results and Discussion:

(a) What did you observe from procedure 1?

(b) What did you observe from procedure 2?

(c) Give your conclusion on each step.

Conclusion

What have you learnt? Present your findings from the experiment.

Write a laboratory report in groups and present your report to the rest of the class.

3.8 ACID-BASE TITRATIONS

Upon completion of this topic, learners will be able to:

- suggest a suitable indicator for a given acid-base titration.
- analyze the concentrations of acids and bases using titration.
- draw titration curves.

A. Acid-base indicators

Acid-base indicators are weak organic acids or weak organic bases that indicate whether a solution is acidic, basic or neutral.

Let us consider a weak organic acid that is denoted by HIn. In order to be effective indicators, HIn, and its conjugate base, In^-, must have different color. In solution, the acid ionizes as follows:

$$HIn(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + In^-(aq)$$

If the indicator is in sufficiently acidic medium, the equilibrium, according to Le Chatelier's principle, shifts to the left and the predominant color of the indicator is that of non-ionized form (HIn). On the other hand, in a basic medium, the equilibrium shifts to the right and the color of the solution will be that of the ionized form (In^-).

Since the indicator molecule is a weak acid, the ratio of HIn and In^- is governed by the $[H_3O^+]$ of the test solution.

$$HIn(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + In^-(aq)$$

$$K_{In} = \frac{[In^-][H_3O^+]}{[HIn]}$$

Rearranging this equation gives:

$$\frac{[HIn]}{[In^-]} = \frac{[H_3O^+]}{K_{In}}$$

To illustrate how an indicator works, consider an indicator that has a yellow color in acid form (HIn) and a red color in basic form (In^-). K_{In} is 1.0×10^{-6}. Thus, we have:

$$\frac{[HIn]}{[In^-]} = \frac{[H_3O^+]}{1.0 \times 10^{-6}}$$

The color we observe in a solution of this indicator depends on the ratio of [HIn] to $[In^-]$. In a solution of pH = 4.0, $[H_3O^+]$ is 1.0×10^{-4}, therefore

$$\frac{[HIn]}{[In^-]} = \frac{1.0 \times 10^{-4}}{1.0 \times 10^{-6}} = 100$$

This means that the concentration on HIn is 100 times that of In^-, and so the solution appears yellow.

At pH of 6.0, $[H_3O^+]$ is 1.0×10^{-6} equal concentrations of HIn and In^- give the solution an orange color.

At pH = 7.0, $[H_3O^+]$ is 1×10^{-7}. Here the concentration of In^- is 10 times that of HIn, and so the solution appears red.

Indicators are used in the laboratory for estimating the pH of a solution and to reveal the equivalence point of a titration. Equivalence point is the point at which stoichiometrically equivalent quantities of an acid and a base have been brought together. Some common indicators and their colors in acids and in bases are shown in Table 8.

Table 8

Indicator	Acid Color	Base Color	pH range of Color change
Methyl violet	Yellow	Violet	0.0 – 1.6
Methyl orange	Red/Pink	Yellow	3.2 – 4.4
Bromocresol green	Yellow	Blue	3.8 – 5.4
Methyl red	Red	Yellow	4.8 – 6.0
Litmus	Red	Blue	5.0 – 8.0
Bromothymol blue	Yellow	Blue	6.0 – 7.6
Thymol blue	Yellow	Blue	8.0 – 9.6
Phenolphthalein	Colorless	Pink	8.2 – 10.0
Alizarin yellow R	Yellow	Red	10.1 – 12.0

ACTIVITY 5

Preparation of an indicator from local plants and its use to test acidity and basicity

Procedure

To prepare a natural indictor:

- Select a suitable colored plant material, such as purple cabbage.

Extract the color from the plant material by either:

Boiling it in water.

Crush it with water or alcohol using a mortar and pestle.

Decant the solution from the solid.

To test a natural indicator:

Dip the ends of two strips of filter paper into the indicator and allow them to dry.

Using an eye dropper, apply a drop of strong acid to one strip and a drop of strong base to the other strip.

Record any changes in color.

Add additional drops of acid and base to the strips until no further changes in color are observed.

If an indicator is prepared from purple cabbage, the following colors should be observed:

Initial/Neutral color: **Purple**

Color when exposed to strong acid: **Pink, then Red**

Color when exposed to strong base: **Blue-Green, then Yellow**

You can prepare indicators by using other natural materials like extracts of red cabbage leaves, beetroot, and colored petals of some flowers.

B. Acid-base titration

To determine the concentration of a particular solute in a solution, chemists often carry out a titration. Titrations can be conducted using neutralization, precipitation, or oxidation-reduction reactions.

A titration is a technique in which a solution of known concentration is used to determine the concentration of an unknown solution. Typically, the titrant (the known solution) is added from a burette to a known quantity of the analyte (the unknown solution) until the neutralization reaction is complete. The point at which the acid has completely reacted with or been neutralized by the base, or vice versa, is called the equivalence point of the titration.

According to the definition of normality, the number of equivalents is the normality multiplied by the volume of solution, in litres. If we add enough acid to neutralize a given volume of base, the following equation holds:

$$N_aV_a = N_bV_b$$

Where N_a and V_a refer to the normality, and volume of the acid solution, respectively, and N_b and V_b refer to the normality and volume of the base solution, respectively.

Knowing the volume of titrant added allows the determination of the concentration of the unknown. Often, an indicator is used to signal the end of the reaction. The end point of titration is the pH at which the indicator changes color.

To perform a successful titration, we must use an indicator that changes color at the equivalence point.

ACTIVITY 6

Acid-base Titration

Objective: To use sulfuric acid to determine the concentration of a solution of sodium hydroxide.

In an acid-base titration between sodium hydroxide and hydrochloric acid,

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

the indicator should tell when the numbers of moles of NaOH and HCl are exactly equal, matching the 1:1 ratio in the equation.

For the reaction $2NaOH\ (aq) + H_2SO_4\ (aq) \longrightarrow 2H_2O\ (l) + Na_2SO_4\ (aq)$ the indicator should tell when the number of moles of NaOH is exactly twice the number of moles of H_2SO_4, this time reflecting the 2:1 molar ratio between the reactants. This point of chemical equality is called the equivalence point of the titration. Acid-base indicators show signals by changing color at or very near the equivalence point of the titration.

If the volumes of the substances involved are known, as well as the concentration of the acid, then it is possible to calculate the unknown base concentration.

Procedure

1. Put on your eye protection.
2. Fill the 25 mL pipette with sodium hydroxide. Pour this exact amount into a conical flask to which a few drops of phenolphthalein indicator have been added. Phenolphthalein is pink in alkaline conditions but colorless in acid.
3. A 0.05 mol/dm^3 solution of sulfuric acid is placed in the burette using a funnel until it is filled up exactly to the zero mark (Figure 6a).
4. The funnel is now removed.
5. The sulfuric acid is added to the aqueous sodium hydroxide in small quantities - usually no more than 0.5 mL at a time (Figure 6b). The contents of the flask must be swirled after each addition of acid.
6. The acid is added until the aqueous sodium hydroxide has been neutralised completely. This is shown by the pink color of the indicator just disappearing.
7. Take the final reading on the burette at the end-point (just as neutralisation has taken place). This value should be recorded in Table 9 as the rough value.

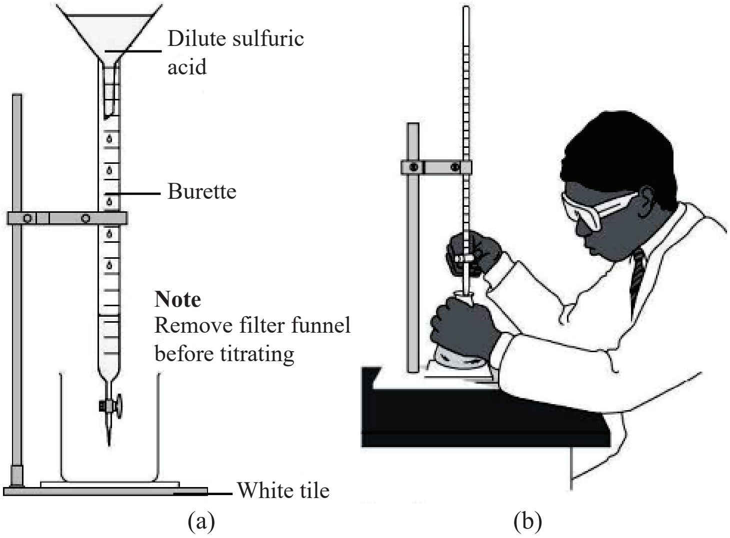


Figure 6. (a) Sulfuric acid is placed in the burette
(b) Addition of H_2SO_4 to the NaOH in small quantities

8. Further titrations need to be carried out until consistent results are obtained (within 0.1 mL of each other).

Results and calculations

Table 9 **Data Table**

	1	2	3	4
Initial burette reading (mL)				
Final burette reading (mL)				
Volume of acid used (mL)				

1. Calculating the concentration of the base:

The chemical equation is:

Sulfuric acid + Sodium hydroxide ⟶ Sodium sulfate + Water

$$H_2SO_4(aq) + 2NaOH \longrightarrow Na_2SO_4(aq) + H_2O(l)$$

From this balanced equation it can be seen that:

The number of moles of sulfuric acid in 2 mL

$$\frac{\text{Average titration volume} \times \text{Molarity}}{1000} = \underline{\hspace{6cm}} \text{ moles}$$

Since 1 mole of sulfuric acid reacts with 2 moles of sodium hydroxide, the number of moles of sodium hydroxide which will react with 2 × ____________ moles of sulfuric acid = ____________________ moles which is found in 25 mL of solution.

The concentration of the base is:

$$\text{moles of base in 25 ML} \times \frac{1000}{25} = \underline{\hspace{6cm}} \text{ mol/L}$$

2. Read about a titration curve and plot a curve using your recorded data?

Conclusion

The concentration of the base sodium hydroxide as a

Molarity = ______________________ M

What have you learnt? Present your findings from the experiment.

Acid-base titration curves

An acid-base titration curve is a plot of the pH of a solution of acid (or base) against the volume of added base (or acid). Such curves are used to gain insight into the titration process. You can use the titration curve to choose an indicator that will show when the titration is complete.

Exercises

A 20.0 mL solution of 0.50 M HCl is titrated with a 0.50 M NaOH solution.

(i) Calculate the pH after the following additions of the NaOH solution:

(a) 0.0 mL
(b) 5.0 mL
(c) 10.0 mL
(d) 20.0 mL
(e) 30.0 mL

(ii) Plot these pH values versus the volume of NaOH(aq) added.

(iii) What is the pH of a solution of strong acid-strong base titration at the equivalence point?

(iv) From the titration curve, show the pH at the equivalence point and identify appropriate indicators for the titration?

Titration of a strong acid and a strong base

Features of the titration curve for the titration of a strong acid with a strong base.

- The pH is low at the beginning of the titration.
- The pH changes slowly until just before the equivalence point.
- Just before the equivalence point, the pH rises sharply.
- At the equivalence point, the pH is 7.0.
- Just past the equivalence point, the pH continues to rise sharply.
- Further beyond the equivalence point, the pH continues to increase, but much less slowly.
- Any indicator whose color changes in the pH range from about 4 to 10 can be used in the titration of a strong acid with a strong base. Methyl violet changes color too soon, and alizarin yellow R too late. So, bromothymol blue and phenolphthalein are preferred for this titration.

Titration of a weak acid and a strong base

Can you predict the pH range at the equivalence point?

In contrast to the titration of a strong acid with a strong base, the titration of a weak acid with a strong base, has these features:

- The initial pH is higher because the weak acid is only partially ionized.
- At the half-neutralization, pH = pK_a. The solution at this point is a buffer solution in which the concentration of the weak acid and its conjugate base are equal.
- The pH is greater than 7 at the equivalence point because the anion of the weak acid hydrolyzes.
- The steep portions of the titration curve just prior to and just beyond the equivalence point is confined to a smaller pH range.

- The choice of indicator for the titration is more limited. The color change must occur in a basic solution. Generally, the midpoint of the pH range in which the indicator changes color must be well above pH 7.

Exercise

A 20.0 mL solution of 0.50 M CH_3COOH is titrated with a 0.50 M NaOH solution.

(i) Calculate the pH after the following additions of the NaOH solution:

(a) 0 mL	(c) 10.0 mL	(e) 25.0 mL
(b) 5.0 mL	(d) 20.0 mL	(f) 30.0 mL

(ii) Identify the solution that corresponds to:
  (a) The inital stage before the addition of NaOH
  (b) Half-way to the equivalence point
  (c) The equivalence point
  (d) Beyond the equivalence point. Is the pH greater than, less than, or equal to 7 at the equivalence point?

(iii) Plot the pH values versus the volume of NaOH added.

ACTIVITY 7

Weak acid-strong base titration

Objective: To study the characteristic features of weak acid-strong base titration.

Theory

In this experiment, we will be looking at how acids and bases react. Specifically, we will be titrating a weak acid with a strong base and observing changes in pH using a pH indicator to find the initial concentration of the acid.

Procedure

1. First, set up your titration apparatus. Use the clamp to attach the burette to the stand. Place one beaker underneath the burette.

   Safety Tip! *Put on your gloves, apron and safety goggles before handling the base.*
2. Now, measure 5 mL of base and pour it into the burette using a funnel to rinse the burette. Make sure the base coats all the sides.
3. Repeat step 2.
4. Fill the burette with 50 mL of base, and let two drops flow through into the beaker to remove any air bubbles.
5. Pour 25 mL of acid into the flask.
6. Add 2-3 drops of phenolphthalein into the acid, and swirl it around. The acid should be clear.
7. Remove the flask from under the burette, and replace it with the flask of acid.
8. Slowly add one drop of base at a time to the acid. Swirl the flask gently with each drop added. When the solution turns pink and keeps that color after swirling, the solution has reached its equivalence point.

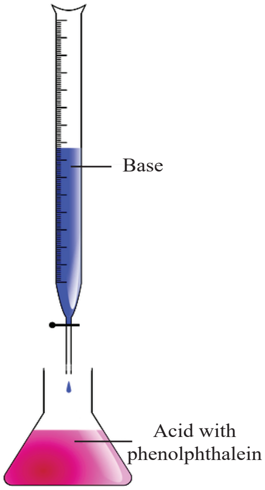


Figure 7. Titration apparatus setup

Results and discussion:

1. Now it's time for the calculations. First, note how much base is left in the burette. Subtract this from the initial amount (50 mL). Convert mL to liters by dividing by 1000. Record this in your notebook.
2. To find the moles of base used, multiply the volume of based used in liters by the molarity of the base. Record this number in your notebook.
3. In this experiment, the ratio of acid to base in the chemical reaction is 1:1, so at the equivalence point, the moles of acid is equal to the moles of base.
4. Convert the initial volume of acid to liters by dividing 25 mL by 1000.
5. Now, divide the moles of acid calculated in step 2 by the volume calculated in step 1 to get the concentration of the acid. Record this in your notebook.
6. Thoroughly wash all your equipment and repeat step 2-3 times. Average the concentration of acid for each trial to get the actual concentration of your acid.

Conclusion

What have you learnt? Present your findings from the experiment.

Evaluate the outcome objectively, taking a candid and unbiased point of view.

Titrations of a weak base and a strong acid

How does the titration curve of a weak base with a strong acid differ from the titration curves you have seen so far? What is the pH at equivalence point?

Consider the titration of ammonia, NH_3, with a strong acid, HCl.

$$HCl\,(aq) + NH_3\,(aq) \longrightarrow NH_4Cl\,(aq)$$

or simply

$$H^+ (aq) + NH_3 (aq) \longrightarrow NH_4^+ (aq)$$

The pH at the equivalence point is less than 7. Why?

Exercises

1. A 25.0 mL sample of 0.1 M NH_3 is titrated with 0.1 M HCl.
    (a) Calculate the pH values of the solution after the following volumes of 0.1 M HCl are added: 0.00 mL, 5.00 mL, 10.00 mL, 15.00 mL, 20.00 mL, 22.00 mL, 24.00 mL, 25.00 mL and 26.00 mL.
    (b) Construct a table and put the pH values corresponding to each volume in the table.
    (c) Draw the titration curve.
    (d) Name the appropriate indicator for this titration.

KEY TERMS

- Strong electrolytes
- Weak electrolytes
- Non-electrolytes
- Arrhenius concept of acids bases
- Brønsted–Lowry Concept of Acids and Bases
- Conjugate Acid–Base Pairs
- Auto-ionisation
- Amphiprotic species
- pH and pOH
- Acid dissociation constant
- Base dissociation constant
- Percent ionization
- Salt hydrolysis
- Lewis Acids and Bases
- Common ion effect
- Buffer Solutions
- Acid-base indicators
- Acid-base titration
- Equivalence point
- Titration Curves
- End point

SUMMARY

Any substance whose aqueous solution contains ions is called an electrolyte. Any substance that forms a solution containing no ions is a non-electrolyte. Electrolytes that are present in solution entirely as ions are strong electrolytes, whereas those that are present partly as ions and partly as molecules are weak electrolytes.

Arrhenius recognized that the properties of acidic solutions are due to H^+ ions and those of basic solutions are due to OH^- ions. The Brønsted-Lowry concept of acids and bases is more general than the Arrhenius concept and emphasizes the transfer of a proton from an acid to a base.

A Brønsted-Lowry acid is a substance that donates a proton to another substance; a Brønsted-Lowry base is a substance that accepts a proton from another substance. Water is an amphiprotic substance, one that can function as either a Brønsted-Lowry acid or base, depending on the substance with which it reacts. The conjugate base of a Brønsted-Lowry acid is the species that remains when a proton is removed from the acid. The conjugate acid of a Brønsted-Lowry base is the species formed by adding a proton to the base. An acid and its conjugate base (or a base and its conjugate acid) are called a conjugate acid-base pair. The acid-base strengths of conjugate acid-base pairs are related: The stronger an acid, the weaker is its conjugate base; the weaker an acid, the stronger is its conjugate base.

Water ionizes to a slight degree, forming $[H^+]$ and $[OH^-]$. The extent of this auto ionization is expressed by the ion product constant for water: $K_w = [H^+][OH^-]$. The K_w expression indicates that the product of $[H^+]$ and $[OH^-]$ is a constant. Thus, as $[H^+]$ increases, $[OH^-]$ decreases. Acidic solutions are those that contain more $[H^+]$ than $[OH^-]$, whereas basic solutions contain more $[OH^-]$ than $[H^+]$.

The concentration of an acid can be expressed in terms of pH: $pH = -\log[H^+]$. The pX notation is also used to represent the negative logarithm of other small quantities, as in pOH and pK_w. The pH of a solution can be measured using a pH meter, or it can be estimated using acid–base indicators.

Weak acids are weak electrolytes; only some of the molecules exist in solution in ionized form. The extent of ionization is expressed by the acid-dissociation constant, K_a. The larger the value of K_a, the stronger is the acid. For solutions of the same concentration, a stronger acid also has a larger percent ionization. The concentration of a weak acid and its K_a value can be used to calculate the pH of a solution.

Weak bases include NH_3, amines, and the anions of weak acids. The extent to which a weak base reacts with water to generate the corresponding conjugate acid and $[OH^-]$ is measured by the base-dissociation constant, K_b.

The acid-base properties of salts can be ascribed to the behavior of their respective cations and anions. The reaction of ions with water, with a reacting change in pH, is called hydrolysis.

The Lewis concept of acids and bases emphasizes the shared electron pair rather than the proton. A Lewis acid is an electron-pair acceptor, and a Lewis base is an electron-pair donor. The Lewis concept is more general than the Brønsted-Lowry concept because it can apply to cases in which the acid is some substance other than H^+.

The common-ion effect tends to suppress the ionization of a weak acid or a weak base. This action can be explained by Le Chatelier's principle. A buffer solution is a combination of either a weak acid and its conjugate base or a weak base and its conjugate acid. The solution reacts in such a way that the pH of the solution remains nearly constant. Buffer systems play a vital role in maintaining the pH of body fluids.

Acid-base indicators are weak organic acids or bases. They change color near the equivalence point in an acid-base neutralization reaction. Titration is a process in which a solution of known concentration is used to determine the concentration of an unknown solution. The pH at the equivalence point of an acid-base titration depends on the extent of hydrolysis of the salt formed in the neutralization reaction. For strong acid strong base titrations, the pH at the equivalence point is 7. For weak acid strong base titrations, the pH at equivalence point is greater than 7. For weak base–strong acid titrations, the pH at the equivalence point is less than 7.

Exercises

1. List what ions you expect to find for each of the following electrolytes. Include the correct charges and the correct number of each ion.
   (a) CaF_2 (b) NH_4Cl (c) Na_3PO_4
2. Calculate the [H^+], pH, [OH^-], and pOH of
   (a) 0.035 M HCl (b) 0.01 M $Sr(OH)_2$
3. The ionization constant for water, K_w is 9.614×10^{-14} at 60˚C. Calculate the [H^+], pH, [OH^-] , and pOH for pure water at 60˚C.
4. Calculate the [H_3O^+], [OH^-] and pOH of human gastric fluid at pH = 3.
5. 0.10 M solutions of acetic acid, chlorus acid, hydrochloric acid and nitrous acid contain the following equilibrium concentrations.

Acid	[Acid]	[Conjugate base]	[H_3O^+]
CH_3COOH	0.099 M	0.0013 M	0.0013 M
Chlorus acid	0.072 M	0.028 M	0.028 M
HF	0.092 M	0.0081 M	0.0081 M
HNO_2	0.093 M	0.0069 M	0.0069 M

   (a) Arrange the solutions of these acids in order of increasing acid strength.
   (b) Which of these acids have the strongest conjugate base?
   (c) Which acid solution has the smallest pH value?
6. A 0.1 M solution of HNO_2 is 7.1% ionized at equilibrium. What is the
   (a) [H^+] and pH, [OH^-] and pOH
   (b) K_a value of HNO_2
7. The pH of a 0.012M solution of a weak base, BOH, was determined to be 11.40. What is the K_b value of the base?

8. Vitamin C (ascorbic acid, $HC_6H_7O_6$) has a K_a of 8.0×10^{-5}. Calculate the pH of a solution made by dissolving 500 mg in 100. mL of water.
9. Calculate the concentration of all species at equilibrium and pH of a solution containing 0.1 mol CH_3COOH in 500 mL of solution?
10. Calculate the pH of a 0.0035 M solution of methylamine.

$$CH_3NH_2(aq) + H_2O\ (aq) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq) \quad K_b = 4.4 \times 10^{-4}$$

11. Why will the solution containing both CH_3COOH and $CH_3COO^-Na^+$ will be less acidic than a solution containing only CH_3COOH in the same concentration?
12. Which one is the most acidic solution 0.10 M HNO_2 or a solution of 0.10 M HNO_2 and 0.10 M $NaNO_2$?
13.
    (i) What is brine solution?
    (ii) What are the three major products of the electrolysis of brine?
    (iii) The two gases producessd in the electrolysis of brine can react to form hydrogen chloride. Write the balanced equation for this?
14. Tell whether 0.1 M solutions of the following salts would be acidic, neutral, or or basic: $BaCl_2$, $CuSO_4$. $(NH_4)_2SO_4$. $ZnCl_2$, and NaCN.
15. What is the effect of adding potassium formate, $HCOO^-K^+$, to a 0.1M solution of formic acid, HCOOH? Explain the effect on
    (a) The dissociation of HCOOH
    (b) The $[H^+]$
    (c) The pH value of the solution
16. The pH of a sodium acetate/acetic acid buffer is 4.5. Calculate the ratio of $[CH_3COOH]/[CH_3COO^-]$.
17. Calculate the pH:
    (a) of a buffer solution containing 0.1 M acetic acid and a 0.1 M solution of sodium acetate.
    (b) when 1.0 mL of 0.10 M HCl is added to 100 mL of the buffer in (a);
    (c) when 1.0 mL of 0.10 M NaOH is added to 100 mL of the buffer in (a);
    (d) of an unbuffered solution containing 1.8×10^{-5} M HCl;
    (e) change of the an unbuffered solution in (d) after adding
        (i) 1.0 mL of 0.1 M NaOH to 100 mL of the solution,
        (ii) 1.0 mL of 0.10 M HCl to 100 mL of the solution.

18. A buffer solution consists of 0.5 M CH_3COOH and 0.5 M $CH_3COO^-Na^+$. Using a chemical equation, show how this buffer resists the change in pH upon addition of little amount of
    (a) NaOH to the buffer
    (b) HCl to the buffer
19. How does the titration of a strong acid with a strong base differ from the titration of a weak acid with a strong base, with respect to the following points?
    (a) Quantity of base required to reach the equivalence point.
    (b) pH at the beginning of the titration.
    (c) pH at the equivalence point.
    (d) pH after addition of a slight excess of base.
    (e) Choice of indicator for determining the equivalence point
20. A 20.0 mL sample of 0.2 M HBr solution is titrated with 0.2 M NaOH solution. Calculate the pH of the solution after the following volumes of the base have been added;
    (a) 15.0 mL
    (b) 19.9 mL
    (c) 20.0 mL
    (d) 35.0 mL
    (e) 20.1 mL

    Draw the titration curve.

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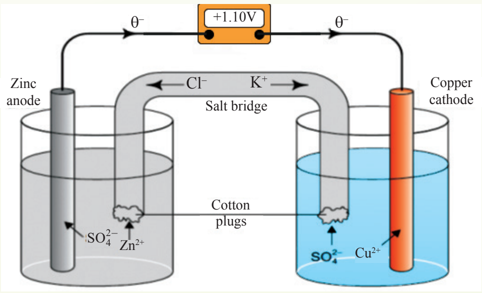
CHAPTER 4

ELECTROCHEMISTRY

Chapter Contents



Chapter Outcomes

By the end of this chapter, you will be able to:

- understand the fundamental concepts related to oxidation-reduction reactions;
- know the application of redox reactions in the production of new substances and electrical energy;
- demonstrate an understanding of fundamental concepts related to the interconversion of chemical and electrical energy;
- identify and describe function of the components of electrolytic and Galvanic cells;
- understand the difference between electrolytic and Galvanic cells;
- know how to solve problems based on Faraday's first and second laws;
- measure, through experiments, the mass of metal deposited by electroplating, and apply Faraday's Law to relate the mass of the metal deposited to the amount of charge passed;
- predict spontaneity of redox reactions and overall cell potentials by studying half-cell reduction potentials;
- determine the emf of an electrochemical cell, experimentally or from given data;
- explain the application of electrochemistry in our daily lives and in industry;
- explain corrosion as an electrochemical process, and describe corrosion-inhibiting techniques
- describe examples of common Galvanic cells and evaluate their environmental and social impact; and
- describe scientific enquiry skills: observing, classifying, comparing and contrasting, communicating, asking questions, measuring, relating cause and effect and problem solving.

4.1 REVIEW OF REDOX REACTIONS/BALANCING OF REDOX EQUATIONS

Upon completion of this topic, learners will be able to:

- define a redox reaction;
- define oxidation and reduction in terms of electron transfer and change in oxidation number;
- describe the oxidizing and reducing agents;
- identify the species that are oxidized and reduced in a given redox reaction and determine the oxidizing and reducing agents;
- balance a given redox reaction, using the change in oxidation-number method; and
- balance a given redox reaction, using the ion-electron method.

In Grade 10, you learned about oxidation, reduction and balancing redox equations in acidic and basic solutions. Review what you have learned by working on the following exercise.

Electrochemistry is best defined as the study of the interchange of chemical and electrical energy. It is primarily concerned with two processes that involve oxidation–reduction reactions: the generation of an electric current from a spontaneous chemical reaction and the opposite process, the use of a current to produce chemical change. The reactions involve electron transfer, and so they are oxidation-reduction (or redox) reactions. Many metals can be purified or electroplated using electrochemical methods. Devices such as automobiles, smartphones, electronic tablets, watches, pacemakers, and many others use batteries for power.

Many important chemical reactions involve oxidation and reduction. In fact, most reactions used for energy production are oxidation-reduction or redox reactions. In humans the oxidation of sugars, fats, and proteins provides the energy necessary for life. Combustion reactions, which provide most of the energy to power our civilization, also involve oxidation and reduction.

Exercises

Discuss the following questions and present your answers to the class.

1. State weather the change represents oxidation, reduction or neither?

(a) $MnO_2 \longrightarrow Mn_2O_3$

(b) $SO_4^{2-} \longrightarrow S^{-2}$

(c) $IO_3^- \longrightarrow I_2$

(d) $CrO_4^{-2} \longrightarrow Cr^{3+}$

(e) $Cr_2O_7^{-2} \longrightarrow CrO_4^{2-}$

2. Which of the following reactions are redox reactions? Explain your answer for each case.
   (a) $Ca(s) + 2H_2O\ (l) \longrightarrow Ca(OH)_2\ (aq) + H_2\ (g)$
   (b) $H_2SO_4\ (aq) + 2NaOH\ (aq) \longrightarrow Na_2SO_4\ (aq) + 2H_2O\ (l)$
   (c) $Si\ (s) + 2Cl_2\ (g) \longrightarrow SiCl_4\ (l)$
3. Identify the species that undergoes oxidation, the species that undergoes reduction, the oxidizing agent, and the reducing agent in each of the reactions given below
   (a) $4HCl + MnO_2 \longrightarrow MnCl_2 + Cl_2 + 2H_2O$
   (b) $3OCl^- \longrightarrow ClO_3{}^- + 2Cl^-$
   (c) $SO_4^{2-} + Br_2 \longrightarrow S_2O_3^{2-} + BrO_3^-$
4. Calculate the oxidation number of Fe in $K_4[Fe(CN)_6]$

Balancing oxidation-reduction (redox) reactions

When we balance a chemical equation, the primary concern is to stick to the principle of

- Conservation of mass and
- Conservation of charge (the total number of e^-s lost must equal the total number of e^-s gained.)

There are two very important methods for balancing redox reactions. They are

1. Oxidation number method and
2. Ion-Electron method

Exercises

1. Balance each of the following chemical equations, using the change in oxidation number method.
   (a) $HNO_3 + H_3AsO_3 \longrightarrow NO + H_3AsO_4 + H_2O$
   (b) $KMnO_4 + H_2SO_4 + H_2O_2 \longrightarrow MnSO_4 + K_2SO_4 + O_2 + H_2O$
   (c) $P_4 + H_2SO_4 \longrightarrow H_3PO_4 + H_2O + SO_2$
2. Balance the following reaction equation in acidic solution:
   (a) $Cu + HNO_3 \longrightarrow Cu^{2+} + NO$
   (b) $Cr_2O_7^{2-} + H_2C_2O_4 \longrightarrow Cr^{3+} + CO_2$
3. Balance the following reaction equation in basic solution:
   (a) $H_2O_2 + Sn^{2+} \longrightarrow H_2O + Sn^{4+}$
   (b) $Al + Cr_2O_7^{2-} \longrightarrow Al^{3+} + Cr^{3+}$

4.2 ELECTROCHEMICAL CELLS

Upon completion of this topic, learners will be able to:

- define Voltaic cell and salt bridge;
- define electrode potential and cell potential;
- construct Zn-Cu Voltaic cell;
- measure the cell potential of Zn-Cu cell using a voltmeter;
- explain how standard electrode potential is measured;
- describe the reactivity of a metal from its position in the activity series;
- calculate cell potential;
- decide whether a given redox reaction is spontaneous or not;
- explain the effect of concentration on cell potential;

The next sections describe battery cells, or voltaic cells (also called galvanic cells). These are kinds of electrochemical cell. An electrochemical cell is a system consisting of electrodes that are dipped into an electrolyte and in which a chemical reaction either uses or generates an electric current. A voltaic, or galvanic, cell is an electrochemical cell in which a spontaneous reaction generates an electric current. In the next sections, we will discuss the basic principles behind voltaic cells and then explore some of their commercial uses.

Construction of Zn-Cu galvanic cell

A voltaic cell consists of two half-cells that are electrically connected. Each half-cell is the portion of an electrochemical cell in which a half-reaction takes place. A simple half-cell can be made from a metal strip that is dipped into a solution of its metal ion.

The Galvanic cell was invented by the British Chemist John Daniell in 1836. It is called the Daniell cell. A diagram of this cell is as shown in Figure 1.

One compartment of the Daniell cell contains a zinc electrode immersed in a solution of zinc sulphate ($ZnSO_4$). The other compartment contains a copper electrode in a solution of copper sulphate ($CuSO_4$). When the two electrodes are connected by a wire, the zinc atoms give up electrons, forming positive ions:

$$Zn\,(s) \longrightarrow Zn^{2+}\,(aq) + 2e^-$$

The zinc ions repel each other and enter the solution. The negative electrons also repel each other and travel through the external wire to the copper electrode, where they are accepted by copper ions from the surrounding solution:

$$Cu^{2+}\,(aq) + 2e^- \longrightarrow Cu\,(s)$$

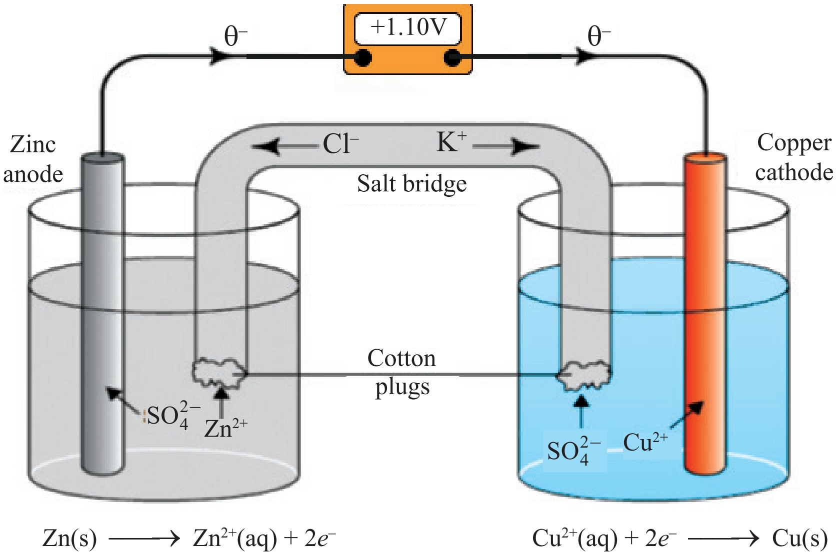


Figure 1. Daniell cell

The resulting copper atoms are deposited as copper metal on the surface of the copper electrode.

Note that the sum of the two half-reactions $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$ is the net reaction that occurs in the voltaic cell; it is called the cell reaction.

The solutions in the two halves of a Galvanic cell must be connected in order to complete the circuit, but they must not mix. The connection can be made through a salt bridge (see Figure 1).

A salt bridge is an inverted U-tube filled with an electrolyte, such as NH_4NO_3 or KCl, chosen so that it does not interfere with the operation of the cell. Regardless of how the cell is constructed, the solutions in each compartment remain more or less separated.

Furthermore, because ions can move into and out of the salt bridge, the solutions remain electrically neutral.

How does the salt bridge maintain the electroneutrality of a solution?

Explain the uses of a salt bridge?

Every Galvanic cell has an oxidation half-reaction and a reduction half-reaction. The compartments in which these reactions occur are referred to as half-cells.

What are the anode and the cathode in a Galvanic cell?

The electrode where oxidation takes place is called the anode, and the electrode where reduction takes place is the cathode. In the Daniell cell, the zinc electrode is the anode and the copper electrode is the cathode.

Once you know which electrode is the anode and which is the cathode, you can determine the direction of electron flow in the external portion of the circuit. Electrons are given up by the anode (from the oxidation half-reaction) and thus flow from it, whereas electrons are used up by the cathode (by the reduction half-reaction) and so flow into this electrode. The anode in a voltaic cell has a negative sign, because electrons flow from it. The cathode in a voltaic cell has a positive sign.

4.3 CELL DIAGRAM

Upon completion of this topic, learners will be able to:

- write the cell reaction from the cell notation.
- define cell potential.
- calculate the quantity of work from a given amount of cell reactant.
- define standard cell potential and standard electrode potential.
- interpret the table of standard reduction potentials.
- determine the relative strengths of oxidizing and reducing agents.
- determine the direction of spontaneity from electrode potentials.
- calculate cell potential from standard potentials.

Cell notation

How do you represent galvanic cells without drawing a diagram?

A cell notation allows us to describe a Galvanic cell without drawing a diagram. It is a shorthand representation of a Galvanic cell. For example, a Daniell cell in which the electrolyte concentrations are each 1 molar is represented as

$$Zn(s)\ |\ Zn^{2+}(1M)\ ||\ Cu^{2+}(1M)\ |\ Cu(s)$$

The anode is written on the left. The cathode on the right and concentrations and other data are given in parentheses. The vertical line (|) indicates phase boundaries, and the double vertical line (||) indicates a salt bridge or a porous partition.

The notation for any Galvanic cell has the following form:

Anode | Anode electrolyte (M) || Cathode electrolyte (M) | Cathode

Exercises

1. Give the overall cell reaction for the voltaic cell:
   $Cr|Cr^{3+}(aq,1\ M)||Ag^{+}(aq,1\ M)|Ag$

Standard reduction potentials

What is the difference between standard reduction potential and cell potential?

The cell potential is the difference between two electrode potentials, one associated with the cathode and the other associated with the anode.

By convention, the potential associated with each electrode is chosen to be the potential for reduction to occur at the electrode. Thus, standard electrode potentials (electrode potentials at a concentration of 1 M) are tabulated for reduction reactions and are denoted as E^o_{red}. The cell potential (E^o_{cell}) is E^o_{red} (cathode) minus the standard reduction potential of the anode reaction, E^o_{red} (anode):

$$E^o_{cell} = E^o_{red}\ (\text{cathode}) - E^o_{red}\ (\text{anode})$$

Because every Galvanic cell involves two half-cells, it is not possible to directly measure the standard reduction potential of a half-reaction. However, if we assign a standard reduction potential to a certain reference half-reaction, we can then determine the standard reduction potentials of the other half-reactions, relative to that reference. The reference half-reaction is the reduction of H^+ (aq) to H_2 (g) under standard conditions, which is given a standard reduction potential of exactly 0.0 V.

$$2H^+(aq,\ 1M) + 2e^- \longrightarrow H_2(g,\ 1\ atm);\ E^o_{red} = 0.0\ V$$

An electrode designed to produce this half-reaction is called a standard hydrogen electrode (SHE). As shown in Figure 2, The SHE consists of platinum wire connected to a piece of platinum foil covered with finely-divided platinum that serves as an inert surface for the reaction. The electrode is encased in a glass tube, so that hydrogen gas can bubble over the platinum, and the solution contains $H^+(aq)$ under standard (1 M) conditions.

The spontaneous reaction in Figure 2, is the oxidation of zinc and the reduction of H^+ :

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

In the Figure 2:

(i) The $Zn^{2+}|Zn$ electrode is the anode, and the SHE is the cathode.
(ii) The cell voltage is 0.76 V.

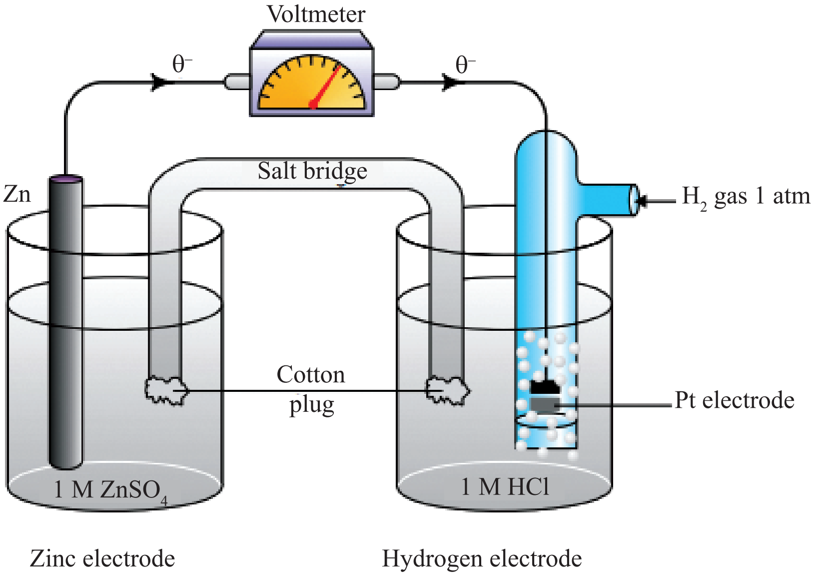


Figure 2. Standard Hydrogen Electrode

By using the defined standard reduction potential of H^+, we can determine the standard reduction potential for Zn^{2+} | Zn half-reaction:

$$E^o_{cell} = E^o_{red}\text{ (cathode)} - E^o_{red}\text{ (anode)}$$

$$0.76\text{ V} = 0.0\text{ V} - E^o_{red}\text{ (anode)}$$

$$E^o_{red}\text{ (anode)} = -0.76\text{ V}$$

Therefore, a standard reduction potential of –0.76 V can be assigned to the reduction of Zn^{2+} to Zn:

$$Zn^{2+}(aq, 1M) + 2e^- \longrightarrow Zn(s);\ E^o_{red} = -0.76\text{ V}$$

Note that we write the reaction as a reduction, even though it occurs in reverse as oxidation.

Whenever we assign a potential to a half-reaction, we write the reaction as a reduction.

The standard reduction potentials for other half-reactions are established in the way that we did for the Zn^{2+}|Zn half-reaction.

In Table 1, the standard reduction potentials of some of the half-reactions are given.

Table 1 **Standard Reduction Potential in Aqueous Solution at 25°C**

Half - Reaction	E°(V)
$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$	+ 2.87
$O_3(g) + 2H^+(aq) + 2e^- \longrightarrow O_2(g) + H_2O$	+ 2.07
$Co^{3+}(aq) + e^- \longrightarrow Co^{2+}(aq)$	+ 1.82
$H_2O_2(aq) + 2H^+(aq) + 2e^- \longrightarrow 2H_2O$	+ 1.77
$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O$	+ 1.70
$Ce^{4+}(aq) + e^- \longrightarrow Ce^{3+}(aq)$	+ 1.61
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O$	+ 1.51
$Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$	+ 1.50
$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$	+ 1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O$	+ 1.33
$MnO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Mn^{2+}(aq) + 2H_2O$	+ 1.23
$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O$	+ 1.23
$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$	+ 1.07
$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O$	+ 0.96
$2Hg^{2+}(aq) + 2e^- \longrightarrow Hg_2^{2+}(aq)$	+ 0.92
$Hg_2^{2+}(aq) + 2e^- \longrightarrow 2Hg(l)$	+ 0.85
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+ 0.80
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+ 0.77
$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)$	+ 0.68

↑ Increasing strength of oxidizing agent

↓ Increasing strength of reducing agent

Increasing strength of oxidizing agent

$MnO_4^-(aq) + 2H_2O + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$	+ 0.59
$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	+ 0.53
$O_2(g) + 2H_2O + 4e^- \longrightarrow 4OH^-(aq)$	+ 0.40
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	+ 0.34
$AgCl(s) + e^- \longrightarrow Ag^+(s) + Cl^-(aq)$	+ 0.22
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow SO_2(g) + 2H_2O$	+ 0.20
$Cu^{2+}(aq) + e^- \longrightarrow Cu^+(aq)$	+ 0.15
$Sn^{4+}(aq) + 2e^- \longrightarrow Sn^{2+}(aq)$	+ 0.13
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	- 0.13
$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$	- 0.14
$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$	- 0.25
$Co^{2+}(aq) + 2e^- \longrightarrow Co(s)$	- 0.28
$PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$	- 0.31
$Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s)$	- 0.40
$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	- 0.44
$Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s)$	- 0.74
$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	- 0.76
$2H_2O + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$	- 0.83
$Mn^{2+}(aq) + 2e^- \longrightarrow Mn(s)$	- 1.18
$Al^{3+}(aq) + 2e^- \longrightarrow Al(s)$	- 1.66
$Be^{2+}(aq) + 2e^- \longrightarrow Be(s)$	- 1.85
$Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s)$	- 2.37
$Na^+(aq) + e^- \longrightarrow Na(s)$	- 2.71
$Ca^{2+}(aq) + 2e^- \longrightarrow Ca(s)$	- 2.87
$Sr^{2+}(aq) + 2e^- \longrightarrow Sr(s)$	- 2.89
$Ba^{2+}(aq) + 2e^- \longrightarrow Ba(s)$	- 2.90
$K^+(aq) + e^- \longrightarrow K(s)$	- 2.93
$Li^+(aq) + e^- \longrightarrow Li(s)$	- 3.05

Increasing strength of reducing agent

In your calculations, be sure to understand these points about the information in Table 1:

1. The E^o_{red} values apply to the half-cell reactions as read in the forward (*left to right*) direction.
2. The more positive E^o_{red}, is the greater is the tendency for the substance to be reduced. For example, the reaction,
   $F_2(g, 1\text{ atm}) + 2e^- \longrightarrow 2F^-(1M)$, $E^0_{red} = +2.87$ V
   has the highest E^o value for all of the half-cell reactions. Thus, F_2 is the strongest oxidizing agent because it has the greatest tendency to be reduced. At the other extreme is the reaction,
   $Li^+(1M) + e^- \longrightarrow Li(s)$, $E^o_{red} = -3.05$ V
   which has the most negative E^o_{red} value. Thus, Li^+ is the weakest oxidizing agent, because it is the most difficult species to be reduced. Alternatively, Li metal is the strongest reducing agent since it gets oxidized most readily.
3. Changing the stoichometric coefficients of a half-cell reaction does not affect the value of E^o_{red}, because electrode potentials are intensive properties. This means that the value of E^o_{red} is unaffected by the size of the electrodes or the amount of solutions present but is dependent on the concentration of the solutions and the pressure of a gas (if any).
   For example,
   $I_2(s) + 2e^- \longrightarrow 2I^-(1M)$; $E^o_{red} = +0.53$ V
   but E^o does not change if we multiply the half-reaction by 2:
   $2I_2(s) + 4e^- \longrightarrow 4I^-(1M)$; $E^o_{red} = +0.53$ V
4. The sign of E^0_{red} changes, but its magnitude remains the same when we reverse a reaction.
5. The more positive the reduction potential, the greater the tendency to accept electrons. As a result, when two half-cells are coupled, the reaction with higher (more positive) reduction potential proceeds as reduction, while the other proceeds as oxidation.

Example

A Galvanic cell consists of a Mg electrode in 1.0 M $Mg(NO_3)_2$ solution and a Ag electrode in 1.0 M $AgNO_3$ solution. Calculate the standard cell potential (*emf*) of this cell at 25°C.

