



TECHNOLOGICAL UNIVERSITY OF THE PHILIPPINES VISAYAS

Capt. Sabi St., City of Talisay, Negros Occidental

**College of Engineering Technology
Office of the College Dean**

LECTURE MODULE

CHEM 124:

**CHEMISTRY FOR THE
ENGINEERS**

DEPARTMENT: BACHELOR OF SCIENCE IN CHEMISTRY

COMPILED BY:

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2020

VISION

The Technological University of the Philippines shall be the premier state university with recognized excellence in engineering and technology at par with leading universities in the ASEAN region.

MISSION

The University shall provide higher and advanced vocational, technical, industrial, technological and professional education and training in industries and technology, and in practical arts leading to certificates, diplomas and degrees.

It shall provide progressive leadership in applied research, developmental studies in technical, industrial, and technological fields and production using indigenous materials; effect technology transfer in the countryside; and assist in the development of small-and-medium scale industries in identified growth center. (Reference: P.D. No. 1518, Section 2)

QUALITY POLICY

The Technological University of the Philippines shall commit to provide quality higher and advanced technological education; conduct relevant research and extension projects; continually improve its value to customers through enhancement of personnel competence and effective quality management system compliant to statutory and regulatory requirements; and adhere to its core values.

CORE VALUES

- T - Transparent and participatory governance
- U - Unity in the pursuit of TUP mission, goals, and objectives
- P - Professionalism in the discharge of quality service
- I - Integrity and commitment to maintain the good name of the University
- A - Accountability for individual and organizational quality performance
- N - Nationalism through tangible contribution to the rapid economic growth of the country
- S - Shared responsibility, hard work, and resourcefulness in compliance to the mandates of the university

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Week No.: 1

TOPIC:
Chemical Safety:
Proper Handling and Storage of Chemical

OBJECTIVES:

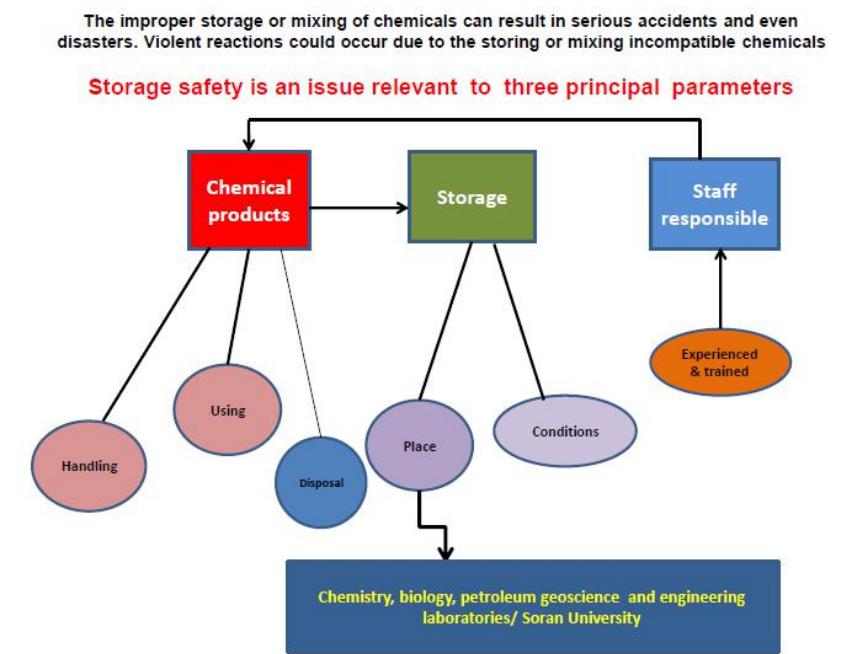
1. Enable students to safely handle and use these hazardous materials.
2. Provide skills and knowledge required to work safely in environments which involve the transport, storage, use and disposal of chemicals
3. Provide skills require, and help to identify the hazards, and explain the controls needed to stay safe working around chemicals.
4. Provide an understanding of working with chemicals.

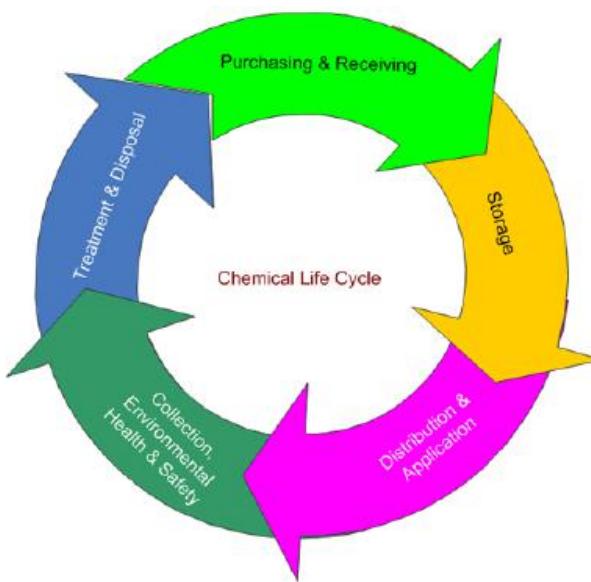
MATERIALS SUPPORT/REFERENCE:

https://www.researchgate.net/publication/309176044_Proper_Handling_and_Storage_of_Chemicals

<https://businesssafety.ie/training/chemical-handling-training>

CONTENTS:





Chemical Storage Guidelines In addition to eliminating hazards that may arise with the use of chemicals, an **appropriate chemical storage system** must be developed. **Improper storage** will increase the chances of an accident occurring. **Examples of improper storage include:**

1. storage of chemicals in alphabetical order or other categories that may bring incompatibles in contact
2. storage of flammables in an ordinary refrigerator
3. storage of chemicals with food

Guidelines can be used to implement a safe storage system for chemicals

A. Rotational Stock System

1. Limit the amount of chemicals present in the laboratories.
2. Ensure that all containers have the following:
 - a. Proper IUPAC Name
 - b. Manufacturer's Name
 - c. Chemical label with associated precautions
 - d. Date the chemical was received
 - e. Date the chemical was first used
3. A first-in, first-out system using the oldest chemicals first should be implemented. This will avoid degradation of older chemicals and their containers.
4. Use the following for maximum storage times:
 - a. When storing untreated chemicals that degrade to unstable forms (e.g. peroxide formers), limit the maximum storage time to one year from purchase or six months from first use.
 - b. For other hazardous chemicals, use the manufacturer's recommended storage time or other indications of degradation (e.g., discoloring of liquids).
 - c. Innocuous material (e.g., sodium chloride, sodium bicarbonate, Buffer Solutions, etc.) can be stored indefinitely or until no further use is desired.

When you have exceeded these periods of time or have no further use of the chemical, contact to have the chemicals removed for proper disposal.

B. Storage

1. General

- a. Do not store anything in the hallway, stairwells, on the floor or in any area accessible to the general public.
- b. Properly label all storage areas (e.g., “Chemical Storage Area”) to warn personnel of the hazards that are present.
- c. Do not store incompatible chemicals in areas where there exists the possibility of reaction.
- d. Ensure that all containers are not corroded, broken, rusted, or leaking. If the container loses its integrity, transfer the chemical to another container or, when transfer is not possible or safe, use secondary containers. Contact for disposal.
- e. In general, limit container size to one gallon in the laboratory. Larger containers should be kept in chemical storage rooms.
- f. Routinely check chemicals that are being stored for possible hazards.
- g. Store reactive chemicals in areas to reduce the possibility of reaction. For instance, keep water reactive chemicals in a controlled, low humidity environment.

2. Shelves

- a. If possible, avoid storing chemicals above shoulder height. Large containers (one gallon or larger), liquids, and corrosive materials should be stored on lower shelves below eye level.
- b. Ensure that shelves are capable of storage. Do not store chemicals on unsturdy shelves.
- c. Do not overcrowd shelves.
- d. Shelves should be impervious to spilled liquids. This can be accomplished by coating the shelves with an epoxy.
- e. See attached illustration for possible guidelines for storage on shelves. If this is not possible, a system of storage should be developed to ensure that incompatible chemicals are not stored together.

3. Refrigerators and Freezers

- a. Do not store chemicals and food together.
- b. When storing flammables, use an approved explosion proof or flammable storage refrigerator.
- c. Only use refrigerators or freezers for storage of chemicals that need to be kept refrigerated or frozen.
- d. Label the refrigerator as to the intended use.

4. Flammable and Combustible Liquids

- a. Flammable and combustible liquids are separated into the following classes according to the National Fire Protection Association (NFPA)

| | | |
|--|---|--|
| Class 1A (Highly Flammable) | Flash Point <73°F (22.8°C) Boiling Point <100°F (37.8°C) | Ex: Ethyl ether, Dimethyl sulfide, Petroleum ether |
| Class 1B Flammable | Flash Point <73°F (22.8°C) Boiling Point >100°F (37.8°C) | Ex: Acetone, Toluene, Ethanol, Ethyl acetate, Hexane, Gasoline |
| Class 1C Flammable | Flash Point >73°F (22.8°C) Boiling Point <100°F (37.8°C) | Ex: Amyl acetate, Bromopentane, Butyric acid, Hexene, Xylene |
| Class II Combustible | Flash Point >100°F (37.8°C) & <140°F (60°C) | Ex: Acetic acid, Cumene, Formaldehyde |
| Class IIIA Combustible | Flash Point >140°F (60°C) & <200°F (93.4°C) | Ex: Benzaldehyde, Ethanolamine, Nitrobenzene |

- b. Do not store flammable or combustible liquids near sources of ignition.
 c. The following are other specifications for storage. For chemical stockrooms, individual evaluations will be necessary and, as a result, may not be bound to these requirements.

1. Not more than 10 gallons of Class I or Class II liquids combined shall be stored outside of a storage cabinet or storage room, except in safety cans.
2. Not more than 25 gallons of Class I or Class II liquids combined shall be stored in safety cans outside of a storage room or storage cabinet.
3. Not more than 60 gallons of Class IIIA liquids shall be stored outside of a storage room or storage cabinet.
4. Any quantity of liquids over this limit must be stored in an inside storage room or storage cabinet.
5. Approved storage cabinets shall not exceed 120 gallons of combustible and flammable liquids and not more than 60 gallons of the total may be flammable liquid. Not more than 3 storage cabinets will be within one fire area of a building.

(Note: A fire area, is “an area of a building separated from the remainder of the building by construction having a fire resistance of at least one hour and having all communicating openings properly protected by an assembly having a fire resistance rating of at least one hour.”)

Guidelines for Chemical Storage Rooms

Entrance to the Chemical Storage room is restricted to authorized personnel only. The doors to the room are locked at all times. All authorized personnel must become familiar with the safety features and regulations before they may enter the storage room



All approved chemical storage rooms and fire-rated cabinets shall be inspected monthly

| DESIGN AND MAINTENANCE | FIRE PROTECTION | ELECTRICAL SAFETY | SAFETY EQUIPMENT |
|---|--|--|--|
| - Location and design of chemical storage rooms and cabinets approved by Physical Plant and Safety Office | -Fire extinguisher adjacent to room | -Chemical storage rooms electronically monitored by Security for heat and fire | -Staff responsible familiar with location and proper use of all safety equipment |
| -Doors locked when room unoccupied | -Extinguisher inspected within last six months | -Wires, cables, switches serviceable | -Eyewash facilities available and operational |
| -Access limited to authorized personnel | -Exit doors unobstructed | -Electrical equipment explosion proof (in chemical storage room only) | -Safety shower available and operational |
| -Warning signs obvious and intact | -Fire lane to building entrance unobstructed | -Containers flammables are dispensed into/from area grounded | -Safety information displayed on door: • Names of person(s) responsible for area • Emergency telephone numbers (Security, Fire Department) • UNB "In Case of Fire" Procedures • Dangerous Goods Class (es) • No Smoking |
| -Ventilation system operational and adequate for removal of hazardous vapors | -'No Smoking' sign clearly displayed | | -First Aid Kit available and complete with supplies |
| -Temperature control adequate | -Fire blanket available | | |
| -Illumination sufficient | | | |
| -Working space sufficient | | | |
| -Aisles unobstructed | | | |
| -Floor in good condition | | | |
| -Area maintained free of unnecessary refuse | | | |



keep your chemicals,
not like in the photos!

Improper storage

| PERSONAL PROTECTION | MATERIALS HANDLING | MATERIAL LABELING | MATERIAL STORAGE | MATERIAL CLEANUP AND DISPOSAL |
|---|---|--|--|---|
| <p>Personal protective equipment available, clean and in good condition:</p> <ul style="list-style-type: none"> • Eye protection (safety glasses, goggles, and face shield) • Hand protection (impervious gloves; latex not acceptable for chemical handling) • Body protection (lab coat, apron, protective suit) • Foot protection • Appropriate respiratory protection (CSA/OSHA) available | <ul style="list-style-type: none"> -Inventory up to date -M.S.D.S. available for all hazardous materials (excluding waste) -Staff responsible for area trained -Protective equipment worn when handling chemicals -Materials transported from storage secured and handled safely | <ul style="list-style-type: none"> -All containers labeled with Supplier or other label -Contents of unlabeled containers verified and proper label applied -All containers display receiving date; stale-dated, where required | <ul style="list-style-type: none"> -All cylinders properly restrained by chain or strap -New inventory segregated from waste -Chemical compatibility observed -Empty containers segregated from new and waste -Containers not leaking or corroded -Containers properly sealed -Drums stacked securely and not higher than two in depth -Carboys on palettes and not piled on top of one another -Volume of hazardous material stored limited for "room" or "cabinet" <p>POTENTIAL HAZARDS No tripping hazards No falling objects No structural defects No sharp objects No evidence of spillage or leakage</p> | <ul style="list-style-type: none"> Commercial spill clean-up kit available and replenished -Staff responsible aware of procedures for clean up and disposal of chemicals -Chemical spills cleaned up promptly -Clean-up materials disposed of as hazardous waste -Out-dated and potentially unstable chemicals removed and disposed of |



Proper storage



Proper storage and handling



Acids stored in a plastic tray



Safe dilution of conc. acids



Proper handling of gas cylinders



Strong acid storage under fume hood

Safe chemical storage cannot be reduced to a list or chart, but should be a process consisting of several major steps carried by the person responsible who is capable to deal with different aspects :

1: Classify All Chemical Products Present & not neglecting at the same time using the following guides:

1. Using the labels of Storage Code: HMIS (Hazardous Materials Identification System)

| Group | Hazard |
|--------|---|
| Red | Flammable. Store in area segregated for flammable reagents. |
| Blue | Health hazard. Toxic if inhaled, ingested or absorbed through skin. Store in secure area. |
| Yellow | Reactive and oxidizing reagent. May react violently with air, water or other substances. Store away from flammable and combustible materials. |
| White | Corrosive. May harm skin, eyes, or mucous membranes. Store away from red-coded, yellow-coded, and blue-coded reagents. |
| Grey | Presents no more than moderate hazard for general chemical storage. |



The color - coded bar

Labels rate hazards in the Health, Flammability and Reactivity sections on a scale from 0 to 4, 0 being the least hazardous and 4 being very hazardous

Hazard Diamond (label)

Provide visible guide to storage compatibility

2. Using the SDS (Safety Data Sheets)

are designed to provide workers and emergency personnel with important safety information to ensure safe handling of hazardous chemicals and appropriate spill response. MSDS's include information such as physical data (melting point, boiling point, flash point etc.), toxicity, health effects, first aid, reactivity, storage, disposal, protective equipment, and spill/leak procedures. Stony Brook University MSDS system provides the campus community with a database of campus specific chemicals. The program also comes with a library of MSDSs which can be printed. If an MSDS is not in the library, the user can request an MSDS through the web page.

Section I - Supplier Information

- Section I - Supplier Information**
- Section II - Hazard Ingredients/Identity Information Section**
- Section III - Physical/Chemical Characteristics**
- Section IV - Fire and Explosion Hazard Data**
- Section V - Reactivity Data**
- Section VI - Health Hazard Data**
- Section VII - Precautions for Safe Handling and Use**



The MSDS should always be consulted if further information is required on storage and chemical incompatibilities of a particular chemical substance.

You can find in below the MSDS Web Links

<http://www.calvin.edu/admin/physicalplant/departments/ehs/policies/hazcom/msds-weblinks.htm>

Or organized into a auto-executing PDF on a CD



3. Using the hazardous symbols

| Symbol | Hazard | Description of hazard | |
|--------|-------------------------------|---|-----------------------------------|
| | explosive | Chemicals that explode. | Hazard symbols Physicochemical |
| | oxidising | Chemicals that react exothermically with other chemicals. | Hazard symbols Physicochemical |
| | extremely flammable | Chemicals that have an extremely low flash point and boiling point, and gases that catch fire in contact with air. | Hazard symbols Physicochemical |
| | highly flammable | Chemicals that may catch fire in contact with air, only need brief contact with an ignition source, have a very low flash point or evolve highly flammable gases in contact with water. | Hazard symbols Physicochemical |
| | toxic | Chemicals that at low levels cause damage to health. | Hazard symbols Health |
| | harmful | Chemicals that may cause damage to health. | Hazard symbols Health |
| | corrosive | Chemicals that may destroy living tissue on contact. | Hazard symbols Health |
| | irritant | Chemicals that may cause inflammation to the skin or other mucous membranes. | Hazard symbols Health |
| | dangerous for the environment | Chemicals that may present an immediate or delayed danger to one or more components of the environment | Hazard symbols Environmental |

4. Record for Chemicals Used And Withdrawn

A book or electronic record is needed for all the chemicals especially for the chemicals that need to be covered by secure storage to record the date, the chemical being used, the person withdrawing the chemical, the amount used and the countersignature by an authorising person is advisable. Specific approval of purchase and use of such high risk chemicals is also strongly recommended

Chemical spills The following equipment should also be provided for dealing with spills:

1. Chemical spill kits
2. Protective clothing, e.g. heavy-duty rubber gloves, overshoes or rubber boots, respirators
3. Scoops and dustpans
4. Forceps for picking up broken glass
5. Mops, cloths and paper towels
6. Buckets
7. Soda ash (sodium carbonate or sodium bicarbonate) for neutralizing acids and corrosive chemicals
8. Sand (to cover alkali spills)
9. Non-flammable detergent

The following actions should be taken in the event of a significant chemical spill:

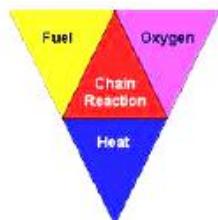
1. Notify the appropriate safety responsible.

2. Evacuate non-essential personnel from the area.
3. Attend to persons who may have been contaminated.
4. If the spilled material is flammable, extinguish all open flames, turn off gas in the room and adjacent areas, open windows (if possible), and switch off electrical equipment that may spark.
5. Avoid breathing vapour from spilled material.
6. Establish exhaust ventilation if it is safe to do so.
7. Secure the necessary items (see above) to clean up the spill

Information regarding storage of compressed and liquefied gases

| | |
|---|--|
| Compressed gas cylinders and liquefied gas containers | <ul style="list-style-type: none"> -Should be securely fixed (e.g. chained) to the wall or a solid bench so that they are not inadvertently dislodged -Must be transported with their caps in place and supported on trolleys -Should be stored in bulk in an appropriate facility at some distance from the laboratory. This area should be locked and appropriately identified -Should not be placed near radiators, open flames other heat sources, sparking electrical equipment or in direct sunlight |
| Small, single-use gas cylinders | Must not be incinerated |

- The main high-pressure valve should be turned off when the equipment is not in use and when the room is unoccupied
- Rooms where flammable gas cylinders are used and/or stored should be identified by warning notices on the doors



In order to be successful at controlling and extinguishing a fire, one must first know and understand the components – known as the “**fire tetrahedron**

Types and uses of fire extinguishers

| Type | Use for | Do not use for |
|--|--|--|
| Water | Paper, wood, fabric | Electrical fires, flammable liquids, burning metals |
| Carbon dioxide (CO ₂) extinguisher gases | Flammable liquids and gases electrical fires | Alkali metals, paper |
| Dry powder | Flammable liquids and gases, alkali metals, electrical fires | Reusable equipment and instruments, as residues are very difficult to remove |
| Foam | Flammable liquids | Electrical fires |

Principles of safe storage

Do not store chemicals alphabetically as a general group. This may result in incompatibles appearing together on a shelf. Separate chemicals into their organic and inorganic families and then into related and compatible groups.

Three principles can be applied to help provide safe storage of laboratory chemicals : Segregation , separation and ventilation The aims should be:

1. To **segregate incompatible chemicals from each other**

2. To **separate** hazardous chemicals from unsuitable conditions for reasons of their toxicity, flammability or reactivity (eg preventing exposure to: unsuitable temperatures; air; moisture; sources of ignition; sunlight; unauthorised access)

3. To provide adequate **ventilation** which will remove or dilute malodorous, noxious, toxic or flammable vapours and prevent their build-up

-All chemicals should be labeled and dated upon receipt in the lab and on opening. This is especially important for peroxide-forming chemicals.

-Solutions should be labeled and dated when prepared.

Some Basic Principles of Chemical Storage

-- Store like materials with like. It is essential to segregate incompatible substances to prevent dangerous interactions.

-- All newly purchased chemicals should have a label on them identifying their hazard category (e.g. flammable, corrosive, oxidising, toxic etc.). A list of commonly used chemicals that should be segregated should be available to assist storage.

- Store the minimum stock levels of hazardous chemicals in the laboratory

- Dispose of hazardous chemicals that are no longer required

- Store large breakable containers, particularly of liquids, below shoulder height .

- Ensure containers and bottle tops are sealed properly to avoid unnecessary leakage of fumes / vapors

- Never carry a bottle containing chemicals by its top, for example always carry Winchester bottles (2.5 liters) in carriers or baskets that are capable of providing proper support, and support the base of the bottle in use.

Chemicals should be separately stored by chemical class as follows:

Solids

- oxidizing solids
- flammable solids
- water reactive solids
- all other solids

Liquids

- acid liquids
- caustic liquids
- oxidizing liquids
- perchloric acid solutions
- flammable or combustible liquids
- water reactives
- all other liquids

Gases

- toxic gases
- flammable gases
- oxidizing and inert gas

Storage of specific chemicals

Flammable Solvents - e.g. alcohols, toluene, hexane The vapor above the liquid of these solvents represents the main source of danger from flammable liquids. This vapor is very susceptible to ignition by naked flames, sparks from electric switches (e.g. thermostats) electric motors or from sparks produced electrostatically by friction. Precautions must therefore be taken to prevent contact between any of these and concentrated vapours of flammable liquids.

Flammable solvents should be stored in specialised metal flammable solvent containers (cabinets) which should be:

- clearly labelled
- positioned away from doors or other means of escape from the laboratory.
- No more than 50 litres of flammable material may be kept in any one laboratory room to reduce the risk of a serious laboratory fire.
- iodinebleach, – hypochlorite Flammable solvents must never be stored with oxidising agents (e.g. sodium -and other halogens, hydrogen peroxide, nitric acid, potassium permanganate etc.) reducing agents (e.g. ...etc) or concentrated acids (e.g. concentrated sulphuric or lithium aluminum hydride, borohydridesodium hydrochloric acids).
- Working volumes of flammable solvents (i.e. those kept on the bench) should not exceed 500 ml, and the solvent must be kept in a suitable closed vessel. - Flammable solvents should not be stored in fume hoods or vented cabinets, since the airflow will fan any fire and may also spread the fire to other parts of the building via the ventilation ducting.
- Flammable solvents must never be stored in a refrigerator unless they are known to be spark proof.
- All laboratory fridges are spark proofed to avoid the possibility of an internal light or thermostat control unit providing a source of ignition for vapours produced from flammable substances.

Chlorinated solvents (e.g. chloroform, dichloromethane (DCM) trichloroethylene)

Chlorinated solvents are best stored in ventilated cabinets separately from flammable (non-chlorinated) solvents because violent reactions can result from the mixing of certain flammable and chlorinated solvents and toxic gases such as phosgene (as well has hydrogen chloride and chlorine) can be produced.

- They should not be stored with alkali metals such as lithium, potassium or sodium, since any mixing can cause an explosion.
- They can be stored in metal containers if ventilated storage is not available-

Acids and Alkalies

Acids and alkalies are both corrosive substances. They must be stored separately since any accidental mixing of concentrated materials will generate large quantities of heat and fumes.

- They can be sorted in a vented or metal cabinet so long as they are in a containment tray to prevent any spillages.
- Consideration must be given to the effects of corrosive fumes on any metal in the fittings and construction of the container.
- The use of ventilated cabinets are recommended where possible, allowing the removal of fumes at source.

-- All containers / bottle tops must be suitably sealed to avoid unnecessary leakage of fumes (NB parafilm can be used to seal container lids but should be checked/replaced at regular intervals).

Oxidizers (e.g. peroxides, perchlorates and nitrates)

-Oxidizing substances should be stored in a metal cabinet and away from organic matter such as wood and paper (NB oxidizing agents should never be sorted in a wooden cabinet!).

-- Oxidizing agents must never be stored with flammable solvents or reducing agents since fires and explosions can result

-- After any spillage, even without a naked flame or heat.

Perchloric acid is an extremely strong oxidizing agent (especially in the concentrated form), which can react explosively with organic materials. It should ideally be stored separately on a metal tray of sand within a cabinet, away from organic materials or dehydrating agents such as sulfuric acid.

Typical classes requiring segregated storage in a laboratory are:

Acids

Bases

(Highly flammable liquids (ie those with a flash point of 32°C or lower

Chlorinated solvents

Malodorous or noxious chemicals

Toxic chemicals and poisons

Oxidising reagents

Highly reactive compounds eg pyrophoric or air / moisture sensitive controlled drugs

Regulated chemicals (eg subject to chemical or biological weapons legislation)

Temperature sensitive compounds

Radioactive materials

Incompatibility of Common Laboratory Chemicals

The improper storage or mixing of chemicals can result in serious accidents and even disasters. Violent reactions could occur due to the storing or mixing incompatible chemicals. The following is a list of some incompatible common laboratory chemicals. Before storing or mixing any chemicals, consult this list or the chemicals' MSDS. This is only a partial list that includes some of the more common academic laboratory chemicals. Please note that the

absence of a chemical from the list does not mean that it is necessarily safe to mix it with any other chemical! You should always check with the MSDS if in doubt.

| Chemical | Incompatible with |
|------------------------------------|--|
| Acetic acid | Chromic acid, nitric acid, hydroxyl compounds, ethylene glycol, perchloric acid, peroxides, permanganates |
| Acetylene | Chlorine, bromine, copper, fluorine, silver, mercury |
| Acetone | Concentrated nitric acid and sulphuric acid mixtures |
| Alkali and alkaline earth metals | Water, carbon tetrachloride or other chlorinated hydrocarbons, carbon dioxide, halogens |
| Ammonia (anhydrous) | Mercury(e.g., in manometers), chlorine, calcium hypochlorite, iodine, bromine, hydrofluoric acid (anhydrous) |
| Ammonium nitrate | Acids, powdered metals, flammable liquids, chlorates, nitrates, sulphur, finely divided organic combustible materials |
| Aniline | Nitric acid, hydrogen peroxide |
| Arsenical materials | Any reducing agent |
| Azides | Acids |
| Calcium oxide | water |
| Carbon (activated) | Calcium hypochlorite, all oxidizing agents |
| Chlorates | Ammonium salts, acids, powdered metals, sulphur, finely divided organic or combustible materials |
| Chromic acid and chromium trioxide | Acetic acid, naphthalene, camphor, glycerol. Alcohol, flammable liquids in general |
| Chlorine | Ammonia, acetylene, butadiene, butane, methane, propane (or other petroleum gases), hydrogen, sodium carbide, benzene, finely divided metals, turpentine |
| Copper | Acetylene, hydrogen peroxide |
| Chlorine dioxide | Ammonia, methane, phosphine, hydrogen sulphide |
| Flammable liquids | Ammonium nitrate, chromic acid, hydrogen peroxide, nitric acid, sodium peroxide, halogens |
| Cyanides | acids |
| Hydrocyanic acid | Nitric acid, alkali |

General rules regarding chemical incompatibilities

To avoid fire and/or explosions, substances in the left-hand column of the table should be stored and handled so that they cannot come into contact with the corresponding substances in the right-hand column

Separation

Physical separation by means of **storage cupboards** which physically divide incompatible classes of hazardous chemicals

The cupboards may need specific properties or provide separation by means of distance. They will also need to provide secondary containment (eg spill trays or bunded shelves) and security (eg locks / bolted to wall).

Special means of separation

under nitrogen to exclude air or moisture, under controlled temperature, or other specialist storage arrangements (eg gas cylinders)

Determine the proper storage facility (the place to store the chemicals including cupboards)

Cupboard function

1. Strong enough to carry the weight of the stored material
2. compatible with the material stored
3. easily cleanable
4. Supported with shelves sufficiently strong to bear the load
5. Secure against unauthorised use / access / theft

Control of access will be required for certain classes of chemicals, which will include:

- Extremely toxic
- Poisons
- Controlled drugs
- Regulated chemicals eg certain chemical weapon precursors, biological toxins and explosives / de-sensitised explosives
- Certain 'high risk' other materials depending on local procedures eg carcinogens, teratogens, mutagens and highly reactive
- Radioactive

A number of facilities are used for the storage of these chemical substances, some of which are specially designed for the purpose.

These include:

Acid Cabinets These are made of acid resistant materials and should contain a tray, to contain any leakage or spillage.

Flammable Solvent Cabinets These are made of fire resistant material with a minimum fire resistance of 30 minutes as required by British Standard 476. A metal spill tray is used to contain spillages.

Ventilated Cabinets These are cabinets fitted with forced ventilation and may be free-standing with their own extract system or positioned beneath a fume cupboard and attached to its duct. Ventilated cabinets are designed to safely store chemicals that give off noxious fumes and smells. These fumes are sucked away by forced ventilation. They should be used to store materials such as mercaptans and amines that have a strong smell; or lachrymators. If you do not have a ventilated cabinet, these noxious chemicals can be stored in sealed secondary containers that should only be opened in a fume cupboard.

It should be noted that fume cupboards are not designed or intended for the storage of chemicals. The working surfaces of fume cupboards should therefore be kept clear of materials and containers when these are not needed for the ongoing work activities. Excess storage of chemicals in fume cupboards disrupts the airflow resulting in a lower level of protection to users.



Aspects of safe storage of laboratory chemicals

- Minimise or restrict the quantities stored and avoiding over-ordering

2. Authorize purchases and maintain records of location, keeper and quantities
3. Obtain and keep available hazard information on the materials purchased and check existing information is up to date.
4. Labels and signs eg on bottles: date of purchase, name of the chemical, name of purchaser or "keeper"
5. Utilize containers that are appropriate and well sealed
6. Use secondary containment (eg spill trays, outer containers or overpacks such as „safepacks") to minimize the consequences of spillage leakage or breakage.
7. Exercise care in handling
8. Tidiness of storage -, overcrowded or limited visibility has to be avoided.
9. Stock control with rotation of material
10. Share stocks
11. Restriction of the quantities of hazardous chemicals.
12. Regular disposal of waste or unwanted / unused chemicals

| Hazard Class of Chemical | Recommended Storage Method | Examples | Incompatibilities |
|----------------------------------|---|--|---|
| Compressed gases - Flammable | Store in a cool, dry area, away from oxidizing gases. Securely strap or chain cylinders to a wall or bench. | Methane, Hydrogen Acetylene, Propane | Oxidizing and toxic compressed gases, oxidizing solids. |
| Compressed gases - Oxidizing | Store in a cool, dry area, away from flammable gases and liquids. Securely strap or chain cylinders to a wall or bench. | Oxygen, Chlorine, Bromine | Flammable gases |
| Compressed gases - Poisonous | Store in a cool, dry area, away from flammable gases and liquids. Securely strap or chain cylinders to a wall or bench. | Carbon monoxide Hydrogen sulfide Nitrogen dioxide | Flammable and/or oxidizing gases. |
| Corrosives - Acids | Store separately in acid storage cabinet. Segregate oxidizing acids (i.e., Chromic, nitric, sulfuric, and perchloric acids) from organic acids | Acetic acid Phenol Sulfuric acid Chromerge Nitric acid Perchloric acid Chromic acid Hydrochloric acid | Flammable liquids, flammable solids, bases, oxidizers |
| Corrosives - Bases | Store in separate corrosive storage cabinet. Store solutions of Inorganic hydroxides in labeled polyethylene containers. | Ammonium hydroxide Sodium hydroxide Calcium hydroxide | Flammable liquids, oxidizers, poisons, and acids |
| Flammable Liquids | Store in flammable storage cabinet and away from sources of ignition. Store highly volatile flammable liquids in an explosion-proof refrigerator. | Acetone, Benzene Diethyl ether, Methanol, Ethanol, Toluene | Glacial acetic acid, Acids, bases, oxidizers, and poisons |
| Flammable Solids | Store in a separate dry, cool area away from oxidizers, corrosives, flammable liquids | Phosphorus, yellow Calcium carbide Picric acid Benzoyl peroxide | Acids, bases, oxidizers, and poisons |
| General Chemicals - Non-reactive | Store on general laboratory benches or shelving preferably behind glass doors and below eye level. | Agar Sodium chloride Sodium bicarbonate Most non-reactive salts | |
| Oxidizers | Store in a spill tray inside a chemical storage cabinet. Separate from flammable and combustible materials. | Ammonium persulfate Ferric chloride Iodine Sodium hypochlorite Benzoyl peroxide Potassium permanganate Potassium dichromate The following are generally considered oxidizing substances: Peroxides, perchlorates, chlorates, nitrates, bromates, superoxides, | Separate from reducing agents, flammables, and combustibles |

| Hazard Class of Chemical | Recommended Storage Method | Examples | Incompatibilities |
|----------------------------|---|---|--|
| Poisons/Toxic Compounds | Store separately in vented, cool, dry area, in unbreakable chemically-resistant secondary containers and in accordance with the hazardous nature of the chemical. | Aniline Carbon tetrachloride Chloroform Cyanides Heavy metals compounds, i.e., cadmium, mercury, osmium Oxalic acid Phenol Formic acid | Flammable liquids, acids, bases, and oxidizers. |
| Water-Reactive Chemicals | Store in dry, cool location, protect from water fire sprinkler. | Sodium metal Potassium metal Lithium metal Lithium aluminum hydride | Separate from all aqueous solutions and oxidizers. |
| Carcinogens | Label all containers as "Cancer Suspect Agents". Store according to the hazardous nature of the chemical, using appropriate security when necessary. | Benzidine Beta-naphthylamine Benzene Methylene chloride Beta-propiolactone | |
| Teratogens | Label all containers as "Suspect Reproductive Hazard". Store according to the hazardous nature of the chemical, using appropriate security when necessary. | Lead and mercury compounds Benzene Aniline | |
| Peroxide-Forming Chemicals | Store in air-tight containers in a dark, cool, dry area. Take care for recommended storage time limits. | Diethyl ether Acetaldehyde Acrylonitrile | |
| Strong Reducing Agents | Store in cool, dry, well-ventilated location. Water reactive. Segregate from all other chemicals. | Acetyl chloride Thionyl chloride Maleic anhydride Ferrous sulfide | |

Look for unusual conditions in chemical storage areas, such as:

- Improper storage of chemicals Leaking or deteriorating containers
- Spilled chemicals Lack of or low lighting levels
- Blocked exits or aisles
- Doors blocked open, lack of security
- Trash accumulation
- Open lights or matches
- Fire equipment blocked, broken or missing
- Lack of information or warning signs ("Flammable liquids", "Acids", "Corrosives", "Poisons", etc.)
- Temperature extremes (too hot or cold in storage area)

Suggested Storage Time Limits for Common Peroxidizable Compounds

Under proper conditions, these chemicals will form explosive peroxides which can be detonated by shock or heat.

| | | |
|--|--------------------------------|------------------------|
| <i>MOST DANGEROUS:</i> Discard after <u>3 months</u> . | | |
| Peroxide formation hazard during storage. | | |
| Diisopropyl ether | | Potassium metal |
| Divinyl acetylene | | Sodium amide |
| Isopropyl ether | | Vinylidene chloride |
| <i>DANGEROUS:</i> Discard after <u>one year</u> . | | |
| Peroxide formation hazard during storage and on concentration (i.e., distillation) of compound. | | |
| Acetal | Dicyclopentadiene | Methyl cyclopentane |
| Acetaldehyde | Diethyl ether | Methyl isobutyl ketone |
| Cumene | 1,4-Dioxane | Tetrahydrofuran |
| Cyclohexene | Ethylene glycol dimethyl ether | Tetrahydronaphthalene |
| Diacetylene | Methyl acetylene | Vinyl ethers |
| <i>DANGEROUS:</i> Discard after <u>one year</u> . | | |
| Peroxide formation causes initiation of hazardous polymerization. | | |
| Acrylic acid | Chloroprene | Tetrafluoroethylene |
| Acrylonitrile | Chlorotrifluoroethylene | Vinyl acetate |
| 1,3-Butadiene | Methyl methacrylate | Vinyl acetylene |
| 2-Butanol | 2-Propanol | Vinyl chloride |
| | Styrene | Vinyl pyridine |

Other safety Tips

1. Do not purchase these compounds in quantities greater than can be used in the specified storage time period.
2. Label containers with receiving, opening and disposal dates. Ethers should be stored in the dark and under nitrogen if possible.
3. Always check for the presence of peroxides before distilling any peroxide-former.
4. Consult safety references (i.e., MSDSs) before working with peroxidizable compounds.
5. If old containers of peroxide-forming chemicals are found, do not move them. Contact the Office of Health and Safety for assistance in disposing of the container.

Laboratory chemical waste

Chemical waste are chemical byproducts, as well as the smaller-scale solvents and other chemicals disposed of.

If chemical waste is not handled or disposed of properly, both the environment and nearby individuals are put at risk by its potentially corrosive, toxic, flammable or explosive nature.

Health and safety legislation varies internationally and dictates the manner in which this waste must be handled and disposed of.

Proper handling of this waste requires:

1. The separation of chemicals that may react with one another, such as salts from acids, hypochlorites and hydroxides from ammonia, and oxidizing substances from combustible substances.
2. After it is properly separated, it should be safely stored in tightly-sealed drums, bottles, tins or jars that will not be corroded or otherwise affected by the contents.
3. It is then transported to a special disposal facility, where it is eliminated according to its compound substance or substances. Most chemical waste, including **chlorinated solvents, are incinerated at a high temperature**, while others **are treated by wet chemical methods**. After it has been incinerated or treated by wet chemistry.
4. The residues are then safe to dispose of in a landfill.

Storage of chemicals and biomaterials in biology laboratories



Infectious or etiologic (disease causing) agents, potentially infectious materials, certain toxins and other hazardous biological materials

BIOHAZARDS

Workers in biological laboratories including microbiology labs; may expose to pathogenic microorganisms, and also to chemical hazards. It is important that they have proper knowledge of the toxic effects of these chemicals, the routes of exposure and the hazards that may be associated with handling and storage.

Material safety data sheets or other chemical hazard information are available from chemical manufacturers and/or suppliers. These should be accessible in laboratories where these chemicals are used, e.g. as part of a safety or operations manual

Routes of exposure

Exposure to hazardous chemicals may occur by:

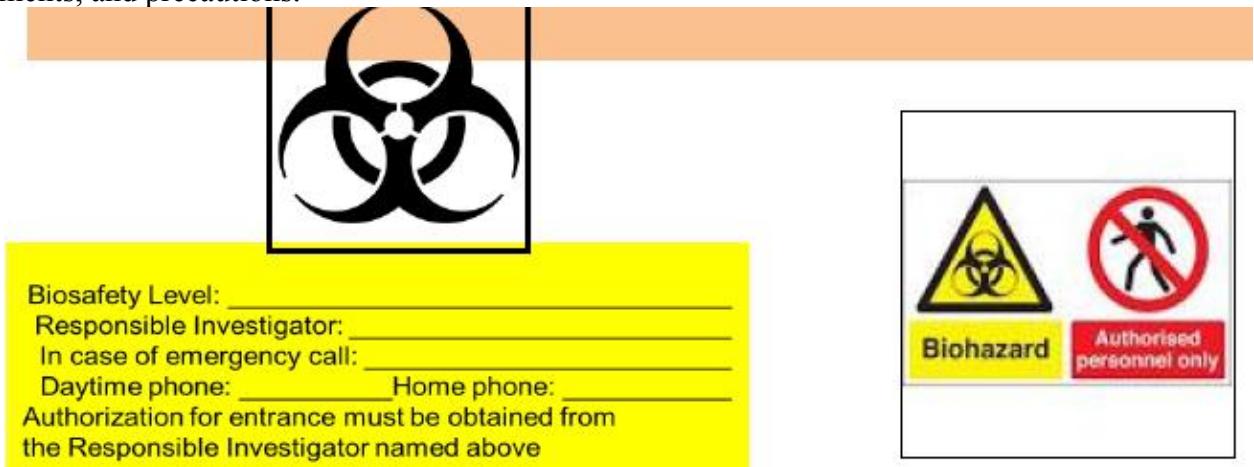
1. Inhalation
2. Contact
3. Ingestion
4. Needle-sticks
5. Through broken skin

Biosafety Basics

Biohazardous materials are infectious agents or other biological materials that present a risk or potential risk to the health of humans, animals or the environment. Biohazardous materials include:

1. Organisms and viruses infectious to humans, animals or plants (e.g. parasites, viruses, bacteria, fungi, prions, rickettsia) cultured human and animal cells
2. Certain types of recombinant DNA
3. Biologically active agents that may cause disease in other living organisms or cause significant impact to the environment or community. (i.e. toxins, allergens, venoms)

Laboratories that contain biohazardous materials should post a biohazard sign at the entry doorway. The sign should include the Biosafety Level, biohazards present, entry requirements, and precautions.



Biosafety Levels (BSL) are levels of containment (1 lowest, 3 highest containment.)

| | |
|--|---|
| | Green - Biosafety Level 1 Represents a basic level of containment that relies on standard microbiological practices with no special primary or secondary barriers recommended, other than a sink for hand washing. |
| | Blue - Biosafety Level 2 is suitable for work involving agents of moderate potential hazard to personnel and the environment. |
| | Red - Biosafety Level 3 Required for work involving indigenous or exotic agents which may cause serious or potentially lethal disease as a result of exposure by inhalation, and with dangerous and exotic agents that pose a high risk of aerosol-transmitted laboratory infections and life-threatening disease |

Biohazard Level 1: Bacteria and viruses including *Bacillus subtilis*, canine hepatitis, *Escherichia coli*, varicella (chicken pox), as well as some cell cultures and non-infectious bacteria. Gloves and some sort of facial protection.

Biohazard Level 2: Bacteria and viruses that cause only mild disease to humans, or are difficult to contract via aerosol in a lab setting, such as hepatitis A, B, and C, influenza A, Lyme disease, salmonella, mumps, measles, scrapie, dengue fever, and HIV.

Biohazard Level 3: Bacteria and viruses that can cause severe to fatal disease in humans, but for which vaccines or other treatments exist, such as anthrax, West Nile virus, Venezuelan equine encephalitis, SARS virus, tuberculosis, typhus, Rift Valley fever, Rocky Mountain spotted fever, yellow fever, and malaria. Among parasites *Plasmodium falciparum*, which causes Malaria, and *Trypanosoma cruzi*, which causes trypanosomiasis, also come under this level.

Biohazard Level 4: Viruses and bacteria that cause severe to fatal disease in humans, and for which vaccines or other treatments are *not* available, Dengue hemorrhagic ,Argentine hemorrhagic fevers and Bolivian as-Crimean, Lassa fever virus, hantaviruses, Ebola virus, Marburg virus, feverVariola diseases and nCOVID-19. hemorrhagic , and other Congo hemorrhagic fever, with a positive pressure personnel suit Use of a) . smallpox(virussegregated air supply, is mandatory. biolab will contain multiple showers, a and other safety precautions light room, ultraviolet vacuum room, designed to destroy all traces of the biohazard.



The biohazard kit provides everything that is needed to safely absorb, disinfect and dispose of the spill,in one container that can simply be carried to the site where it is needed.

Contents:

- Shakers of Haz-Tab Granules,
- tub of 100 Haz-Tab tablets,
- Haz-Tab Diluter,
- scoops and scrapers,
- paper towels,
- synthetic gloves,
- aprons,
- dispo-bags

Biological waste includes:

-liquids such as used cell culturing media, supernatant, blood or blood fractions (serum), etc., which contain viable biological agents.

-materials considered pathological, including any part of the human body, tissues and bodily fluids, but excluding fluids, extracted teeth, hair, nail clippings and the like that are not infectious

-any part of an animal infected [or suspected to be infected] with a communicable disease.

-non-sharp, solid laboratory waste (empty plastic cell culture flasks and petri dishes, empty plastic tubes, gloves, wrappers, absorbent tissues, etc.) which may be, or is known to be, contaminated with viable biological agents.

-all sharp and pointed items used in medical care, diagnosis, and research, including the manipulation and care of laboratory animals, which should be considered potentially infectious.

- laboratory glassware which is known or suspected to be contaminated with hazardous biological agents.

Materials contaminated with hazardous biological agents must be collected in the appropriate containers and sterilized or disinfected before disposal.

A- Packaging and Treatment

1. **Liquids containing Biohazardous Agents** collected in flasks or bottles designed to withstand autoclaving temperatures.

2. **Solids Containing Biohazardous Agents** should be collected in a yellow Bio Waste plastic 20 litre pail

B. Sterilization and Disinfection

- **Chemical disinfectants** play a useful role in many situations where decontamination is required

- **Autoclaving** (steam sterilization) is the preferred (and generally regarded as the most reliable) method of sterilizing biological waste. Depending on the volume of waste to be sterilized, it may be necessary to extend the duration of exposure to high temperature steam under pressure



Bio-waste containers

PROGRESS CHECK:**A. Multiple Choice Questions:**

1. I have a right to know about chemicals I work with or around
 - A. True
 - B. False
2. I can learn about the hazards of specific chemicals by
 - A. Asking a co-worker
 - B. Reading the Material Safety Data Sheet
 - C. Reading science magazines
 - D. Talking to friends about it
3. Labels on chemical containers
 - A. Tell me basic safety and use information
 - B. Are not required
 - C. Provide all the information I need
 - D. Come in many colors
4. If I use chemicals at work I must
 - A. Be very careful
 - B. Never work alone
 - C. Wear a respirator
 - D. Be specifically trained and authorized
5. Safety Data Sheets provide information about
 - A. Hazards about a specific chemical
 - B. Emergency information
 - C. Information on chemical reactions
 - D. All of the above
6. The correct Personal Protective Equipment can
 - A. Be used when I want to
 - B. Protect me from Chemical hazards
 - C. Cause skin irritation
 - D. Make me work slower
7. On the multi-colored chemical label, Blue represents
 - A. Fire Hazard
 - B. Health Hazard
 - C. Reactivity Hazard
 - D. Personal Protective Equipment
8. On the multi-colored chemical label, Red represents
 - A. Fire Hazard
 - B. Health Hazard
 - C. Reactivity Hazard
 - D. Personal Protective Equipment
9. On the multi-colored chemical label, White represents
 - A. Fire Hazard
 - B. Health Hazard
 - C. Reactivity Hazard
 - D. Special Hazards
10. On the multi-colored chemical label, Yellow represents
 - A. Fire Hazard
 - B. Health Hazard
 - C. Reactivity Hazard
 - D. Personal Protective Equipment

11. Flammable chemicals are stored
- Where ever it is easy to get to
 - In special flammable storage lockers
 - Near water sources
 - In glass containers
12. Spills of Chemicals should be
- Cleaned up by trained employees
 - Reported immediately
 - Prevented by using seal containers
 - All of the above
13. After a biohazard spill is covered with paper towels and disinfectant solution, it must sit for _____ minutes?
- 5
 - 60
 - 30
 - 20
14. The desire to maintain a safe laboratory environment for all begins with _____?
- prevention
 - microbiology
 - ubiquity
 - accidents
15. When a chemical splashes in the eye rinse for _____?
- 10 seconds
 - 5 minutes
 - 30 seconds
 - 15 minutes
- B. Application

1. The sign below indicates what type of safety hazard?



2. The sign below indicates what type of safety hazard?



3. Identify one safety violation in the picture.



TOPICS: ATOMS, IONS and MOLECULES

- 2.1. Atomic Theory
 - 2.1.1. Law of Conservation of Mass
 - 2.1.2. Law of Constant Composition
 - 2.1.3. Law of Multiple Proportions
- 2.2. Dalton's Atomic Theory
- 2.3. Discovering Electrons
 - 2.3.1. The Plum Pudding Model
- 2.4. Discovery of the Proton
- 2.5. The Discovery of the Neutron
- 2.6. Atom
 - 2.6.1 Bohr's Model of the Atom
- 2.7. Energy Levels
- 2.8. Electron Cloud Model and the Orbitals
 - 2.8.1 Electron Cloud
 - 2.8.2 Orbitals
- 2.9. The Structure of Atoms
- 2.10. Mass Number and Atomic Number
- 2.11. Isotopes
 - 2.11.1 Natural and Artificial Isotopes
 - 2.11.2. Use of Isotopes
 - 2.11.2.1. Structural Determination
 - 2.11.2.1.1. Nuclear Magnetic Resonance Spectroscopy
 - 2.11.2.1.2 Mass Spectrometry
 - 2.11.2.1.3 Isotopic Labeling
 - 2.11.2.1.4. Study of Photosynthesis
- 2.12. Ion
- 2.13. Symbols
- 2.14. Oxidation Number
 - 2.14.1. Determination of the Oxidation Numbers of an Atom in a Polyatomic Ion
- 2.15. Chemical Formula
- 2.16. Naming of Inorganic Compounds
 - 2.16.1. Binary Compounds
 - 2.16.1.1. Type I Binary Compounds
 - 2.16.1.2 Type II Binary Compounds
 - 2.16.1.3. Type III Binary Compounds – The Binary Covalent Compounds
 - 2.16.1.4. Hydrates
 - 2.16.2 Naming Compounds of Polyatomic Ions
- 2.17. Naming of Inorganic Acids
 - 2.17.1. Naming Binary Acids
 - 2.17.2. Naming of Oxyacids

EXPECTED COMPETENCIES

At the end of the lesson, you must have:

- a. stated the postulates of Dalton's atomic theory;
- b. described the electron cloud and orbitals;
- c. identified the uses of isotopic labeling in structural determination and the primary techniques used to study isotopically-labeled molecules;
- d. described the use of radioactive isotopes in the study of photosynthesis;
- e. described the use of radioactive isotopes in medicine;
- f. described the composition of a chemical compound;
- g. defined ion, cation and anion;
- h. written the symbol of chemical element;
- i. written the chemical formulas of compounds; and
- j. named the compounds given the chemical formulas.

CONTENTS:

2.1. Atomic Theory

John Dalton (1766-1844) is the scientist credited for proposing the atomic theory. This theory explains several concepts that are relevant in the observable world: the composition of a pure gold necklace, what makes the pure gold necklace different than a pure silver necklace, and what occurs when pure gold is mixed with pure copper. Before discussing the atomic theory, this article explains the theories that Dalton used as a basis for his theory: the law of conservation of mass and the law of constant composition.

2.1.1. Law of Conservation of Mass

The law of conservation of mass states that the total mass present in the reactants in a chemical reaction is the same as the total mass present of the products in the chemical reaction, thus conserving the mass. The law of conservation of mass was formulated by Antoine Lavoisier (1743-1794) as a result of his combustion experiment, in which he observed that the mass of his original substance—a glass vessel, tin, and air—was equal to the mass of the produced substance—the glass vessel, “tin calx”, and the remaining air.

In the case of wood turned into ashes. The wood clearly has a greater mass than the ashes. From this observation scientists concluded that mass had been lost without taking into consideration the mass of gases produced during combustion. Figure 2.1 illustrates the law of conservation of mass in the burning of wood.

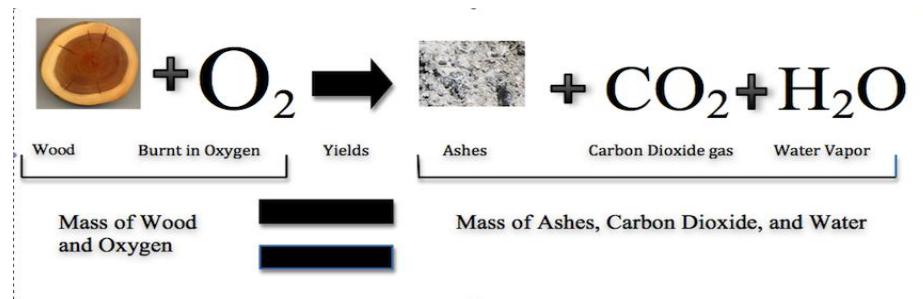


Figure 2.1. Illustration of the Law of Conservation of Mass (constructed by Jessica Thornton using Microsoft Word and Preview -UCD).

2.1.2. Law of Constant Composition

Joseph Proust (1754-1826) formulated the law of constant composition (also called the **law of definite proportions**). This law states that when a compound is broken down into its constituent elements, the masses of the constituents will always have the same proportions. Joseph Proust based this law primarily on his experiments with basic copper carbonate. The illustration below depicts this law; 31 grams of H₂O and 8 grams of H₂O are made up of the same percent of hydrogen and oxygen.

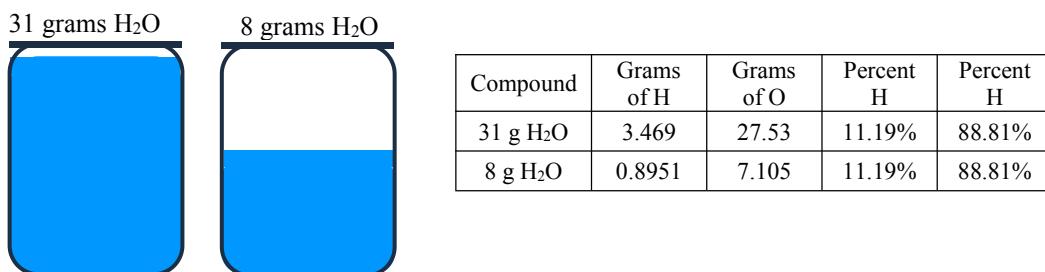


Figure 2.2: Illustration of the Law of Definite Composition (Constructed by Jessica Thornton -UCD)

2.1.3. Law of Multiple Proportions

Another law of combination, the law of multiple proportions which states that if two elements form more than one compound between them, the amounts of one element that combined with a fixed amounts of the second element form in ratios of small whole-numbers.

2.2. Dalton's Atomic Theory

- Each chemical element is composed of tiny indivisible particles that cannot be seen by the unaided eye, called **atoms**. Atoms can neither be created nor destroyed. Pictured below is a helium atom. The purple and red dots represent the neutrons and protons in the nucleus. The black area around the nucleus represent the electron cloud.

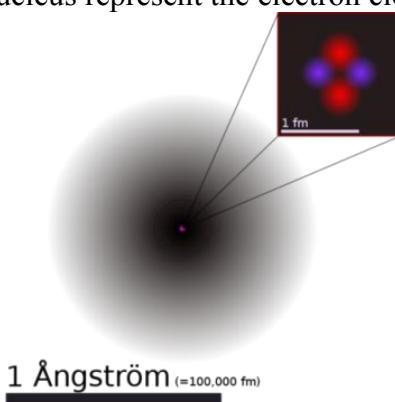


Figure 2.3: Illustration of an Atom (Courtesy of Yzmo on Wikimedia commons, available under Creative Commons-Share Alike 3.0)

- All atoms of an element have the same mass other properties, but the atoms of another element differ from all other elements. For example, gold and silver have different atomic masses and different properties.



Gold

Atomic Mass: 196.97

Silver

Atomic Mass: 107.87

Figure 2.4. (Gold): Courtesy of Chris Ralph that released this image into the public domain.(silver):
Courtesy of <http://resourcescommittee.house.gov/.../photogallery/>

3. In a compound, different elements combine in a simple numerical ratio. The illustration below describes this rule. The second equation for the reaction is incorrect because half of an atom does not exist.



Created by Jessica Thornton

Atomic theory can be used to answer the questions presented above. A pure gold necklace is made up of atoms. A pure gold necklace and a pure silver necklace are different because they have different atoms. Pure gold mixed with pure copper forms rose gold. The gold and copper atoms combine in a simple numerical ratio.

4. Atoms can neither be created nor destroyed. They just rearranged and/or combined forming a different compound or substance(s).

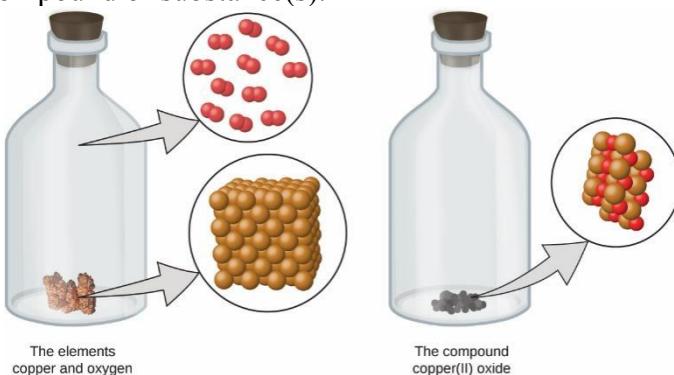


Figure 2.5: When the elements copper (a shiny, red-brown solid, shown here as brown spheres) and oxygen (a clear and colorless gas, shown here as red spheres) react, their atoms rearrange to form a compound containing copper and oxygen (a powdery, black solid). (credit copper: modification of work by <http://images-of-elements.com/copper.php>).

2.3. Discovering Electrons

Michael Faraday's (1791-1867) invention of the first cathode-ray tube (CRT) led to the discovery of the type of radiation emitted by the negative terminal, which is the cathode, upon the passage of electricity. The observed radiation crosses the vacuum glass tube to the positive terminal which is the anode. The cathode ray tube produced invisible rays that can only be detected by the light emitted by the materials they struck called phosphors. The dotted line in figure 2.6 shows the path of the cathode ray. These cathode rays are influenced by magnetic and electric fields that are deflected similar to the negatively charged materials which prompted J. J. Thompson (1856 – 1940) to conclude cathodes are found in all atoms as the negatively charged particles. George Stoney first to give the name electrons referring to the cathode rays.

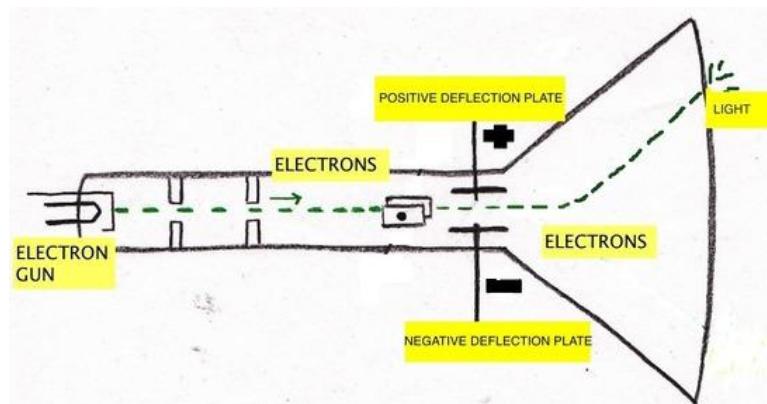


Figure 2.6: The Cathode Ray Tube
(Courtesy: Chem.libretext.com)

2.3.1. The Plum Pudding Model

After the discovery of electrons, Thompson, proposed the plum pudding model of an atom, which states showing the electrons floating in a positively-charged material. This model was named after the plum-pudding dessert.

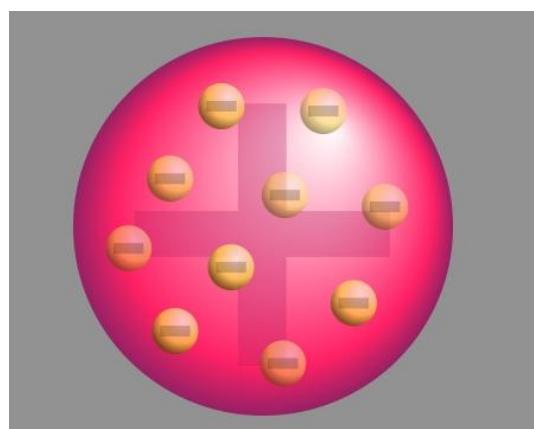


Figure 2.7: The Plum-Pudding Model
Provided courtesy of the Wikipedia Commons

2.4. Discovery of the Proton

In 1909, Ernest Rutherford (1871-1937) studying the inner structure of the atoms, performed series of experiments using alpha particles. Alpha particles being so massive than electrons and carry a positive charge and using the plum-pudding model as . The particles would only be deflected if they happened to come into contact with electrons. According to the plum pudding model, this occurrence would be very unlikely. In order to test his hypothesis, Rutherford shot a beam of alpha particles at a thin piece of gold foil. Around the gold foil Rutherford placed sheets of zinc sulfide. These sheets produced a flash of light when struck by an alpha particle. However, this experiment produced results that contradicted Rutherford's hypothesis. Rutherford observed that the majority of the alpha particles went through the foil; however, some particles were slightly deflected, a small number were greatly deflected, and another small number were thrown back in nearly the direction from which they had come. The figure below shows Rutherford's prediction based off of the plum-pudding model (pink) and the observed large deflections of the alpha particles (gold).

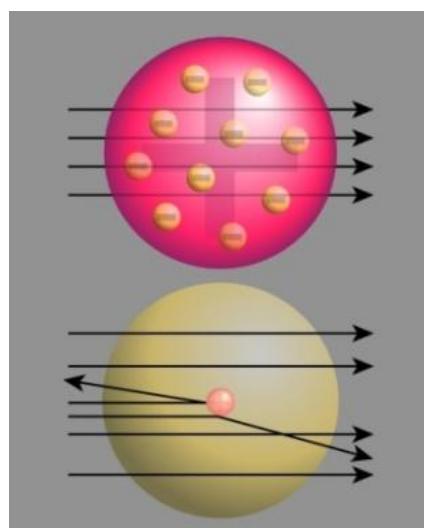


Figure 2.8: Rutherford's Prediction
Provided courtesy of the Wikipedia Commons

To account for these observations, Rutherford devised a model called the nuclear atom. In this model, the positive charge is held in an extremely small area called the nucleus, located in the middle of the atom. Outside of the nucleus the atom is largely composed of empty space. This model states that there were positive particles within the nucleus, but failed to define what these particles are. Rutherford discovered these particles in 1919, when he conducted an experiment that scattered alpha particles against nitrogen atoms. When the alpha particles and nitrogen atoms collided protons were released.

2.5 The Discovery of the Neutron

In 1933, James Chadwick (1891-1974) discovered a new type of radiation that consisted of **neutral** particles. It was discovered that these neutral atoms come from the nucleus of the atom. This last discovery completed the atomic model.

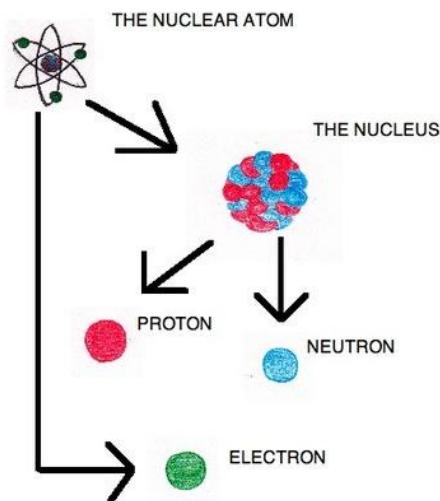


Figure 2.9: The Nuclear Atom
Provided courtesy of the Wikipedia Commons

Example:

When 32.0 g of methane are burned in 128.0 g of oxygen, 88.0 g of carbon dioxide and 72.0 g of water are produced. Which law is this an example of? (a) Law of Definite Proportions (b) Law of Conservation of Mass or (c) Law of Multiple Proportions.

Solution:

The answer is (b) Law of Conservation of Mass. The number of grams of reactants (32.0 g of methane and 128.0 g of oxygen = 160.0 g total) is equal to the number of grams of product (88.0 g of carbon dioxide and 72.0 g of water = 160.0 g total).

Table 1: Charge and mass of three sub atomic particles

| Particle | Charge | Mass (grams) |
|-----------------|---------------|--------------------------|
| Electrons | -1 | 9.1094×10^{-31} |
| Protons | +1 | 1.6726×10^{-24} |
| Neutrons | 0 | 1.6749×10^{-24} |

2.6 Atom

The atom being the smallest and tiniest particle of matter consisting of three subatomic particles: the proton, the neutron, and the electron. Protons together with neutron are found inside the nucleus which carries most of the mass and is positively charged. The electrons are found in an electron cloud surrounding the nucleus.

Rutherford's model of the atom was better than earlier models. But it wasn't the last word. Danish physicist Niels Bohr created a more accurate and useful model. Bohr's model was an important step in the development of modern atomic theory.

2.6.1 Bohr's Model of the Atom

Bohr's research focused on electrons. In 1913, he discovered evidence that the orbits of electrons are located at fixed distances from the nucleus. Remember, Rutherford thought that electrons orbit the nucleus at random. Figure 2.10 below shows Bohr's model of the atom.

In Bohr's atomic model, electrons orbit at fixed distances from the nucleus. These distances are called energy levels.

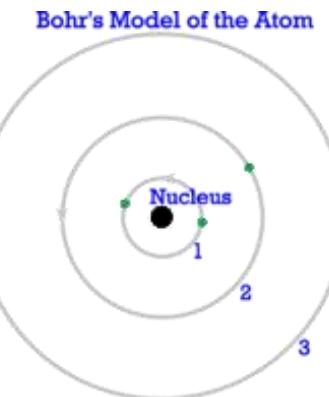


Figure 2.10: The Bohr's Model of the Atom (Provided courtesy of the Wikipedia Commons)

2.7 Energy Levels

Founded on the idea on Bohr's model, are the energy levels. **Energy levels** are regions around the nucleus at fixed distances where electrons are found. They are the only places where electrons can be found. Energy levels are a little like rungs on a ladder. You can stand on one rung or another but not between the rungs. The same goes for electrons. They can occupy one energy level or another but not the space between energy levels.

Figure 2.11 shows the different energy levels around the nucleus. Starting from the level with the least energy is the one closest to the nucleus. Going farther away from the nucleus, the energy in each level increases. Electrons can jump from a lower energy level to a higher energy level and become excited. As you go farther from the nucleus, the levels have more and more energy. Electrons in the lowest energy level are in their **ground state** but they can jump from one energy level to another. As electrons jump from a lower energy level, energy is absorbed and thus turned into their **excited state**. As the electrons jump back to the lower state, energy is emitted or given off.

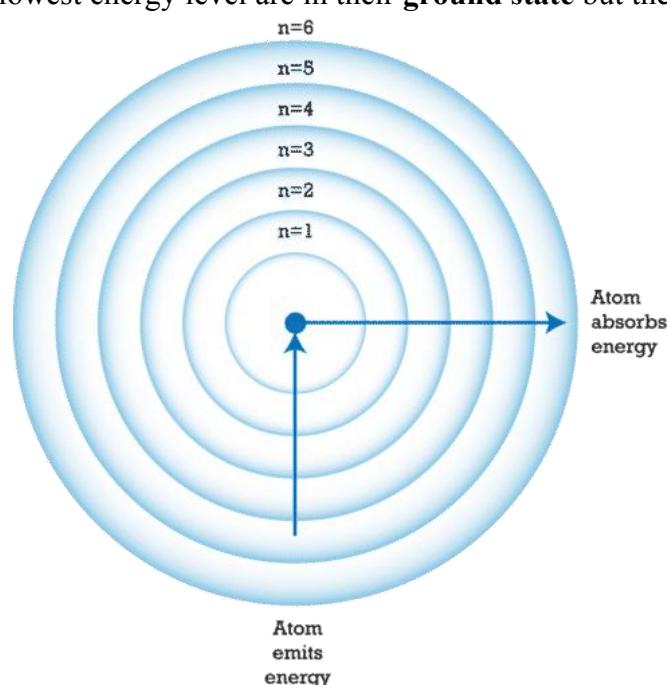


Figure 2.11: This model of an atom contains six energy levels ($n = 1$ to 6). Atoms absorb or emit energy when some of their electrons jump to a different energy level. (Provided courtesy of the Wikipedia Commons)

Seen a firework? When fireworks explode, the atoms in the chemicals composing the fireworks, absorbed energy and so their electrons. Some of the electrons jump to a higher

energy level as they absorbed energy. As they go back to their original energy levels, they give off energy in the form of light. Different atoms have different arrangements of electrons that accounts for the different colors of light given off as shown in figure 2.12.