Solution

Using Table 1, it can be noticed that Ag^+ will oxidize Mg.

We can find the E^o_{cell} by using the principle stated

Ag^+ (1.0 M) + $e^- \longrightarrow Ag^+(s)$, $E^o_{red} = +0.80$ V (*Cathode: higher reduction potential*)

Mg^{2+} (1.0 M) + $2e^- \longrightarrow Mg(s)$, $E^o_{red} = -2.37$ V (*Anode: lower reduction potential*)

$$E^o_{red} = E^o_{red}\,(\text{cathode}) - E^o_{red}\,(\text{anode})$$
$$= E^o_{red}\,(Ag^+/Ag) - E^o_{red}\,(Mg^{2+}/Mg)$$
$$= 0.80\text{ V} - (-2.37\text{ V}) = +3.17\text{ V}$$

The positive value of E^o_{red} shows that the forward reaction is favoured.

Exercises

1. For each of the following galvanic cells, write the anode and cathode half-cell reactions, the overall cell reaction, and calculate the standard cell potential. Use the standard reduction half-cell potentials given in Table 1
   (a) $Zn|Zn^{2+}$ (aq, 1 M)$||Fe^{3+}, Fe^{2+}$ (aq, 1 M)$|Pt$;
   (b) $Zn|Zn^{2+}$ (aq, 1 M)$||Br_2, Br^-$ (aq, 1 M)$|Pt$;
2. Given the following overall reaction,

   Cu^{2+} (1 M) + Mg (s) $\longrightarrow$ Cu (s) + Mg^{2+} (1 M)

   (a) Sketch the Galvanic cell based on the reaction.
   (b) Identify the cathode and anode.
   (c) Show the direction of electron flow through the external circuit

ACTIVITY 1

Electrolytic cells: Chemical energy to electrical energy

The objective of this practical activity is to construct simple electrochemical cells, and to use the results obtained to put metals in an order of reactivity.

To construct an electrochemical cell, two different metals are needed, an electrolyte and, a voltmeter to show the voltage produced. Two half-cells are connected by a salt bridge through which ions can move.

Procedure

1. Take a beaker and fold the piece of copper metal over the top. Clip a crocodile clip to the copper metal, holding it in place in the beaker. Connect the copper metal to the positive terminal of the voltmeter.
2. Fill the beaker with the 1 mol/L copper nitrate solution so that the copper metal dips into it. This is known as a copper half-cell.
3. Take a piece of lead, fold it over the top of the second beaker. Fill the beaker with the 1 mol/L lead(II) nitrate solution so that the lead metal dips into it. Connect the lead metal to the other terminal on the voltmeter. This is a lead half-cell.
4. Finally, connect the two beakers together with a salt bridge which is made from a folded piece of filter paper soaked in potassium chloride solution.

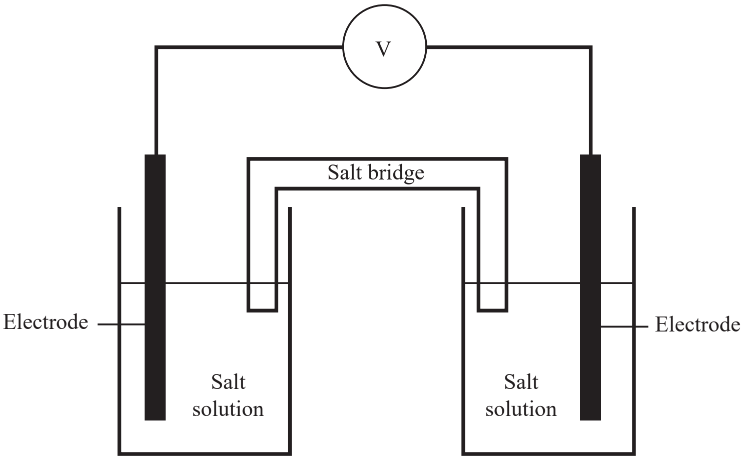


Figure 3. A Galvanic cell to generate electricity

5. You should now see a voltage being recorded on the voltmeter. You have just made an electrochemical cell - a battery. Record the voltage in the results Table 2.
6. Repeat steps 3-5 for the other four metals, each time replacing the beaker and metal connected to the copper half-cell (the lead half-cell in the first case) with half-cells of the other metals in Table 2.

Results and Discussion:

1. Complete the Table as you carry out the experiment.

Table 2

Positive terminal	Negative terminal	Voltage(V)
Copper	Lead	
Copper	Magnesium	
Copper	Iron	
Copper	Zinc	
Copper	Tin	

Conclusions

1. Which combination of metals produces the highest voltage?
2. Which combination of metals produces the lowest voltage?
3. What do you think the voltage would have been if you had used a copper half-cell connected to both terminals of the voltmeter?
4. Which of the metals is the most reactive, and which is the least reactive (not including copper)?
5. Put the metals in order of reactivity with the least reactive first.

6. For the most reactive metal, write an ionic half-equation to show what happens when it is connected to the copper half-cell.
7. What do you think the voltage would have been if you had connected a lead half-cell to a magnesium half-cell to make an electrochemical cell?

Electromotive force (emf)

When electrons move through a wire, they encounter resistance from localised atoms in their paths. The driving force that allows the electrons to overcome this resistance and move around the circuit is called electromotive force (emf). The electromotive force in a Galvanic cell comes from the redox reaction that pushes electrons from the anode to the cathode through the external circuit.

The energy of the moving electrons is used to overcome resistance in the external circuit, and it can be used to do various forms of electrical work. Energy that overcomes resistance appears as heat or as light emitted by a glowing filament. Electrical work is used for starting cars, running watches, radios, and computers, etc.

Electrical work (W) is the product of the emf of the cell and the total charge (in coulombs) that passes through the cell:

$$W = Q \times E$$

where Q is the charge and E is electrical potential.

$$\text{Electrical energy} = \text{Coulombs} \times \text{Volts} = \text{Joules}$$

The total charge is determined by the number of moles of electrons (n) that pass through the circuit.

By definition,

$$Q = nF$$

where F, the Faraday constant, is the total electrical charge contained in 1 mole of electrons.

$$1\ \text{F} = 96{,}500\ \text{C/mol}\ e^-$$

Because $1\ \text{J} = 1\ \text{C} \times 1\ \text{V}$,

We can also express the unit of Faraday as 1 F = 96, 500 J/V. mol e^-.

The measured emf is the maximum voltage that the cell can achieve. This value is used to calculate the maximum amount of electrical energy that can be obtained from the chemical reaction. This energy is used to do electrical work (W_{ele}), so

$$W_{max} = W_{ele} = -nFE_{cell}$$

where, W_{max} is the maximum amount of work that can be done.

What does the negative sign indicate?

The change in free energy (ΔG) represents the maximum amount of useful work that can be obtained from a reaction.

$$\Delta G = W_{max}$$

$$\Delta G = W_{max} = -\,nFE_{cell}$$

$$\Delta G = -\,nFE_{cell}$$

Both n and F are positive quantities, and ΔG is negative for a spontaneous process, so E_{cell} must be positive. Therefore, a positive E_{cell} value corresponds to a negative ΔG value, which is the condition for spontaneity.

For standard state conditions,

$$\Delta G^\circ = -\,nFE^\circ_{cell}$$

Now we can relate E°_{cell} to the equilibrium constant (K) of a redox reaction. The standard free energy change, ΔG°, for a reaction is related to its equilibrium constant, as follows.

$$\Delta G^\circ = -\,RT\ln K$$

If we substitute ΔG° by $-\,nFE^\circ_{cell}$ it becomes $+\,nFE^\circ_{cell} = +\,RT\ln K$

$\Rightarrow \quad nFE^\circ_{cell} = RT\ln K$

$$E^\circ_{cell} = \frac{RT}{nF}\ln K$$

When T = 298 K, the equation can be simplified by substituting for R and F.

$$E^\circ_{cell} = \frac{(8.134\,J/mol\,K)\times(298\,K)}{n(96500\,J/V\,mol)}\ln K = \frac{0.0257\,V}{n}\ln K$$

The natural logarithm (ln) is related to the common logarithm (log) as follows:

$\ln x = 2.303\log x$

$$E^\circ_{cell} = \frac{0.0257\,V \times 2.303\log K}{n} = \frac{0.0592\,V}{n}\log K$$

Therefore, $E^\circ_{cell} = \dfrac{0.0592\,V}{n}\log K$

Thus, if any one of the three quantities ΔG°, K or E°_{cell} is known, the other two quantities can be calculated, using the equations $\Delta G^\circ = -\,RT\ln K$, $\Delta G^\circ = -nFE^\circ_{cell}$ or

$$E^\circ_{cell} = -\Delta G^\circ/nF.$$

Let us summarize the relationships among ΔG°, K and $E°_{cell}$ and characterize the spontaneity of a redox reaction.

Table 3

ΔG°	K	$E°_{cell}$	Reaction under standard state conditions
Negative	>1	Positive	Favours the formation of products
Zero	=1	Zero	Reactants and products are equally favoured.
Positive	<1	Negative	Favours the formation of reactants.

Example

Calculate the standard free energy change for the following reaction at 25°C.

$$Cu^{2+}(aq, 1.0\ M) + Fe(s) \longrightarrow Cu(s) + Fe^{2+}(aq, 1.0\ M)$$

Solution

The relationship between the standard free energy change and the standard cell potential is given by $\Delta G^0 = -nF E^0_{cell}$. First, let us determine E^0_{cell}

The half-reactions are:

Anode (oxidation): $Fe(s) \longrightarrow Fe^{2+}(1.0\ M) + 2e^-$

Cathode (reduction): $Cu^{2+}(1.0\ M) + 2e^- \longrightarrow Cu(s)$

$$E°_{cell} = E°_{red}(\text{cathode}) - E°_{red}(\text{anode})$$

$$E°_{cell} = E°_{red}(Cu^{2+}/Cu) - E°_{red}(Fe^{2+}/Fe)$$

$$= 0.34\ V - (-0.44\ V) = 0.78\ V$$

The overall reaction shows that $n = 2$ (2 moles of electrons are involved). Now we can calculate ΔG°, using the following equation:

$$\Delta G° = -nFE°_{cell} = -(2\,\text{mole})\left(\frac{96500\,C}{1\,\text{mole}}\right)\left(\frac{0.78\,J}{C}\right) = -1.5 \times 10^5\,J$$

The negative value of ΔG° tells us that the forward reaction is spontaneous, that is, iron can reduce copper.

Exercises

1. What is the standard free energy change and the equilibrium constant for the following reaction at room temperature? Is the reaction spontaneous?

$$Sn(s) + 2Cu^{2+}(aq, 1.0\ M) \longrightarrow Sn^{2+}(aq, 1.0\ M) + 2\ Cu^{+}(aq, 1.0\ M)$$

4.4 DEPENDENCE OF EMF ON CONCENTRATION

Upon completion of this topic, learners will be able to:

- calculate the cell potential for non-standard conditions.

What is the effect of change in the concentration of reactants on cell potential?

A change in concentration affects the change of cell potential which is a result of free energy change. According to chemical thermodynamics:

$$\Delta G = \Delta G^{o} + RT \ln Q$$

Where, Q is the reaction quotient, and Q is used to calculate the effect of concentration on ΔG. Since $\Delta G = -nFE_{cell}$ and $\Delta G^{o} = -nFE^{o}_{cell}$, the equation becomes

$$-nFE_{cell} = -nFE^{o}_{cell} + RT \ln Q$$

Dividing each side of the equation by $-nF$ gives

$$E_{cell} = E^{\circ}_{cell} - \frac{RT}{nF} \ln Q$$

This equation gives the relationship between the cell potential and the concentrations of the cell components and is called the Nernst equation.

At 25°C:

$$E_{cell} = E^{0}_{cell} - \frac{\left(8.314 \frac{J}{mol\,K}\right) \times (298\,K)}{n \times \left(96500 \frac{J}{V\,mol}\right)} \ln Q$$

$$E_{cell} = E^{0}_{cell} - \frac{0.0257\,V}{n} \ln Q$$

$$E_{cell} = E^{0}_{cell} - \frac{0.0592\,V}{n} \log Q$$

During the operation of a Galvanic cell, electrons flow from the anode to the cathode, resulting in product formation and a decrease in reactant concentration. Thus Q increases, which means that E_{cell} decreases. Eventually, the cell reaction reaches equilibrium. At equilibrium, there is no net transfer of electrons, so $E_{cell} = 0$ and Q = K, where K is the equilibrium constant.

The above equation enables us to calculate E_{cell} as a function of reactant and product concentrations in a redox reaction.

Example

Predict whether the following reaction would proceed spontaneously, as written at 298 K, given that $[Co^{2+}] = 0.15$ M and $[Fe^{2+}] = 0.68$ M

$$Co\ (s) + Fe^{2+}\ (aq) \longrightarrow Co^{2+}\ (aq) + Fe\ (s)$$

Solution

Because the reaction is not under standard state conditions (concentrations are not 1 M), we need the Nernst equation to calculate the emf (E_{cell}) of a Galvanic cell. The standard emf ($E°_{cell}$) can be calculated, using the standard reduction potentials in Table 1.

The half-cell reactions are

Anode (oxidation): $Co\ (s) \longrightarrow Co^{2+}\ (aq) + 2e^-$

Cathode (reduction): $Fe^{2+}\ (aq) + 2e^- \longrightarrow Fe\ (s)$

$$E^o_{cell} = E^o_{red\ (cathode)} - E^o_{red\ (anode)}$$

$$= -0.44\ V - (-0.28\ V) = -0.16\ V$$

Using the equation

$$E_{cell} = E^0_{cell} - \frac{0.0257\,V}{n} \ln \frac{[Co^{2+}]}{[Fe^{2+}]}$$

$$E_{cell} = -0.16\,V - \frac{0.0257\,V}{2} \ln \frac{0.15}{0.68}$$

$$E_{cell} = -0.16\,V + 0.019\,V = -0.14\,V$$

The reaction is not spontaneous in the forward direction.

4.5 PRINCIPLES OF ELECTROLYSIS

By the end of this section, learners will be able to:

- describe electrolytic cells and their relationship to galvanic cells.
- perform various calculations related to electrolysis.

In galvanic cells, chemical energy is converted into electrical energy. The opposite is true for electrolytic cells.

In electrolytic cells, electrical energy causes non-spontaneous reactions to occur in a process known as electrolysis.

Electrolysis is a process in which electrical energy is used to produce chemical changes. This process is carried out in an electrochemical cell known as an electrolytic or electrolysis cell. A typical electrolysis cell contains a source of direct electric current, an electrolyte and connecting wires that join the source to the electrodes.

Electrodes are strips of metal or graphite that allow electrons to leave or enter the electrolytes. They can be chemically active or inert. Active electrodes directly take part in reactions. Examples include zinc and magnesium. Inert electrodes do not directly take part in chemical reactions. They only serve to transfer electrons. Examples include platinum and graphite.

The electrode connected to the positive terminal of the source is positively charged and is called the anode. It is the electrode through which electrons leave the cell. The electrode connected to the negative terminal of the source is negatively charged and is called the cathode. It is the electrode through which electrons enter the cell.

During electrolysis, the ions of the electrolyte migrate to the electrodes of the opposite charge. The positive ions are attracted to the cathode and are called cations. Since the cathode has excess electrons, the cations will discharge by gaining electrons. This process of gaining electrons is called reduction. The negative ions are attracted by the positive electrode (anode) and are called anions. These ions are discharged by losing electrons at the anode. This process of losing electrons is called oxidation.

Thus, the cathode is the electrode at which reduction occurs and the anode is the electrode at which oxidation takes place.

Difference between Galvanic cell and electrolytic cell

1. Definition of Galvanic cell and electrolytic cell

In galvanic cells there are spontaneous redox processes that allow continuous flow of electrons through the conductor, whereby the chemical energy is converted into electrical energy. In an electrolytic cell, redox reactions take place under the influence of an external source, where the electricity is converted into a chemical energy. The redox reactions are non-spontaneous.

2. Technique of Galvanic cell and electrolytic cell

Galvanic cells generate electricity with the aid of chemical reactions. In electrolytic cells, an electric current is used for development of a chemical reaction, utilizing an external source along the way.

3. Design of Galvanic cell and electrolytic cell

Galvanic cells consists of two different electrodes immersed in solutions of their ions that are separated by a salt bridge. Electrolytic cells consist of an electrolytic container in which two electrodes are connected to a d.c. source. The electrolyte may be a melt or an aqueous solution of some salt, acid or alkali.

4. Electrode polarity in Galvanic cell and electrolytic cell

In galvanic cells, the anode is the negative and the cathode is the positive electrode. In electrolytic cells, the opposite occurs.

5. Application of Galvanic cell and electrolytic cell

Galvanic cells are used as a source of electrical current, and are more commonly referred to as batteries or accumulators. Electrolytic cells have different practical uses, some of them being making hydrogen and oxygen gas for commercial and industrial applications, electroplating, extracting pure metals from alloys and so on.

Discuss with your partner and add more differences between an electrolytic and a galvanic cell?

ACTIVITY 2

Indicator of electrolysis by using phenolphthalein, water, salt, dry cell, speaker wire.

In a glass of water, many of the molecules naturally separate out into hydrogen ions (H^+) that are positively charged and hydroxide ions (OH^-) that are negatively charged. Your electrolysis device causes reactions that pull apart the water even more.

The hydrogen ions (H^+) migrates towards the cathode and bubbles from the negative electrode and the oxygen-containing hydroxide ions (OH^-) migrates towards the anode and bubbles from the positive electrode. At the same time, you also create a change in pH, or the amount of acid and base, in local areas around the electrodes.

At the positive electrode, two oxygen atoms get pulled from two hydroxide ions (OH^-) and combine to make oxygen gas (O_2). This leaves an abundance of free hydrogen ions (H^+) , which makes it more acidic at the positive terminal—so your indicator should show an increase of acid at the positive terminal. Likewise, when hydrogen ions (H^+) combine to make hydrogen gas (H_2) at the negative terminal, an abundance of free hydroxide ions (OH^-) are produced near the negative terminal. Therefore, your indicator should show the production of a base at the negative terminal.

Procedure

Wrap a rubber band lengthwise around the 9-volt battery so that the rubber band lies across both of the battery terminals. Wrap another rubber band lengthwise around the battery so it crosses the first rubber band in a perpendicular fashion.

Slide a stainless steel screw beneath the rubber band and on top of each battery terminal. Each screw should be positioned so that its head is in contact with the terminal. The heads of the screws should point in the same direction and the screws should not touch each other. This is your electrolysis device, and the screws are your electrodes—they will be conducting electricity during the experiment.

Figure 4. Indicator of electrolysis

Put on your safety goggles.

Fill your Petri dish or shallow container with lukewarm water.

Pour epsom salt crystals into the water (about a 1/3 teaspoon if you are using a Petri dish). Stir your solution with a spoon to help dissolve the salt.

Add some of your chosen acid-base indicator to the salt solution until the solution is colored—you will need from a few drops to a few milliliters depending on the type and the concentration of your indicator.

Immerse the exposed ends of the screws in the solution.

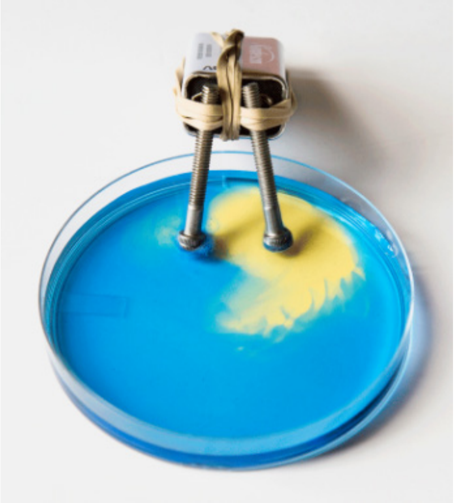


Figure 5. Screws in the solution

Result and observation

What do you notice happening at the dipped ends of each screw? Your screws should begin emitting gas bubbles, and different colors should develop at each electrode.

Did you see bubbles forming at the screw tips? Did one screw emit more bubbles than the other?

Exercises

1. Consider the electrolysis of molten NaCl and $PbBr_2$.
   (a) Identify the ions which migrate towards the anode.
   (b) Identify the ions which migrate towards the cathode.
   (c) Write down the half-reactions at the anode and cathode and cell reactions.
   (d) Write the substances produced at the electrodes.
2. Write the anode, cathode and cell reaction for the electrolysis of H_2O?

4.6 FACTORS INFLUENCING DISCHARGE OF SPECIES

By the end of this section, learners be able to:

- describe the factors that influence the discharge of species.

Preferential discharge

What does preferential discharge mean? What are the factors that affect preferential discharge of ions?

During electrolysis, the cations get attracted towards the negatively charged electrode (cathode) and anions get attracted towards the positively charged electrode (anode). If more than one cations or anions reach an electrode, only one of them preferentially gets discharged at one electrode. Thus, there is a choice amongst the ions that will get discharged on an electrode. This is termed as the preferential discharge of ions during electrolysis.

The preferential discharge of ions is affected by the positions of the ions in the electrochemical series, the nature of the electrodes and the concentration of the ions in the electrolyte.

Let us discuss these factors.

1. Position of ions on the electrochemical series

The electrochemical series is an arrangement of ions according to their reactivity. Ions that are lower down the series will be discharged in preference to those above it on the series.

The figure 6 shows the relative position of ions on the electrochemical series.

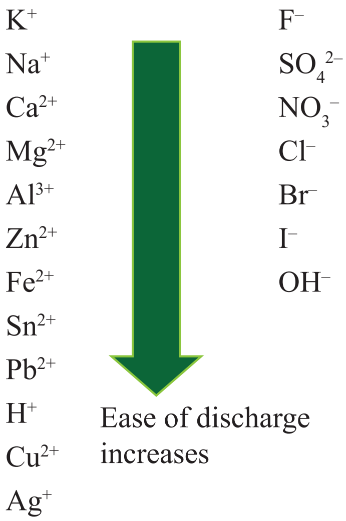


Figure 6. The relative position of some ions on the electrochemical series

2. Nature of the electrodes

How do electrodes affect the preferential discharge of ions?

Inert electrodes, like graphite or platinum, do not affect the product of electrolysis, but reactive or active electrodes, like copper, can affect the product of electrolysis.

For example, in the electrolysis of copper sulphate solutions, using graphite electrodes, oxygen gas is liberated at the anode and copper metal is deposited at the cathode, as shown below.

$$CuSO_4(aq) \longrightarrow Cu^{2+}(aq) + SO_4^{2-}(aq)$$

Anode **:** $4OH^-(aq) \longrightarrow O_2(g) + 2H_2O(l) + 4e^-$

Cathode **:** $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

However, if the electrolysis of copper sulphate is performed using copper electrodes, the copper electrode at the anode dissolves and copper metal will be deposited at the cathode, as indicated below.

Anode **:** $Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$

Cathode **:** $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

3. Concentration of the ions in the electrolyte

If an electrolyte contains a higher concentration of ions that are higher in the electrochemical series than of those that are lower, then the higher ions get discharged in preference to the lower ones. For example, a solution of sodium chloride in water contains two types of anions i.e., the chloride (Cl^-) ions and the hydroxide (OH^-) ions. The hydroxide ions are lower in the electrochemical series than the chloride ions. But if the concentration of chloride ions is much higher than that of the hydroxide ions, then the chloride ions get discharged first.

Electrolysis of common electrolytic cells

A. Electrolysis of concentrated sodium chloride solution (brine solution)

Concentrated solution of sodium chloride (brine solution) contains Na^+, Cl^-, H^+ and OH^- ions. However, the concentrations of H^+ and OH^- are very small. Why? When a potential difference is established across the two electrodes, Na^+ and H^+ ions move towards the cathode, and Cl^- and OH^- ions move towards the anode. At the cathode, the H^+ ions are discharged in preference to the Na^+ ions. Similarly, Cl^- ions are discharged at the anode in preference to the OH^- ions because the concentration of Cl^- ions is very high.

***Cathode* (*reduction*) :** $2H^+(aq) + 2e^- \longrightarrow H_2(g)$

***Anode* (*oxidation*) :** $2Cl^-(aq) \longrightarrow Cl_2(g) + 2e^-$

***Overall reaction* :** $2H^+(aq) + 2Cl^-(aq) \longrightarrow H_2(g) + Cl_2(g)$

Since the Na^+ and OH^- ions remain in the solution, the solution yields NaOH.

ACTIVITY 3

Investigating electrolysis of sodium chloride solution

The aim of this experiment is to electrolyze sodium chloride solution and observe the reaction occurring at the electrodes.

Procedure

1. Prepare 0.1 M sodium chloride solution.
2. Transfer the solution to the beaker.
3. Immerse the graphite electrodes in the sodium chloride solution.
4. Arrange the setup as shown in Figure 7.

Results and Discussion:

1. What do you observe at the surface of the electrodes?
2. Identify the cathode and anode in Figure 7.
3. Name the gases evolved at the cathode and anode.
4. Write the equations for the anode and cathode reactions.

Conclusion

What have you learnt? Present your findings from the experiment.

Write a laboratory report in groups and present your report to the rest of the class.

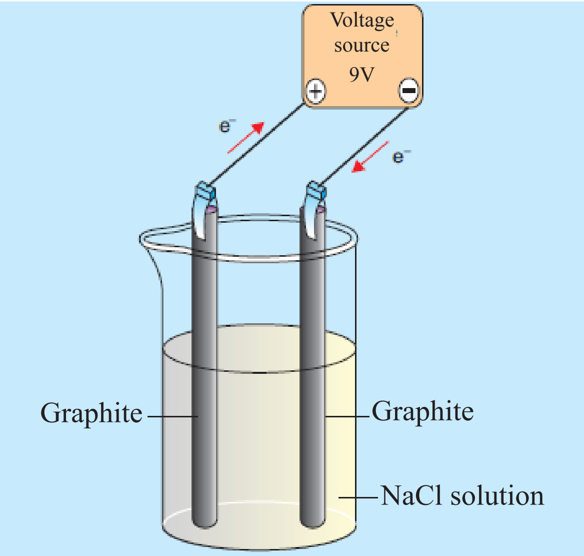


Figure 7 . Electrolysis of sodium chloride solution

B. Electrolysis of dilute sodium chloride solution

Form a group, and discuss each of the following questions. After the discussion, share your ideas with the rest of the class.

1. What is meant by dilute solution?
2.
   (a) List all ions present in dilute sodium chloride solution.
   (b) Identify the ions that migrate towards the anode and the cathode.
   (c) Which ions listed in (A) will be discharged at the cathode and at the anode?
3. Write the electrode half-reactions and overall reaction for the electrolysis of dilute solution of sodium chloride.

C. Electrolysis of dilute sulphuric acid solution

Which ions are discharged at the cathode and anode?

Dilute sulphuric acid solution contains H^+, OH^- and SO_4^{2-} ions. When a potential difference is applied across the two electrodes (anode and cathode), only H^+ ions migrate towards the cathode, and OH^- and SO_4^{2-} ions migrate towards the anode.

At the cathode, H^+ ions are discharged, and at the anode, OH^- ions are discharged in preference to SO_4^{2-} ions because the hydroxide ion is below the SO_4^{2-} ion in the electrochemical series.

***Anode (oxidation)* :** $4OH^-(aq) \longrightarrow 2H_2O\,(l) + O_2\,(g) + 4e^-$

***Cathode (reduction)* :** $[2H^+(aq) + 2e^- \longrightarrow H_2\,(g)] \times 2$

***Overall reaction* :** $2H_2O\,(l) \longrightarrow 2H_2\,(g) + O_2(g)$

Note that the electrolysis of dilute NaCl and dilute H_2SO_4 solutions results in the decomposition of water to oxygen and hydrogen gases.

Quantitative aspects of electrolysis

After completing this subunit, you will be able to:

- State Faraday's first law of electrolysis;
- Write the mathematical expressions for the Faraday's first law of electrolysis;
- Do calculations related to Faraday's first law of electrolysis;
- State Faraday's second law of electrolysis;
- Write the mathematical expressions for Faraday's second law of electrolysis; and
- Do calculations related to Faraday's second law of electrolysis.

Is it possible to calculate the amount of product formed at the electrodes?

The quantitative treatment of electrolysis was developed primarily by Michael Faraday in 1834. His early research on electrolysis led him to propose a relationship between the amount of current passed through a solution and the quantity of substance decomposed or produced by the current.

Faraday's First Law of electrolysis

Faraday's First Law states that "the amount of substance consumed or produced at one of the electrodes in an electrolytic cell is directly proportional to the quantity of electricity that passes through the cell"

If m is the mass of a substance librated or deposited at an electrode due to the passage of charge Q, then according to Faraday's first law of electrolysis,

$$m \propto Q \text{ or } m = zQ$$

Where z is a constant of proportionality called electrochemical equivalent of the substance. It has the same charge which passes due to a steady current I flowing for time t, then the above equation can be written as:

$$m = z \times I \times t$$
$$= z \times Q$$

Show that the general formula of Faraday's first law is given by : $m = \dfrac{MIt}{nF}$

where, m is mass of the substance deposited or liberated, I is current in amperes, t is time in seconds, F is Faradays constant, n is the number of moles of electrons lost or gained, and M is the molar mass of the substance.

For example, in the electrolysis of molten NaCl, the cathode reaction tells us that one Na atom is produced when one Na^+ ion accepts an electron from the cathode. To reduce 1 mole of Na^+ ions, we must supply one mole of electrons (6.02×10^{23} electrons) to the cathode.

In an electrolysis experiment, we generally measure the current that pass through an electrolytic cell in a given period of time. By definition, 1 coulomb of charge is transferred when a 1 ampere current flows for 1 second:

$$1\ \text{C} = 1\ \text{A} \times 1\ \text{s}$$

The charge on 1 mole of electrons is 96,500 C, which is obtained by multiplying 1 mol (6.02×10^{23} electrons) with the charge of electron (1.602×10^{-19} C).

$$\text{Charge of 1 mol of electrons} = 6.02 \times 10^{23}\ \text{electrons} \times 1.602 \times 10^{-19}\ \text{C}$$
$$= 96,485\ \text{C} \simeq 96{,}500\ \text{C} = 1\ \text{F (one faraday)}$$

Therefore, $1\text{F} = 96{,}500\ \text{C mol}^{-1}$.

Example

A current of 1.26 A is passed through an electrolytic cell containing an aqueous solution of H_2SO_4 for 7.44 h. Write the half-cell reactions and calculate the volume of the gases generated at STP (Note that at STP, $P = 1$ atm, and $T = 0°C$ or 273 K).

Solution

Recall that, from the electrolysis of dilute H_2SO_4, we have:

Anode (oxidation) **:** $4OH^- (aq) \longrightarrow 2H_2O\ (l) + O_2\ (g) + 4e^-$

Cathode (reduction) **:** $4H^+ (aq) + 4e^- \longrightarrow 2H_2\ (g)$

Overall reaction **:** $2H_2O\ (l) \longrightarrow 2H_2\ (g) + O_2\ (g)$

First let us calculate the total charge.

Given: $I = 1.26$ A

$t = 7.44\ h = (7.44 \times 60 \times 60)\ \text{s} = 26{,}784\ \text{s}$

$Q = It = (1.26\ \text{A}) \times (26,784\ \text{s}) = 3.37 \times 10^4\ \text{C}$

The above balanced chemical equation shows that for 1 mole of O_2 formed at the anode, 4 moles of electrons are generated. Now let us calculate the number of moles of electrons.

$$96{,}500\ \text{C} = 1\ \text{mol}\ e^-$$

$$1\ \text{C} = \frac{1}{96500\ \text{C}}\ \text{mol}\ e^-$$

$$x = 3.37 \times 10^4 \text{ C} = \frac{1 \text{ mol } e^- \times 3.37 \times 10^4 \text{ C}}{96500 \text{ C}}$$

The number of moles of oxygen becomes:

$$4 \text{ mol } e^- = 1 \text{ mol } O_2 \text{ (observe the anode reaction)}$$

$$0.350 \text{ mol } e^- = x$$

$$x = \frac{0.350 \text{ mol}^{-1} \times 1 \text{ mol } O_2}{4 \text{ mol } O_2} = 0.08750 \text{ mol } O_2$$

$$V = \frac{\text{nRT}}{\text{P}} = \frac{0.0875 \text{ mol} \times 0.0821 \left(\text{L.}\dfrac{\text{atm}}{\text{mol.K}}\right) \times 273 \text{ K}}{1 \text{ atm}}$$

V = 1.96 L or since the volume of 1 mol of a gas at STP is 22.4 L, the volume occupied by 0.0875 mol of O_2 can be obtained using the following relation.

$$1 \text{ mol} = 22.4 \text{ L}$$

$$0.0875 \text{ mol} = x$$

$$x = \frac{0.0875 \text{ mol} \times 22.4 \text{ L}}{1 \text{ mol}} = 1.96 \text{ L}$$

Similarly, for hydrogen, we write

$$4 \text{ mol } e^- = 2 \text{ mol } H_2 \text{ (observe the cathode reaction)}$$

$$0.350 \text{ mol } e^- = x$$

$$x = \frac{0.350 \text{ mole}^- \times 2 \text{ mol } H_2}{4 \text{ mol e}} = 0.175 \text{ mol } H_2$$

The volume of 0.175 mol of H_2 at STP is given by

$$V = \frac{\text{nRT}}{\text{P}} = \frac{0.175 \text{ mol} \times 0.0821 \left(\text{L.}\dfrac{\text{atm}}{\text{mol.K}}\right) \times 273 \text{ K}}{1 \text{ atm}}$$

$$V = 3.92 \text{ L}$$

Note that the volume of H_2 is twice that of O_2.

Exercises

1. Calculate the volume of H_2 and O_2 gases at 25°C and 1.00 atm that will be collected at the cathode and anode, respectively, when an aqueous solution of Na_2SO_4 is electrolyzed for 2 hours with 10 ampere current

Faraday's Second Law of Electrolysis

Faraday's second law of electrolysis states that "when the same quantity of charge (Q) is passed through different electrolytes, then the masses of different substances deposited (m_1, m_2, m_3,...) at the respective electrodes will be directly proportional to their equivalent masses (E_1, E_2, E_3,...)."

$$m \propto E$$

$$\text{or} \qquad m_1 \propto E_1,\ m_2 \propto E_2, \text{ and } m_3 \propto E_3 \text{ etc.}$$

Replacing the proportionality by a proportionality constant k, the equations become:

$$\frac{m_1}{E_1} = \frac{m_2}{E_2} = \frac{m_3}{E_3} = \ldots = k$$

The law can be illustrated by passing the same quantity of electric current through three solutions containing H_2SO_4, $CuSO_4$ and $AgNO_3$, connected in series, as shown in Figure 8.

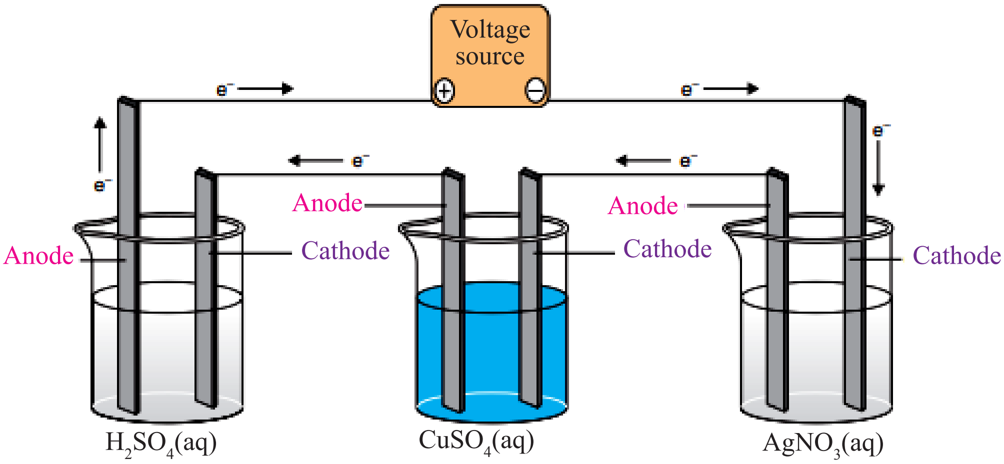


Figure 8 . Solutions connected in series to a battery.

In the first solution, hydrogen and oxygen are liberated. In the second solution copper is deposited and in the third, silver is deposited.

$$\frac{\text{Mass of hydrogen}}{\text{Equivalent mass of } H_2} = \frac{\text{Mass of copper}}{\text{Equivalent mass of copper}} = \frac{\text{Mass of silver}}{\text{Equivalent mass of silver}}$$

Example

In an electrolysis experiment, a current was passed for 5 hours through two cells connected in series. The first cell contains a solution of a salt of gold and the second cell contains copper sulphate solution. 9.85 g of gold was deposited in the first cell. The oxidation number of gold is +3. Find the amount of copper deposited on the cathode in the second cell.

Solution

We know that

$$\frac{\text{Mass of Au deposited}}{\text{Equivalent mass of Au}} = \frac{\text{Mass of Cu deposited}}{\text{Equivalent mass of copper}}$$

Eq. mass of Au = 197/3;

Eq. mass of Cu = 63.5/2 = 31.75

Mass of copper deposited

$$= \frac{\text{Mass of Au deposited} \times \text{Equivalent mass of copper}}{\text{Equivalent mass of Au}} = \frac{9.85\,\text{g} \times \frac{63.5}{2}}{\frac{197}{3}} = 4.7\,\text{g}$$

Exercises

1. Exactly 0.5 Faraday electric charge is passed through three electrolytic cells in series, first containing $AgNO_3$, second $CuSO_4$ and third $FeCl_3$ solution. How many gram of each metal will be deposited assuming only cathodic reaction in each cell?
2. Two cells are connected in series. One contains $AlCl_3$, and the other contains $AgNO_3$ as the electrolytes. What mass of Ag is deposited when 18 g of Al is deposited at cathode?

4.7 BATTERIES

By the end of this section, learners will be able to:

- describe the various batteries, together with their applications.

A battery is an electrochemical cell or series of cells that can be used as a source of direct current at a constant voltage.

The major advantages offered by batteries are convenience and portability.

There are two basic types of batteries:

- Primary battery and
- Secondary battery.

Primary batteries

Primary batteries use redox reactions that cannot be reversed.

Common primary batteries include the dry cell/zinc-carbon battery and alkaline battery.

The dry cell battery/Leclanche cell

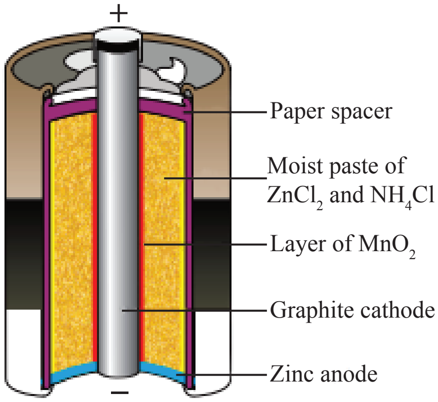


Figure 9. The interior section of a dry cell battery.

The zinc can serves as both a container and the anode electrode. The cathode is a rod made of carbon that is surrounded by a paste of manganese(IV) oxide, zinc chloride, ammonium chloride, carbon powder, and a small amount of water. The reaction at the anode can be represented as the ordinary oxidation of zinc:

$$Zn\,(s) \longrightarrow Zn^{2+}\,(aq) + 2e^- \qquad E^o_{Zn^{2+}/Zn} = -0.76V$$

The reaction that occurs at the cathode is

$$2MnO_2\,(s) + 2NH_4Cl\,(aq) + 2e^- \longrightarrow Mn_2O_3\,(s) + 2NH_3\,(aq) + H_2O\,(l) + 2Cl^-$$

The overall reaction for the zinc–carbon battery can be represented as

$$2MnO_2(s) + 2NH_4Cl(aq) + Zn(s) \longrightarrow Zn^{2+}(aq) + Mn_2O_3(s) + 2NH_3(aq) + H_2O(l) + 2Cl^-(aq)$$

with an overall cell potential which is initially about 1.5 V, but decreases as the battery is used.

Alkaline batteries

- Use alkaline electrolytes, often potassium hydroxide.
- The reactions are

Anode: $Zn(s) + 2OH^-(aq) \longrightarrow ZnO(s) + H_2O(l) + 2e^- \; E°_{anode} = -1.28\ V$

Cathode: $2MnO_2(s) + H_2O(l) + 2e^- \longrightarrow Mn_2O_3(s) + 2OH^-(aq) \; E°_{cathode} = +0.15\ V$

Overall: $Zn(s) + 2MnO_2(s) \longrightarrow ZnO(s) + Mn_2O_3(s) \quad E°_{cell} = +1.43\ V$

Secondary batteries

Secondary batteries are rechargeable. These are the types of batteries found in devices such as smartphones, electronic tablets, and automobiles.

Nickel-cadmium (or Ni-Cd) batteries consist of a nickel (NiO_2) cathode, cadmium-anode, and a potassium hydroxide electrolyte. The positive and negative plates, which are prevented from shorting by the separator, are rolled together and put into the case. This is a "jelly-roll" design and allows the Ni-Cd cell to deliver much more current than a similar-sized alkaline battery.

The reactions are

Anode: $Cd(s) + 2OH^-(aq) \longrightarrow Cd(OH)_2(s) + 2e^-$

Cathode: $NiO_2(s) + 2H_2O(l) + 2e^- \longrightarrow Ni(OH)_2(s) + 2OH^-(aq)$

Overall: $Cd(s) + NiO_2(s) + 2H_2O(l) \longrightarrow Cd(OH)_2(s) + Ni(OH)_2(s)$

The voltage is about 1.2 V to 1.25 V as the battery discharges. When properly treated, a Ni-Cd battery can be recharged about 1000 times.

Cadmium is a toxic heavy metal so Ni-Cd batteries should never be opened or put into the regular trash.

Lead storage battery

The lead acid battery is the type of secondary battery used in automobiles.

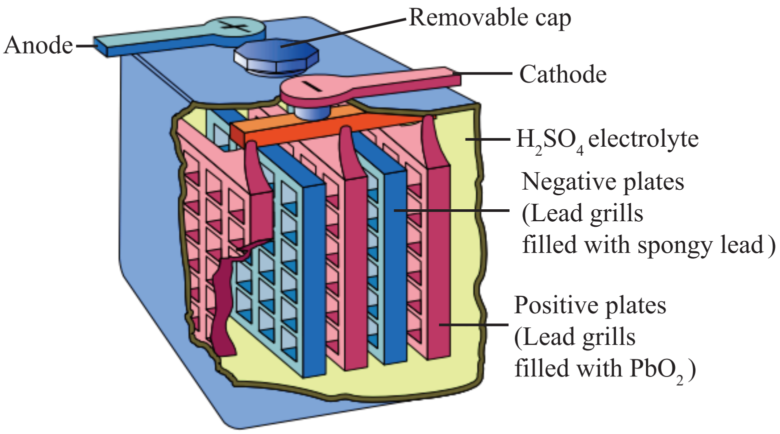


Figure 10. Interior section of a lead storage battery.

It consists of six identical cells joined together in series. Each cell has a lead anode and a cathode made up of lead oxide (PbO_2) packed on a metal plate immersed in an aqueous solution of sulphuric acid which acts as the electrolyte.

The reactions for a lead acid battery are

Anode: $Pb\ (s) + HSO_4^-(aq) \longrightarrow PbSO_4(s) + H^+(aq) + 2e^-$

Cathode: $PbO_2(s) + HSO_4^-(aq) + 3H^+(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O\ (l)$

Overall: $Pb\ (s) + PbO_2(s) + 2H_2SO_4(aq) \longrightarrow 2PbSO_4(s) + 2H_2O\ (l)$

Each cell produces 2V, so six-cells are connected in series to produce a 12V car battery.

Fuel cells

Fuel cells are

- Devices that convert chemical energy into electrical energy.
- Similar to batteries but require a continuous source of fuel, often hydrogen. They continue to produce electricity as long as fuel is available.
- Unlike batteries, fuel cells do not store chemical energy.
- Hydrogen fuel cells have been used to supply power for satellites, space capsules, automobiles, boats, and submarines.

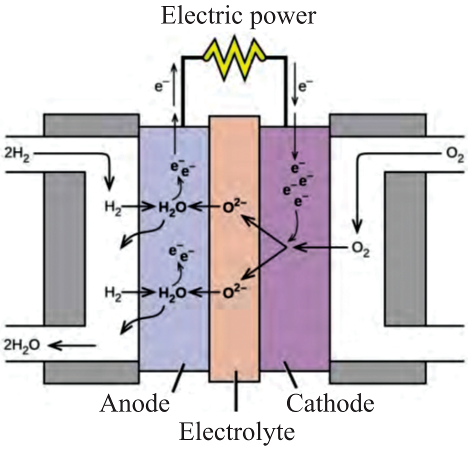


Figure 11. H_2-O_2 Fuel cell

The reactions are

Anode: $2H_2(g) + 4OH^-(aq) \longrightarrow 4H_2O\ (l) + 4e^-$

Cathode: $O_2(g) + 2H_2O\ (l) + 4e^- \longrightarrow 4OH^-(aq)$

Overall reaction: $2H_2(g) + O_2(aq) \longrightarrow 2H_2O\ (l)$

The standard cell potential, can be calculated using the data from Table 1.

$$
\begin{aligned}
E^\circ_{cell} &= E^\circ_{red\ (cathode)} - E^\circ_{red\ (anode)} \\
&= 0.40\ V - (-\ 0.83\ V) \\
&= +1.23\ V
\end{aligned}
$$

Thus, the cell reaction is spontaneous under standard conditions. Note that the reaction is the same as the hydrogen combustion reaction, except that the oxidation and reduction are carried out separately at the anode and the cathode.

4.8 APPLICATION OF ELECTROCHEMICAL CELLS

After completing this section, you will be able to:

- use cell potentials to calculate solution concentrations for sparingly soluble salt.
- describe how to determine equilibrium constant using cell potential.
- explain how reference electrodes allow the pH meter to operate.

In addition to their uses in batteries, electrochemical cells have widespread applications. In this section, we consider three uses in the chemical laboratory.

Determination solubility product of a sparingly soluble salt

Because voltages are relatively easy to measure accurately using a voltmeter, electrochemical methods provide a convenient way to determine the concentrations of very dilute solutions and the solubility products (K_{sp}) of sparingly soluble substances.

To understand how an electrochemical cell is used to measure a solubility product, consider the cell shown in Figure 12, which is designed to measure the solubility product of silver chloride: $K_{sp} = [Ag^+][Cl^-]$. In one compartment, the cell contains a silver wire inserted into a 1.0 M solution of Ag^+; the other compartment contains a silver wire inserted into a 1.0 M Cl^- solution saturated with AgCl.

We can see this by dividing both sides of the equation for K_{sp} by $[Cl^-]$ and substituting:

$$[Ag^+] = K_{sp}/[Cl^-] = K_{sp}/1.0 = K_{sp}.$$

The overall cell reaction is as follows:

$$Ag^+\ (aq,\ concentrated) \longrightarrow Ag^+\ (aq,\ dilute)$$

Thus the voltage of the concentration cell due to the difference in $[Ag^+]$ between the two cells is as follows:

$$E_{cell} = 0 - \frac{0.0592}{1}\log\left(\frac{\left[Ag^{+}\right]dil.}{\left[Ag^{+}\right]conc.}\right) = -0.0592\ V$$

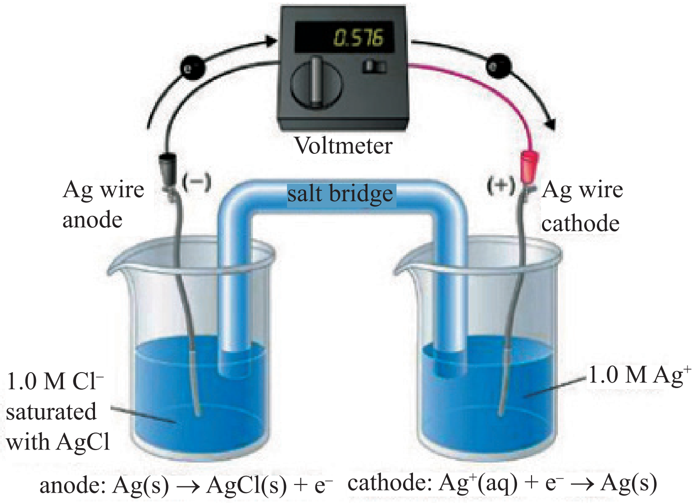


Figure 12. A Galvanic Cell for Measuring the Solubility Product of AgCl

By closing the circuit, we can measure the potential caused by the difference in $[Ag^{+}]$ in the two cells. In this case, the experimentally measured voltage of the concentration cell at 25°C is 0.576 V. Solving for K_{sp},

$$\log K_{sp} = \frac{-E_{cell}}{0.0592\ V} = \frac{-0.576\ V}{0.0592\ V} = -9.73$$

$$K_{sp} = \text{anti}\log\ (10^{-9.73})$$

$$= 1.86 \times 10^{-10}$$

Determination of equilibrium constant

For this chemical equation we have established the Nernst equation:

$$aA + bB \rightleftharpoons cC + dD$$

$$E = E^{0} - \frac{0.0592}{n}\log Q$$

Now at equilibrium point Q = K (equilibrium constant) and cell potential (E) will be zero as rate of forward reaction will be equal to rate of backward reaction. So, the above equation can be written as:

$$0 = E^0 - \frac{0.0592}{n}\log Q$$

$$E^0 = \frac{0.0592}{n}\log Q$$

$$\log K = \frac{nE^0}{0.0592}$$

$$K = 10^{\frac{nE^0}{0.0592}}$$

Thus equilibrium constant (K) can be determined from Nernst equation.

Determination of pH using hydrogen electrode

The concentration dependence of cell voltages provides a convenient means of measuring the concentrations of species in solution. Perhaps the most important solution species we measure on a regular basis is the hydronium ion, H_3O^+ (aq). A pH meter uses cell voltages to determine concentrations of hydronium ions in solution. The probe that is connected to the meter consists of a reference electrode and an electrode that obeys the Nernst equation for hydrogen ions. There are various methods of determination of pH, determination of pH using hydrogen electrode is presented below.

The electrode reaction, written as reduction reaction is

$$H^+ + e^- \longrightarrow 1/2\ H_2\ (1\ \text{atm})$$

The potential of this electrode is given by Nernst equation:

$$E_{(H^+,H_2)} = E^0_{(H^+,H_2)} - \frac{RT}{F} ln \frac{(P_{H_2})^{\frac{1}{2}}}{(H^+)}$$

But $(P_{H_2})^{\frac{1}{2}} = 1$, and $E^0_{(H^+,H_2)} = 0$, and $\frac{RT}{F} = 0.0592$

$$E_{(H^+,\ H_2)} = -0.0592 \log \frac{1}{[H^+]}$$

Here $\log \frac{1}{[H^+]} = pH$

$$E^0_{(H^+,H_2)} = -0.0592\ pH\ \text{at}\ 25°C.$$

A standard hydrogen electrode is coupled with another hydrogen electrode which contains the solution of unknown pH. The e.m.f. of the cell

$$\mathrm{Pt}\left|\mathrm{H}_2\,(1\,\mathrm{atm})\right|\mathrm{H}^+\,(1\,\mathrm{M})\left\|\mathrm{H}^+\,(\text{unknown conc.})\right|\mathrm{H}_2\,(1\,\mathrm{atm})\left|\mathrm{Pt},\right.$$

is found out from the experiment.

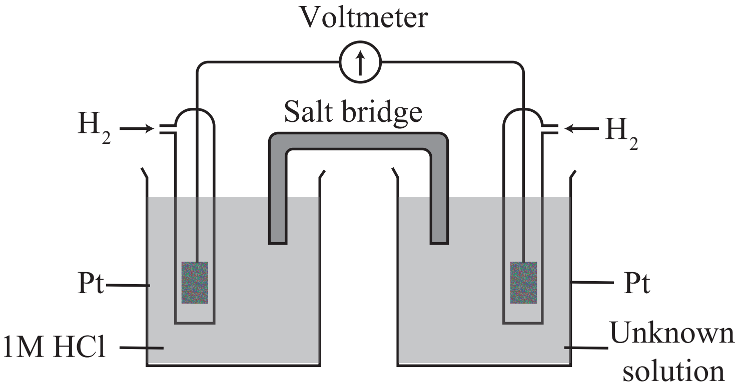


Figure 13. Determination of pH with Hydrogen Electrode

A. The cell potential, E_{cell} is given by:

$$E_{cell} = E_{red,\ cathode} - E_{red,\ anode} = -0.0592\ \mathrm{pH}$$

$$\mathrm{pH} = -\frac{E_{cell}}{0.0592}$$

Thus knowing the value of E_{cell} enables to calculate the pH of the solution.

4.9 CORROSION OF METALS

By the end of this section, learners will be able to:

- explain how electroplating materials can prevent rusting and corrosion.

Corrosion is the deterioration of metals by an electrochemical process. The formation of rust on iron, and the blue-green patina that develops on copper are all examples of corrosion.

In this section, we examine the undesirable redox reactions that lead to corrosion of metals. Corrosion reactions are spontaneous redox reactions in which a metal is attacked by some substance in its environment and converted to an unwanted compound. Since corroded metal often loses its structural integrity and attractiveness, this spontaneous process has great economic impact. Corrosion causes enormous damage to buildings, bridges, ships, and cars.

Corrosion of Iron

Iron will rust when it is exposed to oxygen and water. The main steps in the rusting of iron are:

Anode: $Fe\ (s) \longrightarrow Fe^{2+}(aq) + 2e^{-}$

These electrons reduce oxygen in the air in acidic solutions.

Cathode: $O_2\ (g) + 4H^{+}(aq) + 4e- \longrightarrow 2H_2O\ (l)$ $\qquad E^{o}_{O^{2-}/O_2} = +1.23\ V$

Overall: $2Fe\ (s) + O_2\ (g) + 4H^{+}(aq) \longrightarrow 2Fe^{2+}(aq) + 2H_2O\ (l)$ $E°_{cell} = +1.67\ V$

What we call rust is hydrated iron(III) oxide, which forms when iron(II) ions react further with oxygen.

$$4Fe^{2+}(aq) + O_2\ (g) + (4 + 2x)\ H_2O\ (l) \longrightarrow 2Fe_2O_3{\cdot}xH_2O\ (s) + 8H^{+}(aq)$$

This hydrated form of iron(III) oxide is known as rust. The amount of water associated with the iron oxide varies, so we represent the formula as $Fe_2O_3.xH_2O$.

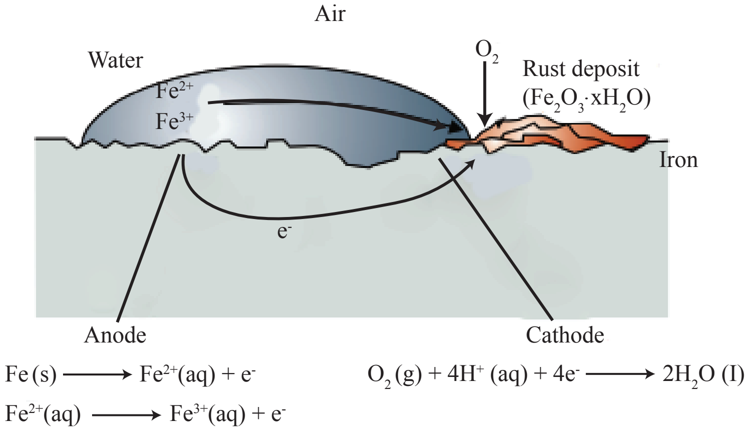


Figure 14. Corrosion of iron in contact with oxygen.

Why does rusting of iron occur rapidly in salt water?

Prevention of corrosion

The corrosion can be prevented by:

- By painting the iron - article
- Alloying the iron with other metals. Stainless steel is mostly iron with a bit of chromium.
- Zinc-plated or galvanized iron, coating iron with a thin layer of zinc.
- Protection of a metal by making it the cathode in an electrochemical cell is called cathodic protection. For example, the rusting of underground iron

storage tanks and pipes can be prevented or greatly reduced by connecting them to a more active metal such as zinc or magnesium by a wire.

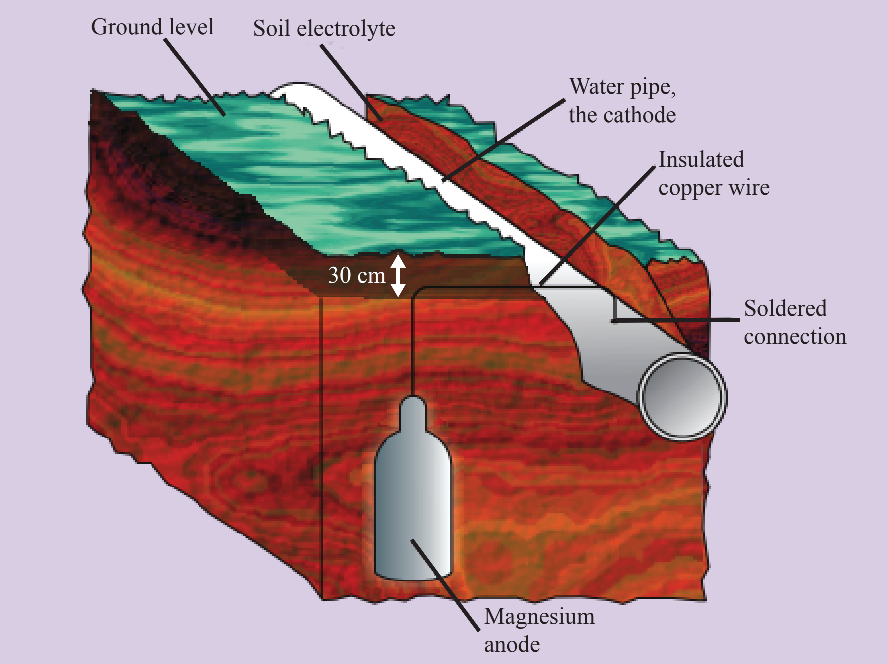


Figure 15. Protection of Iron using Magnesium

The more active metal (lower reduction potential) that is oxidized while protecting the cathode is called sacrificial anode. The metal being protected serves as the cathode, and so does not oxidize (corrode). When the anodes are properly monitored and periodically replaced, the useful lifetime of the iron storage tank can be greatly extended.

4.10 PRACTICAL APPLICATIONS OF ELECTROLYSIS

After completing this section, you will be able to:

- describe selected industrial applications of electrolysis.

Electrolysis has important industrial applications. It is used for:

(a) The production of chemicals like sodium hydroxide, from electrolysis of brine (concentrated NaCl solution), using inert electrodes.

The reactions that take place at the electrodes (when graphite electrodes are used) are as follows:

Anode reaction: $2Cl^{-}\,(aq) \longrightarrow Cl_2\,(g) + 2e^{-}$

Cathode reaction: $2H_2O\,(l) + 2e^{-} \longrightarrow H_2\,(g) + 2OH^{-}\,(aq)$

The overall cell reaction is:

$$2NaCl\,(aq) + 2H_2O\,(l) \longrightarrow 2Na^{+}\,(aq) + 2OH^{-}\,(aq) + Cl_2\,(g) + H_2\,(g)$$

(b) The production of metals and non-metals.

Form a group and discuss each of the following questions. After the discussion, share your ideas with the rest of the class.

1. List non-metals that can be prepared by electrolysis?
2. Write the balanced chemical equation for the dissociation of Al_2O_3 in the molten state?
3. Identify the ions that move to the cathode and the anode during the electrolysis of molten Al_2O_3? Write the half-reactions at the anode, cathode and overall cell reactions.
4. At which electrode will aluminum be produced during the process?
5. Draw a clear sketch showing the main parts in the electrolytic cell?
6. Why cryolite is added in the industrial extraction of aluminum by Hall-Heroult process?
7. Explain why electrolytic reduction rather than chemical reduction is often used to obtain active metals from their compounds?

Refining of aluminium

The metal produced in the greatest quantities by electrolysis is aluminium. Because aluminium is a very reactive metal, it is found in nature as its oxide in an ore called bauxite. Charles M. Hall and Paul Heroult, almost simultaneously discovered a practical electrolytic process for producing aluminium, which greatly increased the availability of aluminium for many purposes.

In the Hall-Héroult process, Al_2O_3 is dissolved in molten cryolite, which melts at lower temperature and is an effective electrical conductor. Graphite rods are employed as anodes and are consumed in the electrolysis.

During electrolysis, Al^{3+} move to the cathode, gain three electrons and become aluminum atom which is collected at the cathode move to the anode, lose two electrons and become oxygen atom which in turn combine to form oxygen molecule.

The overall cell reaction is

$$2Al_2O_3\,(l) \longrightarrow 4\,Al\,(l) + 3O_2\,(g)$$

The aluminum produced in this electrolytic process is 99.5% pure. To be useful as a structural material, aluminum is alloyed with metals such as zinc (used for trailer and aircraft construction) and manganese (used for cooking utensils, storage tanks, and highway signs).

(c) Electrorefining and Electroplating

Form a group and discuss each of the following questions. After the discussion. share your ideas with the rest of the class.

1. Define electrorefining and electroplating?
2. What are the purposes of electrorefining and electroplating?
3. Where do we put the plating metal and the metal to be plated, during electroplating?
4. Does the electrolyte contain dissolved ions of the plating metal or the metal to be plated?
5. Describe the electrorefining of copper. Include the appropriate half-cell reactions.

Electrorefining of metals

Purification of metals is another important application of electrolysis. For example, impure copper from the chemical reduction of copper ore is cast into large slabs that serve as the anodes for electrolytic cells. Aqueous copper sulfate is the electrolyte, and thin sheets of ultrapure copper function as the cathodes. Impure copper is used as the anode and Cu metal is oxidized during electrolysis while pure Cu metal is deposited at the cathode.

The main reactions are

Anode reaction: $Cu \longrightarrow Cu^{2+} + 2e^-$

Cathode reaction: $Cu^{2+} + 2e^- \longrightarrow Cu$

The impure copper anode oxidizes to form Cu^{2+} in the solution. At the cathode reduction takes place to produce pure copper metal. During the electrolysis, the anode decreases but the cathode increases in mass.

Noble metal impurities in the anode are not oxidized at the voltage used; they fall to the bottom of the cell to form a sludge. The Cu^{2+} ions from the solution are deposited onto the cathode, producing copper that is 99.95% pure.

The compounds of very active metals are difficult to decompose, so electrolytic reduction is the only method for obtaining such metals. Sodium, lithium, magnesium, calcium, barium and aluminum are among the metals produced by electrolysis.

Electrolysis is also used in the manufacture of non-metals. For example, fluorine, the most electronegative element, is prepared by the electrolysis of a molten mixture of potassium fluoride and hydrogen fluoride. Chlorine is manufactured by the electrolysis of molten sodium chloride or concentrated sodium chloride (brine) solution. Hydrogen and oxygen are also prepared by electrolysis of water.

Electroplating

The electrolytic deposition of a thin metal film on the surface of a metallic object is called electroplating. It is often done to protect the base metal from corrosion or simply to give it a more pleasant or richer appearance. One of the most familiar examples of electroplating is "chrome plating" in which chromium is plated onto iron and steel surfaces to improve the appearance and protect the object from corrosion. Objects are often plated with thin layers of silver or gold for appearance. In the electroplating process, the object being plated is used as the cathode, and the source of the metal in the coating is usually in the form of a complex metal ion in solution.

ACTIVITY 4

Electroplating using copper

In copper sulfate solution the copper ion is positive, so it moves to the negative wire. Since the wire is attached to an object, the object gets copper-coated with copper ions. This is the same process that is used for gold and silver-plating of objects. This is called electroplating, or plating objects with metal using electricity. Investigate which kinds of objects can be plated.

Procedure

1. Pour copper sulfate solution into a beaker until it is one-half full.
2. Hook the alligator clamps to the negative and positive terminals of the battery.
3. Attach the object to be plated to the alligator clamp coming from the negative terminal.
4. Place both alligator clamps into the copper sulfate solution inside the beaker. They should not touch each other.
5. Observe whether the object gets a different color or stays the same.

Clean-up: Remember to dilute all chemicals used in this lab before pouring down the drain. Put electroplated objects in the proper waste disposal container.

Results and Discussion:

Table 4

Item Tested	Did the object electroplated? (Yes/No)	Qualitative observations – what happened?
Paperclip		
Toothpick		
Straw		

1. What happened to the color of the objects that were electroplated? What color did they get develop?
2. What color did the liquid turn? Why did it change colors?

Conclusion

Based on your findings –

1. What must be placed at the anode? And what must be placed at the cathode?
2. What can you say about the composition of the electrolyte?
3. What other items would you test for possible coin electroplating?

KEY TERMS

- Electrochemistry
- Oxidation
- Reduction
- Voltaic or galvanic cells
- Daniell cell
- Salt bridge
- Cell notation
- Standard reduction potential
- Standard hydrogen electrode
- Electromotive Force
- Cell potential
- Nernst equation
- Electrolytic cells
- Electrolysis
- Preferential Discharge
- Faraday’s First Law of Electrolysis
- Faraday’s Second Law of Electrolysis
- Primary Batteries
- Secondary Batteries
- Fuel Cells
- Corrosion
- Cathodic protection
- Hall Process
- Electrorefining
- Electroplating

SUMMARY

In this chapter we have focused on electrochemistry, the branch of chemistry that relates electricity and chemical reactions. Electrochemistry involves oxidation-reduction reactions, also called redox reactions. These reactions involve a change in the oxidation state of one or more elements.

In every oxidation-reduction reaction, one substance is oxidized (its oxidation state, or number increases) and one substance is reduced (its oxidation state, or number decreases). The substance that is oxidized is referred to as a reducing agent, or reductant, because it causes the reduction of some other substance. Similarly, the substance that is reduced is referred to as an oxidizing agent, or oxidant, because it causes the oxidation of some other substance.

When we balance a chemical equation, the primary concern is to obey the principle of conservation of mass and conservation of charge. Oxidation number method and ion-electron method are two very important methods for balancing redox reactions.

An oxidization-reduction reaction can be balanced by dividing the reaction into two half-reactions, one for oxidation and one for reduction. A half-reaction is a balanced chemical equation that includes electrons.

In oxidation half-reactions the electrons are on the product (right) side of the equation; we can envision that these electrons are transferred from a substance when it is oxidized. In reduction half reactions, the electrons are on the reactant (left) side of the equation. Each half-reaction is balanced separately, and the two are brought together with proper coefficients to balance the electrons on each side of the equation, so the electrons cancel when the half-reactions are added.

A voltaic (or galvanic) cell uses a spontaneous oxidation-reduction reaction to generate electricity. In a voltaic cell, the oxidation and reduction half-reactions often occur in separate half-cells. Each half-cell has a solid surface called an electrode, where the half-reaction occurs. The electrode where oxidation occurs is called the anode; reduction occurs at the cathode. The electrons released at the anode flow through an external circuit (where they do electrical work) to the cathode. Electrical neutrality in the solution is maintained by the migration of ions between the two half-cells through a device such as a salt bridge.

A voltaic cell generates an electromotive force (emf) that moves the electrons from the anode to the cathode through the external circuit.

The origin of emf is a difference in the electrical potential energy of the two electrodes in the cell. The emf of a cell is called its cell potential, E_{cell}, and is measured in volts. The cell potential under standard conditions is called the standard emf, or the standard cell potential, and is denoted E°_{cell}.

A standard reduction potential can be assigned for an individual half-reaction. This is achieved by comparing the potential of the half-reaction to that of the standard hydrogen electrode (SHE), which is defined to have $E^\circ_{red} = 0$ V.

The standard cell potential of a voltaic cell is the difference between the standard reduction potentials of the half-reactions that occur at the cathode and the anode.

The emf, E, is related to the change in the Gibbs free energy, ΔG, where $\Delta G = -nFE$.

Because E is related to ΔG, the sign of E indicates whether a redox process is spontaneous or non-spontaneous: $E > 0$ indicates a spontaneous process, and $E < 0$ indicates a non-spontaneous one. Because ΔG is also related to the equilibrium constant for a reaction , we can relate E to K as well.

The emf of a redox reaction varies with temperature and with the concentrations of reactants and products. The Nernst equation relates the emf under non-standard conditions to the standard emf and the reaction quotient Q.

A concentration cell is a voltaic cell in which the same half-reaction occurs at both the anode and cathode but with different concentrations of reactants in each half-cell. At equilibrium, $Q = K$ and $E = 0$.

A battery is a self-contained electrochemical power source that contains one or more voltaic cells. Batteries are based on a variety of different redox reactions. Several common batteries were discussed. The lead-acid battery, the nickel-cadmium battery, the nickel-metal-hydride battery, and the lithium-ion battery are examples of rechargeable batteries. The common alkaline dry cell is not rechargeable. Fuel cells are voltaic cells that utilize redox reactions in which reactants such as H_2 have to be continuously supplied to the cell to generate voltage.

Unlike electrolytic cells, the anode is negative and the cathode is positive in voltaic cells.

Electrochemical principles help us understand corrosion, undesirable redox reactions in which a metal is attacked by some substance in its environment. The corrosion of iron forming rust is caused by the presence of water and oxygen, and it is accelerated by the presence of electrolytes. The protection of a metal by putting it in contact with another metal that more readily undergoes oxidation is called cathodic protection.

An electrolysis reaction, which is carried out in an electrolytic cell, employs an external source of electricity to drive a non-spontaneous electrochemical reaction.

The quantity of substances formed during electrolysis can be calculated by considering the number of electrons involved in the redox reaction and the quantity of electrical charge that passes into the cell. The quantity of electrical charge is measured in coulombs and is related to the magnitude of the current and the time it flows.

Electrolysis has important industrial applications such as in the production of chemicals like NaOH, in the production of non-metals like Cl_2 and H_2, metals like Na, Al and in purification of metals and electroplating.

Exercises

Part I: Choose the correct answer for each of the following questions

1. In an electroplating experiment 4 ampere electric current is passed for 2 minutes. Hence, m gram Ag is deposited at cathode. If 6 ampere current is passed for 40 second, then what amount Ag is deposited at cathode?
   (a) 2m (b) 4m (c) m/2 (d) m/4
2. 4.5g Al deposited on passing necessary quantity of electricity through Al^{3+} solution. What volume of hydrogen gas will be obtained at STP on passing same quantity of electricity through the solution of H^+(aq) having sufficient concentration? (At. Wt Al=27 g/mol)
   (a) 44.4L (b) 222.4L (c) 1.2L (d) 5.6L
3. Of the following metals those that cannot be obtained by the electrolysis of aqueous solution of their salts are:
   (a) Ag and Mg (c) Mg and Al
   (b) Ag and Al (d) Cu and Cr
4. The weight of silver (Eq. Wt = 108) displaced by the quantity of current which displaced 5600 mL of oxygen at STP is:
   (a) 54g (b) 108g (c) 5.4g (d) 10.8g
5. Oxygen is acting as an oxidizing agent in all of the following except:
   (a) $K + O_2 \longrightarrow KO_2$ (c) $2F_2 + O_2 \longrightarrow 2OF_2$
   (b) $K + O_2 \longrightarrow K_2O$ (d) $2Na + O_2 \longrightarrow Na_2O_2$
6. During electrolysis of an aqueous solution of $AgNO_3$, what would happen to the mass of silver metal deposited if the current is doubled and the electrolysis time is decreased to ½ of its initial value?
   (a) It would decrease to ½ of its value
   (b) It would increase twice the initial value
   (c) It would decrease to ¼ of its initial value
   (d) It would stay the same
7. Electrolytic and Galvanic cells are similar in that:
   (a) The cathode is negative and the anode is positive in both types of cells
   (b) Both types of cells convert electrical energy to chemical energy

(c) The cell reaction in both types of cells are spontaneous redox reactions

(d) The anode and cathode half-reactions are oxidation and reduction respectively in both types of cells

8. Given: $H_2Se + 4O_2F_2 \longrightarrow SeF_6 + 2HF + 4O_2$; which one is true?

(a) The oxidation number of O does not change

(b) F undergoes disproportion reaction

(c) The oxidation number of F changes from 1 to -1.

(d) The oxidation of Se changes from -2 to +6.

9. During the electrolysis of an aqueous solution of $CuSO_4$ using platinum electrodes, the reaction that takes place at the anode is:

(a) $Cu^{2+} + 2e^- \longrightarrow Cu$
(c) $2H_2O \longrightarrow 4H^+ + O_2 + 4e^-$
(b) $Cu \longrightarrow Cu^{2+} + 2e^-$
(d) $4H^+ + O_2 + 4e^- \longrightarrow H_2O$

10. What are the values of b, d, and f in the balanced equation of the following reaction?

Reaction: $aMnO_4^- + bAs_2O_3 + cH_2O \longrightarrow dMn^{2+} + eAsO_4^{3-} + fH^+$

(a) 5, 2, 24
(c) 5, 4, 18
(b) 4, 10, 9
(d) 5, 4, 9

11. In the balanced state of the reaction,
$aBr_2 + bOH^- + cH_2O \longrightarrow dBrO_4^- + eHBr$, what will be the value of d and e respectively?

(a) 8, 2 (b) 2, 6 (c) 6, 2 (d) 2, 14

12. What would be the change in pH of the solution, when electrolysis of $CuSO_4$ is carried out using inert electrodes?

(a) pH increases
(c) no change in pH
(b) pH decreases
(d) can not be predicted

13. Which one of the following relation is correct for Faraday's 2nd law? (m = mass and E = equivalent mass of the substance)

(a) $m_1E_1 = m_2E_2$
(c) $m_1m_2 = E_1E_2$
(b) $m_1E_2 = m_2E_1$
(d) $m_1 = E_2m_2/E_1$

14. How many gram of Ag will be obtained if 5.0 F quantity of electricity is passed through aqueous solution of $AgNO_3$?

(a) 270g (b) 540g (c) 180g (d) 135g

15. During the electrolysis of aqueous solution of NaCl with inert electrodes at the cathode instead of Na^+ reduction of H^+ takes place because:

(a) compared to H^+ standard reduction potential of Na^+ is higher

(b) sodium metal is inactive metal

(c) standard oxidation potential of H^+ is very high

(d) reduction potential of Na^+ is very less

16. What quantity of electricity is required for complete reduction of Ag^+ from 1.0 M , 250 mL of $AgNO_3$ aqueous solution?

(a) 2,412.5 C (c) 4,825 C

(b) 24,125 C (d) 25,250 C

17. Which of the following reactions will not occur spontaneously?

(a) $Cu^{2+} + Pb \longrightarrow Cu + Pb^{2+}$

(b) $Sn^{2+} + Zn \longrightarrow Sn + Zn^{2+}$

(c) $2K^+ + Ca \longrightarrow 2K + Ca^{2+}$

(d) $3Hg^{2+} + 2Al \longrightarrow 3Hg + 2Al^{3+}$

18. In the cell reaction:

$Cu\ (s) + 2Ag^+ (aq) \longrightarrow Cu^{2+} (aq) + 2Ag\ (s)$,

$E^o_{cell} = 0.46$ V. By doubling the concentration of Cu^{2+}, E^o_{cell} will become:

(a) doubled (c) increases but less than double

(b) halved (d) decreases by a small fraction

19. The standard reduction potential for Fe^{2+}/ Fe and Sn^{2+}/ Sn electrodes are –0.44 and –0.14 Volt respectively.

For the cell reaction $Fe^{2+} + Sn \longrightarrow Fe + Sn^{2+}$ the standard emf will be:

(a) +0.30 V (b) –0.58 V (c) +0.58 V (d) –0.30 V

20. The Nerst equation $E = E^o - (RT/nF) \ln Q$ indicates that Q will be equal to K when:

(a) $E = E^0$ (c) $E = 0$

(b) $RT/nF = 1$ (d) $E^0 = 1$

Part II: Short Answer Questions

1. Indicate whether each of the following statements is true or false:

(a) If something is being oxidized, it is formally losing electrons.

(b) For the reaction $Fe^{3+} (aq) + Co^{2+} (aq) \longrightarrow Fe^{2+} (aq) + Co^{3+} (aq)$, $Fe^{3+} (aq)$ is the reducing agent and $Co^{2+}(aq)$ is the oxidizing agent.

(c) If there are no changes in the oxidation state of the reactants or products of a particular reaction, that reaction is not a redox reaction.

(d) A reducing agent gets oxidized as it reacts.

(e) Oxidizing agents can convert CO into CO_2.

(f) A galvanic cell uses a spontaneous redox reaction to produce a current that can be used to do work.

(g) $\Delta G°$ and E^o_{cell} are positive when $K > 1$.

2. Balance the following equations using oxidation number method:
   (a) $FeSO_4 + KMnO_4 + H_2SO_4 \longrightarrow MnSO_4 + Fe_2(SO_4)_3 + K_2SO_4 + H_2O$
   (b) $As_2S_5 + HNO_3 \longrightarrow H_3AsO_4 + H_2SO_4 + NO_2 + H_2O$
3. Balance the following redox equations by the ion electron method:
   (a) $H_2O_2 + Fe^{2+} \longrightarrow Fe^{3+} + H_2O$ (in acidic solution)
   (b) $Cr_2O_7^{2-} + C_2O_4^{2-} \longrightarrow Cr^{3+} + CO_2$ (in acidic solution)
   (c) $CN^- + MnO_4^- \longrightarrow CNO^- + MnO_2$ (in basic solution)
   (d) $I_2 + OH^- \longrightarrow I^- + IO_3^-$(basic)
4. What is a cell diagram? Write the cell diagram for a galvanic cell consisting of an Al electrode placed in a 1 M $Al(NO_3)_3$ solution and a Ag electrode placed in a 1 M $AgNO_3$ solution.
5. Write the equations relating $\Delta G°$ and K to the standard emf of a cell. Define all the terms.
6. Calculate $E°_{cell}$ for the reactions below to be determine which are spontaneous as written:
   (a) $Co\,(s) + H^+(aq) \longrightarrow Co^{+2}(aq) + H_2(g)$
   (b) $Mn^{+2}(aq) + Co^{+3}(aq) \longrightarrow MnO_2(s) + Co^{+2}(aq)$
7. Calculate E^o, and ΔG^o for the following reaction
   $6\,Hg^{2+}(aq) + 2\,Au\,(s) \longrightarrow 3\,Hg_2^{2+}(aq) + 2\,Au^{3+}$
8. The net equation for a given voltaic cell is:
   $Sn\,(s) + 2\,Ag^+ \longrightarrow Sn^{2+} + 2\,Ag\,(s)$
   (a) Write the two half-reactions involved.
   (b) Calculate the net potential of the cell (the voltage), assuming standard conditions.
   (c) Draw a labeled diagram of the voltaic cell. Indicate the flow of electrons in the external circuit (through the wire) and the flow of ions in the solution.
9. Calculate the standard free energy change for the following reaction at 25°C. (Hint use Table 1).
   $Mg(s) + Zn^{2+}\,(1.0\,M) \longrightarrow Zn(s) + Mg^{2+}\,(1.0\,M)$
10. Calculate the volume of H_2 and O_2 gases that, at 25°C and 1.00 atm, will be collected at the cathode and anode, respectively, when an aqueous solution of Na_2SO_4 is electrolyzed for 1.5 h with a 10 A current.

11. A galvanic cell operates through the reaction represented below.

    $3Cu^{2+} (aq) + 2Cr (s) \longrightarrow 3 Cu (s) + 2Cr^{3+} (aq)$

    (a) What is the standard cell potential for the reaction?
    (b) Find the free energy change that occurs for the reaction?
    (c) How would the cell potential differ from the standard cell potential if the cell is assembled so that $[Cu^{2+}]$ is 0.65 M and $[Cr^{3+}]$ is 0.25 M at 25°C?
    (d) Is the reaction thermodynamically favored under the conditions specified in part (C)? Explain.

12. Write the anode, cathode half reactions and cell reactions for the electrolysis of:

    (a) dilute sodium hydroxide
    (b) molten lithium iodide
    (c) molten tin(II) sulfide
    (d) aqueous $CuSO_4$ solution using:
        (i) Graphite electrode
        (ii) Copper electrode

13. Three electrolytic cells A, B and C containing electrolytes $AlCl_3$, $CuSO_4$ and $AgNO_3$ respectively were connected in series. A steady current of 1.287 ampere was passed through the cells for a definite time. After electrolysis 2.158 g of silver were deposited at the cathode. Calculate:

    (i) The total charge passed during electrolysis.
    (ii) The mass of aluminum deposited at cathode of cell A.
    (iii) The mass of Copper deposited at cathode of cell B.

14. Which of the following metals are suitable for use as sacrificial anodes to protect against corrosion of underground iron pipes?

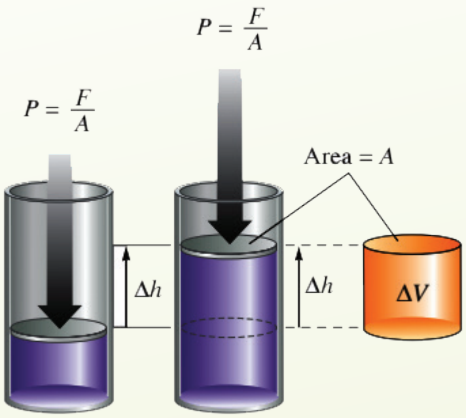
    (a) Al
    (b) Pb
    (c) Mn
    (d) Mg
    (e) Cd

C11CH05

CHAPTER 5

CHEMICAL ENERGETICS

Chapter Contents



Chapter Outcomes

By the end of this chapter, you will be able to:

- perform comparative analysis, on the concept of energetics and interpret related energy level diagrams.
- compare the energy change observed when chemical bonds are formed and broken, and relate these changes to endothermic and exothermic reactions;
- demonstrate scientific enquiry skills including: communicating, measuring, applying concepts and asking questions.

5.1 THERMODYNAMICS

Upon completion of this topic, learners will be able to:

- identify the systems and the surroundings in a chemical process.
- identify the ways in which energy is transferred in the chemical process.
- explain exothermic and endothermic chemical reactions.
- explain internal energy, work and heat in relation to the concept of thermodynamics.
- state the first law of thermodynamics.
- define enthalpy change.
- calculate enthalpy changes from experimental results, including the use of the relationship q = mcΔT.

Thermodynamics is the study of the relationships between heat, work, temperature, and energy.

The laws of thermodynamcis describe how the energy in a system changes and whether the system can perform useful work on its surroundings or not.

To analyze energy changes associated with chemical reactions we must first define the system, or the specific part of the universe that is of interest to us. For chemists, systems usually include substances involved in chemical and physical changes. For example, a system may be a beaker containing a solution of $Ba(OH)_2$ and NH_4NO_3. The surroundings are the rest of the universe outside the system.

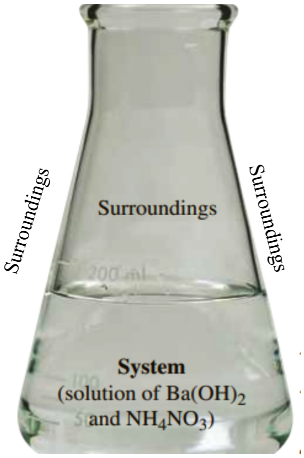


Figure 1. Illustration of a thermodynamic system and surroundings

There are three types of systems. An open system can exchange mass and energy, usually in the form of heat with its surroundings. For example, an open system can consist of a quantity of water in an open container, as shown in Figure 2 (a). If we close the flask, as in Figure 2 (b), so that no water vapor can escape from or condense into the container, we create a closed system, which allows the transfer of energy (heat) but not mass. By placing the water in a totally insulated container, we can construct an isolated system, which does not allow the transfer of either mass or energy, as shown in Figure 2 (c).

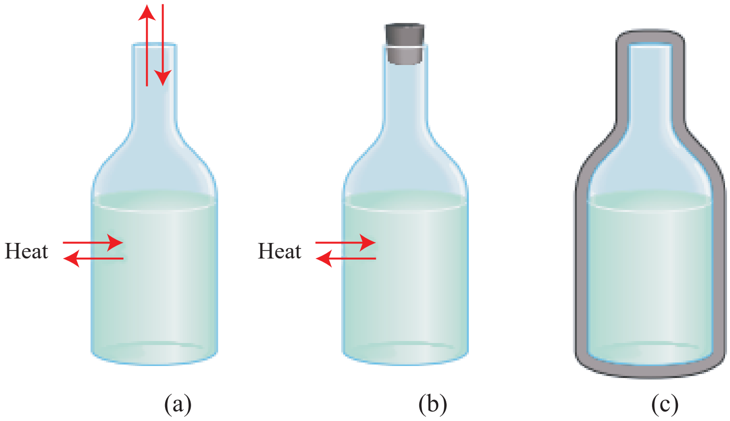


Figure 2. Types of systems

A system is said to be in a certain state if T, P, V, n (observable variables) do not change with time. An equation that relates these observable variables is called an equation of state. An ideal-gas equation is an example of equation of state. A thermodynamic function that depends on the initial and final state of a system, regardless of how that condition was achieved, is called a state function. Examples are energy, volume, pressure, etc. Functions that depend on the path are path functions. Examples are heat and work.

Chemical energy

Reactions that absorb energy from the surroundings are said to be endothermic. When the heat flow is into a system, the process is endothermic. For example, the formation of nitric oxide from nitrogen and oxygen is endothermic:

$$N_2(g) + O_2(g) + \text{Energy}(\text{heat}) \longrightarrow 2NO(g)$$

When a reaction results in the evolution of heat, it is said to be exothermic that is, energy flows out of the system. For example, in the combustion of methane, energy flows out of the system as heat.

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g) + \text{Energy}(\text{heat})$$

Where does the energy, released as heat, come from in an exothermic reaction?

The answer lies in the difference in potential energies between the products and the reactants. Which has lower potential energy, the reactants or the products?

The energy diagram for the combustion of methane is shown in Figure 3, where (PE) represents the change in potential energy stored in the bonds of the products as compared with the bonds of the reactants. In an exothermic process, the bonds in the products are stronger (on average) than those of the reactants. That is, more energy is released by forming the new bonds in the products than is consumed to break the bonds in the reactants. The net result is that the quantity of energy (PE) transferred to the surroundings through heat.

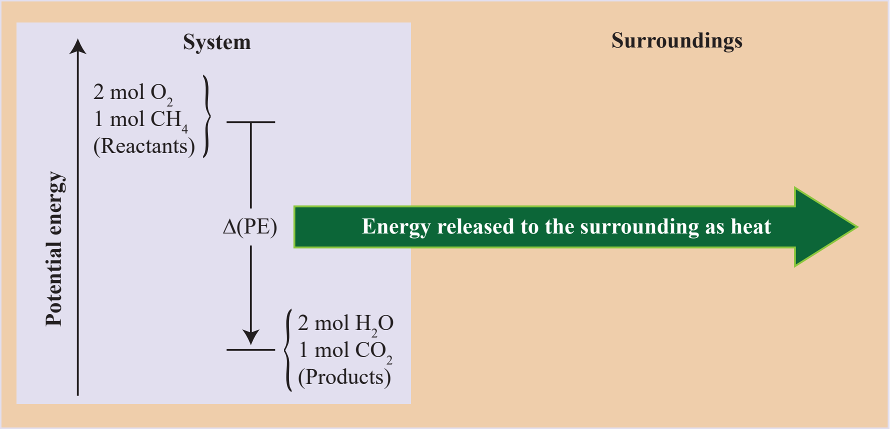


Figure 3. The combustion of methane releases the quantity of energy (PE) to the surroundings via heat flow.

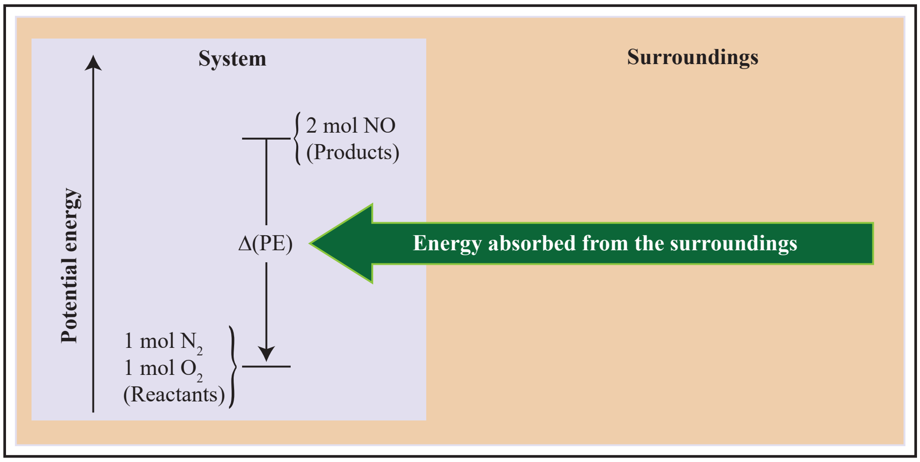


Figure 4. The energy diagram for the reaction of nitrogen and oxygen to form nitric oxide.

For an endothermic reaction, the situation is reversed, as shown in Figure 4. Energy that flows into the system as heat is used to increase the potential energy of the system. In this case, the products have higher potential energy (weaker bonds on average) than the reactants.

Internal energy

The internal energy (E) of a system is the total energy contained within a system, partly as kinetic energy and partly as potential energy.

The kinetic energy component of internal energy consists of various types of molecular motion and the movement of electrons within molecules.

Potential energy is a factor of:

- Attractive and repulsive interaction between molecules;
- Attractive interactions between electrons and nuclei within molecules;
- Repulsive interactions between electrons within molecules; and
- Repulsive interactions between nuclei within molecule.

When a chemical system changes from reactants to products and the product returns to the starting reactant, the internal energy has changed. To determine this change, ΔE, we measure the difference between the systems internal energy after the change (E_{final}) and before the change ($E_{initial}$).

$$\Delta E = E_{final} - E_{intial}$$

Law of conservation of energy

The law of conservation of energy states that energy may be converted from one form to another, but the total quantity of energy remains constant. The energy of the universe is constant. The first law of thermodynamics is a specific statement of the conservation of energy, especially useful in discussing chemical reactions.

The first law of thermodynamics relates the change in internal energy of a physical or chemical change taking place in a container to the flows (transfers) of energy into or out of the container. These energy transfers are of two kinds: work and heat.

Work (W)

Work, is an energy transferred between a system and its surroundings. A common type of work associated with chemical processes is work done by a gas (through expansion) or work done to a gas (through compression).

Suppose we have a gas confined to a cylindrical container that is fitted with a movable piston as shown in Figure 5, where F is the force acting on the piston of area A. Since pressure is defined as force per unit area, the pressure of the gas is:

$$P = \frac{F}{A}$$

Work is defined as a force applied over a given distance, so if the piston moves a distance Δh, as shown in Figure 5, then the magnitude of the work is:

$$\text{Work} = \text{Force} \times \text{Distance} = F \times \Delta h$$

$$\text{Since } P = \frac{F}{A}, \text{ or } F = P \times A, \text{ then}$$

$$\text{Work} = F \times \Delta h = P \times A \times \Delta h$$

The product of the cross-sectional area of the cylinder, A, and the height, Δh, represents the change in volume of the gas, which is designated by the symbol ΔV. By replacing A × Δh with its equivalent, ΔV, we see that the work associated with a gas that expands at constant pressure is described by the following equation:

$$\text{Work} = P \times A \times \Delta h = P\Delta V$$

The product of pressure and a change in volume is usually called "pressure-volume" work. When a gas expands, ΔV is positive, and the work is negative:

$$\text{Work} = -P\Delta V$$

A negative quantity of work signifies that the system loses energy, and that this, energy is transferred from the system to the surroundings.

When a gas is compressed by its surroundings, ΔV is negative, the quantity of work is positive and energy is gained by the system.

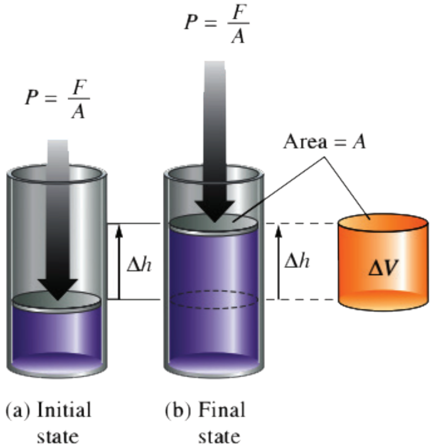


Figure 5. (a) The piston, moving a distance Δh against a pressure P, does work on the surroundings. (b) Since the volume of a cylinder is the area of the base times its height, the change in volume of the gas (ΔV) is given by A × Δh.

Heat (Q)

Heat (thermal energy) is the energy transferred between a system and its surroundings as a result of a difference in their temperatures. Heat passes spontaneously from the region of higher temperature to the region of lower temperature. Heat transfer stops when the system and surroundings reach the same temperature and therefore the system and surroundings are at thermal equilibrium.

The SI unit of heat is joule (J). Another unit of heat is calorie. A calorie (Cal) is the amount of heat, or other energy, necessary to raise the temperature of 1 g of water by 1 degree Celsius. A kilocalorie (kCal) is 1000 calories, and 4.184 Joules is equivalent to 1.0 calorie.