Figure 2.12: Atoms in fireworks give off light when their electrons jump back to a lower energy level.(Provided courtesy of the Wikipedia Commons)

2.8 Electron Cloud Model and the Orbitals

Today, these ideas about electrons are represented by the electron cloud model. The electron cloud is an area around the nucleus where electrons are likely to be in an **orbital**. The figure below shows an electron cloud model for a helium atom.

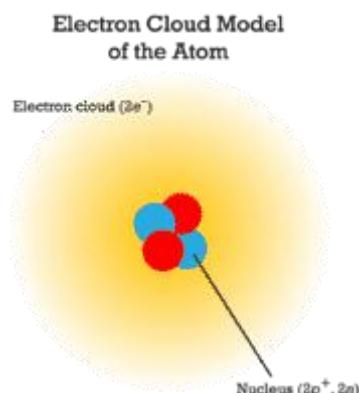


Figure 2.13 The Electron Cloud Model (Provided courtesy of the Wikipedia Commons)

This sketch represents the electron cloud model for helium. What does the electron cloud represent?

2.8.1 Electron Cloud

The electron cloud visualizes the location of electrons in the nucleus of an atom. These electrons and protons are held in place by the **electromagnetic force** in the nucleus. Electrons move around the nucleus very quickly, creating the image of a cloud; however, they actually form **electron shells**. Each electron shell can hold a certain amount of electrons. The first shell holds two electrons, and subsequent shells hold eight electrons (the movement of electrons is discussed in Unit IV). The number of electrons in a given atom is equal to the

number of protons in that atom. However, units of the same element can have different numbers of electrons.

2.8.2 Orbitals

Some regions of the electron cloud are denser than others. These are the regions where the probability of finding the electrons is high called **orbitals**. The first orbital has a maximum of two electrons. Different energy levels in the cloud have different numbers of orbitals. Therefore, different energy levels have different maximum numbers of electrons. Table 2.1 lists the number of orbitals with their corresponding number of electrons for the first four energy levels. The more distance away from the nucleus, the energy levels farther from the nucleus have more orbitals. Therefore, these levels can hold more electrons.

Table 2.2. First Four Energy Levels and Their Orbitals

| Energy Level | Number of Orbitals | Maximum No. of Electrons per orbital |
|--------------|--------------------|--------------------------------------|
| 1 | 1 | 2 |
| 2 | 4 | 8 |
| 3 | 9 | 18 |
| 4 | 16 | 32 |

Figure 2.14 below shows the arrangement of electrons in an atom of magnesium as an example. The most stable arrangement of electrons occurs when electrons fill the orbitals at the lowest energy levels first before more are added at higher levels.

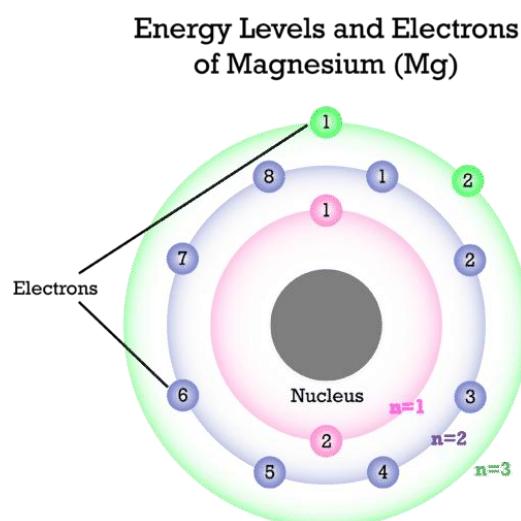


Figure 2.14. This model represents an atom of the element magnesium (Mg). How many electrons does the atom have at each energy level? What is the maximum number it could have at each level? (Provided courtesy of the Wikipedia Commons)

2.9. The Structure of Atoms

An atom is composed of a positively charged nucleus containing the protons and neutrons. The nucleus is then surrounded by negatively charged particles - electrons. The presence of protons in the nucleus account for the positive charges within the nucleus. As earlier discussed, a neutral atom due to the equal number of protons in the nucleus and number of electrons surrounding the nucleus giving a zero charge. Most of an atom's mass is in its nucleus; the mass of an electron is only 1/1836 the mass of the lightest nucleus, that of hydrogen. Although the nucleus is heavy, it is small compared with the overall size of an atom.

The radius of a typical atom is around 1 to 2.5 angstroms (\AA), whereas the radius of a nucleus is about 10^{-5} \AA . If an atom were enlarged to the size of the earth, its nucleus would be only 200 feet in diameter and could easily fit inside a small football stadium. The nucleus of an atom contains protons and neutrons. Protons and neutrons have nearly equal masses, but they differ in charge. A neutron has no charge, whereas a proton has a positive charge that exactly balances the negative charge on an electron. Table 1 lists the charges of these three sub atomic particles, and gives their masses expressed in atomic mass units.

Example 2.1. What is the atomic symbol for bromine, and what is its atomic number? Why is it incorrect to use the letter B? What other element preempts the symbol B? (Refer to the periodic table).

Solution:

Bromine's atomic number is 35, and its symbol is Br; B is the symbol for boron

2.10. Mass Number and Atomic Number

The **atomic number** is equal to the number of protons within the nucleus which is also equal to the number of electrons surround the nucleus. The **mass number** is the sum of the protons and neutron. It is the whole number of an atomic mass. **Atomic mass** a relative mass assigned to an atom which is exactly 1/12th the mass of C-12. The SI unit is expressed in **amu** (atomic mass unit) represented by u.

$$1.0 \text{ amu} = 1.6605 \times 10^{-24} \text{ g} \quad 1.0 \text{ g} = 6.0221 \text{ amu}$$

Oxygen-16 atom is 16.00 amu and carbon-12 atom is 12.00 amu; also hydrogen-1 atom is 1.00 amu.

$$\text{Mass Number} = \text{Number of Protons} + \text{Number of Neutrons}$$

$$\text{Atomic Number} = \text{No. of Protons} = \text{No. of Electrons}$$

$$\text{Mass Number} = \text{Whole Number of Atomic Mass}$$

$$\text{Charge} = \text{Number of protons (+)} + \text{Number of electrons (-)}$$

The number of neutrons in an atom is determined by subtracting the atomic number (number of protons = number of electrons) from the mass number. Using the format notation as:



where X represents the atomic symbol of the specific element, A is the mass number, Z is the atomic number, and C is the charge.

Example 2.2: How many protons, neutrons and electrons are there in an atom of $^{197}_{79}Au$? What is the charge, C?

Solution:

$$\text{Mass Number} = 197$$

$$\text{Atomic Number} = 79$$

$$\text{No. of Electrons} = 79$$

$$\text{No. of Protons} = 79$$

$$\text{No. of Neutron} = \text{Mass number} - \text{Number of neutrons} = 197 - 79 = 118$$

$$C = \text{Number of protons} + \text{Number of electrons} = 79 + (-79) = 0$$

Example 2.3. Give the complete chemical symbol for the atom that has 18 protons, 18 electrons and 22 neutrons.

Solution:

$$\text{Atomic Number} = \text{No. of proton} = \text{No. of electron} = 18$$

$$\text{Mass Number} = \text{Neutron} + \text{Proton} = 22 + 18 = 40$$

$$\text{Charge} = \text{Proton}(+) + \text{Electron} (-) = 18 + (-18) = 0$$

$$\text{Answer: } {}_{18}^{40}\text{Ar}^0$$

Example 2.4. Give the complete chemical symbol for the element that has atomic 10 electrons, 11 protons and 12 neutrons.

Solution:

$$\text{Atomic number} = \text{No. of protons} = 11$$

$$\text{Mass number} = \text{Neutron} + \text{Protons} = 12 + 10 = 23$$

$$\text{Charge} = 11 + (-10) = +1$$

$$\text{Answer: } {}_{11}^{23}\text{Na}^{+1}$$

2.11. Isotopes

Isotopes are atoms of the same element having a different number of neutrons with the same atomic number. The atomic mass of a particular element is equal to the average of the relative abundance of all its isotopes found in nature. For example, there are three naturally occurring isotopes of carbon: carbon-12, carbon-13, and carbon-14. Carbon-12 is the most common of these three, making up about 98.89% of all carbon, whereas carbon-13 has 1.11% natural abundance. Carbon-14 occurs rarely in nature. Atomic masses for other elements use the carbon-12 scale as a reference.

$$\begin{aligned} \text{average atomic mass} &= [\text{mass of carbon-12} \times (\% \text{ natural abundance}/100) + \text{mass of carbon-13} \\ &\quad \times (\% \text{ natural abundance}/100)] \\ &= (12 \times 0.9889) + (13 \times 0.0111) = 12.0111 \text{ u} \end{aligned}$$

Example 2.5. How many protons, neutrons, and electrons are there in an atom of uranium-238? Write the symbol for this isotope.

Solution:

Atomic no. = 92 = no. of protons = no. of electrons (in a neutral atom)
 Atomic mass = 238.03 u
 Mass number = 238
 No. of electrons = no. of protons = 92
 Mass number = protons + neutrons
 Neutrons = mass number – protons = 238 – 92 = 146
 Its symbol is $^{238}_{92}\text{U}$.

Example 2.6. Magnesium (Mg) has three significant natural isotopes: 78.70% of all magnesium atoms have an atomic weight of 23.985 u, 10.13% have an atomic weight of 24.986 u, and 11.17% have an atomic weight of 25.983 u. How many protons and neutrons are present in each of these three isotopes? What are the symbols for each isotope? What is the weighted average of the atomic weights?

Solution:

For isotope ^{24}Mg : 78.70% = 0.7870

Atomic mass = 23.985 u
 No. of protons in Magnesium = 12
 Mass number = 24
 Number of neutrons = Mass number – Protons = 24 – 12 = 12

For isotope ^{25}Mg : 10.13% = 0.1013

Atomic mass = 24.986 u
 Number of protons = 12
 Mass number = 25
 Number of neutrons = 25 – 12 = 13

For isotope ^{26}Mg : 11.17% = 0.1117

Atomic mass = 25.983
 Number of protons = 12
 Mass number = 26 – 12 = 14

Weighted ave. atomic mass = [(atomic mass A x % abundance A) + (atomic mass B x % abundance B) +]

weighted ave. atomic mass = [(23.985 u)(0.7870) + (24.986 u)(0.1013) + (25.983 u)(0.1117)]

$$= 18.876 \text{ u} + 2.531 \text{ u} + 2.902 \text{ u} = 24.31 \text{ u}$$

Note: Percentages abundance of isotopes always equal 100.

2.11.1 Natural and Artificial Isotopes

Most of the elements are having naturally occurring isotopes. There are those occurring more predominantly with greater abundance and there are those occurring only in traces. In the case of mercury, Hg, Mercury, which has seven naturally occurring isotopes: ^{196}Hg , ^{198}Hg , ^{199}Hg , ^{200}Hg , ^{201}Hg , ^{202}Hg , ^{204}Hg ; these have the percent natural abundances of 0.146%, 10.02%, 16.84%, 23.13%, 13.22%, 29.80%, and 6.85%, respectively. It is clear that ^{202}Hg occurs with greatest abundance, and ^{200}Hg is the next most abundant, but the other isotopes only occur in small traces.

There are 20 elements with only artificially produced isotopes. The majority of these are heavier elements; the lightest elements with artificial isotopes are ^{43}Tc and ^{61}Pm . The

other elements that only have artificial isotopes are those with atomic numbers of 84-88 and 89-103, otherwise known as the **actinoids or actinides**, but excluding ^{90}Th and ^{92}U .

Some naturally occurring and artificially produced isotopes are radioactive. The nucleus of a radioactive isotope is unstable; radioactive isotopes spontaneously decay, emitting alpha, beta, and gamma rays until they reach a stability, usually in the state of a different element. Bismuth $^{209}_{83}\text{Bi}$ has the highest atomic and mass number of all the stable nuclides. All nuclides with atomic number and mass number greater than 83 and 209, respectively, are radioactive. However, there are some lighter nuclides that are radioactive.

2.11.2. Use of Isotopes

2.11.2.1. Structural Determination

Structural determination using isotopes is often performed using nuclear magnetic resonance spectroscopy and mass spectrometry.

2.11.2.1.1. Nuclear Magnetic Resonance Spectroscopy

NMR analysis is isotope-dependent, and it often relies on trace isotopes of a molecule for detection. For example, the most abundant isotope of carbon, C-12, is invisible to NMR, whereas the minor isotope C-13 is NMR active, but only comprises 1.1 percent of a given sample of carbon. By replacing C-12 in a molecule with C-13, NMR analysis of that position is greatly enhanced. Similarly, H-1 is an NMR active nucleus, whereas H-2 is NMR invisible, so it is possible to determine where a specific hydrogen atom is by replacing it with H-2 and watching for the disappearance of the corresponding signal.

2.11.2.1.2. Mass Spectrometry

Isotopes of a given element are distinguished using mass spectroscopy which separates each isotope by their respective mass number. A characteristic peak for a specific isotope produced based on their relative abundance ranging from the most intense for the most abundant and the least intense for the least abundant.

Mass spectrometry is a technique for determining the molecular weight of an ionized molecule and fragments of the molecule that appear when the molecule is ionized. The addition of an isotope will change the observed mass of the parent ion—the molecule that is ionized and does not fragment. Adding an isotope will also change the observed mass of any fragment which contains the isotope. If a fragment does not contain the isotope, then its mass will not be changed. This can reveal information about the position of an isotope in a molecule.

2.11.2.1.3. Isotopic Labeling

Isotopic labeling tracks the passage of an isotope through a reaction via metabolic pathway or cell. This gives information on the identity of the reaction product as well as the mechanism of a biochemical pathway.

The reactant is ‘labeled’ by replacing specific atoms with their isotope. The reaction is allowed to occur and the position of the isotopes in the products is measured; this shows the sequence that the isotopic atom followed during the reaction.

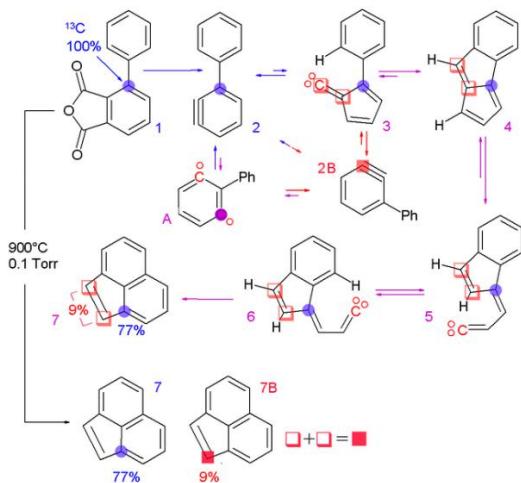


Figure 2.15: Isotopic labeling: A carbon-13 labeled precursor was used to track the position of an atom through a reaction. (Courtesy of the Wikipedia Commons)

.Isotopic labeling comes in several ways in detecting the presence of labeling isotopes: mass, vibrational mode, or radioactive decay. Mass spectrometry and nuclear magnetic resonance detect this difference in an isotope’s mass, while infrared spectroscopy detects the difference in the isotope’s vibrational modes. The radioactive decay can be detected through an ionization chamber or autoradiographs of gels.

An isotopic tracer is used in chemistry and biochemistry to help understand chemical reactions and interactions. In this technique, one or more atoms of a molecule are substituted for a different isotope of the same chemical element. Since the labeled atom—the isotope—has the same number of protons and electrons, it will behave in almost exactly the same way as its unlabeled counterpart. It will not interfere with the reaction being studied. The difference in the number of neutrons, however, means that it can be detected separately from the other atoms of the same element.

Nuclear magnetic resonance and mass spectrometry are used to investigate the mechanisms of chemical reactions. NMR and MS detect isotopic differences; detecting these differences allows information about the position atoms in a product’s structure to be determined. With information about the position of isotopic atoms in products, the reaction pathway can also be determined.

2.11.2.1.4. Study of Photosynthesis

Mass spectrometry has been used to study the ratio of carbon isotopes in various plants to understand the mechanisms of photosynthesis.

The study of the ratio of carbon isotopes in various plants uses spectrometry to understand the mechanism of photosynthesis.

Isotopes in Photosynthesis

Mass spectrometry has been used to study the ratio of isotopes in various plants to understand the mechanisms of photosynthesis. For example, in laboratory experiments,

labeling the atmosphere with oxygen -18 allows us to measure the oxygen uptake by the photorespiration pathway.

Stable carbon isotopes in carbon dioxide are utilized differentially by plants during photosynthesis. C3 carbon fixation is a metabolic pathway that converts carbon dioxide and ribulose bisphosphate into 3-phosphoglycerate. This reaction occurs in all plants as the first step of the Calvin cycle. In C4 plants, carbon dioxide is drawn out of malate and into this reaction rather than being drawn directly from the air.

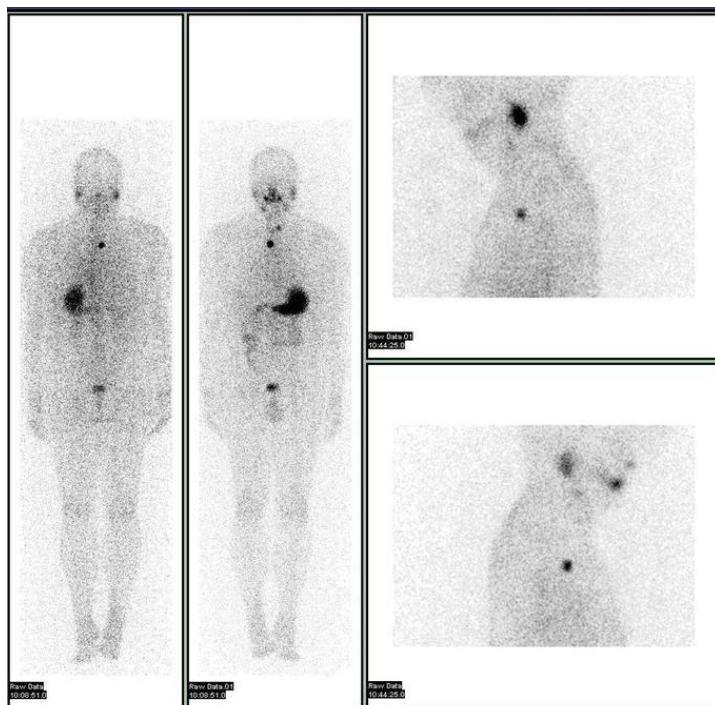
Grasses in temperate environments, such as barley, rice, and wheat, follow a C3 photosynthetic pathway that yields distinctive isotopic ratios. Grasses in hot, arid environments, specifically maize, but also millet, sorghum, sugar cane, and crabgrass, follow a C4 photosynthetic pathway that produces higher ratios of ^{13}C to ^{12}C .

Eating different plants affects the ^{13}C values in the consumer's body tissues. Case studies show that millet and maize eaters can easily be distinguished from rice and wheat eaters. Studying the geographical distribution of dietary preferences through time can illuminate migration paths of people and dispersal paths of different agricultural crops.

Isotopes in Medicine

Nuclear medicine is a medical specialty that involves the application of radioactive substances to diagnose or treat disease which employs procedures where radionuclides are combined with other elements forming a chemical compound. These radiopharmaceuticals, once administered to the patient, can localize to specific organs or cellular receptors. This property of radiopharmaceuticals allows nuclear medicine the ability to image the extent of a disease process in the body. These images are based on cellular function and physiology, rather than on physical changes in the tissue anatomy. Therefore, with some diseases, nuclear medicine studies can identify medical problems at an earlier stage than other diagnostic tests.

Diagnosis



(Courtesy of the Wikipedia Commons)

Figure 2.16: Iodine-123 whole-body scan: These images are scans used in the evaluation of thyroid cancer using the isotope iodine-123.

In nuclear medical imaging, radiopharmaceuticals are taken internally, either intravenously or orally. After this, external detectors capture and form images from the radiation that is emitted by the radiopharmaceuticals. This process is unlike a diagnostic X-ray, where external radiation is passed through the body to form an image. Nuclear medicine differs from most other imaging in that diagnostic tests primarily show the physiological function of the system being investigated, as opposed to traditional anatomic imaging, such as CT or MRI.

Common isotopes that are used in nuclear imaging include: fluorine-18, gallium-67, krypton-81m, rubidium-82, nitrogen-13, technetium-99m, indium-111, iodine-123, xenon-133, and thallium-201.

Treatment

In addition to imaging, radionuclide therapy can be used to treat conditions such as hyperthyroidism, thyroid cancer, and blood disorders. The radiopharmaceuticals used in nuclear medicine therapy emit ionizing radiation that travels only a short distance. This thereby minimizes unwanted side effects and damage to noninvolved organs or nearby structures most commonly used for this therapy are yttrium-90 and iodine-131.

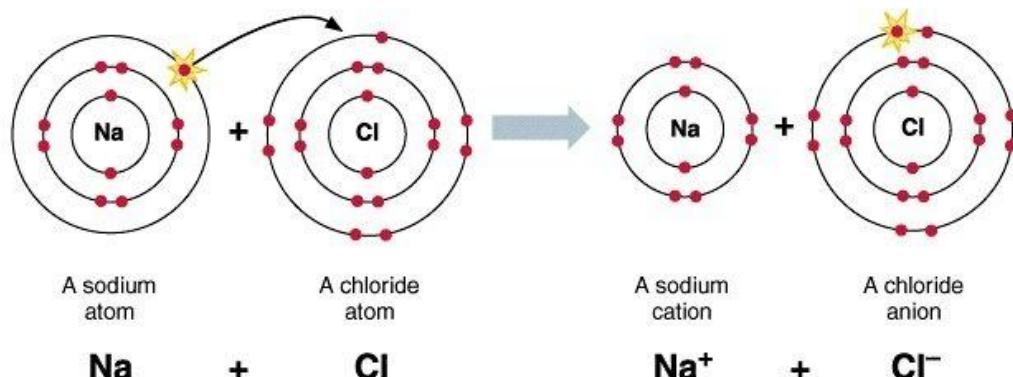
2.12. Ion

An atom is the smallest and the basic unit of matter that consists of a dense nucleus composed of positively charged protons and neutral neutrons, which is surrounded by a cloud of negatively charged electrons. Atoms having the same number of protons and electrons are said to be electrically neutral. In cases where the number of protons is not equal to the number of electrons, the atom is having a net electrical charge. The net electrical charged positive or negative depends upon the number of dominant charged particles.

Once an atom has either more than protons than electrons or more than electrons than protons, the atom is said to carry a charge either positive or negative. Atoms carrying either a positive or negative charge are said to be **ions**.

Ions are formed when an atom gains or losses electrons during chemical reaction. A **valence** electron is the electron or electrons located at the outermost shell of an atom. These valence electrons are the ones involved in the reactions. An atom with more than four valence electrons tends to give up these electrons during chemical reactions resulting to more protons and thus become a positive ion or a **cation**. The charge of a cation depends upon the number of electrons an atom has given up. On the other hand, atoms with valence electron or electrons less than four tends to accept or gain electrons during chemical reactions. This results to more number of electrons than proton and thus becomes a negative charged ion – the **anion**. The charge of the anion depends upon the number of electrons the atom has gained. A common example is sodium. Sodium has eleven electrons and has 1 (less than four) valence electrons. During chemical reaction sodium has to give up its 1 valence electron, thus sodium is a cation and since it has given up 1 electron, it has a +1 charge. In terms of the octet rule an energy level with 2 electrons in the first level is stable and from second level onwards, an eight electron

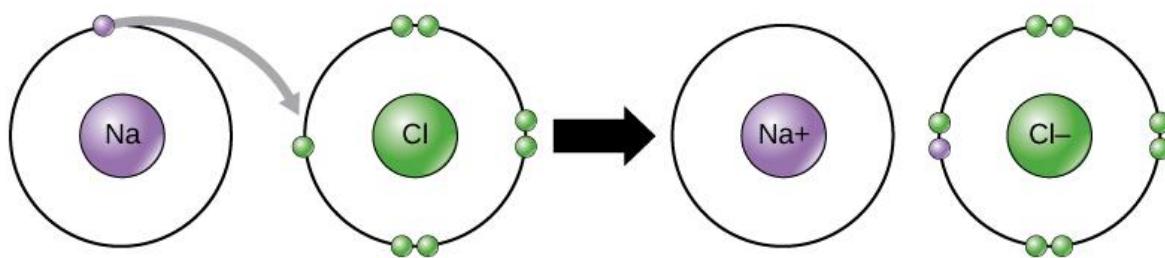
This material is for EDU use only.



is required to become stable. Therefore sodium needs to give up 1 electron to attain a stable configuration (i.e. 2 e⁻ in the first shell and 8 e⁻ in the second shell). On the other hand, chlorine has seven valence electrons (more than four) and tends to gain 1 electron to complete the 8 e⁻ (octet rule). Since chlorine atom gained 1 e⁻, it becomes an anion. The charge is -1 corresponding to the 1 electron gained.

Ionic bonds

We have discussed how sodium atom can lose an electron in forming cation Na⁺ and at how chlorine atom can gain an electron in forming the anion Cl⁻. In reality, however, this process can occur all in one step when sodium gives its electron away to chlorine! We can illustrate this as follows:



Oxidation and reduction of sodium and chlorine.

Figure 2.17 Sodium donates its electron to chlorine to form Na⁺ and Cl⁻.

Image credit: Boundless Learning, CC BY-SA 4.0

An illustration on how an electron is transferred from sodium to chlorine in order to form the ions Na⁺ and Cl⁻. Once these ions are formed, there is a strong electrostatic attraction between them, which leads to the formation of an ionic bond. Ionic bonds are formed by electron transfer and that there is unequal sharing of electrons. .

Covalent bonds and molecules

Sharing of electrons pairs in the formation of compounds results in a **covalent bond**. In a covalent bond, the stability of the bond comes from the shared electrostatic attraction between the two positively charged atomic nuclei and the shared, negatively charged electrons between them.

When atoms combine by forming covalent bonds, the resulting collection of atoms is called a **molecule**. We can therefore say that a molecule is the simplest unit of a covalent compound. As we will now see, there are a variety of different ways to represent and draw molecules.

Representing molecules: chemical formulas

Chemical formulas, or **molecular formulas**, are the shorthand way of representing molecules. In a chemical formula, we use the elemental symbols from the periodic table to indicate which elements are present, and we use subscripts to indicate how many atoms of each element exist within the molecule.

Representing molecules: structural formulas

Chemical formulas only tell us how many atoms of each element are present in a molecule, but structural formulas also give information about how the atoms are connected in space. In structural formulas, we actually draw the covalent bonds connecting atoms. In the last section, we looked at the chemical formula for ammonia, which is NH_3 . Now, let's consider its structural formula:

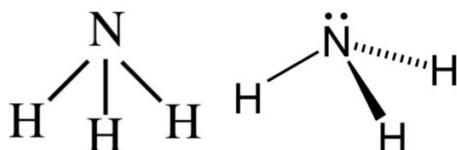


Figure 2.18: Two structural formulas for ammonia.

Two structural formulas for ammonia, NH_3 . The formula on the left gives only a two-dimensional approximation of molecular structure, whereas the formula on the right shows the orientation of atoms in space using dashes going into the plane of the page and wedges coming out of the plane of the page. The two dots on nitrogen in the right formula indicate a lone pair of electrons.

Image credit: left, Physique Applique, CC BY-NC-SA 4.0; right, Wikipedia, CC BY-SA 3.0

The figure above illustrates the structural formula. In this chapter, we will not be discussing the structural formula. We will deal with the molecular or chemical formula.

Covalent vs. ionic compounds: molecules vs. formula units

Now that we've discussed the basics of both covalent and ionic bonding, we need to draw a few necessary distinctions. We know that a group of atoms joined by only covalent bonds is known as a molecule. It should be noted, however, that the word molecule should only be used in reference to covalent compounds. In an ionic compound, such as sodium chloride, there is no such thing as a single molecule of sodium chloride since, in reality, sodium chloride is actually made up of multiple sodium and chloride ions joined together in a large crystal lattice—as we saw in the previous diagram. As such, we refer to one piece of NaCl not as a molecule but as a formula unit. Keep in mind that single formula units, unlike single molecules, largely do not exist in nature—we simply rely on formula units for ease of reference and convenience.

2.13. Symbols

As defined earlier, a chemical symbol is a letter or two-letter word representing the name of the element. The first letter is always written on capital letter and followed by a small letter for a two-word chemical symbol. It should not bear a period.

The first scientist to use symbols for chemical elements was Dalton. He was the one who used the symbols of the elements in a specified quantity, i.e one atom of the element. Later on, Berzilius suggested that we could use one or two letters of the element to form its symbol.

Initially, symbols for the name of elements were derived from the place they originated from. So copper was taken from Cyprus, while gold was meant yellow and so it was denoted accordingly. However, today the International Union of Pure and Applied Chemistry approves the element names.

For example, the chemical symbol for Sodium is Na. This 'Na' is derived from Natrium. Iron is denoted by 'Fe' which comes from the Latin word "Ferrum". H for Hydrogen, hg for mercury.

2.14. Oxidation Number

Ions as discussed as charged atoms. Cations are positively charged while anions are negatively charged. **Monoatomic ion** is either cation or anion of a single atom. For sodium, Na, it has +1 and is written as Na^{+1} . And for chlorine, Cl, it has -1 charge and is written as Cl^{-1} . The charge of an atom is written as the superscript and this is known as the **oxidation number**. We have also the **Polyatomic ion**, a group of atoms carrying a charge either positive or negative. Example we have, CO_3^{2-} , carbonate a polyatomic ion composed of one carbon atom and three oxygen atoms with the -2 charge. Table 2.3 and Table 2.4 list the oxidation numbers of monoatomic ions and polyatomic ions, respectively.

2.14.1 Determination of the Oxidation Numbers of an Atom in a Polyatomic Ion

The oxidation number of atoms are listed in the given table below. There are atoms with variable oxidation numbers or having more than one oxidation number. Take the case for example $\text{Cr}_2\text{O}_7^{2-}$. It is a dichromate polyatomic ion carrying a -2 charge. How do we determine the oxidation number of Cr?

Steps in the Determination of Oxidation Number

1. Free elements or neutral elements are assigned an oxidation number of zero (0). A neutral compound also carries a charge of zero. Cl in its free state is Cl^- , and NaCl is a neutral compound has is assigned a charge of zero: NaCl^0 .
2. Hydrogen in covalent compounds, the oxidation number is +1. In hydrides, hydrogen is -1.
3. Oxygen in covalent compounds, oxidation number is -2. The peroxide, it has -1.
4. The oxidation numbers of a monoatomic ion and polyatomic ion are equal to the charge they carry
5. In covalent compounds, since it contains two nonmetal atoms, the atom which is more electronegative carries the negative charge.
Example: OCl is a covalent compound between two elements in the Group VIIA. Both are considered negative monoatomic ions. However, Cl is more electronegative than O, therefore Cl is considered a negative ion
6. The sum of the oxidation numbers of the atoms in a polyatomic ion is equal to its charge

Example 2.7: What is the oxidation number of Cr in $\text{K}_2\text{Cr}_2\text{O}_7$?

Solution:

Referring to Table 2.3:

The oxidation number of K is +1.

The oxidation number of O is -2.

Solving for the oxidation number of Cr:

$$(\text{No. of K} \times \text{oxidation number of K}) + (\text{No. of Cr} \times \text{oxidation number of Cr}) = \text{charge}$$

$$\text{No. of K} = 2$$

$$\text{No. of Cr} = 2$$

$$\text{No. of O} = 7$$

Charge = 0 ($K_2Cr_2O_7$ is a neutral compound)

$$\begin{aligned} [(2)x(+1)] + [(2)x(Cr)] + [(7)x(-2)] &= 0 \\ +2 + 2Cr - 14 &= 0 \\ 2Cr - 12 &= 0 \\ 2Cr &= 0 + 12 \\ Cr &= \frac{+12}{2} = +6 \end{aligned}$$



Example 2.8: What is the oxidation number of Cr in CrO_4^{-2} ?

Solution:

The oxidation of O is -2.

No. of Cr = 1

No. of O = 4

Charge = -2

Solving for the oxidation number of Cr:

$$\begin{aligned} [(1)x(Cr)] + [(4)x(-2)] &= -2 \\ Cr - 8 &= -2 \\ Cr &= -2 + 8 = +6 \end{aligned}$$

2.15 Chemical Formula

A chemical symbol represents the name of the chemical element. **Chemical formula** serves as the shortest way of writing the name of the chemical compound. It shows the number of atoms of each kind.

Steps for writing a chemical formula

Step 1: First, you have to decide the type of the bond.

If the prefixes are used, then it is a covalent bond. In case there are no prefixes, it is an ionic bond. After deciding move to Step number 2.

Step 2: Write the correct symbol element and the correct formula for the polyatomic ions.

Step 3: Identify the cation and the anion. Always remember to write the cation first, followed by the anion.

Step 4: Determine the oxidation numbers of the cation and the anion by writing as superscripts.

Step 5. Remove the signs and cross-multiply the oxidation numbers – the superscript of the cation becomes the subscript of the anion and the superscript of the anion becomes the subscripts of the cation.

Step 6. Write the correct chemical formula and examine the subscripts.

a). For ions with subscripts 1, no need to write 1 (understood to have one).

$NaCl$ – Sodium has a subscript of 1 from the oxidation number of chlorine which is -1 and chlorine has a subscript of 1 from the oxidation number of sodium which is +1.

$BaCl_2$ – Ba has a subscript of 1 from chlorine which is -1, and Cl has a subscript of 2 from the oxidation number of Ba which is +2.

b) Reduce the subscript to the lowest term possible.

BaS – Ba has +2 and S has -2, thus, Ba_2S_2 . Reducing the subscripts – BaS .

SnO_2 – Sn has +4 and O has -2. Sn_2O_4 . Reducing the subscripts – SnO_2 .

c). Polyatomic ions taken more than once, should be enclosed in a parenthesis.

Fe(OH)_3 – Fe is +3 while a polyatomic OH is -1. Since OH has a subscript of 3, it should be enclosed in a parenthesis.

$(\text{NH}_4)_2\text{CO}_3$ – NH_4 a polyatomic ion with +1 and CO_3 is a polyatomic ion with -2.
 NH_4 has a subscript of 2 and is enclosed in a parenthesis.

- d). Polyatomic ions taken more than once should be enclosed in parenthesis, then in a bracket.
 $\text{Al}_4[\text{Fe}(\text{CN})_6]_3$ – Al is +3 and $\text{Fe}(\text{CN})_6$ is -4. A bracket is used to enclose the polyatomic $\text{Fe}(\text{CN})_6$ as it already contains a parenthesis.

Example 2.9: Write the chemical formula for calcium and sulfate

Solution:

Calcium, Ca is the cation and sulfate, SO_4 is the polyatomic anion. Ca has +2 while SO_4 has -2.
Writing the correct chemical formula: $\text{Ca}_2(\text{SO}_4)_2$ further reducing to the lowest term: CaSO_4

Example 2.10: Write the chemical formula for magnesium and phosphate.

Solution:

Magnesium is the cation with Mg^{+2} while Phosphate is a polyatomic anion with PO_4^{-3} .
 $\text{Mg}_3(\text{PO}_4)_2$.

Example 2.11: Write the chemical formula for aluminum and sulfur.

Solution:

Aluminum is +3 while sulfur is -2. $\text{Al}^{+3} \text{S}^{-2}$. Al_2S_3 .

Table 2.3 Oxidation Numbers of Monoatomic Ions

| I | II | | | | | | | | | | | | | | | | | | | III | IV | V | VI | VII |
|----------|----------------------|----------|----------------------|---------------------------|----------------------------------|--|----------------|----------------|----------|----------------|----------|----------------|----------------|----------------|----------------|----------------------------|----------------------------|---------|---------|-----|----|---|----|-----|
| H +1 | | | | | | | | | | | | | | | | | | | | | | | | |
| Li +1 | B _e +2 | | | | | | | | | | | | | | | | | | | | | | | |
| Na +1 | Mg +2 | | | | | | | | | | | | | | | | | | | | | | | |
| K +1 | Ca +2 | Sc +3 | Ti +4 +3 +2 | V +5 +4 +3 +2 | Cr +6 +5 +4 +3 +2 | Mn +7 +6 +5 +4 +3 +2 | Fe +3 +2 | Co +3 +2 | Ni +2 | Cu +2 +1 | Zn +2 | Ga +3 +2 | Ge +4 +2 | As +5 +3 | Se +6 +4 | Br +7 +5 +3 +1 | Cl +7 +5 +3 +1 | O -2 | F -1 | | | | | |
| Rb +1 | Sr +2 | | | | | | | | | | | | | | | | | | | | | | | |

Table 2.4 Oxidation Numbers/Charges of Polyatomic Ions

| +1 CHARGE | | -1 CHARGE | | -2 CHARGE | | -3 CHARGE | | | | |
|------------------------|------------|---------------------------|----------------------|---------------------------------------|---------------------|-------------------------------|---------------|--|--|--|
| ion | Name | ion | Name | ion | name | ion | name | | | |
| NH_4^+ | ammonium | H_2PO_3^- | dihydrogen phosphite | HPO_3^{2-} | hydrogen phosphite* | PO_3^{3-} | phosphite | | | |
| H_3O^+ | hydronium | H_2PO_4^- | dihydrogen phosphate | HPO_4^{2-} | hydrogen phosphate* | PO_4^{3-} | phosphate | | | |
| Hg_2^{2+} | mercury(I) | HCO_3^- | hydrogen carbonate* | CO_3^{2-} | carbonate | PO_2^{3-} | hypophosphite | | | |
| | | HSO_3^- | hydrogen sulfite* | SO_3^{2-} | sulfite | AsO_3^{3-} | arsenite | | | |
| | | HSO_4^- | hydrogen sulfate* | SO_4^{2-} | sulfate | AsO_4^{3-} | arsenate | | | |
| | | NO_2^- | nitrite | $\text{S}_2\text{O}_3^{2-}$ | thiosulfate | $\text{Fe}(\text{CN})_6^{3-}$ | ferricyanide | | | |
| | | NO_3^- | nitrate | SiO_3^{2-} | silicate | | | | | |
| | | OH^- | hydroxide | C_2^{2-} | carbide | | | | | |
| | | CH_3COO^- | acetate | $\text{C}_2\text{O}_4^{2-}$ | oxalate | | | | | |
| | | CrO_2^- | chromite | CrO_4^{2-} | chromate | | | | | |
| | | CN^- | cyanide | $\text{Cr}_2\text{O}_7^{2-}$ | dichromate | | | | | |
| | | CNO^- | cyanate | $\text{C}_4\text{H}_4\text{O}_6^{2-}$ | tartrate | | | | | |
| | | CNS^- | thiocyanate | MoO_4^{2-} | molybdate | | | | | |
| | | O_2^- | superoxide | O_2^{2-} | peroxide | | | | | |
| | | MnO_4^- | permanganate | S_2^{2-} | disulfide | | | | | |
| | | ClO^- | hypochlorite | | | | | | | |
| | | ClO_2^- | chlorite | -4 CHARGE | | | | | | |
| | | ClO_3^- | chlorate | $\text{P}_2\text{O}_7^{4-}$ | pyrophosphate | | | | | |
| | | ClO_4^- | perchlorate | $\text{Fe}(\text{CN})_6^{4-}$ | ferrocyanide | | | | | |
| | | BrO^- | hypobromite | * | | | | | | |
| | | BrO_2^- | bromite | * | | | | | | |
| | | BrO_3^- | bromate | * | | | | | | |
| | | BrO_4^- | perbromate | * | | | | | | |
| | | IO^- | hypoiodite | * | | | | | | |
| | | IO_2^- | iodite | * | | | | | | |
| | | IO_3^- | iodate | * | | | | | | |
| | | IO_4^- | periodate | * | | | | | | |
| | | AlO_2^- | aluminate | * | | | | | | |
| | | N_3^- | azide | * | | | | | | |

2.16 Naming of Inorganic Compounds

Naming of inorganic and organic compounds follow the system of nomenclature or system of naming set by International Union of Pure and Applied Chemistry (IUPAC). Organic compounds are discussed separately.

2.16.1 Binary Compounds

Binary from the prefix “bi” meaning 2. So binary compounds are compounds containing only two elements. There are three types of binary compounds:

- **Type I** – an ionic compound formed between a metal that forms only one cation and an anion.
- **Type II** – an ionic compound formed between a metal with more than one type of cations and an anion.
- **Type III** – a covalent compound formed between two non-metals.

All binary compounds are named ending in “ide”.

2.16.1.1 Type I Binary Compounds

For **Type I** binary compounds, they are usually from cations of Group 1 and Group 2.

- A cation takes its name from name of the element.

- An anion is named by taking the root of the name of the element and changing the ending to “ide”.

Example 2.12: Give the name of the compound Na_2S .

Solution:

The cation is sodium and the anion is sulfur. Sodium is named first followed by sulfur by changing the end “ur” of sulfur to ’ide” – sulfide. The name is sodium sulfide.

Example 2.13: Give the name of the compound MgI_2 .

Solution:

The cation is magnesium and is named magnesium. The anion is iodine and is named by changing the ending “ine” of iodine to “ide” – iodide. The name is magnesium iodide.

2.16.1.2 Type II Binary Compounds

Type II binary compounds are named in two ways: the Systematic Naming or the Stock System and the Old System.

- Systematic or Stock System

- The name of the cation takes its name from the name of the element. A Roman numeral is added enclosed in parenthesis after the name of the cation. The Roman numeral indicates the oxidation number of the metal cation.

- An anion is named by taking the root of the name of the element and changing the ending to “ide”.

- Tin (II) for Tin +2 and Tin (IV) for Tin +4

- Old System

- The cation is named from the root of the Latin name of the cation (metal) changing the ending “um” to ”ous” for lowest oxidation state, and “ic” for higher/highest oxidation state.

- Tin +2 – from stannum to stannous
- Tin +4 – from stannum to stannic

Example 2.13: Give the name of the compound, CuS, using the Systematic and the Old Systems.

Solution:

CuS, the cation is copper (Cu). Copper has two oxidation states, +1 and +2. Anion sulfur, has an oxidation state of -2. In the given formula, the oxidation number of Cu is +2.

- Systematic Naming: Copper (II) sulfide
- Old System : Cupric sulfide (cuprous is +1 and Cupric is +2).

Example 2.14: Give the name of the compound, PbCl₂, using the Systematic and Old Sytems of naming.

Solution:

Pb has +2 (plumbous) and +4 (plumbic) oxidation states. Cl has -1 oxidation state. Therefore, in this given formula, Pb has +2 oxidation state.

- Systematic Naming: Pb (II) chloride
- Old System: Plumbous chloride

2.16.1.3. Type III Binary Compounds – The Binary Covalent Compounds

This type of compounds are composed of two non-metals. They are named based on the following:

- The first element is named first taking the name of the first element.
- The second element is named taken from the name of the second element ending in “ide”.
- Greek prefixes are added to denote the number of atoms for both elements. However a prefix “mono” is never used for the first element with only one atom.

Table 2.4 lists the Greek prefixes.

Table 2.4 Greek Prefixes

| Number | Prefix | Number | Prefix |
|--------|--------|--------|--------|
| 1 | Mono | 6 | Hexa |
| 2 | Di | 7 | Hepta |
| 3 | Tri | 8 | Octa |
| 4 | Tetra | 9 | Nona |
| 5 | Penta | 10 | Deca |

- If the ending of the name of the first element is a vowel (o or a), and the first letter of the second elements is also a vowel (a or o), the ending vowel (a or o) is dropped at the end of the prefix.

- Nonaoxide – the vowel a in the prefix Nona is dropped giving nonoxide.
- Monooxide is monoxide
- Pantaoxide – the vowel a at the end of the prefix Penta is dropped giving pentoxide.
- The vowel “i” at the end of tri and di are never dropped.

Example 2.15: Give the name of the compound, SO_3 .

Solution:

The covalent compound is composed of three atoms of sulfur and one atom of oxygen.
- the name is sulfur trioxide (not monosulfur trioxide).

Example 2.16: Give the name of the compound, N_2O .

Solution:

The compound is composed of two atoms of nitrogen and one atom of oxygen.
- the name is dinitrogen monoxide.

2.16.1.4 Hydrates

Some ionic compounds occur as hydrates. **Hydrates** are compounds containing number of loosely bound water molecules. The water molecule is called the **water of hydration**.

To name a hydrate, the name of the main chemical compound is named first followed by a Greek prefix added to the word hydrate.

Example 2.17: Give the name of the hydrate, $\text{Ba}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$

Solution:

The name of the main chemical compound is barium hydroxide.
The number of water molecule is 5, and the prefix is penta.
The name is barium hydroxide pentahydrate.

2.16.2 Naming Compounds of Polyatomic Ions

Polyatomic ions are molecules containing two or more atoms carrying a charge. Oxyanions (or oxoanions) are polyatomic ions containing oxygen.

a. With four oxyanions and a halogen bonded to O:

| Prefix | Suffix | Number of O Atoms | Superlative/Comparative | Example | Name |
|--|--------|-------------------|-------------------------|------------------|--------------|
| Per (greater than common) | -ate | 4 | Largest number | ClO_4^- | perchlorate |
| Common | -ate | 3 | Large number | ClO_3^- | chlorate |
| Less than one than common | -ite | 2 | Smaller number | ClO_2^- | chlorite |
| Hypo (lesser than one) – lowest (only one) | -ite | 1 | Smallest number | ClO^- | hypochlorite |

b. With two oxyanions

- ions with most number of O, the name of the non-metal ending in suffix “ate”.
- ions with least number of O, the name of the non-metal ending in suffix “ite”.
 - SO_4^{2-} and SO_3^{2-} . SO_4^{2-} has more O atoms than SO_3^{2-} . SO_4^{2-} is named sulfate and SO_3^{2-} is named sulfite.

Example 2.18: Give the name of the compound, $\text{Ca}(\text{ClO}_3)_2$.

Solution:

Ca is calcium and ClO_3 is chlorate. The name is Calcium chlorate.

Example 2.19 The formula $\text{Mg}(\text{NO}_2)_2$. Is it magnesium nitrate or magnesium nitrite?

Solution:

There are two oxyanions with nitrogen and oxygen. NO_3^- has the most number of oxygen atom while NO_2^- has the least number of oxygen atom. Therefore, NO_3^- and NO_2^- are named as nitrate and nitrite, respectively. The name of compound is magnesium nitrite.

2.17. Naming of Inorganic Acids

2.17.1. Naming Binary Acids

- Binary acids are compounds containing a non-metal covalently bonded to hydrogen. They are named starting with the prefix “hydro” followed by the root of the acid forming element (usually the non-metal) and the suffix “ic” and word acid.

Example 2.20: Name the binary acid, HCl.

Solution:

The binary acid given is composed of the non-metal acid forming element, chlorine covalently bonded to H. The root for the acid forming element is “–chlor” from the element chlorine.

The name is hydro (the prefix) followed by chlor (the root), the ic (the suffix) and the word acid. Hydrochloric acid.

| Name of Acid |
|---|
| HF(<i>aq</i>), hydrofluoric acid |
| HCl(<i>aq</i>), hydrochloric acid |
| HBr(<i>aq</i>), hydrobromic acid |
| HI(<i>aq</i>), hydroiodic acid |
| H ₂ S(<i>aq</i>), hydrosulfuric acid |

2.17.2 Naming of Oxyacids

Oxyacids are acids containing oxygen atom bonded to hydrogen and another element. Also known as **oxoacids** or **ternary acids**.

To name oxyacids: Remove the word hydrogen, then begin with the root name of the anion, replacing the suffix – ate with –ic and the suffix –ite with –ous and add the word acid.

Example 2.21: Give the name of the name of the oxyacid, H₂SO_{3(aq)}.

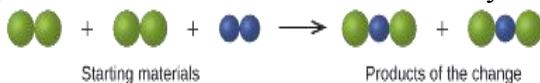
Solution:

The root name of the anion is sulfur. SO₃ is sulfite. The name sulfur + ous (from ite) + acid. The name is sulfurous acid.

Note: Acids have always the subscript (aq) for aqueous in their formulas.

PROGRESS CHECK:

- 2.1. In the following drawing, the green spheres represent atoms of a certain element. The purple spheres represent atoms of another element. If the spheres touch, they are part of a single unit of a compound. Does the following chemical change represented by these symbols violate any of the ideas of Dalton's atomic theory? If so, which one?



- 2.2. Boron has two naturally occurring isotopes, ^{10}B and ^{11}B . We know that 80.22% of its atoms are ^{11}B , atomic weight 11.009 u. From the natural atomic weight given on the inside front cover, calculate the atomic weight of the ^{10}B isotope.
 - 2.3. Boron has two naturally occurring isotopes, boron-10 and boron-11, with the masses of 10.013 g and 11.009 g, respectively. What is the average atomic mass of boron?
 - 2.4. What is the mass of chlorine-37 (24.23%), if the mass of chlorine-35 (75.77%) is 34.969g and the atomic mass of chlorine is 35.453 g?
 - 2.5. For the atom $^{196}\text{Pt}^{4+}$, indicate the number of protons, neutrons and electrons.
 - 2.6. Write the notation for an atom containing 24 protons, 28 neutrons and 21 electrons.
 - 2.7. Complete the chart below.

2.7. Complete the chart below.

| Element | Protons | Neutrons | Electrons | Charge |
|----------------------------|---------|----------|-----------|--------|
| ^3_2He | | 1 | 2 | 0 |
| $^{129}_{53}\text{I}$ | 53 | | 54 | -1 |
| $^{30}_{14}\text{Si}$ | 14 | | | |
| | | 18 | 18 | 0 |
| $^9_4\text{Be}^{+2}$ | | | 2 | |
| | 3 | 3 | | 0 |
| $^{80}_{35}\text{Br}^+$ | 35 | 45 | | -1 |
| $^{27}_{13}\text{Al}^{+3}$ | 13 | | 10 | |
| $^{35}_{17}\text{Cl}^-$ | | 18 | 18 | -1 |
| $^{15}_7\text{N}$ | 7 | | 7 | |
| | 82 | 126 | | +2 |
| $^{10}_5\text{B}$ | | | | |

- 2.8. Bromine has two naturally occurring isotopes: bromine-79 has a mass of 78.9183 u and an abundance of 50.69%, and bromine-81 has a mass of 80.92 u and an abundance of 49.31%. What is the relative atomic mass of Br?
- 2.9. An isotope of lead has an isotopic mass of 208. Give the appropriate notation for the isotope.
- 2.10. Thallium has two naturally occurring isotopes, ^{203}Tl and ^{205}Tl and has an average atomic mass of 204.39 u. Tl-205 has an abundance of 70.48%. What is the percent natural abundance of Tl-203?
- 2.11. What is the oxidation number of Xe in XeO_6^{-4} ?
- 2.12. What is the oxidation number of S in $\text{S}_2\text{O}_5\text{Cl}_2$?
- 2.13. What is the oxidation number of Ta in $\text{Mo}_8\text{O}_{26}^{-4}$?
- 2.14. What is the oxidation number of P in $\text{Na}_3\text{P}_3\text{O}_9$?
- 2.15. Write the correct chemical formula for the following:
- | | |
|-------------------------|-----------------------------|
| a. tin(II) nitrate | b. calcium bicarbonate |
| c. zinc phosphate | d. calcium hydroxide |
| e. chlorous acid | f. iodine heptafluoride |
| g. dinitrogen pentoxide | h. antimony(III) dichromate |
| i. oxygen difluoride | j. perchloric acid |
| k. aluminum bromide | l. lead(IV) oxide |
| m. ammonium phosphate | n. cuprous sulfite |
| o. ferric cyanide | |
- 2.16. Name each of the following compounds:
- | | |
|---|---|
| a. CS_2 | b. SnS |
| c. CCl_4 | d. P_2O_3 |
| e. $\text{H}_2\text{CO}_{3(\text{aq})}$ | f. $\text{H}_3\text{PO}_{4(\text{aq})}$ |
| g. MgO | h. $\text{HF}_{(\text{aq})}$ |
| i. NaI | j. KH_2PO_4 |
| k. CaH_2 | l. $\text{Au}_2\text{C}_2\text{O}_4$ |
| m. $\text{Ca}(\text{ClO}_3)_2$ | n. $\text{Cu}(\text{OH})_2$ |
| o. SF_6 | |

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Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Atomic_Theory/Atomic_Theory

TOPICS: CHEMICAL STOICHIOMETRY

- 3.1. Mole Concept
- 3.2. Interconverting Masses, Moles and Number of Particles/Molecules/Atoms
- 3.3. Percentage Composition
- 3.4. Derivation of Formulas
 - 3.4.1. Empirical Formula
 - 3.4.2. Molecular Formula
- 3.5. Problems Based on Chemical Equations (Mass-mass- Relationship)
- 3.6. Limiting Reactants
- 3.7. Percent Yield

EXPECTED COMPETENCIES:

At the end of the lesson, you must have:

- a. Explain the concept of stoichiometry as it pertains to chemical reactions;
- b. Use balanced chemical equations to derive stoichiometric factors relating amounts of reactants and products;
- c. Perform stoichiometric calculations involving mass, moles, and molecules;
- d. Identify mole ratios of reactants and products from balanced chemical equation;
- e. Identify the limiting and excess reagents in a reaction mixture and determine the amount (in moles or grams) of excess reagent(s) remaining at the end of a reaction; and
- f. Calculate the theoretical yield, actual yield, and percent yield for a chemical reaction.

CONTENTS/TECHNICAL INFORMATION:

Stoichiometry (“stoy-key-ahm-uh-tree”) from the Greek work “stoicheion” meaning element or part, and “metron” meaning measure. The measure of elements. It involves the relationships between reactants and products in a balanced chemical reaction to obtain the desired quantitative data. It is founded on the law of conservation of mass where the total mass of the reactants is equal to the total mass of the products.

3. 1. Mole Concept

Take the case of fluorine, atomic weight is 19.0 and of Hydrogen is 1.0. An atom of fluorine is 19 times heavier than an atom of hydrogen. Taking 10 fluorine atoms and 10 hydrogen atoms, the mass of the collection of fluorine atoms will be 19 times the mass of the collection of hydrogen atoms. The masses of any two samples of fluorine and hydrogen that contain the same number of atoms will stand in the ratio of 19.0 to 1.0, which is the ratio of their atomic weights.

Suppose, we have 19.0g of fluorine and 1.0g of hydrogen, which are values in grams numerically equal to the atomic weights of the elements. Since their masses stand in the ratio of 19.0 to 1.0, the samples must contain the same number of atoms. In fact, a sample of any element that has a mass in grams numerically equal to the atomic weight of the element will contain the same number of atoms

The number is referred to as **Avogadro's number**, named after Amedeo Avogadro, who first interpreted the behavior of gases in chemical reactions in terms of the numbers of

reacting molecules. This has been experimentally determined, 6.023×10^{23} . And the amount of a substance containing Avogadro's number of elementary units is called a **mole** and it is defined as the amount of a substance that contains as many elementary entities as there are atoms in exactly $^{12}_6C$. It is abbreviated as mol and it is an SI base unit.

Then a sample of an element that has a mass in grams numerically equal to the atomic weight of the element is a mole of atoms of the element and contains Avogadro's number of atoms. For example, the atomic weight of Beryllium is 9.0122, thus, $9.0122 \text{ g Be} = 1 \text{ mol Be} = 6.023 \times 10^{23}$ atoms. A mole consists of Avogadro's number of entities. A mole of a molecular substance consists of Avogadro number of molecules and has a mass in grams numerically equal to the molecular weight or molar mass of the substance. For example, the molecular weight of H_2O is 18.02, thus,

$$18.02 \text{ g of } \text{H}_2\text{O} = 1 \text{ mol of } \text{H}_2\text{O} = 6.023 \times 10^{23} \text{ H}_2\text{O molecules}$$

Since a molecule of water contains two H atoms and one O atom, a mole of H_2O contains two moles of H atoms and one mole of O atom. When the term mole is used, the type of entity being measured must be specified. For example, a mole of H atoms contains 6.023×10^{23} atoms of H and has a mass of 1.01g. A mole of H_2 molecules contains 6.023×10^{23} molecules of H_2 and has a mass of 2.02g

For ionic substances, the term "1 mol of BaCl_2 " means that the sample contains Avogadro's number of formula units – the entity specified. One mole of BaCl_2 , has therefore, a mass of 208.3 g, the formula weight of BaCl_2 . In reality, one mole of BaCl_2 contains:

$$1 \text{ mol Ba}^{+2} = 6.023 \times 10^{23} \text{ Ba}^{+2}\text{ ions} = 137.3 \text{ g barium}$$

$$2 \text{ mol Cl}^{-} = 2(6.023 \times 10^{23}) \text{ Cl}^{-} \text{ ions} = 2(35.5) \text{ g Cl}^{-} = 71.0 \text{ g chlorine}$$

Which together make up : $1 \text{ mol BaCl}_2 = 6.023 \times 10^{23} \text{ units BaCl}_2 = 208.3 \text{ g BaCl}_2$

Sample Problem 3.1. What number of moles of Calcium is present in 151 g of Ca?

Solution:

First we can state the problem this way:

$$\text{? mol Ca} = 151 \text{ g Ca}$$

Next, let us derive a conversion factor to solve the problem. The atomic weight of one mole of Ca is 40.08, therefore;

$$\text{? mol Ca} = 151 \text{ g Ca} \times \frac{1 \text{ mol Ca}}{40.08 \text{ g Ca}} = 3.77 \text{ mol Ca}$$

Sample Problem 3.2. How many grams of hydrochloric acid, HCl, must be taken in order to get 0.225 mol of HCl?

Solution:

We can state the problem this way:

$$\text{? g HCl} = 0.225 \text{ mol HCl}$$

The formula weight of HCl is 36.45 (1H + 1Cl). Therefore,

$$1 \text{ mol HCl} = 36.45 \text{ g HCl}$$

The unit that must be eliminated in this problem is mol HCl, and the conversion factor must have this unit in the denominator.

$$\text{? g HCl} = 0.225 \text{ g mol HCl} \times \frac{36.45 \text{ g HCl}}{1 \text{ mol HCl}} = 8.20 \text{ g HCl}$$

3.2. Interconverting Masses, Moles and Numbers of Particles

Conversion of mass to moles and of moles to mass are frequently encountered in calculations using the mole concept. These calculations are made easy through dimensional analysis, as shown:

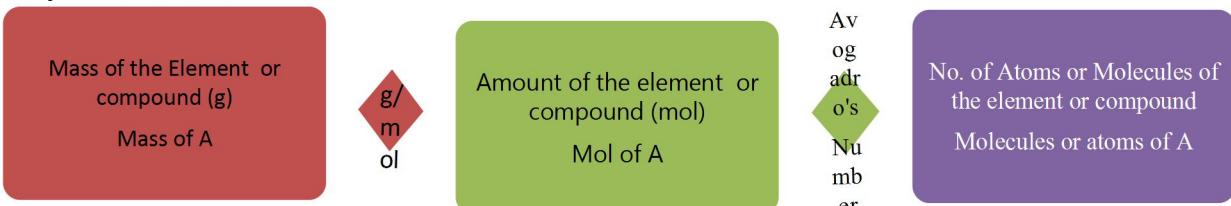


Figure 3.1. Mass – Mol – Molecules/Atoms Relationships for Element

$$\text{? mol A} = \text{mass A, grams} \times \frac{\text{mol A}}{\text{grams A}}$$

Given mass Molar Mass Avogadro's Number

$$\text{? molecules A} = \text{mass A, grams} \times \frac{\text{mol A}}{\text{grams A}} \times \frac{6.023 \times 10^{23} \text{molecules A}}{1 \text{mol A}} = \text{molecules A}$$

$$\text{? atoms A} = \text{mass A, grams} \times \frac{\text{mol A}}{\text{grams A}} \times \frac{6.023 \times 10^{23} \text{molecules A}}{1 \text{mol A}} \times \frac{\text{Number of atoms A}}{1 \text{molecule A}} = \text{atoms A}$$

Sample Problem 3.3. Calculate the number of moles of sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, in 2.24 g of this substance.

Solution:

Given:

$$\text{gC}_{12}\text{H}_{22}\text{O}_{11} = 2.24 \text{ g}$$

Molecular Weight of $\text{C}_{12}\text{H}_{22}\text{O}_{11}$:

$$\begin{aligned}
 12 \text{ C} &= 12 \times 12.0 = 144.0 \\
 22 \text{ H} &= 22 \times 1.0 = 22.0 \\
 11 \text{ O} &= 11 \times 16.0 = 176.0 \\
 \text{Total} &\quad 346.0 \text{ g/mol}
 \end{aligned}$$

$$\text{Moles of C}_{12}\text{H}_{22}\text{O}_{11} = ?$$

The molecular weight of the substance gives the conversion factor for the conversion of grams to moles. One mole of $\text{C}_6\text{H}_{12}\text{O}_6$ has a mass of 180 g.

$$\text{? mol C}_{12}\text{H}_{22}\text{O}_{11} = 2.24 \text{ g C}_{12}\text{H}_{22}\text{O}_{11} \times \frac{1 \text{ mol C}_{12}\text{H}_{22}\text{O}_{11}}{346 \text{ g C}_{12}\text{H}_{22}\text{O}_{11}} = 6.47 \times 10^{-3} \text{ mol}$$

Sample Problem 3.4. How many atoms are there in 755 g Na_2CO_3 ?

Solution:

Molar mass:

$$\begin{aligned}
 2 \text{ atoms Na} &= 2 \times 23.0 = 46.0 \\
 1 \text{ atom C} &= 1 \times 12.0 = 12.0 \\
 3 \text{ atoms O} &= 3 \times 16.0 = 48.0 \\
 6 \text{ atoms} &\quad 106.0 \text{ g/mol}
 \end{aligned}$$

$$\begin{aligned}
 \text{? atoms Na}_2\text{CO}_3 &= 755 \text{ g Na}_2\text{CO}_3 \times \frac{1 \text{ mol Na}_2\text{CO}_3}{106 \text{ g Na}_2\text{CO}_3} \times \frac{6.022 \times 10^{23} \text{ molecules Na}_2\text{CO}_3}{1 \text{ mol Na}_2\text{CO}_3} \times \frac{6 \text{ atoms Na}_2\text{CO}_3}{1 \text{ molecule Na}_2\text{CO}_3} \\
 \text{? atoms Na}_2\text{CO}_3 &= 2.57 \times 10^{25} \text{ atoms}
 \end{aligned}$$

3.3. Percentage Composition

The **percentage composition** of a compound can be readily calculated from the formula of the compound. The subscripts of a formula give the number of moles of each element in a mole of a compound. Using this information and the atomic weights of the elements, we will be able to obtain the number of grams of each element contained in a mole of the compound. The percentage of a given element is 100 times the mass of the element divided by the mass of a mole of the compound.

Given: Chemical Formula A₂B: 2 mol A and 1 mol B

% Composition:

$$\% \text{ A} = (\text{mass A} / \text{mass A}_2\text{B}) = [2(\text{atomic mass A}) / (\text{mass A}_2\text{B})] \times 100\%$$

$$\% \text{ B} = (\text{mass B} / \text{mass A}_2\text{B}) = [1(\text{atomic mass B}) / (\text{mass A}_2\text{B})] \times 100\%$$

Sample Problem 3.5. What is the percentage of Fe in Fe₂O₃?

Solution:

One mole of Fe₂O₃ contains

2 mol Fe = 2 (55.8) g Fe = 111.6 g Fe (55.8 is the atomic weight of Fe)

3 mol O = 3 (16.0) g O = 48.0 g O (16.0 is the atomic weight of O)

Total 159.6g (159.6 is the formula weight/molecular weight of Fe₂O₃)

So the percentage of Fe in Fe₂O₃ is:

$$\% \text{ Fe} = \frac{111.6 \text{ g Fe}}{159.6 \text{ g Fe}_2\text{O}_3} \times 100\% = 69.92\% \text{ Fe in Fe}_2\text{O}_3$$

$$\% \text{ Fe} = \frac{48.0 \text{ g O}}{159.6 \text{ g Fe}_2\text{O}_3} \times 100\% = 30.08\% \text{ O in Fe}_2\text{O}_3$$

Sample Problem 3.6. Nicotine is a compound that contains carbon, hydrogen and nitrogen. If a 2.50g of sample of nicotine is burned in oxygen, 6.78g of CO₂, 1.94g of H₂O, and 0.432g of N₂ are the products of combustion. What is the percentage composition of nicotine?

Solution:

First, we'll calculate the quantity of each element present in 2.50g sample of nicotine. We are given masses of CO₂, H and N₂. Nitrogen as an inert gas, its mass does not change. We need to solve the mass of C and H. In this case, the mass of CO₂ can be converted to the mass of C; while the mass of H₂O can be converted to the mass of H.

$$\text{?g C} = 6.78 \text{ g CO}_2 \times \frac{12 \text{ g C}}{44 \text{ g CO}_2}$$

$$\text{One mole of CO}_2: 1 \text{ C} = 12.0 \text{ g and } 2 \text{ O} = 2 \times 16.0 = 32; (12.0 + 32.0 = 44.0 \text{ g CO}_2)$$

$$\text{?g C} = 6.78 \text{ g CO}_2 \times \frac{12 \text{ g C}}{44 \text{ g CO}_2} = 1.85 \text{ g C}$$

$$\text{? g H} = 1.94 \text{ g H}_2\text{O}$$

$$\text{One mole H}_2\text{O}: 2 \text{ H} = 2(1.0) = 2 \text{ and } 1 \text{ O} = 16.0; (2 + 16.0 = 18.0 \text{ g H}_2\text{O})$$

$$\text{? g H} = 1.94 \text{ g H}_2\text{O} \times \frac{2 \text{ g H}}{18 \text{ g H}_2\text{O}} = 0.216 \text{ g H}$$

In a combustion such as the one described, the nitrogen does not combine with oxygen but is evolved as N₂. Hence the sample contained 0.432 g N.

So, the quantity of each element present in the 2.50g nicotine sample is used to determine the percentage composition of nicotine.

$$\text{? \% C} = \frac{1.85 \text{ g}}{2.50 \text{ g}} \times 100\% = 74.0\% \text{ C}$$

$$\text{? \% H} = \frac{0.216 \text{ g}}{2.50 \text{ g}} \times 100\% = 8.64\% \text{ H}$$

$$\text{? \% N} = \frac{0.432 \text{ g}}{2.50 \text{ g}} \times 100\% = 17.3\% \text{ N}$$

3.4. Derivation of Formulas

3.4.1. Empirical Formula

Empirical formula can be derived from the chemical analysis data of a compound. The analysis gives the proportion by mass of the elements that make up the compound. **Empirical formula** or the simplest formula indicates the atomic proportions of the compound – the relative numbers of atoms of various types that make up the compound.

Since a mole of atoms of an element contains the same number of atoms as a mole of atoms of any other element, the ratio by moles is the same as the ratio by atoms. The number of moles of each element present in a sample of the compound is obtained from the mass of each element present. The simplest whole-number ratio by moles (which is the same as the ratio by atoms) is used to write the empirical formula.

Steps in the Derivation of Empirical Formula

1. If the data are given in terms of percentage composition, base the calculation on a 100.0g sample of the compound. In this instance, the number of grams of each element present in the sample will be numerically equal to the percentage of that element present in the compound. There is no need to find percentages if the data are given in terms of the number of grams of each element present in a sample of the compound.
2. Convert the number of grams of each element present in the sample to the number of moles of atoms of each element. The conversion factors needed are derived from the fact that 1 mol of atoms of an element (numerator) is an atomic weight in grams (denominator).
3. Divide each of the values obtained in step 2 by the smallest value. If every number obtained in this way is not a whole number, multiply each number by the same simple integer in such a way that whole numbers will result.
4. A ratio by moles of atoms in the same as a ratio by atoms. The whole numbers obtained in step 3 are the subscripts of the empirical formula.

Given: % Mass A; % Mass B (100g Total)

$$\text{Given \% mass A} = \frac{\text{gA}}{\text{gA}} \times \frac{1 \text{ molA}}{\text{molA or molB (whichever is lower)}} = \text{whole number (Subscript of A)}$$

$$\text{Given \% mass B} = \frac{\text{gB}}{\text{gB}} \times \frac{1 \text{ molB}}{\text{molA or molB (whichever is lower)}} = \text{whole number (Subscript of B)}$$

Sample Problem 3.7. What is the empirical formula of a compound that contains: 43.6% P and 56.4% O?

Solution:

$$\begin{array}{ll} \text{mass P} = 43.6\% = 43.6 \text{ g} & \text{mass O} = 56.4\% = 56.4 \text{ g} \quad 100.0 \text{ g Total} \\ \text{Atomic Mass: P} = 31.0; & \text{O} = 16.0 \\ ? \text{ mol P} = 43.6 \text{ g P} \times \frac{1.0 \text{ mol P}}{31.0 \text{ g P}} = 1.41 \text{ mol; } ? \text{ mol O} = 56.4 \text{ g O} \times \frac{1.0 \text{ mol O}}{16.0 \text{ g O}} = 3.52 \text{ mol O} \end{array}$$

Mole Ratios

Is the ratio of the number of moles of A to the number of moles of B. The number of moles cancel giving a unitless quotient.

In the case of P and O, solving for the mole ratio, the one with the lower value is the denominator. P has 1.41 mol while O has 3.52 mol, use mol P as the denominator.

$$\text{P} = \frac{1.41 \text{ mol}}{1.41 \text{ mol}} = 1.00 \text{ (subscript of P);} \quad \text{O} = \frac{3.52 \text{ mol}}{1.41 \text{ mol}} = 2.50 \text{ (subscript of O)}$$

$\text{P}_1\text{O}_{2.5}$. Notice that subscripts should be whole numbers, however, O has a subscript of 2.5. We can get the whole number by multiplying both by 2.

$(\text{PO}_{2.5})_2 = \text{P}_2\text{O}_5$ is the empirical formula and the simplest whole-number ratio is 2 to 5.

Sample Problem 3.8. Caffeine, which occurs in coffee, tea and kola nuts is a stimulant for the central nervous system. A 1.261 g sample of pure caffeine contains 0.624g C, 0.065 g H, 0.364 g N and 0.208 g O. What is the empirical formula of caffeine?

Solution:

Given:

$$\begin{array}{ll} \text{Mass of sample} = 1.261 \text{ g} & \\ \text{Mass of C} = 0.624 \text{ g} & \text{Mass of H} = 0.065 \text{ g} \\ \text{Mass of N} = 0.364 \text{ g} & \text{Mass of O} = 0.208 \text{ g} \end{array}$$

Since the given are in terms of grams of each element present in the sample, there's no need to convert the data into percentages. We can readily calculate the number of moles of each element present in the sample:

$$\begin{array}{l} ? \text{ mol C} = 0.624 \text{ g C} \times \frac{1 \text{ mol C}}{12.0 \text{ g C}} = 0.052 \text{ mol C} \\ ? \text{ mol H} = 0.065 \text{ g H} \times \frac{1 \text{ mol H}}{1.0 \text{ g H}} = 0.065 \text{ mol H} \\ ? \text{ mol N} = 0.364 \text{ g N} \times \frac{1 \text{ mol N}}{14.0 \text{ g N}} = 0.026 \text{ mol N} \\ ? \text{ mol O} = 0.208 \text{ g O} \times \frac{1 \text{ mol O}}{16.0 \text{ g O}} = 0.013 \text{ mol O} \end{array}$$

Mole Ratios: O has the lowest number of moles:

$$\begin{array}{l} \text{C} = \frac{0.052 \text{ mol}}{0.013 \text{ mol}} = 4 \text{ (subscript of C)} \\ \text{H} = \frac{0.065 \text{ mol}}{0.013 \text{ mol}} = 5 \text{ (subscript of H)} \\ \text{N} = \frac{0.026 \text{ mol}}{0.013 \text{ mol}} = 2 \text{ (subscript of N)} \\ \text{O} = \frac{0.013 \text{ mol}}{0.013 \text{ mol}} = 1 \text{ (subscript of O)} \end{array}$$

Therefore, the empirical formula for caffeine is, C₄H₅N₂O.

3.4.2. Molecular Formula

The **molecular formula** of a substance gives the number and type of each atom in a molecule of a substance. The molecular formula of a substance can be derived from the empirical formula if the molecular weight of the compound is given or known.

Deriving the chemical formula follows through the process of deriving the empirical formula of the unknown substance. The resulting ratio of the actual molecular given (given in the problem) to the formula weight of the empirical formula is multiplied to the subscripts of the empirical formula.

Sample Problem 3.9. In our sample problem 6.7, what is the molecular formula of the oxide of phosphorus that has the empirical formula of P₂O₅, if the molecular weight of this compound is 284?

Solution:

Formula weight of the empirical formula: P = 31.0 ; O = 16.0

$$FW = (2)(31.0) + (5)(16.0) = 62.0 + 80.0 = 142.0 \text{ g/mol}$$

$$\text{Ratio} = \frac{284 \text{ g/mol}}{142 \text{ g/mol}} = 2, \text{ so } (P_2O_5)2 = P_4O_{10} \text{ is the molecular formula.}$$

Sample Problem 3.10. In sample problem 6.8, the molecular weight of caffeine is 194 and the empirical formula of caffeine is C₄H₅N₂O. What is the empirical formula of caffeine?

Solution:

Formula weight of the empirical formula:

$$4C = (4)(12.0) = 48.0$$

$$5H = (5)(1.0) = 5.0$$

$$2N = (2)(14.0) = 28.0$$

$$1O = (1)(16.0) = 16.0$$

$$97.0 \text{ g/mol}$$

$$\text{Ratio} = \frac{194}{97.0} = 2; \text{ so } (C_4H_5N_2O)2 = C_8H_{10}N_4O_2 \text{ is the molecular formula for caffeine.}$$

Sample Problem 3.11. Glucose a simple sugar, is a constituent of human blood and tissue fluids and a principal source of energy for cells. The compound contains 40.0% C, 6.73% H and 53.3% and has a molecular weight of 180.2. What is the molecular formula of glucose?

Solution:

Deriving the empirical formula:

$$? \text{ mol C} = 40.0\% \text{ C} = 40.0 \text{ g-C} \times \frac{1 \text{ mol C}}{12 \text{ g-C}} = 3.33 \text{ mol C}$$

$$? \text{ mol H} = 6.73\% \text{ H} = 6.73 \text{ g-H} \times \frac{1 \text{ mol H}}{1 \text{ g-H}} = 6.73 \text{ mol H}$$

$$? \text{ mol O} = 53.3\% \text{ O} = 53.3 \text{ g-O} \times \frac{1 \text{ mol O}}{16 \text{ g-O}} = 3.33 \text{ mol O}$$

Mole ratios: The lowest value is 3.33.

$$C = \frac{3.33}{3.33} = 1; \quad H = \frac{6.73}{3.33} = 2.02 \approx 2; \quad O = \frac{3.33}{3.33} = 1, \text{ the empirical formula is CH}_2\text{O.}$$

Deriving the molecular formula:

$$\begin{aligned}1\text{C} &= (1)(12.0) = 12.0 \\2\text{H} &= (2)(1.0) = 2.0 \\1\text{O} &= (1)(16.0) = 16.0 \\&\quad \quad \quad 30.0 \text{ g/mol}\end{aligned}$$

Ratio = $\frac{180.2}{30.0} = 6.00$, so the molecular formula is $(\text{CH}_2\text{O})_6 = \text{C}_6\text{H}_{12}\text{O}_6$.

Therefore the empirical formula is CH_2O and the formula weight is:

$$\text{C} = 1 \times 12.0 = 12.0$$

$$\text{H} = 2 \times 1.0 = 2.0$$

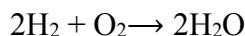
$$\text{O} = 1 \times 16.0 = 16.0$$

$$\quad \quad \quad 30.0 \text{ g/mol}$$

Ratio = $\frac{180.2}{30.0} = 6.0$; therefore multiplying each atom by 6 gives $\text{C}_6\text{H}_{12}\text{O}_6$ as the molecular formula.

3.5. Problems Based on Chemical equations (Mass-mass Relationship)

A chemical equation can be interpreted in so many different ways. The chemical equation for example:



On the simplest level, it shows that hydrogen reacts with oxygen producing water. On the atomic-molecular level, it states:



If we consider 2 N molecules of hydrogen, where N is Avogadro's number which is equal to 6.023×10^{23} . Then,



Avogadro's number of molecules is one mole of molecules. The equation can also be read as:



The last interpretation is the one that will enable us to solve stoichiometric problems. The coefficients of the chemical equation give the ratios, by moles, in which the substances react and are produced. According to the equation, then:

2 mol of H_2 reacts with 1 mol of O_2 ,

10 mol of H_2 would require 5 mol O_2 ,

There are three steps in the solution to a problem where the quantities of substances are expressed in grams instead of moles.

1. The amount of the substance given in the problem is converted from grams to moles by using the formula weight of the substance.
2. The stoichiometric ratio derived from the coefficients of the chemical equation (which is a mole ratio) is used to convert the moles of substance given into the moles of substance sought.
3. The value for moles of a substance sought is converted into grams of substance sought by using the formula weight of the substance sought.

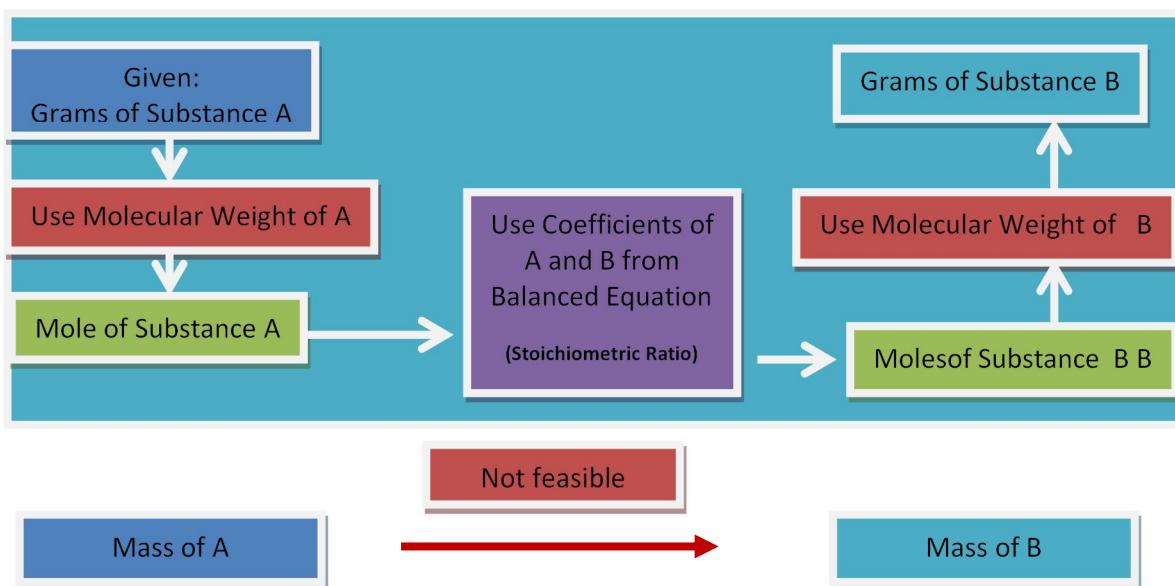


Figure 3.2. Interconversion Process from Mass of Substance A to Mass of Substance B

Sample Problem 3.12. Chlorine can be prepared by the reaction:



- How many grams of HCl are required to react with 25.0 g of $\text{MnO}_{2(s)}$?
- How many grams of Cl_2 are produced by the reaction?

Solutions:

First, let us balance the equation:



Atomic Mass:

$$\text{Mn} = 55.0; \text{ O} = 16.0; \text{ Cl} = 35.5; \text{ H} = 1.0$$

$$\text{a). ? g HCl} = 25.0 \text{ g MnO}_2$$

Mass of MnO_2 (substance A) is given and the mass of HCl (substance B) is sought. So let us concentrate on them.



The stoichiometric relationship (SR) between A and B: 1 mol $\text{MnO}_2 \approx 4$ mol HCl

Molar Mass:

$$\text{HCl} = (1.0) + (35.5) = 36.5 \text{ g/mol}$$

$$\text{MnO}_2 = (55.0) + (2)(16.0) = 55.0 + 32.0 = 87.0 \text{ g/mol}$$

$$\text{? g HCl} = 25.0 \text{ g MnO}_2 \times \frac{1 \text{ mol MnO}_2}{87.0 \text{ g MnO}_2} \times \frac{4 \text{ mol HCl}}{1 \text{ mol MnO}_2} \times \frac{36.5 \text{ g HCl}}{1 \text{ mol HCl}} = 42.0 \text{ g HCl}$$

Mass A Molar Mass A SR Molar Mass B Mass B
 b). Follow the same procedure as in a:



The stoichiometric relationship (SR) between (A) MnO_2 and (B) Cl_2 : 1 mol $\text{MnO}_2 \approx 1$ mol Cl_2

Molar Mass:

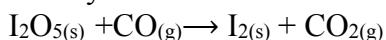
$$\text{MnO}_2 = (55.0) + (2)(16.0) = 55.0 + 32.0 = 87.0 \text{ g/mol}$$

$$\text{Cl}_2 = (2)(35.5) = 71.0 \text{ g/mol}$$

$$\text{? g Cl}_2 = 25.0 \text{ g MnO}_2 \times \frac{1 \text{ mol MnO}_2}{87.0 \text{ g MnO}_2} \times \frac{1 \text{ mol Cl}_2}{1 \text{ mol MnO}_2} \times \frac{71.0 \text{ g Cl}_2}{1 \text{ mol Cl}_2} = 20.4 \text{ g Cl}_2$$

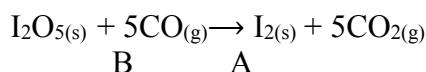
Mass A Molar Mass A SR Molar Mass B Mass B

Sample Problem 3.13. The amount of carbon monoxide in a sample of a gas can be determined by the reaction:



If a gas sample liberates 0.192 g of I₂, how many grams of CO were present in the sample?

Solution:



Stoichiometric relationship: 5 mol CO \approx 1 mol I₂

Atomic Mass:

$$\text{I} = 127.0; \quad \text{C} = 12.0; \quad \text{O} = 16.0$$

Molar Mass:

$$\text{I}_2 = (2)(127.0) = 254.90 \text{ g/mol}$$

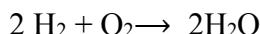
$$\text{CO} = (12.0) + (16.0) = 28.0 \text{ g/mol}$$

$$\text{? g CO} = 0.192 \text{ g I}_2 \times \frac{1 \text{ mol I}_2}{254.9 \text{ g I}_2} \times \frac{5 \text{ mol CO}}{1 \text{ mol I}_2} \times \frac{28.0 \text{ g CO}}{1 \text{ mol CO}} = 0.106 \text{ g CO}$$

Mass A Molar Mass A SR Molar Mass B Mass B

3.6. Limiting Reactants

In some problems, quantities are given for two or more reactants. For example, we are asked how much H₂O can be prepared from 2 mol of H₂ and 2 mol of O₂. The chemical equation is shown,



It shows that 2 mol of H₂ will react with only 1 mol of O₂. However, in the problem, 2 mol H₂ and 2 mol O₂ are given indicating that more O₂ has been supplied than can be used. When all of the H₂ has been consumed, reaction will stop. It is at this point where only 1 mol of O₂ has been consumed and 1 mol of O₂ remained unreacted. The amount of H₂ supplied limits the reaction and determines how much H₂O will be formed. Hydrogen, therefore is the **limiting reactant**.

Limiting reactant is the reactant that is completely consumed in a reaction. The other reactants are called sometimes as **excess reactants**. In our example H₂ is the limiting reactant, meaning that once all the H₂ has been used up, the reaction stops. O₂ is the excess reactant with some leftover when reaction stops.

Whenever the quantities of two or more reactants are given in a problem, we must determine which one limits the reaction before the problem can be solved.

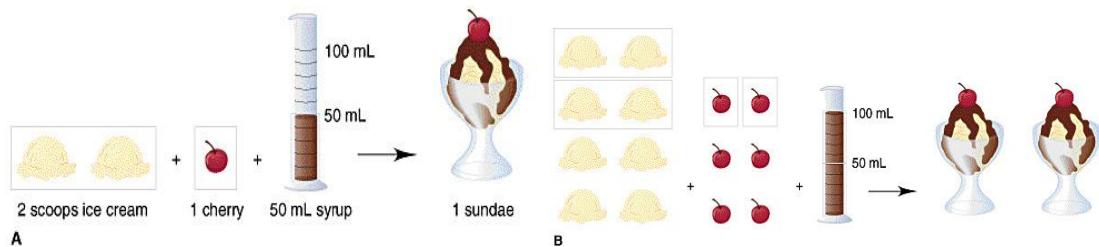
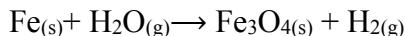


Figure 3.3. An Ice Cream – Sundae Analogy for Limiting Reactions

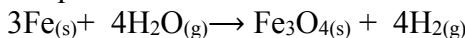
In Figure 3.3. A, to make one sundae, you need 50 mL of syrup, one cherry and two scoops of ice cream. In figure 3.3. B, you have ten scoops of ice cream, 100 mL of syrup, six cherries. You can only make two sundaes for 100 mL syrup. Meaning you have excess four cherries and four scoops of ice cream. Thus, the limiting reactant is the syrup.

Sample Problem 3.14. How many moles of H₂ can be theoretically prepared from 4.00 mol of Fe and 5.00 mol of H₂O? The chemical equation for the reaction is:



Solution:

First, let us balance the equation.

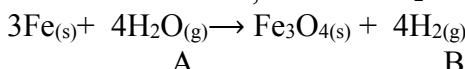


Solve for the mole ratios:

$$\text{Fe mole ratio} = \frac{\text{no. of moles given in the problem}}{\text{no. of moles in a balanced equation}} = \frac{4.00 \text{ mol Fe}}{3.00 \text{ mol Fe}} = 1.33$$

$$\text{H}_2\text{O mole ratio} = \frac{\text{no. of moles given in the problem}}{\text{no. of moles in a balanced equation}} = \frac{5.00 \text{ mol H}_2\text{O}}{4.00 \text{ mol H}_2\text{O}} = 1.25$$

H₂O has lower mole ratio than that of Fe, therefore H₂O is the limiting reactant.



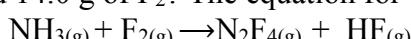
Stoichiometric Relationship: 4 mol H₂O ≈ 4.00 mol H₂

Solving for the moles of H₂, let us start with the H₂O as the limiting reactant:

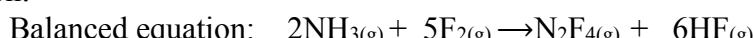
$$? \text{ mol H}_2 =$$

$$\begin{array}{ccc} ? \text{ mol H}_2 & = 5.00 \text{ mol H}_2\text{O} \times \frac{4.00 \text{ mol H}_2}{4.00 \text{ mol H}_2\text{O}} & = 5.00 \text{ mol H}_2 \\ \text{Mol A} & \text{SR} & \text{Mol B} \end{array}$$

Sample Problem 3.15. How many grams of N₂F₄ can be theoretically prepared from 4.00 g NH₃ and 14.0 g of F₂? The equation for the chemical reaction is:



Solution:



Converting mass to moles:

$$\text{Atomic mass: N} = 14.0; \quad \text{H} = 1.00; \quad \text{F} = 19.00$$

Molar Mass:

$$\text{NH}_3: (14.0) + (3)(1.00) = 14.0 + 3.00 = 17.0 \text{ g/mol}$$

$$\text{F}_2: (2)(19.0) = 38.0 \text{ g/mol}$$

$$\text{N}_2\text{F}_4: (2)(14.0) + (4)(19.0) = 28.0 + 76.0 = 104 \text{ g/mol}$$

Mass:

$$\text{NH}_3 = 4.00 \text{ g}; \text{F}_2 = 14.0 \text{ g}$$

Determining the limiting reactant:

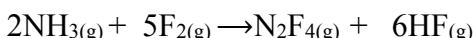
$$? \text{ mol NH}_3 = 4.00 \text{ g NH}_3 \times \frac{1.00 \text{ mol NH}_3}{17.0 \text{ g NH}_3} = 0.235 \text{ mol NH}_3$$

$$? \text{ mol F}_2 = 14.0 \text{ g F}_2 \times \frac{1.00 \text{ mol F}_2}{38.0 \text{ g F}_2} = 0.368 \text{ mol F}_2$$

Solving for mole ratios:

$$\text{NH}_3 = \frac{0.235}{2} = 0.118 \quad ; \quad \text{F}_2 = \frac{0.368}{5} = 0.0735$$

F₂ has lower mole ratio, therefore the limiting reactant.



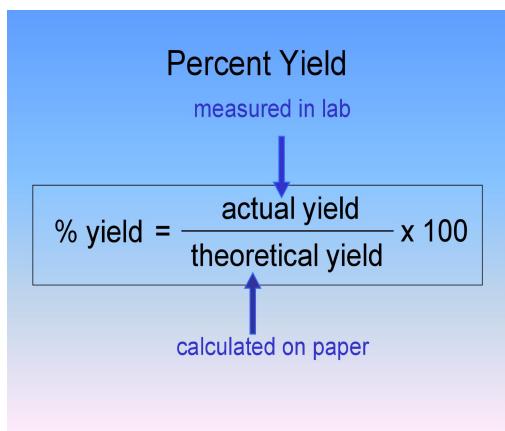


Solving for the mass of N₂F₄(B):

$$? \text{ g N}_2\text{F}_4 = 14.0 \text{ g F}_2 \times \frac{1.00 \text{ mol F}_2}{38.0 \text{ g F}_2} \times \frac{1.00 \text{ mol N}_2\text{F}_4}{5.00 \text{ mol F}_2} \times \frac{104 \text{ g N}_2\text{F}_4}{1.00 \text{ mol N}_2\text{F}_4} = 7.66 \text{ g N}_2\text{F}_4$$

Mass A Molar Mass A SR Molar Mass B Mass B

3.7. Percent Yield



The quantity of product calculated to form when all of the limiting reactant reacts is the **theoretical yield**. The amount of the product which is actually obtained in a reaction is called the **actual yield**. In all cases, actual yield is always less than the theoretical yield. It can never be greater than theoretical yield. There are so many reasons for this difference. Some parts of the reactants may not react, or they may react to in a way different from that desired. Additionally, it is not always possible to recover all of the reaction product from the reaction mixture. The **percent yield** of a reaction relates the actual yield to the theoretical (calculated) yield.

$$\text{Percent yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100\%$$

Sample Problem 3.16. If 4.80 g of N₂F₄ is obtained from the experiment in the above problem. What is the percent yield?

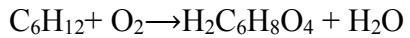
Solution:

The theoretical or calculated yield based on the previous example is 7.66 g. The actual yield is 4.80g. Then the percent yield, therefore:

$$\text{Percent yield} = \frac{4.80 \text{ g}}{7.66 \text{ g}} \times 100\% = 62.7\%$$

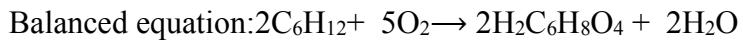
Sample Problem 3.17. Adipic acid, H₂C₆H₈O₄, is a material used for the production of nylon.

It is made commercially by a controlled reaction between cyclohexane, C₆H₁₂ and O₂:



Assume that you carryout this reaction starting with 25.0 g cyclohexane, and that cyclohexane is the limiting reactant, a) what is the theoretical yield of adipic acid? b) If you obtain 33.5 g of adipic acid from your reaction, what is the percent yield of adipic acid?

Solutions:



Molar Mass:

Cyclohexane (C₆H₁₂) = 84.0 g

Adipic acid (H₂C₆H₈O₄) = 146.0 g

Cyclohexane (C₆H₁₂) is the limiting reactant.

a). Stoichiometric relationship (SR): $2 \text{ mol C}_6\text{H}_{12} \approx 2 \text{ mol H}_2\text{C}_6\text{H}_8\text{O}_4$

$$\frac{? \text{ g H}_2\text{C}_6\text{H}_8\text{O}_4}{\text{Mass A}} = \frac{25.0 \text{ g C}_6\text{H}_{12}}{\text{Molar Mass A}} \times \frac{1.00 \text{ mol C}_6\text{H}_{12}}{84.0 \text{ g C}_6\text{H}_{12}} \times \frac{2.00 \text{ mol H}_2\text{C}_6\text{H}_8\text{O}_4}{2.00 \text{ mol C}_6\text{H}_{12}} \times \frac{146.0 \text{ g H}_2\text{C}_6\text{H}_8\text{O}_4}{1.00 \text{ mol H}_2\text{C}_6\text{H}_8\text{O}_4} = \frac{43.5 \text{ g}}{\text{Mass B}}$$

b). Percent Yield:

$$\text{Percent Yield} = \frac{33.5 \text{ g}}{43.5 \text{ g}} \times 100\% = 77.0\%$$

Take note that actual yield is always smaller than the theoretical yield.

PROGRESS CHECK:

- 3.1. How many moles and how many molecules are there in 750g of
 a) H₂ b) H₂O c) H₂SO₄? How many atoms?
- 3.2. Determine the mass in grams of
 a) 3.0×10^{20} O₂ molecules b) 3×10^{-3} mol O₂
- 3.3. Arrange the following formula in terms of increasing percentage of Sulfur
 i. a) CaSO₄ b) SO₂ c) H₂S d) Na₂S₂O₃
 ii. a) BaSO₄ b) SO₃ c) H₂SO₄ d) Na₂SO₄
- 3.4. Arrange the following formulas in order of increasing percentage of nitrogen
 a) NaNO₃ b) NH₃ c) NO₂ d) NH₄NO₃
- 3.5. What mass of lead is theoretically obtained from 15.0 kg galena ore that is 72% PbS?
- 3.6. Graphite is the crystalline form of carbon used in “lead pencils”. How many moles of carbon are in 315 mg of graphite?
- 3.7. How many grams of phosphorus and of oxygen are theoretically needed to make 6.000 g P₂O₅?
- 3.8. The mineral hematite is Fe₂O₃. Hematite ore contains unwanted material called gangue, in addition to Fe₂O₃. If 5.000 kg of ore contains 2.7845 g of Fe, what percentage of the ore is Fe₂O₃?
- 3.9. Cinnamaldehyde, a compound found in cinnamon oil, contains carbon, hydrogen and oxygen. The combustion of 6.50g sample of the compound yields 19.49 g CO₂, and 3.54 g H₂O. What is the percentage composition of cinnamaldehyde?
- 3.10. Silver sulfide, Ag₂S, occurs in nature as the mineral argentite, which is an ore of silver. How many grams of silver are theoretically obtainable from 250.0 g of an impure ore that is 70.00% Ag₂S?
- 3.11. Myristic acid, obtained from coconut oil is 73.61% C, 12.38% H and 14.01% O. What is the empirical formula of myristic acid? (C₇H₁₄O)
- 3.12. The molecular weight of saccharin is 183.18 and the compound is 45.90% C, 2.75% H, 26.20% O, 17.50% S and 7.65% N. What is the molecular formula of saccharin? (C₇H₅O₂SN)
- 3.13. Vanillin, the active flavoring agent of vanilla bean contains 63.14% C, 5.31% H, and 31.55% O. What is the empirical formula of vanillin? (C₈H₈O₃)
- 3.14. The molecular weight of cholesterol is 386 and the compound contains 83.9% C, 12% H and 41% O. What is the molecular formula of cholesterol?
- 3.15. Styrene, a compound substance used to make a Styrofoam cup and insulation, contains 92.3% C, and 7.7 % H by mass and has a molecular weight of 106. What is the molecular formula?

- 3.16. Caffeine, a stimulant found in coffee, contains 49.5% C; 5.15% H; 28.9% N and 16.45% O by mass and has a molecular weight of 195. What is its molecular formula?
- 3.17. Monosodium Glutamate (MSG) a flavor enhancer in certain foods contains 35.51% C, 4.7% H, 37.85% O, 8.29% N and 13.60% Na and has a molecular weight of 169. What is the molecular formula of monosodium glutamate?
- 3.18. A combustion analysis of toluene, a common organic solvent gives 5.86 g CO₂ and 1.37 mg H₂O. If the compound contains only C and H, what is the empirical formula?
- 3.19. Menthol, a substance we can smell in mentholated cough drops, is composed of C, H and O. A 0.1005-g sample of menthol is combusted, producing 0.2829 g CO₂, and 0.1159 g H₂O. What is the empirical formula for the menthol? If the compound has a molecular weight of 156, what is its molecular formula?
- 3.20. Nicotine, a component of tobacco, is composed of C, H and N. A 5.20-mg sample of nicotine was combusted producing 14.242 mg CO₂ and 4.083 mg H₂O. What is the molecular formula of nicotine if the substance has a molecular weight of 160.0?
- 3.21. How many carbon atoms are there in a 1.00 carat diamond? Diamond is pure carbon and one carat is exactly 0.20g.
- 3.22. How many grams of sulfuric acid, H₂SO₄ must be taken in order to get 0.25 mol of H₂SO₄?
- 3.23. 4.92 g hydrated magnesium sulfate crystals (MgSO₄·xH₂O) gave 2.40 g of anhydrous magnesium sulfate on heating to a constant mass. Determine the value of x.
- 3.24. What is the maximum number of grams of NH₄SCN_(s) that can be prepared from 9.00 g of CS_{2(l)} and 3.00 g of NH_{3(g)}? The equation for the reaction is:

$$\text{CS}_{2(l)} + 2\text{NH}_{3(g)} \rightarrow \text{NH}_4\text{SCN}_{(s)} + \text{H}_2\text{S}_{(g)}$$
 (ans: 6.71 g NH₄SCN_(s))
- 3.25. Consider the reaction Al_(s) + Cl_{2(g)} → AlCl_{3(s)}. a mixture of 1.5 mol of Al and 3.0 mol of Cl₂ are allowed to react. a.) what is the limiting reactant? b) how many moles of AlCl₃ are formed?
- 3.26. A strip of zinc metal weighing 2.00 g is placed in an aqueous solution containing 2.50 g of silver nitrate, causing the following reaction to occur:

$$\text{Zn}_{(s)} + \text{AgNO}_{3(aq)} \rightarrow \text{Ag}_{(s)} + \text{Zn(NO}_3)_2{}_{(aq)}$$

 a) Which is the limiting reactant?
 b) How many grams of Ag will form?
 c) How many grams of Zn(NO₃)₂ will form?
 d) How many grams of the excess reactants will be left at the end of the reaction?
- 3.27. A student reacts benzene, C₆H₆, with bromine, Br₂, to prepare bromobenzene, C₆H₅Br:

$$\text{C}_6\text{H}_6 + \text{Br}_2 \rightarrow \text{C}_6\text{H}_5\text{Br} + \text{HBr}$$

 a) What is the limiting reactant?
 b) What is the theoretical yield of bromobenzene in this reaction when 30.0 g of benzene reacts with 65.0 g of bromine? 60.3 g

- c) If the actual yield of bromobenzene was 56.7 g, what was the percentage yield?(94%)
- 3.28. Marble (calcium carbonate) reacts with hydrochloric acid solution to form calcium chloride solution, water and carbon dioxide. Find the percent yield of carbon dioxide if 3.65 g is collected when 10.0 g of marble reacts.
- 3.29. When 56.6 g of calcium and 30.5 g nitrogen gas undergo a reaction that has a 93.0% yield, what mass (g) of calcium nitride is formed?
- 3.30. Silicon Carbide is an important ceramic material made by reacting sand (silicon dioxide, SiO_2) with powdered carbon at a high temperature. Carbon monoxide is also formed. When 100.0 kg of sand is processed, 51.4 kg of SiC is recovered. What is the percent yield of SiC from this process?

TOPICS: ELECTRONIC STRUCTURE OF ATOMS

- 4.1. Dalton's Atomic Theory
- 4.2. Postulates of the Atomic Theory
 - 4.2.1. The Law of Conservation of Mass
 - 4.2.2. The Law of Definite Composition
 - 4.2.3. Law of Multiple Proportions
- 4.3. The Electron
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- 4.4. The Proton
- 4.5. The Neutron
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 - 4.10.1.1. The Wave nature of Light
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- 4.11. Quantum Numbers
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 - 4.11.2. Pauli's Exclusion Principle
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- 4.15. Electronic Configuration and the Periodic Table
- 4.16. Property Trends
 - 4.16.1. Atomic Size Trend
 - 4.16.2. Ionization Energy
 - 4.16.3. Electron Affinity
- 4.17. Electronic Configuration of Ions
 - 4.17.1. Main Group Ions

EXPECTED COMPETENCIES:

At the end of the lesson, you must have:

- a. listed, defined, and described the three quantum numbers and know what possible combinations of quantum numbers are allowed;
- b. stated the atomic orbital names based on quantum numbers;

- c. applied the Aufbau principle to determine the configuration for any atom or ion;
- d. related the electronic configuration to the of an atom of an element to its position on the periodic table;
- e. applied Hund's rule to determine electron configuration using an orbital diagram (electrons in individual orbitals with spins);
- f. defined the term 'electron configuration';
- g. written the electron configurations for the elements of the periodic table;
- h. demonstrated how electron orbitals are filled in accordance with Aufbau Principle, Pauli's Exclusion Principle and Hund's Rule;
- i. described the structure of the atom;
- j. stated the location, relative charge, and atomic mass of the sub-atomic particles; and
- k. defined atomic number.

CONTENTS/ TECHNICAL INFORMATION

4.1. Dalton's Atomic Theory

It was in the fifth century B.C., when Leucippus and Democritus believed matter is subdivided into smallest particle, atom – an indivisible particle and is derived from the Greek word “atomos” meaning “uncut”. However, the theory about the atom was rejected by Aristotle in the fourth century B.C, as he believed as matter to be endlessly divided into smaller particles.

For approximately two centuries, the atomic theory remained just a mere speculation. It was until Robert Boyle in his book The Sceptical Chymist, published in 1661, and by Sir Isaac Newton in his books Principia, and Opticks published in 1687 and 1704, respectively where they finally recognized atoms and its existence.

John Dalton made a name in the history of chemistry for proposing the atomic theory which he developed from 1803 to 1808 and presented it in his book A New System of Chemical Philosophy (Part I – 1808 and Part II – 1810).

Dalton's atomic theory explains the laws governing a chemical change and a quantitative concept of assigning relative masses to the atoms of different elements.

4.2. Postulates of the Atomic Theory

1. All matter is made up of tiny indivisible particles of an element called atom.
2. All atoms of the same element are identical in mass, size and other properties alike, and atoms of different elements are also in mass, size and other properties.
3. Since atoms cannot be divided, atoms can never be created nor destroyed in a chemical reaction it can only combine with another element to form a new substance.
4. Atoms can be rearranged or combined with other elements to form a compound in a fixed whole number ratios.

The limitations of the Dalton's postulates include:

1. Exclusion of subatomic particles.
2. Isotopes and isobars were not considered.
3. Certain complex organic compounds do not observe the simple ratios of the atoms
4. It cannot explain the allotropes

4.2.1. The Law of Conservation of Mass

Referring to the definition of an atom as an indivisible tiny particle and as per Dalton's postulate, this atom cannot be created nor destroyed, much more that it cannot be converted into another atom, the law of conservation of mass states that in a chemical reaction, the total mass of substances produced (products) will always be equal to the total mass of the entering substances (reactants) whether the atoms undergo combination or decomposition.

It was Lavoisier who first experimented mercury with oxygen and found out that the mass of mercury plus the mass of oxygen in the reactant and the mass of mercuric oxide produced are always equal.

Let's take water, H_2O , for example:

| | | | |
|---------------------|----------------------------------|----------------|----------------------------------|
| Formation reaction: | | | |
| For one mole of: | H_2 | + O_2 | $\rightarrow \text{H}_2\text{O}$ |
| Mass is | 2 g | 16 g | 18 g |
| | Total mass of reactants (before) | | Total mass of product |
| (after) | | 18 g | 18 g |

4.2.2. The Law of Definite Composition

The law of definite composition or the **Proust Law** (in honor of Joseph Proust) states that chemical compounds always contain the same elements combined in the same exact proportion by mass.

Consider again water, it is composed of two elements, hydrogen and oxygen. The following results are obtained from a mass analysis of 10.00g of water:

| Analysis by Mass (grams/10.0g) | Mass Fraction (parts/1.00part) | Percent by Mass (parts/100parts) |
|-----------------------------------|-----------------------------------|-------------------------------------|
| 1.11g hydrogen | 0.111 hydrogen | 11.1% hydrogen |
| 8.89g oxygen | 0.889 oxygen | 88.9% oxygen |
| ----- | ----- | ----- |
| 10.00g | 1.000 part by mass | 100.0% by mass |

Solving for the mass of the element in the sample:

$$\text{Mass of element in sample} = \text{mass of compound in sample} \times \frac{\text{mass of element in compound}}{\text{mass of compound}}$$

Sample Problem 4.1. Pitchblende is the most important compound of uranium. Mass analysis of an 82.4-g sample shows that it contains 71.4g uranium, with oxygen the only other element. How many grams of uranium are in 102kg of pitchblende?

Solution:

Solving for the mass (kg) of uranium in 102kg of pitchblende:

$$\text{Mass (g) of pitchblende} = 102\text{kg} \times \frac{1000\text{ g}}{1\text{ kg}} = 1.02 \times 10^5\text{ g}$$

$$\text{Mass (g) uranium} = \text{mass (g) of pitchblende} \times \frac{\text{mass (g) uranium in pitchblende}}{\text{mass (g) of pitchblende}}$$

$$= 1.02 \times 10^5 \text{ g pitchblende} \times \frac{71.4 \text{ kg uranium}}{84.2 \text{ g pitchblende}} = 8.65 \times 10^4 \text{ g uranium}$$

Sample Problem 4.2. How many metric tons (t) of oxygen in a sample of pitchblende that contains 2.3 tons (t) of uranium?

Solution:

Pitchblende is composed of uranium and oxygen.

$$\text{Mass (t) pitchblende} = 2.3 \text{ t uranium} \times \frac{84.2 \text{ t pitchblende}}{71.4 \text{ t uranium}} = 2.7 \text{ t pitchblende}$$

$$\text{Mass (t) oxygen} = 2.7 \text{ t pitchblende} \times \frac{(84.2 \text{ t pitchblende} - 71.4 \text{ t uranium})}{84.2 \text{ t pitchblende}} = 0.41 \text{ t oxygen}$$

4.2.3 Law of Multiple Proportions

The **law of multiple proportions** states that “when two elements react to form more than one compounds, the amount of one element that combined with the fixed amount of the other can be expressed as a ratio of small whole numbers”.

Carbon for instance, can form two compounds with oxygen; carbon monoxide and carbon dioxide. In carbon monoxide, one atom of oxygen combined with one atom of carbon, and in carbon dioxide, two atoms of oxygen combined with one atom of carbon. These compounds have very different properties. Carbon monoxide is a deadly gas produced from the incomplete combustion of carbon containing materials while carbon dioxide is not. It is used for putting out fire (as CO₂ fire extinguisher).

Mass analysis shows the following:

Carbon Monoxide; 57.1% by mass oxygen and 42.9% by mass carbon

Carbon Dioxide: 72.7% by mass oxygen and 27.3% by mass carbon

| | Carbon Monoxide | Carbon Dioxide |
|-----------------------------------|----------------------------|----------------------------|
| Mass, g oxygen/100 g compound | 57.1 | 72.7 |
| Mass, g carbon/100 g compound | 42.9 | 27.3 |
| Mass, (g) oxygen/Mass, (g) carbon | $\frac{57.1}{42.9} = 1.33$ | $\frac{72.7}{27.3} = 2.66$ |

If we will have to divide the mass of oxygen per gram of carbon in carbon dioxide by that in carbon monoxide, we will obtain a ratio of small whole numbers:

$$\frac{2.66 \text{ g oxygen}}{1.33 \text{ g oxygen}} \frac{\text{carbon in carbon dioxide}}{\text{carbon in carbon monoxide}} = \frac{2}{1}$$

So, the ratio of oxygen in the two compounds (CO and CO₂) is 1:2, a small whole number ratio.

4.3. The Electron

As part of the limitations the Dalton's postulates, Dalton's model of the atom, representing the atom viewed as a tiny, indivisible particle, like that of minute billiard ball, the existence of subatomic particles was not predicted. The discovery of electrons and the atomic nucleus followed years after experiments that led to their discovery were conducted.

Investigations were conducted discovering the nature of electric current by allowing current to pass through a vacuum glass tube fitted with two metal electrodes that led to the discovery of cathode rays by Julius Plücker in 1859. The rays were called **cathode rays** because they originated at the negative electrode (cathode) moving towards the positive electrode (anode).

A conclusion was made after several observations of the properties of cathode rays confirming these cathode rays consist mainly of negatively charged particles present in all matter. The rays appear when these particles are in collision with the few remaining gas molecules in the vacuum tube. Cathode ray particles were later on called **electrons**.

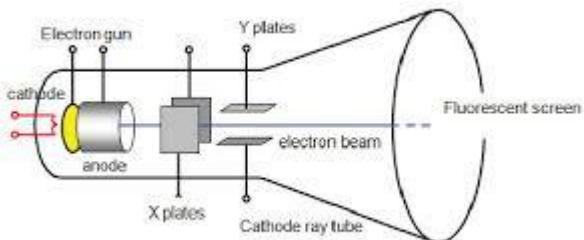


Figure 4.1. Cathode Ray



Figure 4.2. The Electron

4.3.1. Mass and Charge of the Electron

Charge/Mass Ratio

In 1897, British Physicist, J.J. Thomson (1856-1940) was able to the value of q/m , the ratio of the mass of a cathode ray particle to its charge. His experiment resulted to the value of q/m which is -1.7588×10^8 C/g (coulomb/gram). The coulomb is the SI unit of electric charge. One coulomb is the quantity of charge passing through a given point in an electric circuit in one second at one ampere current.

Charge, in 1909, Robert A. Millikan, performed the first precise measurement of the electron by observing the movement of oil droplets in an apparatus containing electrically charged plates and an x-ray source, known as the Millikan Oil Drop experiment. Very small drops of oil pick up electrons acquiring electric charge. The oil drops are allowed to settle between two horizontal plates determining the mass of a particular drop by measuring its rate of fall.

Once the plates are being charged, it altered the rate of fall of the drop due to the attraction of the negatively charged drop to the upper positive plate. The amount of charged on the plates were adjusted so that the drop will stop falling and remain suspended. The charge on the drop is then calculated from the mass of the drop and the charge on the plates after making adjustments. If different oil droplets picked up different number of electrons and he reasoned that this minimum charge must be the charge of the electron itself. The value he calculated is the $-e = q$ called a unit electrical charge. The electron then has a unit negative charge, $-e$, -1.602×10^{-19} C (coulomb).

Mass, calculating the mass of the electron from the value of q/m or $\frac{-e}{q/m}$:

$$\text{Mass of electron} = \frac{-1.6022 \times 10^{-19} C}{-1.7588 \times 10^8 C/g} = 9.1096 \times 10^{-28} \text{ g}$$

4.4. The Proton

The discovery of the electrons gave the scientist the idea that electrons are present in all matter and that many raised questions about its structure when in fact matter and atoms are neutral. Scientists were puzzled on the atom containing a negatively charge particle. If that is so, there must be a positively charge something within the atom that balances the charges causing it to become neutral.

In 1910, Ernest Rutherford (1871-1937) tested the plum-pudding model – spherical atom composed of diffuse positively charged matter with electrons embedded like “raisin in a plum pudding” proposed by Thomson and obtained an unexpected result.

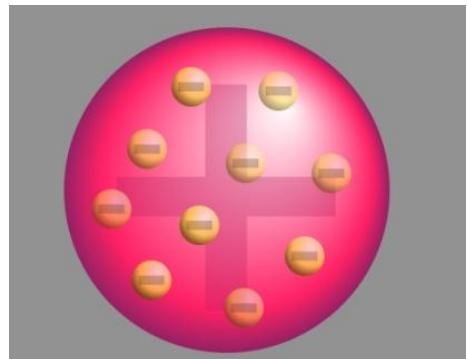


Figure 4.3. The Plum-Pudding Model
Provided courtesy of the Wikipedia Commons

The experimental set-up, where a tiny, dense, positively charged alpha (α) particles emitted from radium are aimed at gold foil. A circular zinc-sulfide screen registers the scattering (deflection) of the alpha particles by emitting light flashes when the particles strike it.

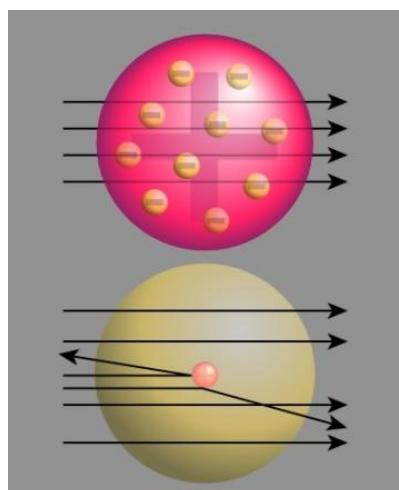


Figure 4.4. Rutherford's Prediction
Provided courtesy of the Wikipedia Commons

Rutherford, thought that something smaller, dense and are having a positive charge within the gold atoms responsible for repelling few alpha particles.

Rutherford's conclusion includes:

- An atom is occupied by electrons
 - At the center of atom is a tiny region containing all the positive charges, the **nucleus**
- He proposed, within the nucleus is a **proton**, the positively charged particle.



Figure 4.5. The Proton

4.5. The Neutron

It was then James Chadwick, in 1932, who published the result of his work establishing the existence of an electrically neutral particle with mass approximately equal to that of a hydrogen atom, he called **neutrons**.

Table 4.1. Sub-atomic Particles

| Particle | Mass | | Charge |
|----------|----------------------------|------------------------|--------|
| | Grams | Atomic Mass Unit (amu) | |
| Proton | 1.672649×10^{-24} | 1.007276 | + |
| Neutron | 1.674954×10^{-24} | 1.008665 | 0 |
| Electron | 9.109535×10^{-28} | 0.0005485803 | - |

4.6. Structure of the Atom

The Dalton's model of an indivisible particle gave way to the current model of an atomic structure.

Protons and neutrons are within the nucleus of the atoms. Protons are positively charge particles and the uncharged neutrons so neutral. The presence of the positively charge protons inside the nucleus of which its number is equal to that of the number of negatively charged electrons surrounding the nucleus making the atom neutral.

Another young scientist, in 1913, Niels Bohr, a Danish physicist, suggested a model for the H atom which explained the line spectrum of this element. Hydrogen having one electron and a nucleus consisting of a single proton. Bohr's theory includes the following:

1. Hydrogen atom consists of an electron that can exist only in certain circular **orbits or the energy levels or shells**.

These energy levels are designated by the capital letters K, L, M, N, O.... or n with values 1, 2, 3 and are found in an arranged order around the nucleus.

2. The energy level or n closest to the nucleus (closest to the positive charged) has the smallest radius and therefore lowest energy. The K energy level or n=1 has lowest energy and smallest radius. As the distance from the nucleus increases (K, L, M, N, O,... or n = 1, 2, 3, 4, 5..), the radius increases so with the energy.

3. An electron is in its **ground state**, if it is in the first energy level or in the first shell or n=1, closest to the nucleus.

4. Electrons in any shell or energy level found away from the nucleus are in their **excited states**. An electron in the second energy level, in the third energy level are in the **first excited state**, and **second excited state**, respectively and so forth.

As the electron jumps farther away from the nucleus, it absorbs a photon (that is **absorption**) whose energy is equal to the difference between the lower and higher energy levels. On the other hand, after the electron jumped from a higher energy level and returned to the lower energy level (closer to the nucleus) it emits (emission process) photon with an energy equal to the difference of two levels.

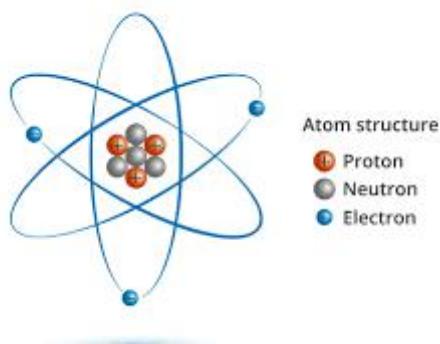


Figure 4.6. Structure of the Atom

4.7. Atomic Symbols

1. Atomic Number, Z, is equal to the number of positive charges in the nucleus. Since proton has a +1 charge, therefore, Z = number of protons.
2. The Mass Number, A, of any atom is equal to the total number of protons and neutrons (collectively called as nucleons) in the nucleus.

$$\begin{aligned} A &= \text{number of neutrons} + \text{number of protons (Z)} \\ \text{Number of neutrons} &= A - \text{number of protons (Z)} \end{aligned}$$

The mass number therefore is the total number of nucleons, and not the mass of the nucleus. Mass number is approximately equal to atomic mass in whole number.

In a neutral atom, the number of protons is equal to the number of electrons.

3. Symbol, the symbol ${}^A_Z X$, represents an element X with atomic number, Z and mass number, A. Thus ${}^{41}_{19} K$, an element potassium with atomic number 19 and mass number 41.

Atomic mass unit, u, a unit of mass equal to one-twelfth the mass of a ${}^1_6 C$ atom. Atomic weight is the average mass of atoms of an element relative to the mass of ${}^1_6 C$ atom taken exactly as 12 u.

Sample Problem 4.3. How many protons, neutrons, and electrons are in:

a) ${}^{11}_5 Q$ b) ${}^{41}_{20} R$ c) ${}^{131}_{53} X$

What do elements, Q, R and X represent?

Solutions:

| | | | |
|------------------|-----------------|---------------|-------------|
| a) protons = 5; | electrons = 5; | neutrons = 6 | Q is Boron |
| b) protons = 20; | electrons = 20; | neutrons = 21 | R Calcium |
| c) protons = 53; | electrons = 53; | neutrons = 78 | X is Iodine |

4.8. Ions

Are charged particles. Monoatomic ions are ions formed from a single atom by the loss or gain of one or more electrons. It is represented by ${}_{Z}^{A}X^{\pm y}$, where y could be positive for lost of electrons and negative for gained of electrons.

Recall that neutral atoms have an *equal* number of protons and electrons. The result of this is that the total positive charge of the protons exactly cancels the total negative charge of the electrons, so that the atom itself has an overall charge, or net charge, of zero.

However, if an atom gains or loses electrons, the balance between protons and electrons is upset, and the atom becomes an ion - a species with a net charge. Let's first look at what happens when a neutral atom loses an electron:

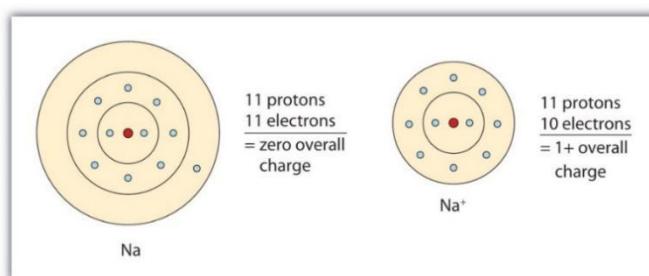
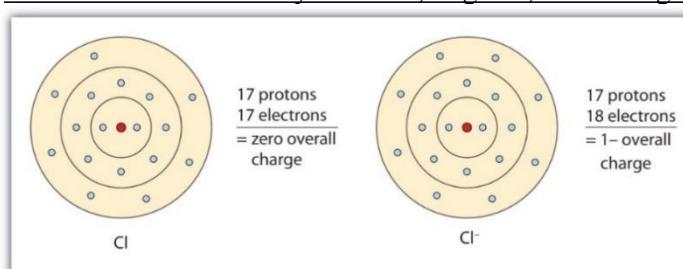


Figure 4.7. A neutral sodium atom, Na, loses one electron to form a cation, Na⁺.

Image credit: [Introduction to Chemistry: General, Organic, and Biological, CC BY-NC-SA 3.0](#)



The reduction of chlorine to chloride.

Figure 4.8. A neutral chlorine atom, Cl, gains an electron to form an anion, Cl⁻.

Image credit: [Introduction to Chemistry: General, Organic, and Biological, CC BY-NC-SA 3.0](#)

In the diagram above, we see a neutral atom of sodium, Na, losing an electron. The result is that the sodium ion, Na⁺, has 11 protons, but only 10 electrons. Thus, the sodium ion has a net charge of 1+, and it has become a cation - a positively charged ion.

Next, we'll look at the formation of an anion - an ion with a net negative charge.

Sample Problem 4.4. How many protons, neutrons, and electrons are in?

- a) ${}_{13}^{27}\text{Al}^{+3}$ b) ${}_{16}^{32}\text{S}^{-2}$

Solutions:

a) protons = 13 neutrons = 14

electrons = number of protons - charge of ion = 13 - (+3) = 10 (lost 3 electrons)

b) protons = 16 neutrons = 16

electrons = number of protons - charge of ion = 16 - (-2) = 18 (gained 2 electrons)

4.9. Isotopes

Isotopes are atoms of the same element having the same atomic number but different mass number. Chlorine for instance has two isotopes occurring in nature:

$^{35}_{17}\text{Cl}$ 17 protons; 18 neutrons and 17 electrons and

$^{37}_{17}\text{Cl}$ 17 protons; 20 neutrons and 17 electrons

Both atoms have 17 protons and 17 electrons, they differ in number of neutrons resulting to the differences in their atomic mass.

4.9.1. Atomic Masses (Atomic Weights)

Mass spectrometer is used to determine the atomic masses. Most elements are occurring in nature as mixtures of isotopes. In these cases, the instruments determine the relative amount of each isotope present in the element as well as the atomic mass of each isotope. Going back to chlorine for instance, $^{35}_{17}\text{Cl}$ having atomic mass of 34.969 u at 75.77% while $^{37}_{17}\text{Cl}$ having atomic mass of 36.966 u at 24.23%. The atomic weight of chlorine is taken as the weighted average of the atomic masses of the natural isotopes.

Weight average = (abundance * mass of $^{35}_{17}\text{Cl}$) + (abundance * mass of $^{37}_{17}\text{Cl}$)

Weighted average = $(0.7577 * 34.969) + (0.2423 * 36.966) = 26.496 + 8.957 = 35.453$ u

The accepted value for the atomic weight of chlorine is 35.453 ± 0.001 u.

In the periodic table, the atomic number of an element is found above the symbol of the element, while the atomic weight is found below the symbol of the element.

Sample Problem 4.5. Carbon occurs in nature as a mixture of $^{12}_{6}\text{C}$ and $^{13}_{6}\text{C}$. The atomic mass of $^{12}_{6}\text{C}$ is exactly 12 u, by definition, and the atomic mass of $^{13}_{6}\text{C}$ 13.003.

The atomic weight of carbon is 12.011 u. What is the atom percent of $^{12}_{6}\text{C}$ in natural carbon?

Solution:

Atomic weight of C = (abundance of $^{12}_{6}\text{C}$)(mass of $^{12}_{6}\text{C}$) + (abundance of $^{13}_{6}\text{C}$)(mass of $^{13}_{6}\text{C}$)
Let x be equal to the abundance of $^{12}_{6}\text{C}$, the $(1-x)$ is the abundance of $^{13}_{6}\text{C}$. Therefore:

$$(x)(12.000) + (1-x)(13.003) = 12.011$$

$$12.000x + 13.003 - 13.003x = 12.011$$

$$12.000x - 13.003x = 12.011 - 13.003$$

$$-1.003x = -0.992$$

$$x = \frac{-0.992}{-1.003} = 0.989$$

$$^{12}_{6}\text{C} = 0.989 \text{ and } ^{13}_{6}\text{C} = 1 - x = 1 - 0.989 = 0.011$$

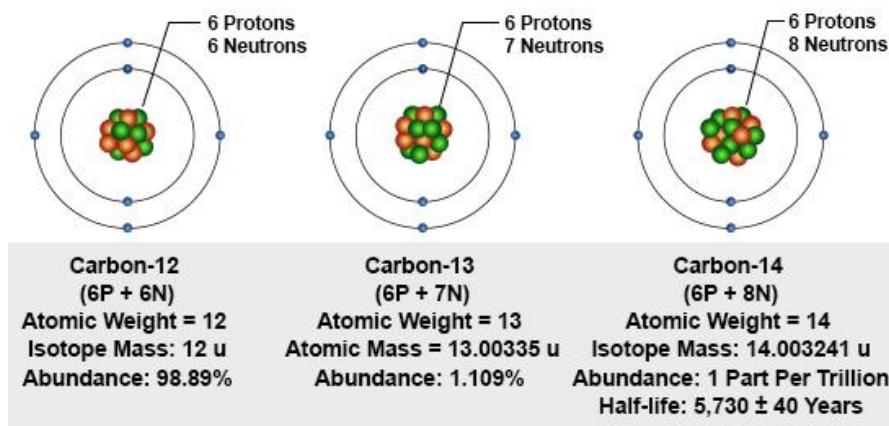


Figure 4.9 Natural Isotopes of carbon

4.10. Electronic Structure of Atoms

Electromagnetic radiation also called electromagnetic energy or radiant energy (such as visible light, microwaves, x-rays, infra-red, etc.) consists of energy propagated by electric and magnetic fields decreasing and increasing in intensity as they move through space.

4.10.1. Dual Nature of Light

4.10.1.1. The Wave Nature of Light

The following terms are used to describe wave properties of electromagnetic radiation:

1. The wavelength, λ (Greek lambda), describes the distance between two similar points on two successive waves i.e. distance from crest to the next crest or from trough to the next trough).
2. Frequency of the radiation, v (Greek nu), describes the number of cycles in a given second, expressed in Hertz ($1 \text{ Hz} = 1 \text{ s}^{-1}$).
3. Speed of wave, c , describes the distance it moves per unit of time. In a vacuum, all electromagnetic waves travel at the same speed, regardless of wavelength, $2.9979 \times 10^8 \text{ m/s}$, a physical constant referred as the speed of light.
4. The amplitude, α , refers to the height of a crest or the depth of a trough. For an electromagnetic wave, it is related to the intensity or brightness of visible light.

4.10.1.2. The Particle Nature of Light

Blackbody radiation gives the explanation on the light given off by an object being heated.

When a solid object is subjected to about 100K, Iodine begins to emit visible light as can be observe in the red glow of smoldering coal. At about 1500K, the light becomes brighter and more orange, like that of an electric heating coil. At temperatures higher than 2000K, the lighter is still brighter and whiter, like that emitted by the filament of a light bulb. These changes in intensity and wavelength of emitted light as objects are heated explains the blackbody radiation, the light given by a hot blackbody.

In 1900, German physicist Max Planck, proposed that a hot glowing object could emit or absorb only certain quantities of energy:

$$E = nhv$$

Where E is the energy of the radiation, v is the frequency, n is any positive integer (1, 2, 3,) called a quantum number, and h is **Planck's constant**; $h = 6.6261 \times 10^{-34} \text{ J}\cdot\text{s}$ (Joule·second).

Such radiation emitted by hot object must be emitted by the atom. If each atom can emit only certain quantities of energy, it follows then that each atom has only certain quantities of energy such that the energy of the atom is quantized – occurring in fixed quantities, rather than being continuous. Each change in atom's energy occurs when the atom absorbs or emits one or more “packets” or definite amounts of energy. Each packet of energy is called a **quantum** (meaning fixed quantity, its plural form, quanta).

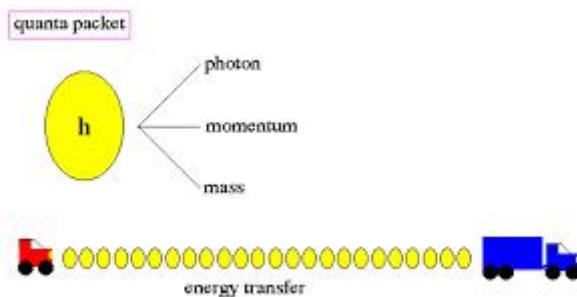


Figure 4.10. The Quanta

Founded on Planck's ideas, Albert Einstein in 1905, proposed that light itself is particulate, quantized into tiny bundles of energy called **photons**.

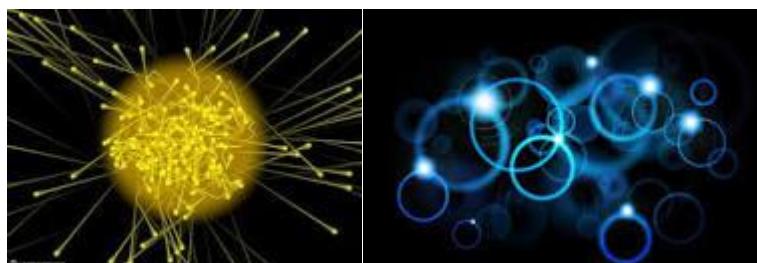


Figure 4.11. Photons

4.10.2. Wave Mechanics

In 1924, Louis de Broglie proposed that electrons and other particles behave as though it moves in a wave.

In 1927, German physicist Werner Heisenberg, postulated the Heisenberg **uncertainty principle** which states that it is impossible to determine simultaneously the exact position and the momentum (mass multiplied by speed) of a body as small as the electron. The more precisely we try to determine one of these values, the more uncertain we are of the other.

In 1926, Erwin Schrödinger derived an equation for the quantum-mechanical model which served as the basis for wave mechanics. The equation is written in terms of a wave function, Ψ (psi), for an electron. Each wave function corresponding to a definite energy state

for the electron pertaining to a region in space where there is a high probability that electron may be found – **orbital**.

4.11. Quantum Numbers

Quantum mechanics examines the wave nature of objects on the atomic scale. Atomic orbitals are specified by three quantum numbers (Table 4.2) which form part of the solution of the Schrödinger equation indicating the size, shape and orientation of the orbital in space.

1. **The principal quantum number, n** , corresponds to a positive integer 1, 2, 3, etc. identifying the shell or energy level to which the electron is located. The larger the value of n , the farther the shell is from the nucleus, the higher the energy of the electron in that shell.
2. The **angular quantum number, l** , corresponds to an integer from 0 to $(n - 1)$. It identifies the shape of the orbital.

$$l = 0, 1, 2, 3, 4, 5, \dots, (n - 1)$$

notation = s, p, d, f, g, h, ..., (sublevels or subshells)

For an orbital with $n = 1$, can only have 1 value for $l = 0$, for $n = 2$, l can have only two values either 0 or 1 and so forth.

3. The **magnetic quantum number, m_l** , corresponds to an integer from $-l$ through 0 to $+l$, which describes the orientation of the orbital in space around the nucleus. An orbital with $l = 0$ can have only $m_l = 0$. An orbital with $m_l = 1$ can have one of the three m_l values, -1, 0, +1 – there are three possible orbital with $l = 1$, each with its own orientation. The first three quantum numbers (n, l, m_l) arise from solutions to the Schrödinger equation.
4. The **magnetic spin quantum number, m_s** , describes the electron completely. It can have two values, $+\frac{1}{2}, -\frac{1}{2}$ indicating two electrons spinning at opposite directions. The spin magnetic moments of these two electrons cancel each other. Each orbital can hold two electrons with opposite spins.

Table 4.2. Quantum Numbers (Orbitals of the first Three Shells)

| Property/ Symbol | Value | Quantum Numbers | | | | | | | | | | | |
|-----------------------------|------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|
| | | 1 | 2 | | | 3 | | | 4 | | | 5 | |
| n | 1, 2, 3, 4, 5, 6, 7 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
| Subshell, l | 0 to $(n-1)$ | 0 | 0 | 1 | | | 0 | 1 | | | 2 | | |
| Orbital, m_l | $-l$ to 0 to $+l$ | 0 | 0 | -1 | 0 | +1 | 0 | -1 | 0 | +1 | -2 | -1 | 0 |
| m_s | $+\frac{1}{2}, -\frac{1}{2}$ | $+\frac{1}{2}$ $-\frac{1}{2}$ |
| No. of Orbital/ shell | 1, 3, 5, 7... | 1 | 1 | 3 | | | 1 | 3 | | | 5 | | |
| Number | 1, 2, 3, 4... | 2 | 2 | 6 | | | 2 | 6 | | | 10 | | |

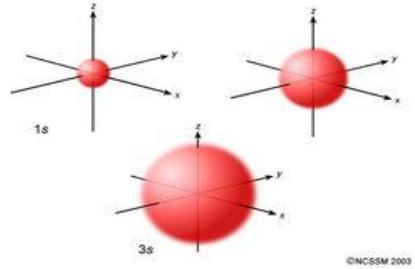
| | | | | | | | | |
|-------------------------------------|---------------------|----|----|---|----|---|--|----|
| of electrons/ subshell | | | | | | | | |
| Total Number of Electrons/ shell | 1, 2, 3, 4, 5, 6... | 2 | 8 | | | | | 18 |
| Subshell Notation | 1s, 2s, 2p, 3s, 3p | 1s | 2s | 2p | 3s | 3p | 3d | |
| | | 1s | 2s | 2p _x 2p _y 2p _z | 3s | 3p _x 3p _y 3p _z | 3d _{xy} 3d _{xz} 3d _{yz} 3d _{x²-y²} ³ d _{z²} | |

Note: s = 2 e⁻; p = 6 e⁻; d = 10 e⁻ and f = 14 e⁻.

The initial letters are used to identify the first four notations : s → sharp (with 2 electrons), p → principal (with 6 electrons → p_x, p_y and p_z); d → diffuse (with 10 electrons → d_{yz}, d_{xy}, d_{z²}, d_{xz}, d_{x²-y²}) and the f → fundamentals (with 14 electrons).

4.11.1. Shapes of the Orbitals

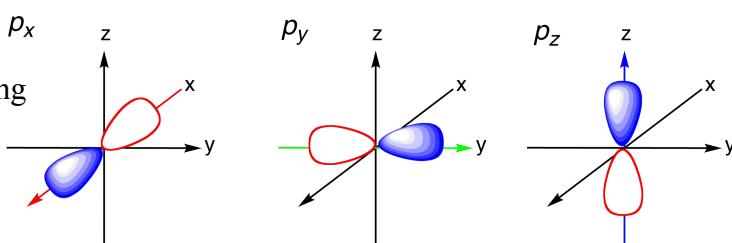
s – orbital



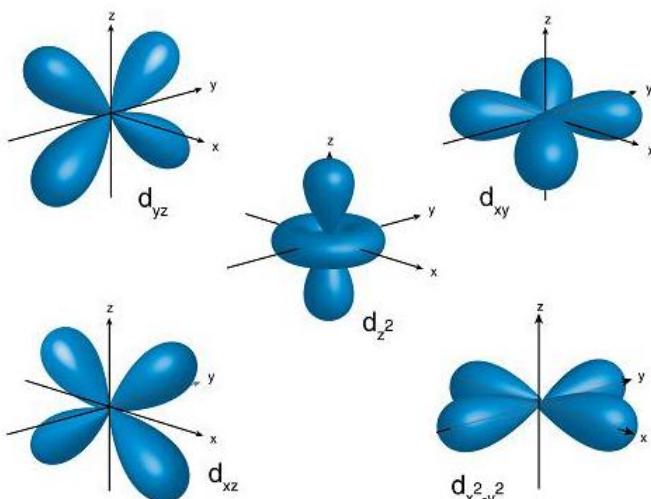
An **s orbital** is a sphere. It is spherically symmetric around the nucleus of the atom, can be compared to a hollow ball made of a fluffy material with the nucleus at its center. The electron gets bigger as distance from the nucleus increases. It is an orbital with $l=0$ with $m_l=0$.

orbital has the shape of a pair of lobes or peanuts on opposite sides of the nucleus, thus resembling dumbbell shape.

There are three p orbitals indicating their orientations. The p_x – along the x-axis, p_y along the y-axis and the p_z – along the z-axis. An electron in a p orbital has equal probability of being in either half. No p orbital in the first energy level



The three p orbitals are aligned along perpendicular axes in the second energy level.

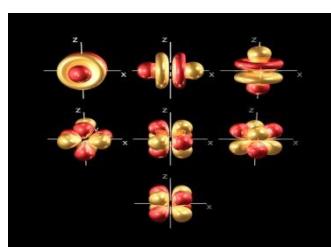


The **d orbital** starts at the third level, consisting of a set of five d orbitals of complicated shapes and names. There are two d orbital groups. The first group are composed 3d_{xy}, 3d_{xz} and 3d_{yz} orbitals. The names tell you where these orbitals lie in the x-y plane, the x-z plane, and the y-z plane, respectively. Each orbital consisting of four lobes, each of the lobes is pointing between two of the axes, not along them. The second group contains the 3d_{x²-y²} and 3d_{z²} orbitals. Their lobes pointing along the various axes. The 3d_{x²-y²} orbital looks exactly like the first group,

except that the lobes are pointing along the x and y axes, not between them. The 3d_{z²} is

like a p orbital wearing a doughnut around its waist. It is an orbital with $l=2$ and m_l values of -2, -1, 0, +1, +2 corresponding to the five d orbitals.

f Orbital



Starting at the fourth energy level, there are seven orbitals in addition to 4s, 4p and 4d orbitals, the f orbitals.

The f orbitals are somewhat complicated and are not discussed further.

4.11.2. Pauli's Exclusion Principle

Introduced by Wolfgang Pauli which states that no two electrons can have the same four quantum number set even if the two electrons have the same values for n , l , m_l they will always differ in their m_s values indicating two electrons paired in a single orbital with opposite spins. The electrons may have the same three sets of quantum numbers, but they will always differ in their spins.