The temperature change experienced by an object when it absorbs a certain amount of energy is determined by its heat capacity. Heat capacity is defined as the amount of heat energy required to raise its temperature by 1° (or 1 K). For pure substances, heat capacity is usually given for a specified amount of the substance. The heat capacity of 1 mol of a substance is called its molar heat capacity. In all thermodynamic calculations temperature must be expressed in Kelvin (K).

Heat capacity of 1g of a substance is called its specific heat. Specific heat of a substance can be determined experimentally by measuring the temperature change (ΔT) for a known mass (m) of a substance that gains or loses a specific quantity of heat, q

$$\text{Specific heat}\,(c) = \frac{\text{Quantity of heat transferred}}{(\text{Grams of substance}) \times (\text{Temperature change})}$$

$$= \frac{q}{m \times \Delta T}, \qquad \text{where } \Delta T = T_{\text{final}} - T_{\text{initial}}$$

Table 1 Specific heat of some common substances

Substance	**Specific heat ($Jg^{-1}K^{-1}$)**
Aluminium, Al (s)	0.90
Gold, Au (s)	0.13
Carbon (graphite)	0.72
Carbon (diamond)	0.50
Copper, Cu (s)	0.38
Iron, Fe (s)	0.45
Mercury, Hg (l)	0.14
Water, H_2O (l)	4.18
Ethanol, C_2H_5OH (l)	2.46

Example

A flask containing 8.0 × 10^2 g of water is heated, and the temperature of the water increases from 20°C to 85°C. How much heat did the water absorb?

$$q = c \times m \times \Delta T = c \times m \times (T_{final} - T_{initial})$$

$$= 4.184 \frac{J}{g.°C} \times 8.0 \times 10^2\, g \times (85 - 20)°C$$

$$= 4.184 \frac{J}{g.°C} \times 8.0 \times 10^2\, g \times (65)°C$$

$$= 220{,}000\, J = 220\, kJ$$

Because the temperature increased, so water absorbed heat and q is positive.

Exercises

1. How much heat is required to raise the temperature of 250 g of water from 22°C to near its boiling point, 98°C?
2. What is the molar heat capacity of water?

ACTIVITY 1

Exothermic and endothermic processes

After examining each reaction in the laboratory, you should be able to classify them as exothermic or endothermic.

SAFETY

The chemicals can be toxic, please handle with care. Wear your goggles at all times. Be sure to rinse and dry your thermometer after each use.

PROCEDURE

In Part 1 you will study the reaction between acetic acid and sodium bicarbonate (baking soda). An equation for the reaction is

$$CH_3COOH + NaHCO_3 \longrightarrow CH_3COO^-Na^+ + H_2O + CO_2$$

Step 1: Add approximately 5 mL of acetic acid to a large test tube.

Step 2: Record the temperature of the acetic acid. Place your hand on the outside of the beaker to gauge the temperature.

Step 3: Add a small spatula of sodium bicarbonate to the acetic acid.

Step 4: Gently stir (with the thermometer) until all the sodium bicarbonate has been dissolved.

Observe the temperature, record any temperature change and other observations.

Step 5: Discard the solution and clean your equipment.

In part 2 You will study the reaction between HCl and Zn metal. An equation for the reaction is:

$$HCl + Zn \longrightarrow ZnCl_2 + H_2$$

Step 1: Add approximately 5 mL of hydrochloric acid to a test tube.

Step 2: Record the temperature of the hydrochloric acid. Place your hand on the outside of the beaker and feel the temperature of the beaker.

Step 3: Add a small piece of zinc to the hydrochloric acid.

Step 4: Gently stir (with the thermometer) until all the zinc has been dissolved.

Observe the temperature, record any temperature change and other observations.

Step 5: Discard the solution and clean your equipment.

Analysis

1. For these reactions, was heat transferred from the system to the surroundings or from the surroundings to the system?
2. Explain which one is an exothermic process and which is an endothermic process?
3. Was ΔH solution positive or negative?
4. Draw and label the enthalpy diagram for these processes.

First law of thermodynamics

The first law of thermodynamics, which is a restatement of the law of conservation of energy, states that the total amount of energy in the universe is constant. When a system undergoes any chemical or physical change, the accompanying change in its internal energy, ΔE, is given by the heat added to the system, q, plus the work done by the system, W.

$$\Delta E = q + W$$

Thermodynamic quantities always consist of two parts:

- A number plus units, which gives the magnitude of the change; and
- A sign that indicates the direction of the flow.

The sign reflects the system's point of view. For example, if a quantity of energy flows into the system as heat, q is equal to +q, where the positive sign indicates that the system's energy is increasing.

On the other hand, when energy flows out of the system as heat, q equal to –q, where the negative sign indicates that the system's energy is decreasing.

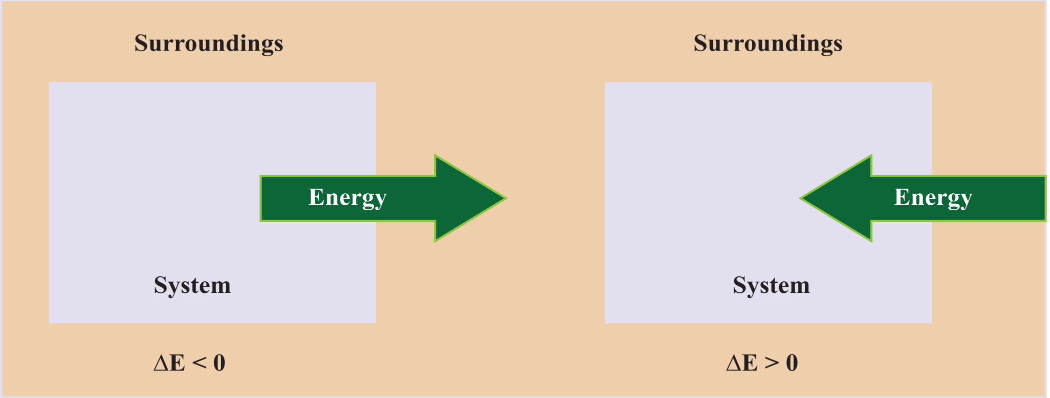


Figure 6. (a)Energy flow out of the system. (b) Energy flow into the system.

This suggests that we need sign conventions to be used with the first law of thermodynamics. The conventions are as follows:

- If heat is absorbed by the system, $q > 0$. If work is done on a system, $W > 0$.
- If heat is given off by a system, $q < 0$. If work is done by a system, $W < 0$.

Example

A gas does 135 J of work while expanding and at the same time, it absorbs 156 J of heat. What is the change in internal energy?

Solution

Note that heat is absorbed by the system (a positive quantity, +156 J) and work is done by the system (a negative quantity, –135 J). Because more heat is absorbed than work done, the internal energy increases: $\Delta E = q + W$

$$\Delta E = (+156\,J) + (-135\,J) = +21\,J$$

Exercises

1. Calculate ΔE for a process in which the system absorbs 65 J of heat and 12 J of work is done on it by the surroundings.
2. A balloon is inflated to its full size by heating the air inside it. In the final stages of this process, the volume of the balloon changes from 4.00×10^6 L to 4.50×10^6 L by addition of 1.3×10^8 J of energy as heat. Assuming the balloon expands against a constant pressure of 1.0 atm, calculate ΔE for the process.

Enthalpy and enthalpy changes

When a reaction occurs against a constant external pressure (say the atmosphere), the heat of reaction equals the change of another thermodynamic quantity, this one called the enthalpy and denoted by the symbol H. The enthalpy of a thermodynamic system is defined as its internal energy, E, plus pressure, P, times volume, V.

$$H = E + PV$$

Because E, P, and V are state functions, H is also a state function. This means that for a given temperature and pressure, a change in enthalpy does not depend on the pathway between two states.

In addition, enthalpy is an extensive property (it depends on the amount of substance). And like the internal energy, we are normally interested only in changes of the property enthalpy.

Consider a process carried out at constant pressure, where the only work allowed is pressure-volume work ($w = -p\Delta V$). Under these conditions the expression:

$$\Delta E = q_p + W$$

Becomes

$$\Delta E = q_p - p\Delta V$$

Or

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

where q_p is the heat at constant pressure. We will now relate q_p to the change in enthalpy.

The definition of enthalpy is $H = E + PV$. Therefore,

$$(\text{Change in H}) = (\text{Change in E}) + (\text{Change in PV})$$

Or

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

Since P is constant, the change in PV is caused only by a change in volume. Thus

$$\Delta(PV) = P\Delta V$$

and

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

This expression is identical to the one we obtained for q_p:

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

Thus, for a process carried out at constant pressure, where the only work allowed is that from a volume change,

$$\Delta H = q_p$$

At constant pressure (where only PV work is allowed), the change in enthalpy (ΔH) of the system is equal to the energy flow as heat. This means that for a reaction studied at constant pressure, the flow of heat is a measure of the change in enthalpy for the system. For a chemical reaction, the enthalpy change is given by the equation

$$\Delta H = H_{\text{product}} - H_{\text{reactant}}$$

Changes of state

In this section, we examine what happens when any of the three forms of matter is converted to either of the other two. These changes of state are often called phase changes. The six most common phase changes are shown in Figure 7.

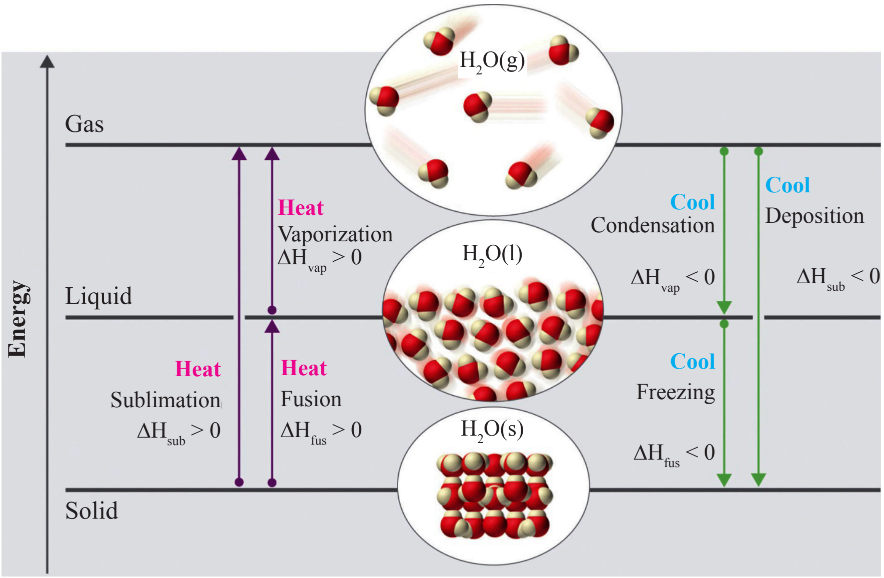


Figure 7. The three phases of matter and the processes that interconvert them when the temperature is changed

Phase changes are always accompanied by a change in the energy of a system. For example, converting a liquid, in which the molecules are close together, to a gas, in which the molecules are, on average, far apart, requires an input of energy (heat) to give the molecules enough kinetic energy to allow them to overcome the intermolecular attractive forces. The stronger the attractive forces, the more energy is needed to overcome them.

Any transition from a more ordered to a less ordered state (solid to liquid, liquid to gas, or solid to gas) requires an input of energy; it is *endothermic process*. Conversely, any transition from a less ordered to a more ordered state (liquid to solid, gas to liquid, or gas to solid) releases energy; it is *exothermic process*.

Energy changes that accompany phase changes

The enthalpy associated with any phase change can be experimentally quantified and tabulated. Each particular phase change has an associated heat and is given a particular name.

For example, the enthalpy change for melting is defined as the enthalpy change for changing from a solid to a liquid at the melting temperature. For water this would be

$H_2O(s, 0°C) \rightleftharpoons H_2O(l, 0°C)$

The process of going from solid to liquid is referred as fusion. The enthalpy for this change is ΔH_{fusion}. This a change in enthalpy,

$$\Delta H_{fusion} = H_f - H_i = H_{liquid} - H_{solid}$$

Because of this, the enthalpy for the opposite process, freezing, will be exactly equal but opposition in sign.

$$\Delta H_{freezing} = H_{solid} - H_{liquid} = -\Delta H_{fusion}$$

This means that only one value is tabulated. Typically it is the endothermic process. Thus, for solid/liquids the fusion value is tabulated. For liquids/gases you will find tabulated data for $\Delta H_{vaporization}$. Again for the opposite process (gas to a liquid) the enthalpy is equal but opposite in sign.

$$\Delta H_{vaporization} = -\Delta H_{condensation}$$

The same follows for the solid/gas phase transitions of sublimation (solid to gas) and deposition (gas to solid).

$$\Delta H_{sublimation} = -\Delta H_{deposition}$$

Experimental data analysis

We can measure the enthalpy change of some reactions by a technique called calorimetry. The apparatus used is called a calorimeter. A simple calorimeter can be a polystyrene drinking cup (Figure 8), a vacuum flask or a metal can.

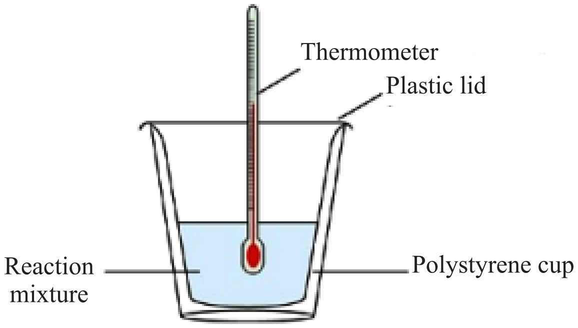


Figure 8. A polystyrene cup can act as a calorimeter for finding some enthalpy changes.

When carrying out experiments in calorimeters, we use known amounts of reactants and known volumes of liquids. We also measure the temperature change of the liquid in the calorimeter as the reaction occurs.

Calorimetry relies on the fact that it takes 4.18 J of energy to increase the temperature of 1 g of water by 1°C.

The heat transferred for a known number of moles of reactants in the calorimeter is given by:

$$q = mc\Delta T$$

We can scale this up to get the enthalpy change per mole of a defined reactant or product. The relationship we then use is:

$$\Delta H = -mc\Delta T$$

Note: A rise in temperature is given a positive sign. So the value of ΔH is negative for an exothermic reaction. A fall in temperature is given a negative sign. So the value of ΔH is positive for an endothermic reaction.

ACTIVITY 2

The enthalpy change of neutralisation reaction by an experiment

SAFETY: Perform this activity in the presence of a teacher while observing safety aspects, which have been already explained.

We can find the enthalpy change of neutralisation of sodium hydroxide with hydrochloric acid by mixing equal volumes of known equimolar concentrations of acid and alkali together in a polystyrene cup.

Procedure

1. Place 50 cm^3 of 1.0 M hydrochloric acid in the cup and record its temperature.
2. Add 50 cm^3 of 1.0 M sodium hydroxide (at the same temperature) to the acid in the cup.
3. Stir the reaction mixture with the thermometer and record the highest temperature

In this experiment most of the heat is transferred to the solution, as the polystyrene cup is a good insulator. Cooling of the warm solution is not a great problem since the reaction is rapid so the maximum temperature is reached before much cooling of the warm solution has occurred. However, there are still heat losses to the air and to the thermometer, which make the result less exothermic than the data book value of -57.1 kJ mol^{-1}.

Results and calculations

Record the temperature as follows:

Initial temperature of NaOH ....

Temperature of the mixture of NaOH and HCl ....

Change in temperature, ΔT = ...

The total mass of the solution is 100 g (100 mL), and the specific heat of the solution is ....

Analysis

1. Calculate the heat of neutralization.
2. Is the value obtained for the heat of neutralization larger or smaller than 57.1 kJ? Why?
3. If more acid is added after neutralization, no more rise in temperature will take place. What is the reason?

5.2 STANDARD ENTHALPY CHANGE

Upon completion of this topic, learners will be able to:

- define and use the term standard conditions.
- define and use the term enthalpy change with particular reference to enthalpy changes of reaction, formation, combustion and neutralization.

Standard conditions

To make any fair comparison of enthalpy changes, we must use the same conditions, called standard conditions. These are:

- Pressure of 101 kPa (approximately normal atmospheric pressure)
- Temperature of 298 K (25°C)
- Each substance involved in the reaction is in its normal physical state (solid, liquid or gas) at 101 kPa and 298 K.

The symbol (^{0}) is used to indicate that the enthalpy change refers to a reaction carried out under standard conditions.

The information in the equation:

$$C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l) \quad \Delta H_c{}^0 = -2803\,kJ$$

shows us that when one mole of glucose reacts with six moles of oxygen gas to form six moles of carbon dioxide gas and six moles of water in the liquid state, the standard enthalpy change is -2803 kJ.

We can describe enthalpy changes according to the type of chemical reaction taking place. These includes

- Enthalpy change of combustion
- Enthalpy change of formation
- Enthalpy change of neutralisation.

In more general cases we can use the term:

- Enthalpy change of reaction.

A. Standard enthalpy of combustion, ΔH_c^0

The standard enthalpy change of combustion, ΔH_c^0 is the enthalpy change when one mole of a substance is burnt in excess oxygen under standard conditions. The reactants and products must be in their standard states.

Enthalpy changes of combustion are always exothermic. The substances combusted can be either elements or compounds.

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \quad \Delta H_c^0 = -890.3\,kJ\,mol^{-1}$$

B. Standard enthalpy of formation, ΔH_f^0

The standard enthalpy of formation, ΔH_f^0, is the change in enthalpy in the reaction when one mole of a substance is formed from the elements in their standard states. By definition, the standard enthalpy of formation of the most stable form of any element is zero.

Take the element oxygen as an example. Molecular oxygen (O_2) is more stable than the other allotropic form of oxygen, ozone (O_3), at 1 atm and 25°C. Thus, we can write:

$$\Delta H_f^0\ (O_2) = 0, \text{ but } \Delta H_f^0\ (O_3) = 142.2 \text{ kJ/mol.}$$

Table 2 Standard enthalpies of formation, ΔH_f^o, of some substances at 25°C.

Substance	ΔH_f^0 (kJ/mol)	Substance	ΔH_f^0 (kJ/mol)
Br_2 (l)	0	C_3H_8 (g)	-103.85
HBr (g)	-36.2	C_6H_6 (l)	-48.99
C (Graphite)	0	I_2 (s)	0
C (Diamond)	1.90	HI (g)	25.9
CO (g)	-110.5	Mg (s)	0
CO_2 (g)	-393.5	MgO (s)	-601.8
Ca (s)	0	$MgCO_3$ (s)	-1112.9
CaO (s)	-635.6	N_2 (g)	0
$CaCO_3$ (s)	-1206.9	NH_3 (g)	-46.3
Cl_2 (g)	0	NO (g)	90.3

Substance	**ΔH_f^0 (kJ/mol)**	**Substance**	**ΔH_f^0 (kJ/mol)**
HCl (g)	-92.3	NO_2 (g)	33.85
F_2 (g)	0	N_2O (g)	81.56
HF (g)	-271.6	N_2O_4 (g)	9.66
H (g)	218.2	O (g)	249.4
H_2 (g)	0	O_2 (g)	0
H_2O (g)	-241.8	O_3 (g)	142.2
H_2O (l)	-285.8	S (Rhombic)	0
H_2O_2 (l)	-187.6	S (Monoclinic)	0.30
SO_2 (g)	-296.1	H_2S (g)	-20.15
SO_3 (g)	-395.2		

Enthalpy changes of formation can be exothermic or endothermic. We write the formula of the compound in square brackets after $\Delta H_f{}^0$ to help us when we do calculations involving enthalpy changes. Examples are:

$$2Fe(s) + \frac{3}{2}O_2(g) \longrightarrow Fe_2O_3(s) \qquad \Delta H_f{}^0\left[Fe_2O_3(s)\right] = -824.2 \text{ kJ mol}^{-1}$$

$$2C(\text{Graphite}) + 2S(s) \longrightarrow CS_2(l) \qquad \Delta H_f{}^0\left[CS_2(l)\right] = +98.7 \text{ kJ mol}^{-1}$$

C. Enthalpy of reaction, $\Delta H_r{}^0$

The importance of the standard enthalpies of formation is that once we know their values, we can readily calculate the standard enthalpy of a reaction, $\Delta H_r{}^0$, defined as the enthalpy of a reaction measured at 1 atm. For example, consider the hypothetical reaction:

$$aA + bB \longrightarrow cC + dD$$

where a, b, c, and d are stoichiometric coefficients. For this reaction $\Delta H_r{}^0$ is given by

$$\Delta H_r{}^0 = \left[c\Delta H_f{}^0(C) + d\Delta H_f{}^0(D)\right] - \left[a\Delta H_f{}^0(A) + b\Delta H_f{}^0(B)\right]$$

We can generalize as:

$$\Delta H_r{}^0 = \sum n\Delta H_P{}^0(\text{products}) - \sum m\Delta H_r{}^0(\text{reactants})$$

where m and n denote the stoichiometric coefficients for the reactants and products.

Example

The standard enthalpies of formation of NH_3, H_2O and NO are –46.2, –241.8 and 90.3 kJ/mol, respectively. Calculate the enthalpy of the reaction:

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

Solution

The convenient way to begin this kind of calculation is to list ΔH_f^0 under the formula of each substance in the equation:

$$\begin{array}{cccc} 4NH_3(g) + & 5O_2(g) \longrightarrow & 6H_2O(l) + & 4NO(g) \\ -46.2\text{ kJ} & 0 & -241.8\text{ kJ} & 90.3\text{ kJ} \end{array}$$

Now we can multiply these ΔH_f^0 values by the numbers of moles given by the coefficients in the equation. In substituting these values into the general equation for, ΔH_f^0 remember that we must subtract the sum of the terms for the reactants from the sum of the terms for products.

$$\Delta H_r^0 = \left(6\Delta H_f^0[H_2O] + 4\Delta H_f^0[NO]\right) - \left(4\Delta H_f^0[NH_3] + 5\Delta H_f^0[O_2]\right)$$

$$\Delta H_r^0 = 6(-241.8\text{kJ}) + 4(90.3\text{kJ}) - (4(-46.2\text{kJ}) + 5(0\text{kJ}))$$

$$= -1450.8\text{kJ} + 361.2\text{kJ} + 184.8\text{kJ} - 0\text{kJ}$$

$$= -904.8\text{ kJ}$$

Exercises

1. Using the standard enthalpies of formations given in Table 2, calculate the $\Delta H°$ for the reaction:

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

2. Compare the quantity of heat produced by combustion of 1.00 g of propane, C_3H_8, with that produced by 1.00 g of benzene, C_6H_6.

A. Enthalpy of neutralization, ΔH^0_{neut}

The standard molar enthalpy of neutralization, ΔH^0_{neut} is the change in enthalpy when one mole of an acid or a base is completely neutralized. For example, the heat of neutralization for:

$$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l) \qquad \Delta H^0_{neut} = -56.2\text{ kJ/mol}$$

For any acid-base reaction the ionic equation is:

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$$

The other ions in solution (Cl^- and Na^+) are spectator ions and take no part in the reaction.

5.3 HESS'S LAW

Upon completion of this topic, learners will be able to:

- calculate change in enthalpy of a reaction using Hess' Law.
- calculate change in standard enthalpy of a reaction using tables of change in enthalpy of formation.

Many compounds cannot be directly synthesized from their elements. In some cases, the reaction proceeds too slowly, or side reactions produce substances other than the desired compound. In these cases, ΔH_f^o can be determined by an indirect approach, which is based on Hess's law of heat summation, or simply Hess's law.

Hess's law can be stated as follows: When reactants are converted to products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps. Hess's law is based on the fact that because H is a state function, ΔH depends only on the initial and final state (that is, only on the nature of reactants and products).

Let us understand the importance of this law with the help of an example. For example, we can think of the reaction of carbon with oxygen to form carbon dioxide as occurring either directly or by a two-step process. The direct process is written:

$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H^0 = -393.5 \text{ kJ}$$

In the two-step process, first carbon monoxide is formed:

$$\text{Step 1}: C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$$

Then, carbon monoxide reacts further to form carbon dioxide:

$$\text{Step 2}: CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$$

The equation describing the overall reaction is the sum of these two chemical changes. Because the CO produced in Step 1 is consumed in Step 2, the net change is:

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

According to Hess's law, the enthalpy change of the reaction is equal to the sum of the enthalpy changes of the steps. We can apply the data from the experimental enthalpies of combustion in Table 5.2 to find the enthalpy change of the entire reaction from its two steps:

$$\text{Step 1}: C(s)+\frac{1}{2}O_2(g)\longrightarrow CO(g) \qquad \Delta H^0=-111\text{kJ}$$

$$\text{Step 2}: CO(g)+\frac{1}{2}O_2(g)\longrightarrow CO_2(g) \qquad \Delta H^0=-283\text{kJ}$$

$$\text{Sum}: C(s)+O_2(g)\longrightarrow CO_2(g) \qquad \Delta H^0=-393.5\text{kJ}$$

The result is shown in Figure 9. We see that ΔH of the overall reaction is the same whether it occurs in one step or two steps. This finding (overall ΔH for the reaction = Sum of Δ*H* values for reaction "steps" in the overall reaction) is true in general for chemical and physical processes.

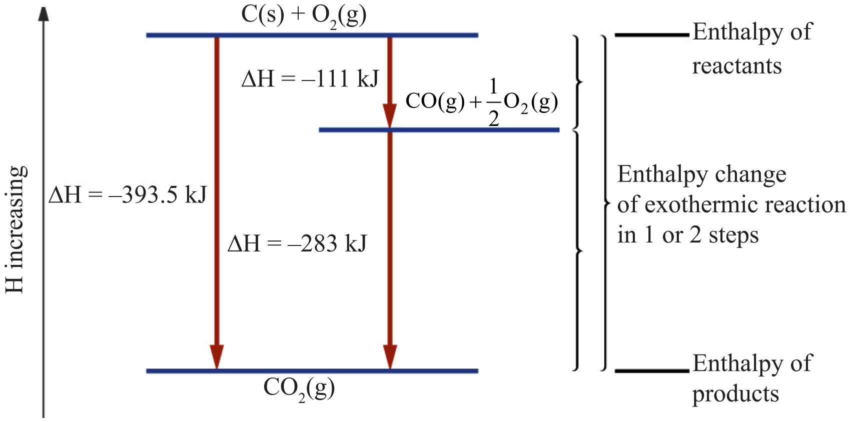


Figure 9. The formation of $CO_2(g)$ from its elements can be thought of as occurring in two steps, which sum upto the overall reaction, as described by Hess's law.

To apply Hess's law, you can generally expect to do the following:

- Reverse certain equations and change the signs of their ΔH values.
- Multiply certain quantities and their ΔH values by appropriate factors. The factors may be whole numbers or fractions.

Exercises

1. Calculate ΔH for the process:

$$N_2(g) + 2O_2(g) \longrightarrow 2NO_2(g)$$

from the following information:

$$N_2(g)+O_2(g)\longrightarrow 2NO(g) \qquad \Delta H=180.5\text{kJ}$$

$$NO(g)+\frac{1}{2}O_2(g)\longrightarrow NO_2(g) \qquad \Delta H=-57.06kJ$$

2. Aluminum chloride can be formed from its elements:

   (i) $2Al(s) + 3Cl_2(g) \longrightarrow 2AlCl_3(s) \quad \Delta H° = ?$

   Use the reactions below to determine the ΔH° for reaction (i):

   (ii) $HCl(g)\longrightarrow HCl(aq) \qquad \Delta H^o(ii)=-74.8kJ$

   (iii) $H_2(g)+Cl_2(g)\longrightarrow 2HCl(g) \qquad \Delta H^o(iii)=-185kJ$

   (iv) $AlCl_3(aq)\longrightarrow AlCl_3(s) \qquad \Delta H^o(iv)=+323kJ/mol$

   (v) $2Al(s)+6HCl(aq)\longrightarrow 2AlCl_3(aq)+3H_2(g) \quad \Delta H^o(v)=-1049kJ$

5.4 BOND ENTHALPY

Upon completion of this topic, learners will be able to:

- explain energy transfers during chemical reactions in terms of breaking and making chemical bonds.
- use bond energies to calculate enthalpy change of reaction.
- carry out calculations using bond energy data.

Bond enthalpy

Why is bond energy defined only for gases?

A measure of the stability of a molecule is its bond enthalpy, which is the enthalpy required to break a particular bond in 1 mole of gaseous molecules. This energy is generally expressed in kilojoules per mole of bonds (kJ/mol).

The experimentally determined bond enthalpy of the diatomic hydrogen molecule, for example, is:

$$H_2(g)\longrightarrow H(g)+H(g) \qquad \Delta H^0=436.4\,kJ/mol$$

This equation tells us that breaking the covalent bonds in 1 mole of gaseous H_2 molecules requires 436.4 kJ of energy.

Bond dissociation enthalpy

It is easy to understand bond-dissociation enthalpy for diatomic molecules because there is only one bond (single, double or triple) per molecule. We can represent bond dissociation energy as an enthalpy change or a heat of reaction. The enthalpy change for the reverse reaction, which is bond formation, is the negative of the bond-dissociation energy. For example

Bond breaking: $Cl_2(g) \longrightarrow Cl(g) + Cl(g) \qquad \Delta H^0 = +243\,kJ/mol$

Bond forming: $Cl(g) + Cl(g) \longrightarrow Cl_2(g) \qquad \Delta H^0 = -243\,kJ/mol$

Notice that the bond energy is always a positive quantity; energy is always required to break chemical bonds. Conversely, energy is released when a bond is formed between two gaseous atoms or molecular fragments. Of course, greater the bond energy, stronger the bond.

Calculations involving bond enthalpies

How do we apply bond energies to calculate ΔH?

The enthalpy of the reaction is estimated as the total energy required to break the bonds minus the total bond energies of the new bonds formed.

$$\Delta H = \sum(\text{bond enthalpies of bonds broken}) - \sum(\text{bond enthalpies of bonds formed})$$

Table 3 Average bond energies of some substances (kJ/mol).

Bond	Bond Energy	Bond	Bond Energy
H – H	436	N – H	389
H – F	565	N – N	163
H – Cl	427	N – O	201
H – Br	366	N – F	272
H – I	295	N – Br	243
C – H	413	N – I	159
C – C	348	O – H	463
C – N	305	O – F	190
C – O	358	O – Cl	203
C – F	485	O – I	234
C – Cl	328	F – F	155
C – Br	276	Cl – F	253
C – I	240	Br – Br	193

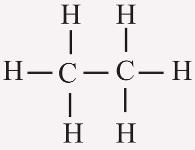
Multiple bonds			
C = C	614	N = N	418
C ≡ C	839	N = O	607
C ≡ N	615	O = O	498
C = O	799	N ≡ N	945
C ≡ O	1072		

Example

Estimate ΔH for the following reaction:

$$\mathrm{C_2H_6(g)+\frac{7}{2}O_2(g)\longrightarrow 2CO_2(g)+3H_2O(g)}$$

Solution



$$\mathrm{H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H\,(g)+\frac{7}{2}\,O=O(g)\longrightarrow 2O=C=O(g)+3H-O-H(g)}$$

$$\Delta\mathrm{H}=\left(6(\mathrm{C-H})+(\mathrm{C-C})+\frac{7}{2}(\mathrm{O=O})\right)-\left(4(\mathrm{C=O})+6(\mathrm{H-O})\right)$$

$$=\left(6\left(413\,\mathrm{kJ\ mol^{-1}}\right)+\left(348\,\mathrm{kJ\ mol^{-1}}\right)+\frac{7}{2}\left(498\,\mathrm{kJ\ mol^{-1}}\right)\right)$$

$$-\left(4\left(799\ \mathrm{kJ\ mol^{-1}}\right)+6\left(463\,\mathrm{kJ\ mol^{-1}}\right)\right)$$

$$=4558\,\mathrm{kJ\ mol^{-1}}-5974\ \mathrm{kJ\ mol^{-1}}=\ -1416\ \mathrm{kJ\ mol^{-1}}$$

Exercises

1. Using bond energies given in Table 3, estimate ΔH for each of the following gas phase reactions.

   (a) $\mathrm{CH_3OH(g)+HBr(g)\longrightarrow CH_3Br(g)+3H_2O(g)}$

   (b) $\mathrm{CO(g)+H_2O(g)\longrightarrow H_2(g)+CO_2(g)}$

Limitations of bond enthalpies

Bond energy is affected by other atoms in the molecule. The O–H bond in water has a slightly different bond energy value to the O–H bond in ethanol. In ethanol, the oxygen is connected to a carbon atom rather than another hydrogen atom. We call these bond energies exact bond energies. The O–H bond is in a different environment. Identical bonds in molecules with two (or more) types of bonds have different bond energies when we measure them. It takes more energy to break the first O–H bond in water than to break the second. For these reasons we use average bond energies taken from a number of bonds of the same type but in different environments.

5.5 IONIC SYSTEMS

Upon completion of this topic, learners will be able to:

- discuss the concept of ionic systems.

Lattice enthalpy

Much of the stability of ionic compounds results from the packing of the oppositely charged positive and negative ions together.

A measure of just how much stabilization results from this packing is given by the lattice enthalpy. This quantity is the energy change occurring when gaseous ions come together to form one mole of a solid ionic compound, or the enthalpy change required for one mole of the solid ionic substance to be separated completely into ions far removed from one another.

The lattice energy plays a crucial role in ionic compound formation, but it is difficult to measure it directly. Nevertheless, the lattice energies of many compounds have been determined using Hess's law. Lattice energies can be calculated using a Born-Haber cycle.

Born-Haber cycle

Let's use the Born-Haber cycle to determine the lattice enthalpy of CsF(s). CsF is a nearly ideal ionic compound because Cs is the least electronegative element and F is the most electronegative element. To construct a thermochemical cycle for the formation of CsF, we need to know its enthalpy of formation, ΔH_f, which is defined by the following chemical reaction:

$$Cs(s) + \frac{1}{2}F_2(g) \longrightarrow CsF(s)$$

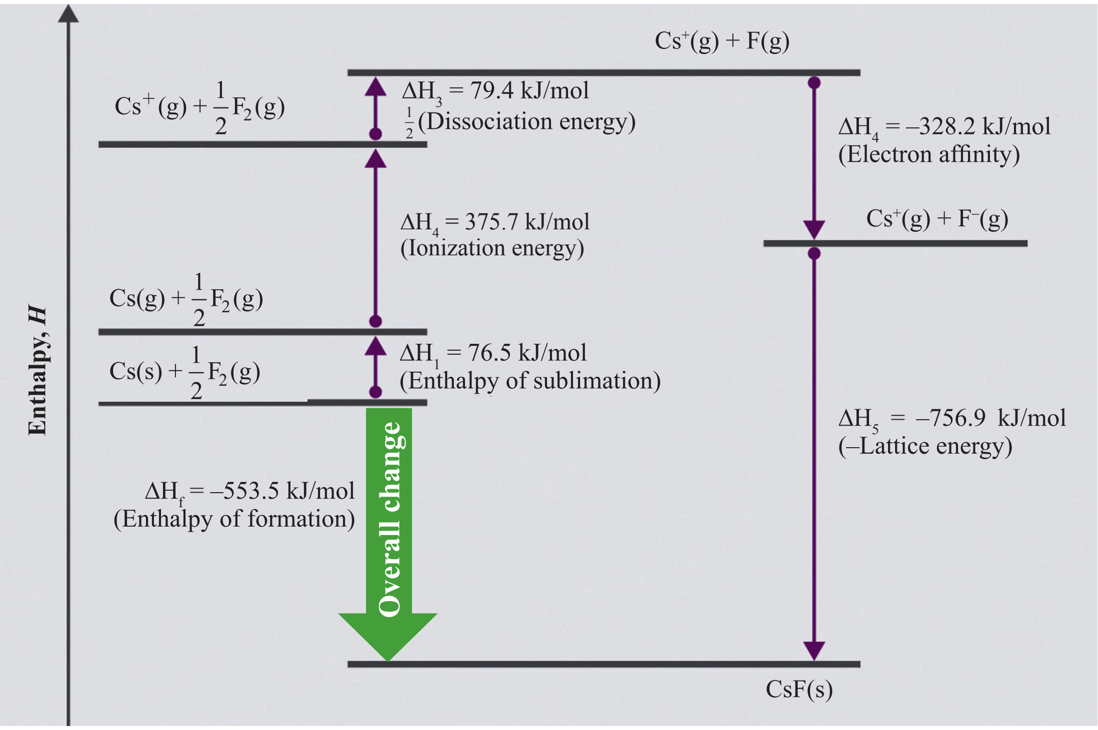


Figure 10. The Born–Haber cycle illustrating the enthalpy changes involved in the formation of solid cesium fluoride from its elements

Reaction 1

$$Cs\ (s) \longrightarrow Cs\ (g) \qquad \Delta H_1 = IE_1 = 76.5 \text{ kJ/mol}$$

This equation describes the sublimation of elemental cesium, the conversion of the solid directly to a gas. The accompanying enthalpy change is called the enthalpy of sublimation (ΔH_{sub}).

Reaction 2

$$Cs\ (g) \longrightarrow Cs^{+}\ (g) + e^{-} \qquad \Delta H_2 = IE_1 = 375.7 \text{ kJ/mol}$$

This equation describes the ionization of cesium, so the enthalpy change is the first ionization energy of cesium.

Reaction 3

$$\frac{1}{2}F_2(g) \longrightarrow F(g) \qquad \Delta H_3 = \tfrac{1}{2}D = 79.4 \text{ kJ/mol}$$

This equation describes the dissociation of fluorine molecules into fluorine atoms, where D is the energy required for dissociation to occur. We need to dissociate only ½ mol of F_2(g) molecules to obtain 1 mol of F(g) atoms.

Reaction 4

$$F\ (g) + e^- \longrightarrow F^-(g) \qquad \Delta H_4 = EA = -328.2\ kJ/mol$$

This equation describes the formation of a gaseous fluoride ion from a fluorine atom; the enthalpy change is the electron affinity of fluorine.

Reaction 5

$$Cs^+(g) + F^-(g) \longrightarrow CsF\ (s) \qquad \Delta H_5 = -U$$

This equation describes the formation of the ionic solid from the gaseous ions.

If the enthalpy of formation of CsF from the elements is known (ΔH_f = -553.5 kJ/mol at 298 K), then the thermochemical cycle shown in Figure 10 has only one unknown, the quantity ΔH_5 = -U. From Hess's law, we can write:

$$\Delta H_f = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5$$

We can rearrange this equation to give:

$$\Delta H_5 = U = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 - \Delta H_f$$

Substituting the appropriate values into this equation gives:

U = (76.5kJ/mol + 375.7 kJ/mol + 79.4 kJ/mol -328.2 kJ/mol) – (–553.5 kJ/mol)
= 756.9 kJ/mol

Exercise

1. Calculate the lattice energy of calcium chloride given that:
   Heat of sublimation of Ca = 178 kJ/mol.
   Enthalpy of dissociation of Cl_2 = +243.4 kJ/mol.
   Enthalpy of formation of $CaCl_2$ = –795.8 kJ/mol.
   The electron affinity of Cl = –348.7 kJ/mol and
   IE_1 and IE_2 for Ca are +590 kJ mol^{-1} and +1145 kJ mol^{-1} respectively.

Enthalpy of solution

Heat of solution, or enthalpy of solution, ΔH_{soln}, is the heat generated or absorbed when a certain amount of solute dissolves in a certain amount of solvent. The quantity ΔH_{soln} represents the difference between the enthalpy of the final solution and the enthalpies of its original components (that is, solute and solvent) before they are mixed. Thus,

$$\Delta H_{soln} = H_{soln} - H_{components}$$

Neither H_{soln} nor $H_{components}$ can be measured, but their difference, ΔH_{soln}, can be readily determined with a constant-pressure calorimeter. Like other enthalpy changes, ΔH_{soln} is positive for endothermic (heat-absorbing) processes and negative for exothermic (heat-generating) processes.

Dissolving an ionic compound such as NaCl in water involves complex interactions among the solute and solvent species. However, for the sake of analysis we can imagine that the solution process takes place in two separate steps. First, the Na^+ and Cl^- ions in the solid crystal are separated from each other and converted to the gaseous state:

$$\text{Energy} + NaCl(s) \longrightarrow Na^+(g) + Cl^-(g)$$

The lattice energy of NaCl is 788 kJ/mol. Next, the “gaseous” Na^+ and Cl^- ions enter the water and become hydrated:

$$Na^+(g) + Cl^-(g) \xrightarrow{H_2O} Na^+(g) + Cl^-(g) + \text{Energy}$$

The enthalpy change associated with the hydration process is called the heat of hydration, ΔH_{hydr} (heat of hydration is a negative quantity for cations and anions). Applying Hess’s law, it is possible to consider ΔH_{soln} as the sum of two related quantities, lattice energy (U) and heat of hydration (ΔH_{hydr}), as shown in Figure 11.

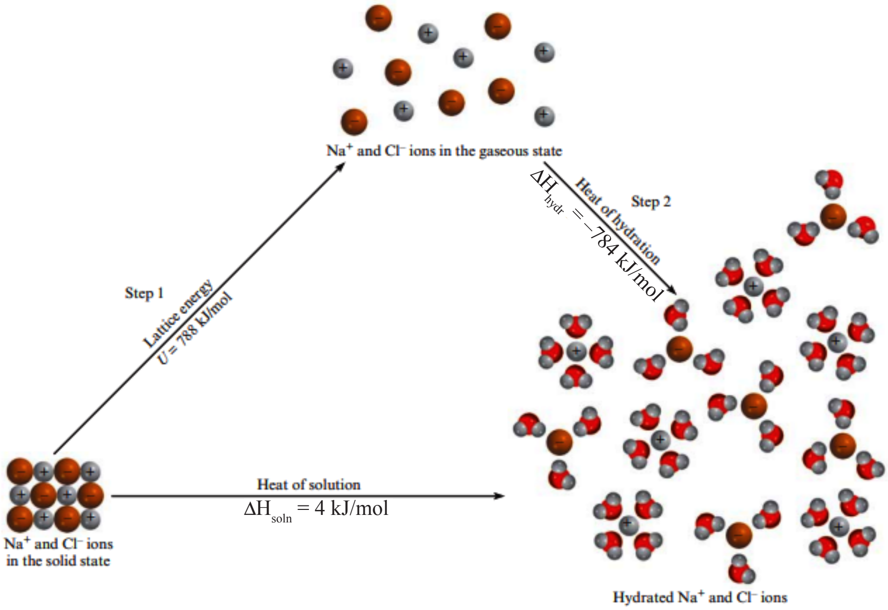


Figure 11. The disolution process for NaCl.

$$\Delta H_{soln} = U + \Delta H_{hydr}$$

$$NaCl(s) \longrightarrow Na^{+}(g) + Cl^{-} \qquad U = 788 \text{ kJ/mol}$$

$$Na^{+}(g) + Cl^{-}(g) \xrightarrow{H_2O} Na^{+}(g) + Cl^{-}(g) \qquad \Delta H_{hydr} = -784 \text{ kJ/mol}$$

$$NaCl(s) \xrightarrow{H_2O} Na^{+}(g) + Cl^{-}(g) \qquad \Delta H_{soln} = U + \Delta H_{hydr} = 4 \text{kJ/mol}$$

Thus, when 1 mole of NaCl dissolves in water, 4 kJ of heat will be absorbed from the surroundings. We would observe this effect by noting that the beaker containing the solution becomes slightly colder.

ACTIVITY 3

Determining heat of solution

When a solution is formed, there is an energy change that results from the interaction of two forces–the intermolecular forces among dissolving particles and the attractive forces between solute and solvent particles. How can this change be observed?

Procedure:

1. Pour 50 mL of water into an Erlenmeyer flask and place a thermometer as shown in Figure 12.

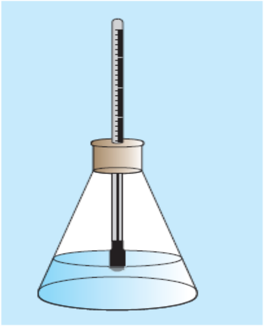


Figure 12. Apparatus to measure the heat of solution of sodium hydroxide.

2. Record the initial temperature of the water.
3. Remove the cork, along with the thermometer, and add 4 g of sodium hydroxide pellets.
4. Replace the cork gently, stir the contents, and note the highest temperature reading.
5. Determine the heat of the solution of sodium hydroxide.
6. Repeat the experiment, using 4 g of $CuSO_4$.
7. Repeat the experiment, using 1 M aqueous solution of H_2SO_4.

Results and Discussion:

1. Feel the bottom of the beaker, and record your observations.
2. Copy and complete the following table.

Table 4

Chemical	Initial temperature of the solvent	Maximum temperature of the solution	Heat of solution
NaOH			
$CuSO_4$			
H_2SO_4			

Conclusion

1. Which dissolving process is exothermic, and which is endothermic? Write down your conclusion.
2. In your conclusion explain how an energy change occurs when solutions are formed?
3. Present your findings to your teacher.

Limitations of ionic model

In our model of an ionic lattice, we have thought of the ions as being spherical in shape. This is not always the case. In some cases, the positive charge on the cation in an ionic lattice may attract the electrons in the anion towards it. This results in a distortion of the electron cloud of the anion and the anion is no longer spherical (Figure 13). We call this distortion ion polarisation. The ability of a cation to attract electrons and distort an anion is called the polarising power of the cation.

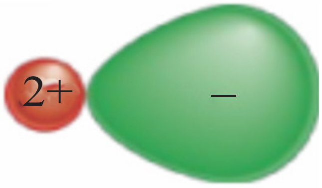


Figure 13. Ion polarisation. A small highly charged cation can distort the shape of the anion.

Factors affecting ion polarisation

The degree of polarisation of an anion depends on:

- The charge density of the cation.
- The ease with which the anion can be polarised: its polarisability.

An anion is more likely to be polarised if:

- The cation is small.
- The anion is large.

5.6 FUELS

Upon completion of this topic, learners will be able to:

- define fuel.
- list the three major fossil fuels.
- identify several sources of fuels.

A chemical fuel is a substance existing in any form of solid, liquid or gas. In the burning of fuel, the chemical energy of fuel is converted into heat energy. A chemical fuel is a substance existing in any form of solid, liquid or gas. The heat energy liberated by complete burning of a unit mass or volume of fuel is known as its calorific value. Beneath the earth and sea, the plant and fossils have been converted to fuels while lying under earth's heat and pressure for millions of years. Thus chemical fuels are also called as fossil fuels. A chemical fuel mainly contains carbon and hydrogen as its main constituents. Therefore chemical fuels are also named as hydrocarbon fuels. Coal, petroleum, and natural gas are examples of chemical fuels.