For example, two electrons paired in a given 1s orbital, they have (n , l , m_l , m_s) quantum sets corresponding to: $n = 1$, $l = 0$, $m_l = 0$. They have the same n , l , m_l but they will differ in m_s which is either $-\frac{1}{2}$ or $+\frac{1}{2}$ but not both. Therefore one set of quantum number $(1,0,0,-\frac{1}{2})$ for the first electron and $(1,0,0,+\frac{1}{2})$ for the second electron. Meaning one electron spinning counterclockwise while the other one clockwise direction.

Sample Problem 4.6. What values of the angular momentum (ℓ) and magnetic quantum numbers are allowed for a principal quantum number, $n = 3$? How many possible orbitals are allowed?

Solutions:

$$n = 3$$

Values for $l = 0$ to $(n-1)$ $l = 0$ to $(3-1) = 0$ to $2 = 0, 1, 2$

Determining m_1 values for each:

For $l = 0$; $m_l = 0$ (1 orbital = s orbital with 2 electrons)

For $l=1$; $m_l = -1, 0, +1$ (3 orbitals = p orbital with 6 electrons)

For $l = 2$; $m_l = -2, -1, 0, +1, +2$ (5 orbitals = d orbital with 10 electrons)

Referring to the m_l values $(0, -1, 0, +1, -2, -1, 0, +1, +2)$ a total of nine, therefore there are nine (9) orbitals with $n = 3$.

Referring to the number of orbitals (1 orbital, 3 orbitals and 5 orbitals) giving a total of 9 orbitals. Therefore, the total number of orbitals for a given n value is n^2 and for $n = 3$, $(3)^2 = 9$.

Sample Problem 4.7. Give the name, magnetic quantum numbers and numbers of orbitals for each subshell with the given n and l quantum numbers:

- a) $n = 3, l = 2$ b) $n = 2, l = 0$ c) $n = 5, l = 1$ d) $n = 4, l = 3$

Solutions:

| | n | l | Possible Values of m_l | Subshell /Sublevel | No. of Orbitals |
|-----|-----|-----|---------------------------|---|-----------------|
| (a) | 3 | 2 | -2, -1, 0, +1, +2 | 3d (d has 5 orbitals and n is 3) | 5 |
| (b) | 2 | 0 | 0 | 2s ($l = 0$ refers to an s orbital and n is 2) | 1 |
| (c) | 5 | 1 | -1, 0, +1 | 5p (p has 3 orbitals and n is 5) | 3 |
| (d) | 4 | 3 | -3, -2, -1, 0, +1, +2, +3 | 4f (f has 7 orbitals and n is 4). | 7 |

To check for the number of orbitals in each sublevel or subshell, $(2l + 1)$.

Sample Problem 4.8. What is wrong with each of the following quantum number designation and/or sublevel name?

| | n | l | m_l | Subshell |
|-----|-----|-----|-------|----------|
| (a) | 1 | 1 | 0 | 1p |
| (b) | 4 | 3 | +1 | 4d |
| (c) | 3 | 1 | -2 | 3p |

Solutions:

Let us complete the table for quantum numbers:

- a) $n = 1, l = 0, m_l = 0$ b) $n = 4, l = 3, m_l = +1$ c) $n = 3, l = 1, m_l = -2$

| n | 1 | 2 | | | | 3 | | | | | 4 | | | | | | | | | | | | | | | |
|-----------|---|---|----|---|----|---|----|---|----|----|---|----|---|----|----|----|---|----|----|----|----|----|---|----|----|----|
| l | 0 | 0 | 1 | | 0 | 1 | | 2 | | | | 0 | 1 | | 2 | | | | 4 | | | | | | | |
| m_l | 0 | 0 | -1 | 0 | +1 | 0 | -1 | 0 | +1 | +2 | 0 | -1 | 0 | +1 | -2 | -1 | 0 | +1 | +2 | -3 | -2 | -1 | 0 | +1 | +2 | +3 |
| Sub shell | 1 | 2 | 2 | 2 | 2 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
| | s | s | p | p | p | s | p | p | p | d | d | d | d | d | s | p | p | p | d | d | d | d | f | f | f | f |

Answering the question using the data on the table:

- a) A subshell with $n = 1$ and $l = 1$, can have only $l = 0$ and not $l = 1$. The only possible subshell is 1s ($n = 1$ has no 1p).
- b) A subshell with $n = 4$ and $l = 3$, is an f subshell. It should be 4f.
- c) A subshell with $n = 3$ and $l = 1$, can only have -1, or 0 or +1 for m_l , not -2. It is a 3p subshell.

The correct answers are tabulated below:

| | n | l | m_l | Subshell |
|-----|-----|-----|-------|----------|
| (a) | 1 | 0 | 0 | 1s |
| (b) | 4 | 3 | +1 | 4f |

| | | | | |
|-----|---|---|---------------|----|
| (c) | 3 | 1 | -1 or 0 or +1 | 3p |
|-----|---|---|---------------|----|

4.12. Quantum Mechanics and the Periodic Table

Quantum mechanics serves to provide the theoretical framework for the periodic table.

Electronic configuration is one way of arranging or distributing the electrons in an atom. It is done by **electronic notation** using symbols of the subshells 1s, 2s, 2s and so on with subscripts indicating the number of electrons in the subshells. Another way is by the **orbital diagram**. A dash or a box is used to represent an orbital and electrons are represented by arrows pointing up (\uparrow) and pointing down (\downarrow) showing spin in opposite directions ($m_s; +\frac{1}{2}, \uparrow$, or $-\frac{1}{2}, \downarrow$).

4.12.1. Orbital Filling (aufbau principle and the Hund's Rule)

Aufbau principle from the German word “aufbauen” – meaning to “build-up” suggested by Wolfgang Pauli. And the **Hund's Rule**, which states that the electrons are distributed among the orbitals of the subshell, giving the maximum number of unpaired electrons with parallel spins – meaning all unpaired electrons spin in the same directions; thus, m_s values of these electrons are having the signs.

These will be elaborated further in our discussions.

4.13. Electronic Notation/Configuration

| | | | | |
|----|----|---------------------------|----|--|
| 1s | | | | |
| 2s | 2p | | | |
| 3s | 3p | 3d | | |
| 4s | 4p | 4d | 4f | |
| 5s | 5p | 5d | 5f | |
| 6s | 6p | <i>6d, 6f don't exist</i> | | |
| 7s | 7p | <i>7d, 7f don't exist</i> | | |

Figure 4.12. Filling Order of the Periodic Table

4.13.1 Full Electronic Notation:

| | | |
|-----------------|---|-----------------------------|
| First Period | : 1s ² | (Helium, ₂ He) |
| Second Period | : 2s ² 2p ⁶ | (Neon, ₁₀ Ne) |
| Third Period | : 3s ² 3p ⁶ | (Argon, ₁₈ Ar) |
| Fourth Period | : 4s ² 3d ¹⁰ 4p ⁶ | (Krypton, ₃₆ Kr) |
| Fifth Period | : 5s ² 4d ¹⁰ 5p ⁶ | (Xenon, ₅₄ Xe) |
| Sixth Period | : 6s ² 4f ¹⁴ 5d ¹⁰ 6p ⁶ | (Radon, ₈₆ Rn) |
| Seventh period: | : 7s ² 5f ¹⁴ 6d ¹⁰ 7p ⁶ | |

or $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^2 5f^{14} 6d^{10} 7p^6$

Sample Problem 4.9. Write the full electronic notation of $_{17}\text{Cl}$:

Solution:

| | | | |
|--------------------|------------------------|-------------|----------------------|
| $_{17}\text{Cl}$: | 1 st Period | $1s^2$ | 2 |
| | 2 nd Period | $2s^2 2p^6$ | 8 |
| | 3 rd period | $3s^2 3p^5$ | 7 Total 17 electrons |

Or $_{17}\text{Cl}$: $1s^2 2s^2 2p^6 3s^2 sp^5 = 17$ total electrons

Sample Problem 4.10. Write the full electronic notation of $_{16}\text{S}$:

Solution:

| | | | |
|-------------------|------------------------|-------------|----------------------|
| $_{16}\text{S}$: | 1 st period | $1s^2$ | 2 |
| | 2 nd period | $2s^2 2p^6$ | 6 |
| | 3 rd period | $3s^2 3p^4$ | 6 Total 16 electrons |

Or: $_{16}\text{S}$: $1s^2 2s^2 2p^6 3s^2 sp^4 = 16$ total electrons

4.13.2. Condensed Electronic Notation

Looking at the full electronic notation, 1st period takes up to $_{2}\text{He}$, 2nd period takes up to $_{10}\text{Ne}$, 3rd period takes up to $_{18}\text{Ar}$, 4th period takes up to $_{36}\text{Kr}$, 5th period takes up to $_{54}\text{Xe}$ and the 6th period to $_{86}\text{Rn}$.

Each of these have complete electronic notation are called the noble gases. They have $s^2 p^6$ (except for He) in the outer shell having eight electrons in the valence shell. To shorten the full electronic notation, we can use the noble gas as our basis – the noble configuration or the condensed configuration.

Sample Problem 4.11. Write the noble gas configuration for $_{17}\text{Cl}$:

Solution:

First, let us refer to the full electronic notation of Cl:

| | | | |
|--------------------|------------------------|-------------|----------------------|
| $_{17}\text{Cl}$: | 1 st Period | $1s^2$ | 2 |
| | 2 nd Period | $2s^2 2p^6$ | 8 |
| | 3 rd period | $3s^2 3p^5$ | 7 Total 17 electrons |

Take note that 1st period (or period 1), is He a noble gas and 2nd period (or period2) is Neon, another noble gas. 1st period is complete without extra electrons also 2nd period. Since we only have three period, let us consider the noble in the 2nd period – Ne, then followed by the electronic notation of the third period the noble gas being enclosed in a bracket.

So, the condensed or noble gas configuration for $_{17}\text{Cl}$ is: $[\text{Ne}]3s^2 3p^5$.

Sample Problem 4.12. Write the full electronic notation and noble gas configuration for $_{18}\text{Ar}$.

Solution:

$_{18}\text{Ar}$:

| | | | |
|--------------------|------------------------|-------------|---|
| $_{18}\text{Ar}$: | 1 st Period | $1s^2$ | 2 |
| | 2 nd Period | $2s^2 2p^6$ | 8 |

3rd period $36^2 3p^8$

8 Total 18 electrons

Take note that all the periods have complete configuration (with eight valence electrons except for He) and that they are all noble gases. As customarily done, the noble gas in the next lower level is taken as the basis. The next lower noble gas is neon. In this case, the noble gas configuration for $_{18}Ar$ is: [Ne]36²3p⁸.

4.13.3. Orbital Diagram

- Hydrogen has an atomic number of 1, and therefore having 1 electron: $_1H$

Electronic Notation: 1s¹ - the superscript 1 represent the electron

Orbital Diagram:



1s

- Helium has an atomic number of 2, and therefore having 2 electrons: $_2He$

Electronic Notation: 1s² - the superscript 2 represent the electron

Orbital Diagram:



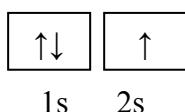
1s

- Lithium, $_3Li$

- Helium has an atomic number of 2, and therefore having 2 electrons: $_2He$

Electronic Notation: 1s²2s¹

Orbital Diagram:



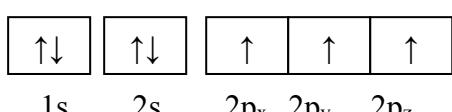
1s 2s

In this case, the exclusion principle of filling the orbitals applies which says that an orbital can hold no more than two electrons.

- Nitrogen, $_7N$

Electronic Notation: 1s² 2s² 2p³

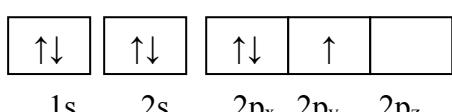
Orbital Diagram:

1s 2s 2p_x 2p_y 2p_z

Notice, nitrogen has 7 electrons. Two electrons for the 1s orbital, another two electrons for the 2s and the three remaining electrons for the three 2p orbitals. Based on Hund's rule, the last electrons enter the empty 2p_z orbital parallel to the other two (p_x and p_y). In short, empty boxes for orbitals should be filled first.

Electronic Notation: 1s² 2s² 2p³

Orbital Diagram:

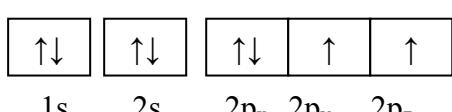
1s 2s 2p_x 2p_y 2p_z

This is violating the Hund's rule.

- Oxygen, $_8O$

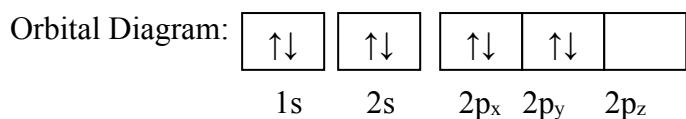
Electronic Notation: 1s² 2s² 2p⁴

Orbital Diagram:

1s 2s 2p_x 2p_y 2p_z

- Nitrogen, $_7N$

Electronic Notation: $1s^2 \quad 2s^2 \quad 2p^3$



This is violating the Hund's rule.

4.13.3.1. Partial Orbital Diagrams

Just like electronic notation, orbital diagram also observes a shorter way of writing the orbital diagrams for higher number of electrons.

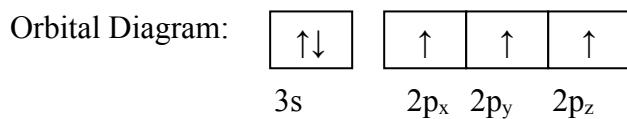
Sample Problem 4.13. Write the full electronic notation, the noble gas configuration and the partial orbital diagram for $_{15}P$:

Solutions:

- Phosphorus, $_{15}P$

Electronic Notation: $[1s^2 2s^2 2p^6]3s^2 3p^3$

Noble gas configuration: $[\text{Ne}]3s^2 3p^3$



Notice, that in writing the partial orbital diagram, the orbital diagram for the noble gas [Ne] has been omitted.

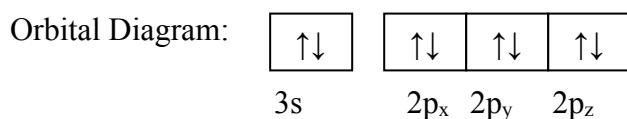
Sample Problem 4.14. Write the full electronic notation, the noble gas configuration and the partial orbital diagram for $_{18}\text{Ar}$:

Solutions:

- Phosphorus, $_{18}\text{Ar}$

Electronic Notation: $[1s^2 2s^2 2p^6]3s^2 3p^6$

Noble gas configuration: $[\text{Ne}]3s^2 3p^6$



4.14. Period 4: The First Transition Metals

We have been discussing elements in the 1st to 3rd periods. This time we will discuss the electronic configurations for the transition elements with filled d orbitals.

Factors affecting the filling patterns of transition elements:

1. Shielding and penetration of energy on the subshell

The 4th period has filled 3d subshell, but the 4s subshell is filled first. This is due to shielding and penetration effects. A 3d electron spending most of the time outside the filled inner n, 1 and 2 levels, this is shielded from the nuclear charge. The outermost electrons in the 4s penetrates closer to the nucleus and is subjected to greater attraction resulting to a slightly lower energy 4s orbital than the 3d and is filled first.

2. Order of filling 4s and 3d orbitals

Except for K and Ca which are alkali and alkaline earth metals, respectively, will not be included.

Referring to the data below, starting with the first transition metal, Scandium (Sc) its 3d orbitals have equal energy and its last electron can occupy any one of the 3d orbital.

Since Sc has a noble gas configuration of [Ar]4s²3d¹, filling the 3d orbitals takes place one at a time just like with p orbital except for chromium and copper.

| | 4s | 3d | | | | | 4p |
|-------|----|----|----|----|----|----|----|
| 19K: | ↑ | | | | | | |
| 20Ca: | ↑↓ | | | | | | |
| 21Sc: | ↑↓ | ↑ | | | | | |
| 22Ti: | ↑↓ | ↑ | ↑ | | | | |
| 23V: | ↑↓ | ↑ | ↑ | ↑ | | | |
| 24Cr: | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | |
| 25Mn: | ↑↓ | ↑ | ↑ | ↑ | ↑ | ↑ | |
| 26Fe: | ↑↓ | ↑↓ | ↑ | ↑ | ↑ | ↑ | |
| 27Co: | ↑↓ | ↑↓ | ↑ | ↑ | ↑ | ↑ | |
| 28Ni: | ↑↓ | ↑↓ | ↑↓ | ↑ | ↑ | ↑ | |
| 29Cu: | ↑ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | |
| 30Zn: | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | |
| 31Ga: | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑ | |
| 32Ge: | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑ | ↑ |
| 33As: | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑ | ↑ |
| 34Se: | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑ |
| 35Br: | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑ |
| 36Kr: | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑↓ |

3. Half-filled and Filled Subshells' Stability

Referring to the data table above, take note that V with the configuration [Ar]4s²3d³, follows the usual order of filling. However, Cr with the configuration [Ar]4s²d⁴, did not follow the usual order of filling. Its last electron did not fill the fourth empty d orbital instead Cr has one electron in the 4s subshell and five in the 3d subshell, making them half-filled with the configuration [Ar]4s¹3d⁵.

^{24}Cr :



As Cu follows next to Ni with configuration [Ar]4s²3d⁸, it is expected to have a configuration of [Ar]4s²3d⁹, however, the 4s subshell of Cu is half-filled with one electron, and the 3d subshell is filled with 10 electrons.

^{29}Cu :



Categories of Electrons

1. **Inner Core electrons** – they fill all the lower energy of an atom.
2. **Outer electrons** – those with the highest energy level and are usually found farthest from the nucleus.
3. **Valence electrons** – they are involved in forming compounds. For main group elements, valence electrons are the outer electrons.

Sample Problem 4.15. Using the periodic table and assuming a regular filling pattern, give the full and condensed (noble gas configuration), partial orbital diagram, and the number of inner electrons of each of the following:

a) ^{19}K b) ^{43}Tc c) ^{82}Pb

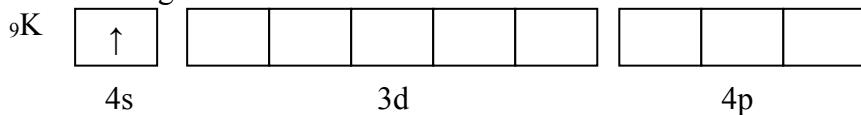
Solutions:

a) Full notation: ^{19}K : $1s^22s^22p^63s^23p^64s^1$

| | | | |
|------------------------|--------------|---|----------------|
| 1 st period | : $1s^2$ | } | Inner Electron |
| 2 nd period | : $2s^22p^6$ | | |
| 3 rd period | : $3s^23p^6$ | | |
| 4 th period | : $4s^1$ | | |

Condensed: ^{19}K : $[\text{Ar}]4s^1$

Partial Orbital diagram:



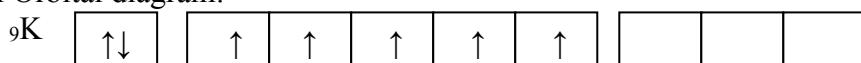
Inner electron: 18

b) Full notation: ^{43}Tc :

| | |
|------------------------|---------------------|
| 1 st period | : $1s^2$ |
| 2 nd period | : $2s^22p^6$ |
| 3 rd period | : $3s^23p^6$ |
| 4 th period | : $4s^23d^{10}4p^6$ |
| 5 th period | : $5s^24d^5$ |

Condensed: ^{43}Tc : $[\text{Kr}]5s^24d^5$

Partial Orbital diagram:



5s

4d

5p

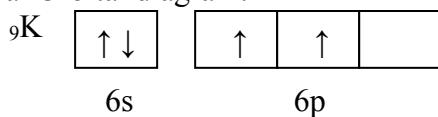
Inner Electron: 36

c). Full notation: ^{43}Tc :

| | |
|------------------------|---|
| 1 st period | : 1s ² |
| 2 nd period | : 2s ² 2p ⁶ |
| 3 rd period | : 3s ² 3p ⁶ |
| 4 th period | : 4s ² 3d ¹⁰ 4p ⁶ |
| 5 th period | : 5s ² 4d ¹⁰ 5p ¹ |
| 6 th period | : 6s ² 4f ¹⁴ 5d ¹⁰ 6p ² |

Condensed: ^{82}Pb : [Xe]6s²4f¹⁴5d¹⁰6p²

Partial Orbital diagram:



Inner Electrons: 78

4.15. Electronic Configuration and the Periodic Table

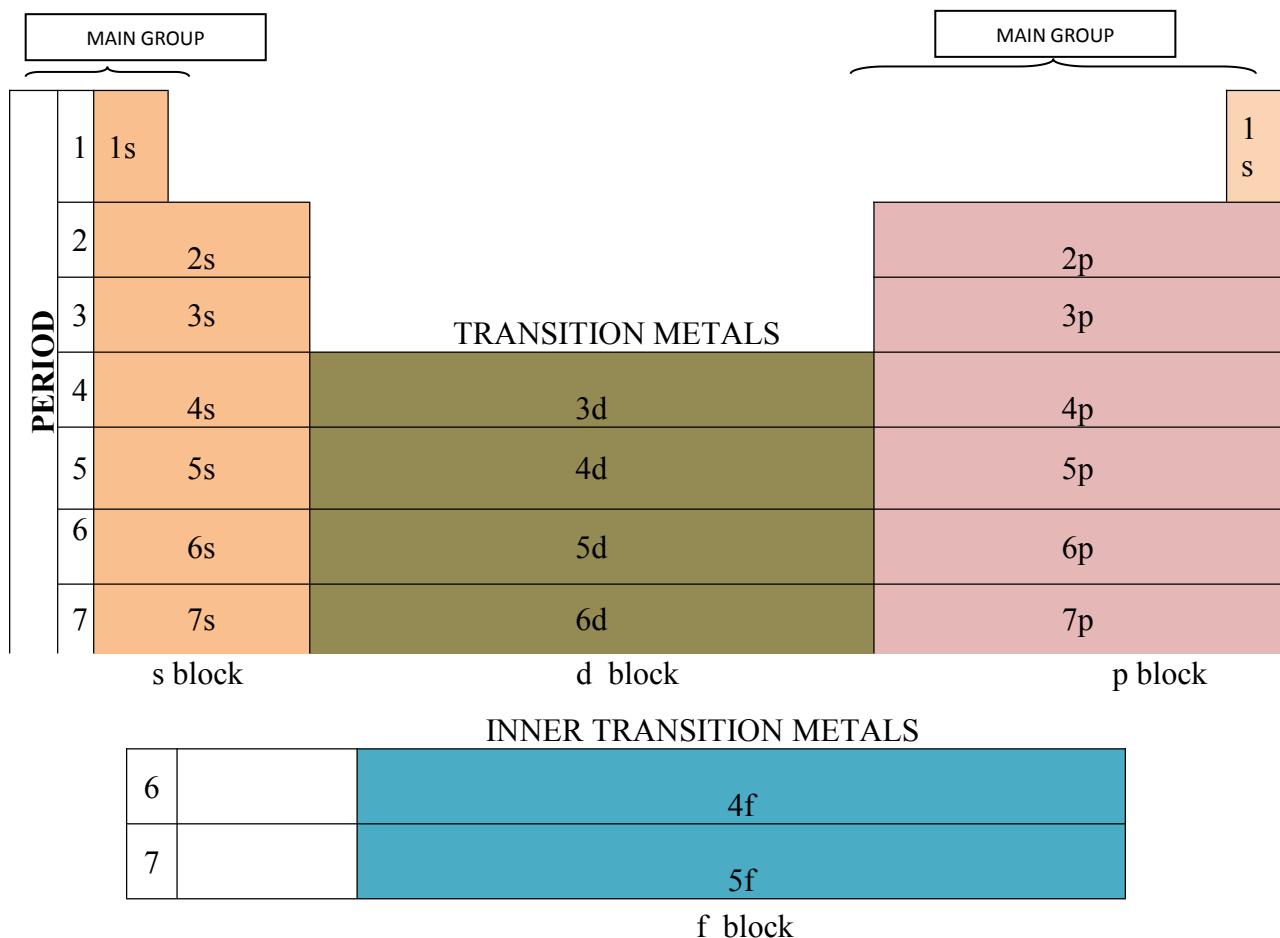


Figure 4.13. Periodic and the Filling of the Orbital

Recall the aufbau principle, the German word meaning – “to build up” which describes the transfer of electrons from element to element as in the electronic configuration.

This electron added transferring from one element to the next as referred in the aufbau principle is called **differentiating electron**.

Electronic configurations of an atom can be derived from the periodic table. From Figure 4.13, notice that the periodic table can be divided into an “s” block, a “p” block, a “d” block and the “f” block. The principal quantum number of the differentiating electron represents the period number for the s block and the p block (notice: we have 1s for period 1; 2s and 2p for period 2). Period number (n) for the d block which is (n-1). Look at 3d starts at period 4 and 4d at period 5 and soon. For the f block we have period number minus 2 (n-2). 4f starts at period 6 while 5f starts at period 7 (n-2).

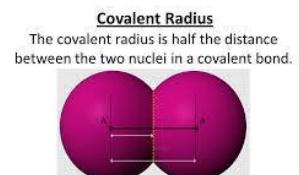
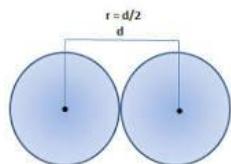
The number of unpaired electrons in an atom, ion or molecule is determined by magnetic properties. Substances with unpaired electrons and are drawn into a magnetic field are called **paramagnetic**. **Diamagnetic** are substances having paired electrons. They are repelled by a magnetic field.

4.16. Property Trends

4.16.1. Atomic Size Trend

Element's atomic size slightly varies from substance to substance. Atomic sizes can be defined according to the following:

- Metallic radius for metals and is one-half the distance between adjacent nuclei of individual atoms.
- Covalent radius for non-metallic molecules and is half the distance between nuclei of bonded atoms.



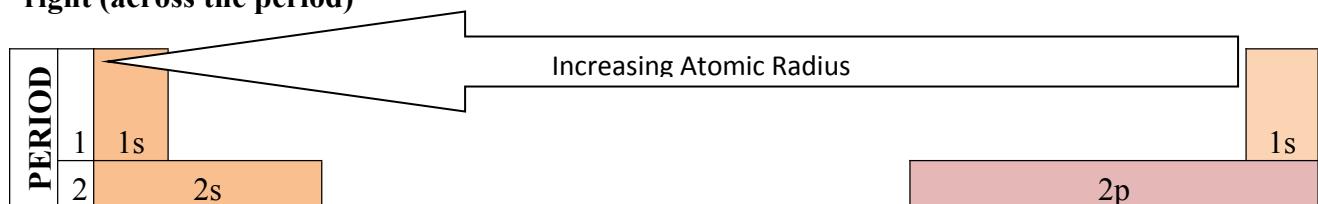
Sample Problem 4.16. Using the periodic table, rank each set of main group elements in order increasing atomic size.

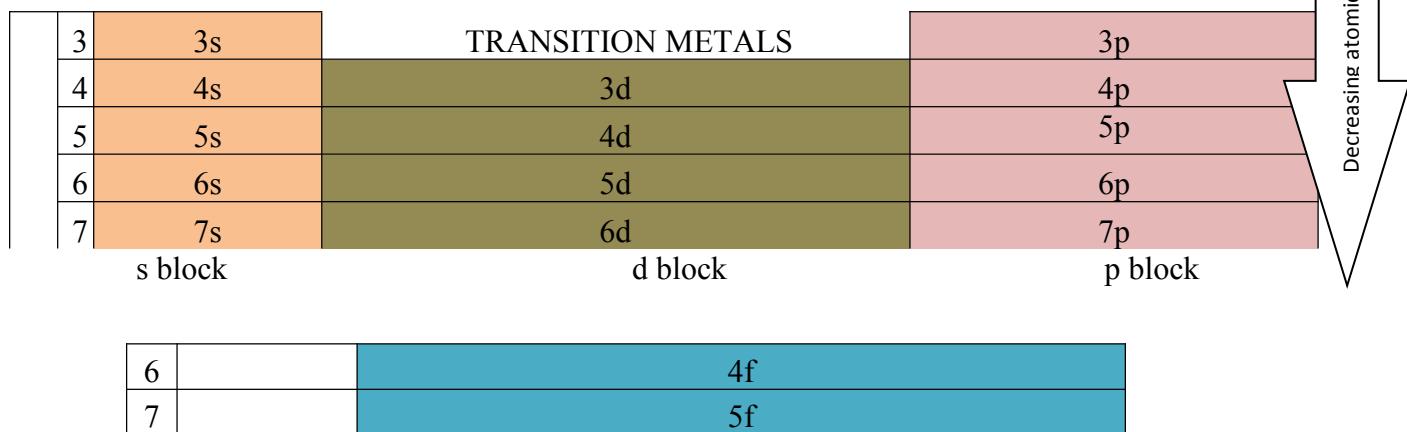
- a) Ca, Mg, Sr b) K, Ga, Ca c) Br, Rb, Kr d) Sr, Ca, Rb

Solutions:

- a) Ca, Mg and Sr – they belong to the same group, Mg is in period 2, Ca in period 3 and sr in period 4. Atomic radius increases from top to bottom (down the group): Mg, followed by Ca then Sr.
- b) K, Ga, Ca they both belong to the same period number. However, atomic radius decreases across a period, therefore: Ga, Ca and K.
- c) Br, Rb, Kr – Br is in group 7 period number 4, Kr is in group 18, period number 4 (Kr is farther to the right and has lower atomic radius than Br) while Rb is in group 1 period 5. Kr then, Br and finally Rb.
- d) Sr, Ca, Rb – Ca and Sr belong to group 2 but Ca is in period 4. Sr has bigger atomic radius than Ca. Rb and Sr are in the same period. However, Rb is in group 1 and Sr in group 2. Rb has bigger atomic radius than Sr. Ca followed by Sr and finally Rb,

Atomic radius generally increases from top to bottom and decreases from left to right (across the period)





HIGHER TRANSITION METALS

4.16.2. Ionization Energy

It is the energy required to completely knock down an electron from atoms or ions. Atoms having a lower ionization energy form cation while atoms having higher ionization energy form anions during reaction.

Ionization energy generally decreases from top to bottom (down the group) and generally increases from left to right (across the period).

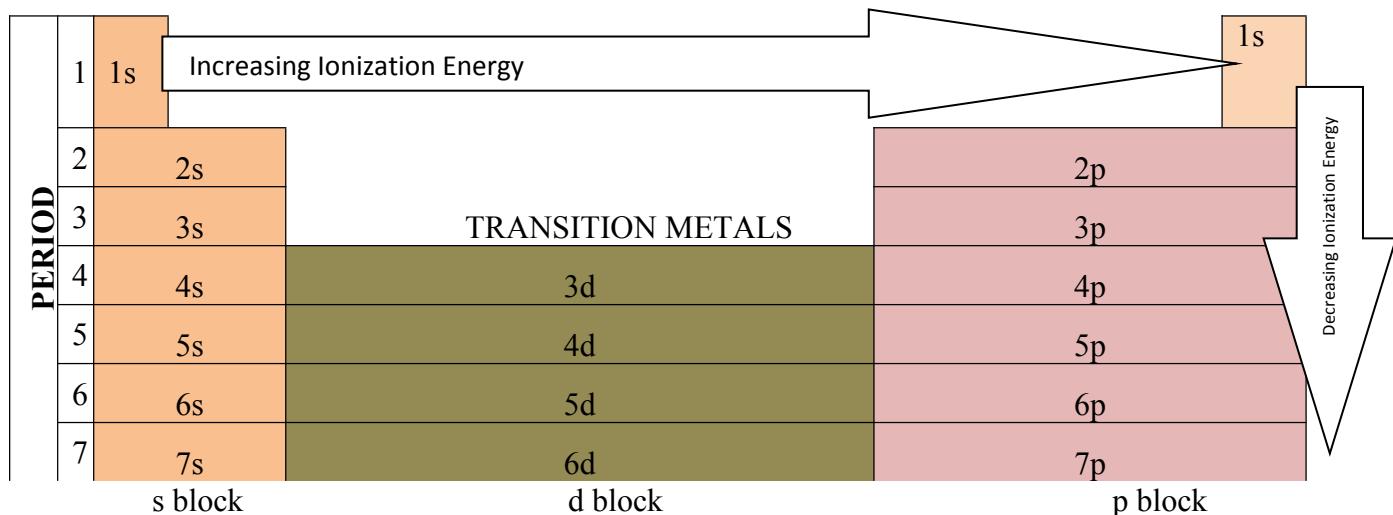


Figure 4.15. Ionization Energy

Sample Problem 4.17. Using the periodic table only, rank the elements in each set in order of decreasing ionization energy:

- a) Kr, He, Ar b) Sb, Te, Sn c) K, Ca, Rb d) I, Xe, Cs

Solutions:

- a) Kr, He, Ar – Kr and He, and Ar are all in group 8, Kr in period 4, Ar in period 3 while He in period 1. He has the highest ionization energy followed by ar and finally Kr. He, Ar, Kr.
- b) Sb, Te, Sn – they are all in period 5. Sn in group 14, Sb in group 15 and Te in group 16. Te is at the farthest right, the followed by Sb and Sn: Te, Sb, Sn.

- c) K, Ca, Rb–K and Rb are in the same group (1). K is in period 4 while Rb is in period 5. K has higher ionization energy than Rb. K and Ca are in the same period (4) but Ca is in group 2, and has higher ionization energy than K: Ca, K, Rb.
 - d) I, Xe, Cs –I and Xe are in the same period (5), I is in group 17, Xe 18, Xe has higher ionization energy than I. Xe is in period 5 while Cs is in period 6, xe has higher ionization energy than Cs. Xe, I, Cs.

4.16.3. Electron Affinity

Electron affinity is the energy change associated with the process of adding electrons to a gaseous atom or ion. Take note that an electron affinity refers to a process of producing a negative ion from a neutral atom – gain of electron while an ionization energy refers to a process of producing a positive ion from a neutral atom – loss of electron.

Electron affinity increases (with many exceptions) across a period (from left to right) and decreases (with many exceptions) from bottom to the top (going up the group).

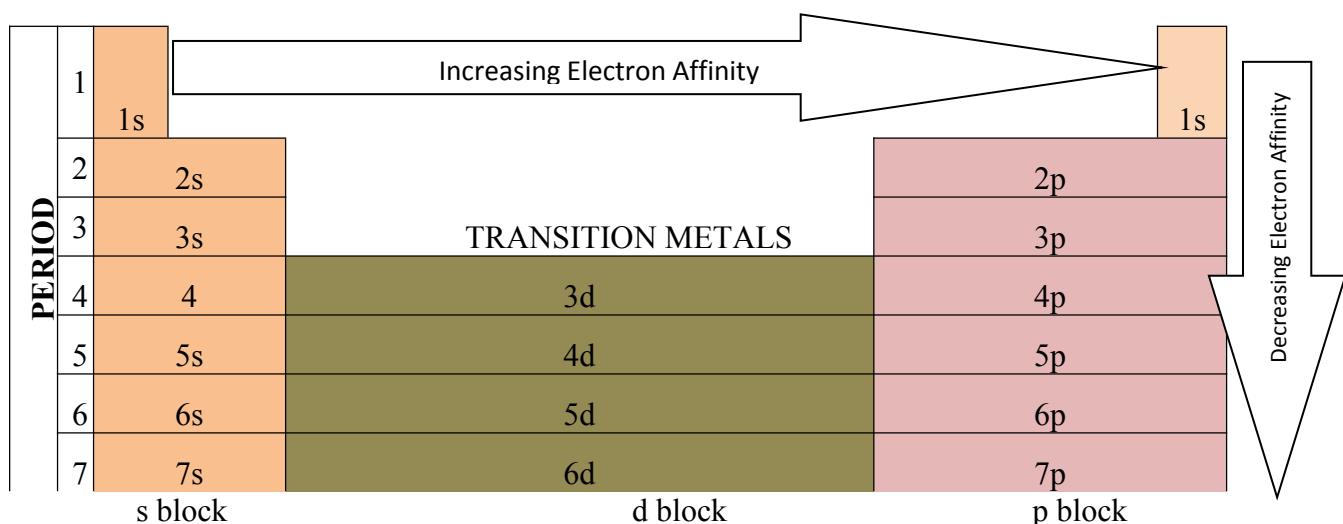


Figure 5.5. Electron Affinity

4.17. Electronic Configurations of Ions

4.17.1. Main Group Ions

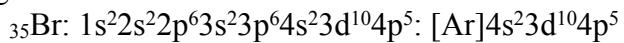
1. Ions with a noble gas configuration

Noble gases' atoms have very low reactivity because of their filled highest energy level, making elements at either end of a period form ions attaining a filled outer level, the noble gas configuration. Their ions are **isoelectric** (Greek work iso meaning same) with the noble gas.

Group 1A (1) and group 2A(a) elements become isoelectric with the previous noble gas by losing electrons. In the case of Na for example, $_{11}^{\text{Na}}$ is isoelectric with neon (Ne):

$_{11}\text{Na}$: $1s^2 2s^2 2p^6 3s^1$: $[\text{He}]2s^2 2p^6 \textcolor{red}{3s}^1 \rightarrow e^- + \text{Na}^+$ (losing 1 outer electron – 3s and becomes a cation - of +1 charge). Take note that $[\text{He}]2s^2 2p^6$ corresponds to Ne and is isoelectric with Ne.

Group 6 A (16) and group 7A (17) become isoelectric with the next noble gas by gaining electrons.



$[\text{Ar}] 4s^2 3d^{10} 4p^5 + \text{e}^- \rightarrow [\text{Ar}] 4s^2 3d^{10} 4p^6$ (added 1 electron in its outer shell – 4p and becomes an anion – of -1 charge. Note that $\text{Ar}4s^2 3d^{10} 4p^6$ is actually Kr and is isoelectric with Kr.

2. Ions without a noble gas configuration

Group 3A (13) and group 5A (15) metals do not form ions with noble gas configuration (except for aluminum). They form cations with two different stable configurations:

a) Pseudo-noble gas configuration

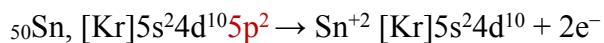
Metal atoms emptying highest energy level attaining stability empty ns and np subshells and filled inner (n-1)d subshells. The (n-1) d¹⁰ configuration is the pseudo-noble gas configuration.

${}_{50}\text{Sn}$: $[\text{Kr}] 5s^2 4d^{10} 5p^2 \rightarrow \text{Sn}^{+4} [\text{Kr}] 4d^{10} + 4\text{e}^-$ (Sn loses four electrons from 5s and 5p become an Sn^{+4} ion).

b) Inert pair configuration

Metal atoms can attain a stable configuration with filled ns and (n-d) subshells retaining ns² electrons.

In the case of ${}_{50}\text{Sn}$, $[\text{Kr}] 5s^2 4d^{10} 5p^2$, losing four electrons from 5s and 5p becomes Sn^{+4} . However, if Sn loses its two electrons from 5p and retaining the 5s electrons and with filled 5s and 4d subshells:



It is impossible for group 3A(13) and group 5A(15) metals to attain noble gas configurations.

Sample Problem 4.18. Using the condensed or noble gas configurations, write equations representing the formation of ion(s) of the following elements:

a) ${}_{53}\text{Iodine}$

b) ${}_{19}\text{K}$

c) ${}_{49}\text{In}$

Solutions:

a) ${}_{53}\text{Iodine}$

| | | | |
|------------------------|-----------------------------------|------------------------|--|
| 1 st period | : 1s ² | 4 th period | : 4s ² 3d ¹⁰ 4p ⁶ |
| 2 nd period | : 2s ² 2p ⁶ | 5 th period | : 5s ² 4d ⁵ |
| 3 rd period | : 3s ² 3p ⁶ | | |

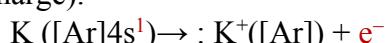
$[\text{Kr}] 5s^2 4d^5$ (7 electrons in the outermost shell. Iodine needs to gain 1 electron to form an anion of -1 charge).

$\text{I} ([\text{Kr}] 5s^2 4d^5) + 1\text{e}^- \rightarrow \text{I}^- ([\text{Kr}] 5s^2 4d^6)$ ($[\text{Kr}] 5s^2 4d^6$ corresponds to Xe and is isoelectric with Xe).

b) ${}_{19}\text{K}$

| | |
|------------------------|-----------------------------------|
| 1 st period | : 1s ² |
| 2 nd period | : 2s ² 2p ⁶ |
| 3 rd period | : 3s ² 3p ⁶ |
| 4 th period | : 4s ¹ |

$\text{K} [\text{Ar}] 4s^1$ (K needs to lose 1 electron from 4s to attain the argon configuration and form a cation of +1 charge).



c) ${}_{49}\text{In}$

| | |
|------------------------|--|
| 1 st period | : 1s ² |
| 2 nd period | : 2s ² 2p ⁶ |
| 3 rd period | : 3s ² 3p ⁶ |
| 4 th period | : 4s ² 3d ¹⁰ 4p ⁶ |
| 5 th period | : 5s ² 4d ¹⁰ 5p ¹ |

In ([Kr]5s²4d¹⁰**5p¹**) → In⁺ ([Kr]5s²4d¹⁰) + **e⁻** (Indium loses the 5p electron and forms a cation of +1 charge- with an inert pair)

In ([Kr]**5s²4d¹⁰5p¹**) → In⁺³([Kr]4d¹⁰) + **3e⁻** (Indium loses the 5s and 5p electrons and forms a cation of +3 charge – with pseudo-noble gas configuration., filled 4d subshell).

PROGRESS CHECK:

- 4.1. Write the atomic symbol for (a) an ion fluoride that contains 9 protons and 10 neutrons in the nucleus and 10 extranuclear electrons? (b) an ion of iron that contains 26 protons and 30 neutrons in the nucleus and 24 extranuclear electrons?
- 4.2. What is the atomic weight of magnesium to four significant figures? The element consists of 78.99% $^{24}_{12}Mg$ atoms (mass, 23.99 u), 10.00% $^{25}_{12}Mg$ atoms (mass, 24.99 u), and 11.00% $^{26}_{12}Mg$ atoms (mass, 25.98 u).
- 4.3. Complete the following table:

| Symbol | Z | A | Protons | Neutrons | Electrons |
|-----------|----|-----|---------|----------|-----------|
| Cs | 55 | 133 | | | |
| Bi | | 209 | | | |
| | 56 | 138 | | | 56 |
| Sn | | | | 70 | 50 |
| Kr | | 84 | | 48 | |
| Sc^{+3} | | | | 24 | |
| | 8 | | | 8 | 10 |

- 4.4. Silver occurs in nature as a mixture of two isotopes, $^{107}_{47}Ag$, which has an atomic mass of 106.906 u, and $^{109}_{47}Ag$, which has an atomic mass of 108.905 u. The atomic weight of silver is 107.868. What is the percent abundance of each of the two isotopes?
- 4.5. An element consists of 60.10% of an isotope with an atomic mass of 68.926 u, and 39.90% of an isotope with an atomic mass of 70.925 u. What is the atomic weight of the element?
- 4.6. What are the n, l, and possible values for the 2p and 5f subshells?

- 4.7. Supply the missing quantum numbers and subshells.

| | n | l | m_l | Subshell |
|-----|---|---|-------|----------|
| (a) | ? | ? | 0 | 4p |
| (b) | 2 | 1 | 0 | ? |
| (c) | 3 | 2 | -2 | ? |
| (d) | ? | ? | ? | 2s |

- 4.8. For each of the following, give the subshells, the allowable m_l values and the number of orbitals
- a) n = 4; l = 2 b) n=5; l = 1 c) n=2; l = 0 d) n=3; l = 2
- 4.9. For each of the following subshells, give the n and l values and the number of orbitals:
- a) 5s b) 3p c) 4f d) 5g e) 4s f) 3d
- 4.10. Each electron in an atom may be characterized by a set of four quantum numbers (n, l, m_l , m_s). For each of the following, tell how many different sets of quantum numbers are possible, such that each set contains all the values listed:
- a) n = 2, l = , 2 b) n=2, l = 0 c) n= 4, l=2, m_l = +3
 d) n=4, l=3, m_l = -2 e) n=3, l = 1, m_l = 0 f) n=3, l = 1
- 4.11. Give the values for all four quantum numbers for each electron in the ground state of the nitrogen atom writing the positive values for m_l and m_s first.

- 4.14. Give the values for all four quantum numbers for each electron in the ground state of the sodium atom writing the positive values for m_l and m_s first.
- 4.15. Using the periodic table and assuming a regular filling pattern, give the full and condensed (noble gas configuration), partial orbital diagram, and the number of inner electrons of each of the following:
a) $_{38}\text{Sr}$ b) $_{84}\text{Po}$ c) $_{50}\text{Sn}$ d) $_{74}\text{W}$
- 4.16. From its partial (valence-level) orbital diagram, write the condensed/noble gas configuration and group number:
- 4.17. Using only the periodic table, rank the elements in each set in order of increasing size:
a) Se, Br, Cl b) I, Xe, Ba
- 4.18. Using the periodic table only, rank the elements in each set in order of decreasing ionization energy:
a) Sb, Sn, I b) Sr, Ca, Ba
- 4.19. Using the condensed or noble gas configurations, write equations representing the formation of ion(s) of the following elements:
a) $_{56}\text{Ba}$ b) $_{8}\text{O}$ c) $_{82}\text{Pb}$

TOPICS: IDEAL GASES AND THE KINETIC MOLECULAR THEORY

- 6.1. Pressure
 - 6.1.1. Atmospheric Pressure
 - 6.1.2. Manometers
- 3.2. Gas Laws
 - 6.2.1. Pressure-Volume Relationship: Boyle's Law
 - 6.2.2. Temperature-Volume Relationship: Charles Law
 - 6.2.3. Quantity-Volume Relationship: Avogadro's Law
 - 6.2.4. General Gas Laws or The Combined Gas Law
 - 6.2.5. The Ideal Gas Equation
- 6.3. The Kinetic Molecular Theory
- 6.4. Partial Pressures and Mole Fractions
- 6.5. Graham's Law of Effusion
- 6.6. Real Gases
 - 6.6.1. Ideal Gas versus Real Gas
 - 6.6.1.1. Attractive Forces versus Repulsive Forces
- 6.7. The Virial Equation of State
- 6.8. The vander Waals Equation of State
 - 6.8.1. Volume Correction

EXPECTED COMPETENCIES:

At the end of the lesson, you must have:

1. described the relationships among pressure, temperature, volume and amount of gases,
2. described the properties and behavior of gases,
3. used kinetic molecular theory to explain the behavior of gas,
4. derived the ideal gas equation from the gas laws,
5. use the ideal-gas equation to determine the density or molar mass of a gas and in stoichiometry calculations,
6. described the assumptions made in the kinetic-molecular theory and used the theory to explain the nature of gas pressure and temperature
7. described how the distribution of speeds and the average speed of gas molecules change with temperature
8. cited the general conditions of P and T under which real gases most closely approximate ideal-gas behavior
9. explained the differences between ideal and real gases,

TECHNICAL SPECIFICATIONS/CONTENTS:

Air is a mixture of gases. We absorb oxygen, O₂, when we breathe air. Air is about 78% N₂-molecules and about 21% O₂ molecules. We have encountered countless of gases which play vital roles in our lives such as Chlorine gas (Cl₂) use for purifying water for drinking purposes. Acetylene gas (C₂H₂) which finds useful in oxy-acetylene welding. Gases also are responsible for the climate change we are now experiencing known as the greenhouse gases such as Carbon dioxide, CO₂, and Methane, CH₄.

They are believed to have molecules in rapid motions. Any two or more gases can be mixed in any proportion to have a perfectly uniform mixture. Gases can expand and fill any container into which they are introduced. Consequently, the volume of the container in which they are held is equal to the volume of the gas introduced. They also can be compressed thus forcing gas molecules to come closer as their molecules are separated by comparatively large distances. And when released from a container, they diffuse and can be detected in all parts of the room as gas molecules are in constant, rapid motion and as such due to their random motion, they strike the wall of the containers which explains the fact why gases exert pressure.

Substances in which under ordinary conditions exist as liquids and solids can also exist as gases often referred to as vapors. Like in the case of water, H₂O, it can exist as liquid water, solid ice or water vapor. Under right conditions, substances can co-exist in all three phases or states of matter, at the same time.

6.1. Pressure

It is the force exerted by matter per unit area. P = F/A. And that the pressure of a gas is equal to the force it exerted on the walls of the containing vessel divided by the surface area of the containing vessel. In an inflated balloon, a gas exerts a pressure on the inside surface of the balloon.

6.1.1. Atmospheric Pressure

The atmosphere exerts a downward force due to gravity. Thus, the pressure exerted by a matter is the product of its mass, multiplied by the acceleration due to gravity. F=ma where F is the force exerted by a matter, m is the mass and a is the acceleration due to gravity which is equal to 9.8m/s².

Pascal is the SI unit for pressure abbreviated as Pa defined as the pressure equivalent to one Newton (N=1kg.m/s²) on a one square meter area (m²)

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

The name given Pascal after the French mathematician Blaise Pascal (1623-16620).

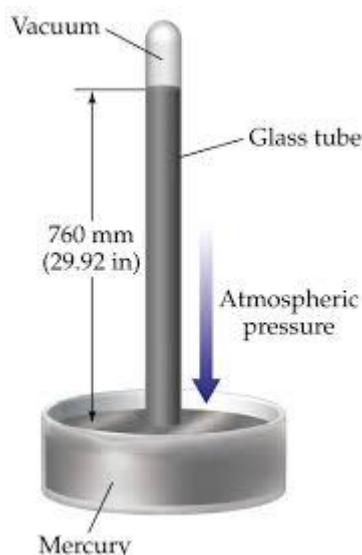


Figure 6.1. The Mercury Barometer

Atmospheric pressure can be measured using a barometer. An instrument devised in the 17th Century by Evangelista Torrecilli, a student of Galileo. It is a tube which is approximately 850mm in length and sealed at one end and is filled with mercury and inverted in an open container (Figure 3.1). The mercury falls in the tube without completely running out. The pressure of the atmosphere on the surface of the mercury in the dish supports the column of mercury inside the tube.

The space inside the tube above the mercury is a nearly perfect vacuum. Mercury is not very volatile at room temperature, and only a small amount of mercury vapor is occupying this space. Thus practically, no pressure is exerted on the upper surface of the mercury in the column. The reference level as shown in Figure 3.1 results from the weight of mercury column alone. And this pressure is equal to the atmospheric pressure outside the tube and the reference level. The height of mercury in the tube serves as a measure of the atmospheric pressure. When the atmospheric pressure rises, it pushes the mercury higher in the tube. Recall that Pressure is the force per unit area. Regardless of the cross-sectional area of the tube, a given atmospheric pressure will support the mercury in the tube to the same height.

Atmospheric pressure varies from day to day and from place to place. The average pressure at sea level and 0°C gives a height of the column of mercury in the tube of 760mm Hg which is called 1 atmosphere (1atm).

Standard atmosphere : 1 atm = 101,325 Pa = 101.325 kPa = 760 torr (for Torrecilli) = 760 mm Hg.

Sample Problem 6.1.

- a). Convert 0.545 atm to torr b). Convert 7.7×10^{-2} torr to atm c). Convert 145.2 kPa to torr

Solutions:

- a. We convert atmosphere to torr using the conversion factor

$$\text{? torr} = (0.545 \text{ atm}) \frac{(760 \text{ torr})}{(1 \text{ atm})} = 414 \text{ torr}$$

- b. We convert torr to atmospheres using the dimensional analysis and the conversion factor:

$$\text{? atm} = \left(7.7 \times 10^{-2}\right) \text{ torr} \frac{(1 \text{ atm})}{(760 \text{ torr})} = 1.0 \times 10^{-4} \text{ atm}$$

c. We use the relationship $760 \text{ torr} = 101.325 \text{ kPa}$

$$\text{? torr} = (145.2 \text{ kPa}) \frac{(760 \text{ torr})}{(101.325 \text{ kPa})} = 1,089 \text{ torr}$$

6.1.2. Manometers

It is a device for measuring pressures of samples of gases patterned after the barometer. The type of manometer shown in Figure 7.2 is consisting of a U-Tube containing mercury. One arm of the U-tube is open to the atmosphere and that atmospheric pressure is exerted on the mercury in this arm. The other arm is connected to a container of a gas in such a way that the gas exerts pressure on the mercury in this arm.

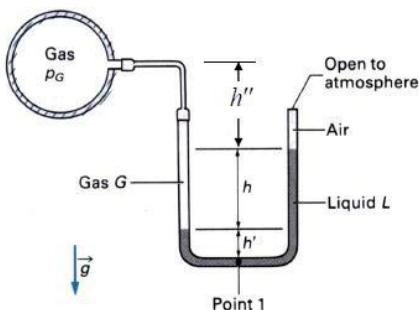


Figure 6.2. U-tube Manometer

If the gas sample has a pressure equal to atmospheric pressure, the mercury would stand at the same level in both arms of the U-tube. In Figure 3.2, the gas pressure is greater

"The Chemistry of Life Blood Pressure

The human heart pumps blood to the parts of the body through arteries, and the blood returns to the heart through veins. When your blood pressure is measured, two valves are reported, such as 120/80 (120 over 80) which is a normal reading. The first measurement is the systolic pressure, the maximum pressure when the heart is pumping. The second is the diastolic pressure, the pressure when the heart is in the resting part of its pumping cycle.

Blood pressure is measured using a pressure gauge attached to a closed, air-filled jacket, or cuff that is applied like a tourniquet in the arm. The pressure gauge may be a mercury manometer or some other device. The air pressure in the cuff is increased using a small pump until it is above the systolic pressure and prevents the flow of blood. The air pump inside the cuff is then slowly reduced until blood just begins to pulse through the artery, as detected by the use of a stethoscope. At this point the pressure in the cuff equals the pressure that the blood exerts inside the arteries. Reading the gauge gives the systolic pressure. The pressure in the cuff is then reduced further until the blood flows freely. The pressure at this point is the diastolic pressure.

6.2. The Gas Laws

A large number of experiments with gases show that there are four variables that are needed to define the physical condition or state of a gas, namely: T – temperature, P-pressure, V-volume and n – number of moles. The equations expressing the relationships among T, P, V and n are called the Gas Laws.

6.2.1. Pressure-Volume Relationship: Boyle's Law

Decreasing the pressure inside the balloon causes the balloon to expand the fact why weather balloons expand as they rise through the atmosphere. Conversely, compressing the gas results to the increase in pressure of the gas inside the balloon. British Chemist Robert Boyle (1627-1691) first investigated the relationship between the pressure of a gas and its volume.

In performing his experiment, Boyle used the J-shaped tube as shown in figure 7.3. A quantity of a gas is trapped in the tube behind a column of mercury. Boyle changed the pressure on the gas by adding mercury to the tube. He found that the volume of the gas decreased as the pressure increased. According to him, doubling the pressure of the gas would decrease the volume of the gas to half its original volume.

Apparatus for Studying the Relationship between Pressure and Volume of a Gas

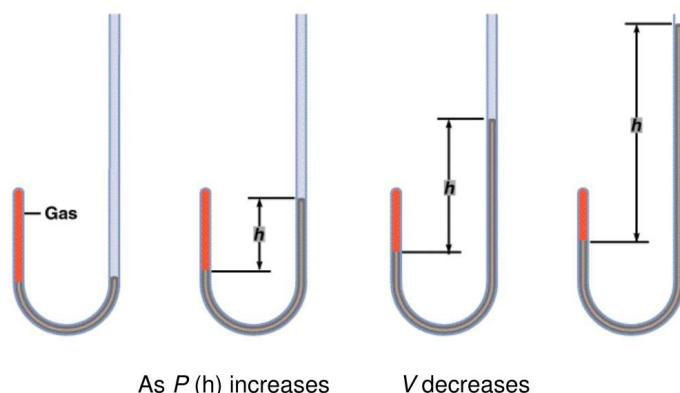


Figure 6.3. J-Apparatus for Measuring the Pressure with Respect to Volume

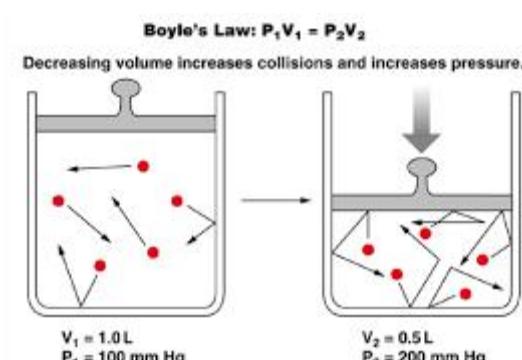


Figure 6.4. Boyle' Law Illustrated

Boyle's Law summarizes these observations “**that the volume of a fixed quantity of a gas maintained at constant temperature is inversely proportional to the pressure**”. In an inversely proportional measurements, one gets smaller when the other gets bigger. Mathematically, Boyle's Law can be expressed:

$$V \propto \frac{1}{P} \text{ converting the proportionality sign with the equality sing using a constant } k,$$

$$V = k \frac{1}{P} \text{ and } k = PV, k_1 = k_2 \text{ at constant Temperature}$$

$K_1 = P_1 V_1$ and $K_2 = P_2 V_2$; where P_1 and P_2 are the initial and final pressures, respectively, and V_1 and V_2 are the initial and final Volumes, respectively.

$$P_1 V_1 = P_2 V_2 \text{ at constant Temperature}$$

The volume of a gas is customarily measured in liters. Liter is equivalent to 1 cubic decimeter ($1 \text{ dm}^3 = 1000 \text{ cm}^3$) and $1 \text{ mL} = 1 \text{ cm}^3$.

Application of the Boyle's Law is every time we breathe air. Between breaths the gas pressure inside the lungs equals atmospheric pressure. The volume of the lungs is governed by the rib cage, which can expand and contract, and the diaphragm, a muscle beneath the lungs. Inhalation occurs when the rib cage expands and the diaphragm moves downward. Both of these actions serve to increase the volume of the lungs, thus decreasing the gas pressure inside the lungs. The atmospheric pressure then forces air into the lungs until the pressure in the lungs once again equals atmospheric pressure. Exhalation involves the reverse process: The rib cage contracts and the diaphragm moves up, both of which decrease the pressure the volume of the lungs. Air is forced out of the lungs by the increase in pressure caused by this reduction in volume.

Sample Problem 6.2. A sample of a gas occupies 345mL under a pressure of 0.72 atm. If the temperature is held constant, what volume will the sample of a gas occupy under a pressure of 0.95atm?

Solution:

$$\text{Given: } V_1 = 345 \text{ mL} \quad P_1 = 0.72 \text{ atm} \quad P_2 = 0.95 \text{ atm} \quad \text{Req'd: } V_2 = ?$$

$$P_1 V_1 = P_2 V_2$$

$$V_2 = \frac{P_1 V_1}{P_2} = \frac{(0.72 \text{ atm})(345 \text{ mL})}{(0.95 \text{ atm})} = 261.5 \text{ mL}$$

6.2.2. Temperature – Volume Relationship: Charles's Law

Hot air expands once heated, that's why hot air balloons rise. The warm air inside the balloon is less dense than the surrounding cool air at the same pressure. The differences in their densities causes the balloon to ascend. Conversely, a balloon will shrink when the gas inside the balloon is cooled.

The temperature and volume relationship of a gas is studied by French scientist Jacques Charles in 1787 and was extended by Joseph Gay-Lussac in 1802.

When gas is heated at constant pressure, gas expands. Data showed that for each Celsius degree rise in temperature, gas volume increases $1/273$ of its value at 0°C keeping the pressure at constant.

Although volume increases regularly with the increase in temperature, the volume is not directly proportional to the Celsius temperature. An increase in temperature from 1°C to 10°C , does not increase the volume tenfold.

In 1848 William Thomson, a British physicist whose title was Lord Kelvin, proposed the absolute temperature scale known as the Kelvin scale. The temperatures are measured in Kelvin in which the volume is directly proportional to the Kelvin scale. On this scale 0K, which is known as absolute zero, equals -273°C. In terms of the Kelvin scale, Charles's Law can be stated “**the volume of a fixed amount of gas maintained at constant pressure is directly proportional to its absolute temperature**”.

$$T(K) = t + 273.15$$

$V \propto T$, having a constant k; $V = kT$ at constant Pressure

$$k_1 = k_2 \text{ then, } k_1 = \frac{V_1}{T_1} \text{ and } k_2 = \frac{V_2}{T_2} \quad \frac{V_1}{T_1} = \frac{V_2}{T_2} \text{ at constant Pressure}$$

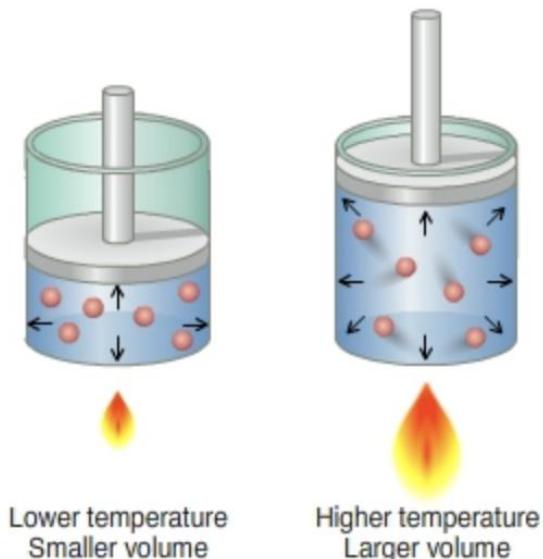


Figure 6.5. Charles' Law Illustrated

Sample Problem 6.3. A volume of a gas has a volume of 80.5mL at 55°C. What volume will the sample occupy at 10°C when the pressure is held constant?

Solution:

Given: $V_1 = 80.5\text{mL}$ $T_1 = 55^\circ\text{C} + 273 = 328\text{K}$ $T_2 = 10^\circ\text{C} + 273 = 283\text{K}$ Req'd: $V_2 = ?$

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

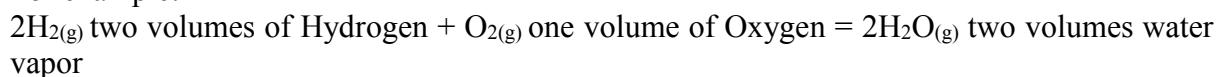
$$V_2 = \frac{V_1 T_2}{T_1} = \frac{(80.5\text{mL})(283\text{K})}{(328\text{K})} = 69.5\text{mL}$$

A balloon blown up inside a warm building will shrink when it is carried to a colder area, like the outdoors. Humans' lung capacity is reduced in colder weather; runners and other athletes may find it harder to perform in cold weather for this reason. Charles' Law, along with a couple other gas laws, is responsible for the rising of bread and other baked goods in the oven; tiny pockets of air from yeast or other ingredients are heated and expand, causing the dough to inflate, which ultimately results in a lighter finished baked good. Car (combustion) engines work by this principle; the heat from the combustion of the fuel causes the cylinder to expand, which pushes the piston and turns the crankshaft.

6.2.3. Quantity-Volume Relationship: Avogadro's Law

When a gas is added to a balloon, the balloon expanded. The volume of a gas is not only affected by the temperature and pressure but also by the amount of a gas. The relationship between the quantity of a gas and its volume was introduced by Joseph Gay-Lussac and Amadeo Avogadro. Gay-Lussac carried-out several experiments on the properties of gases. In 1808, he observed the law of combining volumes "at a given pressure and temperature the volumes of gases that react with one another are in the ratios of small whole number."

For example:



Three years later, interpreted Gay-Lussac's observation by proposing what we referred to as the Avogadro's Hypothesis: "equal volumes of gases at the same temperature and pressure contain equal numbers of molecules." It followed then that approximately 22.4 liters of any gas at 0°C and 1 atmosphere pressure contain 6.02×10^{23} gas molecules for 1 mol of a gas.

Avogadro's Law then from Avogadro's Hypothesis: "the volume of a gas maintained at constant temperature and pressure is directly proportional to the number of moles of the gas."

Doubling the number of moles of a gas will cause the volume to double when temperature and pressure are held constant.

$$V \propto n \text{ at constant Temperature and Pressure; } V = kn$$

6.2.4. General Gas Law or the Combined Gas Laws

According to Boyle's Law: $V \propto \frac{1}{P}$.

According to Charle's Law: $V \propto T$

Combining them: $V \propto \frac{T}{P}$, converting the proportionality sign into an equality sign, let us have k as a constant, we obtain, $V = k \frac{T}{P}$. Suppose condition 1 is represented by K_1 and condition 2 is represented by K_2 , then $k_1 = k_2$

$$k_1 = \frac{P_1 V_1}{T_1} \text{ and } k_2 = \frac{P_2 V_2}{T_2}, \text{ then}$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Sample Problem 6.5. 2.00 L of a gas is collected at 25.0 °C and 745.0 mmHg. What is the volume at STP?

Solution:

Condition 1:

$$V_1 = 2.00 \text{ L} \quad P_1 = 745.0 \text{ mmHg} \quad T_1 = 25.0 \text{ }^\circ\text{C} + 273.15 = 298.15 \text{ K}$$

Condition 2: at STP (Standard Temperature and pressure, where:

$$V_2 = ? \quad P_2 = 760.0 \text{ mmHg} \quad T_2 = 0.0 \text{ }^\circ\text{C} + 273.15 \text{ K} = 273.15 \text{ K}$$

$$V_2 = \frac{P_1 V_1 T_2}{P_2 T_1} = \frac{(745.0 \text{ mmHg})(2.00 \text{ L})(273.15 \text{ K})}{(760.0 \text{ mmHg})(298.15 \text{ K})} = 1.80 \text{ L}$$

6.2.5. Ideal-Gas Equation

Summarizing the preceding gas laws:

$$\text{Boyle's Law} \quad V \propto \frac{1}{P} \text{ at constant } n, T$$

$$\text{Charles's Law} \quad V \propto T \text{ at constant } n, P$$

$$\text{Avogadro's Law} \quad V \propto n \text{ at constant } T, P$$

Combining these gas laws we have:

$$V \propto \frac{nT}{P} \text{ using the proportionality constant } R, \text{ we got: } V = R \left(\frac{nT}{P} \right)$$

Rearranging: $PV = nRT$ - the Ideal Gas Equation known as the equation of state for the ideal gas.

An ideal gas is a hypothetical gas whose pressure, volume and temperature behavior is described completely by the ideal-gas equation.

The R is called the gas constant. The value and unit depends upon the units of P , V , N and T where the temperature is the absolute temperature. The quantity of gas, n , always expressed in moles (mol). Liters and atmosphere (atm) are the units chosen for volume and pressure, respectively.

At STP (standard temperature and pressure), $T=273.15\text{K}$, $V=22.4136\text{L}$ and $P=1\text{atm}$. Therefore:

$$R = \frac{PV}{nT} = \frac{(1\text{ atm})(22.4136\text{ L})}{(1\text{ mol})(273.15\text{ K})} = 0.08206 \frac{\text{L-atm}}{\text{K-mol}}$$

$$\text{Solving for } n = \frac{\text{mass(g)}}{\text{Molar Mass } (\frac{\text{g}}{\text{mol}})} = \frac{m}{MM}, \text{ therefore: } PV = \left(\frac{m}{MM} \right) RT$$

$$\frac{n}{V} = \frac{P}{RT} \text{ multiplying both sides by molar mass (MM); } \frac{n}{V}(MM) = \frac{P}{RT}(MM)$$

Let's check their units:

$$\frac{n}{V}(MM) = \frac{g}{L} = \text{density } (\rho); \frac{P}{RT} = \text{mol/L} \text{ and MM = g/mol; therefore: } \rho = \frac{PM}{RT}$$

Sample Problem 6.6. What is the density of carbon tetrachloride (CCl_4) vapor at 714 torr and 125°C ?

Solution:

$$\text{Given: } P = 714 \text{ torr} \cdot \frac{(1\text{ atm})}{(760 \text{ torr})} = 0.939 \text{ atm} \quad T = 125 + 273.15 = 398.15\text{K}$$

$$\text{MM of } \text{CCl}_4 = (\text{C})(1) + (\text{Cl})(4) = (12)(1) + (35.45)(4) = 153.8\text{g/mol}$$

$$\rho = \frac{(0.939\text{ atm}) \left(\frac{153.8\text{ g}}{\text{mol}} \right)}{(0.08206 \frac{\text{L-atm}}{\text{K-mol}})(398.15\text{ K})} = 4.42\text{ g/L}$$

6.3. Kinetic-Molecular Theory

The kinetic-molecular theory serves as a model that explains the behavior of gas particles as experimental conditions such as temperature or pressure change. It is simply the theory of moving molecules.

This theory was developed over 100 years culminating, in 1857 when Rudolf Clausius published a complete and satisfactory form of the theory.

The Kinetic-Molecular Theory includes the following postulates:

1. Gases consist of large numbers of molecules that are in continuous, random motion (The word molecule is used to designate the smallest particle of any gas, some gases such as the noble gas, consist of individual atoms).