Fuels can be classified mainly on the basis of phase in which they exist normally as solid fuels, liquid fuels, and gaseous fuels.

Solid fuels

A solid fuel is mainly wood and coal. The wood is naturally available by cutting of trees. However, coal may be naturally available or it may be prepared artificially from wood or natural coal.

Naturally available coal

1. **Peat**: It is the first stage of formation of coal deep below the surface of earth. It contains a large amount of moisture content upto 35%. So, it has to be dried before use. Its average calorific value is 23000 kJ/kg.
2. **Lignite**: It comes in the next stage of formation of coal after peat. It also has a large moisture content may be upto 40%. On drying, it becomes brittle and converted to flakes. It is considered superior to Peat. Its calorific value is approximately 25000 kJ/kg.
3. **Bituminous Coal**: It is a superior and naturally available coal containing very less moisture content but high carbon content. Its average calorific value is 33500 kJ/kg.
4. **Anthracite Coal**: It is the final stage of coal formation and contains more than 90% carbon. So it is the most superior quality of naturally available coal. Its burning is smokeless and has a calorific value of approximately 36000 kJ/kg.

Artificially prepared coal

1. **Wood charcoal**: It is prepared by heating of wood with limited supply of air at a temperature nearly 300^{o}C. It is used in metallurgical Industries.
2. **Coke**: It is produced by heating of naturally available coal continuously for two days in the absence of air. This process is known as carbonization of coal as the carbon content increases by removal of moisture and other gases. Due to high carbon content, it has a high calorific value.

Liquid fuels

These are the fuels which are found in liquid state and easier to handle and use, as compared to solid fuels. The naturally available liquid fuel is petroleum which is not used directly as it is mixture of a number of useful substances. Thus before using, it is refined by boiling and condensation process in refineries distilleries to separate into a number of useful substances like petrol, kerosene, fuel oils, lubricating oils, coal tar and others.

1. **Petrol or gasoline**: It is the most light and most volatile liquid fraction of petroleum fuel. It is distilled at a lower temperature upto 200^{o}C by boiling of petroleum, Thereafter cracking process is used to prepare light petrol.
2. **Kerosene**: It is a heavier fraction and less volatile fuel and distilled in boiling range up to 300^{o}C. It is used in Jet engines and also in domestic stoves and ovens.
3. **Diesel Oils**: Diesel oils are the fuels which distillate on further higher temperature up to 370^{o}C. Diesel oils lie between Kerosene and lubricating oils while separating from crude petroleum. These are the fuels which are commercially used in engines and boilers.
4. **Fuel Oils**: Fuel oil is similar to Diesel oil in specific gravity and distillation range, but their composition varies in a wide range. Rather fuel oils are used for industrial purpose.

Gaseous fuels

These are also naturally available or artificially prepared. The natural gas is available under the earth's surface near petroleum fields. It is a mixture of methane, ethane and other like gases.

Gaseous fuels are needed to be compressed for storing in containers and also for effective use. They are difficult to handle and require large heavy containers but their advantage is that they readily catch fire and free from impurities. So combustion is complete and also pollution is less.

The gaseous fuels, which are artificially prepared from other fuels, are categorized as:

1. **Coal gas**: It is obtained by carbonization of coal as discussed earlier in solid fuels. It consists mainly of hydrogen and some hydrocarbons. Its calorific value is approximately 25000 kJ/m^3.
2. **Liquefied petroleum gas**: It is prepared from natural gas by separating lighter hydrocarbons i.e. propane and butane. It is liquefied and stored in cylinders under high pressure. Only under high pressure, a gas can be liquefied at atmospheric temperature. Due to this a large quantity of gas occupies less space in cylinder. LPG is commonly used as cooking gas and also in gas engines and other Industrial processes.
3. **Producer gas**: It is obtained by partial combustion of coal in the presence of air and steam blast. It is used in glass melting process.

Key Terms

- System
- Surroundings
- Equation of state
- State function
- Path functions
- Exothermic reaction
- Endothermic reaction
- Internal energy
- First law of thermodynamics
- Work
- Heat
- Specific heat
- Enthalpy change
- Calorimetry
- Standard enthalpy of combustion
- Standard enthalpy of formation
- Enthalpy of reaction
- Enthalpy of neutralization
- Hess's law
- Bond enthalpy
- Lattice enthalpy
- Born-Haber cycle
- Enthalpy of solution
- Fuels

Summary

Thermodynamics is the study of energy and its transformations. In this chapter we have focused on thermochemistry, the transformations of energy-especially heat-during chemical reactions.

When we study thermodynamic properties, we define a specific amount of matter as the system. Everything outside the system is the surroundings. When we study a chemical reaction, the system is generally the reactants and products. A closed system can exchange energy, but not matter, with the surroundings. Energy can be transferred between the system and the surroundings as work or heat. Work is the energy required to move an object against a force. Heat is the energy that is transferred from a hotter object to a colder one. Energy is the capacity to do work or to transfer heat. There are many forms of energy and they are interconvertible. The law of conservation of energy states that the total amount of energy in the universe is constant.

The internal energy for a system is the sum of its potential and kinetic energies. According to the first law of thermodynamics, the internal energy of a system can be changed by work and heat: $\Delta E = q + w$.

Both q and w have a sign that indicates the direction of energy transfer. When heat is transferred from the surroundings to the system, $q > 0$. Likewise, when the surroundings do work on the system, $w > 0$.

When a gas is produced or consumed in a chemical reaction taking place at constant pressure, the system may perform pressure-volume (P-V) work against the prevailing pressure of the surroundings.

A process that gives off heat to the surroundings is exothermic; a process that absorbs heat from the surroundings is endothermic.

The amount of heat transferred between the system and the surroundings is measured experimentally by calorimety. A calorimeter measures the temperature change accompanying a process. The temperature change of a calorimeter depends on its heat capacity, the amount of heat required to raise its temperature by 1 K. The heat capacity for one mole of a pure substance is called its molar heat capacity; for one gram of the substance, we use the term specific heat.

Enthalpy is a state function. A change in enthalpy ΔH is equal to $\Delta E + P\Delta V$ for a constant-pressure process.

The standard enthalpy of a reaction can be calculated from the standard enthalpies of formation of reactants and products. The enthalpy of formation, ΔH_f, of a substance is the enthalpy change for the reaction in which the substance is formed from its constituent elements. The standard enthalpy change of a reaction, $\Delta H°$, is the enthalpy change when all reactants and products are at 1 atm pressure and a specific temperature, usually 298 K.

Hess's law states that the overall enthalpy change in a reaction is equal to the sum of enthalpy changes for individual steps in the overall reaction.

The heat of solution of an ionic compound in water is the sum of the lattice energy of the compound and the heat of hydration. The relative magnitudes of these two quantities determine whether the solution process is endothermic or exothermic.

Fuels are conveniently classified as solids, liquids and gaseous fuels. The most common fuels are hydrocarbons that are found as fossil fuels, such as natural gas, petroleum, and coal. Coal is the most abundant fossil fuel.

Exercises

Part I: Choose the correct answer for each of the following questions

1. Thermodynamics is not concerned about____.
   - (a) energy changes involved in a chemical reaction.
   - (b) the extent to which a chemical reaction proceeds.
   - (c) the rate at which a reaction proceeds
   - (d) the feasibility of a chemical reaction.
2. An isolated system is a system in which:
   - (a) there is no exchange of energy with the surroundings
   - (b) there is exchange of mass and energy with the surroundings
   - (c) there is no exchange of mass or energy with the surroundings
   - (d) there is exchange of mass with the surroundings
3. When 75.4 J of energy is absorbed by 0.25 mol of CCl_4, what is the change in temperature? The specific heat of CCl_4 is 0.861 J/g.K.
   (a) 17.8 K (b) 21.9 K (c) 2.3 K (d) 9.1 K
4. The molar heat capacity of a compound with the formula C_2H_6SO is 88.0 J/mol.K. the specific heat of this substance is ———— J/g.K.
   (a) 88.0 (b) 1.13 (c) 4.89 (d) 6
5. Which of the following would have the largest temperature change upon gaining 200.0 J of heat?
   (a) 50 g Al, c_{Al} = 0.90 J/g.K (c) 25 g Au, c_{Au} = 0.13 J/g.K
   (b) 50 g Cu, c_{cu} = 0.38 J/g.K (d) 25 g Ag, c_{Ag} = 0.24 J/g.K
6. A 10.0 L sample of an ideal gas at 15.0 atm is allowed to expand against a constant external pressure of 2.00 atm at a constant temperature. Calculate the work in units of kJ for the gas expansion.
   (a) –13.2 kJ (b) 13.2 kJ (c) 23.4 kJ (d) –23.4 kJ
7. Calculate ΔH for the following reaction using the bond energies given below:
   $H{-}H\ (g) + I{-}I\ (g) \longrightarrow 2H{-}I\ (g)$
   Bond energies: H–H = 436 kJ/mol, I–I =151 kJ/mol, H–I = 297 kJ/mol
   (a) +290 kJ (b) –7 kJ (c) +7 kJ (d) –290 kJ

Part II: Short Answer Questions

1. A gas expands in volume from 26.7 mL to 89.3 mL at constant temperature. Calculate the work done (in joules) if the gas expands against a constant pressure of 2.8 atm.
2. The work done to compress a gas is 74 J. As a result, 26 J of heat is given off to the surroundings. Calculate the change in energy of the gas.

3. Define these terms: enthalpy, enthalpy of reaction. Under what condition is the heat of a reaction equal to the enthalpy change of the same reaction?
4. What is the difference between specific heat and heat capacity? What are the units for these two quantities? Which is the intensive property and which is the extensive property?
5. What is meant by standard-state condition? How are the standard enthalpies of an element and of a compound determined?
6. State Hess's law. Describe how chemists use Hess's law to determine the ΔH_f^o of a compound by measuring its heat (enthalpy) of combustion.
7. Define the following terms: enthalpy of solution, heat of hydration, lattice energy.
8. Given the following data:

$$P_4(s) + 6Cl_2(g) \longrightarrow 4PCl_3(g) \qquad \Delta H = -1225.6\,kJ$$

$$P_4(s) + 5O_2(g) \longrightarrow P_4O_{10}(S) \qquad \Delta H = -2967.3\,kJ$$

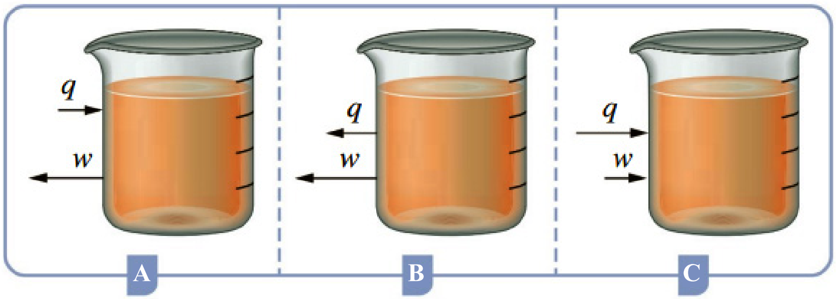
$$PCl_3(g) + Cl_2(g) \longrightarrow PCl_5(g) \qquad \Delta H = -84.2\,kJ$$

$$PCl_3(g) + \frac{1}{2}O_2(g) \longrightarrow Cl_3PO(g) \qquad \Delta H = -285.7\,kJ$$

calculate ΔH for the reaction:

$$P_4O_{10}(s) + 6PCl_5(g) \longrightarrow 10Cl_3PO(g)$$

9. Chemical reactions are run in each of the beakers depicted below (labeled A, B, and C). The magnitude and direction of heat and work for each reaction are represented as arrows, with the length of an arrow depicting the relative magnitude of the heat or work.



For the reaction in each beaker, answer the following and givc reasons for your answer:

(a) Is the reaction endothermic or exothermic?
(b) What is the sign (+ or –) of the work?
(c) What is the sign (+ or –) of the enthalpy of each reaction?
(d) Is there an increase or decrease in internal energy?

10. Are the following processes exothermic or endothermic?
    (a) When solid KBr is dissolved in water, the solution gets colder.
    (b) Natural gas (CH_4) is burned in a furnace.
    (c) When concentrated H_2SO_4 is added to water, the solution becomes very hot.
    (d) $F_2(g) \rightarrow 2F(g)$

11. Identify each of the following reactions as ΔH^o_r, ΔH^o_f, or ΔH^o_{neut}
    (a) $C\ (graphite) + O_2(g) \longrightarrow CO_2(g)$
    (b) $HCl(g) + NH_3(g) \longrightarrow NH_4Cl(s)$
    (c) $H_2(g) + ½\ O_2(g) \longrightarrow H_2O(l)$

12. Give two examples each for a solid, liquid and gaseous fuel along with some important uses?

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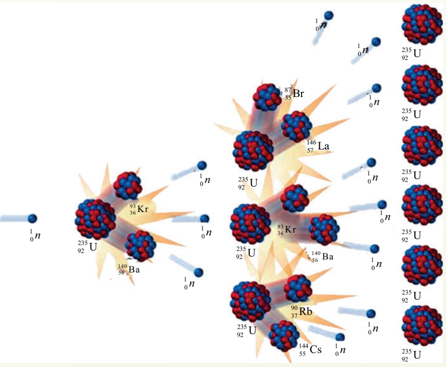
CHAPTER 6

NUCLEAR CHEMISTRY

Chapter Contents



Chapter Outcomes

By the end of this chapter, you will be able to:

- describe radioactivity, including its various applications.
- explain how nuclear reactions differ from chemical reactions.
- describe the types and nature of radiations.
- explain the role of half-life in the stability of the nucleus.
- distinguish between fusion and fission and
- explain the effects and applications of radioactivity.

6.1 DEFINITION AND HISTORY OF RADIOACTIVITY

Upon completion of this topic, learners will be able to:

- describe radioactivity, including its historical development.

Nuclear chemistry is the study of nuclear reactions, with an emphasis on their uses in chemistry and their effects on biological systems. It affects our lives in many ways, particularly in energy and medical applications. In radiation therapy, for example, gamma rays from a radioactive substance such as cobalt-60 are directed to cancerous tumors to destroy them.

The use of nuclear energy for power generation and the disposal of nuclear wastes from power plants are controversial social and political issues. It is imperative, therefore, that as a citizen with a stake in these matters, you have some understanding of nuclear reactions and the uses of radioactive substances.

Nuclear chemistry is the study of reactions involving changes in atomic nuclei. This branch of chemistry began with the discovery of natural radioactivity by Henri Becquerel and grew as a result of subsequent investigations by Pierre and Marie Curie and many others.

In 1896, Henri Becquerel was studying the possible connection between light emission of some uranium compounds after exposure to sunlight and X-ray emission. He wrapped a photographic plate in a lightproof covering and placed a uranium compound on top of it. He then placed them in sunlight. The photographic plate was exposed even though it was protected from visible light, suggesting that it had been exposed to X-rays. When he tried to repeat his experiment, cloudy weather prevented him from placing the experiment in sunlight. To his surprise, the plate was still exposed. This meant that sunlight was not needed to produce the rays that exposed the plate. The rays were produced by radioactive decay.

Radioactive decay is the spontaneous disintegration of a nucleus into a slightly lighter nucleus, accompanied by emission of particles, electromagnetic radiation, or both. The radiation that exposed the plate was nuclear radiation, particles or electromagnetic radiation emitted from the nucleus during radioactive decay.

Uranium is a radioactive nuclide, an unstable nucleus that undergoes radioactive decay. Studies by Marie Curie and Pierre Curie found that of the elements known in 1896, only uranium and thorium were radioactive. In 1898, the Curies discovered two new radioactive metallic elements, polonium and radium. Since that time, many other radioactive nuclides have been identified.

6.2 DIFFERENCE BETWEEN ORDINARY AND NUCLEAR REACTIONS

Upon completion of this topic, learners will be able to:

- explain how nuclear reactions differ from chemical reactions.

Nuclear reactions are not considered to be ordinary chemical reactions. The governing principles for ordinary chemical reactions deal with the rearrangement of electrons; this rearrangement occurs as the result of electron transfer or electron sharing. In nuclear reactions, it is nuclei rather than electron arrangements that undergo change.

Specific atoms, in nuclear chemistry discussions, are called nuclides rather than isotopes. The term nuclide refers to atoms of either the same or different elements.

A nuclide is an atom with a specific atomic number and a specific mass number. In practice, the designation nuclides is used to describe atoms of different elements and the designation isotopes is used to describe different types of atoms of the same element. The species $^{12}_{6}C$ and $^{16}_{8}C$ are nuclides of different elements, while the species $^{12}_{6}C$ and $^{13}_{6}C$ are isotopes of the same element.

Nuclides may be divided into two types based on nuclear stability. Some nuclides have nuclei that are stable and others possess nuclei that are unstable. A stable nuclide is a nuclide with a stable nucleus, a nucleus that does not readily undergo change. Conversely, an unstable nuclide is a nuclide with an unstable nucleus, a nucleus that spontaneously undergoes change. The spontaneous change that unstable nuclei undergo involves emission of radiation from the nucleus, a process by which the unstable nucleus can become more stable. The radiation emitted from unstable nuclei is called radioactivity. Radioactivity is the radiation spontaneously emitted from an unstable nucleus. Nuclides that possess unstable nuclei are said to be radioactive. A radioactive nuclide is a nuclide with an unstable nucleus from which radiation is spontaneously emitted. The term radioactive isotope is sometimes used in place of radioactive nuclide.

With the exception of hydrogen ($^{1}_{1}H$), all nuclei contain two kinds of fundamental particles, called protons and neutrons. All elements having an atomic number greater than 83 are radioactive. For example, the isotope of polonium, polonium-210 ($^{210}_{84}Po$), decays spontaneously to $^{206}_{82}Po$ by emitting an α-particle.

Another type of radioactivity, known as nuclear transmutation, results from the bombardment of nuclei by neutrons, protons, or other nuclei. An example of a nuclear transmutation is the conversion of atmospheric $^{14}_{7}N$ to $^{14}_{6}C$ and $^{1}_{1}H$, which results when the nitrogen isotope captures a neutron (from the sun).

Radioactive decay and nuclear transmutation are nuclear reactions, which differ significantly from ordinary chemical reactions. Table 1 summarizes the differences.

Table 1 Differences Between Nuclear and Chemical Reactions

Chemical Reactions	Nuclear Reactions
Atoms are rearranged by the breaking and forming of chemical bonds.	Elements (or isotopes of the same elements) are converted from one to another.
Only electrons in atomic or molecular orbitals are involved in the breaking and forming of bonds.	Protons, neutrons, electrons, and other elementary particles may be involved.
Reactions are accompanied by absorption or release of relatively small amounts of energy.	Reactions are accompanied by absorption or release of tremendous amounts of energy.
Rates of reaction are influenced by temperature, pressure, concentration, and catalysts.	Rates of reaction normally are not affected by temperature, pressure, and catalysts.

6.3 TYPES AND NATURE OF RADIATIONS

Upon completion of this topic, learners will be able to:

- describe the types and nature of radiations.
- write a nuclear equation.
- write balanced nuclear equations.

Nature of radiations

The first information concerning the nature of the radiation emanating from naturally radioactive materials was obtained by Rutherford in 1898-1899. Using an apparatus similar to that shown in Figure 1, he found that if radiation from uranium is passed between electrically charged plates, it split into three components. This finding indicates the presence of three different types of emissions from naturally radioactive materials.

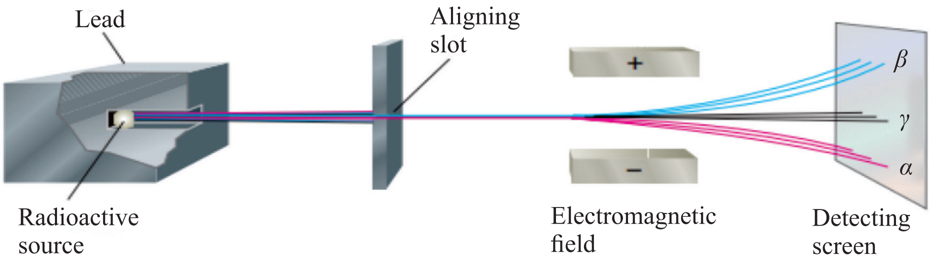


Figure 1. The effect of an electromagnetic field on alpha, beta, and gamma radiation.

Rutherford chose to call the three radiation components:

- alpha rays (α-rays) – the positive component;
- beta rays (β-rays) – the negative component; and
- gamma rays (γ-rays) – the uncharged component.

Further research has shown that both alpha particles and beta particles have specific masses and that gamma radiation has no mass – that is, it is a form of energy.

Types of radiations

The three most common kinds of radiation given off when a radionuclide decays are alpha, beta, and gamma radiations.

In terms of modern-day scientific knowledge, Rutherford's three types of "radiation" are characterized as follows:

An alpha particle is a particle in which two protons and two neutrons are present that are emitted by certain radioactive nuclei. The notation used to represent an alpha particle is ${}^{0}_{-1}\alpha$. The numerical superscript indicates a mass of 4 amu.

Alpha particles are identical to the nuclei of helium atoms -4 (${}^{4}_{2}\mathrm{He}$); because of this, an alternative designation for an alpha particle is ${}^{4}_{2}\mathrm{He}$.

A beta particle is a particle whose charge and mass are identical to those of an electron that is emitted by certain radioactive nuclei. Beta particles are not extranuclear electrons; they are particles that have been produced inside the nucleus and then ejected.

The symbol used to represent a beta particle is ${}^{0}_{-1}\beta$. The numerical subscript indicates that the charge on the beta particle is -1; it is the same as that of an electron.

A gamma ray is a form of high-energy radiation without mass or charge that is emitted by certain radioactive nuclei. Gamma rays are similar to X-rays except that gamma rays have higher energy. The symbol for gamma rays is ${}^{0}_{0}\gamma$.

Equations for radioactive decay

The terms parent nuclide and daughter nuclide are often used in descriptions of radioactive decay processes.

A parent nuclide is the nuclide that undergoes decay in a radioactive decay process.

A daughter nuclide is the nuclide that is produced in a radioactive decay process.

Alpha particle decay

Alpha particle decay is the radioactive decay process in which an alpha particle is emitted from an unstable nucleus. It always results in the formation of a nuclide of a different element. The product nucleus has an atomic number that is 2 less than that of the original nucleus and a mass number that is 4 less than that of the original nucleus. We can represent alpha particle decay in general terms by the equation

$${}^{A}_{Z}\mathrm{X} \rightarrow {}^{4}_{2}\alpha + {}^{A\rightarrow 4}_{Z\rightarrow 2}\mathrm{Y}$$

where X is the chemical symbol for the nucleus of the original element undergoing decay and Y is the chemical symbol of the nucleus formed as a result of the decay.

Specific radioactive decay processes are represented using nuclear equations. A nuclear equation is an equation in which the chemical symbols represent atomic nuclei rather than atoms. Both ${}^{211}_{83}\mathrm{Bi}$ and ${}^{238}_{92}\mathrm{U}$ are radionuclides that undergo alpha particle decay. The nuclear equations for these two decay processes are:

$${}^{211}_{83}\mathrm{Bi} \longrightarrow {}^{4}_{2}\alpha + {}^{207}_{81}\mathrm{Tl}$$

$${}^{238}_{92}\mathrm{U} \longrightarrow {}^{4}_{2}\alpha + {}^{234}_{90}\mathrm{Th}$$

In the first equation, ${}^{211}_{83}\mathrm{Bi}$ is the parent nuclide and ${}^{207}_{81}\mathrm{Tl}$ is the daughter nuclide; in the second equation, ${}^{238}_{92}\mathrm{U}$ is the parent nuclide and ${}^{234}_{90}\mathrm{Th}$ is the daughter nuclide.

Nuclear equations differ from ordinary chemical equations in three important ways:

1. The symbols in nuclear equations stand for nuclei rather than atoms. (We do not worry about electrons when writing nuclear equations.)
2. Mass numbers and atomic numbers (nuclear charge) are always specifically included in nuclear equations.
3. The elemental symbols on both sides of the equation frequently are not the same in nuclear equations.

The procedures for balancing nuclear equations are different from those used for ordinary chemical equations. A balanced nuclear equation is a nuclear equation in which the sum of the subscripts (atomic numbers or particle charges) on both sides of the equation are equal, and the sum of the superscripts (mass numbers) on both sides of the equation are equal. Both the preceding nuclear equations are balanced. In the alpha decay of ${}^{211}_{83}\mathrm{Bi}$, the subscripts on both sides total 83, and the superscripts total 211. For the alpha decay of ${}^{238}_{92}\mathrm{U}$, the subscripts total 92 on both sides, and the superscripts total 238.

Beta particle decay

Beta particle decay is the radioactive decay process in which a beta particle is emitted from an unstable nucleus. Beta particle decay, like alpha particle decay, always produces a nuclide of a different element. The mass number of the new nuclide is the same as that of the parent nuclide. However, the atomic number is increased by 1 unit. The general equation for beta decay is

$${}^{A}_{Z}X \longrightarrow {}^{0}_{-1}\beta + {}^{A}_{Z+1}Y$$

Specific examples of beta particle decay are

$${}^{10}_{4}Be \longrightarrow {}^{0}_{-1}\beta + {}^{10}_{5}\beta$$

$${}^{234}_{90}Th \longrightarrow {}^{0}_{-1}\beta + {}^{234}_{91}Pa$$

Both of these nuclear equations are balanced; superscripts and subscripts add to the same sums on both sides of the equation.

Gamma ray emission

Gamma ray emission is the radioactive decay process in which a gamma ray is emitted from an unstable nucleus. For naturally occurring radionuclides, gamma ray emission always takes place in conjunction with an alpha or a beta decay process; it never occurs independently. These gamma rays are often not included in the nuclear equation because they do not affect the balancing of the equation or the identity of the daughter nuclide.

Example

Write a balanced nuclear equation for the decay of each of the following radioactive nuclides. The mode of decay is indicated in parentheses.

(a) ${}^{70}_{31}Ga$ (beta emission)

(b) ${}^{144}_{60}Nd$ (alpha emission)

(c) ${}^{113}_{47}Ag$ (beta emission)

Solution

In each case, the atomic and mass numbers of the daughter nucleus are obtained by writing the symbols of the parent nucleus and the particle emitted by the nucleus (alpha or beta). Then the equation is balanced.

(a) Let X represent the daughter nuclide, the product of the radioactive decay. Then

${}^{70}_{31}Ga \longrightarrow {}^{0}_{-1}\beta + X$

The sum of the superscripts on both sides of the equation must be equal, so the superscript for X must be 70. In order for the sum of the subscripts on both sides of the equation to be equal, the subscript for X must be 32. Then 31 = (-1) + (32). After we determine the subscript of X, we can obtain the identity of X by looking at a periodic table. The element with an atomic number of 32 is Ge (germanium). Therefore,

$$^{70}_{31}\text{Ga} \longrightarrow {}^{0}_{-1}\beta + {}^{70}_{32}\text{Ge}$$

(b) Letting X represent the daughter nuclide, we have, for the alpha decay of $^{144}_{60}\text{Nd}$,

$$^{144}_{60}\text{Nd} \longrightarrow {}^{4}_{2}\alpha + \text{X}$$

We balance the equation by making the superscripts on each side of the equation total 144 and the subscripts total 60. We get

$$^{144}_{60}\text{Nd} \longrightarrow {}^{4}_{2}\alpha + {}^{140}_{58}\text{Ce}$$

(c) Finally, we write

$$^{113}_{47}\text{Ag} \longrightarrow {}^{0}_{-1}\beta + \text{X}$$

In beta emission, the atomic number of the daughter nuclide always increases by 1, and the mass number does not change from that of the parent. The balancing procedure gives us the result

$$^{113}_{47}\text{Ag} \longrightarrow {}^{0}_{-1}\beta + {}^{113}_{48}\text{Cd}$$

Exercises

1. Write a balanced nuclear equation for the decay of the following radioactive nuclides. The mode of decay is indicated in parentheses.
   (a) $^{99}_{43}\text{Tc}$ (beta emission) (b) $^{210}_{84}\text{Po}$ (alpha emission)
2. What changes in atomic number and mass number occur in each of the following types of radioactive decay?
   (a) alpha emission
   (b) beta emission

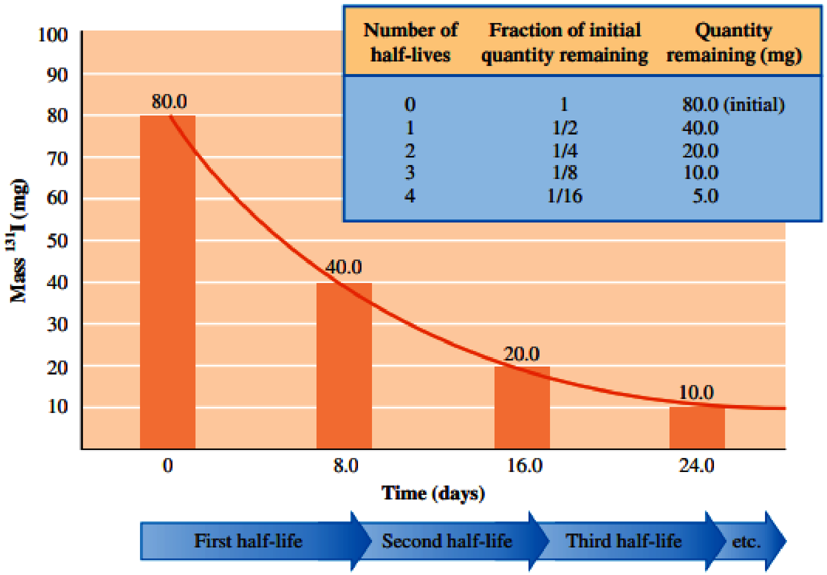
6.4 HALF-LIFE AS A MEASURE OF THE STABILITY OF THE NUCLEUS

Upon completion of this topic, learners will be able to:

- Explain the role of half-life in the stability of the nucleus.
- Define half-life.
- Draw a typical half-life decay curve of a radioactive element.

Radioactive nuclides do not all decay at the same rate. Some decay very rapidly; others undergo disintegration at extremely low rates. This indicates that radionuclides are not all equally unstable. The greater the decay rate, the lower the stability of the nuclide.

The concept of half-life is used to express nuclear stability quantitatively. A half-life ($t_{1/2}$) is the time required for one-half of a given quantity of a radioactive substance to undergo decay. For example, if a radionuclide's half-life is 12 days and you have a 4.00 g sample of it, then after 12 days (1 half-life), only 2.00 g of the sample (one-half of the original amount) will remain undecayed; the other half will have decayed into some other substance. Figure 2 illustrates the radioactive decay curve for a radionuclide.



Number of half-lives	Fraction of initial quantity remaining	Quantity remaining (mg)
0	1	80.0 (initial)
1	1/2	40.0
2	1/4	20.0
3	1/8	10.0
4	1/16	5.0

Figure 2. Decay of 80.0 mg of ^{131}I, which has a half-life of 8.0 days. After each half-life period, the quantity of material present at the beginning of the period is reduced by half.

Calculations involving amounts of radioactive material decayed, amounts remaining undecayed, and time elapsed can be carried out by using the following equation:

$$(\text{Amount of radionuclide undecayed after n half - lives})$$

$$= (\text{Original amount of radionuclide})\left(\frac{1}{2^{n}}\right)$$

Example

Iodine-131 is a radionuclide that is frequently used in nuclear medicine. The half-life of iodine-131 is 8.0 days. How much, in grams, of a 0.32 g sample of iodine-131 will remain undecayed after a period of 32 days?

Solution

First, we must determine the number of half-lives that have elapsed.

$$32 \text{ days} \times \frac{1\,\text{Half-life}}{8.0 \text{ Days}} = 4\,\text{Half-lives}$$

Knowing the number of elapsed half-lives and the original amount of radioactive iodine present, we can use the equation

$$\left(\text{Amount of radionuclide undecayed after n half - lives}\right)$$

$$= \left(\text{Original amount of radionuclide}\right)\left(\frac{1}{2^n}\right)$$

$$= (0.32\,\text{g})\left(\frac{1}{2^4}\right) = (0.32\,\text{g})\left(\frac{1}{16}\right) = 0.020\,\text{g}$$

A tabular summary of the amount of sample remaining after each of the elapsed half-lives yields

Half-lives	0	1	2	3	4
Number of days	0	8	16	24	32
Amount remaining	0.32 g	0.16 g	0.080 g	0.040 g	0.020 g

Exercise

1. The half-life of cobalt-60 is 5.3 years. If 2.0 g of cobalt-60 is allowed to decay for a period of 21.2 years, how many grams of cobalt-60 remain?

ACTIVITY 1

Kinetics and nuclear chemistry

Objective

Students will simulate nuclear decay and graph the data in order to gain an understanding of half-life.

Materials

- One coin per student

Procedure

Start with the entire class standing up; each standing student represents a radioactive nucleus. Have all students flip their coins once. If a student gets heads, he/she remains standing (the nucleus doesn't decay); if a student gets tails, the student sits (the nucleus decays). Record the number of standing students in a table on the board. Have the remaining students flip their coins one more time. Those that get tails should sit. Record the number of standing students. Repeat this cycle until all students are seated. Each round of coin flipping represents one half-life. Graph the data from the Table. To get a smoother graph, you will probably need to repeat the procedure a few times and take an average of the data.

Discussion Questions

The following questions can help students reflect on this exercise. Spend some time discussing in class.

1. The data from this experiment probably did not create a perfectly smooth graph, where exactly half the sample decays after each half-life. If you started with 10 grams of a real radioactive element, however, the graph would look almost perfectly smooth. Why is there a difference?
2. What determined the half-life of the element in this simulation?
3. What determines the half-life of actual radioactive elements?
4. After each half-life, the amount of a radioactive element decreases by half. Will the element ever decay completely, if the amount just keeps getting cut in half?

6.5 NUCLEAR REACTIONS – FISSION AND FUSION IN NUCLEAR REACTORS

Upon completion of this topic, learners will be able to:

- distinguish between fusion and fission.

Nuclear fission

In nuclear fission, a very heavy nucleus splits into more stable nuclei of intermediate mass. This process releases enormous amounts of energy. Nuclear fission may occur spontaneously or when nuclei are bombarded by particles. When Uranium-235 is bombarded with slow neutrons, a uranium nucleus can capture one of the neutrons, making it very unstable. The nucleus splits into medium-mass nuclei with the emission of more neutrons. The mass of the products is less than the mass of the reactants. The missing mass is converted to energy.

Nuclear chain reaction

A chain reaction is a reaction in which the material that starts the reaction is also one of the products and can start another reaction. As shown in Figure 3, two or three neutrons can be given off when Uranium-235 fission occurs. These neutrons can cause the fission of other Uranium-235 nuclei. Again neutrons are emitted, which can cause the fission of still other Uranium-235 nuclei.

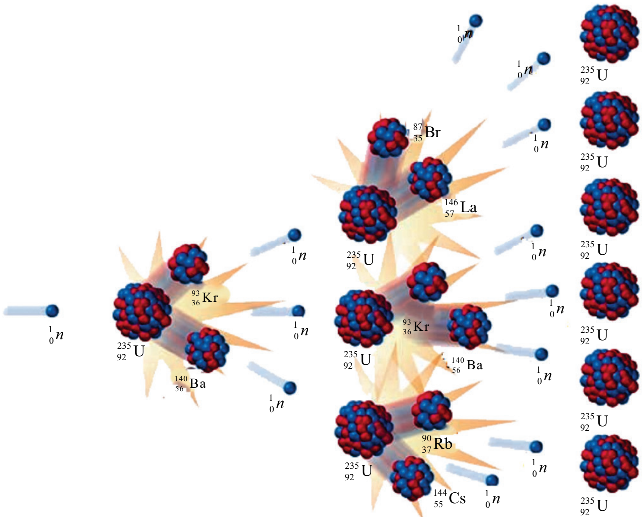


Figure 3. Nuclear Chain Reactions Fission induction of Uranium-235 by bombardment with neutrons.

A chain reaction continues until all of the Uranium-235 atoms have split or until the neutrons fail to strike other Uranium-235 nuclei. If the mass of the Uranium-235 sample is below a certain minimum, too many neutrons escape without striking other nuclei, and the chain reaction stops. The minimum amount of nuclide that provides the number of neutrons needed to sustain a chain reaction is called the critical mass. Uncontrolled chain reactions give the explosive energy to atomic bombs. Nuclear reactors use controlled-fission chain reactions to produce energy and radioactive nuclides.

Nuclear power plants

Nuclear power plants use energy as heat from nuclear reactors to produce electrical energy. They have five main components: shielding, fuel, control rods, moderator, and coolant. The components, shown in Figure 4, are surrounded by shielding. Shielding is radiation-absorbing material that is used to decrease exposure to radiation, especially gamma rays, from nuclear reactors. Uranium-235 is typically used as the fissile fuel to produce energy as heat, which is absorbed by the coolant. Control rods are neutron-absorbing rods that help control the reaction by limiting the number of free neutrons. Because fission of Uranium-235 is more efficiently induced by slow neutrons, a moderator is used to slow down the fast neutrons produced by fission. Nuclear power plants can provide competitively priced electricity without emitting greenhouse gases or particulates. Concerns about nuclear power include storage and disposal of spent radioactive fuel, as well as public perception.

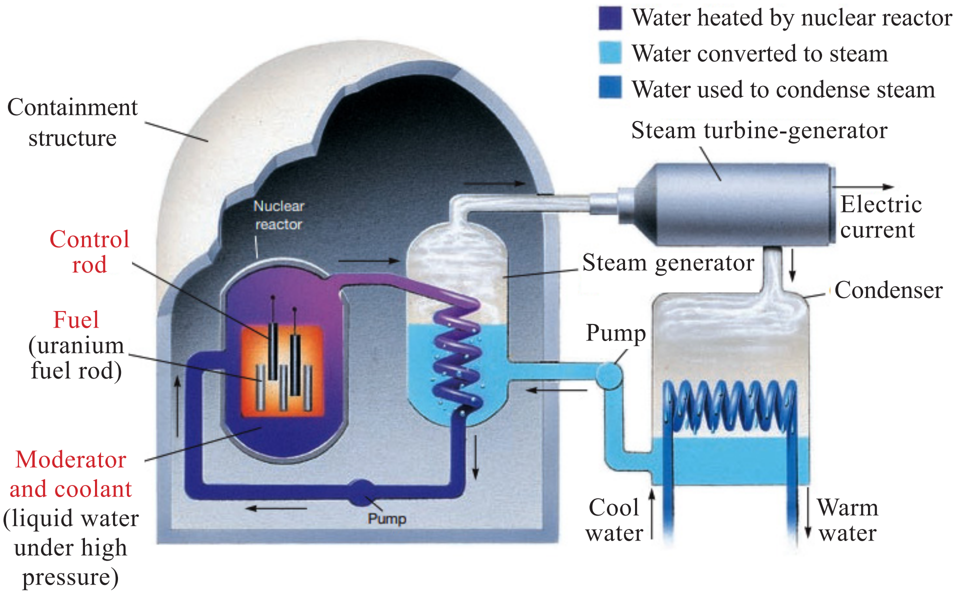


Figure 4. Nuclear power plant

Nuclear fusion

In nuclear fusion, low-mass nuclei combine to form a heavier, more stable nucleus. Nuclear fusion releases even more energy per gram of fuel than nuclear fission. In our sun and stars that are similar to the sun, hydrogen nuclei combine at extremely high temperature and pressure to form a helium nucleus with a loss of mass and release of energy. The net reaction is illustrated in Figure 5.

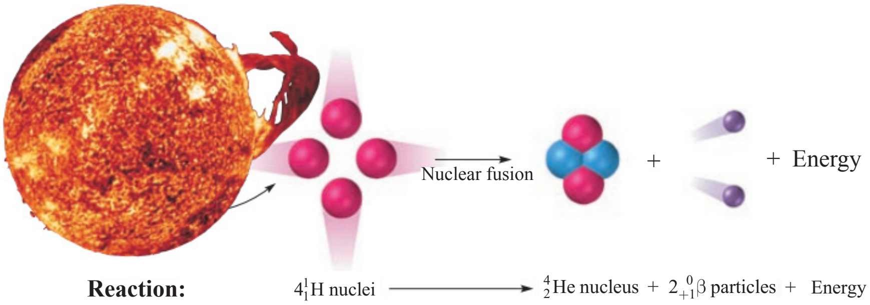


Figure 5. Nuclear Fusion; Fusion of hydrogen nuclei into more stable helium nuclei provides the energy of our sun and other stars.

Fusion is appealing as an energy source because of the availability of light isotopes on Earth and because fusion products are generally not radioactive. Despite this fact, fusion is not presently used to generate energy. The problem is that, in order for two nuclei to fuse, high temperatures and pressures are needed to overcome the electrostatic repulsion between them. Fusion reactions are therefore also known as thermonuclear reactions.

6.6 EFFECTS AND APPLICATION OF RADIOACTIVITY

Upon completion of this topic, learners will be able to:

- comprehend the biological effects of different kinds of radiation.
- explain the effects and applications of radioactivity.

Effects of radioactivity

We are continuously bombarded by radiation from both natural and artificial sources. We are exposed to infrared, ultraviolet, and visible radiation from the sun; radio waves from radio and television stations; microwaves from microwave ovens; X-rays from medical procedures; and radioactivity from natural materials. Understanding the different energies of these various kinds of radiation is necessary in order to understand their different effects on matter.

When matter absorbs radiation, the radiation energy can cause atoms in the matter to be either excited or ionized. In general, radiation that causes ionization, called ionizing radiation, is far more harmful to biological systems than radiation that does not cause ionization. The latter, called non-ionizing radiation, is generally of lower energy, such as radiofrequency electromagnetic radiation or slow-moving neutrons.

Most living tissue contains at least-water by mass. When living tissue is irradiated, water molecules absorb most of the energy of the radiation. Thus, it is common to define ionizing radiation as radiation that can ionize water, a process requiring a minimum energy of 1216 kJ/mol. Alpha, beta, and gamma rays (as well as X-rays and higher-energy ultraviolet radiation) possess energies in excess of this quantity and are therefore forms of ionizing radiation.

When ionizing radiation passes through living tissue, electrons are removed from water molecules, forming highly reactive H_2O^+ ions. An H_2O^+ ion can react with another water molecule to form an H_3O^+ ion and a neutral OH molecule:

$$H_2O^+ + H_2O \longrightarrow H_3O^+ + OH$$

The unstable and highly reactive OH molecule is a free radical, a substance with one or more unpaired electrons, as seen in the Lewis structure $\cdot\underset{\cdot\cdot}{\ddot{\text{O}}}-\text{H}$. The OH molecule is also called the hydroxyl radical, and the presence of the unpaired electron is often emphasized by writing the species with a single dot, ·OH. In cells and tissues, hydroxyl radicals can attack biomolecules to produce new free radicals, which in turn attack yet other biomolecules. Thus, the formation of a single hydroxyl radical can initiate a large number of chemical reactions that are ultimately able to disrupt the normal operations of cells.

The damage produced by a radiation depends on the activity and energy of the radiation, the length of exposure, and whether the source is inside or outside the body. Gamma rays are particularly harmful outside the body because they penetrate human tissue very effectively, just as X-rays do. Consequently, their damage is not limited to the skin. In contrast, most alpha rays are stopped by skin, and beta rays are able to penetrate only about 1 cm beyond the skin surface (Figure 6). Neither alpha rays nor beta rays are as dangerous as gamma rays, unless the radiation source somehow enters the body. Within the body, alpha rays are particularly dangerous because they transfer their energy efficiently to the surrounding tissue, causing a considerable damage.

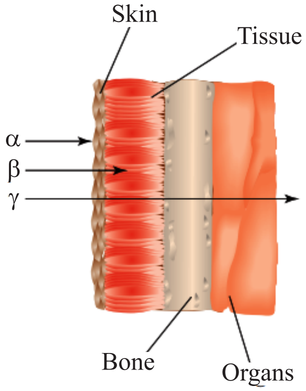


Figure 6. Relative penetrating abilities of alpha, beta, and gamma radiation.

In general, the tissues damaged most by radiation are those that reproduce rapidly, such as bone marrow, blood-forming tissues, and lymph nodes. Extended exposure to low doses of radiation cause cancer. In light of the biological effects of radiation, it is important to determine whether any levels of exposure are safe.

Application of radioactivity

Radioactivity is used to determine the mechanisms of chemical reactions, to trace the movement of atoms in biological systems and the environment, and to date historical artifacts. Nuclear reactions are also used to generate electricity. Other areas of application of radioactivity include medical therapy and diagnosis, food preservation, and pest control.

Explain how radioactivity is applicable in food preservation and pest control?

KEY TERMS

- Nuclear chemistry
- Radioactive decay
- Nuclear reaction
- Radioactive nuclide
- Radioactivity
- Nuclear transmutation
- Alpha radiation

SUMMARY

Some atoms possess nuclei that are unstable. To achieve stability, these unstable nuclei spontaneously emit energy (radiation). Such atoms are said to be radioactive.

The types of radiation emitted by naturally occurring radioactive nuclei are alpha, beta, and gamma. These radiations can be characterized by mass and charge values. Alpha particles carry a positive charge, beta particles carry a negative charge, and gamma radiation has no charge.

The procedures for balancing nuclear equations are different from those for balancing ordinary chemical equations. In nuclear equations, mass numbers and atomic numbers (rather than atoms) balance on both sides.

Every radionuclide decays at a characteristic rate given by its half-life. A half-life is the time required for half of any given quantity of a radioactive substance to undergo decay.

Nuclear fission is the splitting of a large nucleus into two smaller nuclei and one or more neutrons. When the free neutrons are captured efficiently by other nuclei, a chain reaction can occur.

Nuclear reactors use the heat from a controlled nuclear fission reaction to produce power.

Nuclear fusion, the type of reaction that occurs in the sun, is the combination of two light nuclei to form one heavy nucleus. Fusion takes place only at very high temperatures.

Radioactive isotopes are easy to detect and thus make excellent tracers in chemical reactions and in medical practice.

The biochemical effects of radiation depend on the energy, ionizing ability, and penetrating ability of the radiation. Alpha particles exhibit the greatest ionizing effect, and gamma rays have the greatest penetrating ability. High-energy radiation damages living systems by causing ionization and the formation of free radicals.

Exercises

Part I: Choose the correct answer for each of the following questions

1. Which of the following statements concerning the nature of emissions from naturally occurring radioactive materials is incorrect?
   (a) Alpha particles carry a positive charge.
   (b) Beta particles have a mass less than that of alpha particles.
   (c) Gamma particles have a mass of 1 amu.
   (d) Alpha particles have a mass of 4 amu.
2. The loss of an alpha particle by a radionuclide causes which of the following?
   (a) Both its atomic number and its mass number increase.
   (b) Both its atomic number and its mass number decrease.
   (c) Its atomic number increases, and its mass number decreases.
   (d) Its atomic number decreases, and its mass number increases.
3. Which is the daughter nuclide for the alpha decay of polonium-212?
   (a) Lead-208 (c) Radon-208
   (b) Lead-216 (d) Radon-216
4. The beta decay of a nuclide of $^{234}_{90}Th$ produces a nuclide of which of the following?
   (a) Element-88 (c) Element-91
   (b) Element-89 (d) Element-92
5. Which of the following amount of a radio active sample remains undecayed after three half-lives have elapsed?
   (a) 1/3 of the original amount (c) 1/4 of the original amount
   (b) 1/9 of the original amount (d) 1/8 of the original amount
6. The half-life of cobalt-60 is 5.2 years. Thus what happens to a sample of cobalt-60 after 5.2 years?
   (a) It breaks in half.
   (b) It turns into cobalt-30.
   (c) It contains one-half as many cobalt-60 atoms as it did originally.
   (d) It contains twice as many cobalt-60 atoms as it did originally
7. Forms of ionizing radiation include all of the following except one. Which is the exception?
   (a) Visible light (c) Alpha particles
   (b) X-rays (d) Ultraviolet light
8. Which of the following statements about natural radioactive emissions is incorrect?

(a) Beta particles are emitted from nuclei at speeds of up to 0.9 times the speed of light.
(b) Alpha particles cannot penetrate the body's outer layers of skin.
(c) Alpha and beta particles and gamma radiation are all capable of knocking electrons off atoms with which they collide.
(d) A piece of aluminum foil will stop both alpha particles and gamma radiation.

9. Generation of electricity in a nuclear power plant and generation of energy within the sun involve which of the following processes, respectively?
(a) Nuclear fission and nuclear fusion
(b) Nuclear fusion and nuclear fission
(c) Nuclear fission and nuclear fission (both the same process)
(d) Nuclear fusion and nuclear fusion (both the same process)

10. How many neutrons are produced as a result of the following fission reaction?

$$\text{Neutron} + \text{U-235} \longrightarrow \text{I-135} + \text{Y-97} + ?$$

(a) 4-neutrons
(b) 5-neutrons
(c) 6-neutrons
(d) 7-neutrons

Part II: Short Answer Questions

1. The half-life of cesium-137 is 30.2 years. How long will it take for a sample of cesium-137 to decay to 1/8 of its original mass?
2. Briefly describe how a nuclear fission reactor operates.
3. Write the nuclear equation for the decay of phosphorus-32 to sulfur-32 by beta emission. A phosphorus-32 nucleus emits a beta particle and gives a sulfur-32 nucleus.
4. Write balanced nuclear equations for the following processes: (a) Rubidium-90 undergoes beta emission; (b) Polonium-210 decays by emitting a single alpha particle; (c) Radium-226 emits alpha radiation.
5. Give the symbol for (a) a bata particle, (b) an alpha particle, (c) gamma radiation.
6. Describe the purposes of the five major components of a nuclear power plant.
7. How does the penetrating ability of gamma rays compare with that of alpha particles and beta particles?
8. How do nuclear reactions differ from ordinary chemical reactions?
9. Complete the following nuclear equations and identify X in each case:

(a) $^{135}_{53}\text{I} \longrightarrow {}^{135}_{54}\text{Xe} + \text{X}$

(b) $^{40}_{19}\text{K} \longrightarrow {}^{0}_{-1}\beta + \text{X}$

(c) $^{204}_{82}\mathrm{Pb} \longrightarrow \mathrm{X} + {}^{4}_{2}\alpha$ (d) $^{59}_{27}\mathrm{Co} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{56}_{25}\mathrm{Mn} + \mathrm{X}$

10. Fill in the blanks in the following radioactive decay series:

(a) $^{232}\mathrm{Th} \xrightarrow{\alpha}$ ______ $\xrightarrow{\beta}$ ______ $\xrightarrow{\beta}$ $^{228}\mathrm{Th}$

(b) $^{235}\mathrm{U} \xrightarrow{\alpha}$ ______ $\xrightarrow{\beta}$ ______ $\xrightarrow{\alpha}$ $^{227}\mathrm{Ac}$

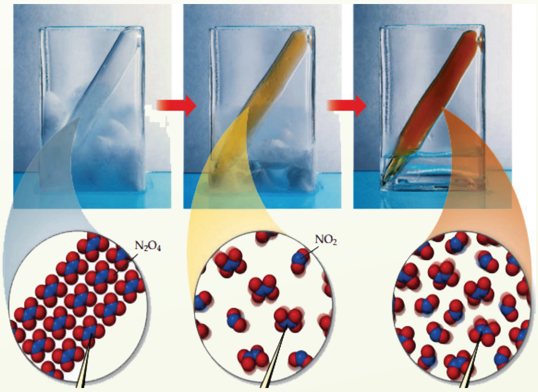
11. In the thorium decay series, thorium-232 loses a total of 6 α-particles and 4 β-particles in a 10-stage process. What is the final isotope produced?
12. Determine the half-life of a radionuclide if after 5.4 days the fraction of undecayed nuclides present is 1/16?
13. What nuclide undergoes nuclear fission to give barium-143, rubidium-94, and three neutrons?
14. Identify which of the following characteristics apply to the fission process, which to the fusion process, and which to both processes.
    (a) An extremely high temperature is required to start the process.
    (b) An example of the process occurs in the sun.
    (c) Neutrons are needed to start the process

C11CH07

CHAPTER 7

CHEMICAL EQUILIBRIUM

Chapter Contents



Chapter Outcomes

By the end of this chapter, you will be able to:

- discuss the general principles of equilibrium, including the mathematical relationships between k_p and k_c.
- write the equilibrium constant expression for homogeneous and heterogeneous equilibria.
- predict the direction of a net reaction towards equilibrium and calculate equilibrium concentrations.
- discuss the factors that can affect the position of an equilibrium.
- use Le Châtelier’s principle to predict the changes.

Introduction

It is generally observed that many of the chemical reactions do not proceed to completion when they are carried out in a closed container. This implies that the reactants are not completely converted into the products. Instead, after some time the concentration of reactants do not undergo further decrease and the reaction appears to have stopped. This state of the system in which no further net change occurs is called a state of equilibrium.

Equilibrium can be attained for the physical and chemical processes. The equilibrium achieved in physical processes such as dissolution of salt, evaporation of water, etc., is called physical equilibrium, whereas the equilibrium achieved in chemical processes such as decomposition of calcium carbonate or reaction between hydrogen and iodine is called chemical equilibrium.

The equilibrium situation raises many interesting questions such as:

- What is the equilibrium state and how is it recognised?
- What is the molecular behaviour when state of equilibrium is reached?
- What are the factors which alter the state of equilibrium?

In this chapter, we shall seek answers to the above questions.

7.1 GENERAL PRINCIPLES OF EQUILIBRIUM

Upon completion of this topic, learners will be able to:

- discuss the general principles of equilibrium.
- state the Law of Mass Action.

Reversible reactions

In most reactions two or more substances react to form products which themselves react to give back the original substances. Thus A and B may react to form C and D which react to reform A and B.

$$A + B \longrightarrow C + D \text{ (Forward reaction)}$$

$$A + B \longleftarrow C + D \text{ (Reverse reaction)}$$

A reaction which can go in the forward and backward direction simultaneously is called a reversible reaction. Such a reaction is represented by showing a pair of arrows between the reactants and products.

$$A + B \rightleftharpoons C + D$$

The arrow pointing right indicates the forward reaction, while that pointing left shows the reverse reaction.

The conversion between nitrogen dioxide, and dinitrogen tetroxide, shows us visible evidence of the reversibility of a reaction.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

The reactant N_2O_4 is a colorless gas, and the product NO_2 is a brown gas. Figure 1 shows a sample of frozen N_2O_4 inside a sealed tube. The solid N_2O_4 vaporizes as it is warmed above its boiling point, and the gas turns darker as the colorless N_2O_4 gas dissociates into brown NO_2 gas. Eventually, even though there is still N_2O_4 in the tube, the color stops getting darker because the system reaches equilibrium. We are left with an equilibrium mixture of N_2O_4 and NO_2 in which the concentrations of the gases no longer change as time passes. Because the reaction is in a closed system, where no gases can escape, equilibrium will eventually be reached.

An equilibrium mixture results because the reaction is reversible: N_2O_4 can form NO_2, and NO_2 can form N_2O_4. This situation is represented by writing the equation for the reaction with two half arrows pointing in opposite directions:

$$\underset{\text{Colorless}}{N_2O_4(g)} \rightleftharpoons \underset{\text{Brown}}{2NO_2(g)}$$

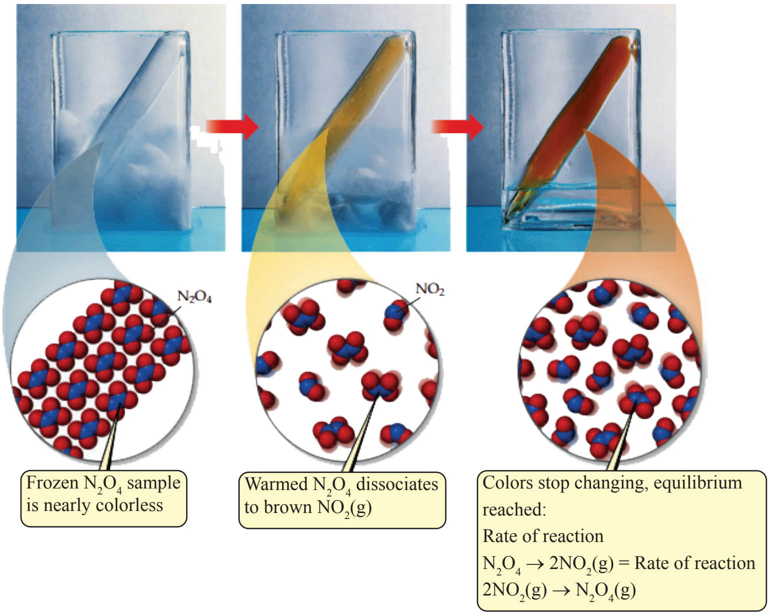


Figure 1. The equilibrium between N_2O_4 and NO_2.

In a chemical equilibrium, the forward and reverse reactions do not stop, rather they continue to occur at the same rate, leading to constant concentrations of the reactants and the products. Plots showing how the reaction rates and concentrations change with respect to time are shown in Figure 2.

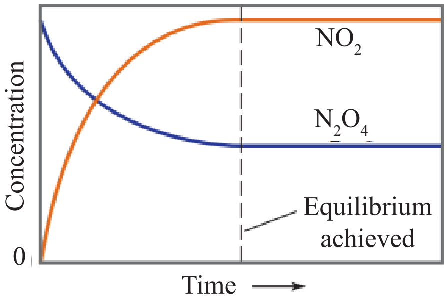


Figure 2. A mixture of N_2O_4 *and* NO_2 *moves toward equilibrium.*

Nature of chemical equilibrium: its definition

Let us consider the reaction

$$A + B \rightleftharpoons C + D$$

If we start with A and B in a closed vessel, the forward reaction proceeds to form C and D. The concentrations of A and B decrease and those of C and D increase continuously. As a result the rate of forward reaction also decreases and the rate of the reverse reaction increases. Eventually, the rate of the two opposing reactions become equal and the system attains a state of equilibrium.

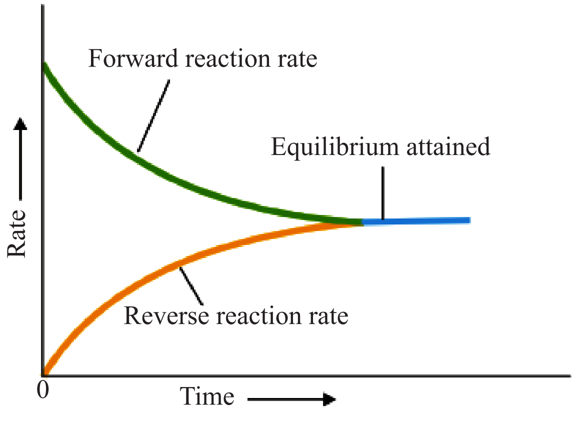


Figure 3. At equilibrium the forward reaction rate equals the reverse reaction rate.

Thus chemical equilibrium may be defined as: the state of a reversible reaction when the two opposing reactions occur at the same rate and the concentrations of reactants and products do not change with time.

Exercises

1. Define dynamic equilibrium. When a reaction reaches equilibrium, does that mean the concentrations of reactants and products are equal?
2. List and describe at least five characteristics of a chemical equilibrium?

Furthermore, the true equilibrium of a reaction can be attained from both sides. Thus the equilibrium concentrations of the reactants and products are the same whether we start with A and B, or C and D.

ACTIVITY 1

Reversible and irreversible chemical reactions

This practical activity is an experiment to demonstrate reversible and irreversible chemical reactions.

Procedure

1. Place about 2 mL of 0.1 M $CoCl_2$ solution in a test tube. Record the color of the solution.
2. Add about 3 mL of concentrated HCl to the test tube. Record the color of the solution.

Warning: HCl can burn skin and clothing.

1. Add enough water to the test tube until a color change occur. Record the color.
2. Add about 2 mL of 0.1 M $CoCl_2$ to another test tube. Add concentrated HCl a drop at a time until the solution turns purple. If the solution becomes blue, add water until it turns purple.
3. Place the test tube in an ice bath with table salt sprinkled into the ice water. Record the color of the solution in the test tube.
4. Place the test tube in a hot water bath. Use a non mercury thermometer to determine that the temperature is at least 70ºC. Record the solution's color.

Observation and Analysis

1. Using equation for the reaction you just observed explain your observations of color in Steps 1-3.
2. Is this reaction reversible or irreversible? What is your evidence?
3. Describe how the equilibrium shifts when energy is added or removed.
4. From your observations of color in Steps 5 and 6, determine whether the reaction is exothermic or endothermic.

Conclusion

What characteristics of a chemical reaction make it reversible or irreversible?

What can you conclude from the experiment? Write a short report on your observation.

Law of mass action

Science is fundamentally empirical – it is based on experiment. The development of the equilibrium concept is typical. From their observations of many chemical reactions, two Norwegian chemists, Cato Maximilian Guldberg (1836-1902) and Peter Waage (1833-1900), proposed in 1864 the law of mass action as a general description of the equilibrium condition.

We can write the conclusions in modern terms: For any reaction at equilibrium,

$$\mathrm{aA} + \mathrm{bB} \rightleftharpoons \mathrm{mM} + \mathrm{nN}$$

The rate of the forward reaction (r_f) depends upon the concentrations of A and B and is given by

$$r_f \propto [\mathrm{A}]^a\,[\mathrm{B}]^b \text{ or } r_f = \mathrm{kg}\,[\mathrm{A}]^a\,[\mathrm{B}]^b$$

where [A] and [B] are the concentrations of A and B respectively.

The rate of the reverse reaction is given by the expression:

$$r_b \propto [\mathrm{M}]^m\,[\mathrm{N}]^n \text{ or } r_b = k_b\,[\mathrm{M}]^m\,[\mathrm{N}]^n$$

where [M] and [N] are the concentrations of M and N respectively. k_f and k_b are rate constants for the forward and reverse reactions, respectively.

At equilibrium, the rate of the forward reaction is equal to the rate of the reverse reaction.

Therefore, $$r_f = r_b$$

$$k_f\,[\mathrm{A}]^a\,[\mathrm{B}]^b = k_b\,[\mathrm{M}]^m\,[\mathrm{N}]^n$$

The ratio of k_f and k_b is represented by K_{eq}.

$$K_{eq} = \frac{k_f}{k_b} = \frac{[\mathrm{M}]^m\,[\mathrm{N}]^n}{[\mathrm{A}]^a\,[\mathrm{B}]^b}$$

Since K_{eq} represents the reaction at equilibrium it is known as equilibrium constant. [M], [N], [A] and [B] are concentrations at equilibrium.

The law of mass action is a relation that states the values of the equilibrium constant expression, K_{eq} are constant for a particular reaction at a given temperature, whatever equilibrium concentrations are substituted.

7.2 FACTORS INFLUENCING EQUILIBRIUM

Upon completion of this topic, learners will be able to:

- state Le Châtelier's principle.
- explain Le Châtelier's principle as it relates to factors influencing equilibrium.
- state what happens to an equilibrium when a reactant or product is added or removed.
- describe the effect of a pressure change on chemical equilibrium.
- apply Le Châtelier's principle when the temperature is altered.
- compare the effect of a catalyst on the rate of reaction with its effect on equilibrium.

Chemical equilibrium represents a balance between forward and reverse reactions. Changes in experimental conditions may disturb the balance and shift the equilibrium position so that more or less of the desired product is formed. Variables that can be controlled experimentally are concentration, pressure, volume, and temperature. Here we will examine how each of these variables affects a reacting system at equilibrium. In addition, we will examine the effect of a catalyst on equilibrium.

Le Châtelier's principle

We can qualitatively predict the effects of changes in concentration, pressure, and temperature on a system at equilibrium by using Le Châtelier's principle, which states that if a system at equilibrium is disturbed by a change in temperature, pressure, or concentration of reactant or product, the system will shift its equilibrium position so as to nullify the effect of the disturbance.

Effect of change in reactant or product concentration

When the concentrations of species in the reaction are altered, the equilibrium shifts until a new state of balance is attained. Le Châtelier's principle states that the shift is in the direction that minimizes or reduces the effect of the change. Therefore, if a chemical system is already at equilibrium and the concentration of any substance in the reaction mixture is increased (either reactant or product), the system reacts to consume some of that substance. Conversely, if the concentration of a substance is decreased, the system reacts to produce some of that substance.

There is no change in the equilibrium constant when we change the concentrations of reactants or products.

Example

Arsenic can be extracted from its ores by first reacting the ore with oxygen (called roasting) to form solid , which is then reduced using carbon:

$$As_4O_6(s)+6C(s) \rightleftharpoons As_4(g)+6CO(g)$$

Predict the direction of the shift of the equilibrium position in response to each of the following changes in conditions.

(a) Addition of carbon monoxide.

(b) Addition or removal of carbon or tetra-arsenic hexoxide (As_4O_6).

(c) Removal of gaseous arsenic (As_4).

Solution

(a) Le Châtelier's principle predicts that the shift will be away from the substance whose concentration is increased. The equilibrium position will shift to the left when carbon monoxide is added.

(b) Since the amount of a pure solid has no effect on the equilibrium position, changing the amount of carbon or tetraarsenic hexoxide will have no effect.

(c) If gaseous arsenic is removed, the equilibrium position will shift to the right to form more products.

Exercise

1. What happens to the equilibrium if $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$
   - (a) $O_2(g)$ is added to the system,
   - (b) NO is removed?

ACTIVITY 2

The equilibrium between Fe^{3+} and $Fe(CNS)^{2+}$

Some reactions involving iron compounds are suitable for illustrating Le Chatelier's Principle because they also involve clear colour changes.

One such equilibrium is:

$$\underset{\text{Yellow}}{Fe^{3+} + CNS^-} \rightleftharpoons \underset{\text{Red}}{Fe(CNS)^{2+}}$$

This experiment will be used to demonstrate the effects of concentration changes on an equilibrium mixture. Adding hydrochloric acid reduces the concentration of Fe^{3+} by forming a complex ion containing iron and chlorine. This causes a shift of equilibrium to the left. The equilibrium can be shifted to the right hand side by adding some potassium thiocyanate solution.

Procedure:

<u>NB</u>: Wear your safety glasses.

1. Mix about 5 cm^3 of solutions of iron(III) chloride and potassium thiocyanate in a beaker. Note the formation of the red complex.

$$\underset{\text{Yellow}}{Fe^{3+} + CNS^-} \rightleftharpoons \underset{\text{Red}}{Fe(CNS)^{2+}}$$

Since the red complex is formed, the equilibrium must lie on the right hand side of the equation.

2. Divide the mixture into three portions in separate boiling tubes (Figure 4). Keep one of these as a control.

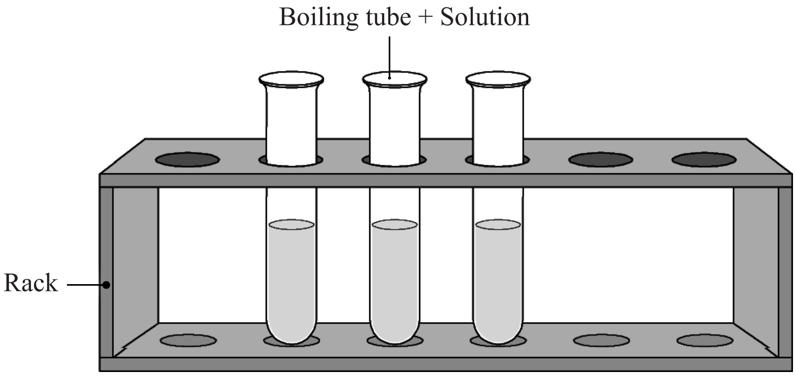


Figure 4. Mixture of $FeCl_3$ and KCNS in separate boilling tubes

3. Using a fume cupboard, add some concentrated hydrochloric acid to the second tube until the red colour disappears. Based on Le Châtelier's Principle, the red colour disappears as the equilibrium is shifted to the left hand side to replace the Fe^{3+} ions removed.
4. Add an equivalent amount of water to the third tube, and compare. This comparison should indicate that the extent of lightening of the colour is not due to a dilution effect.
5. To the second tube, add some potassium thiocyanate solution. The red complex reforms because the equilibrium is shifted to the right.

Questions relating to the experiment

1. Why is a control used in this experiment?
2. When potassium thiocyanate solution is added to a solution of iron(III) chloride, a colour change occurs. Describe the colour change, and explain why it happens.
3. Why does adding hydrochloric acid reverse the colour change referred to in question 2?
4. How can it be shown that it is the chloride ions in the hydrochloric acid that cause this reversal?
5. Why is water added in step 4 of the procedure?
6. Name a substance other than hydrochloric acid that can reverse the colour change referred to in question 2.

Conclusion

What have you learnt? Present your findings from the experiment.
Evaluate the outcome objectively.

Effects of volume and pressure changes

Basically, there are three ways to change the pressure of a reaction system involving gaseous components at a given temperature:

- Add or remove a gaseous reactant or product at constant volume.
- Add an inert gas (one not involved in the reaction) at constant volume.
- Change the volume of the container.

We have already considered the addition or removal of a reactant or product.

When an inert gas is added at constant volume, there is no effect on the equilibrium position. The addition of an inert gas increases the total pressure but has no effect on the concentrations or partial pressures of the reactants or products (assuming ideal gas behavior). Thus the system remains at the original equilibrium position.

A pressure change obtained by changing the volume can affect the yield of products in a gaseous reaction if the reaction involves a change in total moles of gas. When the volume of the container holding a gaseous system is reduced, the system responds by reducing its own volume. This is done by decreasing the total number of gaseous molecules in the system.

Suppose we have a mixture of gaseous nitrogen, hydrogen, and ammonia at equilibrium. If we suddenly reduce the volume, what will happen to the equilibrium position? The reaction system can reduce its volume by reducing the number of molecules present. Consequently, the reaction:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

will shift to the right, thus reducing the total number of gaseous molecules present. The new equilibrium position will be further to the right than the original one. That is, the equilibrium position will shift toward the side of the reaction involving the fewer number of gaseous molecules in the balanced equation.

When the container volume is increased, the system will shift in the direction that increases its volume. An increase in volume in ammonia production will produce a shift to the left to increase the total number of gaseous molecules present.

Examples

Predict the shift in equilibrium position that will occur for each of the following processes when the volume is reduced.

(a) $P_4(s) + 6Cl_2(g) \rightleftharpoons 4PCl_3(l)$

(b) $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$

(c) $PCl_3(g) + 3NH_3(g) \rightleftharpoons P(NH_2)_3 + 3HCl(g)$

Solution

(a) Since P_4 and PCl_3 are a pure solid and a pure liquid, respectively, we need to consider only the effect of the decrease in volume on Cl_2. The position of the equilibrium will shift to the right, since the reactant side contains six gaseous molecules and the product side has none.

(b) Decreasing the volume will shift the given reaction to the right, since the product side contains only one gaseous molecule and the reactant side has two.

(c) Both sides of the balanced reaction equation have four gaseous molecules. A change in volume will have no effect on the equilibrium position. There is no shift in this case.

Effect of change of temperature

The effect of change in temperature on an equilibrium reaction can be easily predicted by the following version of the Le Châtelier's principle.

When temperature of a reaction is increased, the equilibrium shifts in a direction in which heat is absorbed.

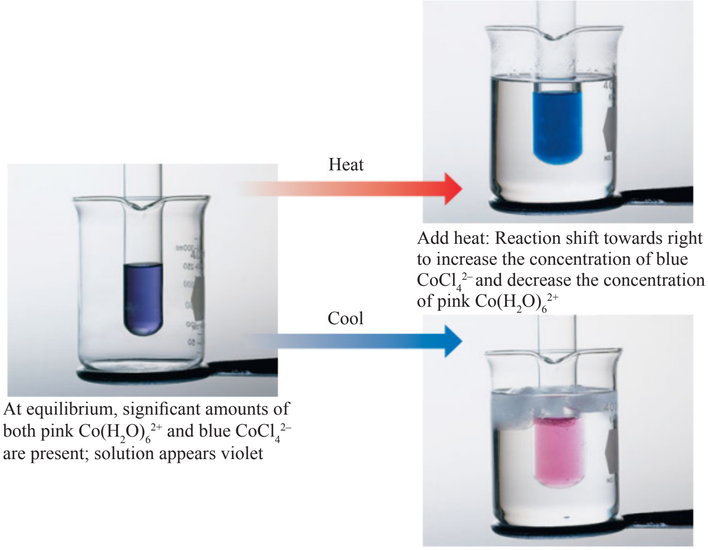
For example, consider the equilibrium established when cobalt(II) chloride, ($CoCl_2$) is dissolved in hydrochloric acid, HCl(aq), in the endothermic reaction,

$$\underset{\text{Pale pink}}{Co(H_2O)_6^{2+}(aq)} + 4Cl^-(aq) \rightleftharpoons \underset{\text{Deep blue}}{CoCl_4^{2-}(aq)} + 6H_2O(l) \qquad \Delta H > 0,$$

because $Co(H_2O)_6^{2+}$ is pink and $CoCl_4^{2-}$ is blue, the position of this equilibrium is readily seen from the color of the solution (Figure 5). When the solution is heated it turns blue, indicating that the equilibrium has shifted to form more $CoCl_4^{2-}$. Cooling the solution leads to a pink solution, indicating that the equilibrium has shifted to produce more $Co(H_2O)_6^{2+}$.

In an endothermic reaction, heat is absorbed as reactants are converted to products. Thus, increasing the temperature causes the equilibrium to shift to the right, in the direction of making more products, and K_{eq} increases. In an exothermic reaction, the opposite occurs: Heat is produced as reactants are converted to products. Thus, increasing the temperature in this case causes the equilibrium to shift to the left, in the direction of making more reactants, and K_{eq} decreases.

Cooling a reaction has the opposite effect. As we lower the temperature, the equilibrium shifts in the direction that produces heat. Thus, cooling an endothermic reaction shifts the equilibrium to the left, decreasing K_{eq}, as shown in Figure 5, and cooling an exothermic reaction shifts the equilibrium to the right, increasing K_{eq}.



At equilibrium, significant amounts of both pink $Co(H_2O)_6^{2+}$ and blue $CoCl_4^{2-}$ are present; solution appears violet

Add heat: Reaction shift towards right to increase the concentration of blue $CoCl_4^{2-}$ and decrease the concentration of pink $Co(H_2O)_6^{2+}$

Remove heat: Reaction shif towards left to decrease the concentration of blue $CoCl_4^{2-}$ and increase the concentration of pink $Co(H_2O)_6^{2+}$

Figure 5. Temperature and Le Châtelier's principle.

Effect of catalyst on the position of equilibrium

A catalyst has no effect on the equilibrium composition of a reaction mixture. It merely speeds up the attainment of equilibrium. This is due to the fact that the catalyst changes the rate of the forward reaction and the reverse reaction by the same extent so the equilibrium is not affected. We can therefore conclude that a presence of a catalyst does not alter the equilibrium constant, nor does it shift the position of an equilibrium system.

7.3 THE EQUILIBRIUM CONSTANT

Upon completion of this topic, learners will be able to:

- define the equilibrium-constant expression and equilibrium constant.
- explain the nature of equilibrium constant, performing simple related calculations.
- define homogeneous equilibrium and heterogeneous equilibrium.
- obtain K_c for a reaction that can be written as a sum of other reactions of known K_c values.
- give a qualitative interpretation of the equilibrium constant based on its value.
- define reaction quotient, Q.
- describe the direction of reaction after comparing Q with K_c.

The equilibrium constant expression for a reaction is an expression obtained as the product of the concentration of products divided by the product of the concentration of reactants, each concentration term raised to a power equal to the coefficients in the chemical equation.

For the previous general reaction,

$$\mathrm{aA + bB \rightleftharpoons mM + nN}$$

you have:

$$K_c = \frac{[\mathrm{M}]^{\mathrm{m}}[\mathrm{N}]^{\mathrm{n}}}{[\mathrm{A}]^{\mathrm{a}}[\mathrm{B}]^{\mathrm{b}}}$$

The constant K_c, the equilibrium constant, is the numerical value obtained when we substitute molar equilibrium concentrations into the equilibrium-constant expression. The subscript c on the K_c indicates concentrations expressed in molarity that are used to evaluate the constant.

When all the reactants and the products are in the gaseous state, their concentrations can be written in terms of partial pressures. In such cases the equilibrium constant is denoted by K_p.

The expression for K_p is:

$$K_p = \frac{(\mathrm{P_M})^{\mathrm{m}}(\mathrm{P_N})^{\mathrm{n}}}{(\mathrm{P_A})^{\mathrm{a}}(\mathrm{P_B})^{\mathrm{b}}}$$

Writing equilibrium constant expressions

To use equilibrium constants, we must express them in terms of reactant and product concentrations. Our only guide is the Law of Mass Action, which is the general formula for finding equilibrium concentrations. However, because the reacting species are not always in the same phase, there may be more than one way to express the equilibrium constant for the same reaction. To begin with, we will consider reactions in which the reactants and products are in the same phase.

Homogeneous equilibria

The term homogeneous equilibrium applies to reactions in which all reacting species are in the same physical state.

For a homogeneous reaction, rules followed while writing the expression for the equilibrium constant are:

- The concentrations of all the substances formed as products are written in the numerator.
- The concentrations of all the reactants are written in the denominator.
- Each concentration term is raised to the power of its respective coefficient as written in the balanced chemical reaction.

For the formation of ammonia,

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

expression of the equilibrium constant in terms of molarity is:

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

The expression for K_p is:

$$K_p = \frac{\left(P_{NH_3}\right)^2}{(P_{N_2})\left(P_{H_2}\right)^3}$$

Exercise

1. Write the equilibrium-constant expression K_c for the equation

   (a) $2NO_2(g) + 7H_2(g) \rightleftharpoons 2NH_3(g) + 4H_2O(g)$

   (b) $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$

   (c) $HF(aq) \rightleftharpoons H^+(aq) + F^-(aq)$

Units of the equilibrium constant

In the equilibrium expression for a particular reaction, the concentrations are given in units of moles/litre or mol/L, and the partial pressure are given in atmospheres (atm). The units of K_c and K_p, depend on the specific reaction.The unit of K_c of a reaction depends upon the number of moles of the reactants and products involved in the reaction.

Therefore, for a general reaction;

$$aA + bB \rightleftharpoons mM + nN$$

For concentration of reactants and products given in mol. L^{-1} the unit of K_c will be:

$$K_c = \frac{[M]^m [N]^n}{[A]^a [B]^b} = \frac{[mol.L^{-1}]^m [mol.L^{-1}]^n}{[mol.L^{-1}]^a [mol.L^{-1}]^b} = (mol.L^{-1})^{(m+n)-(a+b)}$$

The unit of K_p is decided by the unit of pressure. If the partial pressure is expressed in atm, then the unit of K_p, will be:

$$K_p = \frac{(P_M)^m (P_N)^n}{(P_A)^a (P_B)^b} = \frac{(atm)^m (atm)^n}{(atm)^a (atm)^b} = (atm)^{(m+n)-(a+b)}$$

It may be noted, however, that the units are often omitted when equilibrium constants are listed in Tables.

Heterogeneous equilibria

A heterogeneous equilibrium results from a reversible reaction involving reactants and products that are in different phases.

Rules for Writing Expression for the Equilibrium Constant for a Heterogeneous Reaction:

- The concentration terms of products are written in the numerator and the concentration terms of reactants are written in the denominator raised to the power of their respective coefficient in the balanced chemical equation.
- While writing the expression for K_c, the molarity of gaseous reactants and products and species present in the solution are written.
- Concentration terms of solids and pure liquids do not appear in the expression, as they are taken to be unity.
- While writing the expression for K_p, partial pressures of only the gaseous reactants and products are written in the expression for the equilibrium constant.

The decomposition of calcium carbonate upon heating to form calcium oxide and carbon dioxide is an example of a heterogeneous equilibrium. If the reaction is carried out in a closed vessel, the following equilibrium is attained:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

The two solids and one gas constitute three separate phases. At equilibrium, we might write the equilibrium constant as:

$$K_c = \frac{[CO_2][CaO]}{[CaCO_3]}$$

But $CaCO_3$ and CaO are pure solids. The concentration of a pure solid (or liquid) is fixed and cannot vary. Thus the concentrations of pure solids or liquids are not included in the equilibrium constant expression. Ignoring the concentrations of $CaCO_3$ and CaO, the equilibrium constant expression for the decomposition of $CaCO_3$ is written as:

$$K_c = [CO_2]$$

In terms of partial pressures $K_p = P_{CO_2}$.

Exercise

1. Write expressions for the equilibrium constants K_c and K_p for the equilibria:

   (a) $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$

   (b) $3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$

Calculating equilibrium constants

If we can measure the equilibrium concentrations of all the reactants and products in a chemical reaction, calculating the value of the equilibrium constant is straightforward. We simply insert all the equilibrium concentrations into the equilibrium-constant expression for the reaction.

Often we do not know the equilibrium concentrations of all species in an equilibrium mixture. If we know the equilibrium concentration of at least one species, however, we can generally use the stoichiometry of the reaction to deduce the equilibrium concentrations of the others. The following steps outline the procedure:

1. Tabulate all known initial and equilibrium concentrations of the species that appear in the equilibrium constant expression.
2. For those species for which initial and equilibrium concentrations are known, calculate the change in concentration that occurs as the system reaches equilibrium.
3. Use the stoichiometry of the reaction (that is, the coefficients in the balanced chemical equation) to calculate the changes in concentration for all other species in the equilibrium constant expression.
4. Use initial concentrations from step 1 and changes in concentration from step 3 to calculate equilibrium concentrations not tabulated in step 1.
5. Determine the value of the equilibrium constant.

Example

A mixture of 0.10 mol of NO, 0.050 mol of H_2, and 0.10 mol of H_2O is placed in a 1.0 L vessel at 300 K. The following equilibrium is established:

$$2NO(g) + 2H_2(g) \rightleftharpoons N_2(g) + 2H_2O(g)$$

At equilibrium [NO] = 0.062 M. Calculate K_c?

Solution

$$\text{Concentration} = \frac{\text{No. of moles}}{\text{Volume}}$$

$$\text{Initial concentration of NO} = \frac{0.10 \text{ mol}}{1 \text{ L}} = 0.10 \text{ M}$$

$$\text{Initial concentration of } H_2 = \frac{0.05 \text{ mol}}{1 \text{ L}} = 0.05 \text{ M}$$

$$\text{Initial concentration of } H_2O = \frac{0.10 \text{ mol}}{1 \text{ L}} = 0.10 \text{ M}$$

The ICE Table of the above reaction is given below.

	2NO	$2H_2$	N_2	$2H_2O$
Initial (I) concentration	0.10mol/L	0.05mol/L	0	0.10mol/L
Change (C)	−2x	−2x	+x	+2x
Equilibrium (E) concentration	(0.10−2x) mol/L	(0.05−2x) mol/L	x mol/L	(0.10+2x) mol/L

Compare the equilibrium concentration of NO with that in ICE table.

$$(0.10 - 2x) = 0.062$$

$$2x = 0.038$$

$$x = 0.019$$

The equilibrium concentrations are calculated as shown below:

$$[H_2] = (0.05 - 2x)\text{mol/L} = (0.05 - 2 \times 0.019)\text{mol/L} = 0.012\text{mol/L}.$$

and,

$$[N_2] = x = 0.019 \text{ mol/L}$$

$$[H_2O] = (0.10 + 2x)\text{mol/L} = (0.10 + 2 \times 0.019)\text{mol/L} = 0.138 \text{ mol/L}$$

Hence, the equilibrium concentrations are:

$$[H_2] = 0.012 \text{ mol/L}$$

$$[N_2] = 0.019 \text{ mol/L}$$

$$[H_2O] = 0.138 \text{ mol/L}$$

The equilibrium constant calculation is as follows:

$$K_c = \frac{[N_2][H_2O]^2}{[NO]^2[H_2]^2} = \frac{0.019\text{mol}/\text{L} \times (0.138 \text{ mol}/\text{L})^2}{\left(0.012\frac{\text{mol}}{\text{L}}\right)^2\left(0.062\frac{\text{mol}}{\text{L}}\right)^2} = 6.53 \times 10^2 \text{L}/\text{mol}$$

Exercises

1. Consider the formation of ammonia from nitrogen and hydrogen:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

This reaction is initiated with 0.50 M N_2 and 0.85 M H_2 and no NH_3. At equilibrium, the concentration of N_2 was 0.25 M. What is the value of K_c?

2. 1.25 mol NOCl was placed in a 2.50 L reaction chamber at 427°C. After equilibrium was reached, 1.10 moles NOCl remained. Calculate the equilibrium constant for the reaction.

$$2NOCl\ (g) \rightleftharpoons 2NO(g) + Cl_2(g)$$

Equilibrium constant for the sum of reactions

It is possible to determine the equilibrium constants for various chemical reactions and then use them to obtain the equilibrium constants of other reactions.

The useful rules are as follows:

1. The equilibrium constant of a reaction in the reverse direction is the inverse (or reciprocal) of the equilibrium constant of the reaction in the forward direction:

$$A + B \rightleftharpoons C + D \qquad K_1$$

$$C + D \rightleftharpoons A + B \qquad K = 1/K_1$$

2. The equilibrium constant of a reaction that has been multiplied by a number is equal to the original equilibrium constant raised to a power equal to that number.

$$A + B \rightleftharpoons C + D \qquad K_1$$

$$nA + nB \rightleftharpoons nC + nD \qquad K = K_1^{\,n}$$

3. If a given chemical equation is obtained by taking the sum of other equations, the equilibrium constant for the given equation equals the product of the equilibrium constants of the added equations.

$$1.\ A + B \rightleftharpoons C + D \qquad K_1$$
$$2.\ C + F \rightleftharpoons G + A \qquad K_2$$
$$3.\ B + F \rightleftharpoons D + G \qquad K_3 = (K_1)(K_2)$$

Example

The equilibrium constants for the following reactions at 1300 K are given:

$$2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g);\ K_c = 4.0 \times 10^{-14}$$
$$2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g);\ K_c = 1.0 \times 10^{-12}$$

Determine the value of K_c for the reaction:

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

Solution

To obtain the desired overall equation:

(i) Reverse and multiply by ½

$$H_2(g) + \tfrac{1}{2}\,O_2(g \rightleftharpoons H_2O(g)\ ;\ Kc_{\text{i}} = \frac{1}{\sqrt{4.0\times10^{-14}}} = \frac{1}{2.0\times10^{-7}} = 5\times10^{6}$$

(ii) Multiply the second equation by ½

$$CO_2(g) \rightleftharpoons CO(g) + \tfrac{1}{2}\,O_2(g);\ Kc_{\text{ii}} = \sqrt{1.0\times10^{-12}} = 1.0\ \times\ 10^{-6}$$

Then the equilibrium constant, k_c for the reaction $H_2(g) + CO_2(g) \rightleftharpoons CO(g) + H_2O(g)$ becomes:

$$K_c = (Kc_{\text{i}})(Kc_{\text{ii}}) = 5 \times 10^{6} \times 1.0 \times 10^{-6} = 5$$

Exercise

1. Given that, at 700 K, K_p = 54.0 for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ and $K_p = 1.04 \times 10^{-4}$ for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, determine the value of K_p for the reaction

$$2NH_3(g) + 3I_2(g) \rightleftharpoons 6HI(g) + N_2(g) \text{ at 700K?}$$

Applications of the equilibrium constant

What does the equilibrium constant tell us?

The equilibrium constant helps us to predict the direction in which a reaction mixture will proceed to achieve equilibrium and to calculate the concentrations of reactants and products once equilibrium has been reached. In this section we will look at the following uses of the equilibrium constant:

1. Qualitatively interpreting the equilibrium constant

By merely looking at the magnitude of K_c, you can tell whether a particular equilibrium favors products or reactants.

If K_c for a reaction

$$\underbrace{aA + bB}_{\text{Reactants}} \rightleftharpoons \underbrace{mM + nN}_{\text{Products}}$$

is large, the equilibrium mixture is contains more of products. If K_c is small, the equilibrium mixture is contains more of reactants. When the equilibrium constant is neither large nor small (around 1), neither reactants nor products are favored. The equilibrium mixture contains appreciable amounts of both reactants and products.

Consider the synthesis of ammonia from its elements.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

At 25°C, the equilibrium constant K_c equals 4.1×10^8. This means that the product concentrations is 4.1×10^8 times larger than the reactant concentrations. In other words, at this temperature the reaction favors the formation of ammonia at equilibrium.

Exercise

1. The equilibrium constant K_c for the reaction

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

equals 4.6×10^{-31} at 25ºC. Does the equilibrium mixture contain predominantly reactants or products?

ACTIVITY 3

The variation of K_c/K_p

Nitrogen dioxide (NO_2) and dinitrogen tetraoxide (N_2O_4) exist together in equilibrium.

$$2NO_2(g) \rightleftharpoons N_2O_4(g) \quad \Delta H = -58\frac{kJ}{mol}$$

A gas syringe contains a sample of an equilibrium mixture of the two gases. The mixture is brown in color.

The plunger is pulled out to reduce the pressure of the gaseous equilibrium mixture. The colour of the mixture first of all changes to light brown as it now occupies a larger volume. However, it then goes darker brown in colour as a new equilibrium is established.

State why the color of the mixture changes from light brown to a darker brown. Justify your answer.

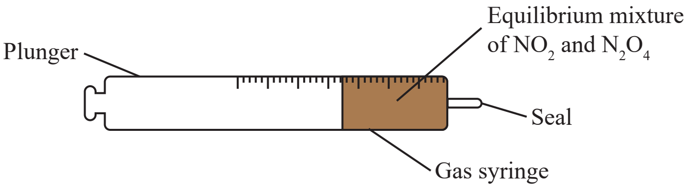


Figure 6. Equilibrium mixture of NO_2 *and* N_2O_4 *in a gas syringe*

Here it is to be noted that the pressure is not the only factor to have changed. The volume has changed as well. However, it is important to remember: 'An increase in volume, at constant temperature, will shift the equilibrium to the side where there are more moles of gas'.

Hence, the increase in volume produces the same result as the decrease in pressure.

Procedure

- The nitrogen dioxide/dinitrogen tetraoxide mixture can be generated by heating lead(II) nitrate in a boiling tube connected to the gas syringe with a rubber tubing.
- Be careful to place a pad of cotton wool in the neck of the boiling tube since lead(II) nitrate decompose on heating, so work in a fume cupboard.
- When sufficient gas mixture has been collected, disconnect the rubber tubing and seal the end of the gas syringe with a plastic cap.
- You can now increase or decrease the pressure of the gas in the syringe by pushing or pulling the plunger.
- When pushing the plunger you may have to hold your finger over the plastic cap. Be sure to wear protective gloves if you do this.

Result and observation

- Observe the relative variation in their colour intensity (compared to the one at room temperature).
- Determine the direction of shift in the equilibrium position of the reaction.

$$2NO_2\,(g) \rightleftharpoons N_2O_4(g)$$

- Interpret your observations appropriately and explain the variation of K_c/K_p.

Conclusion

What conclusions can you draw from this practical activity?

2. Predicting the direction of reaction

The law of mass action not only describes equilibrium systems but also provides important information about systems not yet at equilibrium. The reaction quotient, Q, has the same algebraic form as K_c, but the given concentrations, not specifically the equilibrium concentrations, are used in the calculation. Comparing Q with K_c enables us to predict in which direction a reaction will proceed to achieve equilibrium.

The reaction quotient, Q, is a number obtained by substituting reactant and product concentrations or partial pressures at any point during a reaction into an equilibrium constant expression. Therefore, for the general reaction

$$aA + bB \rightleftharpoons mM + nN$$

the reaction quotient in terms of molar concentrations is:

$$Q_c = \frac{[M]^m [N]^n}{[A]^a [B]^b}$$

(A related quantity Q_p can be written for any reaction that involves gases by using partial pressures instead of concentrations.)

Although we use what looks like the equilibrium constant expression to calculate the reaction quotient, the concentrations we use may or may not be the equilibrium concentrations.

To determine whether or not we are at equilibrium, or in which direction the reaction proceeds to achieve equilibrium, we compare the values of Q_c and K_c or Q_p and K_c. Three possible situations are as follows:

- $Q = K$: The system is at equilibrium; no shift will occur.

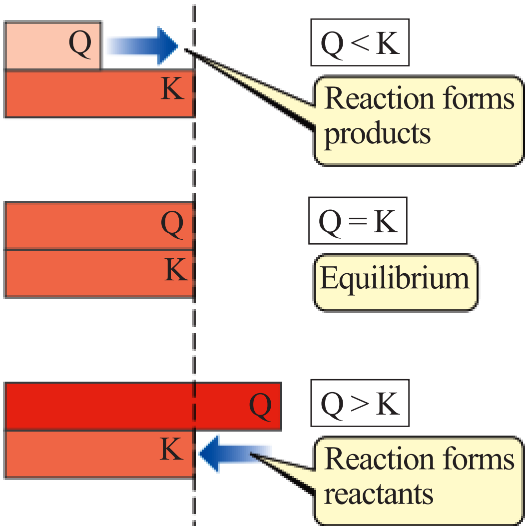


Figure 7. Predicting the direction of a reaction by comparing Q and K at a given temperature.