- a. Gas is a collection of a large number of atoms or molecules.
 - b. Atoms or molecules making up the gas are very small particles like a point (dot) on a paper with a small mass.
 - c. The particles are always in constant motion. Because of lack of interactions and the free space available, the particles randomly move in all directions but in a straight line.
2. The volume of all the molecules of the gas is negligible compared to the total volume in which the gas is contained.
- a. Particles are generally far apart such that their inter-particle distance is much larger than the particle size and there is large free unoccupied space in the container. Compared to the volume of the container, the volume of the particle is negligible (zero volume).
 - b. Because of motion, gas particles, occupy the total volume of the container whether it is small or big and hence the volume of the container to be treated as the volume of the gases.
3. Attractive and repulsive forces between gas molecules are negligible.
- a. Particles are independent. They do not have any (attractive nor repulsive) interactions among them.
4. The average kinetic energy of the molecules is proportional to the absolute temperature. At any given temperature the molecules of all gases have the same kinetic energy.
- a. Energy can be transferred between molecules during collisions, but the average kinetic energy of the molecules does not change with time, as long as the temperature of the gas remains constant. Meaning the collision is perfectly elastic.
 - b. Since the particles are always in motion, they have average kinetic energy proportional to the temperature of the gas.
 - c. Moving particles may collide with other particle or container. But the collisions are perfectly elastic. Collisions do not change the energy or momentum of the particle.
 - d. Collision of the particles on the walls of the container exerts a force on the walls of the container. Force per unit area is the pressure. The pressure of the gas is thus proportional to the number of particles colliding (frequency of collisions) in unit time per unit area on the wall of the container.

6.4. Partial Pressures and Mole Fractions

So far, we have considered the behaviour of pure gases – consisting of only one gas. How about those mixtures of two or more gases?

John Dalton while studying the properties of air observed that “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 that particular gas in a mixture of gases is called the partial pressure of that gas and is called the Dalton’s Law of Partial Pressures.

Let, P_T be the total pressure and $P_1, P_2, P_3, P_4, \dots$ and so forth be the partial pressures of the gases in the mixture. Dalton’s Law then follows:

$$P_T = P_1 + P_2 + P_3 + P_4 + \dots$$

Let n_t be the total number of moles and n_1, n_2, n_3, n_4 and so forth be the number of moles of gas 1, gas 2, gas 3 and gas 4, respectively and that $n_t = n_1, n_2, n_3, n_4 + \dots$

If each of the gas obeys the ideal-gas equation:

$$P_1 = n_1 \left(\frac{RT}{V} \right) \quad P_2 = n_2 \left(\frac{RT}{V} \right) \quad P_3 = n_3 \left(\frac{RT}{V} \right) \quad P_4 = n_4 \left(\frac{RT}{V} \right) \text{ and so forth....}$$

And that $P_T = (n_1, n_2, n_3, n_4, \dots) \left(\frac{RT}{V} \right) = n_t \left(\frac{RT}{V} \right)$

If n_1 mol of gas 1 and n_2 mol of gas 2 are mixed the total number of moles of the gases in the mixture is $n_t = n_A + n_B$. The ratio of the number of moles A (n_A) to the total number of moles of gases in the mixture is called the mole fraction of gas 1, X_1 .

$$X_1 = \frac{n_1}{n_1+n_2} = \frac{n_1}{n_t} \text{ and for the mole fraction of gas 2; } X_2 = \frac{n_2}{n_1+n_2} = \frac{n_2}{n_t}$$

and the partial pressure of gas 1 is

$$P_1 = \left(\frac{n_1}{n_1+n_2} \right) P_T = X_1 P_T$$

and the partial pressure of gas 2 is

$$P_2 = \left(\frac{n_2}{n_1+n_2} \right) P_T = X_2 P_T$$

Note that the sum of the mole fraction is equal to 1; $X_1 + X_2 = 1.0$

$$\frac{n_1}{n_1+n_2} + \frac{n_2}{n_1+n_2} = 1$$

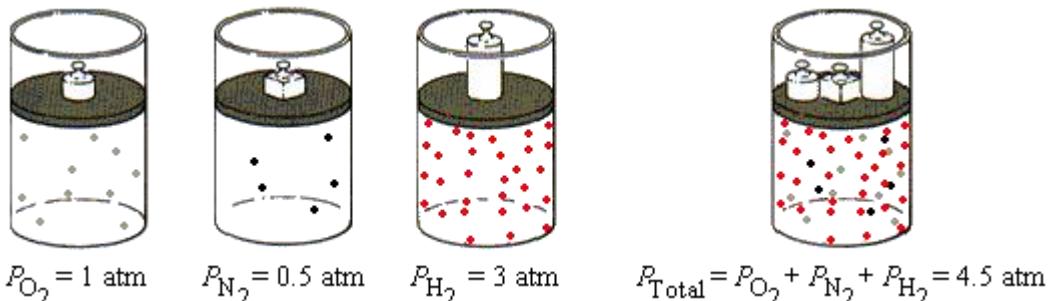


Figure 6.6. Dalton's Theory of Partial Pressure Illustrated

Sample Problem 6.7. A mixture of 4.0g of oxygen and 4.0g of helium has a total pressure of 0.900atm. What is the partial pressure of oxygen?

Solution:

$$\text{Given: } 4.0\text{g O}_2 \times \frac{1\text{ mol O}_2}{32\text{ g O}_2} = 0.125 \text{ mol O}_2 ; 4.0\text{g He} \left(\frac{1\text{ mol He}}{4.0\text{ g He}} \right) = 1 \text{ mol He}$$

$$\text{Mole Fraction of O}_2: X_{O_2} = \frac{n_{O_2}}{n_{O_2} + n_{He}} = \frac{0.125 \text{ mol}}{0.125 \text{ mol} + 1.00 \text{ mol}} = 0.111$$

$$\text{The partial pressure of O}_2 \text{ is: } P_{O_2} = X_{O_2} + P_T = (0.111)(0.900\text{atm}) = 0.0999\text{atm}$$

$$\text{The partial pressure of He is: } P_{He} = 0.900\text{atm} - 0.0999\text{atm} = 0.8001\text{atm}$$

6.5. Graham's Law of Effusion

Effusion is the escape of gas molecules through a tiny hole into an evacuated space. **Diffusion** is the spread of one substance throughout a space or throughout another substance. Take the case for example the molecules of a perfume diffuse throughout a room.

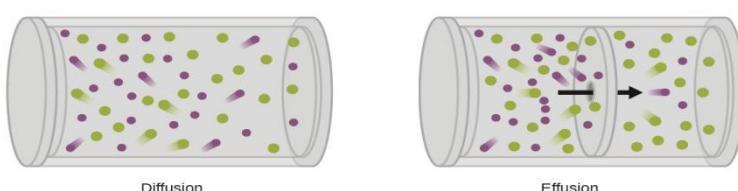


Figure 6.6. Diffusion and Effusion Illustrated

Thomas Graham in 1846, discovered that the effusion rate of any gas is inversely proportional to the square root of its molar mass. Suppose we have two gases at the same temperature and pressure in containers with identical pinholes. If the rates of effusion of the two substances r_A and r_B , with their respective molar masses, M_A and M_B . Graham Law states:

$$\frac{r_A}{r_B} = \sqrt{\frac{M_B}{M_A}}$$

For example, in the case of air and Helium. Helium escapes more rapidly than air. As a result, balloons filled with Helium deflates more quickly than balloons filled with air.

In the process of simple effusion, the rate of escape is faster than lighter molecules.

Sample Problem 6.8. An unknown gas composed of homonuclear diatomic molecules effuses at a rate that is only 0.355 times that of O_2 at the same temperature. What is the identity of the unknown gas?

Solution:

Given: $MM\ O_2 = (2)(16) = 32\text{g/mol}$

Let r_x and M_x be the rate of effusion and molar mass of the unknown gas

$$r_x = 0.355 \times r_{O_2}$$

Then: $\frac{r_x}{r_{O_2}} = 0.355 = \sqrt{\frac{32\text{ g/mol}}{M_x}} = (0.355)^2 = (\sqrt{\frac{32\text{ g/mol}}{M_x}})^2$ (squaring both sides)

$M_x = \frac{32\text{ g/mol}}{(0.355)^2} = \frac{32\text{ g/mol}}{0.216} = 254\text{ g/mol}$ Since we are told that the unknown gas is composed of homonuclear diatomic molecules, its molar mass is twice the atomic mass. The unknown gas is therefore, I_2 .

6.6. Real Gases

Previously, we discussed the gas laws that described the behavior of the ideal gases and the Kinetic Molecular Theory which explains this behavior on a molecular theory.

Let's discuss the limitations of the KMT and the ideal gas description when it comes to describing real gases. An ideal gas obeys $PV=nRT$ at all pressures and temperatures. The KMT gives us the molecular basis as to why the ideal gases behave this way.

6.6.1. Ideal Gas Vs. Real Gas

Again, according to KMT, an ideal gas has molecules so infinitely small. So small that we can neglect the molecular volume of the gas. Whereas we're gonna treat the molecule of a gas a point particle. KMT also explained about the intermolecular forces of attraction of a gas that they don't have any interactions with one another. However, real gases do have volumes and they also exert attractive forces on each other. We can treat all gases as ideal gases on all conditions because it will come to a point where the intermolecular force of attraction as well as the size of the gas molecules become significant enough to influence its behavior.

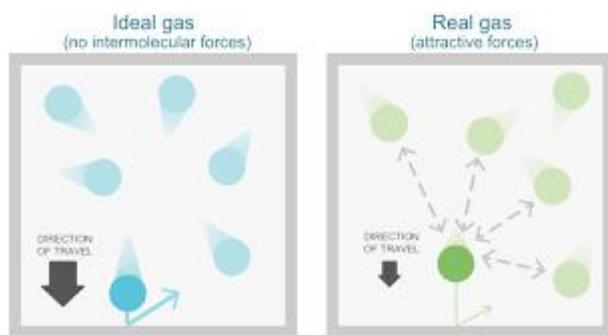


Figure 6.7. Ideal Gas Molecules Vs. Real Gas Molecules

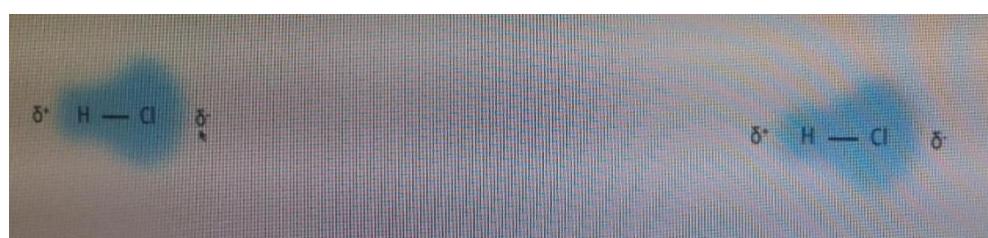
One particular case is when have a condition in which the intermolecular forces of attraction will cause the gas to start liquefying. This is now the part where we will have to consider intermolecular forces of attraction because we have phase changes.

Let's consider Boyle's Law, so we could start seeing the deviation of an ideal gas from a real gas. Looking at the ideal gas isotherm, Boyle's Law tells us the relationship between pressure and volume at constant temperature and number of moles. Overall we know that there is inverse relationship so we can draw isotherms. In the curve, it describes the behavior at T_1 , even if we start decreasing the temperatures to T_2 , T_3 and T_4 we still have the same relationship between pressure and volume.

For the real gas isotherms, we can see deviations. For T_1 , we can still observe a nice P-V curve. However, if we start decreasing the temperature to T_2 , this is where we start changes in the shape of the P-V curve different from our typical smooth curve for ideal gas. Further decreasing the temperatures to T_3 and T_4 , some discontinuities in the plots are seen. Bear in mind that if we start decreasing the temperatures shall we say for a container of water vapor. What happens when we start decreasing the temperatures. What would happen to all the water vapor? Of course the water vapor will start to condense. The kinetic energy of the gas is not enough to escape the intermolecular force of attraction which causes condensation of a gas into liquid. Actually, in particular parts of the curve, we have a liquid and a vapor parts and in between this is where we have the phase changes.

6.6.1.1. Attractive Vs. Repulsive Forces

Referring to the model in figure (at right), we have $\text{HCl}_{(g)}$ which is a polar molecule. There is partially negative portion (H)



at the left side and a partially positive (Cl) portion at the right side. We expect that HCl is having the dipole-dipole interaction and that is an attractive force. At a point however, these two HCl molecules are far apart from one another. At this particular condition the distance is pretty much approaching infinity which occurs at really low pressure and high temperature.

Why do we need to have really low pressure because for gases pressure is inversely proportional to volume. So, if the pressure is really really low, we have very large volumes. If the volume is large, it implies that the distance between two molecules is very very large so the particles are super far from one another. And at high temperature, so that there is no

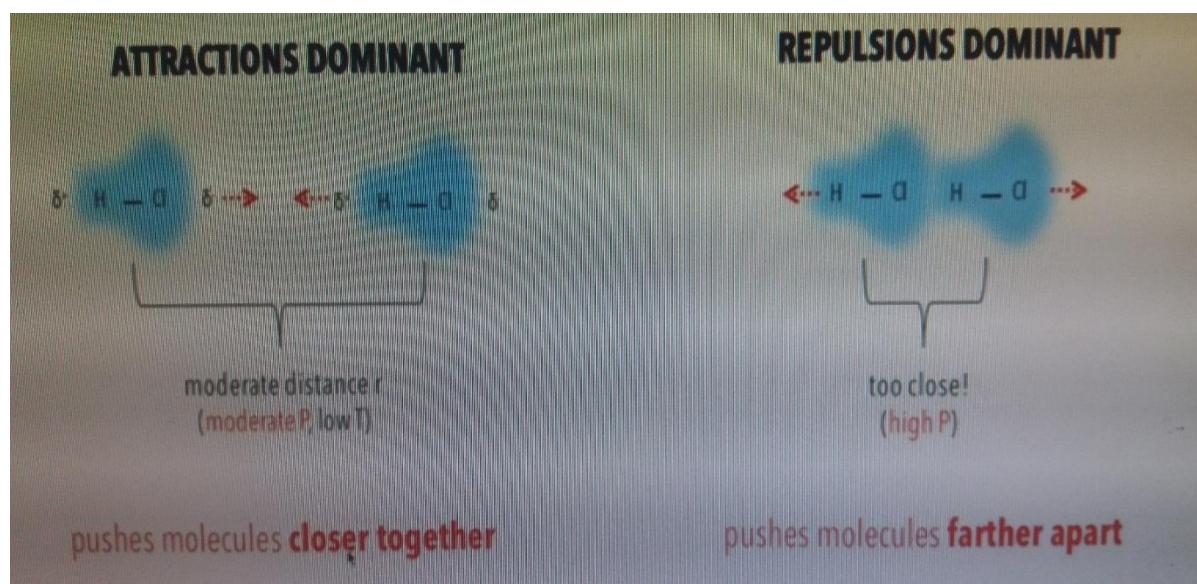
chance for the two molecules to approach one another, so that the dipoles will take hold of one another.

Bringing these two molecules closer to one another at a moderate distance between each other occurring at moderate pressure and low temperature. At this point, we now have a small space between these two molecules such that they could attractive interaction. The partial positive charge of the other molecule is close enough to the partial negative charge of the other molecule such that they can have the dipole-dipole interaction.

When these two molecules approach one another, and they going to be drawn even closer to one another. If we force them a little bit closer to one another, that's when they start repelling each other. This occurs at very high pressure.

Imagine, a container with a gas and the pressure is increased, the molecules are drawn closer to each other. Considering a very short distance which is unfavorable because molecules are made up of positive nuclei and negatively charged electron cloud. As the become way too close to one another they start repelling each other. The negatively charged electron clouds will start forcing their way into their space causing them to repel each other. If two molecules come closer to each other they're going to push away one another.

In terms of compressibility, if attractions are dominant, the gas becomes more compressible. It is easier to compress the gas repulsion is dominant. Overall, we could say that the real gas volume. If attractive forces are dominant, the real gas volume is smaller than the ideal gas volume (as the molecules have no attractions to each other). If repulsive forces are dominant, the real gas volume is going to be larger than the ideal gas volume.



Compressibility Factor, Z

It is the ratio of the real gas volume to the ideal gas volume at the same conditions,

$$Z = \frac{V_{real}}{V_{ideal}},$$

If $Z < 1$; volume of real gas is less than ideal gas volume – attractive forces dominant, the gas is more compressible.

If $Z > 1$; volume of real gas is greater than ideal gas volume – repulsive forces dominant, the gas is less compressible.

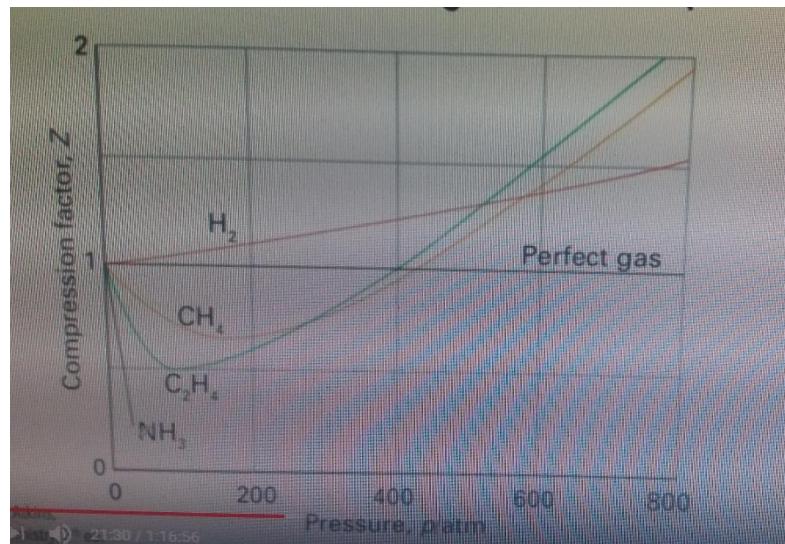
If $Z = 1$; volume of real gas is equal to the volume of ideal gas

$$\text{For 1 mol of a gas: } V_{ideal} = \frac{RT}{P} \quad Z = \frac{V_{real}}{\left[\frac{RT}{P}\right]} = \frac{PV_{real}}{RT}$$

Let's look at the variation of Z of certain gas at varying temperature. In the chart, we have the low temperature, moderate and high temperatures. The Z value of 1 corresponds to the ideal gas or perfect gas regardless of the pressure and temperature. For real gases, varies based on the temperature.

6.7. The Virial Equation of State

Referring to the figure below, all these curves were determined experimentally. So the volume of this gases were measured at different conditions. The compression factor calculated at different pressure and temperatures.



The general equation fitting to the curve is:

$$Z = 1 + B'P + C'P^2 + \dots \text{ where: } B' \text{ and } C' \text{ are the Virial Coefficients.}$$

B' is the second Virial Coefficient (could be + or -). If B' is positive, a curve similar to H_2 , repulsions dominate. If B' is negative, attractive forces dominate

C' is the third Virial Coefficient and is always positive.
Virial coefficient varies with temperature and the type of gas.

Using the molar volume:

$$Z = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \dots$$

$$Z = 1 + B'P + C'P^2 \quad \text{and} \quad Z = \frac{PV_m}{RT} \text{ substituting to the formula:}$$

$$\frac{PV_m}{RT} = 1 + B'P + C'P^2 ; PV_m = RT(1 + B'P + C'P^2) - \text{Virial Equation of State}$$

Another equation:

$$PV_m = ZRT ; \quad PV_m = RT\left(1 + \frac{B}{V_m} + \frac{C}{V_{m^2}} + \dots\right) - \text{another form of Virial Equation for state.}$$

We have discussed about how our gas equation of state should reduce to the ideal gas equation of state at the limiting conditions, namely: low pressures, when pressure approaches zero and the molar volume approaches infinity.

As P approaches zero ($P \rightarrow 0$), $B'P$ is equal to 0 and $C'P^2$ is also equal to 0 such that the equation reduces to $PV_m = RT$. Since $V_m = \frac{V}{n}$, therefore, $PV = nRT$.

Another case, $PV_m = RT (1 + \frac{B}{V_m} + \frac{C}{V_{m^2}} + \dots)$ as V_m approaches infinity ($V_m \rightarrow \infty$) and when an infinity term is at the denominator, the whole term is equal to 0 such that $\frac{B}{V_m} = 0$ and $\frac{C}{V_{m^2}} = 0$.

Therefore: $PV_m = RT$; again $V_m = \frac{V}{n}$ such that: $PV = nRT$.

Sample Problem 6.9. Calculate the pressure exerted by 0.275 moles of N₂ gas in a 0.500 L flask at 273 K. The value of B for N₂ at 273 K is -10.5 cm³/mole.

Solution:

$$V = 0.500 \text{ L} \times \frac{1000 \text{ cm}^3}{1.0 \text{ L}} = 500 \text{ cm}^3 \times \frac{1.0 \text{ m}^3}{1000000 \text{ cm}^3} = 0.000500 \text{ m}^3 = 5.00 \times 10^{-4} \text{ m}^3$$

$$B = -10.5 \text{ cm}^3/\text{mole} = -1.05 \times 10^{-5} \frac{\text{m}^3}{\text{mol}}$$

$$n = 0.275 \text{ mol}$$

$$T = 273 \text{ K}$$

$$R = 8.3145 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

$$\text{Solving for } V_m = \frac{5.00 \times 10^{-4} \text{ m}^3}{0.275 \text{ mol}} = 1.82 \times 10^{-3} \frac{\text{m}^3}{\text{mol}}$$

$$\text{Solving for P: } P = \frac{RT}{V_m} \left(1 + \frac{B}{V_m}\right)$$

$$P = \frac{8.3145 \frac{\text{J}}{\text{mol} \cdot \text{K}} (273 \text{ K})}{1.82 \times 10^{-3} \frac{\text{m}^3}{\text{mol}}} \left(1 + \frac{-1.05 \times 10^{-5} \frac{\text{m}^3}{\text{mol}}}{5.00 \times 10^{-4} \frac{\text{m}^3}{\text{mol}}}\right) = 1.247 \text{ J/m}^3$$

6.8. The vander Waals Equation for State

Proposed by Johannes vander Waals in 19th century, a model to explain the different behavior of real gases versus ideal gases. He considered the different assumptions of the KMT, that limits the ideal gas equation. Assumptions are: gases have no volume and gases molecules do not interact. He added corrective terms to the ideal gas equation to account for the volume of gas molecules and interactions.

$P_{\text{ideal}}V_{\text{ideal}} = nRT$; Pressure will be affected by the interaction of molecules and volume will also be affected by the volume of actual molecule.

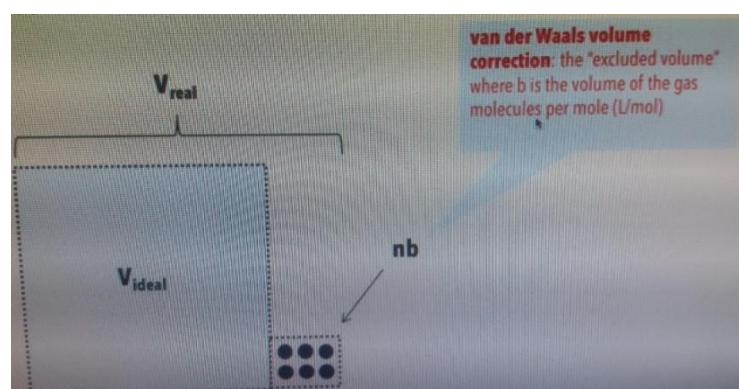
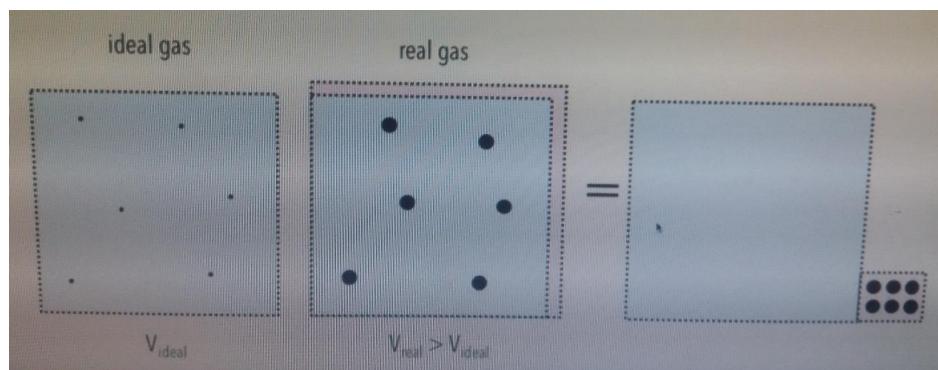
$P_{\text{ideal}} = P_{\text{real}} + P'$ and $V_{\text{ideal}} = V_{\text{real}} + V'$. P' and V' are the corrected pressure and volume, respectively.

$(P_{\text{real}} + P')(V_{\text{real}} + V') = nRT$ - basis for the van der Waals equation of state.

6.8.1. Volume Correction

Consider again an ideal gas having an ideal volume and considered the molecules as point particles. The actual gas molecules do not occupy space.

Real gas molecules do occupy a significant amount of space. Bear in mind that since our gas molecules occupy some space the real gas is going to be larger than the ideal gas.



$$V_{\text{real}} = V_{\text{ideal}} + nb \text{ (corrected van der Waals equation)}$$

PROGRESS CHECK:

- 6.1. A container holds 500. mL of CO₂ at 20° C and 742 torr. What will be the volume of the CO₂ if the pressure is increased to 795 torr?
- 6.2. A gas tank holds 2785 L of propane, C₃H₈, at 830. mm Hg. What is the volume of the propane at standard pressure?
- 6.3. A balloon contains 7.20 L of He. The pressure is reduced to 2.00 atm and the balloon expands to occupy a volume of 25.1 L. What was the initial pressure exerted on the balloon?
- 6.4. A sample of neon occupies a volume of 461 mL at STP. What will be the volume of the neon when the pressure is reduced to 93.3 kPa?
- 6.5. The volume of a sample of gas at 50°C is 2.50L. Assume that the pressure is held constant. a). What is the volume of the gas at -10. °C? b). At what temperature (in °C) would the volume be 1.25 L? c). At what temperature (in °C) would the volume be 2.75 l?
- 6.6. Carbon dioxide is usually formed when gasoline is burned. If 30.0 L of CO₂ is produced at a temperature of 1.00×10^3 °C and allowed to reach room temperature (25.0 °C) without any pressure changes, what is the new volume of the carbon dioxide?
- 6.7. When 50.0 L of oxygen at 20.0 °C is compressed to 5.00 L, what must the new temperature be to maintain constant pressure?
- 6.8. What volume will 10.0 g of CO_{2(g)} occupy at 27 °C and 2.00 atm?
- 6.9. What is the density of NH_{3(g)} at 1.00 °C and 1.15 atm?
- 6.10. a). Cyclopropane is a gas that is used as a general anesthetics. The gas has a density of 1.50 g/L at 50. °C and 0.948 atm. What is the molecular weight of cyclopropane? b). The empirical formula of cyclopropane is CH₂. What is the molecular formula of the compound?
- 6.11. Calcium Hydride, CaH_{2(s)}, reacts with water to yield H_{2(g)} and Ca(OH)_{2(s)}. a). Write the balanced equation for this reaction. b). How many grams of CaH_{2(s)} is required to prepare 3.00 L of H_{2(g)} at STP?
- 6.12. A chemical engineer uses waste CO₂ from a manufacturing process, instead of chlorofluorocarbons, as a “blowing agent” in the production of polystyrene. Find the density (in g/L) of CO₂ and the number of molecules per liter a). at STP, and b). at room conditions (20 °C and 1.00 atm).
- 6.13. An empty 149-ml flask weighs 68.322 g before a sample of volatile liquid is added. The flask is then placed in a hot (95.0 °C) water bath, the barometric pressure is 740 torr. The liquid vaporizes and the gas fills the flask. After cooling, flask and condensed liquid together weighs 68.997 g. What is the molar mass of the liquid?
- 6.14. A sample of argon gas at STP occupies 56.2 L. Determine the number of moles of argon and the mass in the sample.

6.15. The initial temperature of a 1.00 L sample of argon is 20 °C. The pressure is decreased from 720.0 mm Hg to 360 mm Hg and the volume increases to 2.14 L. What was the change in temperature of the argon?

6.16. A 20.0-L container is filled with helium and the pressure is 150.0 atm at 30.0 °C temperature. How many 5.00 L balloons can be filled when the temperature is 22.0 °C and the pressure is 755 mmHg?

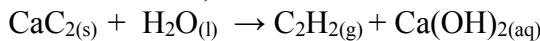
6.17. A sample of nitrogen gas occupies a volume of 2.00 L at 756 mm Hg and 0.00 °C. The volume increases by 2.00 L and the temperature decreases to 137.0 K. What is the final pressure exerted on the gas?

6.18. The partial pressure of $\text{CH}_{4(\text{g})}$ is 0.225 atm and of $\text{C}_2\text{H}_{6(\text{g})}$ is 0.165 atm in a mixture of two gases. a). What is the mole fraction of each gas in the mixture? b). If the mixture occupies 9.73 L at 35 °C, what is the total number of moles of gas in the mixture? c). How many grams of each gas is present?

6.19. To study O_2 uptake by muscle at high altitude, a physiologist prepares an atmosphere consisting of 79 mole % N_2 , 17 mole % $^{16}\text{O}_2$ and 4.0 mole % $^{18}\text{O}_2$. (The isotope $^{18}\text{O}_2$ will be measured to determine O_2 uptake). The total pressure is 0.75 atm to stimulate high altitude. Find the mole fraction and partial pressure of $^{18}\text{O}_2$ in the mixture.

6.20. To prevent the presence of air, noble gases are placed over highly reactive chemicals to act as inert “blanketing” gases. A chemical engineer puts a mixture of noble gases consisting of 5.50 g of He, 15.0 g of Ne, and 35.0 g of Kr in a piston cylinder assembly at STP. Calculate the partial pressure of each gas.

6.21. Acetylene, C_2H_2 , an important fuel in welding, is produced in the laboratory when calcium carbide, CaC_2 , reacts with water;



For a sample of acetylene collected over water, total gas pressure (adjusted to barometric pressure) is 738 torr and the volume is 523 mL. At the temperature of the gas (23 °C), the vapour pressure of water is 21 torr. How many grams of acetylene are collected?

6.22. If it takes 1.25 min for 0.010 mol of He to effuse, how long will it take for the same amount of ethane (C_2H_6) to effuse?

6.23. What is the molecular weight of gas X if it effuses 0.876 times as rapidly as $\text{N}_{2(\text{g})}$?

6.24. At 25°C and 0.500 atm, the density of N_2 is 0.572 g/L. the rate of effusion of N_2 gas through an apparatus is 9.50 mL/s. a). What is the density of a sample of a gas that effuses at a rate of 6.28 mL/s through the same apparatus under the same conditions b). What is the molecular weight of the gas?

6.25. If equal amounts of helium and argon are placed in a porous container and allowed to escape, which gas will escape faster and how much faster?

6.26. Two porous containers are filled with hydrogen and neon respectively. Under identical conditions, $\frac{2}{3}$ of the hydrogen escapes in 6 hours. How long will it take for half the neon to escape?

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TOPICS: ELECTROCHEMISTRY

- 7.1. Balancing Oxidation-Reduction Equations**
 - 7.1.1. Oxidation-Reduction Reactions**
 - 7.1.2. Half-Reactions**
- 7.2. The Ion-Electron Method**
 - 7.2.1. Reactions Occurring in Acid Solutions**
 - 7.2.2. Reactions occurring in Alkaline or Basic Solution**
- 7.3. Electrochemical Cell**
 - 7.3.1. Electrodes & Charge**
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- 7.6. Electrolysis**
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- 7.8. Batteries**
 - 7.8.1. Lead-Acid Storage Battery**
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 - 7.8.3. Nickel-Cadmium, Nickel Metal-Hydride, and Lithium-Ion Batteries**
- 7.9. Fuel Cells**
- 7.10. Preventing the Corrosion of Iron**

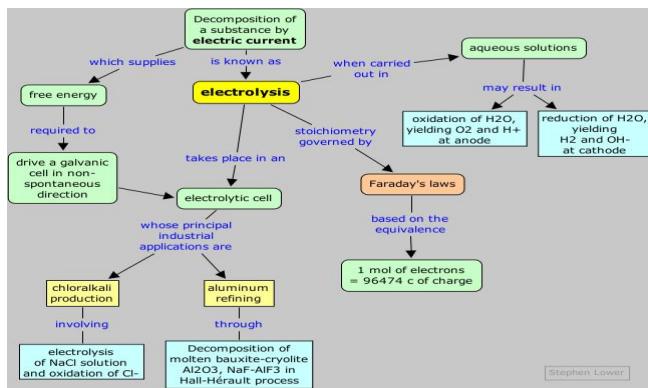
EXPECTED COMPETENCIES

At the end of the lesson, you must have:

1. defined oxidation-reduction (Redox) reactions,
2. balanced oxidation-reduction reaction by the addition of H^+ and OH^- ,
3. written and balance half-cell reactions,
4. described electrochemical cells,
5. described voltaic cells,
6. differentiated voltaic cell from electrolytic cell,
7. calculated cell under standard and non-standards conditions,
8. described electrolysis,
9. described different industrial electrolytic processes,
10. described the different batteries,
11. described fuel cells; and

12. explained how to control corrosion.

CONTENTS



theoretical as well as practical importance. Chemical reactions can be used in producing electrical energy (in cells that are called either voltaic or galvanic cells). This electrical energy can be used to bring about chemical transformations (in electrolytic cells). Additionally, the study of electrochemical processes leads to an in-depth understanding, as well as to systematize, oxidation-reduction phenomena taking place outside cells.

All chemical reactions are fundamentally electrical in nature since all types of chemical bonding involved electrons. Electrochemistry, however, is primarily the study of oxidation-reduction reaction. In other words, **electrochemistry** is that branch of chemistry dealing with the relationship between chemical change and electrical work.

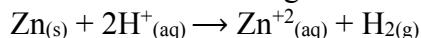
The relations between chemical change and electrical energy have

7.1. Balancing Oxidation-Reduction Equations

7.1.1. Oxidation-Reduction Reactions

Chemical reactions in which the oxidation number of one or more substance changes is called as **redox**.

We have discussed balancing chemical equations by inspection and by the number of electrons lost and gained. As discussed in the previous topics, **oxidation** refers to the loss of electrons, on the other hand, **reduction** refers to the gain of electrons. Consider the reaction:

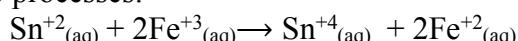


In the course of the reaction, the oxidation number of Zinc increases from zero in $\text{Zn}_{(s)}$ to +2 in $\text{Zn}^{+2}_{(aq)}$ whereas that of H decreases from +1 in $\text{H}^{+}_{(aq)}$ to zero in $\text{H}_{2(g)}$.

In any redox reaction, both oxidation and reduction must occur. So, if one substance is oxidized, then another is reduced. The substance that makes it possible for another substance to be oxidized is called the **oxidizing agent**, or the **oxidant**. The oxidizing agent removes electrons from another substance by acquiring them itself, thus oxidizing agent is itself reduced. Similarly, a **reducing agent**, or **reductant**, is the substance that gives up electrons, thereby causing another substance to be reduced. The reducing agent is oxidized in the process.

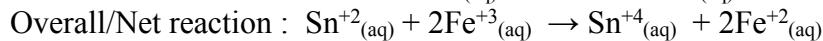
7.1.2. Half-Reactions

Although oxidation and reduction must take place simultaneously, it is often convenient to consider them as separate processes. Example: the oxidation of Sn^{+2} by Fe^{+3} can be considered into two processes:

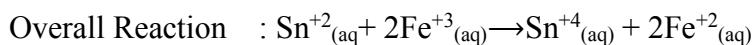
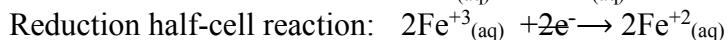


1. The oxidation of Sn^{+2} , and
2. The reduction of Fe^{+2}

Oxidation half-cell reaction: $\text{Sn}^{+2(\text{aq})} \rightarrow \text{Sn}^{+4(\text{aq})} + 2e^-$



Note that in the oxidation process, electrons are shown as products while in the reduction process, electrons are shown on the reactant side of the equation. Equations that show either oxidation or reduction alone are called **half-reactions or partial equations**. In the overall redox reactions the number of electrons lost in the oxidation half-reaction must equal the number of electrons gained in the reduction half-reaction. When this condition is attained and each half-reaction is balanced, the electrons on each side cancel when the two reactions are added to have the overall balance oxidation-reduction equation. See below:



The use of half-reactions provides a general method for balancing oxidation-reduction equations.

7.2. The Ion-Electron Method

The ion-electron method of balancing redox reaction equations employs partial equations that represents the half-cell or half-reaction. As discussed, one partial equation for oxidation and the other partial equation for the reduction. The final equation is obtained by combining the partial equations in such a way that the number of electrons lost equals the number of electrons gained.

Steps in balancing redox reaction by ion-electron method:

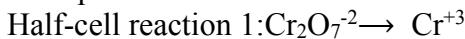
1. Divide the equation into two skeleton partial equations/half-cells/half-reactions.
Balance the atoms other than O and H. .
2. Balance the O and H atoms in each partial equation.
 - a. For reactions in acid solution:
 - i. For every O atom that is needed, add one H_2O to the side of the partial skeleton that is deficient in oxygen,
 - ii. Add H^{+} where needed to balance the hydrogen.
 - b. For reactions in alkaline solutions
 - i. For every O atom that is needed, add one H_2O to the side of the partial skeleton that is deficient in oxygen,
 - ii. For every H atom that is needed, add one H_2O to the side of the partial skeleton that is deficient in hydrogen, then add one OH^{-} to the opposite side.
3. Balance the net charge. Add electrons to the most positive side to balance the charges on both sides.
4. Multiply one or both partial equations by numbers that will make the number of electrons lost in one partial equation equal the number of electrons gained in the other partial equation.
5. Add the partial equations. In addition, cancel terms found at opposite sides of the final equation and add terms that are found in the side.
6. Check the net charges of both sides.

Take note that there are two slightly different procedures employed in balancing the equation by the ion-electron method. One is for reactions taking place in acid solution, and the other one for reactions taking place in alkaline solution.

7.2.1. Reactions Occurring in Acid Solutions

Sample Problem 7.1. $\text{Cr}_2\text{O}_7^{2-} + \text{Cl}^- \rightarrow \text{Cr}^{+3} + \text{Cl}_2$ occurring in acid solution

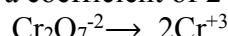
1. Two skeleton partial equation for the half-reactions: Let's take the case of partial equation 1 first:



2. The reaction is taking place in an acid solution, H_2O and H^+ can be added where needed.
3. For half-cell reaction 1, let us balance first atom other than H and O. In this case, we have Cr.

- a. There are 2 Cr atoms in the reactant.

- b. To balance Cr we need to add a coefficient of 2 to Cr in the product.

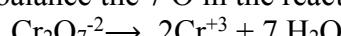


4. To balance the O:

- a. There are 7 atoms of O in the reactant. No O in the product.

- b. For every O that is required, one water must be added to the side that requires O.

We need to add 7 H_2O to the product to balance the 7 O in the reactant.

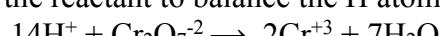


5. We have balanced the O atoms. We now have to balance the H.

- a. For every H atom needed, add H^+ to the side that requires H.

- b. We have added 7 H_2O in the product, giving 14H atoms in the product.

- c. So, 14 H^+ must be added to the reactant to balance the H atoms.



- d. That balances both sides.

6. Let us now balance the net charge. Take note of the charges of the following:

- a. H^+ - has charge of +1 (monoatomic ion)

- b. $\text{Cr}_2\text{O}_7^{2-}$ – has charge of -2 (polyatomic ion)

- c. Cr^{+3} – has a charge of +3 (monoatomic ion)

- d. H_2O – has no charge at all (neutral compound) and its charge is zero (0).

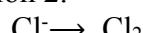
| 14H^+ | $+$ | $\text{Cr}_2\text{O}_7^{2-}$ | \rightarrow | 2Cr^{+3} | $+$ | $7\text{H}_2\text{O}$ |
|------------------|-----|------------------------------|---------------|-------------------|-----|-----------------------|
| 14 (+1) | | 1 (-2) | | 2(+3) | | 7(0) |
| +14 | | -2 | | +6 | | 0 |
| +14 + (-2) = +12 | | | | +6 + 0 = +6 | | |
| | | | | +12 ≠ +6 | | |

- e. We need to add electrons to the most positive side. Take note that electrons have negative charges.

- f. +12 (reactant) is more positive than +6 (product). Electrons must be added to the reactant.

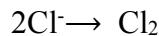
| 6e^- | $+$ | 14H^+ | $+$ | $\text{Cr}_2\text{O}_7^{2-}$ | \rightarrow | 2Cr^{+3} | $+$ | $7\text{H}_2\text{O}$ |
|-----------------------|-----|----------------|-----|------------------------------|---------------|-------------------|-----|-----------------------|
| 6(-1) | | 14 (+1) | | 1 (-2) | | 2(+3) | | 7(0) |
| -6 | | +14 | | -2 | | +6 | | 0 |
| (-6) + 14 + (-2) = +6 | | | | | | +6 + 0 = +6 | | |
| | | | | | | +6 = +6 | | |

7. Next, we will balance half-cell reaction 2.



- a. We only have Cl. No more other atoms to balance.

- b. To balance Cl, a coefficient of 2 must be added to Cl^- .



8. Proceed to net charge.

a. Cl^- - has a charge of -1.

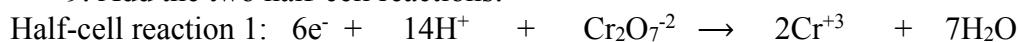
b. Cl_2 – is a diatomic molecule and does not carry a charge. Its charge is zero (0).

| | | |
|----------------|---------------|---------------|
| 2Cl^- | \rightarrow | Cl_2 |
| $2(-1)$ | | $1(0)$ |
| | | $-2 \neq 0$ |

c. The product is more positive (0) than the reactant (-2). Electrons must be added to the product to balance the net charge.

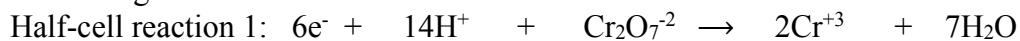
| | | | |
|----------------|---------------|---------------|----------|
| 2Cl^- | \rightarrow | Cl_2 | $+ 2e^-$ |
| $2(-1)$ | | $1(0)$ | $2(-1)$ |
| -2 | | $0 + (-2)$ | |
| | | $-2 = -2$ | |

9. Add the two half-cell reactions:



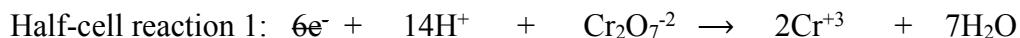
a. We need to balance the electrons lost and gained to cancel them.

b. To balance, we need to multiply half-cell reaction 2 by 3 on both sides to bring the electrons lost to 6. Multiply half-cell reaction 1 by 1 on both sides considering that we have 6 electrons gained.



c. Taking the algebraic sum, cancel common terms found opposite with each other.

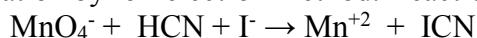
Add common terms on the same side.



10. Check the net charge.

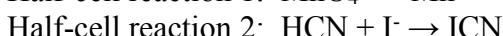
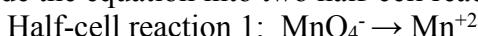
| | | | | | | |
|----------------|------------------|--------------------------------|---------------|----------------|---------------------|-------------------------|
| 6Cl^- | $+ 14\text{H}^+$ | $+ \text{Cr}_2\text{O}_7^{2-}$ | \rightarrow | 3Cl_2 | $+ 2\text{Cr}^{+3}$ | $+ 7\text{H}_2\text{O}$ |
| $6(-1)$ | $14(+1)$ | $1(-2)$ | | $3(0)$ | $2(+3)$ | $7(0)$ |
| -6 | $+14$ | -2 | | 0 | $+6$ | 0 |
| | | | | $+6 = +6$ | | |

Sample 7.2. Balance the equation by ion-electron method. Reaction occurring in acid solution.



Solution:

1. Divide the equation into two half-cell reaction:



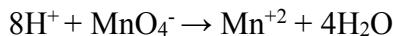
2. Starting with Half-cell reaction 1: $\text{MnO}_4^- \rightarrow \text{Mn}^{+2}$

a. Mn is already balanced.

b. We have four O atoms in the reactant. Add four H_2O in the product to balance the O.



c. We have balanced the O. Since we have added $4\text{H}_2\text{O}$, that gives 8H atoms in the product. We need to add 8H^+ to the reactant to balance the H.



3. Balance the net charge.

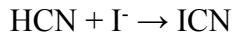
- a. H^+ - has a charge of +1
- b. MnO_4^- - has a charge of -1
- c. Mn^{+2} - has a charge of +2
- d. H_2O - has a charge of 0.

| $8\text{H}^+ + \text{MnO}_4^- \rightarrow \text{Mn}^{+2} + 4\text{H}_2\text{O}$ | | | |
|---|-------|-------|------|
| 8(+1) | 1(-1) | 1(+2) | 4(0) |
| +8 | 1- | +2 | 0 |
| $+7 \neq +2$ | | | |

4. +7 (reactant) is more positive than +2 (product). We need to add electrons to the reactant to balance the charge.

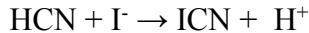
| $5\text{e}^- + 8\text{H}^+ + \text{MnO}_4^- \rightarrow \text{Mn}^{+2} + 4\text{H}_2\text{O}$ | | | | |
|---|-------|-------|-------|------|
| 5(-1) | 8(+1) | 1(-1) | 1(+2) | 4(0) |
| 6- | +8 | 1- | +2 | 0 |
| $+2 = +2$ | | | | |

5. Half-cell reaction 2:



6. Everything is balanced except H. Take note that there is no O atom. We need to balance only the H.

7. To balance the H, we need to add 1 H^+ in the product to balance the H.



8. Balance the net charge.

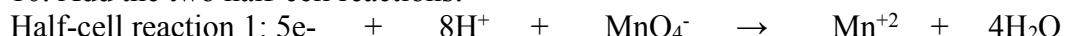
- a. HCN – has a charge of 0 (neutral compound)
- b. I^- - has charge of -1
- c. ICN – has a charge of 0
- d. H^+ - has a charge of +1

| $\text{HCN} + \text{I}^- \rightarrow \text{ICN} + \text{H}^+$ | | | | |
|---|-------|------|-------|--|
| 1(0) | 1(-1) | 1(0) | 1(+1) | |
| 0 | 1- | 0 | +1 | |
| $-1 \neq +1$ | | | | |

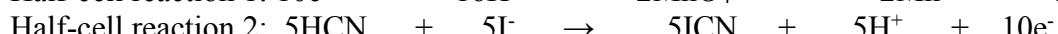
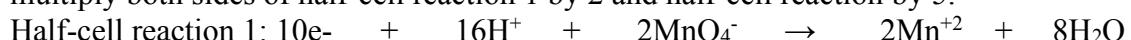
9. +1 (product) is more positive than -1 (reactant). We need to add 2e- in the product to balance the charge.

| $\text{HCN} + \text{I}^- \rightarrow \text{ICN} + \text{H}^+ + 2\text{e}^-$ | | | | |
|---|-------|------|-------|-------|
| 1(0) | 1(-1) | 1(0) | 1(+1) | 2(-1) |
| 0 | 1- | 0 | +1 | -2 |
| $-1 \neq -1$ | | | | |

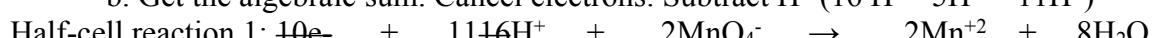
10. Add the two half-cell reactions:



a. 5e- gained against 2e- lost. To balance the electrons lost and gained, we need to multiply both sides of half-cell reaction 1 by 2 and half-cell reaction by 5.



b. Get the algebraic sum. Cancel electrons. Subtract H^+ ($16\text{H}^+ - 5\text{H}^+ = 11\text{H}^+$)



11. Checking the net charge.

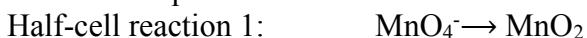
| | | | | | | | | | | | | |
|-----------|---|-----------------|---|--------------------------------|---|------------------|---|------|---|-------------------|---|-------------------|
| 5HCN | + | 5I ⁻ | + | 2MnO ₄ ⁻ | + | 11H ⁺ | → | 5ICN | + | 2Mn ⁺² | + | 8H ₂ O |
| 5(0) | | 5(-1) | | 2(-1) | | 11(+1) | | 5(0) | | 2(+2) | | 8(0) |
| 0 | | -5 | | -2 | | +11 | | 0 | | +4 | | 0 |
| $+4 = +4$ | | | | | | | | | | | | |

7.2.2. Reactions occurring in Alkaline or Basic Solution

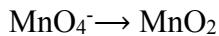
In balancing reactions occurring in acidic solutions, H₂O molecules and H⁺ are added to balance H and O atoms. In reactions occurring in basic or alkaline solutions, H⁺, H₂O molecules and OH⁻ are used to balance the H and O atoms.

Sample Problem 7.3. MnO₄⁻ + N₂H₄ → MnO₂ + N₂ in alkaline solution

- Divide the equation to two half-cell reactions



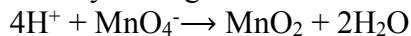
- Half-cell reaction 1:



a. There are four O atoms in the reactant against only two O atoms in the product. We need to add 2 H₂O molecules to the product to balance the O.

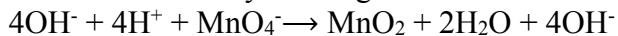


b. We need to balance the H by adding 4H⁺ to the reactant to balance the H.

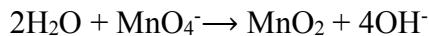


c. We have balanced all species in the reaction. However, this is occurring in an alkaline or basic solution and we need to remove H⁺ from the equation.

d. To do this, we have added 4H⁺, so need to add OH⁻ at both sides equivalent to the number of H⁺ added. In this particular example, we have added 4H⁺, therefore we must add 4 OH⁻ to both sides in order to remove H⁺ by forming H₂O.



e. The 4OH⁻ + 4H⁺ in the reactant combines to form 4H₂O molecules. And the H₂O molecules are subtracted (4H₂O - 2H₂O = 2H₂O).



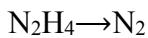
- Balancing the net charge:

| | | | | | | |
|-------------------|---|-------------------------------|---|------------------|---|------------------|
| 2H ₂ O | + | MnO ₄ ⁻ | → | MnO ₂ | + | 4OH ⁻ |
| 2(0) | | 1(-1) | | 1(0) | | 4(-1) |
| 0 | | -1 | | 0 | | -4 |
| $-1 \neq -4$ | | | | | | |

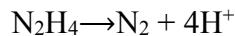
a. -1 (reactant) is more positive than -4 (product). We must add 3e⁻ to the reactant to balance the charge.

| | | | | | | | | |
|-----------------|---|-------------------|---|-------------------------------|---|------------------|---|------------------|
| 3e ⁻ | + | 2H ₂ O | + | MnO ₄ ⁻ | → | MnO ₂ | + | 4OH ⁻ |
| 3(-1) | | 2(0) | | 1(-1) | | 1(0) | | 4(-1) |
| -3 | | 0 | | -1 | | 0 | | -4 |
| $-4 = -4$ | | | | | | | | |

- Half-cell reaction 2



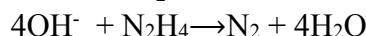
a. No O atom only H atoms. We need to add 4H⁺ only to the product to balance H.



b. We have added 4H^+ to balance the H^+ , we must add the same number of OH^- to both side to remove H^+ added.



c. $4\text{H}^+ + 4\text{OH}^-$ combines to form $4\text{H}_2\text{O}$ molecules.



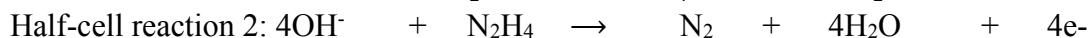
5. Balancing the net charge

| 4OH^- | $+$ | N_2H_4 | \rightarrow | N_2 | $+$ | $4\text{H}_2\text{O}$ |
|----------------|-----|------------------------|---------------|--------------|-----|-----------------------|
| $4(-1)$ | | $1(0)$ | | $1(0)$ | | $4(0)$ |
| -4 | | 0 | | 0 | | 0 |
| | | | | $-4 \neq 0$ | | |

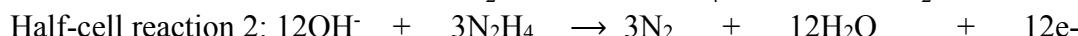
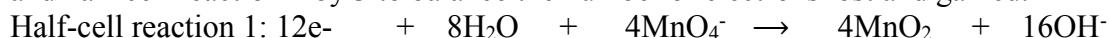
a. 0 (product) is more positive than -4 (reactant). We must add $4e^-$ to the product to balance the charge.

| 4OH^- | $+$ | N_2H_4 | \rightarrow | N_2 | $+$ | $4\text{H}_2\text{O}$ | $+$ | $4e^-$ |
|----------------|-----|------------------------|---------------|--------------|-----|-----------------------|-----|---------|
| $4(-1)$ | | $1(0)$ | | $1(0)$ | | $4(0)$ | | $4(-1)$ |
| -4 | | 0 | | 0 | | 0 | | -4 |
| | | | | $-4 = -4$ | | | | |

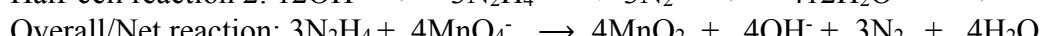
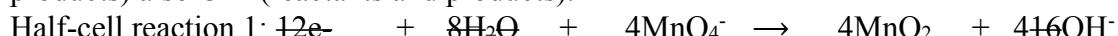
6. Add the two half-cell reactions:



a. $3e^-$ gained against $4e^-$ lost. We must multiply both sides of half-cell reaction 1 by 4 and half-cell reaction 2 by 3 to balance the number of electrons lost and gained.

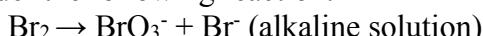


b. get the algebraic sum. Cancel electrons. Subtract H_2O molecules (reactants and products) also OH^- (reactants and products).



| $3\text{N}_2\text{H}_4$ | $+$ | 4MnO_4^- | \rightarrow | 4MnO_2 | $+$ | 4OH^- | $+$ | 3N_2 | $+$ | $4\text{H}_2\text{O}$ |
|-------------------------|-----|-------------------|---------------|-----------------|-----|----------------|-----|---------------|-----|-----------------------|
| $3(0)$ | | $4(-1)$ | | $4(0)$ | | $4(-1)$ | | $3(0)$ | | $4(0)$ |
| 0 | | -4 | | 0 | | -4 | | 0 | | 0 |
| | | | | $-4 = -4$ | | | | | | |

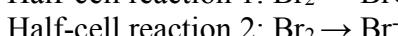
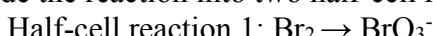
Sample Problem 7.4. Consider the following reaction:



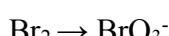
In this type of reaction, Br_2 undergoes both oxidation (loss of electrons) and reduction (gain of electrons). This type of reaction is called **disproportionation** or **auto-oxidation-reduction reaction**.

Solution:

1. Divide the reaction into two half-cell reactions:



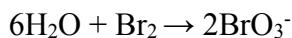
2. Half-cell reaction 1:



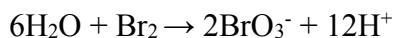
a. We need to balance the Br first.



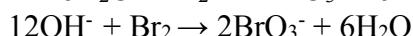
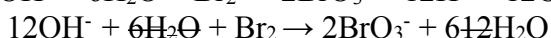
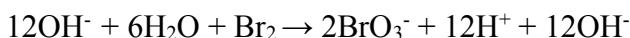
b. There are six O atoms in the product. Six H₂O molecules must be added to the reactant to balance O.



c. We have added six H₂O molecules in the reactant giving 12 H atoms. To balance the H, 12H⁺ must be added to the product.



d. Since this is in alkaline/basic solution, H⁺ must be removed. As a rule, OH⁻ must be added to both sides to cancel H⁺ by forming H₂O. The number of OH⁻ is equal to the number of H⁺ added.



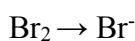
3. Take the net charge.

| 12OH^- | $+$ | Br_2 | \rightarrow | 2BrO_3^- | $+$ | $6\text{H}_2\text{O}$ |
|-----------------|-----|---------------|---------------|-------------------|-----|-----------------------|
| 12(-1) | | 1(0) | | 2(-1) | | 6(0) |
| -12 | | 0 | | -2 | | 0 |
| | | | | $-12 \neq -2$ | | |

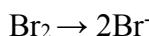
a. -2 (product) is more positive than -12 (reactant). We need to add 10e⁻ to the product to balance the charges.

| 12OH^- | $+$ | Br_2 | \rightarrow | 2BrO_3^- | $+$ | $6\text{H}_2\text{O}$ | $+$ | 10e^- |
|-----------------|-----|---------------|---------------|-------------------|-----|-----------------------|-----|----------------|
| 12(-1) | | 1(0) | | 2(-1) | | 6(0) | | 10(-1) |
| -12 | | 0 | | -2 | | 0 | | -10 |
| | | | | $-12 = -12$ | | | | |

4. Half-cell reaction 2:



a. Balance Br.



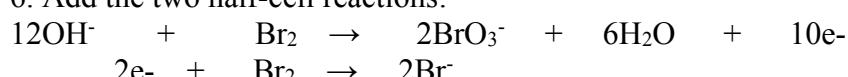
5. No H nor O atom. Let us proceed to the net charges.

| $\text{Br}_2 \rightarrow 2\text{Br}^-$ | |
|--|-----------|
| 2(0) | 2(-1) |
| 0 | $\neq -2$ |

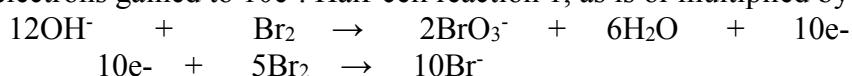
a. 0 (reactant) is more positive than -2 (product). We need to add two electrons to the reactant to balance the charges.

| 2e^- | $+$ | Br_2 | \rightarrow | 2Br^- |
|---------------|-----|---------------|---------------|----------------|
| 2(-1) | | 2(0) | | 2(-1) |
| | | | | $-2 \neq -2$ |

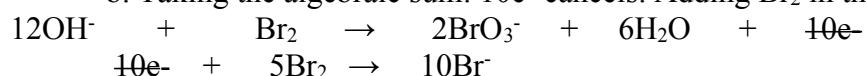
6. Add the two half-cell reactions:



a. There are 10e⁻ lost against 2e⁻ gained. To balance the number of electrons gained/lost, we need to multiply both sides of half-cell reaction 2 by 5 to bring the number of electrons gained to 10e⁻. Half-cell reaction 1, as is or multiplied by 1.



b. Taking the algebraic sum: 10e⁻ cancels. Adding Br₂ in the reactants.



7. Checking the net charges:

| | | | | | | | | |
|-----------------|---|----------------|---------------|-------------------|---|-----------------------|---|-----------------|
| 12OH^- | + | 6Br_2 | \rightarrow | 2BrO_3^- | + | $6\text{H}_2\text{O}$ | + | 10Br^- |
| 12(-1) | | 6(0) | | 2(-1) | | 6(0) | | 10(-1) |
| -12 | | 0 | | -2 | | 0 | | -10 |
| $-12 = -12$ | | | | | | | | |

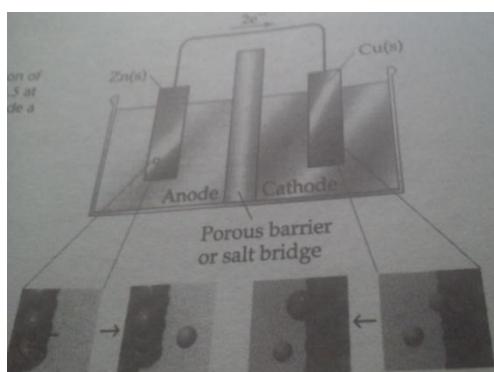
7.3. Electrochemical Cell

An electrochemical cell contains two electrodes (anode and cathode); a liquid-liquid junction separates two electrodes. Oxidation-reduction or **redox reactions** take place in electrochemical cells. There are two types of electrochemical cells. Spontaneous reactions occur in galvanic (voltaic) cells; nonspontaneous reactions occur in electrolytic cells. Both types of cells contain electrodes where the oxidation and reduction reactions occur. Oxidation occurs at the electrode termed the **anode** and reduction occurs at the electrode called the **cathode**.

7.3.1. Electrodes & Charge

The anode of an electrolytic cell is positive (cathode is negative), since the anode attracts anions from the solution. However, the anode of a galvanic cell is negatively charged, since the spontaneous oxidation at the anode is the *source* of the cell's electrons or negative charge. The cathode of a galvanic cell is its positive terminal. In both galvanic and electrolytic cells, oxidation takes place at the anode and electrons flow from the anode to the cathode.

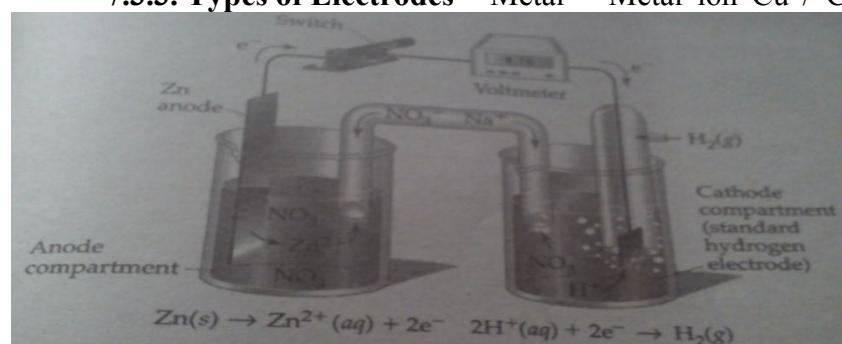
7.3.2. Galvanic or Voltaic Cells



The redox reaction in a galvanic cell is a spontaneous reaction. For this reason, galvanic cells are commonly used as batteries. Galvanic cell reactions supply energy which is used to perform work. The energy is harnessed by situating the oxidation and reduction reactions in separate containers, joined by an apparatus that allows electrons to flow. A common galvanic cell is the Daniell cell.

7.3.3. Types of Electrodes Metal – Metal ion Cu / Cu++ Ion – Ion (redox) Pt / Fe⁺⁺⁺, Fe⁺⁺ Gas Pt / H₂, H⁺ Metal – insoluble salt Hg / Hg₂Cl₂ / KCl

Voltaic Cell using Standard Hydrogen Electrode (SHE)

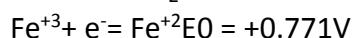
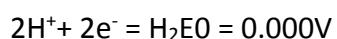


Sign of the electrode potential, E^0 is positive when the half – cell is spontaneous as cathode. And is negative when the half – cell behaves as anode. It is a measure of the driving force for the half – reaction.

7.3.3.1. Liquid Junction

Serves as galvanic contact between electrodes (can be a salt bridge or porous membrane). Salt bridge, very commonly used – an intermediate compartment filled with saturated KCl solution and fitted with porous barrier at each end or agar solidified incorporating saturated KCl. Salt bridge minimizes liquid junction potential (diffusion potential) that develops when any two phases such as two solutions are in contact with each other. This potential (if not corrected) introduces errors and interferences in the measured cell potentials. With introduction of a salt bridge, two liquid junction potentials are created; but they tend to cancel each other.

7.3.3.2. E^0 is Referenced to a Standard Hydrogen Electrode (Refer to figure below).



E^0 is independent of number of moles of reactant or product. Positive means reaction is spontaneous with respect to Hydrogen electrode. In accordance with the recommendations of IUPAC, the present practice is to use reduction potentials. $E_{cell} = E_{right} - E_{left}$. Standard Hydrogen Electrode (SHE) is the reference point.

Electrode

Types of electrochemical cells

Galvanic

Chemical energy to electrical energy

Spontaneous/Reversible/Thermodynamic

Cathode (+)

Anode (-)

$AG^0 < O, E^0_{cell} > O$

Eg: Dry cell Daniel cell

Electrolytic

Electrical to chemical energy

Non spontaneous/Kinetic cell

irreversible

Cathode (-)

Anode (+)

$AG^0 > O, E^0_{cell} < O$

Eg: Electroplating, Impressed current;cathodic protection

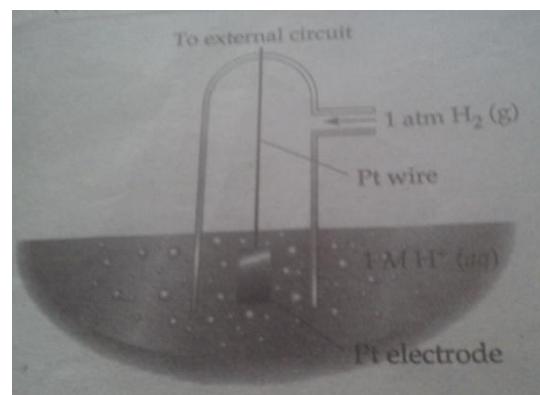
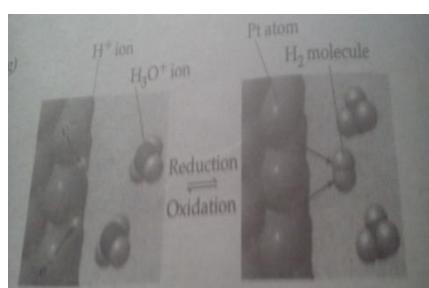


Figure 7.1 Standard Hydrogen Electrode



Electrodes (anode, cathode) in the presence of electrolyte

Driving force for electrochemical reaction is the potential difference between the electrodes, E_{cell} . $\Delta G = - nFE_{cell}$, n = moles of electrons in half reaction, $F = 96500C$, $\Delta G^0 = - RT\ln K$ Nernst relationship: $E = E^0 + \ln \frac{P_{products}}{P_{reactants}}$

$Eh = E^0 + \log \text{ at } 25^\circ\text{C}$ Where E^0 is the standard electrode potential, is the ratio between activities of oxidized and reduced species. **Daniel cell** is an example of a galvanic cell - contains zinc immersed in zinc sulfate solution and copper in copper sulfate solution separated by a diaphragm or salt bridge.

7.4. Voltaic Cell Notation

Cell notation is used to describe the components of a voltaic cell. The notation for the Zn/Cu^{+2} cell is:

Steps:

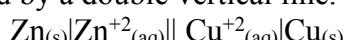
1. It is written in compartments. The anode (oxidation half-cell) and the cathode (reduction half-cell) compartments. A single vertical line represents a phase boundary within the compartment.

In the Zn/Cu^{+2} , Zn is written first (to the left) so it is the anode - oxidation. Cu^{+2} is written next (to the right), so is the cathode - reduction.



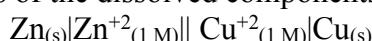
A single vertical line separates $\text{Zn}_{(s)}$ from $\text{Zn}^{+2}_{(aq)}$ and $\text{Cu}^{+2}_{(aq)}$ from $\text{Cu}_{(s)}$.

2. Combining the two compartments with the anode compartment to the left and the cathode compartment to the left, separated by a double vertical line.



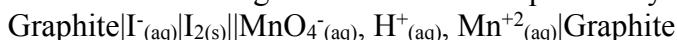
The double vertical line separates the anode compartment from the cathode (which also indicates a salt bridge (take note that ions in the salt bridge are not included in the voltaic cell notation)).

3. If required, the concentrations of the dissolved components are enclosed in parentheses.



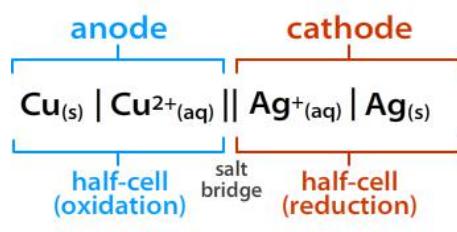
$\text{Zn}^{+2}_{(aq)}$ and $\text{Cu}^{+2}_{(aq)}$ having 1 M concentrations.

4. A comma separates the half-cell components that are in the same phase. Half-cell components usually appearing in the same order as in the half-cell reaction. Electrodes are at the far left for the anode and at the far right for the cathode separated by a single vertical line.



The anode and the cathode compartments are separated by a double vertical line (salt bridge). Solid graphite serves as the electrodes immersed in the compartments.

Cell Diagram



Graphic by Shamsher Singh

Sample Problem 7.5. What is the E^0_{cell} for the voltaic cell: $\text{Mg}|\text{Mg}^{+2}||\text{Sn}^{+2}|\text{Sn}$

Solution:

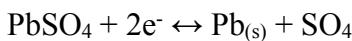
Half-cell reaction (anode) : $\text{Mg}_{(s)} \rightarrow \text{Mg}^{+2}_{(aq)} + 2\text{e}^-$ $E^0_{\text{red}} = -2.363\text{V}$

Half-cell reaction (cathode): $\text{Sn}^{+2}_{(aq)} + 2\text{e}^- \rightarrow \text{Sn}_{(s)}$ $E^0_{\text{red}} = -0.136\text{V}$

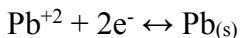
Overall reaction: $\text{Sn}^{+2}_{(aq)} + \text{Mg}_{(s)} \rightarrow \text{Mg}^{+2}_{(aq)} + \text{Sn}_{(s)}$

$$E^0_{\text{cell}} = E^0_{\text{red}}(\text{cathode}) - E^0_{\text{red}}(\text{anode}) = -0.136\text{V} - (-2.363\text{V}) = -0.136\text{V} + 2.363\text{V} = +2.227\text{V}$$

Sample Problem 6.6. Given the following:



$$E^0_{\text{red}} = -0.359\text{V}$$



$$E^0_{\text{red}} = -0.126\text{V}$$

- a). Write the notation for a cell that uses these half-reactions
 b). Write the equation for the cell reaction

Solution:

a). $\text{Pb}^{+2} + 2\text{e}^- \leftrightarrow \text{Pb}_{(\text{s})}$, $E^0_{\text{red}} = -0.126\text{V}$ has the greater tendency for reduction and is the cathode



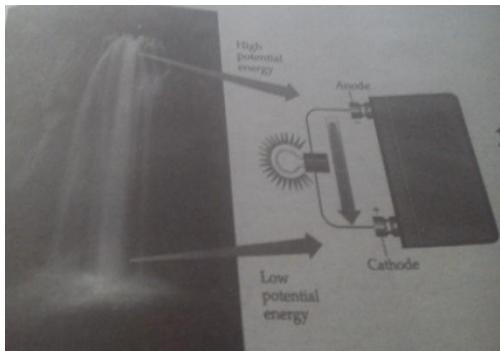
b). Half-cell reaction (anode): $\text{Pb}_{(\text{s})} + \text{SO}_4^{2-} \leftrightarrow \text{PbSO}_4 + 2\text{e}^-$ $E^0_{\text{red}} = +0.359\text{V}$

Half-cell reaction (cathode) : $\text{Pb}^{+2} + 2\text{e}^- \leftrightarrow \text{Pb}_{(\text{s})}$ $E^0_{\text{red}} = -0.126\text{V}$

Overall reaction: $\text{Pb}^{+2} + \text{SO}_4^{2-} \leftrightarrow \text{PbSO}_4$ $E^0_{\text{red}} = +0.233\text{V}$

7.5. Cell EMF

7.5.1. Cell EMF Under Standard Conditions



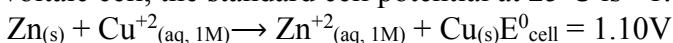
Water in the waterfalls, flows spontaneously due to the differences in potential energy between the top of the hills and the stream below. This can be compared to the flow of electrons. In that, electron flows from the anode of the voltaic cell to the cathode because of a difference in potential energy. The potential energy of electrons is higher in the anode than in the cathode, and that they spontaneously flow through an external circuit from the anode to the cathode. That is electrons flow spontaneously toward the electrode with the more positive electrical potential.

The potential difference, or the difference in potential energy per electrical charge between two electrodes is measured in units of volts. One volt (V), is the potential energy difference required to produce 1 joule of energy to a charge of 1 coulomb(C).

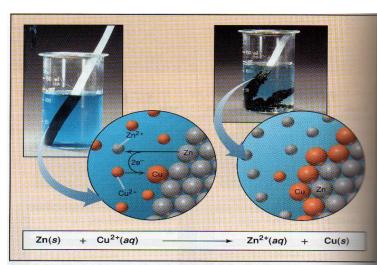
$$1\text{V} = 1\text{J/C}$$

Try to recall from your basic chemistry that one electron has a charge of $1.60 \times 10^{-19}\text{ C}$. The difference between the two electrodes of a voltaic cell provides the driving force that pushes electrons through the external circuit. And we call this potential difference the **electromotive (causing electron motion) force, or emf**. The emf of the cell, denoted by E_{cell} , is called the **cell potential**. Since E_{cell} is expressed in Volts, it is often referred to as voltage cell. For any cell reaction that proceeds spontaneously, such as in a voltaic cell, the cell potential will be positive.

The emf of a particular voltaic cell depends on the specific reactions occurring at the cathode and the anode. The concentrations of the reactants and products, and the temperature, which is assumed to be at 25°C unless otherwise stated. This discussion will be focused on cells that are operated at 25°C under standard conditions. At standard conditions, 1M concentrations for reactants and products and at 1 atm pressure for those that are gases. Under standard conditions, the emf is called the **standard emf**, or the **standard cell potential** and is denoted by E^0_{cell} . For example, the Zn-Cu voltaic cell, the standard cell potential at 25°C is +1.10V:



The superscript 0 indicates standard-state conditions.



7.5.2. Standard Reduction (Half-Cell) Potentials

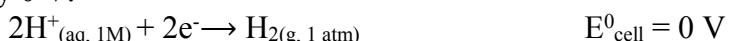
The emf, or cell potential, of a voltaic cell, E^0_{cell} depends on the particular cathode and anode half-cells involved. We could, in principle, tabulate the standard cell potentials for all possible cathode/anode combinations but it is not necessary to undertake such arduous task. Rather, we can assign a standard potential to each individual half-cell and then use these half-cell potentials to determine E^0_{cell} .

The **cell potential** is the difference between two electrode potentials, the first one is the one associated with the cathode and the other one is associated with the anode. By convention, the potential associated with each electrode is chosen to be the potential for reduction to occur at that electrode. Thus, standard electrode potentials are tabulated for reduction reactions; they are referred to as **standard reduction potentials** denoted by E^0_{red} . The cell potential E^0_{cell} , is given by the standard reduction potential of the cathode reaction, E^0_{red} (cathode), minus the standard reduction potential of the anode reaction, E^0_{red} (anode).

$$E^0_{\text{cell}} = E^0_{\text{red}}(\text{cathode}) - E^0_{\text{red}}(\text{anode})$$

For all spontaneous reactions at standard conditions, $E^0_{\text{cell}} > 0$.

Since every voltaic cell involves two half-cells, it is not possible to measure the standard reduction potential of a half-reaction directly. Assigning a standard reduction potential to a certain reference half-reaction, we can determine the standard reduction potentials of other half-reactions relative to that reference. The reference half-reaction is the reduction of $\text{H}^{+}_{(\text{aq})}$ to $\text{H}_{2(\text{gas})}$ under standard conditions, which assigned a standard reduction potential of exactly 0 V.



An electrode designed to produce this half-reaction is called as the **standard hydrogen electrode (SHE)** or the **normal hydrogen electrode (NHE)**. SHE consists of a platinum wire connected a piece of platinum foil covered with finely divided platinum serving as an inert surface for the reaction. The electrode is encased in a glass tube so that hydrogen gas under standard conditions (1 atm) can bubble over the platinum and the solution contains $\text{H}_{+(\text{aq})}$ under standard (1 M) conditions.

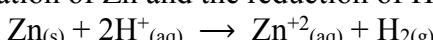
There are two suggested methods to determine the E^0_{cell} :

1. Using the standard reduction potential as reduction process and solving the E^0_{cell} using the formula:

$$E^0_{\text{cell}} = E^0_{\text{red}}(\text{cathode}) - E^0_{\text{red}}(\text{anode})$$

2. Identifying the half-cell reaction undergoing oxidation and the one undergoing reduction, then reversing the reduction potential in the table and taking the algebraic sum.

For example, the oxidation of Zn and the reduction of H^{+} :



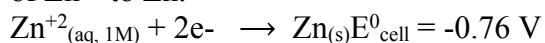
Notice that the Zn^{+2}/Zn electrode is the anode and the SHE is the cathode and the cell voltage is +0.76 V. Using the defined standard potential of H^{+} ($E^0_{\text{red}} = 0$). Thus we can determine the standard reduction potential for the Zn^{+2}/Zn half-reaction:

$$E^0_{\text{cell}} = E^0_{\text{red}}(\text{cathode}) - E^0_{\text{red}}(\text{anode})$$

$$+0.76 \text{ V} = 0 \text{ V} - E^0_{\text{red}}(\text{anode})$$

$$E^0_{\text{red}}(\text{anode}) = -0.76 \text{ V}$$

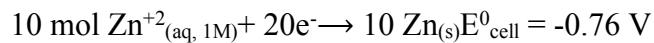
Therefore, a standard reduction potential of -0.76 V can be assigned to the reduction of Zn^{+2} to Zn.



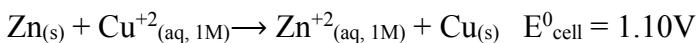
Take note that the reaction is represented as reduction though it is “running in reverse” as an oxidation. Assigning an electrical potential to a half-reaction, it is always written as a reduction. The standard reduction potentials for other half-reactions can be

established from other cell potentials in a way analogous to that process for the Zn^{+2}/Zn half-reactions. Appendix lists some standard reduction potentials. These standard reduction potentials, often called half-cell potentials, can be combined to calculate the emfs of a large variety of voltaic cells.

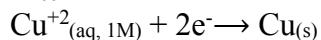
Since electrical potential measures potential energy per electrical charge, standard reduction potentials are intensive property, meaning, if the amount of a substance is increased in a redox reaction, both the energy and charges involved are increased but the ratio of energy (joules) to electrical charge (C) remains constant ($V=J/C$). Thus changing the stoichiometric coefficient in a half-reaction does not affect the value of the standard reduction potential. For example, E^0_{red} for the reduction of 10 mol Zn^{+2} is the same as that for the reduction of 1 mol Zn^{+2} :



Sample Problem 7.7. For the Zn-Cu+2 voltaic cell:



Given that the standard reduction potential of Zn^{+2} to $Zn_{(\text{s})}$ is -0.76 V , calculate the E^0_{cell} for the reaction of Cu^{+2} to $Cu_{(\text{s})}$.

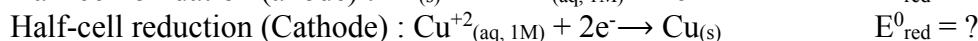
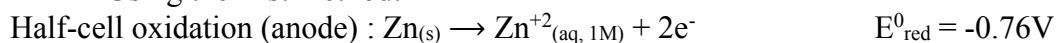


Solution:

E^0_{cell} and E^0_{red} for Zn^{+2} are given and we are asked to calculate E^0_{red} for Cu^{+2} .

Step: In the voltaic cell, Zn is oxidized (from 0 in the $Zn_{(\text{s})}$ to $+2 Zn^{+2}_{(\text{aq}, 1M)}$) and is therefore the anode. Thus, the given E^0_{red} for Zn^{+2} is E^0_{red} (anode). Because Cu^{+2} is reduced (from $+2$ in the $Cu^{+2}_{(\text{aq}, 1M)}$ to 0 in the $Cu_{(\text{s})}$), then it should be in the cathode half-cell. Thus, the unknown reduction potential for Cu^{+2} is E^0_{red} (cathode). Knowing E^0_{cell} and E^0_{red} (anode), we can solve for E^0_{red} (cathode).

Using the first method:



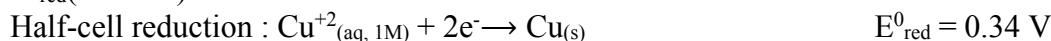
$$E^0_{\text{cell}} = 1.10 \text{ V}$$

Solving for E^0_{red} (cathode):

$$E^0_{\text{cell}} = E^0_{\text{red}}(\text{cathode}) - E^0_{\text{red}}(\text{anode})$$

$$1.10 \text{ V} = E^0_{\text{red}}(\text{cathode}) - (-0.76 \text{ V})$$

$$E^0_{\text{red}}(\text{cathode}) = 1.10 \text{ V} - 0.76 \text{ V} = 0.34 \text{ V}$$

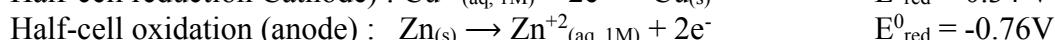
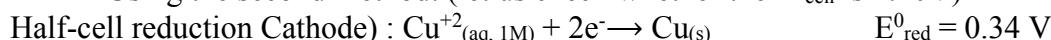


Checking:

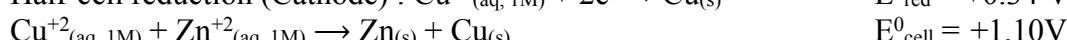
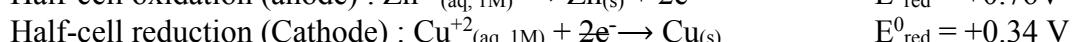
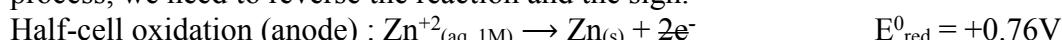
This reduction potential agrees with the one listed in the appendix.

Note: The standard reduction potential for Cu^{+2} can be presented as $E^0_{Cu^{+2}} = 0.34 \text{ V}$, and that for Zn^{+2} as $E^0_{Zn^{+2}} = -0.76 \text{ V}$. The subscript identifies the ion that is reduced in the reduction half-cell.

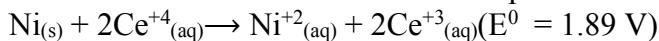
Using the second method: (let us check whether the E^0_{cell} is 1.10 V)



Since, the given data in the table are the reduction process and for the oxidation process, we need to reverse the reaction and the sign.

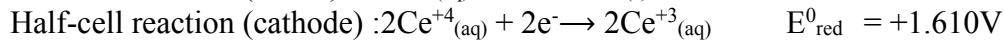
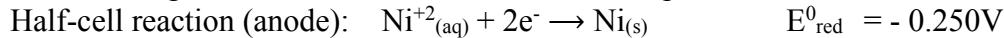


Sample Problem 7.8. Using standard reduction potentials, calculate the standard emf for each of the following reaction decide whether the reaction is spontaneous.



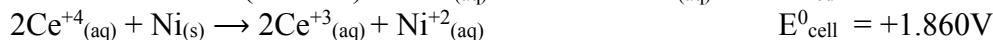
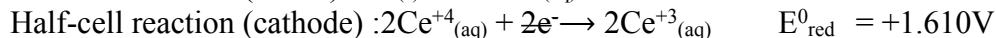
Solution:

Using the first method: From the reduction potential table



$$E_{\text{cell}}^0 = E_{\text{red}}^0(\text{cathode}) - E_{\text{red}}^0(\text{anode}) = +1.610\text{V} - (-0.250 \text{ V}) = 1.610\text{V} + 0.250\text{V} = 1.860\text{V}$$

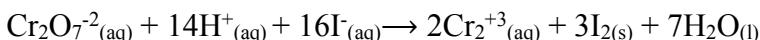
Using the second method (reversing the anode and its sign):



Since the overall emf is positive, the reaction is spontaneous.

The problems can be solved using either first or second method.

Sample Problem 7.9. Using the standard reduction potential based in the appendix, calculate the standard emf for the voltaic cell based on the reaction:



Solution:

We are given the equation for the redox reaction and asked to use data in the appendix to calculate that standard emf (standard potential) for the associated voltaic cell.

Step 1: Identify the two half reactions (cathode and anode).

- Let us determine first the oxidation numbers of all the species present.
- Oxygen has -2 and hydrogen has +1 in the reactant and in the product.
- I from -1 in the reactant to 0 ($\text{I}_2_{(s)}$) - oxidized (oxidation).
- For Cr, we have: $\text{Cr}_2\text{O}_7^{-2}$

$\text{Cr}_2\text{O}_7^{-2} = -2$, solving for Cr;

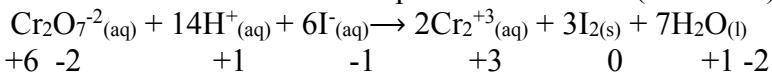
$$2(\text{Cr}) + 7(-2) = -2$$

$$2\text{Cr} - 14 = -2$$

$$2\text{Cr} = -2 + 14$$

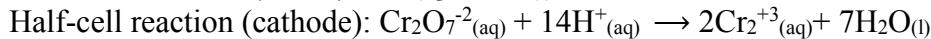
$$\text{Cr} = \frac{12}{2} = +6$$

- Cr from +6 in the reactant to +3 in the product – reduced (reduction).



Step 2. $\text{Cr}_2\text{O}_7^{-2}_{(aq)}$ and $14\text{H}^+_{(aq)}$ produces $2\text{Cr}^{+3}_{(aq)}$ and $7\text{H}_2\text{O}_{(l)}$ as reduction. $16\text{I}^-_{(aq)}$ is oxidized to $3\text{I}_2_{(s)}$.

Step 3. Half-cell reaction (anode) : $6\text{I}^-_{(aq)} \rightarrow 3\text{I}_2_{(s)}$



Step 4. To determine the number of electrons lost/gained, we need to balance the charges.

Half-cell reaction (anode) : $2\text{I}^-_{(aq)} \rightarrow \text{I}_2_{(s)}$

- Taking the net charge.

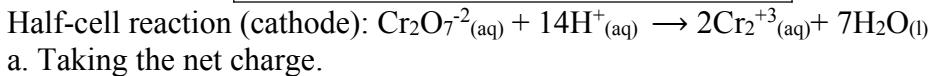
| | |
|--|------|
| $6\text{I}^-_{(aq)} \rightarrow 3\text{I}_2_{(s)}$ | |
| 6(-1) | 3(0) |
| -6 | 0 |

- Balancing the net charge by adding electrons to the most positive side.

c.

| | | | | |
|----------------------|---------------|---------------------|-----|--------|
| $6\text{I}^-_{(aq)}$ | \rightarrow | $3\text{I}_2_{(s)}$ | $+$ | $6e^-$ |
| 6(-1) | | 3(0) | | 6(-1) |

| | | |
|-----------|---|----|
| -6 | 0 | -6 |
| $-6 = -6$ | | |

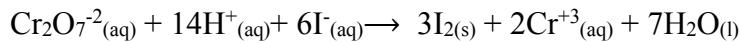
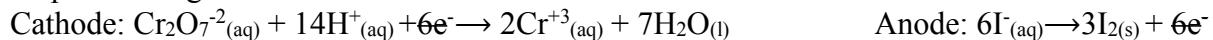


| $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$ | $+ 14\text{H}^+(\text{aq})$ | $\rightarrow 2\text{Cr}_2^{+3}(\text{aq})$ | $+ 7\text{H}_2\text{O}(\text{l})$ |
|---|-----------------------------|--|-----------------------------------|
| 2(-1) | 14(+1) | 2(+3) | 7(0) |
| -2 | +14 | +6 | 0 |
| $+12 > +6$ | | | |

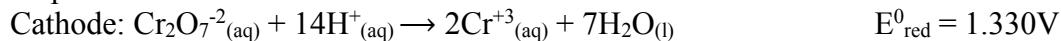
b. Balancing the net charge by adding electrons to the most positive side.

| 6e^- | $+ \text{Cr}_2\text{O}_7^{2-}(\text{aq})$ | $+ 14\text{H}^+(\text{aq})$ | $\rightarrow 2\text{Cr}_2^{+3}(\text{aq})$ | $+ 7\text{H}_2\text{O}(\text{l})$ |
|---------------|---|-----------------------------|--|-----------------------------------|
| 6(-1) | 2(-1) | 14(+1) | 2(+3) | 7(0) |
| -6 | -2 | +14 | +6 | 0 |
| $+6 > +6$ | | | | |

Step 5. Adding the two half-reactions:

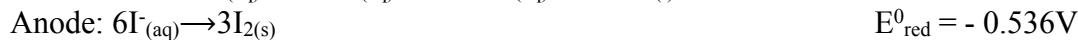
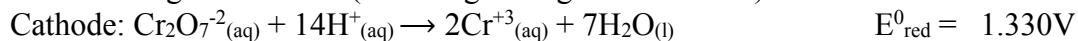


Step 6. We can use these values then for the calculations:



$$E^0_{\text{cell}} = E^0_{\text{red}}(\text{cathode}) - E^0_{\text{red}}(\text{anode}) = 1.33 \text{ V} - 0.536 \text{ V} = 0.794 \text{ V.}$$

Using method two (reversing the sign of the anode):



Although we have different coefficients, the value of E^0_{cell} is not multiplied by the coefficients. As we have noted the standard reduction potential is an intensive property, so it is not dependent of the specific stoichiometric coefficients.

The cell potential, 0.794V, is a positive number. As noted earlier, a voltaic cell must have a positive emf (spontaneous) in order to operate.

For each of the half-cells in a voltaic cell, the standard reduction potential provides a measure of the driving force for the reaction to occur. The more positive the value of E^0_{red} , the greater the driving force for reduction under standard conditions. In any voltaic cell operating under standard conditions, the reaction at the cathode has a more positive value of E^0_{red} than does the reaction at the anode.

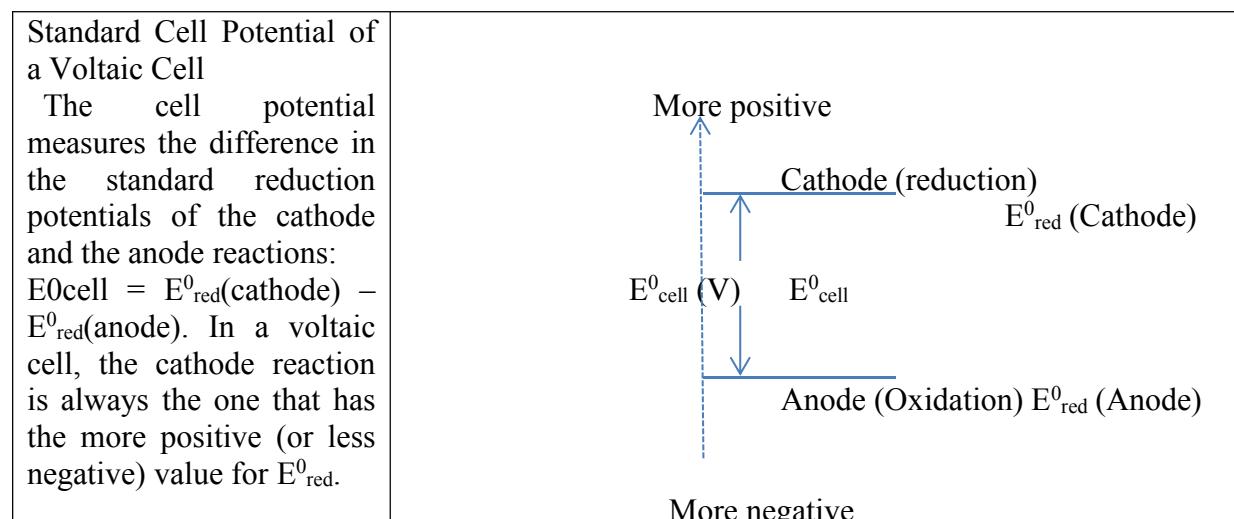
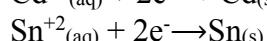
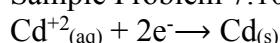


Figure 7.2. The Standard Potential of a Voltaic Cell

Sample Problem 7.10: A voltaic cell is based on the following two standard half-reactions:



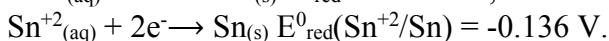
By using the data in the appendix, determine a) the half reactions that occur at the cathode, and b) the standard cell potential

Solution:

a). Determining the half-reaction taking place at the cathode.

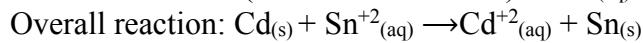
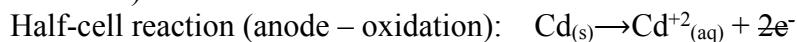
Step 1: Refer to the E^0_{red} for two half-reactions in the appendix and use these values to compare and to predict the cathode and anode of the cell and to calculate its standard cell potential, E^0_{cell} . The cathode will have the reduction with the more positive E^0_{red} value. The anode will have the less positive E^0_{red} . To write the half-reaction at the anode, we reverse the half-reaction written for the reduction, so that the half-reaction is written as an oxidation.

Step 2. $\text{Cd}^{+2(aq)} + 2e^- \rightarrow \text{Cd}_{(s)}$ $E^0_{\text{red}} = -0.403 \text{ V}$, and



Step 3. $E^0_{\text{red}}(\text{Sn}^{+2}/\text{Sn}) = -0.136 \text{ V}$ has more positive (less negative) E^0_{red} value, and is the cathode.

Step 4. Writing the cathode (half-cell reaction – reduction) and the anode (half-cell reaction – oxidation):

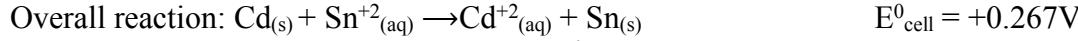
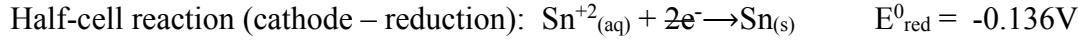


b). The cell potential is:

$$E^0_{\text{cell}} = E^0_{\text{red}}(\text{cathode}) - E^0_{\text{red}}(\text{anode})$$

$$E^0_{\text{cell}} = (-0.136 \text{ V}) - (-0.403 \text{ V}) = 0.267 \text{ V}$$

Using the second method: reversing the E^0_{red} for anode:



Note: That it is important that the E^0_{red} values of both half-reactions are negative; the negative values merely indicate how these reductions compare to the reference reaction, the reduction of $\text{H}^{+}(aq)$. Yet the cell potential for the reaction is positive, as it must be for a voltaic cell.

7.5.3. Cell emf Under Non-Standard Conditions

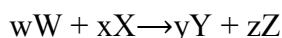
We have discussed calculating the emf of a cell when the reactants and products are under standard conditions. As a voltaic cell is discharged, however, the reactants of the reaction are consumed and the products are generated, so the concentrations of these substances changed. In this case, the emf, progressively drops until $E = 0$ at which point, we can say the cell is “dead”. At this point, the concentrations of the reactants and products cease to change since they are at equilibrium. The emf generated under non-standard conditions can be calculated by using an equation first derived by Walther Nernst (1864-1941), a German chemist who established many of the theoretical foundations of electricity.

The Nernst Equation

The dependence of the cell emf on concentration can be obtained from the dependence of the free-energy change on concentration. Let's consider the free-energy change, ΔG , is related to the standard free-energy change, ΔG^0 .

$$\Delta G = \Delta G^0 + RT \ln Q$$

Where ΔG is the free energy change for a chemical reaction, ΔG^0 is the standard free-energy change for that reaction. R is 8.13143 J/(K-mol), T is the absolute temperature and Q is the reaction quotient, a fraction derived from the activities of the substances involved in the reaction. For the hypothetical reaction,



$$Q = \frac{[a_Y]^y [a_Z]^z}{[a_W]^w [a_X]^x}$$

where the small letters represent the coefficients of the balanced chemical equations.

The numerator of Q is the product of the activity terms for the substances on the right of the chemical equation. The denominator of Q is the product of the activity terms for the substances on the left of a chemical equation. Since the activity of a pure solid is assumed to be unity at all times, the activity for a solid is always equal to 1. For purposes of discussion, it is assumed that the activity of a substance in a solution is given by the molar concentrations of the substance and the activity of a gas is equal to the partial pressures of the gas in atmospheres.

Since $\Delta G = -nFE$ and $\Delta G^0 = -nFE^0$,

substituting to the equation gives: $\Delta G = \Delta G^0 + RT \ln Q$

$$-nFE = -nFE^0 + RT \ln Q,$$

$$\text{solving for } -E = \frac{-nFE^0}{nF} - \frac{RT \ln Q}{nF} = -E^0 - \frac{RT \ln Q}{nF} E = \frac{-E^0}{-1} + \left(-\frac{RT \ln Q}{nF} \right)$$

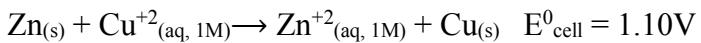
$$E^0 - \frac{RT}{nF} \ln Q; \text{ gives the Nernst Equation}$$

It is expressed in common (base 10) logarithms, which is related to natural logarithms by a factor of 2.303: $\ln Q = 2.303 \log Q$, substituting to the equation, gives:

$$E = E^0 - \frac{2.303 RT}{nF} \log Q, \text{ T at } 25^\circ\text{C} (298.15 \text{ K}), \text{ and } R = 8.314 \frac{J}{mol \cdot K}, \text{ and } F = 96500 \frac{J}{V \cdot mol}$$

$$E = E^0 - \frac{(2.303)(8.314 \frac{J}{mol \cdot K})(298.15 K)}{(n)(96500 \frac{J}{V})} \ln Q = E^0 - \frac{0.0592V}{n} \log Q \quad (n \text{ is the number of electrons involved}).$$

This equation can be used to determine the emf produced by a cell under non-standard conditions or to determine the concentration of a reactant or product by measuring the emf of the cell.



In this particular case, $n = 2.00$ (two electrons are transferred from Zn to Cu^{+2}), and the standard emf is 1.10 V. At 298 K, the Nernst equation gives:

$$E = 1.10\text{V} - \frac{0.0592V}{(2.00)} \log \frac{[\text{Zn}^{+2}]}{[\text{Cu}^{+2}]}, \text{ take note only Zn}^{+2} \text{ and Cu}^{+2} \text{ are included. Zn}_{(\text{s})} \text{ and Cu}_{(\text{s})}$$

are not included in the Q. Given if, $[\text{Cu}^{+2}]$ is 5.00M and $[\text{Zn}^{+2}]$ is 0.050 M we have

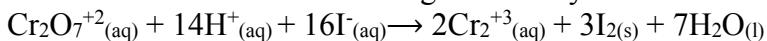
$$E = 1.10\text{V} - \frac{0.0592V}{(2.00)} \log \frac{[0.050]}{[5.00]} = 1.10\text{V} - \frac{0.0592V}{(2.00)} \log (0.010) = \frac{0.0592V}{(2.00)}$$

$$E = 1.10\text{V} - \frac{0.0592V}{(2.00)} (-2.0) = 1.10\text{V} + 0.0592\text{V} = 1.16\text{V}$$

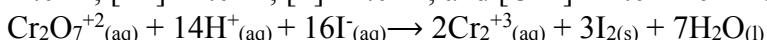
Thus, increasing the concentration of the reactant (Cu^{+2}) and decreasing the concentration of the product (Zn^{+2}) relative to standard conditions increases the emf of the cell ($E = 1.16$ V) relative to the standard conditions ($E^0 = 1.10$ V). This helps us understand why the emf of the voltaic cell drops as the cell discharges. As reactants are converted to products, the value of Q increases, so the value of E decreases, eventually reaching $E=0$. Since $\Delta G = -nFE$, it follows that $\Delta G = 0$ when $E = 0$. Recall then that the system is at equilibrium when $\Delta G = 0$. Thus when $E = 0$, the cell reaction has reached equilibrium, and no net reaction is occurring.

In general, increasing the concentration of reactants or decreasing the concentration of the products increases the driving force for the reaction, resulting in a higher emf. Conversely, decreasing the concentration of the reactants or increasing the concentration of the products decreases the emf.

Sample Problem 7.11. Calculate the emf at 298K generated by the cell:



When, $[\text{Cr}_2\text{O}_7^{+2}] = 2.0 \text{ M}$; $[\text{H}^+] = 1.0 \text{ M}$; $[\text{I}^-] = 1.0 \text{ M}$; and $[\text{Cr}^{+3}] = 1.0 \times 10^{-5} \text{ M}$:

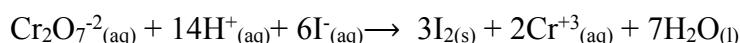


Solution:

This problem has been solved in the previous example.

Cathode: $\text{Cr}_2\text{O}_7^{+2}_{(\text{aq})} + 14\text{H}^{+}_{(\text{aq})} + 6\text{e}^- \rightarrow 2\text{Cr}^{+3}_{(\text{aq})} + 7\text{H}_2\text{O}_{(\text{l})} \quad E^0_{\text{red}} = 1.33\text{V}$

Anode: $6\text{I}^{-}_{(\text{aq})} \rightarrow 3\text{I}_2_{(\text{s})} + 6\text{e}^- \quad E^0_{\text{red}} = 0.54\text{V}$



$n = 6.0$ (6 electrons involved)

$$E^0_{\text{cell}} = E^0_{\text{red}}(\text{cathode}) - E^0_{\text{red}}(\text{anode}) = 1.33 \text{ V} - 0.54 \text{ V} = 0.79 \text{ V}$$

Solving for Q:

$$Q = \frac{[\text{Cr}^{+3}]^2}{[\text{Cr}_2\text{O}_7^{+2}][\text{H}^+]^{14}[\text{I}^-]^6} = \frac{[1.0 \times 10^{-5}]^2}{[2.0][1.0]^{14}[1.0]^6} = \frac{1.0 \times 10^{-10}}{2.0} = 5.0 \times 10^{-11}$$

Solving for E:

$$E = 0.79 \text{ V} - \frac{0.0592V}{6.0} \log 5.0 \times 10^{-11}$$

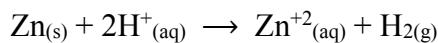
$$E = 0.79 \text{ V} - \frac{0.0592V}{6.0} (-10.3) = 0.79 \text{ V} + 0.10 \text{ V} = 0.89 \text{ V}$$

The result is qualitatively what we expect. Because the concentration of $\text{Cr}_2\text{O}_7^{+2}$ (a reactant) is above 1 M and the concentration of Cr^{+3} (a product) is below 1M, the emf is greater than E^0 .

Sample Problem 7.12. If the voltage of Zn-H⁺ cell is 0.45 V at 25⁰C when $[\text{Zn}^{+2}] = 1.0 \text{ M}$ and $P_{\text{H}_2(g)} = 1.0 \text{ atm}$, what is the concentration of H⁺?

Solution:

The cell reaction is:



Solution:

Identifying the cathode and anode half-cell reactions:

Analyzing the reaction: Zn from 0 to +2 losing 2e⁻ (oxidation – anode), thus H⁺ to H₂ gaining 2e⁻ (reduction – cathode).

Cathode: 2H⁺_(aq, 1M) + 2e⁻ → H_{2(g)}, 1 atm - involving gases (reduction) $E_{\text{Red}}^0 = 0.000V$

Anode: Zn_(s) → Zn⁺²_(aq, 1M) + 2e⁻ - aqueous solution (oxidation) $E_{\text{Red}}^0 = -0.760V$

$$E_{\text{cell}}^0 = E_{\text{Red(Cathode)}}^0 - E_{\text{Red(anode)}}^0 = 0.000V - (-0.763V) = 0.763V$$

$$E^0 = +0.760 V$$

$$E = 0.450V$$

$$n = 2.0$$

$$[\text{Zn}^{+2}] = 1.0 \text{ M}; P_{\text{H}_2(\text{g})} = 1.0 \text{ atm}$$

Solving for Q:

$$Q = \frac{[\text{Zn}^{+2}] [\text{H}_2(\text{g})]}{[\text{H}^+]^2} = \frac{[1.0\text{M}][1.0 \text{ atm}]}{[\text{H}^+]^2}$$

Option 1: Solving the [H⁺_(aq)] using 1.0 atm pressure

$$0.450V = 0.760 V - \frac{0.0592V}{2.0} \log \frac{[1.0\text{M}][1.0 \text{ atm}]}{[\text{H}^+]^2} = 0.763 V - \frac{0.0592V}{2.0} \log \frac{1.0}{[\text{H}^+]^2}$$

$$\log \frac{1.0}{[\text{H}]^2} = -2 \log \text{H}, \text{ so}$$

$$0.450V = 0.763 V - \frac{0.0592V}{2.0}(-2 \log \text{H}^+)$$

$$0.450V - 0.763 V = 0.0592V (\log \text{H}^+)$$

$$-0.313V = 0.0592V (\log \text{H}^+)$$

$$\log [\text{H}^+] = \frac{-0.310}{0.0592} = -5.2$$

$$[\text{H}^+] = -\text{antilog } 5.29 = 6.3 \times 10^{-6} \text{ M}$$

This example shows how a voltaic cell whose cell reaction involves H⁺ that can be used to measure [H⁺] or pH. A pH meter is especially designed voltaic cell with a voltmeter calibrated to read pH directly.

Sample Problem 7.13.

In a test of a new reference electrode, a chemist constructs a voltaic cell consisting of a Zn/Zn⁺² half-cell and an H₂/H⁺ half-cell under the following conditions:

$$[\text{Zn}^{+2}] = 0.010 \text{ M} \quad [\text{H}^+] = 2.5 \text{ M} \quad P_{\text{H}_2} = 0.30 \text{ atm}$$

Calculate E_{cell} at 298.15K.

Solution:

Identifying the half-cell reactions for cathode and anode:

Zn/Zn⁺² – oxidation (anode)

H₂/H⁺ - reduction (cathode)

Half-cell (anode) : Zn_(s) → Zn⁺² + 2e⁻ $E_{\text{red}}^0 = -0.76V$

Half-cell (cathode): 2H⁺ + 2e⁻ → H_{2(g)} $E_{\text{red}}^0 = 0.00V$

Overall reaction: 2H⁺ + Zn_(s) → Zn⁺² + H_{2(g)}

$$E_{\text{cell}}^0 = E_{\text{red(cathode)}}^0 - E_{\text{red(anode)}}^0 = 0.00V - (-0.76V) = 0.76V$$

$$n = 2.0 \text{ (2e- lost/gained)}$$

$$[\text{Zn}^{+2}] = 0.010 \text{ M}$$

$$[\text{H}^+] = 2.5 \text{ M}$$

$$P_{\text{H}_2} = 0.30 \text{ atm}$$

Solving for Q:

$$Q = \frac{[\text{Zn}^{+2}](\text{H}_2)}{[\text{H}_{(\text{aq})}^+]^2} = \frac{[0.010](0.30)}{[2.5]^2} = 4.8 \times 10^{-4}$$

Solving for E_{cell} at 298.15K (25°C),

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^0 - \frac{0.0592V}{(2.0)} \log Q = 0.76V - \frac{0.0592V}{2.0} \log (4.8 \times 10^{-4}) \\ &= 0.76V - \frac{0.0592V}{2.0} (-3.32) = 0.76V + 0.0983V = 0.86V \end{aligned}$$

Another Option: For consistency of units, let us convert atm to mol/L (M):

Using the PV = nRT

Rearranging the equation gives:

$$\frac{n}{V} = \frac{P}{RT} = \frac{0.30 \text{ atm}}{(0.08206 \frac{\text{L-atm}}{\text{K-mol}})(298.15\text{K})} = 0.012 \frac{\text{mol}}{\text{L}} = 0.012 \text{ M}$$

Solving for Q:

$$Q = \frac{[\text{Zn}^{+2}](\text{H}_2)}{[\text{H}_{(\text{aq})}^+]^2} = \frac{[0.010](0.012)}{[2.5]^2} = 1.9 \times 10^{-5}$$

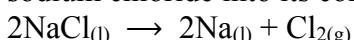
Solving for E_{cell} at 298.15K:

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^0 - \frac{0.0592V}{(2.0)} \log Q = 0.76V - \frac{0.0592V}{2.0} \log (1.9 \times 10^{-5}) \\ &= 0.76V - \frac{0.0592V}{2.0} (-4.7) = 0.76V + 0.139V = 0.90V \end{aligned}$$

This type of problems can be solved using either of the options (using atm as unit for pressures or converting atm to M).

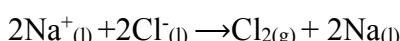
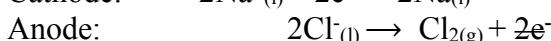
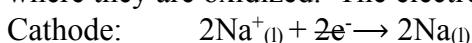
7.6. Electrolysis

Voltaic cells(or galvanic cells, a device in which the transfer of electrons takes place through an external pathway rather than directly between reactants) are based on spontaneous oxidation-reduction reactions. Conversely, it is possible to use electrical energy to cause non-spontaneous redox reactions. For example, electricity can be used to decompose molten sodium chloride into its component elements:



Such types of processes driven by an outside source of electrical energy are called **electrolysis** reactions and are taking place in **electrolytic cells**.

An electrolytic cell consists of two electrodes in a molten salt or solution. It is driven by a battery or some source of direct electric current. The battery is acting as an electron pump, pushing the electrons into one electrode and pulling them from the other. Like in the voltaic cell, the electrode at which reduction occurs – **cathode**, and the electrode at which oxidation occurs – **anode**. In the electrolysis of molten NaCl, sodium ions pick up electrons and reduced to Na metal at the cathode. As the Na^+ ions near the cathode are depleted, additional Na^+ ions migrate in. Similarly, there is net movement of Cl^- ions to the anode, where they are oxidized. The electrode reactions for the electrolysis of molten NaCl:



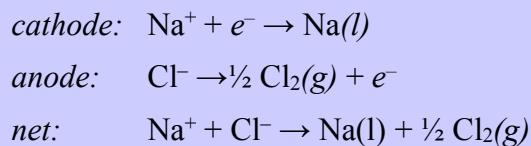
In a voltaic cell (or any other source of direct current) the electrons emanate from the negative terminal to the external circuit. In this case, the electrolytic cell is part of the external circuit connected to the voltage source. Thus, the electrode of the electrolytic cell

that is connected to the negative terminal of the voltage source is the cathode of the cell. It receives electrons that are used to reduce a substance. The electrons that are removed during the oxidation process at the anode travel to the positive terminal of the voltage, thus completing the circuit of the cell.

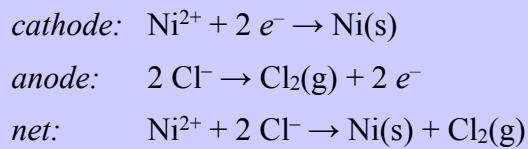
Electrolysis also refers to the decomposition of a substance by an electric current. The electrolysis of sodium and potassium hydroxides, first carried out in 1808 by Sir Humphrey Davey, led to the discovery of these two metallic elements and showed that these two hydroxides which had previously been considered un-decomposable and thus elements, were in fact compounds:

"By means of a flame which was thrown on a spoon containing potash, this alkali was kept for some minutes at a strong red heat, and in a state of perfect fluidity." One pole of a battery of copper-zinc cells was connected to the spoon, and the other was connected to platinum wire which dipped into the melt. "By this arrangement some brilliant phenomena were produced. The potash appeared to be a conductor in a high degree, and as long as the communication was preserved, a most intense light was exhibited at the negative wire, and a column of flame, which seemed to be owing to the development of combustible matter, arose from the point of contact." The flame was due to the combustion in the air of metallic potassium. In another experiment, Davey observed "small globules having a high metallic luster, precisely similar in visible characters to quicksilver, some of which burnt with explosion and bright flame, as soon as they were formed, and others remained, and were merely tarnished, and finally covered by a white film which formed on their surfaces."

Electrolysis of molten alkali halides is the usual industrial method of preparing the alkali metals:

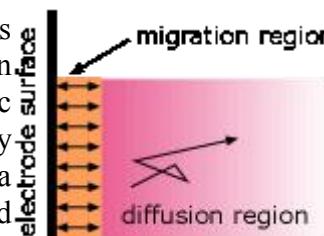


Ions in aqueous solutions can undergo similar reactions. Thus if a solution of nickel chloride undergoes electrolysis at platinum electrodes, the reactions are



Both of these processes are carried out in electrochemical cells which are forced to operate in the "reverse", or non-spontaneous direction, as indicated by the negative for the above cell reaction. The free energy is supplied in the form of electrical work done on the system by the outside world (the surroundings). This is the only fundamental difference between an **electrolytic cell** and the **galvanic cell** in which the free energy supplied by the cell reaction is extracted as work done on the surroundings.

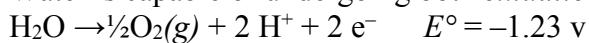
A common misconception about electrolysis is that "ions are attracted to the opposite-charged electrode." This is true only in the very thin interfacial region near the electrode surface. Ionic motion throughout the bulk of the solution occurs mostly by **diffusion**, which is the transport of molecules in response to a concentration gradient. **Migration**— the motion of a charged particle due to an applied electric field, is only a minor player, producing only about one non-random jump out of around 100,000 random ones for a 1 volt



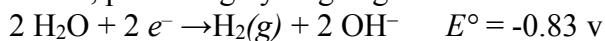
cm^{-1} electric field. Only those ions that are near the interfacial region are likely to undergo migration.

7.6.1. Electrolysis in Aqueous Solution

Water is capable of undergoing both *oxidation*, releasing oxygen at the anode,



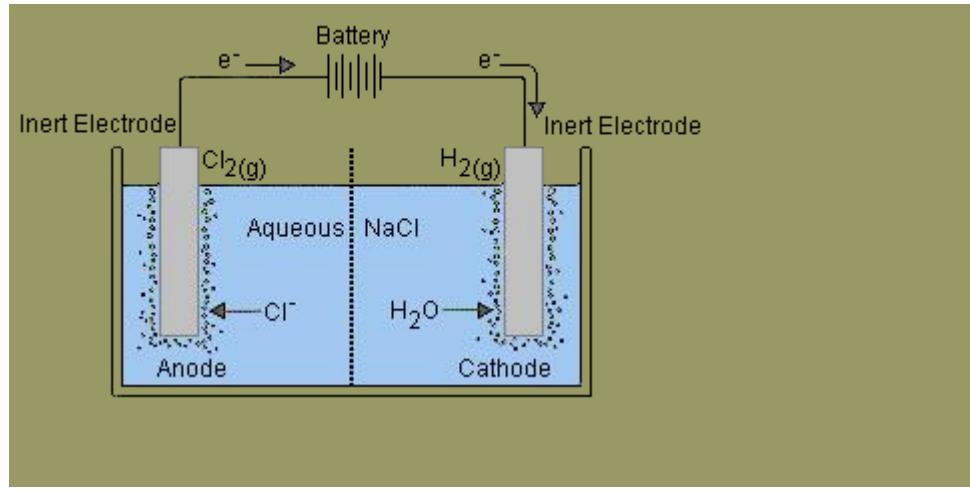
and *reduction*, producing hydrogen gas at the cathode.



Thus if an aqueous solution is subjected to electrolysis, one or both of the above reactions may be able to compete with the electrolysis of the solute.

For example, if we try to electrolyze a solution of sodium chloride, hydrogen is produced at the cathode instead of sodium:

| | | |
|----------|--|--|
| cathode: | $2 \text{H}_2\text{O} + 2 \text{e}^- \rightarrow \text{H}_2(\text{g}) + 2 \text{OH}^-$ | $E = +0.41 \text{ v } ([\text{OH}^-] = 10^{-7} \text{ M})$ |
| anode: | $\text{Cl}^- \rightarrow \frac{1}{2}\text{Cl}_2(\text{g}) + \text{e}^-$ | $E^\circ = -1.36 \text{ v}$ |
| net: | $\text{Cl}^- + \text{H}_2\text{O} \rightarrow 2 \text{H}_2(\text{g}) + \frac{1}{2}\text{Cl}_2(\text{g}) + 2 \text{OH}^-$ | $E = -0.95 \text{ v}$ |

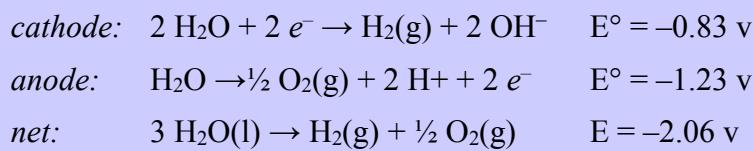


Reduction of Na^+ ($E^\circ = -2.7 \text{ v}$) is energetically more difficult than the reduction of water (-0.83 v), so in aqueous solution the latter will prevail.

Electrolysis of salt ("brine") is carried out on a huge scale and is the basis of the *chloralkali* industry.

7.6.2. Electrolysis of Water

Pure water is an insulator and cannot undergo significant electrolysis without adding an electrolyte. If the object is to produce hydrogen and oxygen, the electrolyte must be energetically more difficult to oxidize or reduce than water itself. Electrolysis of a solution of sulfuric acid or of a salt such as NaNO_3 results in the decomposition of water at both electrodes:



Electrolytic production of hydrogen is usually carried out with a dilute solution of sulfuric acid; for a concise summary of the chemistry and energetics. This process is generally too expensive for industrial production unless highly pure hydrogen is required. However, it becomes more efficient at higher temperatures, where thermal energy reduces the amount of electrical energy required, so there is now some interest in developing high-temperature electrolytic processes. Most hydrogen gas is manufactured by the steam reforming of natural gas.

7.6.3. Industrial Electrolytic Process

For many industrial-scale operations involving the oxidation or reduction of both inorganic and organic substances, and especially for the production of the more active metals such as sodium, calcium, magnesium, and aluminum, the most cost-effective reducing agent is electrons supplied by an external power source. The two most economically important of these processes are described below.

7.6.3.1. The Chloralkali Industry

The electrolysis of brine is carried out on a huge scale for the industrial production of chlorine and caustic soda (sodium hydroxide). Because the reduction potential of Na^+ is much higher than that of water, the latter substance undergoes decomposition at the cathode, yielding hydrogen gas and OH^- .

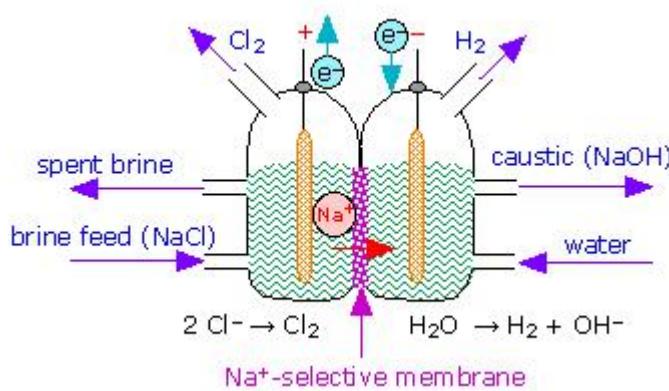
| | | | |
|-------------------|---|-------------------|-----|
| anode reactions | $2 \text{Cl}^- \rightarrow \text{Cl}_{2(\text{g})} + 2 e^-$ | -1.36 v | i |
| cathode reactions | $4 \text{OH}^- \rightarrow \text{O}_{2(\text{g})} + 2 \text{H}_2\text{O} + 4 e^-$ | -0.40 v | ii |
| | $\text{Na}^+ + e^- \rightarrow \text{Na}_{(\text{s})}$ | -2.7 v | iii |
| | $\text{H}_2\text{O} + 2 e^- \rightarrow \text{H}_{2(\text{g})} + 2 \text{OH}^-$ | $+0.41 \text{ v}$ | iv |

A comparison of the E° 's would lead us to predict that the reduction (ii) would be favored over that of (i). This is certainly the case from a purely energetic standpoint, but as was mentioned in the section on fuel cells, electrode reactions involving O_2 are notoriously slow (that is, they are kinetically hindered), so the anodic process here is under kinetic rather than thermodynamic control. The reduction of water (iv) is energetically favored over that of Na^+ (iii), so the net result of the electrolysis of brine is the production of Cl_2 and NaOH ("caustic"), both of which are of immense industrial importance:





A modern industrial chloralkali plant

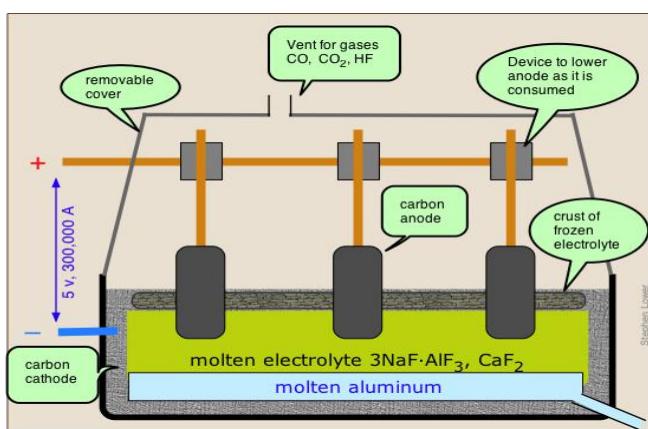
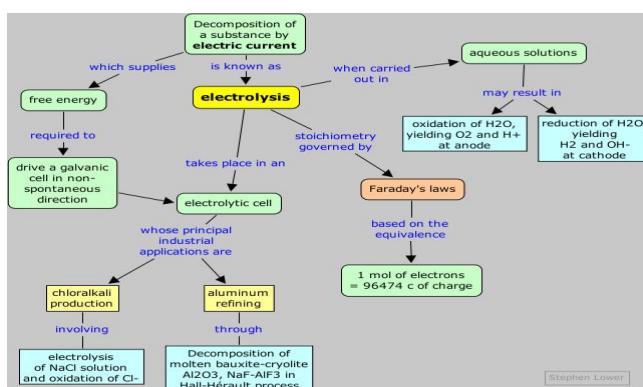


Since chlorine reacts with both OH^- and H_2 , it is necessary to physically separate the anode and cathode compartments. In modern plants this is accomplished by means of an ion-selective polymer membrane, but prior to 1970 a more complicated cell was used that employed a pool of mercury as the cathode. A small amount of this mercury would normally find its way into the plant's waste stream, and this has resulted in serious pollution of many major river systems and estuaries and devastation of their fisheries.

7.6.3.2. Electrolytic Refining of Aluminum

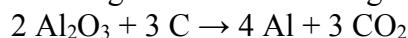
Aluminum is present in most rocks and is the most abundant metallic element in the earth's crust (eight percent by weight.) However, its isolation is very difficult and expensive to accomplish by purely chemical means, as evidenced by the high E° (-1.66 v) of the Al^{3+}/Al

couple. For the same reason, aluminum cannot be isolated by electrolysis of aqueous solutions of its compounds, since the water would be electrolyzed preferentially. And if you have ever tried to melt a rock, you will appreciate the difficulty of electrolyzing a molten aluminum ore! Aluminum was in fact considered an exotic and costly metal until 1886, when Charles Hall (U.S.A) and Paul Héroult (France) independently developed a practical electrolytic reduction process.



The Hall-Héroult process takes advantage of the principle that the melting point of a substance is reduced by admixture with another substance with which it forms a homogeneous phase. Instead of using the pure alumina ore Al_2O_3 which melts at 2050°C , it is mixed with cryolite, which is a natural mixture of NaF and AlF_3 , thus reducing the temperature required to a more

manageable 1000°C. The anodes of the cell are made of carbon (actually a mixture of pitch and coal), and this plays a direct role in the process; the carbon gets oxidized (by the oxide ions left over from the reduction of Al³⁺ to CO, and the free energy of this reaction helps drive the aluminum reduction, lowering the voltage that must be applied and thus reducing the power consumption. This is important, because aluminum refining is the largest consumer of industrial electricity, accounting for about 5% of all electricity generated in North America. Since aluminum cells commonly operated at about 100,000 amperes, even a slight reduction in voltage can result in a large saving of power. The net reaction is:



However, large quantities of CO and of HF (from the cryolite), and hydrocarbons (from the electrodes) are formed in various side reactions, and these can be serious sources of environmental pollution.

7.7. Stoichiometry of Electrolysis

Charges flowing through an electrolytic cell produces products at the electrodes. The more the charges that flow, the more products are formed.

In this section, we will apply the relationship between charges and products formed determined experimentally in the 1832 by Michael Faraday. The **Faraday's law of electrolysis**: the amount of substance deposited or liberated at any electrode is directly proportional to the amount of charge passed.

It usually involved calculation of current, mass of material or time. One mole of electric charge (96,500 coulombs), when passed through a cell, will discharge half a mole of a divalent metal ion such as Cu²⁺. This relation was first formulated by Faraday in 1832 in the form of two laws of electrolysis:

1. The weights of substances formed at an electrode during electrolysis are directly proportional to the quantity of electricity that passes through the electrolyte.

2. The weights of different substances formed by the passage of the same quantity of electricity are proportional to the equivalent weight of each substance.

The *equivalent weight* of a substance is defined as the molar mass, divided by the number of electrons required to oxidize or reduce each unit of the substance. Thus one mole of V³⁺ corresponds to three equivalents of this species, and will require three faradays of charge to deposit it as metallic vanadium.

Most stoichiometric problems involving electrolysis can be solved without explicit use of Faraday's laws. The "chemistry" in these problems is usually very elementary; the major difficulties usually stem from unfamiliarity with the basic electrical units:

- current (amperes) is the rate of charge transport; 1 amp = 1 C/sec.

- power (watts) is the rate of energy production or consumption;

$$1 \text{W} = 1 \text{J/sec} = 1 \text{volt-amp}; 1 \text{watt-sec} = 1 \text{J}, 1 \text{kw-h} = 3600 \text{J}.$$

Steps relative to the stoichiometric calculations of substances oxidized or reduced.



Note: Current is the rate of flow of electricity. An ampere (amp) is the one associated with the flow of 1 C (Coulomb) past a point per second.

Sample Problem 7.14. The charge of a single electron is 1.6022×10^{-19} C. Calculate the Avogadro's number from the fact that $1F = 96500$ C.

Solution:

$$1F = 96500 \text{ C}$$

$$\text{Charge for } 1e^- = 1.6022 \times 10^{-19} \text{ C}$$

$$? \text{ number of electrons} = 96,500 \text{ C} \times \left(\frac{1 e^-}{1.6022 \times 10^{-19} \text{ C}} \right) = 6.023 \times 10^{23} e^-$$

Recall the Avogadro's number is dependent upon the variables:

- for molecules = 6.023×10^{23} molecules
- for ions = 6.023×10^{23} ions, etc.

Sample Problem 7.15. In the electrolysis of CuSO_4 , how much copper is plated out on the cathode by a current of 0.750 A in 10.0 min?

Solution:

$$\text{Atomic mass: Cu} = 63.5 \quad \text{S} = 32.0 \quad \text{O} = 16.0$$

$$A = \frac{1 \text{ C}}{\text{s}} = 0.750 \frac{\text{C}}{\text{s}}$$

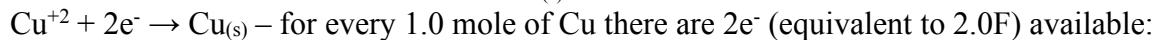
$$1 \text{ F} = 96,500 \text{ C}$$

$$t = 10.0 \text{ min.} \times \frac{60 \text{ s}}{\text{min}} = 600. \text{ s}$$

Using dimensional analysis:

$$? \text{ no. of Faradays (F)} = 600. \text{ s} \left(\frac{0.750 \text{ C}}{\text{s}} \right) \left(\frac{1 \text{ F}}{96500 \text{ C}} \right) = 4.66 \times 10^{-3} \text{ F}$$

Half-cell reaction for the formation of $\text{Cu}_{(s)}$:



$$1 \text{ mol Cu}_{(s)} \cong 63.5 \text{ g} \cong 2F$$

$$? \text{ g Cu}_{(s)} = 4.66 \times 10^{-3} \text{ F} \left(\frac{63.5 \text{ g Cu}_{(s)}}{2.0 \text{ F}} \right) = 0.148 \text{ g}$$

Sample Problem 7.16. The half-reaction for formation of magnesium metal upon electrolytes of molten MgCl_2 is $\text{Mg}^{+2} + 2e^- \rightarrow \text{Mg}_{(s)}$. Calculate the mass of Mg formed upon passage of 60.0 A for a period of 4.00×10^3 s.

Solution:

$$A = 60.0$$

$$t = 4.00 \times 10^3 \text{ s}$$

$$C = A \times t = A \times s$$

$$\text{Atomic mass: Mg} = 24.3$$

$$? \text{ g Mg} = (60.0 \text{ A}) (4.00 \times 10^3 \text{ s}) \left(\frac{1.0 \text{ mole } e^-}{96500 \text{ C}} \right) \left(\frac{1.0 \text{ mol Mg}}{2.0 \text{ mole } e^-} \right) \left(\frac{24.3 \text{ g Mg}}{1.0 \text{ mol Mg}} \right) = 30.2 \text{ g Mg}$$

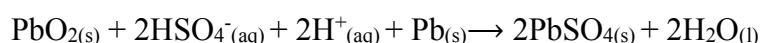
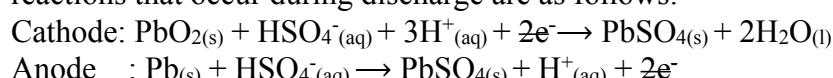
7.8. Batteries

A battery is a portable self-contained electrochemical power source that consists of one or more voltaic cells. The common 1.5 V batteries used to power flashlights and many consumer electronic devices are single voltaic cells. Greater voltages can be achieved by using multiple voltaic cells in a single battery, as in the case of 12-V automotive batteries. When cells are connected in series (with the cathode of one attached to the anode of another), the battery produces a voltage that is the sum of the emfs of the individual cells. The electrodes of batteries are marked following the convention- the cathode is labeled with a plus sign and the anode with a minus sign.

An oxidation-reduction reaction produces a cell emf that can be used to drive electrons from the anode to the cathode through an external circuit, thereby producing electric current. As the battery operates, reactants are converted to products and the emf of the battery drops, eventually to zero. Some batteries are primary cells, meaning they can't be recharged. A **primary cell** must be discarded or recycled after its emf drops to zero. A **secondary cell** can be recharged from an external power source after its emf has dropped.

7.8.1. Lead-Acid Storage Battery

Lead-acid storage battery used in automobiles is one of the most common batteries. A 12-V automotive battery consists of six voltaic cells in series, each producing 2V. The cathode of each cell consists of lead dioxide, PbO_2 , packed on a metal grid. The anode of each cell is composed of lead. Both electrodes are immersed in sulfuric acid. The electrode reactions that occur during discharge are as follows:



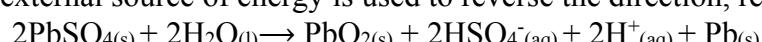
The standard cell potential can be obtained from the standard reduction potential from the appendix:

$$E_{\text{cell}}^0 = E_{\text{cathode}}^0 - E_{\text{anode}}^0 = (+1.685 \text{ V}) - (-0.356 \text{ V}) = +2.041 \text{ V}$$

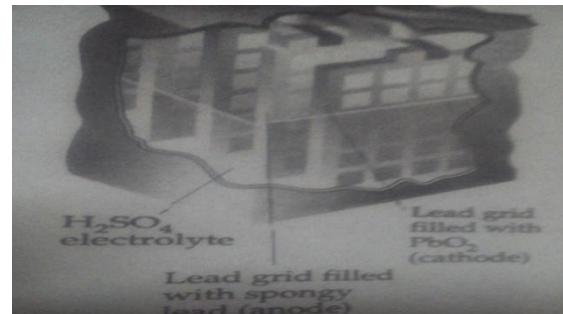
The reactants Pb and PbO_2 , between which electron transfer occurs, serve as the electrodes. Since these reactants are solids, there is no need to separate the cell into anode and cathode compartments; the Pb and PbO_2 cannot come into direct physical contact unless one electrode plate touches the other. To keep the electrode from touching, wood or glass-fiber spacers are placed between them.

Using a reaction whose reactants and products are solids has another benefit. Because solids are excluded from reaction quotients, the relative amounts of $\text{Pb}_{(s)}$, $\text{PbO}_{2(s)}$ and $\text{PbSO}_{4(s)}$ have no effect on the emf of the lead storage battery, helping the battery maintain a relatively constant emf during discharge. The emf does vary somewhat with use because the concentration of H_2SO_4 varies with the extent of cell discharge.

One advantage of a lead-acid battery is that it can be recharged. During recharging an external source of energy is used to reverse the direction, regenerating $\text{Pb}_{(s)}$ and $\text{PbO}_{2(s)}$:



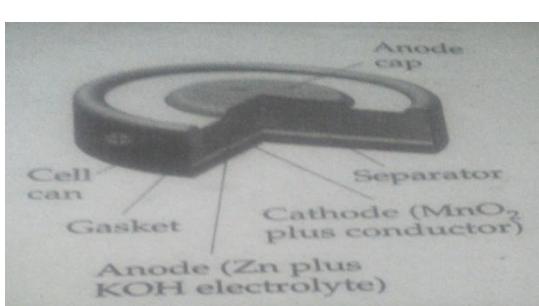
In an automobile the energy necessary for recharging the battery is provided by a generator driven by the engine. Recharging is possible because PbSO_4 formed during discharge adheres to the electrodes. As the external source forces electrons from one electrode to another, the PbSO_4 is converted to Pb at one electron and to PbO_2 at the other.



7.8.2. Alkaline Battery

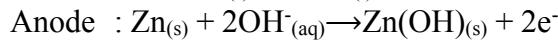
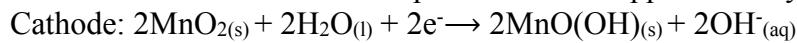
The most common primary (non-rechargeable) battery is the alkaline battery. The anode of this battery consists of powdered zinc metal immobilized in a gel in contact with a

concentrated solution of KOH (hence, the name alkaline battery). The cathode is a mixture of $\text{MnO}_{2(s)}$ and graphite, separated from the anode by



a porous fabric separator. The battery is sealed in a steel can to reduce the risk of leakage of the concentrated KOH.

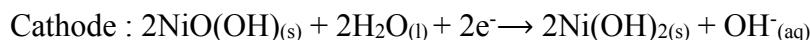
The cell reaction is complex but can be approximately represented as follows:



The emf of an alkaline battery is 1.55 V at room temperature. The alkaline battery provides far superior performance over the older dry cells that are also based on MnO₂ and Zn as the electrochemically active substances.

7.8.3. Nickel-Cadmium, Nickel Metal-Hydride, and Lithium-Ion Batteries

The tremendous growth in high power demand portable electronic devices such as cellular phones, notebook computers, and video recorders has increased the demand for light-weight, readily rechargeable batteries. Recently, the most common rechargeable battery is the Nickel-Cadmium (Nicad) battery. During discharged, cadmium metal is oxidized at the anode of the battery while nickel-oxyhydroxide , NiO(OH)_(s), is reduced at the cathode. Electrode reactions:



As in the lead-acid battery, the solid reaction products adhere to the electrodes, which permits the electrode reactions to be reversed during charging. A single nicad voltaic cell has an emf of 1.30 V. Nicad battery packs typically contain three or more cells in series in order to produce the higher emfs needed by most electronic devices.

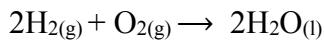
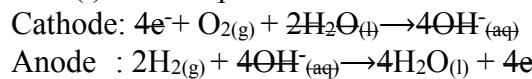
Nickel-Cadmium batteries have drawbacks. Cadmium is considered as a toxic heavy-metal. Its use increases the weight of batteries and provides an environmental hazard. But some of these problems have been reduced with the development of nickel-metal-hydride (NiMH) batteries. The cathode reaction of these batteries is very different. The anode consists of metal alloy, such as ZrNi₂, that has the ability in absorbing hydrogen atoms . In the course of the oxidation at the anode, the hydrogen atoms are released as H₂O, a process which is reversed during charging.

The ever newest rechargeable battery that has gained large acceptance to consumer electronic devices is the lithium-ion (Li-Ion) battery. Since lithium is a very light element, Li-ion batteries achieve a greater energy-density – the amount of energy stored per unit mass – than nickel-based batteries. The technology of Li-ion battery is very different from that of the other batteries described, and it is based on the ability of lithium ions to insert themselves into certain layered solids. For example, Li ions can be inserted into layers of graphite. During discharge, lithium ions migrate between two different layered materials that serve as the anode and cathode of the cell.

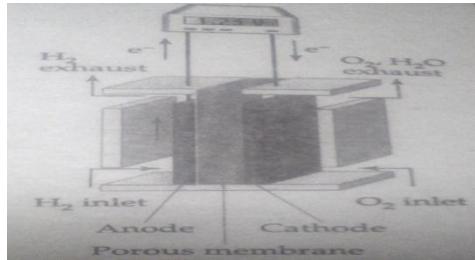
7.9. Fuel Cells

Many substances serve as fuels. The thermal energy released during combustion is often converted to electrical energy. The heat may convert water to steam which drives a turbine that is used to drive the generator. Only 40% at maximum of the energy produced during combustion is converted to electricity; the rest is lost as heat. The direct production of electricity from fuels by a voltaic cell, could in principle, produce higher rates of conversion of the chemical energy of the reaction. Voltaic cells that perform this conversion using conventional fuels, such as H₂ and CH₄, are called **fuel cells**. Fuel cells are not batteries since they are not self-contained systems.