- $Q > K$: In this case, the ratio of initial concentrations of products to initial concentrations of reactants is too large. To reach equilibrium, a net change of products to reactants must occur. The system shifts to the left, consuming products and forming reactants, until equilibrium is achieved.

- *Q* < *K*: In this case, the ratio of initial concentrations of products to initial concentrations of reactants is too small. The system must shift to the right, consuming reactants and forming products, to attain equilibrium.

These relationships are summarized in Figure 7.

Exercise

1. At the start of a reaction, there are 0.249 mol N_2, 3.21×10^{-2} mol H_2, and 6.42×10^{-4} mol NH_3 in a 3.50 L reaction vessel at 375°C. If the equilibrium constant (K_c) for the reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

is 1.2 at this temperature, decide whether the system is at equilibrium. If it is not, predict which way the net reaction will proceed.

3. Calculating equilibrium concentrations

The approach in solving problems of this type is similar to the one we used for evaluating equilibrium constants: We tabulate initial concentrations or partial pressures, changes in those concentrations or pressures, and final equilibrium concentrations or partial pressures. Usually we end up using the equilibrium constant expression to formulate an equation that must be solved for an unknown quantity.

In these types of problem it will be very helpful to use the following approach.

1. Express the equilibrium concentrations of all species in terms of the initial concentrations and a single unknown x, which represents the change in concentration.
2. Write the equilibrium constant expression in terms of the equilibrium concentrations. Knowing the value of the equilibrium constant, solve for x.
3. Having solved for x, calculate the equilibrium concentrations of all species.

The following example illustrates the application of this three-step procedure.

Example

A 1.000 L flask is filled with 1.000 mol of $H_2(g)$ and 2.000 mol of $I_2(g)$ at 448°C. The value of the equilibrium constant K_c for the reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

at 448°C is 50.5. What are the equilibrium concentrations of H_2, I_2, and HI in mole/L?

Solution

First, we note the initial concentrations of H_2 and I_2:

$$[H_2] = 1.000\text{ M and } [I_2] = 2.000\text{ M}$$

Second, we construct a Table in which we tabulate the initial concentrations:

	$H_2(g)$ +	$I_2(g)$ $\rightleftharpoons$	$2HI(g)$
Initial concentration (M)	1.000	2.000	0
Change in concentration (M)			
Equilibrium concentration (M)			

Third, we use the stoichiometry of the reaction to determine the changes in concentration that occur as the reaction proceeds to equilibrium. The H_2 and I_2 concentrations will decrease as equilibrium is established and that of HI will increase. Let's represent the change in concentration of H_2 by x. The balanced chemical equation tells us the relationship between the changes in the concentrations of the three gases. For each x mol of H_2 that reacts, x mol of I_2 are consumed and 2x mol of HI are produced:

	$H_2(g)$ +	$I_2(g)$ $\rightleftharpoons$	$2HI(g)$
Initial concentration (M)	1.000	2.000	0
Change in concentration (M)	-x	-x	+2x
Equilibrium concentration (M)			

Fourth, we use initial concentrations and changes in concentrations, as dictated by the stoichiometry, to express the equilibrium concentrations. With all entries, the table now looks like this:

	$H_2(g)$ +	$I_2(g)$ $\rightleftharpoons$	$2HI(g)$
Initial concentration (M)	1.000	2.000	0
Change in concentration (M)	-x	-x	+2x
Equilibrium concentration (M)	1.000 – x	2.000 – x	+2x

Fifth, we substitute the equilibrium concentrations into the equilibrium constant expression and solve for x:

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(2x)^2}{(1.000 - x)(2.000 - x)} = 50.5$$

Expand this expression to obtain a quadratic equation in x. Solving the quadratic equation leads to two solutions for x:

$$x = 2.323 \text{ or } 0.935$$

On substituting 2.323 for x into the expressions for the equilibrium concentrations, we find negative concentrations of H_2 and I_2. Because a negative concentration is not chemically meaningful, we reject this solution. We then use to find the equilibrium concentrations:

$$[HI] = 1.000 - x = 0.065\ M$$

$$[I_2] = 2.000 - x = 1.065\ M$$

$$[H_2] = 2x = 1.87\ M$$

Finally we can check our solution by putting these numbers into the equilibrium constant expression to assure that we correctly calculated the equilibrium constant.

Exercise

1. For the equilibrium:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \quad K_c = 0.36 \text{ at } 100^{\circ}C$$

a sample of 0.25 mol N_2O_4 is allowed to dissociate and come to equilibrium in a 1.5 L flask at 100°C. What are the equilibrium concentrations of NO_2 and N_2O_4?

7.4 RELATIONSHIP BETWEEN K_p & K_c

Upon completion of this topic, learners will be able to:

- demonstrate the mathematical relationship between K_p & K_c.

If concentrations are provided, K_c is easier to use. If the problem makes use of partial-pressure data, then K_p is generally more convenient. But if the equilibrium constant is in one set of units and the concentrations are in the other, then we must convert either the concentrations or the equilibrium constant to match.

Relation between K_c and K_p

For the general reaction:

$$aA(g) + bB(g) \rightleftharpoons mM(g) + nN(g)$$

$$K_c = \frac{[M]^m[N]^n}{[A]^a[B]^b} \quad \text{and} \quad K_p = \frac{(P_M)^m(P_N)^n}{(P_A)^a(P_B)^b}$$

It is assumed that all the gaseous species behave like an ideal gas. The relationship between the partial pressure of a gas and its molar concentration comes from the ideal gas law:

$$PV = nRT$$

$$P = \left(\frac{n}{V}\right) RT = CRT$$

Where, n/V = C is the molar concentration-the units are moles per liter, n = amount of the gaseous species in moles, R = Gas constant, T = Temperature in kelvin, V = Volume of the reaction mixture, and C = Molarity.

For the pressure of any species, substitute [n/V] × RT for P

$$K_p = \frac{\left(\frac{n_M}{V} \times RT\right)^m \left(\frac{n_N}{V} \times RT\right)^n}{\left(\frac{n_A}{V} \times RT\right)^a \left(\frac{n_B}{V} \times RT\right)^b}$$

We can substitute square brackets for $\frac{n}{V}$.

$$K_p = \frac{([M] \times RT)^m ([N] \times RT)^n}{([A] \times RT)^a ([B] \times RT)^b}$$

and collect all the RT terms:

$$K_p = \frac{([M])^m ([N])^n}{([A])^a ([B])^b} \times \frac{(RT)^{m+n}}{(RT)^{a+b}}$$

We can recognize that the first term is equal to K_c

$$K_p = K_c \times (RT)^{m+n-a-b}$$

and the second term is $(RT)^{\Delta n}$, so

$$K_p = K_c (RT)^{\Delta n}$$

here Δn = (m + n) – (a + b) for gaseous species.

When the number of gaseous reactants and products are equal then, a + b = m + n. Therefore, Δn = 0 and hence $K_p = K_c$.

Exercise

1. For which of the following reaction $K_p = K_c$?
   (a) $2NOCl\,(g) \rightleftharpoons 2NO\,(g) + Cl_2\,(g)$
   (b) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

(c) $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl\,(g)$

(d) $PCl_3\,(g) + Cl_2\,(g) \rightleftharpoons PCl_5(g)$

KEY TERMS

- Chemical equilibrium
- Reversible reactions
- Law of mass action
- Le Châtelier's Principle
- Equilibrium constant expression
- Equilibrium constant
- Homogeneous Equilibrium
- Heterogeneous Equilibrium
- Reaction quotient

SUMMARY

A chemical reaction can be in a state in which the forward and reverse processes occur at the same rate. This condition is called **chemical equilibrium**, and it results in the formation of an equilibrium mixture of the reactants and products of the reaction. The composition of an equilibrium mixture does not change with time if temperature is held constant.

The relationship between the concentrations of the reactants and products of a system at equilibrium is given by the law of mass action. For an equilibrium equation of the form $aA + bB \rightleftharpoons mM + nN$ the equilibrium constant expression is written as:

$$K_c = \frac{[M]^m [N]^n}{[A]^a [B]^b}$$

where K_c is a constant called the equilibrium constant.

When the equilibrium system of interest consists of gases, it is often convenient to express the concentrations of reactants and products interms of gas pressures:

$$K_p = \frac{(P_M)^m (P_N)^n}{(P_A)^a (P_B)^b}$$

K_c and K_p are related by the expression $K_p = K_c\,(RT)^{\Delta n}$

The value of the equilibrium constant changes with temperature. A large value of K_c indicates that the equilibrium mixture contains more products than reactants and therefore lies toward the product side of the equation. A small value for the equilibrium constant means that the equilibrium mixture contains less products than reactants and therefore lies toward the reactant side. The equilibrium constant expression and the equilibrium constant of the reverse of a reaction are the reciprocals of those of the forward reaction. If a reaction is the sum of two or more reactions, its equilibrium constant will be the product of the equilibrium constants for the individual reactions.

Equilibria for which all substances are in the same phase are called homogeneous equilibria; in heterogeneous equilibria two or more phases are present. The concentrations of pure solids and liquids are left out of the equilibrium-constant expression for a heterogeneous equilibrium.

The reaction quotient, Q, is found by substituting reactant and product concentrations or partial pressures at any point during a reaction into the equilibrium-constant expression. If the system is at equilibrium, $Q = K$.

If $Q \neq K$, however, the system is not at equilibrium.

When $Q < K$, the reaction will move toward equilibrium by forming more products (the reaction proceeds from left to right); when $Q > K$, the reaction will proceed from right to left. Knowing the value of K_{eq} makes it possible to calculate the equilibrium amounts of reactants and products.

Le Châtelier's principle states that if a system at equilibrium is disturbed, the equilibrium will shift to minimize the effect of the disturbance according to this principle, if a reactant or product is added to a system at equilibrium, the equilibrium will shift to consume the added species. The effects of removing reactants or products and of changing the pressure or volume of a reaction mixture can be similarly deduced. For example, if the volume of the system is reduced, the equilibrium will shift in the direction that decreases the number of gas molecules.

The enthalpy change for a reaction indicates how an increase in temperature affects the equilibrium: For an endothermic reaction, an increase in temperature shifts the equilibrium to the right; for an exothermic reaction, a temperature increase shifts the equilibrium to the left. Catalysts affect the speed at which equilibrium is reached but do not affect the magnitude of K_{eq}.

Exercises

Part I: Choose the correct answer for each of the following questions

1. Which of the following is incorrect?
   (a) Equilibrium constant can never be a negative number.
   (b) Pure solids and liquids are excluded from equilibrium constant expressions because the ratio of moles of a substance to volume occupied by the substance is constant.

(c) The concentrations used to calculate Q_c must be equilibrium concentration so that $Q_c = K_c$.

(d) When Q is greater than K, then a net forward reaction will bring the system to equilibrium.

2. Which of the following conditions characterizes a system in a state of chemical equilibrium?

(a) The concentrations of reactants and products are equal.

(b) Reactants are being consumed at the same rate at which products are converted to reactants.

(c) The rate of the forward reaction has dropped to zero.

(d) Reactant molecules no longer react with each other

3. What is the equilibrium constant expression for the following reaction?

$$C_3H_8(g) + 5O_2(g) \rightleftharpoons 3CO_2(g) + 4H_2O(l)$$

(a) $\dfrac{[C_3H_8][O_2]}{[CO_2][H_2O]}$

(b) $\dfrac{[CO_2]^3}{[C_3H_8][O_2]^5}$

(c) $\dfrac{[C_3H_8][O_2]^5}{[CO_2]^3[H_2O]^4}$

(d) $\dfrac{[CO_2]^3[H_2O]^4}{[C_3H_8][O_2]^5}$

4. The following reaction is initiated and the concentrations are measured after ten minutes:

$$A(g) + 3B(g) \rightleftharpoons AB_3(g);\ K_c = 1.33 \times 10^{-2}$$

$[A] = 2$ M $[B] = 2$ M $[AB_3] = 4$ M, Is the reaction in equilibrium?

(a) Yes, it is.

(b) No, because $Q > K$.

(c) No, and $[AB_3]$ must increase to establish equilibrium.

(d) No, because $Q < K$.

5. In which of the following reactions is $K_p < K_c$?

(a) $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$

(b) $2NOBr(g) \rightleftharpoons 2NO(g) + Br_2(g)$

(c) $2BrCl(g) \rightleftharpoons Cl_2(g) + Br_2(g)$

(d) $I_2(g) \rightleftharpoons 2I(g)$

6. The equilibrium constant, K_c, is 2.48×10^2 at a certain temperature for the reaction:

$$2NO(g) \rightleftharpoons N_2(g) + O_2(g)$$

For which of the following sets of conditions is the system at equilibrium?

(a) A 1.0 L flask that contains 0.1 mol NO, 2.0 mol N_2 and 2.0 mol O_2

(b) A 2.0 L flask that contains 0.2 mol NO, 1.24 mol N_2 and 4.0 mol O_2

(c) A 3.0 L flask that contains 0.3 mol NO, 6 mol N_2 and 3 mol O_2

(d) A 2.0 L flask that contains 0.1 mol NO, 0.62 mol N_2 and 4.0 mol O_2

7. Which statement best describes Le Châtelier's Principle?

(a) When a change is made to a system at equilibrium, equilibrium can never be restored.

(b) A system at equilibrium will respond to a change by moving in the direction that reduces the effect of the change as it returns to equilibrium.

(c) A system at equilibrium will always remain at equilibrium.

(d) A system at equilibrium will not be affected by a change in concentration.

8. For the following reaction which of the given changes would shift the equilibrium to the right (favor the forward reaction)?

$$2NOCl(g) + 75\ kJ \rightleftharpoons 2NO(g) + Cl_2(g)$$

(i) Add more NOCl.

(ii) Remove some Cl_2.

(iii) Lower the temperature.

(iv) Add more NO.

(a) II, III, and IV

(b) I, II, and III

(c) I and II

(d) I and III

9. A catalyst has the following effects on an equilibrium reaction

(i) A catalyst increases the rate of the chemical reaction by making available a low energy pathway for the conversion of reactants to products.

(ii) It increases the rate of forward and reverse reactions that pass through the same transition state and does not affect equilibrium.

(iii) It lowers the activation energy for the forward and reverse reactions by exactly the same amount.

Which of the above statement(s) is/are correct?

(a) Only (i)

(b) (i) and (ii)

(c) (i), (ii) and (iii)

(d) (ii) and (iii)

10. If K_1 and K_2 are the equilibrium constants of the reactions (i) and (ii) respectively. What is the relationship between the two constants?

(i) $SO_2(g) + ½O_2(g) \rightleftharpoons SO_3(g)$; K_1

(ii) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$; K_2

(a) $(K_1)^2 = \frac{1}{K_2}$

(c) $K_1 = \frac{1}{K_2}$

(b) $K_2 = K_1^{\ 2}$

(d) $K_1 = K_2$

Part II: Short Answer Questions

11. At 327°C, the equilibrium concentrations are $[CH_3OH] = 0.15$ M, $[CO] = 0.24$ M, and $[H_2] = 1.1$ M for the reaction:

$$CH_3OH(g) \rightleftharpoons CO(g) + 2H_2(g)$$

Calculate K_p at this temperature.

12. At a particular temperature, 8.0 moles of NO_2 is placed into a 1.0 L container and the NO_2 dissociates according to the reaction:

$$2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$$

At equilibrium the concentration of NO(g) is 2.0 M. Calculate K_c for this reaction.

13. At 2000°C the equilibrium constant for the reaction:

$2NO(g) \rightleftharpoons N_2(g) + O_2(g)$ is $K_c = 2.4 \times 10^3$. If the initial concentration of NO is 0.175 M, what are the equilibrium concentrations of NO, N_2 and O_2?

14. Heating solid sodium bicarbonate in a closed vessel establishes the following equilibrium:

$$2NaHCO_3(s) \rightleftharpoons 2Na_2CO_3(g) + H_2O(g) + CO_2(g)$$

What would happen to the equilibrium position if:

(a) Some of the CO_2 were removed from the system;

(b) Some solid Na_2CO_3 were added to the system.

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CHAPTER 8

CHEMICAL KINETICS

Chapter Contents

Chapter Outcomes

By the end of this chapter, you will be able to:

- describe what is meant by reaction rate and perform activities that determine it.
- demonstrate an understanding of the factors that affect the rate of a reaction.
- discuss the rate laws and the concept of collision theory.
- determine reaction rates, using experimental data and calculations.
- determine the rate laws and order of reactions from data on initial concentrations and reaction rates.
- understand that most reactions occur as a series of elementary steps in reaction mechanisms.

Chemical reactions require varying lengths of time for completion. For example, rusting of iron could start while ripening of fruits may be completed in few days. Other reactions, like the combustion of gasoline or the explosion of gunpowder occur in few seconds. Can you add more examples from your daily life?

The study of the rate, or speed, of a reaction has important applications. In the manufacture of ammonia from nitrogen and hydrogen, you may wish to know what conditions will help the reaction to proceed in a commercially feasible length of time. The area of chemistry that is concerned with reaction rates is called chemical kinetics. One of the main goals of chemical kinetics is to understand the steps by which a reaction takes place. This series of steps is called the reaction mechanism. Understanding the mechanism allows us to find ways to facilitate the reaction.

In this chapter, we will consider the fundamental ideas of chemical kinetics. We will explore rate laws, reaction mechanisms, activation energy, and collision theory.

8.1 REACTION RATES

Upon completion of this topic, learners will be able to:

- define reaction rate.
- relate the changes in concentration over time to the rate of reaction.
- calculate the instantaneous rate of reaction from experimental data.
- use stoichiometry to relate the rate of reaction to the changes in the concentrations of reactants and products.
- understand the factors that affect the rate of chemical reactions.

Rate is change per unit time. The reaction rate is the change in concentration per unit time.

$$\text{Rate} = \frac{\text{Change in concentration of reactants or products}}{\text{Time}}$$

$$\text{Rate} = \frac{\Delta C}{\Delta t}$$

The rate of a reaction can be expressed in units of mol L^{-1} s^{-1}.

Consider a chemical reaction of the type

$$\text{Reactant} \longrightarrow \text{Product}$$

Initially, at $t = 0$, only the reactant is present. As the reaction progresses and time elapses, the reactant concentration decreases during the reaction, so Δ [reactant] is negative. The product increases in concentration, and Δ [product] is positive.

For this simple reaction, the rate of a reaction is the amount of product formed or the amount of reactant used up per unit time. Later, we will modify this definition of reaction rate for more complex reactions, because reaction stoichiometry must be included.

$$\text{Rate} = -\frac{\Delta[\text{Reactant}]}{\Delta t} = \frac{\Delta[\text{Product}]}{\Delta t}$$

As the reactant is consumed, $[\text{reactant}]_{\text{final}} < [\text{reactant}]_{\text{initial}}$, the change in concentration of reactant is negative. However, the rate of a reaction is always expressed as a positive number. Thus, a negative sign is introduced in the rate expression to make the rate positive.

Consider the gas-phase reaction:

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

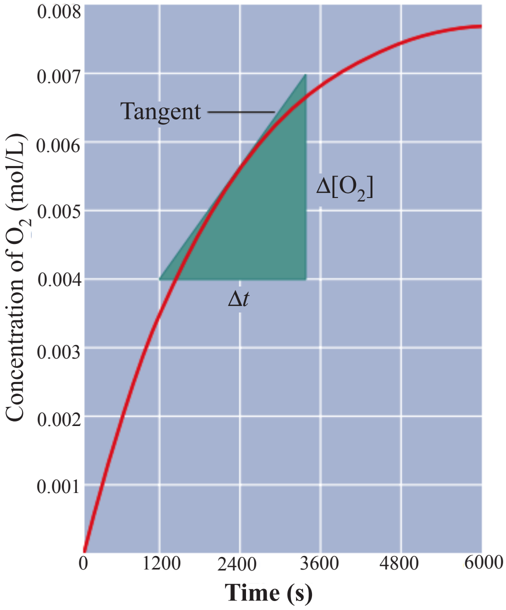


Figure 1. The instantaneous rate of reaction.

The rate for this reaction could be found by observing the increase in molar concentration of O_2 produced. In a given time interval, Δt, the molar concentration of oxygen, $[O_2]$, in the reaction vessel increases by the amount $\Delta[O_2]$. The rate of the reaction is given by:

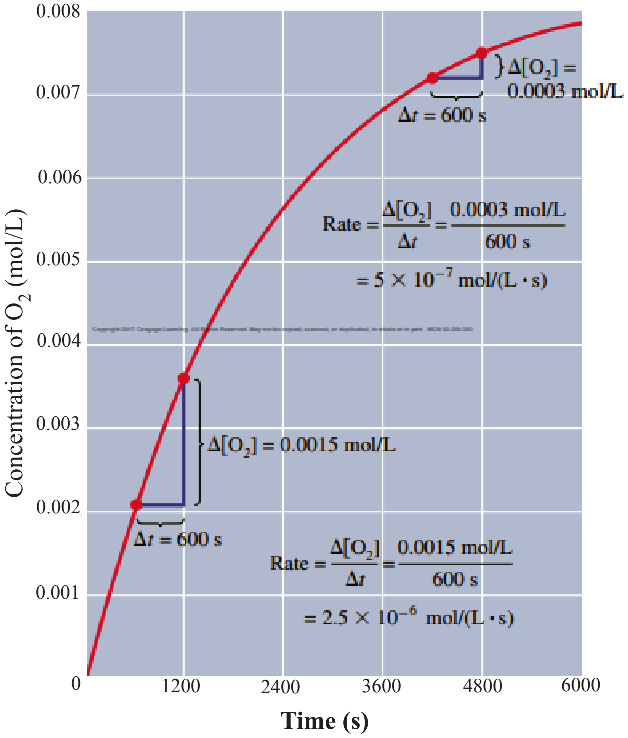
$$\text{Rate of formation of oxygen} = \frac{\Delta[O_2]}{\Delta t}$$

This equation gives the average rate over the time interval Δt. If the time interval is very short, the equation gives the instantaneous rate, that is, the rate at a particular instant of time. The instantaneous rate is also the value of $\Delta[O_2]/\Delta t$ for the tangent at a given instant (the straight line that just touches the curve of concentration versus time at a given point). See Figure 1.

Figure 2 shows the increase in concentration of O_2 during the decomposition of N_2O_5. It shows the calculation of average rates at two positions on the curve. For example, when the time changes from 600 s to 1200 s (Δt = 600 s), the O_2 concentration increases by 0.0015 mol/L (= $\Delta[O_2]$). Therefore,

$$\text{Average rate of formation of } O_2 = \frac{\Delta[O_2]}{\Delta t} = \frac{0.0015\,\text{mol/L}}{600\,\text{s}} = 2.5\times10^{-6}\,\text{mol/(L.s)}$$

Later, during the time interval from 4200 s to 4800 s, the average rate is 5×10^{-7} mol/(L.s). Note that the rate decreases as the reaction proceeds.



Time	$[O_2]$
0	0.0000
600	0.0021
1200	0.0036
1800	0.0048
2400	0.0057
3000	0.0063
3600	0.0068
4200	0.0072
4800	0.0075
5400	0.0077
6000	0.0078

Figure 2. Calculation of the average rate.

Rate and reaction stoichiometry

Because the amounts of products and reactants are related by stoichiometry, any substance in the reaction can be used to express the rate of reaction. In the case of the decomposition of N_2O_5 to NO_2 and O_2, we gave the rate in terms of the rate of formation of oxygen, $\Delta[O_2]/\Delta t$. However, we can also express it in terms of the rate of decomposition of N_2O_5.

$$\text{Rate of decomposition of } N_2O_5 = -\frac{\Delta[N_2O_5]}{\Delta t}$$

Note the negative sign. It always occurs in a rate expression for a reactant in order to indicate a decrease in concentration. Thus, because $[N_2O_5]$ decreases, $\Delta[N_2O_5]$ is negative.

The rate of decomposition of N_2O_5 and the rate of formation of oxygen are easily related. Two moles of N_2O_5 decompose for each mole of oxygen formed, so the rate of decomposition of N_2O_5 is twice the rate of formation of oxygen. To equate the rates, you must divide the rate of decomposition of N_2O_5 by 2 (its coefficient in the balanced chemical equation).

$$\text{Rate of formation of } O_2 = \frac{1}{2}\left(\text{Rate of decomposition of } N_2O_5\right)$$

$$\frac{\Delta[O_2]}{\Delta t} = -\frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t}$$

In general, for the reaction:

$$aA + bB \longrightarrow cC + dD$$

The rate of reaction is given by:

$$r = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

where r is the rate of reaction, A and B are reactants, C and D are products, and a, b, c, d are stoichiometric coefficients.

Examples

Write the rate expressions for the following reactions, in terms of the disappearance of the reactants and the appearance of the products:

(a) $3O_2(g) \longrightarrow 2O_3(g)$

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

Solution

(a) Here, the coefficients are 3 and 2, so,

$$r = -\frac{1}{3}\frac{\Delta[O_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[O_3]}{\Delta t}$$

(b) For this reaction:

a. $$r = -\frac{1}{4}\frac{\Delta[NH_3]}{\Delta t} = -\frac{1}{5}\frac{\Delta[O_2]}{\Delta t} = \frac{1}{4}\frac{\Delta[NO]}{\Delta t} = \frac{1}{6}\frac{\Delta[H_2O]}{\Delta t}$$

Exercise

1. For the reaction: $2NOCl\,(g) \longrightarrow 2NO\,(g) + Cl_2\,(g)$
   (a) Express the rate of reaction in terms of the concentration of NOCl.
   (b) Relate the rate of reaction of NOCl with the rate of reaction of NO and Cl_2.
2. Consider the formation of ammonia from the elements:

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

   The rate of disappearance of N_2 was 0.14 M/s.
   (a) What is the rate of the reaction?
   (b) What is the rate of disappearance of hydrogen?
3. Iodide ion is oxidized by hypochlorite ion in basic solution.

   $$I^-(aq) + ClO^-(aq) \longrightarrow Cl^-(aq) + IO^-(aq)$$

   In 1.00 M NaOH at 25°C, the iodide-ion concentration at different times was as follows:

Time	$[I^-]$
2.00 s	0.00169 M
8.00 s	0.00101 M

Calculate the average rate of reaction of I^- during this time interval.

Factors that affect reaction rates

The rates at which reactants are consumed and products are formed during chemical reactions vary greatly. We can identify five factors that affect the rates of chemical reactions. These are: (i) chemical nature of the reacting substances (ii) surface area of the reactants (iii) temperature of the reactants (iv) concentration of the reactants, and (v) presence of a catalyst.

(i) Nature of the reactants

The rate of a reaction depends on the nature of the participating substances. Reactions that appear similar may have different rates under the same conditions, depending on the identity of the reactants. For example, when small pieces of the metals iron and sodium are exposed to air, the sodium reacts completely with air overnight, whereas the iron is barely affected. The active metals calcium and sodium both react with water to form hydrogen gas and a base. Yet calcium reacts at a moderate rate, whereas sodium reacts more vigorously.

(ii) Surface area of reactants

Which form of Zinc metal is easier to dissolve in dilute HCl, large pieces of Zn or powdered Zn? Why?

Why large pieces of wood smolder, smaller pieces burn rapidly?

The area of contact between the phases determines the rate of reaction in heterogenous reaction. If a reaction involves a solid with a gas or liquid, the surface area of the solid affects the reaction rate. Because the reaction occurs at the surface of the solid, the rate increases with increasing surface area. When the size of particles is minimized, contact between the atoms, ions, or molecules in the solid state maximizes with those in a different phase.

A finely divided solid has more surface area available for reaction than does one large piece of the same substance. Thus a liquid will react more rapidly with a finely divided solid than with a large piece of the same solid. For example, large pieces of iron react slowly with acids; finely divided iron reacts much more rapidly. A wood fire burns faster if the logs are chopped into smaller pieces.

ACTIVITY 1

Effect of temperature on reaction rate

Objective: To study the effect of temperature on the rate of the reaction between sodium thiosulphate and hydrochloric acid.

Procedure:

1. Take 25 mL of 0.1 M $Na_2S_2O_3$ solution in a test tube and 25 mL of 0.5 M HCl solution in another test tube.
2. Prepare 3 such sets and maintain them at different temperatures. Set (i) at 0°C [by keeping them in a ice bath as shown in Figure 3 (a)]. Set (ii) at room temperature. Set (iii) at 40°C (by heating the two solutions in a water bath).
3. Put a cross sign on a white cardboard and place a clean dry 100 mL beaker above it.
4. Now, pour the contents of set (i) in the beaker and start a stopwatch immediately.

5. Carefully stir the mixture with a thermometer and record the time taken for the cross to disappear [Figure 3 (b)].
6. Repeat steps 3, 4, and 5 with set 2 and set 3 respectively.
7. Tabulate your results as temperature in °C versus time in minutes.

Observations and analysis:

1. What was the appearance of the mixture at the start of the reaction, and at the end of the reaction? Explain the changes using the equation for the reaction
2. Plot the graph of rate against time.
3. Under which condition of temperature does the cross take:
   (a) the shortest time to disappear, and
   (b) the longest time to disappear.
4. Draw a conclusion about the relationship between the average reaction rate and temperature.

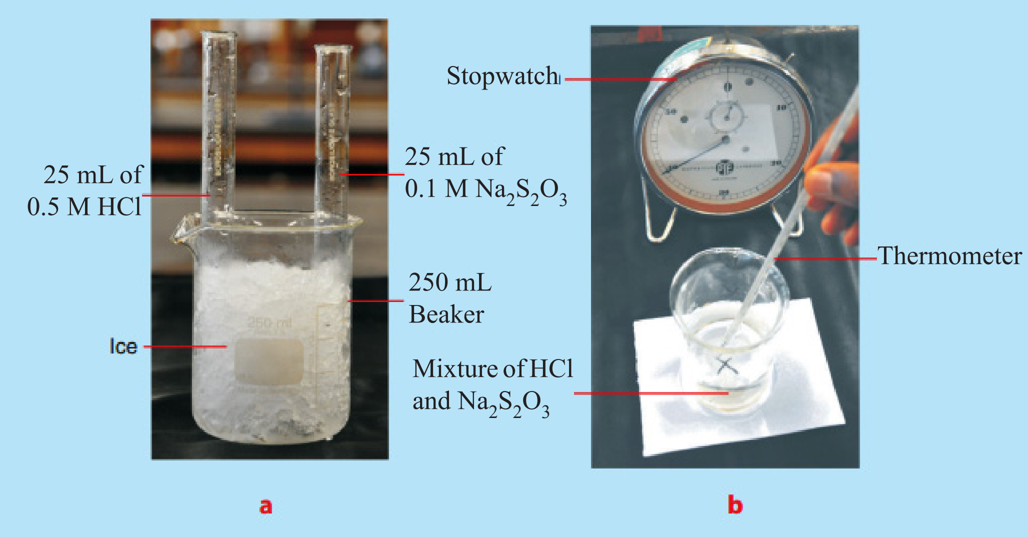


Figure 3. Laboratory setup for the study of the effect of temperature on reaction of $Na_2S_2O_3$ *and HCl.*

(iii) Temperature of reactants

Temperature usually has a major effect on the rate of a reaction. Chemical reactions typically occur faster at higher temperatures. Food can spoil quickly when left on the kitchen counter. However, the lower temperature inside of a refrigerator slows that process so that the same food remains fresh for days. We use a burner or a hot plate in the laboratory to increase the speed of reactions that proceed slowly at ordinary temperatures. In many cases, an increase in temperature of only 10°C will approximately double the rate of a reaction in a homogeneous system.

(iv) Concentration of reactants

ACTIVITY 2

Effect of concentration on reaction rate

Objective: To determine the rate of the reaction of magnesium with 0.1M and 5M of sulfuric acid.

Theory

Effect of concentration and pressure

The rate of a chemical reaction can be changed by altering the concentration of a reactant in solution, or the pressure of a gaseous reactant. If the concentration or pressure is increased:

- the reactant particles become closer
- there is a greater chance of the particles colliding
- the rate of reaction increases

To show the effect of a change in concentration of a reactant, the reaction between magnesium and sulfuric acid will be used.

Procedure

(a)

1. Take 20 mL of 0.1M H_2SO_4 into a beaker.
2. Add 1 cm long magnesium ribbon into the beaker as shown in Figure 4.
3. Note how fast the reaction occurs.

(b)

1. Take 20 mL of 5M H_2SO_4 into beaker.
2. Add 1cm long magnesium ribbon into the beaker as shown in Figure 4
3. Observe how fast the reaction occurs.

Observations and Analysis

1. In which of the reactions does the evolution of gas bubble faster? (*a*) or (*b*).
2. Write the balanced chemical equation.
3. What do you conclude from the experiment?
4. How increasing the concentration of H_2SO_4 affects the rate of a reaction?

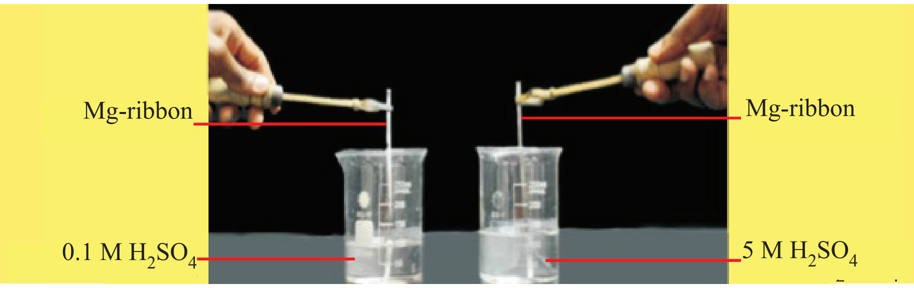


Figure 4. The effect of concentration on the rate of a reaction.

5. Plot the concentration of the acid on the x-axis and the reaction time on the y-axis.

Conclusion

Summarize and explain what happened in your experiment.

Your conclusion should be based solely on your results. Look back at the purpose of your experiment and assess whether or not you met your goal in performing the experiment.

What can you conclude from the experiment? Write a short report on your observation.

Why does wood burn more rapidly in pure oxygen than in air?

When the concentration of one or more reactants increases, rate of reaction increases. This is because increasing the concentration produces more contacts between the reacting particles, which results in increasing the rate of reaction. In the case of reactions that involve gaseous reactants, an increase in pressure increases the concentration of the gases which leads to an increase in the rate of reaction.

For example, in a polluted atmosphere where the concentration of sulfur dioxide is high, calcium carbonate deteriorates more rapidly than in less polluted air. Similarly, phosphorus burns much more rapidly in an atmosphere of pure oxygen than in air, which is only about 20% oxygen.

(v) Presence of a catalyst

Some chemical reactions proceed quite slowly. Sometimes their reaction rates can be increased dramatically by the presence of a catalyst. A catalyst is a substance that changes the rate of a chemical reaction without itself being permanently consumed. The action of a catalyst is called catalysis. The effect of catalysts on the rate of chemical reaction is illustrated in Figure 5.

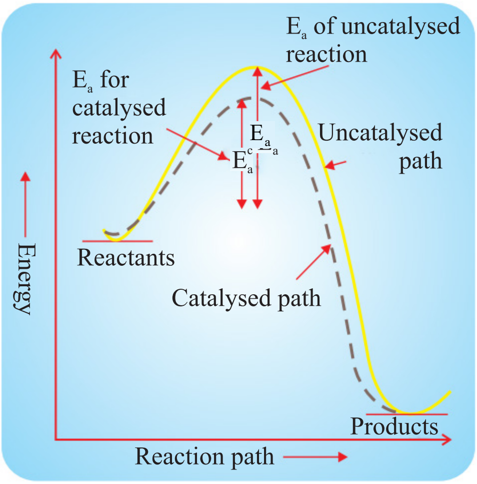


Figure 5. Comparsion of activation energies of a catalysed and an uncatalysed reaction.

A catalyst provides an alternative energy pathway or reaction mechanism in which the potential-energy barrier between reactants and products is lowered.

Because the catalyst is not consumed by the reaction, it does not appear in the balanced chemical equation (although its presence may be indicated by writing its formula over the arrow). Catalysts may participate in one step along a reaction pathway and be regenerated in a later step.

A solution of pure hydrogen peroxide, H_2O_2, is stable, but when hydrobromic acid, HBr(aq), is added, H_2O_2 decomposes rapidly into H_2O and O_2.

$$2H_2O_2 \xrightarrow{HBr(aq)} 2H_2O(l) + O_2(g)$$

Here HBr acts as a catalyst to speed up the decomposition of H_2O_2.

A catalyst that is in the same phase as all the reactants and products in a reaction system is called a homogeneous catalyst. When its phase is different from that of the reactants, it is called a heterogeneous catalyst. Metals are often used as heterogeneous catalysts. The catalysis of many reactions is promoted by adsorption of reactants on the metal surfaces, which increases the concentration of the reactants.

Example (1): $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$; $V_2O_5(s)$ as catalyst.

Example (2): $OCl^-(aq) + I^-(aq) \longrightarrow OI^-(aq) + Cl^-(aq)$; $OH^-(aq)$ as inhibitor.

Example (1) represents heterogeneous catalysts as state of reactants and catalyst is different while example (2) represents homogeneous catalyst as both reactants and catalyst are in same state.

Describe how negative catalysts or inhibitors decreases the rate of reaction?

ACTIVITY 3

Effect of catalyst on reaction rate

Objective: To investigate the effect of a catalyst on rate of decomposition reaction of hydrogen peroxide.

Theory

Hydrogen peroxide is a commonly used chemical compound with the formula H_2O_2. In pure liquid form, it has a distinctive pale blue colour. Diluted solutions of H_2O_2 can be safely decomposed in the presence of proper catalyst.

A catalyst makes the decomposition reaction of hydrogen peroxide faster because it provides an alternative pathway with a lower activation energy.

Activation energy is just a term used to express the *minimum energy* required in order for a reaction to take place.

If no catalyst is present, hydrogen peroxide will decompose at a very, very slow rate.

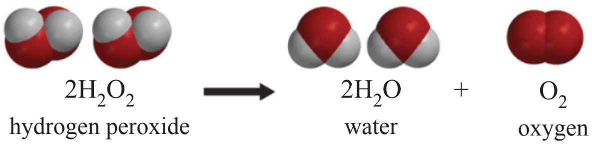


Figure 6. Decomposition reaction of H_2O_2

When a catalyst is added, an alternative pathway through which the reaction can form water and oxygen gas is introduced. The speed of a catalyzed reaction will *increase* because this alternative pathway has a lower activation energy.

Procedure

1. Setup the apparatus as shown in Figure 7. Set the volume of the gas syringe at 0 mL. Add 25.0 mL of 0.1 M H_2O_2 solution, but without manganese(IV) oxide, MnO_2, and start stopwatch immediately.
2. Record the volume of gas collected in the gas syringe at minute intervals until each reaction is almost complete.
3. Repeat steps 1 and 2 with 1 g of MnO_2.

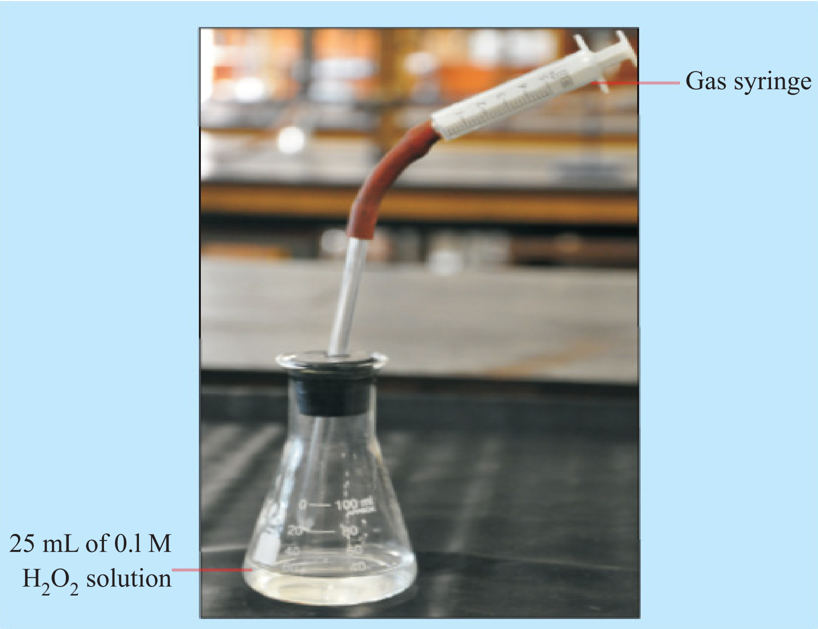


Figure 7. Investigating the effect of managanese(IV) oxide on the decomposition of hydrogen peroxide.

Observations and analysis:

1. Identify the gas and write a balanced chemical equation for the reaction.

2. Under which condition does the gas syringe contain more of the gas? Give an explanation for this observation.
3. Describe the appearance of MnO_2 before and after the reaction.
4. Plot graphs of rate on the vertical axis and time (minutes) on the horizontal axis for two different sets of readings. Which set of reading were used? Why?
5. Draw a conclusion about the reaction rate:
   (a) in the presence of a catalyst;
   (b) in the absence of a catalyst

Conclusion

How your results addressed the objective.

What have you learnt? Present your findings from the experiment.

8.2 INTRODUCTION TO RATE LAWS

Upon completion of this topic, learners will be able to:

- define a rate constant and rate law to express the dependence of the rate of reaction on the concentration of the reactants.
- use rate laws to calculate reaction rates.
- identify the reaction order from the rate law.

By a study of numerous reactions it is shown that: the rate of a reaction is directly proportional to the reactant concentrations, each concentration being raised to some power. A rate law or rate equation for a chemical reaction is an equation that relates the rate of a reaction to the concentrations or pressures of reactants raised to their powers. Thus for a substance A undergoing reaction,

$$A \longrightarrow B$$

The rate law or rate equation for this reaction is written as:

$$\text{Rate} \propto [A]^n \text{ or Rate} = k[A]^n$$

The proportionality constant k, called the rate constant, and n, called the order of the reaction.

Note that n is not stoichiometric coefficient in the balanced equation and it is determined experimentally. The order of a reaction can be positive or negative and can be an integer or a fraction.

Note two important points about rate law or rate equation:

The concentrations of the products do not appear in the rate law because the reaction rate is being studied under conditions where the reverse reaction does not contribute to the overall rate.

The value of the exponent n must be determined by experiment; it cannot be written from the balanced equation.

For reactions involving more than one reactant, the order of a reaction is the sum of the powers to which all concentrations are raised in the rate law expression. For the general reaction,

$$aA + bB \longrightarrow cC + dD$$

we can write the rate law expression as:

$$r = k[A]^n [B]^m$$

The reaction is nth order w.r.t. A, mth order w.r.t. B, and (n + m)th order overall. Note that the order of a reaction is not necessarily the same as the stoichiometric coefficients in the balanced equation for the reaction.

Consider a reaction with the rate equation,

$$r = k[A]^2[B]$$

The reaction with the rate equation given above is described as “second-order w.r.t. A” and “first-order w.r.t. B.” The overall reaction order is described as a third-order reaction overall, because the sum of the exponents on [A] and [B] is 3.

Types of rate laws

Notice that the rate law we have used to this point expresses rate as a function of concentration. For example, for the decomposition of NO_2 we have defined:

$$\text{Rate} = -\frac{\Delta[NO_2]}{\Delta t} = k[NO_2]^n$$

which tells us (once we have determined the value of n) exactly how the rate depends on the concentration of the reactant, NO_2. A rate law that expresses how the rate depends on concentration is technically called the differential rate law, but it is often simply called the rate law. Thus when we use the term the rate law in this text, we mean the expression that gives the rate as a function of concentration.

A second kind of rate law, the integrated rate law, also will be important in our study of kinetics. The integrated rate law expresses how the concentrations depend on time. A given differential rate law is always related to a certain type of integrated rate law, and vice versa. That is, if we determine the differential rate law for a given reaction, we automatically know the form of the integrated rate law for the reaction.

This means that once we determine experimentally either type of rate law for a reaction, we also know the other one.

Which rate law we choose to determine by experiment often depends on what types of data are easiest to collect. If we can conveniently measure how the rate changes as the concentrations are changed, we can readily determine the differential (rate/concentration) rate law. On the other hand, if it is more convenient to measure the concentration as a function of time, we can determine the form of the integrated (concentration/ time) rate law. We will discuss how rate laws are actually determined in the next several sections.

Exercises

1. Why are we interested in determining the rate law for a reaction? How does it help us?

8.3 DETERMINING THE FORM OF THE RATE LAW

Upon completion of this topic, learners will be able to:

- use initial concentrations and initial rates of reactions to determine the rate law and rate constant.
- define a rate law to express the dependence of the rate of reaction on the concentrations of the reactants.
- identify the reaction order from the rate law.

Most often, chemists obtain experimental data and determine the rate law. The first step is to determine the order by deciding which exponent explains the observed behavior. Suppose a reaction of the type,

$$\text{A} \longrightarrow \text{products}$$

is under study. The data are inspected to find how the initial rate varies with the initial concentration of A, $[A]_0$. The objective is to find the value of the exponent in the rate equation, rate = $k[A]^n$, where n is the order of the reaction. Table 1 shows the dependence of rate on concentration when the value of the rate constant (k) is 1.

Table 1 Change in initial rate with change in $[A]_0$ for rate = $k[A]^n$

For a reaction of	If $[A]_0$ is doubled	If $[A]_0$ is tripled
Zero-order (n = 0)	rate is unchanged	rate is unchanged
First-order (n = 1)	rate is doubled	rate is tripled
Second-order (n = 2)	rate is quadrupled (x 2^2)	rate is 9 times greater (x 3^2)

First, we will consider the decomposition of dinitrogen pentoxide in carbon tetrachloride solution:

$$2N_2O_5(soln) \longrightarrow 4NO_2(soln) + O_2(g)$$

Data for this reaction at 45°C are listed in Table 2 and plotted in Figure 8.