The most promising fuel-cell system involves the reaction of $\text{H}_{2(\text{g})}$ and $\text{O}_{2(\text{g})}$ to form $\text{H}_2\text{O(l)}$ the sole product. The electrode reactions under basic conditions are as follows:



The standard emf of an H_2 - O_2 fuel cell is +1.23 V, reflecting the large driving force for the reaction of H_2 and O_2 to form water.



Until today, fuel cells are too impractical as they require high operating temperatures for the cell reaction to occur at an appreciable rate. Newly developed semipermeable membranes and catalysts allow for the operation of H_2 - O_2 fuel cells below 100°C .

7.10. Preventing the Corrosion of Iron

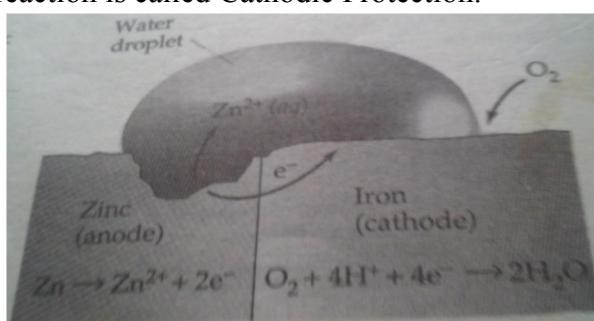
To protect iron against corrosion, it is often coated with paint or another metal strip such as tin or zinc. This surface coating would simply prevent oxygen and water from being in contact with each other. In cases where the surface coating is broken, then corrosion begins.

Galvanized iron, is the iron which is coated with zinc layer to prevent iron from corrosion.

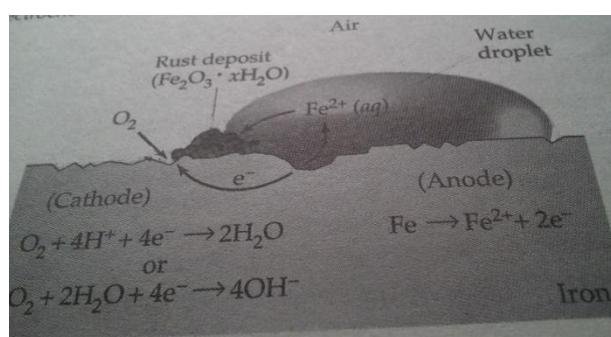


The E°_{red} value for the reduction of Fe^{+2} is less negative (more positive) than that for the reduction of Zn^{+2} , meaning iron (Fe) is easier to reduce than zinc (Zn). So, if the zinc coating is broken, the galvanized iron is exposed to oxygen and water, the zinc will serve as the anode for the reaction, thus zinc will be corroded instead of iron.

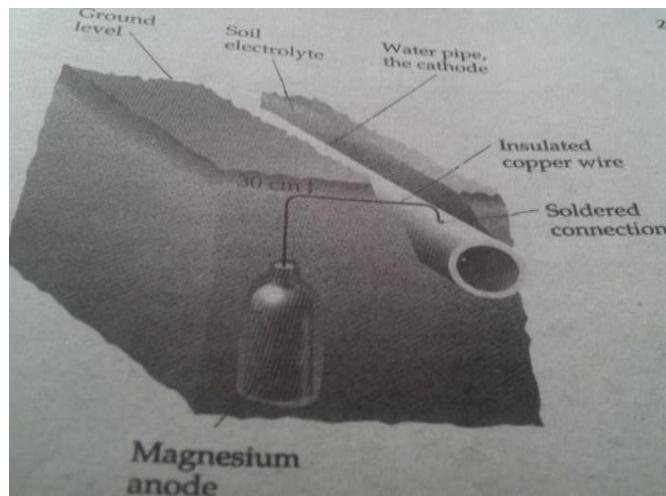
This method of protecting the iron by making it the cathode for the electrochemical reaction is called Cathodic Protection.



Corrosion of iron in contact with water



Cathodic protection of iron in contact with zinc



Cathodic protection of iron water pipe. The magnesium anode is surrounded by mixtures of gypsum, sodium sulfate and clay to promote conductivity of ions. In effect, the pipe serves as the cathode of the voltaic cell.

PROGRESS CHECK

7.1. Complete and balance the following by ion-electron method. Reactions are taking place in acidic solution.

- $\text{Cu}_{(s)} + \text{NO}_3^-_{(aq)} \rightarrow \text{Cu}^{+2}_{(aq)} + \text{NO}_2_{(g)}$
- $\text{Mn}^{+2}_{(aq)} + \text{NaBiO}_3_{(s)} \rightarrow \text{Bi}^{+3}_{(aq)} + \text{MnO}_4^-_{(aq)}$

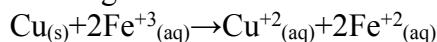
7.2. Complete and balance the following by ion-electron method. Reactions are taking place in alkaline solution.

- $\text{NO}_2^-_{(aq)} + \text{Al}_{(s)} \rightarrow \text{NH}_3_{(aq)} + \text{Al(OH)}_4^-_{(aq)}$
- $\text{Cr(OH)}_3_{(s)} + \text{ClO}^-_{(aq)} \rightarrow \text{CrO}_4^{-2}_{(aq)} + \text{Cl}_2_{(g)}$

7.3. Write the half-cell reactions for each of the following cells:

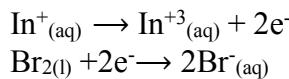
- $\text{Ag}|\text{Ag}^+||\text{H}^+|\text{H}_2|\text{Pt}$
- $\text{Pt}|\text{Cr}_2\text{O}_7^{2-}, \text{Cr}^{+3}, \text{H}^+||\text{Br}^-|\text{Br}_2_{(l)}|\text{Pt}$

7.4. Describe in shorthand notation a galvanic cell for which the cell reaction:



7.5. One beaker contains 0.15 M $\text{Cd}(\text{NO}_3)_2$ and a Cd metal electrode. The other beaker contains 0.20 M AgNO_3 and a Ag metal electrode. Write the anode and cathode half-cell reactions, overall reactions and the cell notation.

7.6. A voltaic cell based on the half-reactions:

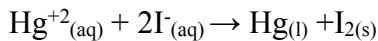


The standard emf for this cell is 1.46 V. Using the data in the appendix, calculate, E^0_{red} for the reduction of In^{+3} to In^{+1} :

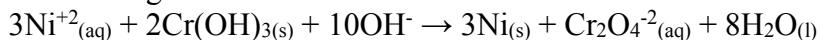
7.7. A voltaic cell is based on Co^{+2}/Co half-cell and a AgCl/Ag half-cell.

- What reaction occurs at the anode?
- What is the standard cell potential (E^0_{cell})?

7.8. Using the standard reduction potentials listed in the appendix, determine whether the following reaction is spontaneous under standard conditions:

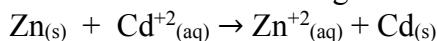


7.9. Consider the following reaction:



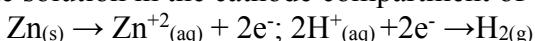
- What is the value of n for the reaction?
- Use data in the appendix to calculate ΔG^0 for the reaction.

7.10. A voltaic cell is constructed that uses the following reaction and operates at 298K:



- What is the emf of the cell under standard conditions?
- What is the emf of this cell when $[\text{Cd}^{+2}] = 1.50\text{M}$, $[\text{Zn}^{+2}] = 0.150\text{M}$?

6.11. What is the pH of the solution in the cathode compartment of the cell



when $P_{\text{H}_2} = 1.0 \text{ atm}$, $[\text{Zn}^{+2}]$ in the anode compartment is 1.0M and cell emf is 0.542V?

7.12. A voltaic cell is constructed with two hydrogen electrodes. Electrode 1 has $P_{H_2} = 1.00$ atm and an unknown concentration of $H^{+}_{(aq)}$. Electrode 2 is a hydrogen electrode ($[H^+] = 1.00$ M, $P_{H_2} = 1.00$ atm). At 298 K, the cell voltage is measured to be 0.211V and the electrical current is observed to flow from electrode 1 through the external circuit to electrode 2. What is the $[H^+]$ for the solution in electrode 1? What is its pH?

7.13. A concentration cell is constructed with two $Zn_{(s)}-Zn^{+2}_{(aq)}$ half-cells. The first cell has $[Zn^{+2}] = 1.35\text{M}$ and the second cell $[Zn^{+2}] = 0.000375\text{M}$. a). Which half-cell is the anode b). What is the emf of the cell?

7.14. A technician plates a faucet with 0.86 g Cr metal by electrolysis of aqueous $\text{Cr}_2(\text{SO}_4)_3$. If 12.5 min is allowed for the plating what current is need?

7.15. Using a current of 4.75 A, how many minutes does it take to place a sculpture of with 1.50 g of Cu from a CuSO_4 solution?

7.16. In the electrolysis of CuSO_4 , how much copper is plated out on the cathode by a current of a 0.75A in 10 min?

7.17 a). What mass of copper is plated out in the electrolysis of CuSO_4 , in the same time that it takes to deposit 1.00g of Ag in a silver coulometer that is arranged in series with CuSO_4 cell? b).

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chem.libretexts.org/Bookshelves/Analytical_Chemistry/Supplemental_Modules_(Analytical_Chemistry)/Electrochemistry#:~:text=Electrochemistry%20is%20the%20study%20of%20chemical%20processes%20that%20cause%20electrons,("redox")%20reaction.

TOPIC/S: NUCLEAR CHEMISTRY

- 10.1. The Nucleus
- 10.2. The Radioactive Decay
- 10.3. Balancing Nuclear Reactions
- 10.4. Rate Law and Half-life
- 10.5. Radioactive Dating
- 10.6. Radioactive Decay Series
- 10.7. Detection of Radiation
- 10.8. Nuclear Transmutation
- 10.9. Effects of Nuclear Radiation on Matter
- 10.10. Radioisotope Tracers
- 10.11. Other Applications of Ionizing Radiation
- 10.12. Nuclear Fusion
- 10.13. Nuclear Fission

EXPECTED COMPETENCIES

At the end of the lesson, you must have:

- 1. defined nucleus,
- 2. described, explained and calculated radioactive decays,
- 3. balanced nuclear reactions,
- 4. explained rate law and radioactive decay series,
- 5. described nuclear transmutations,
- 6. enumerated different radioisotope traces,
- 7. enumerated different applications of ionizing radiations,
- 8. defined nuclear fusion and nuclear fission; and
- 9. differentiated nuclear fusion from nuclear fission.

CONTENTS

Nuclear chemistry is the study that deals with the changes occurring within the atomic nuclei opposed to traditional chemistry, which involves changes to electronic structures of atoms.

Table 10 .1 Differences between Nuclear Reactions and Chemical Reactions

| Chemical Reactions | Nuclear Reactions |
|--|---|
| A new substance is formed, but atoms never change identity. - When Na and Cl ₂ gas combines, they form a new substance NaCl but the identities of Na and Cl remain. | A new atom of different element is formed - When $^{215}_{84}Po$ undergoes alpha decay, $^{211}_{82}Pb$ a totally different atom is formed. |
| Involves electrons in the orbitals causing breaking and forming of bonds. - Na with electron configuration 1s ² 2s ² 2p ⁶ 3s ¹ – during reaction, only the outermost electron of Na in the 3s, is the one involved the reaction. | Nuclear particles, neutrons and protons are involved. - $^{1}_1p + ^{0}_1e \rightarrow ^{1}_0n$ a proton is transformed into a neutron when a nucleus interacts with the electron. |
| Reactions accompanied by relatively small changes in energy. | Reactions accompanied by relatively large changes in energy |
| Rates of reactions are influenced by temperature, concentration and the addition of catalysts. | Reaction rates are not influenced by temperature, catalysts but depend on the number of nuclei. |

10.1. The Nucleus

We have discussed the nucleus of the atom. Each specific atom – a nuclide is characterized by atomic number (Z) and the mass number (A). A nucleus is considered to contain protons and neutrons and particles collectively called as nucleons.

Lighter elements with approximately equal numbers of protons and neutrons (with the ratio of neutron to proton of 1) have stable nuclei. Stable heavier nuclei on the other hand, contain more neutrons than protons. As the atomic number increases, more and more protons are present in the nucleus, thus more and more excess of neutrons are required in overcoming the effects of repulsive forces between protons. This causes the neutron/proton ratio to increase with the increasing atomic number until approximately 1.5 neutron/proton ratio.

There is a limitation to the number of protons that can be present in the nucleus regardless on the number of neutrons present. $^{209}_{83}Bi$ is considered as the largest stable nuclei. Existing nuclei larger than this, are radioactive.

Nuclides with even protons and even neutrons are the most naturally occurring stable nuclides. 2_1H , 6_3Li , $^{10}_5B$, $^{14}_7N$, and $^{180}_{73}Ta$ having odd number of protons and odd number of neutrons. Two elements ($_{43}Tc$, $_{61}Pm$) with atomic number less than 83 having odd number atomic number have never been proven to occur in nature.

Nuclides with number of protons or number neutrons 2, 8, 20, 28, 50 and 82 are having nuclear stability. These numbers are referred to as magic numbers which indicate close nuclear shells similar to that of the atomic numbers of the noble gases 2, 10, 18, 36 and 54 indicating stable electronic notations. Generally, elements with atomic numbers equal to that of the magic numbers have larger number of stable isotopes.

10.2. Radioactive Decay

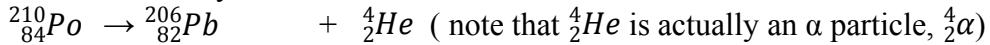
Radioactivity is exhibited by an unstable nucleus with the emission of radiation due to spontaneous disintegration.

Modes of radioactive decay:

- When a nuclide of one element undergoes decay process, radiation is emitted associated with a change of a nuclide into different element. Nuclide decays with the formation of nuclide of lower energy and the excess energy is released through radiation emitted and recoiled.

a). Alpha (α) decay

Involves the emission of an alpha, α , particles consisting of 2 protons and 2 neutrons, similar to that of the ${}_2^4He$ nuclei. Elements with atomic number more than 83 are considered radioactive and exhibit decays. Alpha emission is the most common way for a heavy unstable nucleus to attain stability.

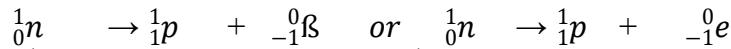


The emission of an alpha, α , particle reduces the number of protons by two and the number of neutrons by two.

b). Beta (β) decay

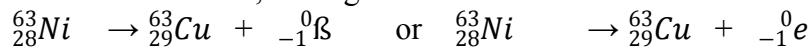
Different modes of β decays:

- **Negatron emission, β^-** particles (or ${}_{-1}^0e$) ejected when a neutron is converted into a proton which stays at the nucleus:



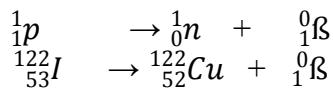
The symbol ${}_{1}^1p$ indicates a nuclear proton. ${}_{1}^1H$ indicates a free proton and e to indicate an orbital electron from a particle.

Nickel which is radioactive, undergoes β^- emission to become a stable Cu-63.



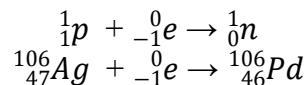
β^- emission results in the decrease of number of neutrons by 1 and the increase in the number of protons by 1, hence the number of nucleons does not change. The mass number does not change but the atomic number is increased by 1 (atomic number of the next higher element).

- **Positron emission, β^+** , an antiparticle of an electron and is expelled from the nucleus through the process in which a proton in the nucleus is converted into a neutron and a positron. The positron has the same mass as an electron but of opposite charge.



This results in an increase in the number of neutrons by 1 and a decrease in the number of protons by 1. The mass number remains the same but the atomic number is decreased by 1 forming an element with the next lower atomic number.

- **Electron Capture (EC)** occurs when an electron in a lower energy level interacts with the nucleus transforming a proton into a neutron.

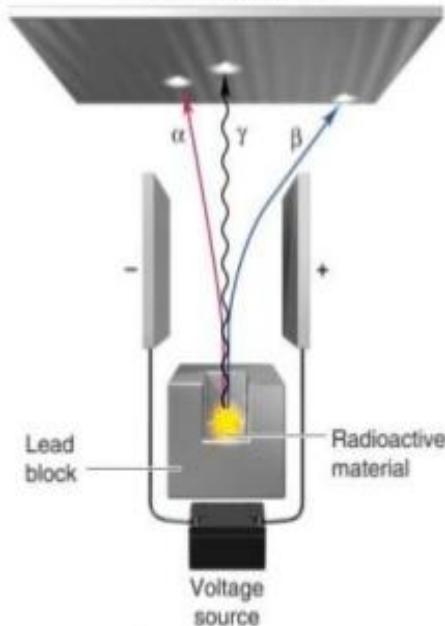


In this process, the electron from an inner electron level is captured by the nucleus converting the proton into a neutron. Electron capture is like positron emission (in terms of net effect) resulting to a decrease in the number of proton and an increase in proton in the product nucleus. The mass number remains the same, atomic number is decreased by 1 (or an element with next lower atomic number).

- c). **Gamma (γ) emissions** or the gamma rays involve emission of γ photons or γ rays from an excited nucleus. Gamma emission usually accompanies β^- decay.

Gamma, γ emission does not cause the atomic number or the mass number to change because γ rays have no mass nor mass. In the process where a particle and an antiparticle annihilate each other, two γ rays are emitted.

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ZnS-coated screen
(or photographic plate)



The positively charged α particles curve toward the negative plate, the negatively charged β particles curve towards the positive plate, and the γ rays are not affected by the electric field.

Figure .1: How the three types of radioactive emissions behave in an electric field

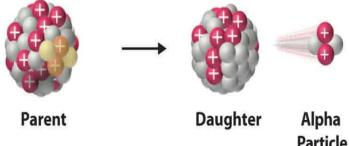
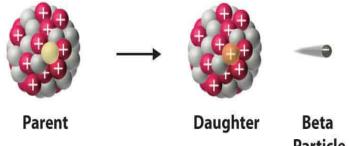
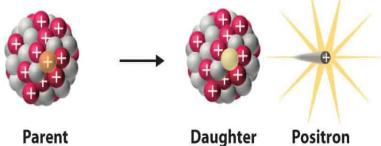
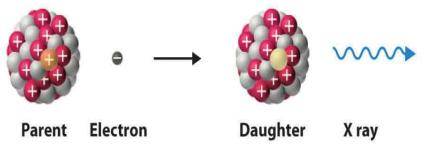
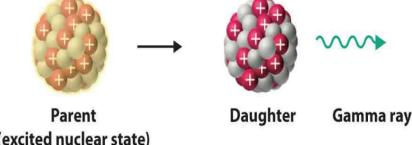
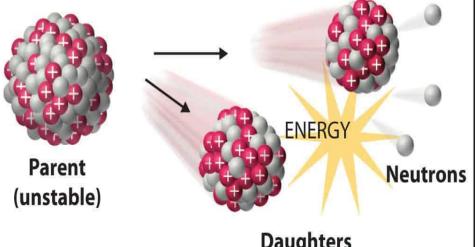
| Decay Type | Radiation Emitted | Generic Equation | Model |
|---------------------|---------------------|--|--|
| Alpha decay | $\frac{4}{2}\alpha$ | ${}_{Z}^A X \longrightarrow {}_{Z-2}^{A-4} X' + \frac{4}{2}\alpha$ |  |
| Beta decay | $\frac{0}{-1}\beta$ | ${}_{Z}^A X \longrightarrow {}_{Z+1}^{A} X' + \frac{0}{-1}\beta$ |  |
| Positron emission | $\frac{0}{+1}\beta$ | ${}_{Z}^A X \longrightarrow {}_{Z-1}^{A} X' + \frac{0}{+1}\beta$ |  |
| Electron capture | X rays | ${}_{Z}^A X + \frac{0}{-1}e \longrightarrow {}_{Z-1}^{A} X' + \text{X ray}$ |  |
| Gamma emission | $\frac{0}{0}\gamma$ | ${}_{Z}^A X^* \xrightarrow{\text{Relaxation}} {}_{Z}^{A} X' + \frac{0}{0}\gamma$ |  |
| Spontaneous fission | Neutrons | ${}_{Z+Y}^{A+B+C} X \longrightarrow {}_{Z}^{A} X' + {}_{Y}^{B} X' + {}_{0}^1 n$ |  |

Figure 10.2. Radioactive Decay Mechanism

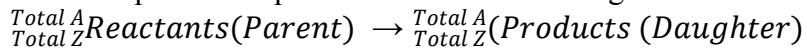
10.3. Balancing Nuclear Reactions

Ordinary chemical equations are designed to represent formation and breaking of bonds – chemical bonds. In nuclear equations, atomic symbols represent nuclei with mass number and atomic number.

In balancing a nuclear reactions:

1. The reactants are called as the parent and the products as daughter.
2. The superscripts which give the mass numbers (A) and the subscripts give the atomic number (Z).

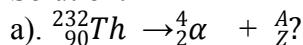
3. The sum of the superscripts of the species involved in the parent must be equal to the superscripts of the species involved in the daughter.
4. The sum of the subscripts of the species involved in the parent must be equal to the sum of the subscripts of the species involved in the daughter.



Sample Problem 10.1. Write the balanced equation for the following:

- a). Naturally occurring thorium-232 undergoes α decay.
- b). Zirconium-86 undergoes electron capture
- c). ${}_{2}^{4}\text{He} + {}_{7}^{14}\text{N} \rightarrow {}_{1}^{1}\text{H} + {}_{Z}^{A}?$

Solution:

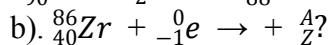
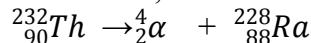


The sum of the mass numbers (A) on the parent side = The sum of the mass numbers (A) on the daughter side:

$$232 = 4 + A; A = 232 - 4 = 228$$

The sum of the atomic numbers (Z) on the parent side = The sum of the atomic numbers (Z) on the daughter side:

$$90 = 2 + Z; Z = 90 - 2 = 88; \text{Ra}$$

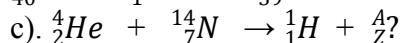
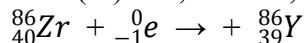


The sum of the mass numbers (A) on the parent side = The sum of the mass numbers (A) on the daughter side:

$$86 + 0 = A; A = 86$$

The sum of the atomic numbers (Z) on the parent side = The sum of the atomic numbers (Z) on the daughter side:

$$40 + (-1) = Z; Z = 39; \text{Y}$$



The sum of the mass numbers (A) on the parent side = The sum of the mass numbers (A) on the daughter side:

$$4 + 14 = 1 + A$$

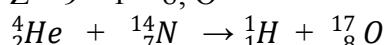
$$A = 18 - 1 = 17$$

The sum of the atomic numbers (Z) on the parent side = The sum of the atomic numbers (Z) on the daughter side:

$$2 + 7 = 1 + Z$$

$$9 = 1 + Z$$

$$Z = 9 - 1 = 8; \text{O}$$



10.4. Rate Law and Half-Life

Decay rate or Activity (A), is equal to the change in the number of nuclei (N) divided by the change in time (t) for a radioactive sample simply referring to the amount of radiation from its source for a given time.

$$\text{Decay rate (Activity) } A = -\frac{\Delta N}{\Delta t}$$

Notice of a negative sign in the expression because the number of nuclei is decreasing (radioactive substance disappears).

The SI unit of radioactivity is the **becquerel (Bq)**, equivalent to one disintegration/second (d/s). **Curie (Ci)**, is a unit frequently used.

$$1 \text{ Ci} = 1 \text{ Curie} = 3.70 \times 10^{10} \text{ d/s}$$

$$1 \text{ mCi} = 1 \text{ milliCurie} = 3.70 \times 10^7 \text{ d/s}$$

$$1 \mu\text{Ci} = \text{microCurie} = 3.70 \times 10^4 \text{ d/s}$$

The number of atoms present in a sample of a radioactive nuclide is proportional to its activity.

$$A \propto N$$

To convert the proportionality sign into an equality sign, let us introduce a constant, k , the decay constant characteristic of a nuclide. The higher the k value, the higher the rate of decay.

$$A = kN$$

Substituting, the equation for A , gives

$$-\frac{\Delta N}{\Delta t} = kN$$

Activity is a first-order process and is dependent only on the amount of radioactive substance present.

Rearranging equation $-\frac{\Delta N}{\Delta t} = kN$ gives

$$-\frac{\Delta N}{N} = k\Delta t$$

Expressing in a differential form

$$-\frac{dN}{N} = kt$$

Integrating overtime gives the equation for finding the remaining nuclei, N_1 after a given time, t :

$$\frac{N_1}{N_0} = -kt \quad \text{or} \quad N_1 = N_0 e^{-kt} \quad \text{or} \quad \ln \frac{N_0}{N_1} = kt \quad \text{or}$$

$$-\frac{dN}{N} = kt$$

$$-2.303 \log \left(\frac{N_1}{N_0} \right) = kt \quad \text{or}$$

$$\log \left(\frac{N_0}{N_1} \right) = \frac{kt}{2.303}$$

Half-life ($t_{1/2}$) is the time required for half the sample of a nuclei to decay. The remaining number of nuclei is halved after each half-life. Activity is dependent upon the number of nuclei, thus activity is halved after each succeeding half-life.

Where N_1 is the amount of nuclei at $t=0$. To solve for $t_{1/2}$, let's assign $N_1 = \frac{1}{2}N_0$.

Solving for $t_{1/2}$ gives:

$$\frac{N_0}{N_1} = 2 \text{ substituting to } \log \left(\frac{N_1}{N_0} \right) = \frac{kt}{2.303} \text{ gives}$$

$$\log 2 = \frac{kt_{1/2}}{2.303}$$

$$t_{1/2} = \frac{2.303 \log 2}{k} = \frac{0.693}{k}$$

Take note that N_0 and N_1 can be expressed in terms of atoms, moles or any mass unit provided consistency in the units is observed.

Half-life is not dependent on the number of nuclei and is inversely proportional to the decay constant.

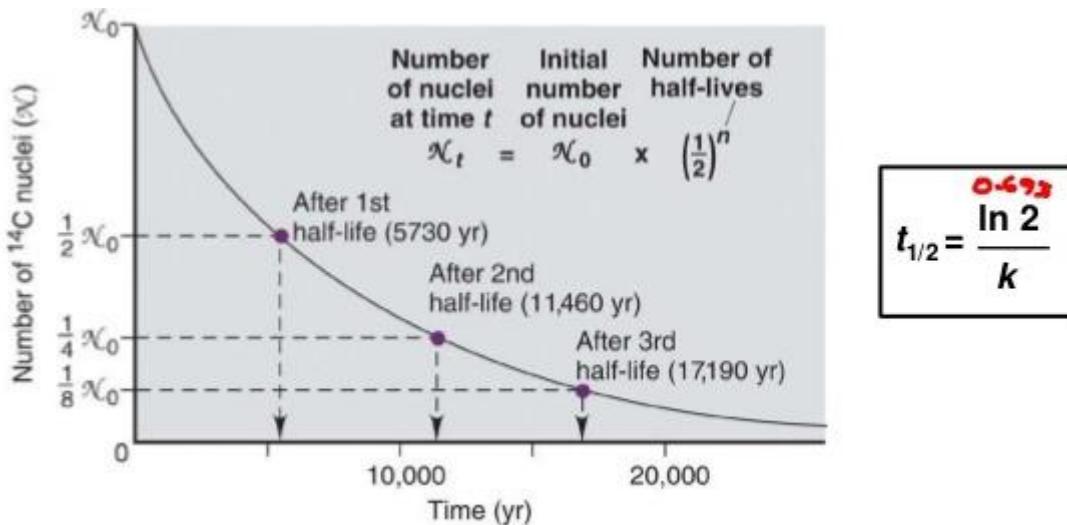


Figure 10.3. Decay of Carbon-14

Sample Problem 10.2. Strontium-90 is a radioactive by-product of nuclear reactor and behaves biologically like calcium. When ^{90}Sr is ingested by mammals it is found in their milk and eventually in the bones of those drinking the milk. If a sample of ^{90}Sr has an activity of $1.2 \times 10^{12} \text{ d/s}$, what are the activity and the fraction of nuclei that have decayed after 59 years ($t_{1/2}$ of $^{90}\text{Sr} = 29 \text{ yrs}$)?

Solution:

$$\text{Fraction of nuclei that decayed} = \frac{N_o - N_1}{N_o} = \frac{A_o - A_1}{A_o}$$

$$N_o = A_o = 1.2 \times 10^{12} \text{ d/s}; t = 59 \text{ yrs}; t_{1/2} = 29 \text{ yrs}$$

$$\text{Since } k \text{ is characteristic to a nuclei, solving for } k \text{ using } t_{1/2} = \frac{\ln 2}{k} \text{ gives:}$$

$$k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{29 \text{ yrs}} = 0.024/\text{yr}$$

$$\ln \frac{N_o}{N_1} = \ln \frac{A_o}{A_1} = kt \quad \text{and} \quad \ln A_o - \ln A_1 = kt$$

$$-\ln A_1 = kt - \ln A_o \text{ dividing both sides by } -1$$

$$\ln A_1 = -kt + \ln A_o$$

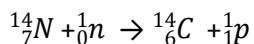
$$\ln A_1 = -(0.024/\text{yr})(59 \text{ yrs}) + \ln(1.2 \times 10^{12} \text{ d/s}) = -1.4 + 27.81 = 26.4$$

$$A_1 = 2.9 \times 10^{11} \text{ d/s}$$

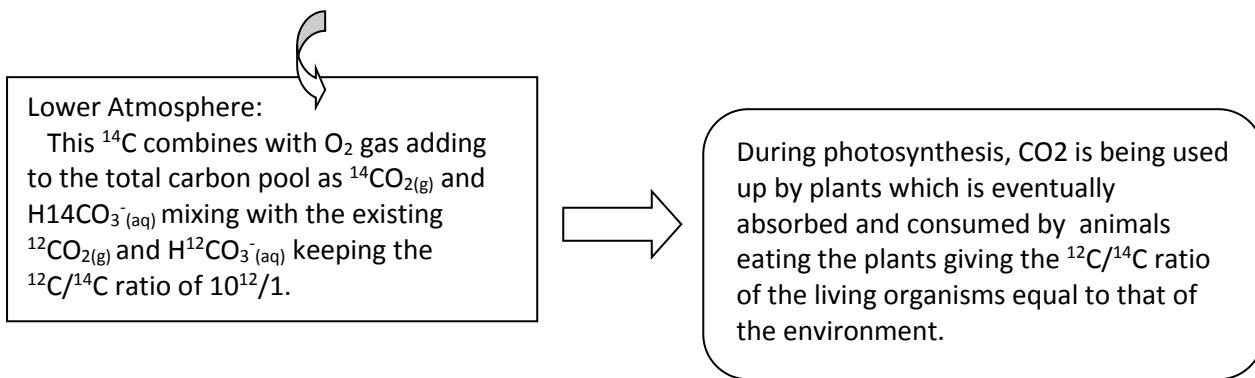
$$\text{Fraction decayed} = \frac{A_o - A_1}{A_o} = \frac{1.2 \times 10^{12} \text{ d/s} - 2.9 \times 10^{11} \text{ d/s}}{1.2 \times 10^{12} \text{ d/s}} = 0.76$$

10.5. Radiocarbon Dating

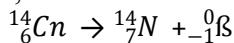
Cosmic rays of higher energy consisting of protons, from the outer space enter the atmosphere initiating series of nuclear reactions producing some neutrons bombarding ordinary ^{14}N atoms forming ^{14}C .



This keeps the amount of ^{14}C in the atmosphere to be constant.



As organisms die, absorption and release of CO_2 stop. Thus, the $^{12}\text{C}/^{14}\text{C}$ ratio decreases steadily. As the body decays, the amount of ^{14}C decreases:



The time elapse for the death of the body is taken from the differences in the ratio of $^{12}\text{C}/^{14}\text{C}$ in the living organism to the dead organism. The activity of the object decreases also. The age of an object can be determined using the radiocarbon activity of the object, the radio

Radioisotope dating or carbon dating uses isotopes in determining the ages of bodies or objects.

The age of an object can be determined using the radioisotope activity of the object, the radioisotope activity of living organisms and the half-life of ^{14}C which is 5730 years.

The equation, $\ln \frac{N_o}{N_1} = \ln \frac{A_o}{A_1} = kt$, where $A_o=N_o$ is the activity in the living organism while $A_1=N_1$ is the activity in the object or body of unknown age. Solving for the age of the object, t:

$$t = \frac{1}{k} \ln \frac{A_o}{A_1}$$

Sample Problem 10.3. The charred bones of a sloth in a cave in Chile represent the earliest evidence of human presence at the southern tip of South America. A sample of the bone has a specific activity of 5.22 d/min per gram of carbon (d/min-g) if the $^{12}\text{C}/^{14}\text{C}$ ratio for the living results in a specific activity of 15.3d/min-g, how old are the bones ($t_{1/2}$ for ^{14}C = 5730 years)?

Solution:

$$t_{1/2} \text{ for } ^{14}\text{C} = 5730 \text{ years}$$

$$A_o = 15.3 \text{ d/min-g}$$

$$A_1 = 5.22 \text{ d/min-g}$$

Solving for k:

$$k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{5730 \text{ yrs}} = 1.21 \times 10^{-4} / \text{yr}$$

Solving for t:

$$t = \frac{1}{k} \ln \frac{A_o}{A_1} = \frac{1}{1.21 \times 10^{-4} / \text{yr}} \ln \frac{15.3 \frac{\text{d}}{\text{min}} \text{g}}{5.22 \frac{\text{d}}{\text{min}} \text{g}} = 8.89 \times 10^3 \text{ years}$$

Sample Problem 10.4. A sample of a wooden artifact is found to undergo 9.0 d/m-m-g of carbon (^{14}C). What is the approximate age of the artifact? The half-life of ^{14}C is 5730 years, and the radiocarbon activity of wood recently cut down is 15 d/min-g of carbon. ^{14}C .

Solution:

$t_{1/2}$ for ^{14}C = 5730 years

$A_0 = 15 \text{ d/min-g}$

$A_1 = 9.0 \text{ d/min-g}$

$$\text{Solving for } k: k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{5730 \text{ yrs}} = 1.21 \times 10^{-4} / \text{yr}$$

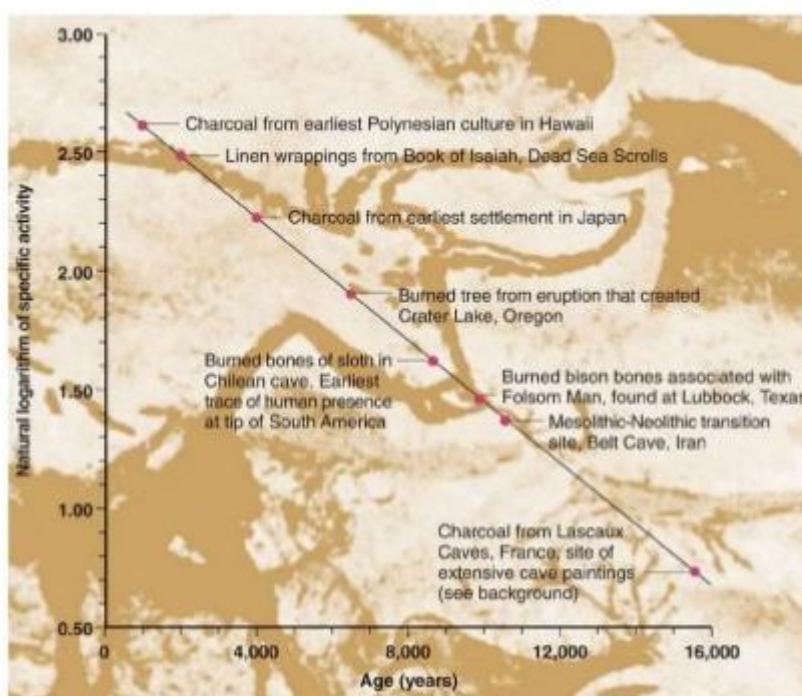
$$\text{Solving for } t: t = \frac{1}{k} \ln \frac{A_0}{A_1} = \frac{1}{1.21 \times 10^{-4} / \text{yr}} \ln \frac{15 \frac{\text{d}}{\text{min-g}}}{9.0 \frac{\text{d}}{\text{min-g}}} = 4.2 \times 10^3 \text{ years}$$

$$\text{Or: } \log\left(\frac{N_0}{N_1}\right) = \frac{kt}{2.303}$$

$$\log \frac{15 \frac{\text{d}}{\text{min-g}}}{9.0 \frac{\text{d}}{\text{min-g}}} = \frac{(1.21 \times 10^{-4} / \text{yr})k}{2.303}$$

$$k = \frac{(0.222)(2.303)}{1.21 \times 10^{-4} / \text{yr}} = 4.2 \times 10^3 \text{ years}$$

Radioactive or radiocarbon dating finds its interesting applications to many historical finds and objects. The Dead Sea scrolls determined to be about 200 years old, the age of the Solar System including Earth to be about 4.7 billion years, etc.

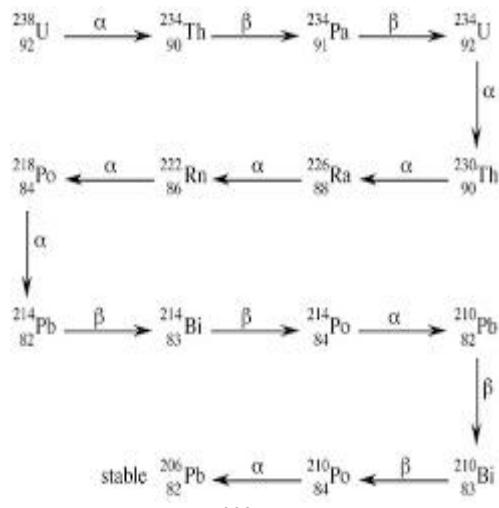


$$t = \frac{1}{k} \ln \frac{A_0}{A_t}$$

Figure 10.4 Ages of Objects determined by Radioactive Dating

10.6. Radioactive Decay Series

A parent nuclide can undergo series of decay that leads to the formation of a stable nuclide daughter. This process of succession is known as **decay series** or **disintegration series**.

Figure 19.5. ^{238}U Decay Series

The figure above illustrates the series of decay of ^{238}U finally leading to the stable nuclide of ^{206}Pb . With the given routes, the series consists of 14 steps having 8 α decays and 6 β^- decays.

10.7. Detection of Radiation

Ionization counter detects radioactive emissions by ionizing the gas which produces free electrons with gaseous cations that are attracted to the electrodes thereby producing electric current.

A **scintillation counter** detects radioactive emissions due to their ability to excite atoms causing them to emit light. ZnS coats the window of a sensitive photoelectric tube and the flashes of light which ZnS emitted when its struck by radioactive emissions cause pulses of electric current that pass through the photoelectric tube. These signals are amplified to operate various counting devices.

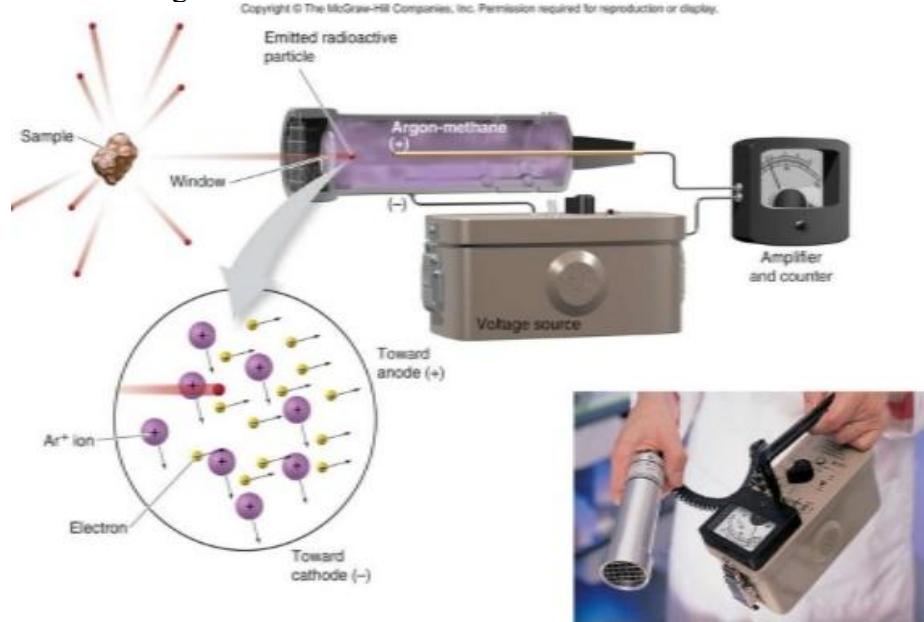


Figure 10.6. Detection of Radiation using a Scintillation Counter

Wilson Cloud Chamber the device used to detect paths of ionizing particles from radioactive decay. When ionizing particles pass through air, ions are produced with the path of radiation. The chamber, consists of a sealed environment with supersaturated vapor of alcohol or water.

As the piston moves which causes the air in the chamber to expand and cool rapidly. This makes the air to become supersaturated with the vapor of the liquid. Droplets of the liquid condense on the ions formed by the particles as they move along the chamber making the paths of these particles visible.

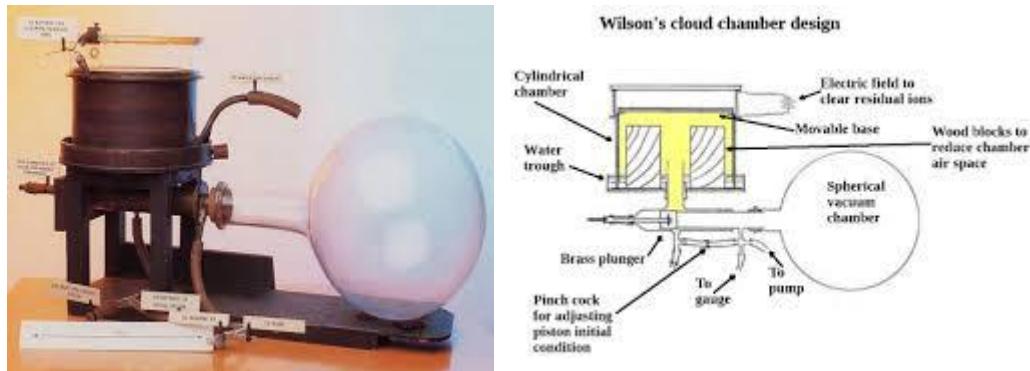


Figure 10.7. Wilson Cloud Chamber

Geiger-Müller counter use for detecting and measuring ionizing radiation. A Geiger-Müller tube is a device used for detecting and measuring all types of radiation: alpha, beta and gamma radiation. It consists of a pair of electrodes surrounded by a gas, usually He or Ar, with high voltage electrodes across them. When radiation enters the tube it ionizes the gas. The ions (and electrons) are attracted to the electrodes and an electric current is produced. A scaler counts the current pulses, and one obtains a "count" whenever radiation ionizes the gas.

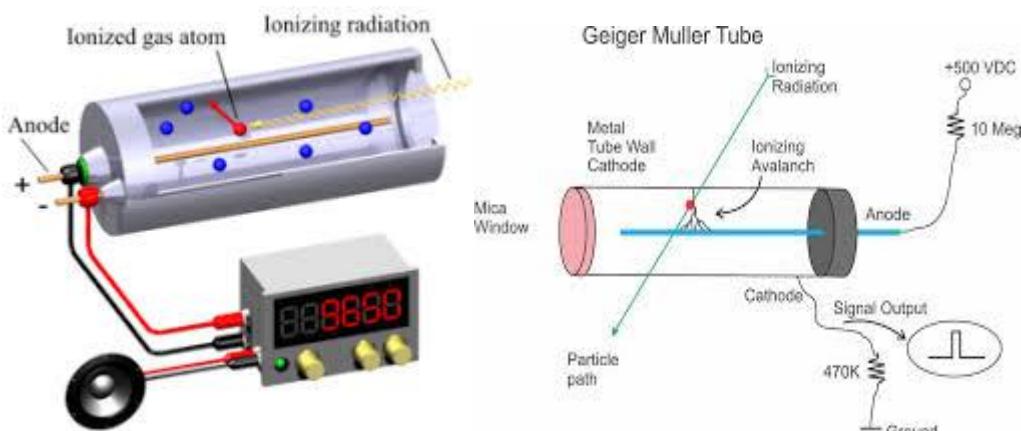
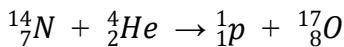


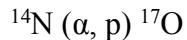
Figure 10.8. Geiger-Müller Counter

10.8 Nuclear Transmutation

It is the induced conversion of the nucleus of one element into the nucleus of another element and is achieved by high-energy bombardment of a nuclei using a particle accelerator



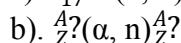
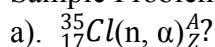
The above transmutation reaction can be described using a short-hand notation:



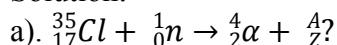
Particle accelerators were invented beginning in the 1930s to impart high kinetic energies to particles in an electric field in combination with a magnetic field.

Linear accelerator is a series of separated tubes of increasing length which, through the source of alternating voltage, change their charge from positive to negative synchronizing with the movement of the particle through them.

Sample Problem 10.5. Write the equations for the following induced nuclear reactions:



Solution:



$$35 + 1 = 4 + A$$

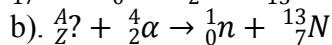
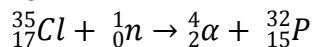
$$36 - 4 = A$$

$$32 = A$$

$$17 + 0 = 2 + Z$$

$$17 - 2 = Z$$

$$15 = Z$$



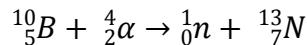
$$A + 4 = 1 + 13$$

$$A + 4 = 14$$

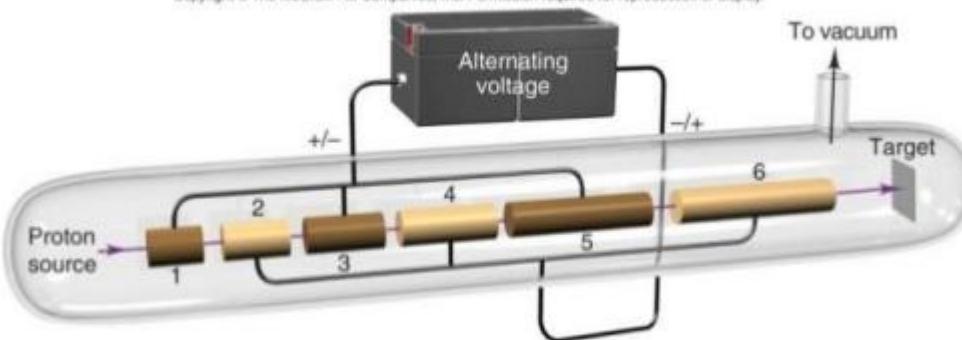
$$A = 14 - 4 = 10$$

$$Z + 2 = 0 + 7$$

$$Z = 7 - 2 = 5$$



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The linear accelerator uses a series of tubes with alternating voltage. A particle is accelerated from one tube to the next by repulsion.

Figure 10.9. Schematic Diagram of a Linear Accelerator

The **cyclotron** invented in 1930 by E. O. Lawrence, employs linear accelerator principle but uses electromagnets giving the particle a spiral path to save space. It uses the synchronously increasing magnetic field making the path of a particle circular instead of spiral.

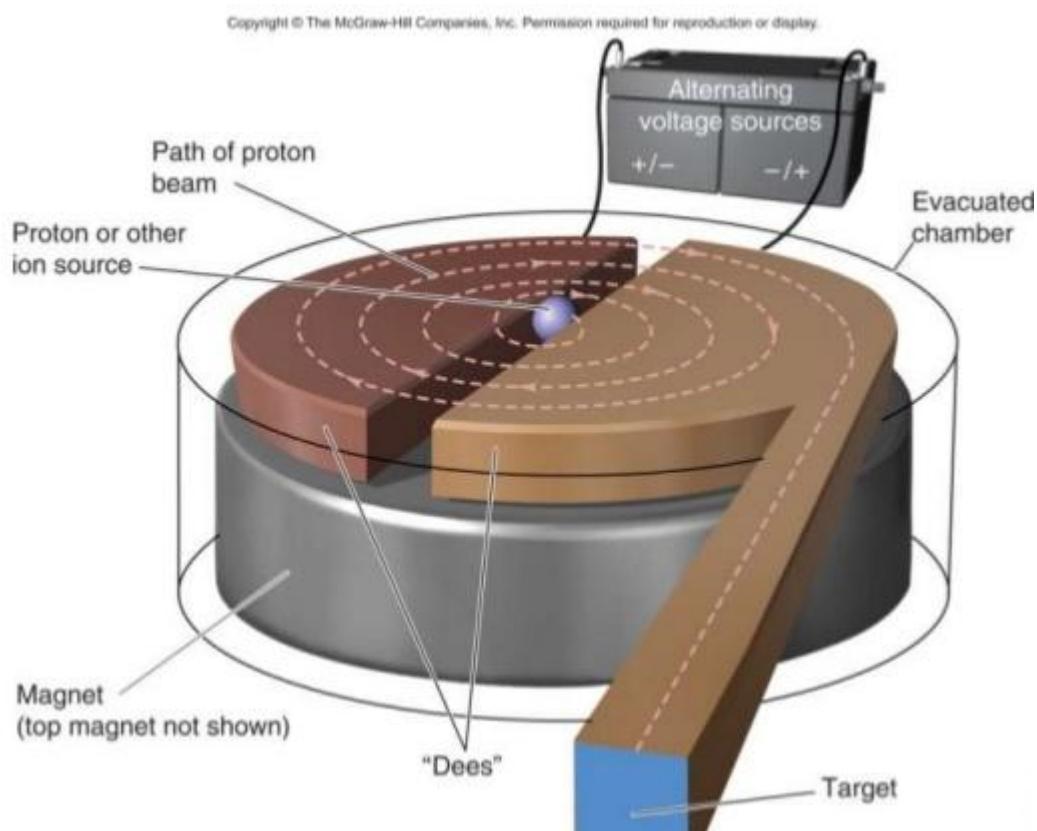
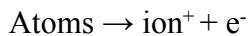


Figure 10.10. Schematic Diagram of a Cyclotron

10.9. Effects of Nuclear Radiation on Matter

All radioactivity causes ionization in surrounding matter, as emissions colliding with atoms dislodging electrons.



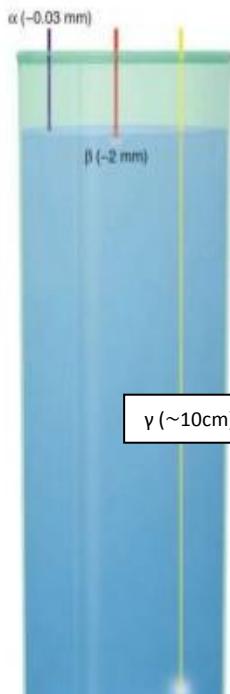
For every ionization process, cation and free electron are formed of which the number of cation-electron pairs formed is directly proportional to the energy of the **ionizing radiation**. A natural ionizing radiation is called **background radiation**. Ionizing radiation alters bonds in DNA that can cause harmful. It has also a beneficial cause that allows species to evolve.

A unit for radiation dose is used to measure the effects of ionizing radiation. Becquerel and curie measure the number of decays in a given time but not their energy. The measure of the amount of energy absorbed per kg of body tissue gives the number of cation-electron pairs produced by the given amount of a living body tissue. The SI unit is **Gray (Gy)**, is equal to 1 joule of energy absorbed per kg of body tissue ($1 \text{ Gy} = 1 \text{ J/kg}$). Another unit often used is **rad** (radiation absorbed dose) equivalent to $0.01 \text{ J/kg} = 0.01 \text{ Gy}$.

In measuring actual tissue damage, the difference in the strength of the radiation, exposure time and type of tissue must be accounted for. This is done by multiplying the number of rads by RBE (Relative Biological Effectiveness) factor, depending upon the effect a given type of radiation has on a given body part giving the resulting product as **rem (roentgen equivalent for man)**, the unit of dosage of radiation which is equivalent to a given amount of damage to tissue in human.

$$\text{no. of rems} = \text{no. of rads} \times \text{RBE} \text{ and is always expressed in millirems (} 10^{-3} \text{ rem)}$$

1 rem = 0.01 Sv (sievert – the SI unit for dosage equivalent, the same as in rems but with absorbed dose in grays).



The effect of radiation on living tissue depends on both the penetrating power and the ionizing ability of the radiation.

Penetrating power is **inversely related** to the mass, charge, and energy of the emission.

Figure 10.11. Penetrating Power of Radioactive Emissions

Penetrating Power of Particles

- **Alpha particles, α** - are massive and highly charged which can interact with matter most strongly of the three emissions, thus they penetrate so little that a piece of paper, light clothing or even the outer layer of skin can stop α radiation. If ingested, α radiation can cause grave localized internal damaged through extensive ionization.

- **Beta particles (β^-) and positron (β^+)** – they have less charge and much less mass than they interact less strong with matter. Though they have less chance of causing ionization, however, they have more destructive external source because they penetrate deeper. Only a specialized heavy clothing or a piece of metal with 0.50cm thickness can stop these particles.

- **Gamma rays, γ** – they are neutral, massless that interact least with matter but penetrate most. It requires several inches of lead block to stop them. It is dangerous as it can ionize many layers of living tissue.

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| Dose (rem) | Effect | Lethal Dose | |
|-----------------------|---|-----------------------|--------------------|
| | | Population (%) | No. of Days |
| 5–20 | Possible late effect; possible chromosomal aberrations | — | — |
| 20–100 | Temporary reduction in white blood cells | — | — |
| 50+ | Temporary sterility in men (100+ rem = 1-yr duration) | — | — |
| 100–200 | "Mild radiation sickness": vomiting, diarrhea, tiredness in a few hours Reduction in infection resistance Possible bone growth retardation in children | — | — |
| 300+ | Permanent sterility in women | — | — |
| 500 | "Serious radiation sickness": marrow/intestine destruction | 50–70 | 30 |
| 400–1000 | Acute illness, early deaths | 60–95 | 30 |
| 3000+ | Acute illness, death in hours to days | 100 | 2 |

Figure 10.12. Typical radiation Doses From natural and Artificial Sources

10.10. Radioisotopes Tracers

Isotopes of some elements exhibit a very similar chemical and physical behavior. A small amount of radioactive isotope mixed with the stable isotopes will undergo the same chemical reactions, and can act as a tracer.

They are used to study reaction pathways, track physiological functions, trace material flow, identify components of a substance from a very small sample, and diagnose a wide variety of medical conditions.

- Reaction pathways

Traces can be used to understand both simple and complex reaction pathways.

- Inorganic systems: periodate-iodide reaction
- Biochemical pathways: photosynthesis

Material Flow

Used for studying solid surfaces and flow of materials. Atoms of metals that are hundreds of layers deep within a solid exchange with metal ions from surrounding solution, in a matter of minutes. Tracers to study material movement has been used in semiconductor chips, paints, metal plating, detergent actions, in the corrosion process, etc.

Studying the volume and flow of large bodies of water employs tracers. To name a few applications of tracers: study the surface and deep ocean currents circulating around the globe, the mechanism of hurricane formation, and the mixing of troposphere and stratosphere.

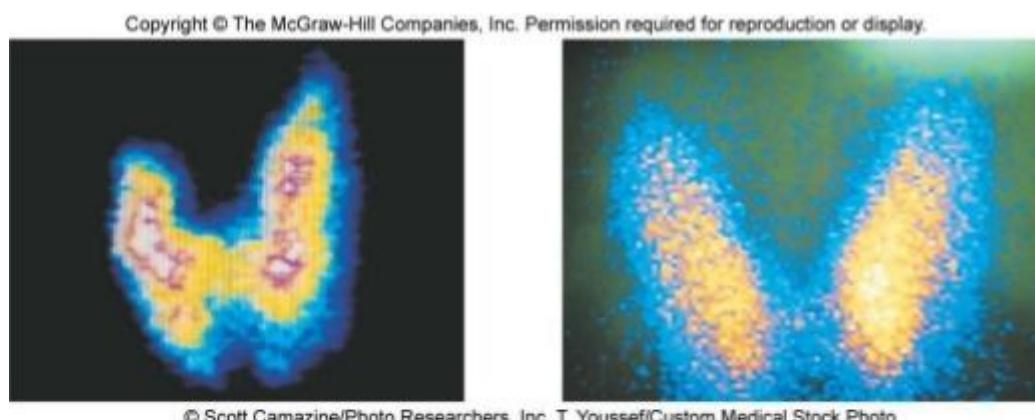
In the industry, tracers are used to study material flow during manufacturing processes, the diffusion of fungicide into lumber, porosity and leakage of oil and gas wells in geological formations.

Activation Analysis

Neutron Activation Analysis (NAA), by bombarding neutrons on a non-radioactive sample where a small fraction of its atom to radioisotopes, exhibiting characteristic patterns of decays such as γ -ray spectra revealing the presence of the elements. It used in forensic analysis for detecting traces of ammunition on a suspect's hands or traces of arsenic in the victim's hair due to poisoning. Another example of its use, a painting which was considered a 16th – century Dutch masterpiece was shown to be a counterfeit (20th – century forgery) as its micro-sized sample of pigments was found to contain much less silver and antimony traces than the pigments used by the Dutch master, through NAA.

Medical Diagnosis

Scope in terms of its application is in medical science. Specific organs and other body parts are observed employing tracers with half-lives of a few minutes to a few days. The use of radioisotopes to assess thyroid function is one. Healthy thyroid glands incorporate dietary I⁻ into iodine-containing hormones at a known rate. The patient drinks a solution containing a trace amount of Na¹³¹I and being scanned by a scanning monitor.



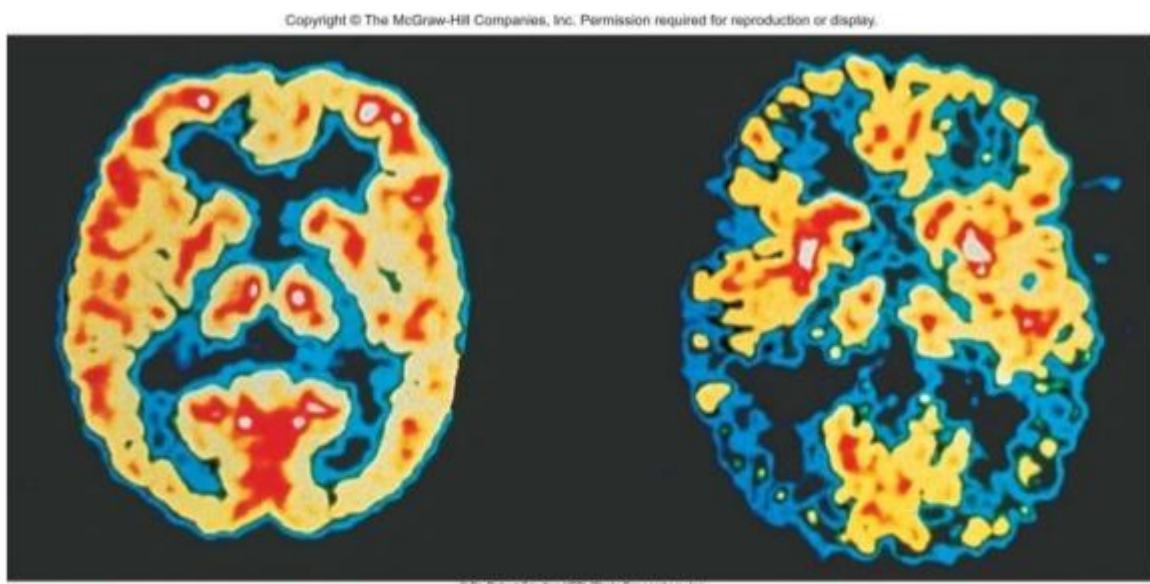
This ¹³¹I scan shows an asymmetric image that is indicative of disease.

A ⁹⁹Tc scan of a healthy thyroid.

Figure 19.13. Use of Radioisotopes to Scan the Image of Thyroid Gland

| Isotope | Body Part or Process |
|---|-----------------------------------|
| ^{11}C , ^{18}F , ^{13}N , ^{15}O | PET studies of brain, heart |
| ^{60}Co , ^{192}Ir | Cancer therapy |
| ^{64}Cu | Metabolism of copper |
| ^{59}Fe | Blood flow, spleen |
| ^{67}Ga | Tumor imaging |
| ^{123}I , ^{131}I | Thyroid |
| ^{111}In | Brain, colon |
| ^{42}K | Blood flow |
| $^{81\text{m}}\text{Kr}$ | Lung |
| $^{99\text{m}}\text{Tc}$ | Heart, thyroid, liver, lung, bone |
| ^{201}TI | Heart muscle |
| ^{90}Y | Cancer, arthritis |

Figure 10.14. Some Radioisotopes Used as Medical Tracers



These PET scans show brain activity in a normal person (*left*) and in a patient with Alzheimer's disease (*right*). Red and yellow indicate relatively high activity within a region.

Figure 10.15. PET and Brain Activity

10.11. Other Applications of Ionizing Radiation

- Radiation therapy

- Cancer cells divide more rapidly than normal cells and are therefore, susceptible to radioisotopes interfering with cell division killing more cancer cells than normal ones.¹⁹⁸Au and ⁹⁰Sr implants decaying into γ -emitting ⁹⁰Y are used to destroy pituitary and breast tumor cells, also γ rays from ⁶⁰Co is used to destroy tumors of the brain and other body parts.

- Destruction of microbes

- Irradiation of foods causes to increase its shelf-life by killing microorganisms that cause spoilage. This practice was opposed, the method makes fresh fruits, grains and seeds for longer periods preserved for longer periods but irradiation might affect the nutritional value or can produce harmful by-products. Irradiation destroys newer, more resistant bacterial strains that survive the increasing use of more common antibiotics in animal feed.

- Insect control

Sterilizing by radiation captured males and being released to mate, decreasing the number of off-spring.

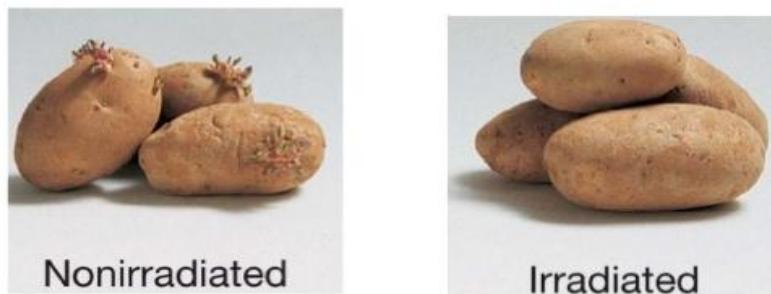
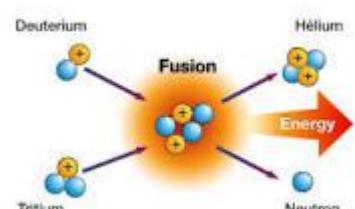


Figure 10.16. Increased Shelf-Life of Irradiated Food

10.12. Nuclear Fusion

Nuclear fusion is a process by which two very light nuclei of elements are fused or combined to give heavier nuclei releasing energy. Nuclei are made up of protons and neutrons, however, the mass of the nucleus is always less than the sum of the individual masses of the protons and neutrons constituting it. The difference is a measure of the nuclear binding energy holding the nucleus together. The **binding energy** is the energy required to pull the nucleons of a nucleus apart.



Nuclei undergoing fusion reaction carry with them positive charges causing them to repel each other strongly. In order for the nuclei to get closer enough together to fuse, they need very high energies to overcome the forces of repulsion, a very high temperature is required for fusion reaction which are sometimes referred to as **thermonuclear reactions**.

At higher temperatures of fusion reactions, all molecules are dissociated into atoms, forming cations and electrons. This state of matter, a highly dense, extremely hot gas consisting of cations and electrons which is known as **plasma**.

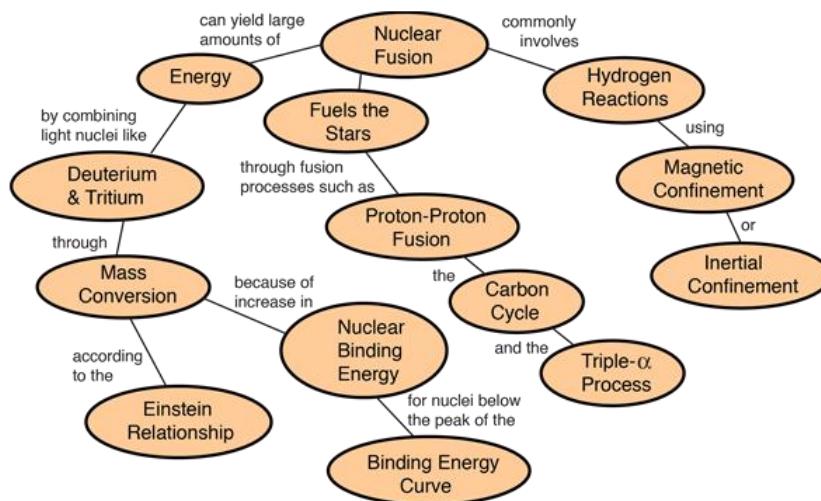
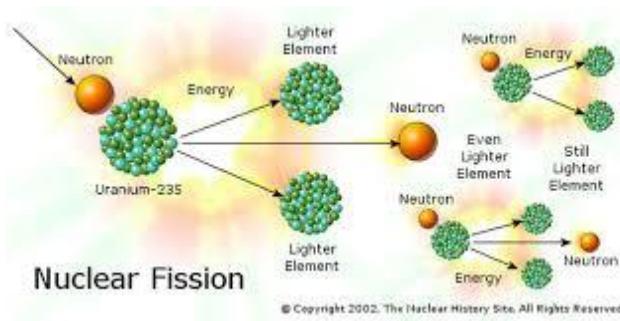
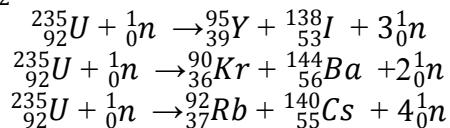


Figure 10.17. Nuclear Fusion Process

10.13. Nuclear Fission



be induced by protons (${}_1^1H$), deuterons (${}_2^2H$) and α (${}_2^4He$). Fissions of given nuclei may occur in many different ways and may produce three sets of products resulting from the slow-neutron-induced fission of ^{235}U :



All the indicated product nuclides (primary-fission-fragments) in the equations are β^- radioactive. Though neutrons are expelled in the fission reactions as shown in the equations, the primary fission products (nuclei in the intermediate range) with too high neutron/proton ratio.

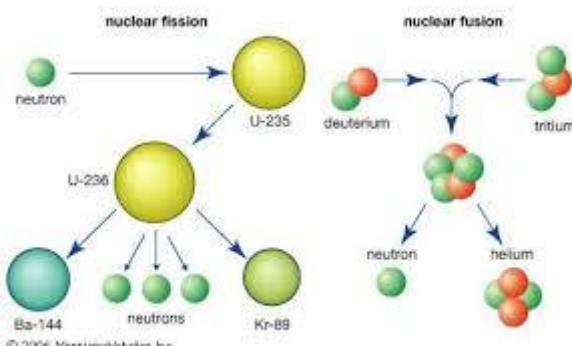


Figure 19.18 Fission and Fusion Reactions

PROGRESS CHECK

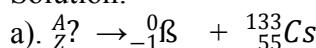
10.1. Write the nuclear equation for the nuclear reaction in which a nuclei undergoes β^- decay and changes to cesium-133.

10.2. Write the equations for the following examples of nuclear decay:

- a). α emission by $^{193}_{83}Bi$
- b). β^- by $^{27}_{12}Mg$
- c). β^+ by $^{68}_{34}Se$
- d). electron capture by $^{71}_{32}Ge$

10.3. Write the nuclear equation for the nuclear reaction in which a nuclei undergoes β^- decay and changes to cesium-133.

Solution:



10.4. Write the balanced equations for the following nuclear reactions:

- a). $^{27}_{13}Al + {}_2^4He \rightarrow {}_0^1n + {}_{Z?}^A$
- b). $^{30}_{15}P \rightarrow {}_{14}^{30}Si + {}_{Z?}^A$
- c). $^{238}_{92}U + {}_0^1n \rightarrow {}_{Z?}^A$
- d). $^{239}_{92}U + {}_{-1}^0\beta \rightarrow {}_{Z?}^A$

10.5. Write the equations for the following induced nuclear reactions:

- a). $^{75}_{33}As(d, 2n)_{Z?}^A$
- b). $^{24}_{12}Mg(d, \alpha)_{Z?}^A$
- c). $^{209}_{83}Bi(p, 8n)_{Z?}^A$
- d). ${}_{Z?}^A(d, p) {}_{33}^{76}As$
- e). ${}_{Z?}^A(\alpha, p) {}_{22}^{48}Ti$

10.5. Sodium-24 ($t_{1/2} = 15h$) is used to study blood circulation. If a patient is injected with an aqueous solution of $^{24}NaCl$ whose activity is $2.5 \times 10^9 \text{ d/s}$, how much of the activity is present in the patient's body and excreted fluids after 4.0 days?