Table 2 **Concentration/Time Data for the Reaction**

$$2N_2O_5(soln) \longrightarrow 4NO_2(soln) + O_2(g) \text{ (at 45°C)}$$

$[N_2O_5]$ (mol/L)	Time (s)
1.00	0
0.88	200
0.78	400
0.69	600
0.61	800
0.54	1000
0.48	1200
0.43	1400
0.38	1600
0.34	1800
0.30	2000

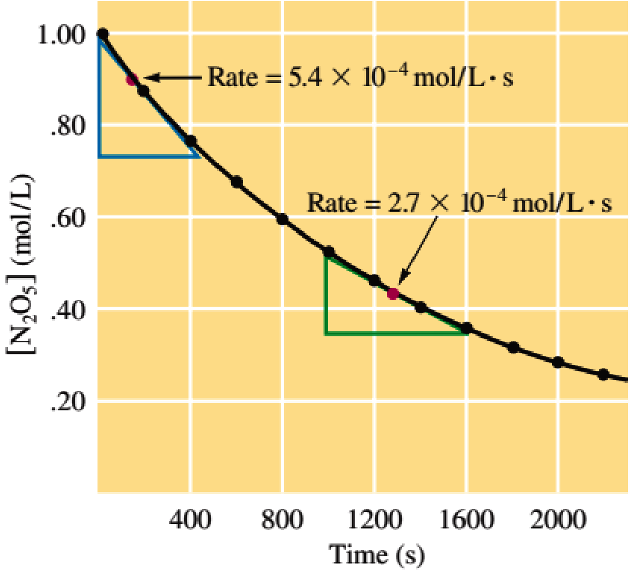


Figure 8. A plot of the concentration of N_2O_5 as a function of time for the reaction

$$2N_2O_5(\text{soln}) \longrightarrow 4NO_2(\text{soln}) + O_2(g) \text{ (at 45°C)}$$

Evaluation of the reaction rates at N_2O_5 concentrations of 0.90 M and 0.45 M, by taking the slopes of the tangents to the curve at these points (Figure 8), yields the following data:

$[N_2O_5]$	Rate (mol L^{-1} s^{-1})
0.90 M	5.4×10^{-4}
0.45 M	2.7×10^{-4}

Note that when $[N_2O_5]$ is halved, the rate is also halved. This means that the rate of this reaction depends on the concentration of N_2O_5 to the first power. In other words, the (differential) rate law for this reaction is:

$$\text{Rate} = -\frac{d[N_2O_5]}{dt} = k[N_2O_5]$$

Thus the reaction is first order w.r.t. N_2O_5.

Method of initial rates

One widely used method of determining the order of a reaction is called the initial rate method. The technique utilizes several experiments in which the initial concentrations of all substances are accurately known but are different in each experiment.

To use this method, we select two sets of rate data that differ in the concentration of only one reactant and set up a ratio of the two rates and the two rate laws. After cancelling terms that are equal, we are left with an equation that contains only one unknown, the coefficient of the concentration that varies. We then solve this equation for the coefficient.

Exercises

The initial rate of a reaction $A + B \longrightarrow C$ was measured for several different initial concentrations of A and B, and the results are as follows:

Experiment Number	[A] (M)	[B] (M)	Initial Rate (M/s)
1	0.100	0.100	4.0×10^{-5}
2	0.100	0.200	4.0×10^{-5}
3	0.200	0.100	1.60×10^{-4}

Using these data, determine the:

(a) Rate law for the reaction,

(b) Rate constant,

(c) Rate of the reaction when [A] = 0.050 M and [B] = 0.100 M.

8.4 THE INTEGRATED RATE LAW

Upon completion of this topic, learners will be able to:

- evaluate concentration-time behaviors to write a rate law.
- relate the differential and integrated forms of the rate law.
- calculate the concentration-time behavior for a zero-order, first-order, and second order reaction from the rate law and the rate constant.
- relate half-life and rate constant, and calculate concentration-time behavior from the half-life of a zero-order, first-order, and second order reaction.

A rate law tells us how the rate of reaction depends on the concentration of the reactants at a particular moment. But, often we would like to have a mathematical relationship that shows how a reactant concentration changes over a period of time. A rate law can be transformed into a mathematical relationship between concentration and time using calculus. Therefore, an integrated law relates concentration to reaction time.

We will proceed by first looking at reactions involving a single reactant:

$$\mathrm{A} \longrightarrow \text{products}$$

The above reaction have a rate law of the form:

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

We will develop the integrated rate laws individually for the cases n = 1 (first order), n = 2 (second order), and n = 0 (zero order).

(a) First-order rate laws

A first-order reaction is a reaction whose rate of reaction depends on the reactant concentration raised to the first power. For a chemical reaction of the form:

$$\mathrm{A} \longrightarrow \text{products}$$

where the kinetics are first order in [A], the differential rate law is of the form:

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

and the integrated first-order rate law is:

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

where *ln* is the natural logarithm, and $[A]_0$ and [A] are the concentrations of A at times t = 0 and t = t, respectively. It should be understood that t = 0 need not correspond to the beginning of the experiment. It can be any time at which we choose to start monitoring the change in the concentration of A.

There are three important things to note about integrated rate equation for 1^{st} order reaction

1. The equation shows how the concentration of A depends on time. If the initial concentration of A and the value of the rate constant k are known, the concentration of A at any time can be calculated.
2. The equation $\ln[A] = -kt + \ln[A]_0$ has the form of the linear equation $y = mx + b$, in which m is the slope of the line that is the graph of the equation. Thus, a plot of ln [A] versus t gives a straight line with a slope of k (or m). This graphical analysis allows us to calculate the rate constant k. Figure 9 shows the characteristics of first-order reactions.

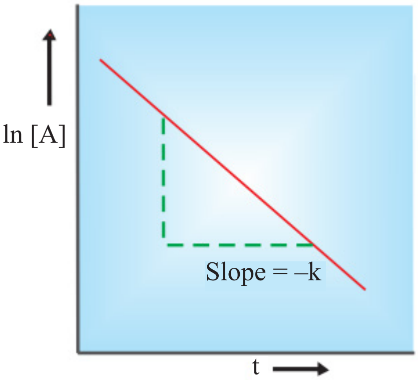


Figure 9. Plot for a reaction that is first-order with respect to A

The observation that plot of ln[A] versus time is a straight line confirms that the reaction is first-order in A and first-order overall, i.e., Rate = k[A]. The slope is equal to –k. Conversely, if the plot is not a straight line, the reaction is not first order.

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

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

For a first order reaction, r = k[A]. To obtain the units of k for this rate law, we write

$$k = \frac{r}{[A]} = \frac{M/s}{M} = \frac{1}{s} \text{or } s^{-1}$$

Example

The rate constant for the first-order decomposition of cyclobutane, C_4H_8 at 500°C is s 9.2×10^{-3} s^{-1}

$$C_4H_8 \longrightarrow 2C_2H_4$$

How long will it take for 80.0% of a sample of C_4H_8 to decompose?

Solution

We use the integrated form of the rate law to answer questions regarding time:

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

There are four variables in the rate law, so if we know three of them, we can determine the fourth. In this case we know $[A]_0$, [A], and k, and need to find t.

The initial concentration of C_4H_8, $[A]_0$, is not provided, but the provision that 80.0% of the sample has decomposed is enough information to solve this problem. Let x be the initial concentration, in which case the concentration after 80.0% decomposition is 20.0% of x or 0.200x. Rearranging the rate law to isolate t and substituting the provided quantities yields:

$$t = \ln\frac{[x]}{[0.200x]} \times \frac{1}{k}$$

$$t = \ln\frac{0.100\,\text{mol}/\text{L}}{0.020\,\text{mol}/\text{L}} \times \frac{1}{9.2 \times 10^{-3}\,s^{-1}}$$

$$t = 1.609 \times \frac{1}{9.2 \times 10^{-3}\,s^{-1}} = 1.7 \times 10^{2}\,s$$

(b) Half-life of a first-order reaction

The time required for a reactant to reach half of its original concentration is called the half-life of a reaction and is designated by $t_{1/2}$.

A general formula for the half-life of a first-order reaction can be derived from the integrated rate law for the general reaction,

$$A \longrightarrow \text{products}$$

If the reaction is first order in [A],

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

By definition, when $t = t_{½}$, $[A] = \frac{[A]_0}{2}$.

Then for $t = t_{½}$, the integrated rate law becomes:

$$\ln\left(\frac{[A]_0}{[A]_0/2}\right) = kt_{½}$$

$$\ln(2) = kt_{½}$$

Substituting the value of ln(2) and solving for $t_{½}$ gives:

$$t_{½} = \frac{0.693}{k}$$

This is the general equation for the half-life of a first-order reaction. This equation can be used to calculate $t_{½}$ if k is known, or k if $t_{½}$ is known. Note that for a first-order reaction the half-life does not depend on concentration.

Exercises

1. Iodine-131 decays to Xenon-131 according to the equation:

   $$\text{I-131} \longrightarrow \text{Xe-131} + \text{electron}$$

   The decay is first-order with a rate constant of 0.138 d^{-1}. How many days will it take for 90% of the iodine-131 in a 0.500 M solution of this substance to decay to Xe-131?
2. A certain first-order reaction has a half-life of 20.0 minutes.
   (a) Calculate the rate constant for this reaction.
   (b) How much time is required for this reaction to be 87.5% complete?

(c) Second-order rate laws

For a general reaction involving a single reactant,

$$A \longrightarrow \text{products}$$

which is second order in A, the rate law can be defined as:

$$\text{Rate} = -\frac{d[A]}{dt} = k[A]^2$$

Integration of this differential rate law yields the integrated second-order rate law:

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

Note the following characteristics of the integrated second-order rate law:

1. A plot of 1/[A] versus t will produce a straight line with a slope equal to k as shown in Figure 10.

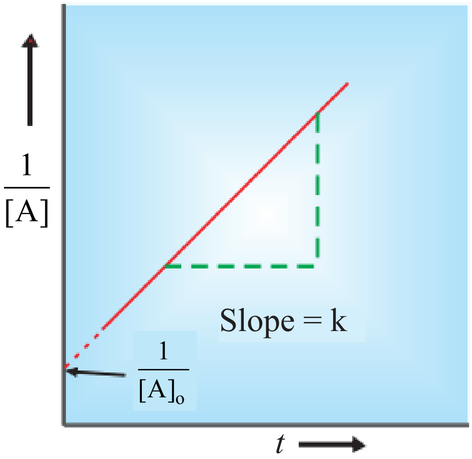


Figure 10. A Plot for a reaction that is second-order with respect to A and overall a second-order reaction.

2. The integrated second-order rate equation shows how [A] depends on time and can be used to calculate [A] at any time t, provided k and $[A]_0$ are known. From the rate law

$$r = k[A]^2$$

we can determine the units of k by writing:

$$k = \frac{r}{[A]^2} = \frac{M/s}{M^2} = M^{-1}s^{-1}$$

Example

Nitrosyl chloride, NOCl, decomposes slowly to NO and Cl_2 as shown in the equation below:

$$2NOCl \longrightarrow 2NO + Cl_2$$

$$r = k[NOCl]^2$$

The rate constant, k equals 0.020 L mol^{-1} s^{-1} at a certain temperature. If the initial concentration 0.050 M, what will be the concentration after 30 minutes?

Solution

The integrated rate equation for this reaction is given by:

$$\frac{1}{[NOCl]} = kt + \frac{1}{[NOCl]_0}$$

$$\frac{1}{[NOCl]} = \left(0.020\,L\,mol^{-1}\,s^{-1}\right)\left(1800\,s\right) + \frac{1}{0.050\,M}$$

$$\frac{1}{[NOCl]} = 56\,L\,mol^{-1}$$

$$[NOCl] = 0.018\ mol\ L^{-1}$$

(d) Second order half-life

When one half-life of a second-order reaction has elapsed ($t = t_{1/2}$), by definition, [A] = $[A]_0/2$. The integrated second-order rate law then becomes

$$\frac{1}{[A]_0/2} = kt_{1/2} + \frac{1}{[A]_0}$$

and $\frac{1}{[A]_0} = kt_{1/2}$. Solving for $t_{1/2}$ gives the expression for the half-life of a second-order reaction:

$$t_{1/2} = \frac{1}{k[A]_0}$$

Exercise

1. The reaction 2A → B is second order with a rate constant of 51 M^{-1} min^{-1} at 24°C.

(a) Starting with $[A]_0 = 0.0092$ M, how long will it take for $[A] = 3.7 \times 10^{-3}$ M?

(b) Calculate the half-life of the reaction.

(e) Zero-order rate laws

A zero-order reaction is a reaction whose rate of reaction does not depend on the reactant concentration. For the general reaction

$$A \longrightarrow \text{products}$$

the zero order rate law is written as the equation

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

For a zero-order reaction, the rate is constant. It does not change with concentration as it does for first-order or second-order reactions.

The integrated rate law for a zero-order reaction is:

$$[A] = -kt + [A]_0$$

This is a linear equation with the form of y = mx + b. For a zero-order reaction, a plot of [A] versus-time is a straight line, whose slope is – k.

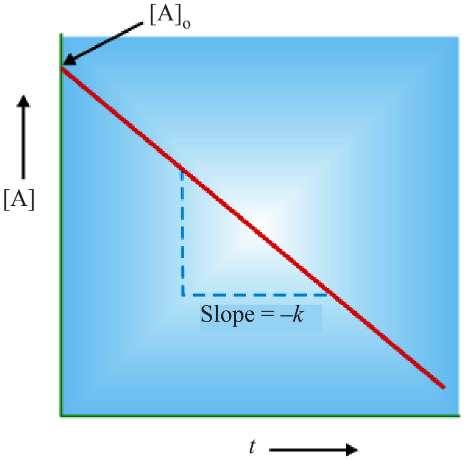


Figure 11. A plot of [A] versus t for a zero-order reaction.

For a zero order reaction, the rate constant k is given by the expression:

$$k = \frac{d[A]}{dt} = \frac{\text{mol}}{L} \times \frac{1}{\text{time}}$$

Thus the units of k are mol L^{-1} $time^{-1}$. Time may be given in seconds, minutes, days or years.

(f) Zero-order half life

The expression for the half-life of a zero-order reaction can be obtained from the integrated rate law. By definition, $[A] = [A]_0/2$ when $t = t_{½}$, so

$$\frac{[A]_0}{2} = -kt_{½} + [A]_0$$

$$kt_{½} = \frac{[A]_0}{2}$$

$$t_{½} = \frac{[A]_0}{2k}$$

Zero-order reactions are most often encountered when a substance such as a metal surface or an enzyme is required for the reaction to occur.

Exercise

1. The decomposition of HI into hydrogen and iodine on a gold surface is zero order in HI. The rate constant for the reaction is 0.050 s^{-1}. If you begin with a 0.500 M concentration of HI, what is the concentration of HI after 5 seconds?

(g) Integrated rate laws for reactions with more than one reactants

So far we have considered the integrated rate laws for simple reactions with only one reactant. Special techniques are required to deal with more complicated reactions. For example, consider the reaction:

$$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \longrightarrow 3Br_2(l) + 3H_2O(l)$$

From experimental evidence we know that the rate law is:

$$\text{Rate} = -\frac{d[BrO_3^-]}{dt} = k[BrO_3^-][Br^-][H^+]^2$$

Suppose we run this reaction under conditions where:

$$[BrO_3^-]_0 = 1.0 \times 10^{-3}\,M,\ [Br^-]_0 = 1.0\,M,\ \text{and}\ [H^+]_0 = 1.0\,M\ .$$

As the reaction proceeds, $[BrO_3^-]$ decreases significantly, but because the Br^- ion and H^+ ion concentrations are so large initially, relatively little of either of these two reactants is consumed. Thus [Br^-] and [H^+] remain approximately constant. In other words, under the conditions where the Br^- ion and H^+ ion concentrations are much larger than the BrO_3^- ion concentration, we can assume that throughout the reaction

$$\left[Br^-\right]=\left[Br^-\right]_0 \text{ and } \left[H^+\right]=\left[H^+\right]_0$$

This means that the rate law can be written as:

$$\text{Rate}=k\left[BrO_3^-\right]\left[Br^-\right]_0\left[H^+\right]_0^2=k'\left[BrO_3^-\right]$$

Where $[BrO^-]_0$ and $[H+]_0$ are constant,

$$k'=k\left[Br^-\right]_0\left[H^+\right]_0^2$$

The rate law Rate = k'[BrO_3^-] is first order. However, since this rate law was obtained by simplifying a more complicated one, it is called a pseudo-first-order rate law. Under the conditions of this experiment, a plot of ln [BrO_3^-] versus t gives a straight line with a slope equal to –k. Since $[Br^-]_0$ and $[H^+]_0$ are known, the value of k can be calculated from the equation:

$$k'=k\left[Br^-\right]_0\left[H^+\right]_0^2$$

which can be rearranged to give:

$$k=\frac{k'}{\left[Br^-\right]_0\left[H^+\right]_0^2}$$

Note that the kinetics of complicated reactions can be studied by observing the behavior of one reactant at a time. If the concentration of one reactant is much smaller than the concentrations of the others, then the amounts of those reactants present in large concentrations will not change significantly and can be regarded as constant. The change in concentration with time of the reactant present in a relatively small amount can then be used to determine the order of the reaction in that component. This technique allows us to determine rate laws for complex reactions.

8.5 REACTION MECHANISMS

Upon completion of this topic, learners will be able to:

- explain reaction mechanism.
- describe the molecularity of a reaction

- Explain what is meant by rate determining step; and
- Use rate equation to suggest possible reaction mechanism for a reaction.

Most chemical reactions occur by a series of steps called reaction mechanism. To understand a reaction, we must know its mechanism, and one of the main purposes for studying kinetics is to learn as much as possible about the steps involved in a reaction. In this section we explore some of the fundamental characteristics of reaction mechanisms.

As an example of a reaction mechanism, let us consider the reaction between nitric oxide and oxygen:

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

the mechanism is thought to involve the steps shown below:

Step 1 $2NO(g) \longrightarrow N_2O_2(g)$

Step 2 $N_2O_2(g) + O_2(g) \longrightarrow 2NO_2(g)$

In the first elementary step, two NO molecules collide to form a N_2O_2 molecule. This event is followed by the reaction between N_2O_2 and O_2 to give two molecules of NO_2. The net chemical equation, which represents the overall change, is given by the sum of the elementary steps:

Elemetary step: $NO(g) + NO(g) \longrightarrow N_2O_2(g)$

Elemetary step: $N_2O_2(g) + O_2(g) \longrightarrow 2NO_2(g)$

Overall reaction: $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$

Species such as N_2O_2 are called intermediates because they appear in the mechanism of the reaction (that is, the elementary steps) but not in the overall balanced equation.

Molecularity of an elementary reaction

Molecularity is defined as the number of species that must collide to produce the reaction indicated by that step. A reaction involving one molecule is called a unimolecular step. Reactions involving the collision of two and three species are termed bimolecular and termolecular, respectively.

Termolecular steps are quite rare because the probability of three molecules colliding simultaneously is very small. Examples of these three types of elementary steps and the corresponding rate laws are shown in Table 3.

Note from Table 3 that the rate law for an elementary step follows directly from the molecularity of that step. For example, for a bimolecular step, the rate law is always second order, either of the form $k[A]^2$ for a step with a single reactant or of the form $k[A][B]$ for a step involving two reactants.

Table 3 **Examples of Elementary Steps and Corresponding Rate Laws**

Elementary Step	Molecularity	Rate Law
$A \longrightarrow \text{Products}$	Unimolecular	$\text{Rate} = k[A]$
$A + A \longrightarrow \text{Products}$ $2A \longrightarrow \text{Products}$	Bimolecular	$\text{Rate} = k[A]^2$
$A + B \longrightarrow \text{Products}$	Bimolecular	$\text{Rate} = k[A][B]$
$A + A + B \longrightarrow \text{Products}$ $2A + B \longrightarrow \text{Products}$	Termolecular	$\text{Rate} = k[A]^2[B]$
$A + B + C \longrightarrow \text{Products}$	Termolecular	$\text{Rate} = k[A][B][C]$

Rate-determining step

In a multi-step reaction, all the elementary reactions do not necessarily proceed at equal rates. One of them might be very rapid, moderate or very slow. The reactants can be converted to products only as fast as they can complete the slowest step. The slowest step in the sequence of steps leading to the formation of products is called the rate determining step. In other words, the slowest step in the mechanism determines the overall rate of the reaction.

The overall rate cannot be faster than that of the slowest step.

$$\text{Overall rate} \rightleftharpoons \text{rate of the slowest step}$$

We can now define a reaction mechanism more precisely. It is a series of elementary steps that must satisfy two requirements:

1. The sum of the elementary steps must give the overall balanced equation for the reaction.
2. The mechanism must agree with the experimentally determined rate law.

Example

The gas-phase decomposition of nitrous oxide (N_2O) is believed to occur *via* two elementary steps:

Step 1 $N_2O \xrightarrow{k_1} N_2 + O$

Step 2 $N_2O + O \longrightarrow N_2 + O_2$

Experimentally the rate law is found to be rate = k[N_2O].

(a) Write the equation for the overall reaction.

(b) Identify the intermediates.

(c) What can you say about the relative rates of steps 1 and 2?

Solution

(a) Adding the equations for steps 1 and 2 gives the overall reaction

$$2N_2O \longrightarrow 2N_2 + O_2$$

(b) Because the O atom is produced in the first elementary step and it does not appear in the overall balanced equation, it is an intermediate.

(c) If we assume that step 1 is the rate-determining step, then the rate of the overall reaction is given by

$$\text{Rate} = k_1\,[N_2O]$$

and $k = k_1$.

Exercise

1. For the decomposition of ozone to oxygen. The balanced reaction is:

$$2O_3(g) \longrightarrow 3O_2(g)$$

The observed rate law is:

$$\text{Rate} = k\frac{[O_3]^2}{[O_2]}$$

A proposed mechanism for this process is:

$$O_3 \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} O_2 + O \qquad \text{Slow}$$

$$O + O_3 \overset{K_2}{\rightleftharpoons} 2O_2 \qquad \text{Fast}$$

Is this an acceptable mechanism for the reaction?

8.6 ACTIVATION ENERGY

Upon completion of this topic, learners will be able to:

- define activation energy.
- relate temperature, activation energy, and rate constant through the Arrhenius equation.

The minimum energy necessary to form a product during a collision between reactants is called the activation energy (E_a). Figure 12 shows the energy relationships for the general reaction of a molecule of A with a molecule of B to form molecules of C and D:

$$A + B \longrightarrow C + D$$

The Figure 12 shows that the energy of the transition state is higher than that of the reactants A and B by an amount equal to E_a, the activation energy. Thus, the sum of the energies of A and B must be equal to or greater than E_a to reach the transition state. After the transition state has been reached, C and D begin to form. ΔH represents the difference in enthalpy between the reactants (A and B) and the products (C and D). The sum of E_a and ΔH represents the activation energy for the reverse reaction:

$$C + D \longrightarrow A + B$$

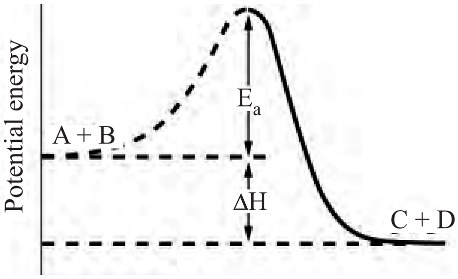


Figure 12. This graph shows the potential energy relationships for the reaction A + B → C + D. The dashed portion of the curve represents the energy of the system with a molecule of A and a molecule of B present, and the solid portion the energy of the system with a molecule of C and a molecule of D present.

The activated complex

The energies of reactants, products, and intermediates are often displayed on an energy level diagram. The vertical axis is potential energy; the horizontal axis, called the reaction coordinate, is a relative scale that begins with the reactants and ends with the products. In the terminology of chemical kinetics, the least-stable (highest energy) arrangement of atoms is called the activated complex, or the transition state.

An activated complex or transition state is a short-lived, high energy state species that is temporarily formed by the collision of reactant molecules before they form products. In the activated complex, the original bonds are lengthened and weakened, and the new bonds are only partially formed. Remember that chemical reactions involve the formation and breaking of chemical bonds and are accompanied by changes in potential energy, which is related to bond energy.

Let us consider the reaction:

$$A_2 + B_2 \longrightarrow 2AB$$

where A_2 and B_2 are the reactants, and AB is the product.

As the reactants, A_2 and B_2, approach each other and collide, they begin climbing up the left side of the potential-energy hill, or barrier. If they have less energy than the energy of activation, E_a, they fail to climb the barrier and, instead, roll back down its left side. In this case, no reaction occurs.

If, however, they have energy that is at least equal to the energy of activation, they climb the barrier, roll down the other side, and convert to products.

In this concept, the level of activation energy required for a reaction is seen as the height of a barrier between the reactants and products. To convert from the reactant condition to the product condition, particles must climb the barrier.

The potential-energy curves in Figure 13 include representations of the barrier.

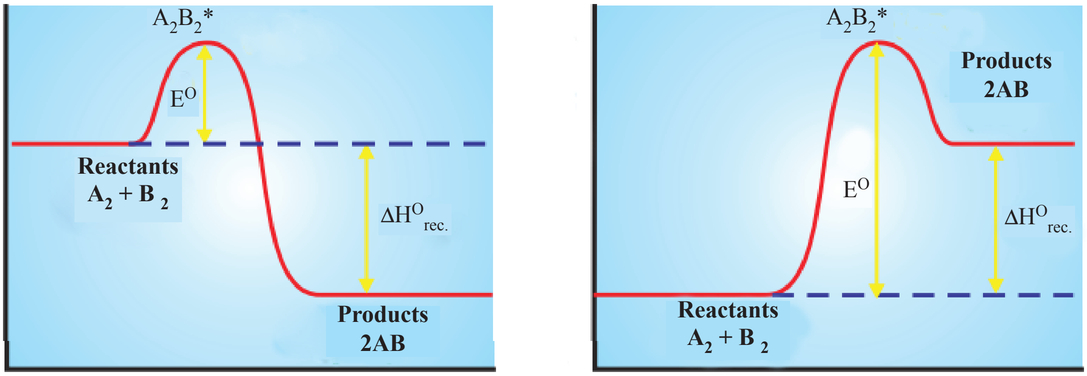


Figure 13. Reaction energy diagrams for a) exothermic and b) endothermic reactions.

A_2B_2* represent the activated complex or transition state.

Arrhenius equation

We can use the Arrhenius equation to relate the activation energy and the rate constant, k, of a given reaction:

$$k = Ae^{-Ea/RT}$$

In this equation, R is the ideal gas constant, which has a value 8.314 J / mol . K, T is temperature on the Kelvin scale, E_a is the activation energy in joules per mole, and A is a constant called the frequency factor, which is related to the frequency of collisions and the orientation of the reacting molecules.

The Arrhenius equation describes quantitatively much of what we have already discussed about reaction rates. For two reactions at the same temperature, the reaction with the higher activation energy has the lower rate constant and the slower rate. The larger value of E_a results in a smaller value for $e^{-E_a/RT}$, reflecting the smaller fraction of molecules with enough energy to react. Alternatively, the reaction with the smaller E_a has a larger fraction of molecules with enough energy to react. This will be reflected as a larger value of $e^{-E_a/RT}$, a larger rate constant, and a faster rate for the reaction. An increase in temperature has the same effect as a decrease in activation energy. A larger fraction of molecules has the necessary energy to react (Figure 14), as indicated by an increase in the value of $e^{-E_a/RT}$.

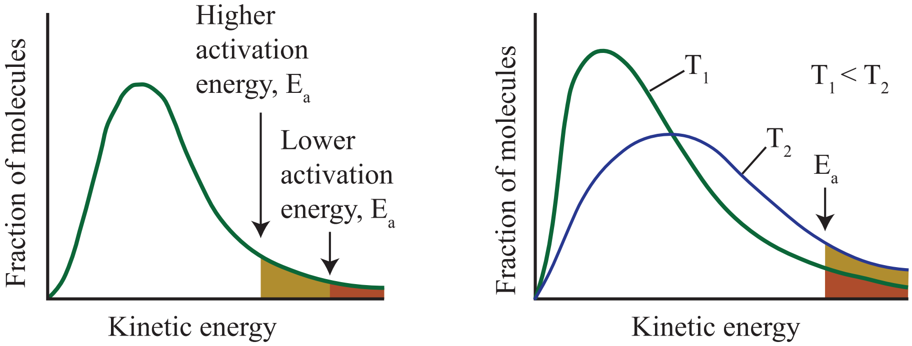


Figure 14. (a) As the activation energy of a reaction decreases, the number of molecules with at least this much energy increases, as shown by the shaded areas. (b) At a higher temperature, T_2*, more molecules have kinetic energies greater than* E_a*, as shown by the yellow shaded area.*

A convenient approach to determining E_a for a reaction involves the measurement of k at different temperatures and using an alternate version of the Arrhenius equation that takes the form of linear equation:

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

Thus, a plot of ln k versus 1/T gives a straight line with a slope $-E_a/R$, from which E_a may be determined. The intercept gives the value of ln A.

Because we need only two experiments to calculate the slope, we can derive an equation that relates the activation energy to the rate constants at two temperatures.

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

Exercise

1. Consider the decomposition of nitrogen dioxide:

$$2NO_2(g) \longrightarrow 2NO(g) + O_2(g)$$

At 650 K, the rate constant is 1.66 L/mols ; at 700 K , it is 7.39 L/mols. Use these rate constants to determine the activation energy.

8.7 COLLISION THEORY

Upon completion of this topic, learners will be able to:

- state collision theory.
- describe how collision theory can be used to explain changes in reaction rate.

The fundamental concept of the collision theory of rate of reaction is that, in order for a reaction to occur between reacting species (atoms, ions or molecules), they must first collide (come in contact). The rate of reaction is directly proportional to the number of collisions per second (the frequency of collision).

$$\text{Rate} \propto \frac{\text{Number of collisions}}{\text{Second}}$$

According to the collision theory, the more collisions there are, the faster the rate of reaction would be. However, not all collisions between reacting species result in a reaction. This is because collisions between reactants can be either effective or ineffective. Effective collisions are collisions that result in a reaction to form the desired products.

In order for a collision between reactants to be effective, the reacting species must be in proper orientation with each other at the time of collision, they must collide with sufficient energy to break or rearrange bonds.

Postulates of the collision theory are summarized below. For a reaction to occur between reactants:

1. The particles of the reacting substances must collide.
2. The particles of the reacting species must have proper orientation.
3. The particles of the reactants must collide with energy greater than or equal to the energy of activation

According to the collision theory, only collisions with proper orientation of reacting species possessing sufficient energy result in a reaction.

Concentration and collision theory

Concentration is one of the factors that influence the rate of reaction of a chemical reaction. The collision theory accounts for the observed increase in the rate of any reaction when the concentrations of reactants are increased. Increasing the concentrations of the reacting species results in higher number of collisions per unit time, and the reaction rate is correspondingly higher.

Temperature and collision theory

As the temperature of the reacting species is raised, the average kinetic energy of the reacting particles increases considerably. This causes the particles of the reactants to collide more frequently and with greater energy. This results in an increase in reaction rate.

Exercise

1. How is the rate of a reaction affected by each of the following?
   (a) Activation energy
   (b) Temperature
   (c) Frequency of collisions
   (d) Orientation of collisions
2. The central idea of the collision theory is that molecules must collide in order to react. Give two reasons why not all collisions of reactant molecules result in product formation.

KEY TERMS

- Rate of a reaction
- Homogeneous catalyst
- Heterogeneous catalysts
- Rate law
- Rate constant
- Order of a reaction
- Differential rate law
- Integrated rate law
- Method of initial rates
- First-order rate law
- Second-order rate law
- Third-order rate law
- Zero-order rate law

- Reaction mechanism
- Intermediates
- Molecularity
- Rate determining step
- Activation energy
- Activated Complex
- Arrhenius equation
- Collision theory

SUMMARY

The rate of a reaction can be expressed either in terms of the decrease in the amount of a reactant or the increase in the amount of a product per unit time. Relations between different rate expressions for a given reaction are derived directly from the stoichiometric coefficients of the equation representing the reaction.

The rate of a chemical reaction is affected by several parameters. Reactions involving two phases proceed more rapidly when there is a greater surface area contact. If temperature or reactant concentration is increased, the rate of a given reaction generally increases as well. A catalyst can increase the rate of a reaction by providing an alternative pathway that causes the activation energy of the reaction to decrease.

Rate laws provide a mathematical description of how changes in the amount of a substance affect the rate of a chemical reaction. Rate laws are determined experimentally and cannot be predicted by reaction stoichiometry. The order of reaction describes how much a change in the amount of each substance affects the overall rate, and the overall order of a reaction is the sum of the orders for each substance present in the reaction. Reaction orders are typically first order, second order, or zero order, but fractional and even negative orders are possible.

Differential rate laws can be determined by the method of initial rates or other methods. We measure values for the initial rates of a reaction at different concentrations of the reactants. From these measurements, we determine the order of the reaction in each reactant. Integrated rate laws are determined by integration of the corresponding differential rate laws. Rate constants for those rate laws are determined from measurements of concentration at various times during a reaction.

The half-life of a reaction is the time required to decrease the amount of a given reactant by one-half. The half-life of a zero-order reaction decreases as the initial concentration of the reactant in the reaction decreases. The half-life of a first-order reaction is independent of concentration, and the half-life of a second-order reaction decreases as the concentration increases.

The sequence of individual steps, or elementary reactions, by which reactants are converted into products during the course of a reaction is called the reaction mechanism. The overall rate of a reaction is determined by the rate of the slowest step, called the rate-determining step. Unimolecular elementary reactions have first-order rate laws, while bimolecular elementary reactions have second-order rate laws. By comparing the rate laws derived from a reaction mechanism to that determined experimentally, the mechanism may be considered as either incorrect or plausible.

Chemical reactions require collisions between reactant species. These reactant collisions must be of proper orientation and sufficient energy in order to result in product formation. The collision theory provides a simple but effective explanation for the effect of many experimental parameters on reaction rates. The Arrhenius equation describes the relationship between the rate constant of a reaction and its activation energy, temperature, and dependence on collision orientation.

Exercises

Part I: Choose the correct answer for each of the following questions

1. Consider the reaction in which ammonia is synthesized from nitrogen and hydrogen gases: $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$
   How is the rate of formation of ammonia related to the rate of consumption of hydrogen?
   (a) The rate of formation of ammonia is half the rate of consumption of hydrogen.
   (b) The rate of formation of ammonia is twice the rate of consumption of hydrogen.
   (c) The rate of formation of ammonia is equal to the rate of consumption of hydrogen.
   (d) The rate of formation of ammonia is two-thirds the rate of consumption of hydrogen.
2. For a collision between molecules to result in a reaction, the molecules must possess a certain minimum energy and ....?
   (a) Exchange electrons.
   (b) Interact with a catalyst.
   (c) Have a favorable orientation relative to each other when they collide.
   (d) Have the same activation energy.
3. Increasing the temperature at which a chemical reaction occurs will also do which of the following?
   (a) Increase the activation energy.
   (b) Cause more reactant collisions to take place in a given time.

(c) Increase the energy of the system, thus decreasing the reaction rate.
(d) Decrease the energy of the system, thus increasing the reaction rate.

4. The following data were obtained for reaction:

$$2A(g) + B(g) + 2C(g) \longrightarrow 3D(g) + 2E(g)$$

Experiment	Initial [A], (M)	Initial [B], (M)	Initial [C], (M)	Initial Rate, (M/s)
1	0.20	0.10	0.10	2.0×10^{-4}
2	0.20	0.30	0.20	6.0×10^{-4}
3	0.20	0.10	0.30	2.0×10^{-4}
4	0.60	0.30	0.40	1.8×10^{-3}

From these initial rate data, determine the rate constant for the reaction?
(a) 1.0×10^{-1}/Ms (c) 1.0×10^{-2}/Ms
(b) 2.0×10^{-1}/Ms (d) 2.0×10^{-2}/Ms

5. The half-life of a first-order reaction:
(a) depends on the reactant concentration raised to the first power.
(b) is inversely proportional to the square of the reactant concentration.
(c) is inversely proportional to the reactant concentration.
(d) is totally independent of the reactant concentration.

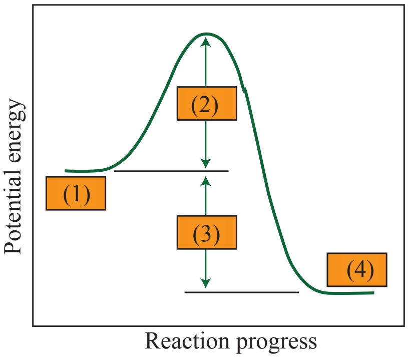
6. In a reaction, A + B $\longrightarrow$ Product, rate is doubled when the concentration of B is doubled, and rate increases by a factor of 8 when the concentrations of both the reactants (A and B) are doubled. The rate law for the reaction can be written as:
(a) Rate = $k[A][B]^2$ (c) Rate = $k[A][B]$
(b) Rate = $k[A]^2[B]^2$ (d) Rate = $k[A]^2[B]$

7. The unit of rate constant for a zero order reaction is:
(a) $\text{mol L}^{-1}\text{ s}^{-1}$
(b) $\text{L mol}^{-1}\text{ s}^{-1}$ (d) s^{-1}
(c) $\text{L}^2\text{ mol}^{-2}\text{ s}^{-1}$

8. The plot of concentration of the reactant vs. time for a reaction is a straight line with a negative slope. The reaction follows:
(a) zero order rate equation (c) second order rate equation
(b) first order rate equation (d) third order rate equation

9. The reaction A $\longrightarrow$ B is a second-order reaction. When the initial concentration of A is 0.50 M, the half-life is 8.0 minutes. What is the half-life if the initial concentration of A is 0.10 M?
(a) 1.6 minutes (c) 40.0 minutes
(b) 8.0 minutes (d) 16.0 minutes

10. In the Arrhenius equation $k = Ae^{\frac{-E_a}{RT}}$, the rate constant:
    (a) decreases with increasing activation energy and increases with temperature.
    (b) increases with activation energy and temperature.
    (c) decreases with activation energy and temperature.
    (d) increases with activation energy and decreasing temperature.

11. 

    Based on the diagram given, activation energy is indicated by number .... and the reaction profile is:
    (a) 2, endothermic (c) 3, endothermic
    (b) 2, exothermic (d) 3, exothermic

12. Species that are formed in one step of reaction mechanism and used up in another step are called:
    (a) catalysts (c) inhibitors
    (b) intermediates (d) activated complexes

13. Which of the following statements associated with mechanisms of chemical reactions is incorrect?
    (a) intermediates do not appear in the net chemical equation or overall rate law.
    (b) the fastest step in a mechanism determines the rate of the reaction.
    (c) in elementary reactions, coefficients give the order with respect to reactants and products.
    (d) a plausible mechanism must account experimentally determined rate law.

14. Which one of the following statements concerning rates of reactions is False?
    (a) The higher the activation energy barrier, the faster the reaction.
    (b) As concentration of a reactant increases, the rate of the reaction increases except for zero-order reactions.

(c) Increasing the concentration of a reactant may increase the rate of a reaction.
(d) Adding a catalyst speeds up the rate of reaction for both the forward and reverse reactions.

15. For a hypothetical reaction, $2A + B \longrightarrow$ Products, the rate constant, $k = 5.6 \times 10^{-6}$ $Lmol^{-1}s^{-1}$. The order of the reaction is:

(a) second
(b) first
(c) half
(d) zero

16. Which of the following statements is *incorrect* about the collision theory of chemical reaction?

(a) All collisions between reacting species result in a reaction.
(b) An activated complex is a short-lived, high energy state species temporarily formed by the collision of reactants.
(c) The number of effective collisions determines the rate of reaction.
(d) The number of ineffective collisions determines the rate of reaction.

17. Which of the following statements is *not correct* about the order of a reaction. The order of a reaction:

(a) is always equal to the sum of the stoichiometric coefficients of reactants in the balanced chemical equation for a reaction.
(b) is the sum of the powers of molar concentration of the reactants in the rate law expression.
(c) is an experimentally determined quantity.
(d) can be a fractional number.

18. The rate law for a reaction is given as rate = $k\,[A]^{½}\,[B]^2$, Which one of the following statements is False?

(a) The overall reaction order is 5/2.
(b) If concentration terms are in M and time in second, then the unit of k for this reaction is $M^{-3}s^{-1}$.
(c) If [A] is quadrupled and [B] is doubled, the reaction rate will increase by a factor of 8.
(d) If only [B] is doubled, the reaction rate will increase by a factor of 4.

19. The reaction of butadiene gas (C_4H_6) with itself produces C_8H_{12} gas as follows:

$$2C_4\,H_6(g) \longrightarrow C_8\,H_{12}(g)$$

The reaction is second order with a rate constant equal to 5.76×10^{-2} L/mol/min under certain conditions. If the initial concentration of butadiene is 0.200 *M*, what is the concentration remaining after 10.0 min?

(a) $[A] = 5.576\ \text{L mol}^{-1}$

(b) $[A] = 0.0196\ \text{mol/L}$

(c) $\frac{1}{[\text{A}]} = 1.79 \times 10^{-1}\ \text{mol L}^{-1}$

(d) $\frac{1}{[\text{A}]} = 5.576\ \text{L mol}^{-1}$

20. The decomposition of ozone into oxygen gas i.e. $2O_3 \rightarrow 3O_2$ proceeds through the following mechanism given below:

(i) $O_3 \underset{K_2}{\overset{K_1}{\rightleftharpoons}} O_2 + O$ ......(fast)

(ii) $O + O_3 \xrightarrow{K_3} 2O_2$ ....(slow)

The rate law expression for the reaction would be

(a) $r = k[O_3]^2[O_2]^{-1}$

(b) $r = k[O_3]^2[O_2]$

(c) $r = k[O_3][O_2]$

(d) $r = k[O_3]^2$

Part II: Short Answer Questions

21. Define reaction rate. Distinguish between initial rate, average rate, and instantaneous rate of a chemical reaction.

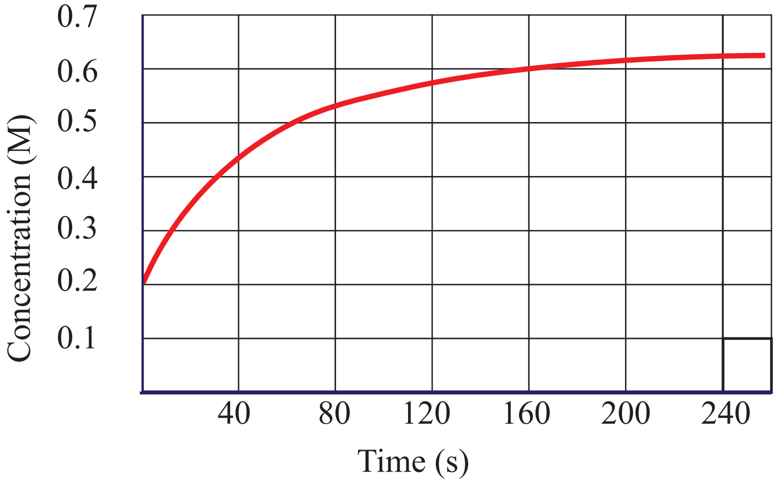
22. Consider the following reaction in aqueous solution:

$5Br^-\ (aq) + BrO_3^-\ (aq) + 6H^+\ (aq) \longrightarrow 3Br_2\ (aq) + 3H_2O\ (l)$ If the rate of disappearance of Br^- (aq) at a particular moment during the reaction is 3.5×10^{-4} M s^{-1}, what is the rate of appearance of Br_2(aq) at that moment?

23. Nitrogen monoxide reacts with chlorine to form nitrosyl chloride.

$$NO(g) + \frac{1}{2}Cl_2(g) \longrightarrow NOCl(g)$$

The figure shows the increase in nitrosyl chloride concentration under appropriate experimental conditions. The concentration of nitrosyl chloride actually starts at zero.



(a) Write an expression for the rate of reaction.

(b) Calculate the average rate of reaction between 40 and 120 seconds.

(c) Calculate the instantaneous rate of reaction after 80 seconds.

(d) Calculate the instantaneous rate of consumption of chlorine 60 seconds after the start of the reaction.

24. Write a rate law for:

$$NO_3(g) + O_2(g) \longrightarrow NO_2(g) + O_3(g)$$

if measurements show the reaction is first order in nitrogen trioxide and second order in oxygen.

25. If the half-life for a reaction is 20 seconds, what would be the second half-life, assuming the reaction is either zero, first, or second order?

26. The radioactive isotope ^{32}P decays by first-order kinetics and has a half-life of 14.3 days. How long does it take for 95.0% of a given sample of ^{32}P to decay?

27. A certain reaction has the following general form:

$$aA \longrightarrow bB$$

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

(a) Determine the rate law, the integrated rate law, and the value of the rate constant for this reaction.

(b) Calculate the half-life for this reaction.

(c) How much time is required for the concentration of A to decrease to 2.50×10^{-3} M

28. The reaction:

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

exhibits the rate law

$$\text{Rate} = k[NO]^2[O_2]$$

Which of the following mechanisms is consistent with this rate law?

(a) $NO + O_2(g) \longrightarrow NO_2 + O$ slow

$O + NO \longrightarrow NO_2$ fast

(b) $NO + O_2 \rightleftharpoons NO_3$ fast equilibrium

$NO_3 + NO \longrightarrow 2NO_2$ slow

(c) $2NO \rightleftharpoons N_2O_2$ fast equilibrium

$N_2O_2 \longrightarrow NO_2 + O$ slow

$O + NO \longrightarrow NO_2$ fast

WHAT IS BULLYING?

Any unwanted written, verbal, graphic, or physical act by an individual or group toward another person(s) that causes harm or distress.

Types of Bullying

- Physical
- Verbal
- Social
- Emotional
- Cyber

Signs of Bullying

- Headaches
- Depression
- Loss of friends
- School absenteeism
- Academic problems

What You Can Do

PREVENT

- Be a role model for positive communication, healthy relationships, and self-care.
- Reinforce acts of kindness, respect, and inclusion.
- Set policies and rules about bullying.

RECOGNIZE

- Know the definition of bullying and its many forms.
- Talk with and actively listen to the youth who confide in you.
- Watch for warning signs of bullying.

INTERVENE

- If you witness bullying behavior
- Respond quickly and consistently to send the message that it is not acceptable.
- Separate the students involved.
- Meet any immediate medical or mental health needs.
- Stay calm and model respectful behavior.

Source: Teacher's Diary on *Cyber-Crime Awareness* by UNODC, Cybercrime and MoE, Republic of Liberia

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TEXTBOOK MANAGEMENT

Student Textbook Assignment Form

School : ____

District : ______________________________Country: __________________________

Teacher : ___________________________________Subject: ______________________

Grade : ____

No.	Name of the Student	Name of the Textbook	Barcode Number	Condition of the TB when received	Date Received	Date Returned	Condition of TB when returned	Signature of Student
1								
2								
3								
4								
5								
6								
7								
8								
9								
10								
11								
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