10.6. A sample of $^{35}_{16}S$, a β^- emitter, has an activity of $0.100 \mu\text{Ci}$. In 20.0 days, the activity of the sample has declined to $0.0853 \mu\text{Ci}$. What is the half-life of $^{35}_{16}S$?

10.7. The radioactive nuclide $^{60}_{27}Co$ has a half-life of 5.27 years. Calculate the mass of $^{60}_{27}Co$ that remains from 0.0100g sample of the nuclide, after 1.00 year has elapsed.

10.8. The half-life of $^{100}_{43}Tc$, a β^- emitter, is 15.8 s. a). How many atoms of $^{100}_{43}Tc$ are present in a sample with an activity of $0.200 \mu\text{Ci}$. b). What is the mass of the sample?

10.9. The radioactive nuclide $^{55}_{27}Co$ has a shelf-life of 17.5 hours. What mass $^{55}_{27}Co$ remains from 0.0100g sample after 24 hours?

10.10. A sample of wood from an Egyptian mummy case has a specific activity of 9.41 d/min-g . How old is the case?

10.11. The carbon from the heartwood of a giant sequoia tree gives 11 counts per minute per gram carbon ($^{14}_6C$), whereas the wood from the outer portion of the tree gives 15 counts per minute per gram carbon ($^{14}_6C$). How old is the tree? ($t_{1/2} = 5730$ years).

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Week No.: 11

TOPIC/S: CHEMISTRY OF THE ENVIRONMENT

- 11.1. Earth's Atmosphere
 - 11.1.1. What gases are pollutants in the atmosphere?
- 11.2. Ozone in the Upper Atmosphere
 - 11.2.1. What is UV?
 - 11.2.2. How is Ozone produced in the Atmosphere?
 - 11.2.3. Chlorofluorohydrocarbons (CFCs)
 - 11.2.4. How do CFCs help depleting ozone?
 - 11.2.4.1. What has been done and what can be done to reduce ozone depletion?
- 11.3. The Troposphere
- 11.4. The Ocean
 - 11.4.1. The Hydrosphere
 - 11.4.1.1. Hydrospheric Processes
 - 11.4.1.2. Common Ions Present in Natural Water
 - 11.4.1.2.1. Hard Water
 - 11.4.1.2.2. Temporary vs. Permanent Hard Water
 - 11.4.1.2.2.1. Lime-Soda Softening
 - 11.4.1.2.2.2. Complexation Treatment
 - 11.4.1.2.2.3. Ion Exchange
 - 11.4.1.2.2.4. Pure Water by Ion Exchange
 - 11.4.1.2.2.5. Reverse Osmosis Water Filter System
 - 11.4.2.2.6. Desalination
 - 11.4.2.2.6.1. Environmental Impact of Seawater Desalination
 - 11.4.2.2.6.2. The Production of Brine
 - 11.4.2.2.6.3. The Impact to Marine Life
 - 11.4.2.2.6.4. The Consumption of Energy
 - 11.5. Sulfur dioxide
 - 11.5.1. Environmental Effects
 - 11.5.2. Health effects
 - 11.5.3. Air Quality Standard
 - 11.5.4. Measuring Sulfur Dioxide
 - 11.6. Why Dissolved Oxygen is Important
 - 11.6.1. Environmental Impact
 - 11.6.1.1. Chemical Oxygen Demand (COD)
 - 11.6.1.2. Biological oxygen Demand (BOD)
 - 11.7. Carbon Monoxide
 - 11.7.1. harmful Effects of CO
 - 11.8. Nitrogen Oxides and Photochemical Smog
 - 11.9. Green Chemistry
 - 11.9.1. Basic Principles of Green Chemistry
 - 11.9.1.1. Prevention
 - 11.9.1.2. Maximize “atom energy”
 - 11.9.1.3. Less Hazard

- 11.9.1.4. Safer Chemicals
- 11.9.1.5. Safer Solvents and Auxiliaries
- 11.9.1.6. Design for Energy Efficiency
- 11.9.1.7. Use of Renewable Feed stocks
- 11.9.1.8. Reduce Derivatives
- 11.9.1.9. Catalysis
- 11.9.1.10. Design for Degradation
- 11.9.1.11. Real-Time Analysis for Pollution Prevention
- 11.9.1.12. Inherently Safer Chemistry for Accident Prevention

EXPECTED COMPETENCIES

At the end of the lesson, you must have:

1. identified different gas pollutants in the atmosphere,
2. defined UV,
3. described ozone and ozone production,
4. described how ozone is depleted,
5. described the troposphere, ocean, etc.,
6. described the hydrosphere,
7. described the harmful effects of sulfur dioxide, carbon monoxide, etc.,
8. Explained nitrogen oxides and photochemical smog, and
9. described green chemistry.

CONTENTS

Environmental chemistry is the scientific study of the chemical and biochemical phenomena that occur in natural places. It should not be confused with green chemistry, which seeks to reduce potential pollution at its source. **Environmental chemistry** is the study of **chemical** processes that occur in water, air, terrestrial and living environments, and the effects of human activity on them. It includes topics such as astrochemistry, atmospheric **chemistry**, **environmental** modelling, geochemistry, marine **chemistry** and pollution remediation.

11.1. Earth's Atmosphere

In the 1800s, scientists, including John Dalton, realized that the atmosphere was composed of a variety of gases. By volume, air is made up of approximately 78% nitrogen, 21% oxygen, and 1% argon, with small amounts of additional gases including water vapor and carbon dioxide. While the three major components have remained relatively constant over time and space, the minor components, which also include methane, sulfur dioxide, ozone, and nitrogen oxides, have varied more widely. These minor components are the major contributors to phenomena like weather, the greenhouse effect, and global warming.

In recent years, additional carbon dioxide has helped trap additional heat being radiating off the planet. Carbon dioxide, water vapor, and other greenhouse gases are adept at stopping heat from leaving the atmosphere, causing the Earth to heat up. Some greenhouse gases are beneficial—without them, Earth would be as cold as the moon—but the recent increase in carbon dioxide has upset the precise balance between too cold, too hot, and just right.

The atmosphere is further classified into multiple layers by temperature, which include the thermosphere, the mesosphere, the stratosphere, and the troposphere. Both air pressure and density increase upon approaching the Earth's surface. The layer closest to the Earth, the troposphere, contains most of the water vapor and is where weather occurs. The next layer, the stratosphere, contains an ozone layer that results from the reaction of ionizing solar radiation with oxygen gas; this ozone layer is responsible for the absorption of UV light.

In the recent past, we have damaged our ozone layer by putting chlorofluorocarbons (CFCs) into the atmosphere. The CFCs have damaged ozone, resulting in a hole in the ozone layer. In recent years, CFCs have been banned and the ozone layer hole is shrinking. Farther from the surface, the mesosphere, the thermosphere, and then the exosphere make up the top layers of our atmosphere. Planes typically fly in the stratosphere.

The atmosphere performs a various beneficial functions for the inhabitants of Earth including: absorbing UV radiation, heating the Earth's surface, and buffering temperature fluctuations.

The atmospheric chemistry studies the chemical composition of the natural atmosphere, the way gases, liquids, and solids in the atmosphere interact with each other and with the earth's surface and associated biota, and how human activities may be changing the chemical and physical characteristics of the atmosphere. It is interesting to note that the 1995 Nobel Prize in Chemistry 1995 was awarded to the atmospheric scientists P. Crutzen, M. Molina and F. S. Rowland. For convenience of study, atmospheric scientists divide the atmosphere as if it consists of four layers. The division is mainly due to temperature variations as the altitude increases. The four layers according to the variation of temperature are.

- Ionosphere (Aurora) or Thermosphere
- Mesosphere
- Stratosphere
- Troposphere

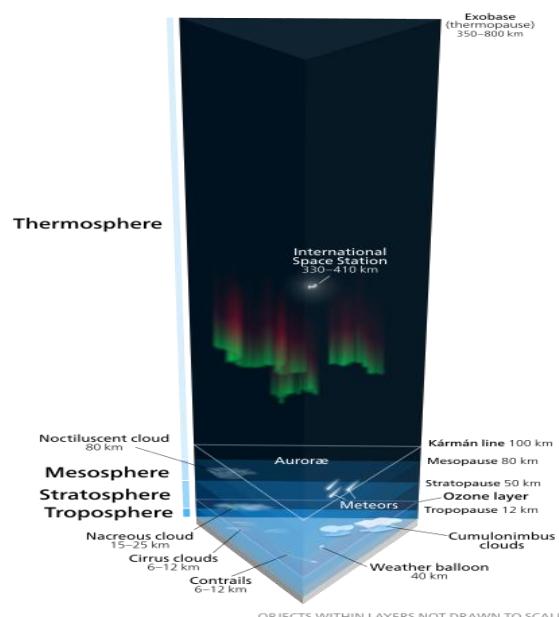
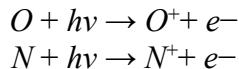


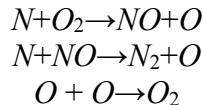
Figure 11.1. Earth's Atmosphere Lower 4 layers of the atmosphere in 3 dimensions as seen diagonally from above the exobase. Layers drawn to scale, objects within the layers are not to scale. Aurorae shown here at the bottom of the thermosphere can actually form at any altitude in this atmospheric layer. Image used with permission from NASA.

Above 100 km is the thermosphere and ionosphere where the temperature increases from 200 K at 100 km to 500 K at 300 km. The temperature goes even higher as the altitude increases. activity as the altitude decrease. In the outer space, most particles consist of single atoms, H, He, and O etc. At lower altitude (200 - 100 km), diatomic molecules N₂, O₂, NO etc are present. The ionosphere is full of electrically charged ions. The UV rays ionizes these gases. The major reactions are:

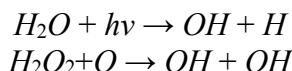
In the ionosphere:



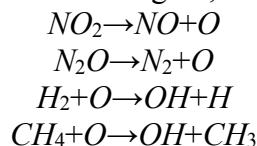
In the neutral thermosphere:



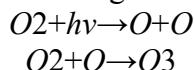
Beyond the neutral thermosphere is the ionosphere and exosphere. These layers are of course interesting for space explorations and environmental concerns and space sciences. The atmosphere in the outer space is more like a plasma than a gas. Below the thermosphere is the mesosphere (100 - 50 km) in which the temperature decreases as the altitude increase. In this region, OH, H, NO, HO₂, O₂, and O₃ are common, and the most prominent chemical reactions are:



Below the mesosphere is the **stratosphere**, in which the temperature increases as the altitude increase from 10 km to 50 km. In this region, the following reactions are common:



Air flow is horizontal in the stratosphere. A thin ozone layer in the upper stratosphere has a high concentration of ozone. This layer is primarily responsible for absorbing the ultraviolet radiation from the sun. The ozone is generated by these reactions:



The troposphere is where all weather takes place; it is the region of rising and falling packets of air. The air pressure at the top of the troposphere is only 10% of that at sea level (0.1 atmospheres). There is a thin buffer zone between the troposphere and the next layer called the tropopause.



Figure 11.2. Space Shuttle Endeavour silhouetted against the atmosphere. The orange layer is the troposphere, the white layer is the stratosphere and the blue layer is the mesosphere. (The shuttle is actually orbiting at an altitude of more than 320 km (200 mi), far above all three layers.). Image used with permission from NASA.

The major components in the region close to the surface of the Earth are N₂ (78%), O₂ (21%), Ar (1%) with variable amounts of H₂O, CO₂, CH₄, NO₂, NO_x, CO, N₂O, and O₃. The ozone concentration in this layer is low, about 8% of the total ozone in the atmosphere is in the troposphere.



Figure 11.3. The Earth's atmosphere: A view of the Earth from space, looking from orbit beyond the exosphere, down through the layers of the thermosphere, mesosphere, and stratosphere, at a thick cloud layer topping the troposphere.

11.1.1. What gases are pollutants in the atmosphere?

From the atmospheric science viewpoint, interactions of all gasses among themselves and their interaction with the environmental elements are of interest. However, for identification purposes, we need to identify the gases produced by man-made process (industry).

Some of the gases due to human activities are:

- Carbon dioxide result from the excess burning of carbon-containing fuel.
- Carbon monoxide produced by automobiles. This odorless and colorless gas is very toxic.
- Ozone produced in the exhaust of internal combustion engine, and the variation of ozone concentration in the stratosphere.
- Nitrogen oxides such as NO, NO₂, N₂O₄; due to the production of NO in the internal combustion engine.
- Methane gas produced due to treatments of large amount of waste.
- Sulfur oxides produced in mining operation and in the combustion of sulfur containing fuel. Sulfur oxide causes the so called *acid rain* problem.
- Chlorofluorocarbons (CFC) are gases used as refrigerant. When disposed into the atmosphere, they cause the ozone concentration to decrease.
- Water vapor is also considered a greenhouse gas, but it is also generated by nature continuously due to radiation from the Sun. Of course, when water vapor condense into a liquid, much energy is released in the exothermal process. Condensation of water vapor causes storms and many of the weather phenomena.

Sample Problem 11.1. If ozone is a beneficial gas in the atmosphere, why is ozone also a gaseous pollutant?

Solution:

Decomposition of ozone releases O, OOH, OH radicals and they are harmful to many living organisms.

11.2. Ozone in the Upper Atmosphere

Most of the ozone in the atmosphere is in the stratosphere of the atmosphere, with about 8% in the lower troposphere. As mentioned there, the ozone is formed due to photo

reaction. The ozone level is measured in Dobson Unit (DU), named after G.M.B. Dobson, who investigated the ozone between 1920 and 1960. One Dobson Unit (DU) is defined to be 0.01 mm thickness of ozone at STP when all the ozone in the air column above an area is collected and spread over the entire area. Thus, 100 DU is 1 mm thick.

11.2.1. What is UV?

In the electromagnetic radiation spectrum, the region beyond the violet (wavelength \sim 400 nanometer nm) invisible to eye detection is called ultraviolet (UV) rays. Its wavelength is shorter than 400 nm.

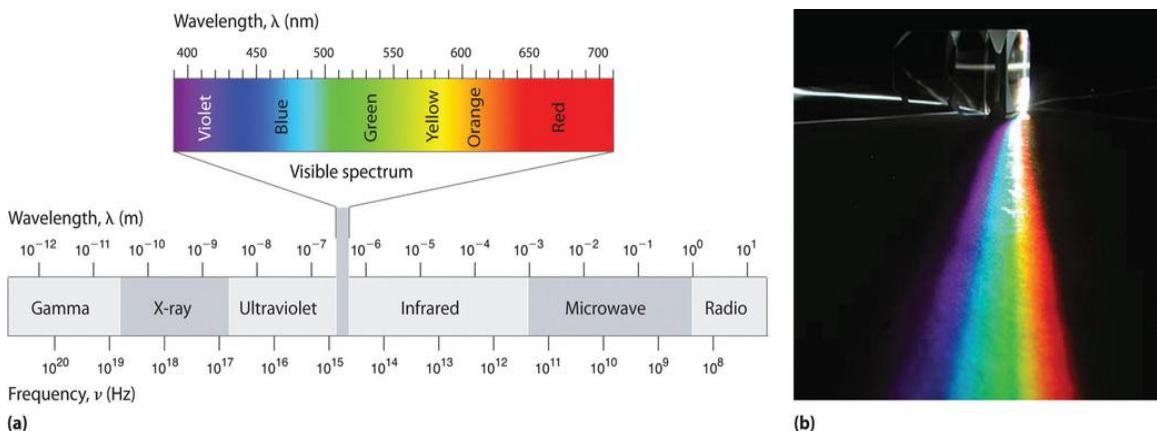


Figure 11.4. (a) This diagram shows the wavelength and frequency ranges of electromagnetic radiation. The visible portion of the electromagnetic spectrum is the narrow region with wavelengths between about 400 and 700 nm. (b) When white light is passed through a prism, it is split into light of different wavelengths, whose colors correspond to the visible spectrum.

UV is divided into three regions:

UV A, wavelength = 400 - 320 nm

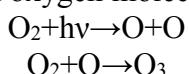
UV B, wavelength = 320 - 280 nm

UV C, wavelength = < 280 nm

Obviously, photons of UV C are the most energetic. UV-A radiation is needed by humans for the synthesis of vitamin-D; however, too much UV-A causes photoaging (toughening of the skin), suppression of the immune system and, to a lesser degree, reddening of the skin, and cataract formation. Ozone strongly absorbs UV B and C, but the absorption decreases as the wavelength increases to 320 nm. Very little UV C reaches the Earth surface due to ozone absorption.

11.2.2. How is Ozone produced in the Atmosphere?

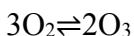
When an oxygen molecule receive a photon ($h\nu$), it dissociates into monoatomic (reactive) atoms. These atoms attack an oxygen molecule to form ozone, O_3 .



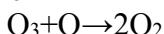
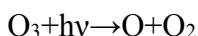
The last reaction requires a third molecule to take away the energy associated with the free radical $O\cdot$ and O_2 , and the reaction can be represented by



The over all reaction between oxygen and ozone formation is:



The absorption of UV B and C leads to the destruction of ozone



A dynamic equilibrium is established in these reactions. The ozone concentration varies due to the amount of radiation received from the sun.

Sample Problem 11.2. The enthalpy of formation of ozone is 142.7 kJ / mol. The bond energy of O₂ is 498 kJ / mol. What is the average O=O bond energy of the bent ozone molecule O=O=O?

Solution:

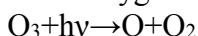
The overall reaction is:



Note that 3 O=O bonds of oxygen are broken, and 4 O-O bonds of ozone are formed. If the bond energy of ozone is E, then

$$E = (3 \times 498 + 286) \text{ kJ} / 4 \text{ mol} = 445 \text{ kJ/mol}$$

The ozone bonds are slightly weaker than the oxygen bonds. The average bond energy is not the bond energy for the removal of one oxygen from ozone.



The techniques used in this calculation is based on the **principle of conservation of energy**.

11.2.3. Chlorofluorohydrocarbons (CFCs)

Chemist Roy J. Plunkett discovered tetrafluoroethylene resin while researching refrigerants at DuPont. Known by its trade name, Teflon, Plunkett's discovery was found to be extremely heat-tolerant and stick-resistant. After ten years of research, Teflon was introduced in 1949. His continued research led to the usage of chlorofluorohydrocarbons known as CFCs or freon as refrigerants.

CFCs are made up of carbon, hydrogen, fluorine, and chlorine. DuPont used a number system to distinguish their product based on three digits. The digits are related to the molecular formulas.

The first digit is the number of carbon atoms minus 1.

The second digit is the number of hydrogen atoms plus 1.

The third digit is the number of fluorine atoms.

For example, CFC (or freon) 123 should have a formula C₂HF₃Cl₂. The number of chlorine atoms can be deduced from the structural formula of saturated carbon chains. CFC's containing only one carbon atom per molecule has only two digits. Freon 12 used for fridge and automobile air conditioners has a formula of CF₂Cl₂. The nontoxic and nonflammable CFCs have been widely used as refrigerants, in aerosol spray, and dry cleaning liquid, foam blowing agents, cleansers for electronic components in the 70s, 80s and early 90s.

In 1973, James Lovelock demonstrated that all the CFCs produced up to that time have not been destroyed, but spread globally throughout the troposphere. (Lovelock's report was later published: J. E. Lovelock, R.J.Maggs, and R.J. Wade, (1974); Nature, **241**, 194) In the article, concentrations of CFCs at some parts per 10¹¹ by volume was measured, and they deducted that with such a concentration, CFCs are not destroyed over the years. In 1974, Mario J. Molina published an article in Nature describing the ozone depletion by CFCs. (see

M.J. Malina and F.S. Rowland, (1974); Nature, **249**, 810) NASA later confirmed that HF was present in the stratosphere, and this compound had no natural source but from the decomposition of CFCs. Molina and Rowland suggested that the chlorine radicals in CFCs catalyze the decomposition of ozone as discussed below.

Sample Problem 11.3. Find the number for CFCl_3 .

Solution:

Let : a be the number of C, b the number of H and c the number of F

$$a = 1 \text{ C atom} - 1 = 0$$

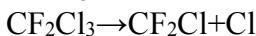
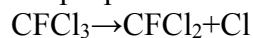
$$b = 0 \text{ H atom} + 1 = 1$$

$$c = 1 \text{ F atom} = 1$$

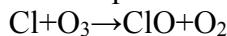
Therefore, the number is CFC-011 or CFC-11

11.2.4. How do CFCs help depleting ozone?

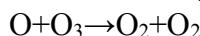
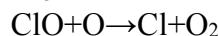
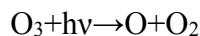
A relatively recent concern is the depletion of ozone, O_3 due to the presence of chlorine in the troposphere, and eventually their migration to the stratosphere. A major source of chlorine is Freons: CFCl_3 (Freon 11), CF_2Cl_2 (Freon 12), $\text{C}_2\text{F}_3\text{Cl}_3$ (Freon 113), $\text{C}_2\text{F}_4\text{Cl}_2$ (Freon 114). Freons decompose in the troposphere. For example,



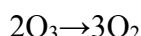
The chlorine atoms catalyze the decomposition of ozone,



and ClO molecules further react with O generated due to photochemical decomposition of ozone:

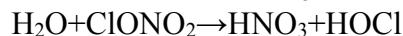
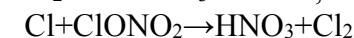


The net result or reaction is



Thus, the use of CFCs is now a world wide concern. In 1987, one hundred and forty nine (149) nations signed the Montreal Protocol. They agreed to reduce the manufacturing of CFCs by half in 1998; they also agree to phase out CFCs.

Ozone depletion in the polar region is different from other regions. The debate of ozone depletion often involves the North and South Poles. In these regions when temperatures drop to 190 K, ice cloud is formed. The ice crystals act as heterogeneous catalyst converting HCl and ClONO_2 into HNO_3 and Cl_2 ,



Both Cl_2 , and HOCl are easily photolyzed to Cl atoms, which catalyze the depletion of ozone. This has just been discussed in the previous section.

11.2.4.1. What has been done and what can be done to reduce ozone depletion?

The U.S. and Canadian governments have banned the use of Freons in aerosol sprays, but their use in air conditioner and cooling machines continue. In order to eliminate Freon in the atmosphere, international concerted effort and determination is required. However, sound and reliable scientific information is required. The banning of CFCs opens a research

opportunity for another invention to find its substitute. Who knows what other problems will the new product bring?

11.3. The Troposphere

A lot of chemistry happens in Earth's atmosphere; there are many different kinds of chemicals in the air. Those chemicals often combine with each other in chemical reactions, making new and different chemicals. This is called "atmospheric chemistry".

Earth's atmosphere has different layers. The lowest layer is called the troposphere. We live in the troposphere. This page explains about atmospheric chemistry in the troposphere.

Most of the gas in our atmosphere is nitrogen. About 4/5ths of the air is nitrogen. What about the other 1/5th? Almost all of it is oxygen, the stuff in the air we need to breathe. There are also very small amounts of a bunch of other chemicals.

Have you heard of greenhouse gases? They are kinds of gases that trap the heat from sunlight in our atmosphere. Earth would be very cold if we didn't have any greenhouse gases. Carbon dioxide and methane are two very important greenhouse gases.

Some of the chemicals in the air come from pollution. When we burn coal in a factory or gasoline in our cars, we make air pollution. Coal and oil have sulfur in them. When they burn, they make chemicals called sulfur oxides. These can turn into sulfuric acid when they mix with water droplets in the air. These droplets of acid can fall to the ground as acid rain. Cars and trucks also give off chemicals called nitrogen oxides. Nitrogen oxides combine with other chemicals to make smog. They also help make nitric acid, which is another acid in acid rain.

Nature also does things to change the chemistry of the troposphere. Volcanoes, lightning, and wildfires all add chemicals to the air or change the ones that are already there. Energy from sunlight can make chemical reactions happen, changing one gas into another. Some chemicals move in cycles between the atmosphere, living creatures, and the oceans. The Carbon Cycle and the Nitrogen Cycles are two important cycles that change the chemistry of the atmosphere.

Table 11.1 This table (below) describes some of the chemicals in the troposphere, and some of the chemical reactions that happen in the air:

| Chemical | Formula | Role in Tropospheric Chemistry |
|-----------------|-------------------------------|--|
| Carbon dioxide | CO ₂ | Carbon dioxide is a kind of greenhouse gas. When we breathe, we take in oxygen and breathe out carbon dioxide. Plants and some kinds of microbes use carbon dioxide during photosynthesis to make food. Burning fuels also puts carbon dioxide into the atmosphere. |
| Carbon monoxide | CO | When things burn, they mostly make carbon dioxide. Sometimes they make carbon monoxide, too. Carbon monoxide is a poisonous gas. Volcanoes and car engines make carbon monoxide. |
| Hydrocarbons | C _x O _y | Hydrocarbons are chemicals made up of hydrogen and carbon atoms. When fuel burns, it puts some hydrocarbons into the air. Hydrocarbons help to make smog, a kind of air pollution. |
| Methane | CH ₄ | Methane is a kind of greenhouse gas. |
| Nitrogen | N ₂ | Most of the gas in Earth's atmosphere is nitrogen. About 4/5ths of the air is nitrogen. The nitrogen cycle explains how nitrogen moves around in the environment. When fuel burns hot, like it does in the engine of a car, nitrogen combines with oxygen to make nitrogen oxides. |
| Nitrogen Oxides | NO & NO ₂ | Nitrogen oxides are a kind of pollution. Burning fuels like gasoline in air makes nitrogen oxides. Most nitrogen oxides come from cars and trucks. They help to make smog. They also mix with water droplets in the air to make nitric acid. Nitric acid is a part of acid rain. |
| Nitric Acid | HNO ₃ | Nitric acid is part of acid rain. Nitric acid forms when nitrogen oxides mix with water droplets in the air. Nitrogen oxides are a kind of pollution that comes from the engines of |

| | | |
|---------------------------|--|---|
| | | cars and trucks. |
| Oxygen & Ozone | O ₂ & O ₃ | About 1/5th of the gas in the atmosphere is oxygen. When you breathe, your body uses the oxygen to keep you alive. Ozone is a special kind of oxygen that has three atoms instead of two. |
| PAN(Peroxyacetyl nitrate) | C ₂ H ₃ O ₅ N | PAN is a kind of air pollution. Smog has PAN in it. PAN forms when nitrogen dioxide, oxygen, and Volatile Organic Compounds (VOCs) get together. |
| Smog | - | Smog is a mixture of smoke and fog. Photochemical smog is a kind of air pollution. It has nitrogen oxides, ozone, VOCs, and PAN in it. |
| Photodissociation | - | When a photon of sunlight breaks apart a molecule. |
| Sulfur Oxides | SO ₂ & SO ₃ | Sulfur dioxide and sulfur trioxide are types of pollution. People make them when we burn coal and oil. Volcanoes also give off sulfur oxides. Sulfur dioxide mixes with water droplets in the air to make sulfuric acid. Sulfuric acid is in acid rain. |
| Sulfuric Acid | H ₂ SO ₄ | Sulfuric acid is in acid rain. Sulfuric acid in the air is made when sulfur dioxide gas mixes with water droplets. The sulfur dioxide gas comes from volcanoes and from coal and oil that people burn for fuel. |

11.4. The Ocean

Water is the most important resource. Without water life is not possible. From a chemical point of view, water, H₂O, is a pure compound, but in reality, you seldom drink, see, touch or use pure water. Water from various sources contains dissolved gases, minerals, organic and inorganic substances.

11.4.1. The Hydrosphere

The total water system surrounding the planet Earth is called the **hydrosphere**. It includes freshwater systems, oceans, atmosphere vapour, and biological waters. The Arctic, Atlantic, Indian, and Pacific oceans cover 71% of the Earth surface, and contain 97% of all water. Less than 1% is fresh water, and 2-3 % is ice caps and glaciers. The Antarctic Ice Sheet is almost the size of North America continent. These waters dominate our weather and climate, directly and indirectly affecting our daily lives. They cover 3.35x10⁸ km². The four oceans have a total volume of 1.35x10⁹ km³.

The sunlight dims by 1/10 for every 75 m in the ocean, and humans barely see light below 500 m. The temperature of almost all of the deep ocean is 4°C (277 K).

The average ocean depth is 4 km, and the deepest point at the Mariana Trench is 10,912 m (35,802 ft), which compares to the height of 8.8 km for Mount Everest.

11.4.1.1. Hydrospheric Processes

Hydrospheric Processes are steps by which water cycles on the planet Earth. These processes include sublimation of ice, evaporation of liquid, transportation of moisture by air, rain, snow, river, lake, and ocean currents. All these processes are related to the physical and chemical properties of water, and many government agencies are set up to study and record phenomena related to them. The study of these processes is called **hydrology**

Among the planets, Earth is the only one in which there are solid, liquid and gaseous waters. These conditions are just right for life, for which water is a vital part. Water is the most abundant substance in the biosphere of Earth. Groundwater is an important part of the water system. When vapor is cooled, clouds and rain develop. Some of the rain percolate through the soil and into the underlying rocks. The water in the rocks is **groundwater**, which moves slowly.

A body of rock, which contains appreciable quantities of water, is called an **aquifer**. Below the **water table**, the aquifer is filled (or saturated) with water. Above the water table is the unsaturated zone. Some regions have two or more water tables. These zones are usually separated by water-impermeable material such as boulder and clay. Groundwater can be brought to the surface by drilling below the water table, and pumped out. The amount of water that can be pumped out depends on the structure of the aquifer. Little water is stored in tight granite layers, but large quantities of water are stored in limestone aquifer layers. In some areas, there are under ground rivers.

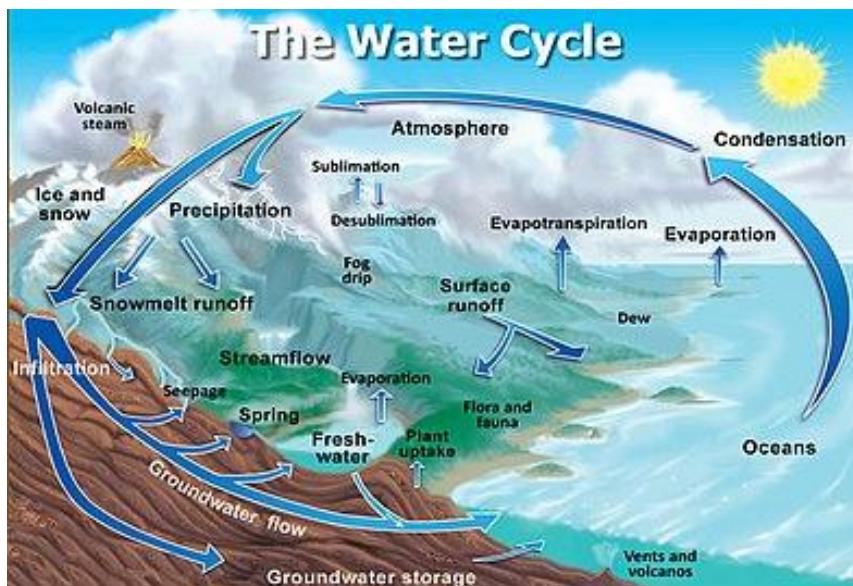


Figure 11.5. The Water Cycle (Hydrospheric Process)

Table 11.2. Ions in Seawater

| Species | Cl^- | Na^+ | SO_4^{2-} | Mg^{2+} | Ca^{2+} | K^+ | HCO_3^- | Br^- | Sr^{2+} | BO_4^{3-} | F^- | H_4SiO_4 | H^+ |
|---------|---------------|---------------|--------------------|------------------|------------------|--------------|------------------|---------------|------------------|--------------------|--------------|--------------------------|--------------|
| mg/Kg | 10,760 | 2,710 | 2,710 | 1,290 | 411 | 399 | 142 | 67 | 8 | 4.5 | 1.3 | 0.5-10 | $10^{-8.35}$ |

11.4.1.2. Common Ions Present in Natural Water

Hydrology is also the study of how solids and solute interact in, and with, water. In this link, the compositions of seawater, composition of the atmosphere, compositions of rain and snow, and compositions of river waters and lake waters are given in details. Table 18.5.118.5.1 list the major ions present in seawater. The composition does vary, depending on region, depth, latitude, and water temperature. Waters at the river mouths contain less salt. If the ions are utilized by living organism, its contents vary according to the populations of organisms.

Dust particles and ions present in the air are nucleation center of water drops. Thus, waters from rain and snow also contain such ions: Ca^{2+} , Mg^{2+} , Na^+ , K^+ , NH_4^+ . These cations are balanced by anions, HCO_3^- , SO_4^{2-} , NO_2^- , Cl^- , and NO_3^- . The pH of rain is between 5.5 and 5.6. Rain and snow waters eventually become river or lake waters. When the rain or snow waters fall, they interact with vegetation, top soil, bed rock, river bed and lake bed, dissolving whatever is soluble. Bacteria, algae, and water insects also thrive. Solubilities of inorganic salts are governed by the kinetics and equilibria of dissolution. The most common ions in lake and river waters are the same as those present in rainwater, but at higher concentrations.

The pH of these waters depends on the river bed and lake bed. Natural waters contain dissolved minerals. Waters containing Ca^{2+} and Mg^{2+} ions are usually called **hard water**.

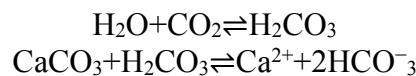
11.4.1.2.1. Hard Water

Minerals usually dissolve in natural water bodies such as lakes, rivers, springs, and underground waterways (ground waters). Calcium carbonate, CaCO_3 , is one of the most common inorganic compounds in the Earth crust. It is the ingredient for both calcite and aragonite. These two minerals have different crystal structures and appearance. This photograph shows crystals of typical Calcite.

Calcium-carbonate minerals dissolve in water, with a solubility product as shown below.



From the solubility product, we can (see example 1) evaluate the molar solubility to be $7.1 \times 10^{-5} \text{ M}$ or 7.1 mg/L (7.1 ppm of CaCO_3 in water). The solubility increases as the pH decrease (increase acidity). This is compounded when the water is saturated with carbon dioxide, CO_2 . Saturated CO_2 solution contains carbonic acid, which help the dissolution due to the reaction:



Because of these reactions, some natural waters contain more than 300 ppm calcium carbonates or its equivalents.

The carbon dioxide in natural water creates an interesting phenomenon. Rainwater is saturated with CO_2 , and it dissolves limestones. When CO_2 is lost due to temperature changes or escaping from water drops, the reverse reaction takes place. The solid formed, however, may be a less stable phase called aragonite, which has the same chemical formula as, but a different crystal structure than that of calcite.

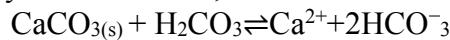
The rain dissolves calcium carbonate by the two reactions shown above. The water carries the ions with it, sips through the crack of the rocks. When it reached the ceiling of a cave, the drop dangles there for a long time before fallen. During this time, the carbon dioxide escapes and the pH of the water increases. Calcium carbonate crystals begin to appear. Calcite, aragonite, stalactite, and stalagmite are four common solids found in the formation of caves.

Natural waters contain metal ions. Water containing calcium, magnesium and their counter anions are called **hard waters**. Hard waters need to be treated for the following applications.

- Heat transfer carrier in boilers and in cooling systems
- Solvents and reagents in industrial chemical applications
- Domestic water for washing and cleaning

11.4.1.2.2. Temporary vs. Permanent Hard Water

Due to the reversibility of the reaction,

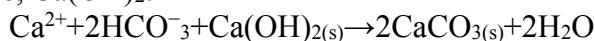


water containing Ca^{2+} , Mg^{2+} and CO_3^{2-} ions is called **temporary hard water**, because the hardness can be removed by boiling. Boiling drives the reverse reaction, causing deposit in pipes and scales in boilers. The deposits lower the efficiency of heat transfer in boilers, and diminish flow rates of water in pipes. Thus, temporary hard water has to be softened before it enters the boiler, hot-water tank, or a cooling system. The amount of metal ions that can be removed by boiling is called **temporary hardness**

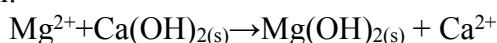
After boiling, metal ions remain due to presence of chloride ions, sulfate ions, nitrate ions, and a rather high solubility of $MgCO_3$. Amount of metal ions that can not be removed by boiling is called **permanent hardness**. **Total hardness** is the sum of temporary hardness and permanent hardness. Hardness is often expressed as equivalence of amount of calcium ions in the solution. Thus, water conditioning is an important topic. The value of water treatment market has been estimated to be worth \$30 billion.

11.4.1.2.2.1. Lime-Soda Softening

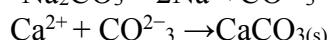
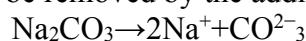
Lime-soda softening is the removal of temporary hardness by adding a calculated amount of hydrated lime, $Ca(OH)_2$:



Adding more lime causes the pH of water to increase, and as a result, magnesium ions are removed by the reaction:



The extra calcium ions can be removed by the addition of sodium carbonate.



In this treatment, the amount of $Ca(OH)_3$ required is equivalent to the temporary hardness plus the magnesium hardness. The amount of sodium carbonate required is equivalent to the permanent hardness. Thus, lime-soda softening is effective if both the temporary and total hardness have been determined. The sodium ion will remain in the water after the treatment. The pH of the water is also rather high depending on the amount of lime and sodium carbonates used.

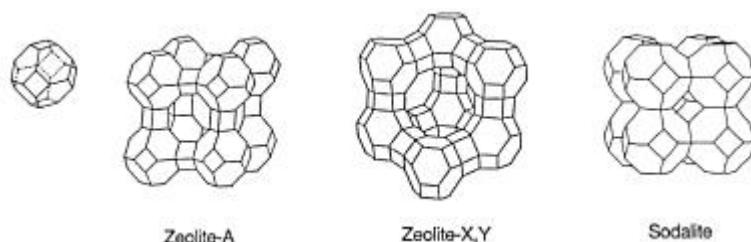
11.4.1.2.2.2. Complexation Treatment

Addition of complexing reagent to form soluble complexes with Ca^{2+} and Mg^{2+} prevents the formation of solid. One of the complexing agents is sodium triphosphate Na_3PO_4 , which is marketed as Calgon, etc. The phosphate is the complexing agent. Other complexing agents such as Na_2H_2EDTA can also be used, but the complexing agent $EDTA^{4-}$ forms strong complexes with transition metals. This causes corrosion problem, unless the pipes of the system are made of stainless steel.

11.4.1.2.2.3. Ion Exchange

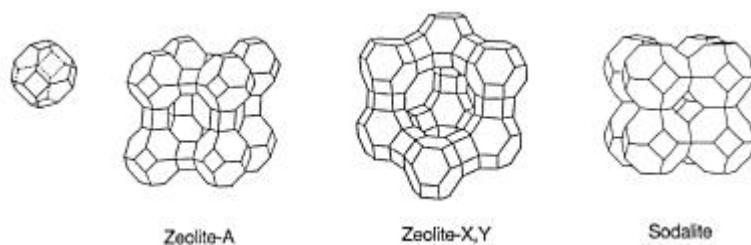
Today, most water softeners are using zeolites and employing ion exchange technique to soften hard water. Zeolites are a group of hydrated crystalline aluminosilicates found in certain volcanic rocks. The tetrahedrally coordinated aluminum and silicon atoms form AlO_4 and SiO_4 tetrahedral groups. They interconnect to each other sharing oxygen atoms forming cage-type structures as shown on the right. This diagram and the next structural diagram are taken from an introduction to zeolites. There are many kinds of zeolites, some newly synthesized.

Whatever kind, the crystal structure of zeolites contains large cages. The cages are connected to each other forming a framework with many cavities and channels. Both positive and negative ions can be trapped in these cavities and channels as shown below.



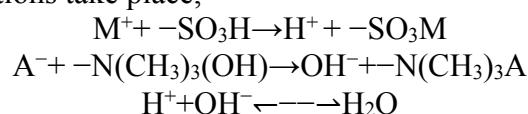
For each oxygen that is not shared in the AlO_4 and SiO_4 tetrahedral groups, a negative charge is left on the group. These negative charges are balanced by trapping alkali metal and alkaline earth metal ions. When more cations are trapped, hydroxide and chloride ions will remain in the cavities and channels of the zeolites.

To prepare a zeolite for water treatment, they are soaked in concentrated NaCl solution. The cavities trap as many sodium ions as they can accommodate. After the treatment, the zeolite is designated as Na-zeolite. Then the salt solution is drained, and the zeolite is washed with water to eliminate the extra salt. When hard water flow through them, calcium and magnesium ions will be trapped by the Na-zeolite. For every Ca^{2+} or Mg^{2+} trapped, two Na^+ ions are released. The treated water contains a rather high concentration of Na^+ ions, but low concentrations of Mg^{2+} and Ca^{2+} . Thus, zeolite ion exchange convert hard water into soft water.



11.4.1.2.2.4. Pure Water by Ion Exchange

In most cases, the resins are polystyrene with functional $-\text{SO}_3\text{H}$ groups attached to the polymer chain for cation exchange resin, and with functional group $-\text{N}(\text{CH}_3)_3^+$ attached to the chain for anion exchange resin. To prepare the resin for making *pure or deionized water*, the cation resin is regenerated with HCl so that the groups are really $-\text{SO}_3\text{H}$. The anion resin is regenerated with NaOH , so that the functional groups are $-\text{N}(\text{CH}_3)_3(\text{OH})$. When water containing any metal ion M^+ and anion A^- passes through the ion exchange resins in two stages, the following reactions take place,



Thus, ion exchange provides *pure water* to meet laboratory requirement.

11.4.1.2.2.5. Reverse Osmosis Water Filter System

This method can also be used to prepare water for domestic and laboratory applications.

Reverse Osmosis water purification process is a simple and straightforward water filtration process. It is accomplished by water pressure pushing tap water through a semipermeable membrane to remove impurities from water. This is a process in which dissolved inorganic solids (such as salts) are removed from a solution (such as water).

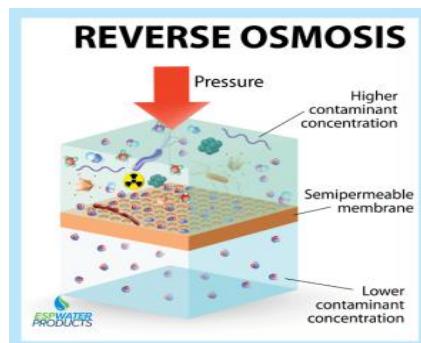


Figure 11.6. The Reverse Osmosis Process (Courtesy of ESP Water Products)

11.4.2.2.6. Desalination

Desalination is defined as process by which excess salts and minerals from water are removed (or) the chemical process of changing seawater into potable water. These processes may be used for municipal, industrial or any commercial uses.

In major desalination methods the feed water is treated and two streams of water are obtained:

- Treated potable fresh water that has less amounts of salt and minerals(treated water or product water)
- Concentrate or brine that has salt and mineral concentrations higher than that of original feed water or saltwater.

Salt water or feed water sources may include sea water, brackish, wells, surface (rivers and streams), wastewater, and industrial feed and process waters. With advancements in technology, desalination processes are becoming cost effective compared to other methods of producing usable water to meet the growing demands. The water that is obtained after desalination should be re-mineralized to be fit for human consumption. The concentrated brine obtained in desalination process must be disposed of in a proper manner back to the sea.

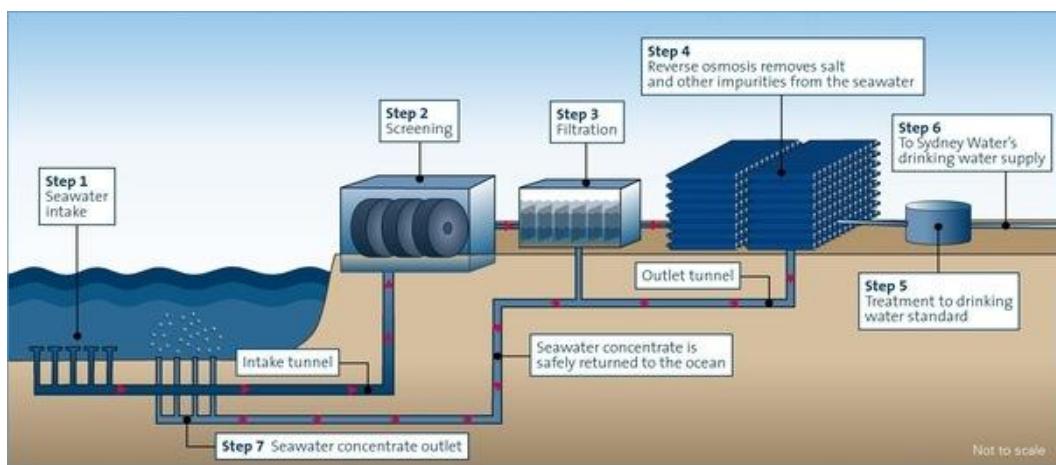


Figure 11.7. Desalination Process

11.4.2.2.6.1. Environmental Impact of Seawater Desalination

Desalination is a process that removes salt and minerals from seawater and turns it into a potable resource. It is extremely helpful in areas experiencing rising water demands due to water scarcity, droughts, growing populations and increased water consumption. With the ocean covering most of the Earth's surface, seawater provides a sustainable, long-term solution to a problem that won't soon dissipate.

By 2015, 18,000 desalination plants had cropped up worldwide, producing 22,870 million gallons of fresh water per day. Experts believe desalination, coupled with future advancements in technology, could be the key to establishing drought-proof communities worldwide.

A clean source of water is still a major concern in many places around the world. However, the process of desalination comes with its own environmental risks. Desalination's role in the future of sustainability will depend on how these risks are addressed and adapted.

11.4.2.2.6.2. The Production of Brine

During the desalination process, half of the collected water will end up as fresh water. The remaining half will be a highly concentrated brine containing a mixture of toxic chemicals. Research shows that desalination plants produce 141.5 million cubic meters of



brine each day, compared to 95 million cubic meters of fresh water. Disposal of this brine can be costly and, if tossed back into the ocean, can be deadly to marine life. But this minor setback could lead to new economic opportunity. Briny discharge is often a source of precious minerals and elements like salt and uranium. Uranium can be resold to reduce overall operating costs and salt can be made commercially available as a de-icing agent. Experts believe this financial benefit could be enough incentive for plants to turn to extraction.

The amount of brine generated can also be reduced through more efficient desalination processes. A modern kind of membrane technology called reverse osmosis is cheaper, requires less energy and produces less brine. Sustainable desalination practices will depend on plants switching over from outdated methods, such as thermal desalination, which sucks in seawater, heats it up to a vapor and then pushes the remaining brine back out to sea.

11.4.2.2.6.3. The Impact to Marine Life

Another concern in the desalination industry is impingement and entrainment. During the intake process, when water from the ocean is sucked in, marine life like fish and crabs can get sucked in and die against the intake screen, called **impingement**. During the treatment process, smaller organisms like fish eggs and plankton can also get sucked in and killed, referred to as **entrainment**.

One way to reduce this threat is to switch from a surface to a subsurface intake process. This means extracting water from beneath the ocean floor instead of on top, where sand can act as a natural filter to protect marine life. This natural filter also reduces the need

for chemicals and energy consumption during the treatment process, which can significantly cut costs.

A subsurface intake process isn't the only solution available to protect marine life. Experts have also found ways to adapt screen openings to incorporate a finer mesh with less space for organisms to enter the intake. Another option is the lower the through-screen velocity. Impingement occurs when the through-screen velocity is so high that crabs and fish are unable to move away when caught. The EPA (Environmental Protection Agency) has determined a velocity lower than or equal to 0.5 feet per second can effectively address marine impacts.

11.4.2.2.6.4. The Consumption of Energy

Energy use is a concern in any industry, and desalination is no different. Worldwide, desalination plants consume more than 200 million kilowatt-hours of energy per day. Energy costs make up about 55% of a desalination plant's operating costs, making them especially vulnerable to price increases. In comparison, a traditional drinking water treatment plant consumes less than 1 kilowatt-hour per cubic meter. Eighty-five percent of Americans support increasing federal investment to rebuild water infrastructure, indicating how we get our water is of high importance to today's consumers.

Desalination plants that adopt the reverse osmosis process — which also produces the least amount of brine — see a major decrease in energy usage, down to three to 10 kilowatt-hours per cubic meter. But researchers are still looking for cheaper and more eco-friendly ways to treat seawater. One method being tested is forward osmosis, which uses a solution of salt and gases to create a pressure difference. Experts say this can lengthen the lifespan of reverse osmosis membranes and reduce the need for disinfectants during treatment.

Solar is also being considered as a solution to high energy consumption. Experts are using the sustainable form of energy as a way to improve the thermal desalination process. The desired outcome is a more efficient water treatment method that requires less startup and integration capital.

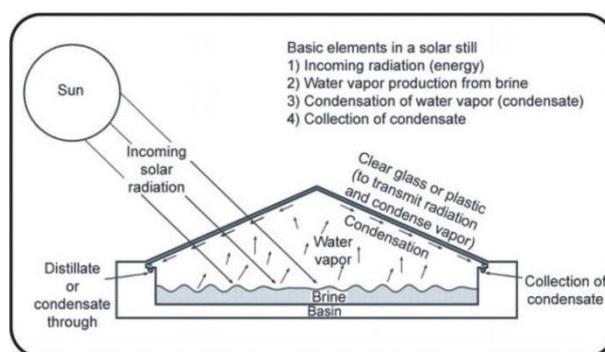


Figure 11.8. Solar Desalination System

11.5. Sulfur dioxide

Sulfur dioxide (SO_2) is a colorless gas with a sharp, irritating odor. It is produced by burning fossil fuels and by the smelting of mineral ores that contain sulfur.

Erupting volcanoes can be a significant natural source of sulfur dioxide emissions.

11.5.1. Environmental Effects

When sulfur dioxide combines with water and air, it forms sulfuric acid, which is the main component of acid rain. Acid rain can:

- cause deforestation
- acidify waterways to the detriment of aquatic life
- corrode building materials and paints.

In areas where there are heavy industries, where the potential for forming acid rain from sulfur dioxide emissions is higher. Weather conditions and low sulfur content of fuels reduce the potential for acid rain.

11.5.2. Health effects

Sulfur dioxide affects the respiratory system, particularly lung function, and can irritate the eyes.

Sulfur dioxide irritates the respiratory tract and increases the risk of tract infections. It causes coughing, mucus secretion and aggravates conditions such as asthma and chronic bronchitis.

11.5.3. Air Quality Standard

The recommended air quality standards for sulfur dioxide are:

- 0.20 parts per million (ppm) for a 1-hour exposure period
- 0.08ppm for a 24-hour exposure period
- 0.02ppm for an annual exposure period.

These standards are designed to protect sensitive individuals, such as children and asthmatics.

Significant concentrations of sulfur dioxide are only measured in near large industrial sources.

11.5.4. Measuring Sulfur Dioxide

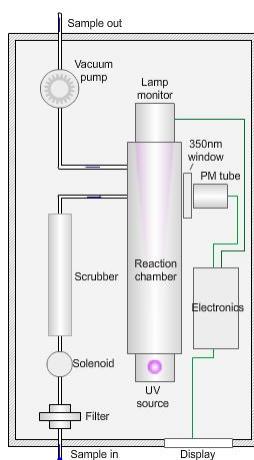


Figure 11.9. Sulfur Analyzer

The sample (shown by the path of the blue dot) is drawn into the analyser by means of the vacuum pump, firstly through a filter to remove particles, and then through a scrubber to remove interfering gases, such as hydrocarbons.

The scrubbed sample passes into a reaction chamber where it is irradiated with ultraviolet (UV) light at 214nm (nanometres) generated by a zinc discharge lamp and a UV bandpass filter.

Sulfur dioxide absorbs UV radiation at wavelengths between 200nm and 240nm. Emission of fluorescence (light-producing) photons at higher wavelengths (around 350nm) follows this absorption of UV radiation by the molecule.

This fluorescence is measured perpendicular to the beam using a photomultiplier (PM) tube and the signal converted to a concentration value.

The measured fluorescence is directly proportional to the concentration of sulfur dioxide in the sample.

11.6. Why Dissolved Oxygen is Important

Dissolved oxygen analysis measures the amount of gaseous oxygen (O_2) dissolved in an aqueous solution. Oxygen gets into water by diffusion from the surrounding air, by aeration (rapid movement), and as a waste product of photosynthesis.

When performing the dissolved oxygen test, only grab samples should be used, and the analysis should be performed immediately. Therefore, this is a field test that should be performed on site.

11.6.1. Environmental Impact

Total dissolved gas concentrations in water should not exceed 110 percent. Concentrations above this level can be harmful to aquatic life. Fish in waters containing excessive dissolved gases may suffer from "gas bubble disease"; however, this is a very rare occurrence. The bubbles or emboli block the flow of blood through blood vessels causing death. External bubbles (emphysema) can also occur and be seen on fins, on skin and on other tissue. Aquatic invertebrates are also affected by gas bubble disease but at levels higher than those lethal to fish.

Adequate dissolved oxygen is necessary for good water quality. Oxygen is a necessary element to all forms of life. Aerobic bacteria consume dissolved oxygen in order to oxidize organic materials meeting their energy requirements. **Biodegradable** materials are organic materials that are oxidized by bacteria. These bacteria need dissolved oxygen.

Natural stream purification processes require adequate oxygen levels in order to provide for aerobic life forms. As dissolved oxygen levels in water drop below 5.0 mg/l, aquatic life is put under stress. The lower the concentration, the greater the stress. Oxygen levels that remain below 1-2 mg/l for a few hours can result in large fish kills.

11.6.1.1. Chemical Oxygen Demand (COD)

The **chemical oxygen demand** (COD) is a measure of water and wastewater quality. The COD test is often used to monitor water treatment plant efficiency. This test is based on the fact that a strong oxidizing agent, under acidic conditions, can fully oxidize almost any organic compound to carbon dioxide. The COD is the amount of oxygen consumed to chemically oxidize organic water contaminants to inorganic end products.

The COD is often measured using a strong oxidant (e.g. potassium dichromate, potassium iodate, potassium permanganate) under acidic conditions. A known excess amount of the oxidant is added to the sample. Once oxidation is complete, the concentration of organics in the sample is calculated by measuring the amount of oxidant remaining in the

solution. This is usually done by titration, using an indicator solution. COD is expressed in mg/L, which indicates the mass of oxygen consumed per liter of solution.

11.6.1.2. Biological oxygen Demand (BOD)

Biochemical oxygen demand, or BOD, measures the amount of oxygen consumed by microorganisms in decomposing organic matter in stream water. BOD also measures the chemical oxidation of inorganic matter (i.e., the extraction of oxygen from water via chemical reaction). A test is used to measure the amount of oxygen consumed by these organisms during a specified period of time (usually 5 days at 20°C). The rate of oxygen consumption in a stream is affected by a number of variables: temperature, pH, the presence of certain kinds of microorganisms, and the type of organic and inorganic material in the water.

BOD directly affects the amount of dissolved oxygen in rivers and streams. The greater the BOD, the more rapidly oxygen is depleted in the stream. This means less oxygen is available to higher forms of aquatic life. The consequences of high BOD are the same as those for low dissolved oxygen: aquatic organisms become stressed, suffocate, and die. Sources of BOD include leaves and woody debris; dead plants and animals; animal manure; effluents from pulp and paper mills, wastewater treatment plants, feedlots, and food-processing plants; failing septic systems; and urban storm water runoff.

Table 11.3. BOD vs COD

| | |
|---|---|
| BOD is the amount of oxygen consumed by bacteria while decomposing organic matter under aerobic conditions. | COD is the amount of oxygen required for the oxidation of total organic matter in water |
| Biological oxidation process. | Chemical oxidation process. |
| Determined by incubating a sealed water sample under specific temperature for 5 days and measuring the loss of oxygen from the beginning of the test. | Determined by incubating a closed water sample with a strong oxidant like potassium dichromate in combination with boiling sulfuric acid under a specific temperature for a specified period. |
| Five days to take the examination. | Can be taken for a few days. |
| Permissible limit is 30mg/L | Permissible limit is 250 to 500 ppm |
| Value is lower than COD value. | Always greater than the BOD value. |
| Capable of oxidizing waste of any kind in the water. | Capable of degrading industrial sewage, but does not measure oxygen consumption of acetate. |

11.7. Carbon Monoxide

CO is a colorless, odorless gas that can be harmful when inhaled in large amounts. CO is released when something is burned. The greatest sources of CO to outdoor air are cars, trucks and other vehicles or machinery that burn fossil fuels. A variety of items in your home such as unvented kerosene and gas space heaters, leaking chimneys and furnaces, and gas stoves also release CO and can affect air quality indoors.

11.7.1. Harmful Effects of CO

Breathing air with a high concentration of CO reduces the amount of oxygen that can be transported in the blood stream to critical organs like the heart and brain.

At very high levels, which are possible indoors or in other enclosed environments, CO can cause dizziness, confusion, unconsciousness and death.

Very high levels of CO are not likely to occur outdoors. However, when CO levels are elevated outdoors, they can be of particular concern for people with some types of heart disease. These people already have a reduced ability for getting oxygenated blood to their hearts in situations where the heart needs more oxygen than usual. They are especially vulnerable to the effects of CO when exercising or under increased stress. In these situations, short-term exposure to elevated CO may result in reduced oxygen to the heart accompanied by chest pain also known as **angina**.

11.8. Nitrogen Oxides and Photochemical Smog

Photochemical smog is a type of air pollution due to the reaction of solar radiation with airborne pollutant mixtures of nitrogen oxides (NO_x) and volatile organic compounds (hydrocarbons). Smog is a byproduct of modern industrialization. Due to industry and the number of motor vehicles, this is more of a problem in large cities that have a warm, sunny and dry climate.

The components of photochemical smog were established during the 1950s. This type of air pollution is formed through the reaction of solar radiation with airborne pollutants like nitrogen oxides and volatile organic compounds. These compounds, which are called primary pollutants, are often introduced into the atmosphere through automobile emissions and industrial processes. Ultraviolet light can split nitrogen dioxide into nitric oxide and monatomic oxygen; this monatomic oxygen can then react with oxygen gas to form ozone. Products like ozone, aldehydes, and peroxyacetyl nitrates are called secondary pollutants. The mixture of these primary and secondary pollutants forms photochemical smog.

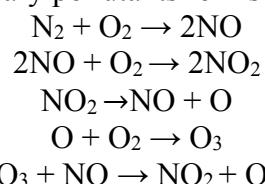


Figure 11.10. Smog in New York City Photochemical smog is composed of primary and secondary pollutants. Primary pollutants include nitrogen oxides and volatile organic compounds as a result of industrial processes, while secondary pollutants are created through the reaction of primary pollutants with ultraviolet light.

11.9. Green Chemistry

Green chemistry, also called sustainable chemistry, is an area of chemistry and chemical engineering focused on the design of products and processes that minimize the use and generation of hazardous substances. Whereas environmental chemistry focuses on the effects of polluting chemicals on nature, green chemistry focuses on technological approaches to preventing pollution and reducing consumption of nonrenewable resources.

Green chemistry overlaps with all subdisciplines of chemistry but with a particular focus on chemical synthesis, process chemistry, and chemical engineering, in industrial applications. To a lesser extent, the principles of green chemistry also affect laboratory practices. The overarching goals of green chemistry—namely, more resource-efficient and inherently safer design of molecules, materials, products, and processes—can be pursued in a wide range of contexts.

New chemistry is required to improve the economics of chemical manufacturing and to enhance the environmental protection. The green chemistry concept presents an attractive technology to chemists, researchers, and industrialists for innovative chemistry research and applications.

Primarily, green chemistry is characterized as reduction of the environmental damage accompanied by the production of materials and respective minimization and proper disposal of wastes generated during different chemical processes. According to another definition, green chemistry is a new technique devoted to the synthesis, processing, and application of chemical materials in such manner as to minimize hazards to humankind and the environment.

Numerous new terms have been introduced associated with the concept of “green chemistry,” such as “eco-efficiency,” “sustainable chemistry,” “atom efficiency” or “atom economy,” “process intensification and integration,” “inherent safety,” “product life cycle analysis,” “ionic liquids,” “alternate feedstocks,” and “renewable energy sources.”

Hence, there is an essential need to improve the synthetic and engineering chemistry either by environmental friendly starting materials or by properly designing novel synthesis routes that reduce the use and generation of toxic substances by using modern energy sources.

11.9.1. Basic Principles of Green Chemistry

Green chemistry is the approach in chemical sciences that efficiently uses renewable raw materials, eliminating waste and avoiding the use of toxic and hazardous reagents and solvents in the manufacture and application of chemical products. Green chemistry takes into account the environmental impact and seeks to prevent or lessen that impact through several key principles outlined below.

Here are the **12 key principles** of green chemistry as formulated by P.T. Anastas and J.C. Warner, in *Green Chemistry: Theory and Practice*, 1998.

11.9.1.1. Prevention

Better to prevent wastes than to treat them after.

This statement is one of the most popular guidelines in process optimization; it describes the ability of chemists to redesign chemical transformations in order to minimize the generation of hazardous waste as an important step toward pollution prevention. By preventing waste generation, the hazards associated with waste storage, transportation, and treatment could be minimized.

This principle is easy to understand and easy to apply, and examples from both industry and academia have proven its significance, relevance, and feasibility. This pillar of green chemistry is still valid; however, we have to conceive it in a broader context, switching from a restricted interpretation of waste based on its quantity to a universal approach to deal

with the topic “waste”: (1) We have to take waste’s multidimensional nature into account. (2) We need to move from a “quantity of waste per quantity of product” principle toward a principle addressing the “quantity of waste generated per function provided by the product.” In this context, we have to aim at making both quality and functionality of products superior. (3) Considering the entire life cycle of a product, we have to address the fact that not only the production process itself generates waste but, moreover, “end-of-life waste” accrues after the product’s life span or its consumption. This encompasses firstly the conversion of such materials up to now considered as waste into valuable products and, secondly, their recyclability.

Generally, moving toward “zero-waste production” and “waste prevention” encompasses the modernization of industrial processes through clean production techniques. These techniques aim at the reduction of gaseous emissions, effluents, solid residues, and noise generation; generally, they are developed to contribute to the protection of climate and environment [2]. However, the most auspicious strategy to prevent waste generation would simply be not producing the desired product. In most scenarios, this will not be practicable; however, it might be reasonable to instead produce completely novel products, which display higher quality and longer durability. Lower quantities of such novel, superior products are sufficient to fulfill a desired function. An alternative approach is to avoid that the product can be transformed into precarious waste, e.g., by making plastics accessible toward biodegradation or by a priori switching toward biodegradable plastic instead of highly recalcitrant petrochemical plastics. According to these ideas, we need to fundamentally reconsider our understanding of waste as hazardous material that needs to be disposed by enhancing the status of waste to a valued resource, which can act as starting material for generation of new products.

11.9.1.2. Maximize “atom economy”

Design synthetic methods to maximize incorporation of all material used into final product.

Atom economy is a concept developed in the early 1990s to evaluate the efficacy of chemical conversions on an element-by-element basis [4]. In analogy to well-established yield calculations, the concept of “atom economy” is based on the ratio of the entire mass of atoms in the target product to the entire mass of atoms in the starting materials. One option to reduce waste generation is to plan such chemical transformations, which maximize the integration of all materials used in the process into the final product, resulting in a number of wasted atoms as low as possible. Hence, selecting such chemical conversion routes, which incorporate the major share of starting materials into desired products, displays higher efficiency and contributes to waste reduction. This concept is nowadays widely implemented in new routes to generate various organic compounds, e.g., such substances that are used in the biomedical and pharmaceutical field.

One factor that is greatly speeding the incorporation of pollution prevention into industrial manufacturing processes is the development of green chemistry. According to an alternative definition, chemical synthesis methods should be designed in such a way to maximize the incorporation of different potentially hazardous materials, such as spinning precarious waste with cement and sand to produce improved paste used in construction applications [8, 9] or to incorporate radioactive wastes as immobilizing material to produce a safe stabilized form of waste. In a similar vein, combining recycled poly(ethylene terephthalate) (PET) waste with cement paste displays a viable strategy for immobilization of hazardous wastes, e.g., radioactive borates.

11.9.1.3. Less Hazard

Design less hazardous chemical synthesis.

In synthetic organic chemistry, effecting a successful chemical transformation in a new way or with a new molecule or in a new order is what matters regarding the principles of green chemistry. Various researchers have clearly demonstrated the direct relation of toxicity and the associated hazards and risks allied with chemical reactions to the matrix of matter present in the reaction vessel. Generally, the holistic toxicity spectrum of products or processes, together with most other sustainability and green chemistry criteria, is highly impacted by the chemistry behind a process and the transformation contributing to a chemical synthesis chain. An exception is identified in such cases where a molecule is produced by purpose, which is designed to display toxicity and/or biologically activity. For example, this scenario is found in the case of various molecules synthesized for pharmaceutical or agricultural applications; such compounds exhibit toxicity and/or impact living organisms.

Selection of compounds and materials to be used to increase the efficacy of chemical transformations is a pivotal point in process development; chemists should dedicate increased attention to the decision on which materials to be put into reaction vessels. It is simple to disregard all the other materials and to dedicate all efforts exclusively to the chemosynthetic pathway, which provides us with the desired product. However, discounting all the other matter present in a production process ultimately results in a high price to be payed, and we finally have to get rid of this scenario. Sometimes, chemists actually produce hazardous molecules, and, therefore, the subsequent principle is dedicated to the design of molecules which are intrinsically safer in their nature

11.9.1.4. Safer Chemicals

Design safer chemicals and products.

Chemical products should be designed to achieve their desired function with at the same time minimizing their toxicity. New products can be designed that are inherently safer, while highly effective for the target application. For example, the direct incorporation of radioactive spent liquid scintillation waste into cement combined with clay materials is considered an added value in the immobilization of the hazardous organic wastes in very cheap materials and natural clay to produce a safe stabilized product easy for handling, transformation, and disposal.

11.9.1.5. Safer Solvents and Auxiliaries

This principle promotes the use of safer solvents and auxiliaries. It is about any substances that do not directly contribute to the structure of the reaction product but are still necessary for the chemical reaction or process to occur. Mostly, reactions of organic compounds take place in liquid milieus, where the solvent acts in different ways: it can enable enhanced contact between the reactants, it can stabilize or destabilize generated intermediates, or it can influence transition states. In addition, the applied solvent also governs the selection of adequate downstream and regeneration processes and recycling or discarding techniques. By taking the ecological effect of chemical processes in consideration, innovative concepts for substitution of volatile organic solvents have become a great challenge in green chemistry. A green solvent should meet numerous criteria such as low toxicity, nonflammability, nonmutagenicity, nonvolatility, and widespread availability among others. Moreover, these green solvents have to be cheap and easy to handle and recycle. Prime examples are provided in the field of extractive recovery of microbial

polyhydroxyalkanoate (PHA) biopolymers, typical intracellular storage materials, from biomass. For this extraction process, which is typically carried out by the use of precarious halogenated solvents, one more and more resorts to less harmful greener solvents, or to new recovery methods which entirely do without any solvents.

11.9.1.6. Design for Energy Efficiency

Usually, energy is used to enhance the human life in important ways. The traditionally used energy sources like coal, oil, and gas are limited in supply, and their combustion releases greenhouse gases. For continuous improvement of life quality, both move toward renewable energy and design for energy efficiency are needed. Designing more efficient processes by choosing the most suitable technologies and unit operations has to go in parallel with selecting proper energy sources. Using an electric motor with energy sources generated from the sun and wind is more effective in ecological terms instead of using fossil fuels. How energy is converted to useful forms and where it gets lost are the most important questions for engineers and designers to help society use energy more effectively.

Consequently, green chemistry includes minimization of energy loss like mechanical friction, fluid drag, and unwanted heat transfer, by improving the layout and insulation of a refrigerator or designing lighter vehicles with enhanced aerodynamic characteristics and lower rolling resistance.

In addition, when developing a new production process, the effect of geographical location of production plants has to be taken into account: ecological comparison of different production scenarios for the same product, in this case bioplastics, clearly demonstrates that different energy production technologies, resources for energy production, and the effect of available energy mixes in different countries become significant for the ecological footprint of a new process.

11.9.1.7. Use of Renewable Feedstocks

According to the principles of green chemistry, a raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable. Using renewable resources like microbial or plant biomass, which are embedded into nature's closed carbon cycle, represents a real option to prepare functional bioproducts in a sustainable way and to contribute to energetic transition.

In the context of the Green Chemistry Principle #7, which addresses the renewable feedstock thematic, we nowadays witness a vast number of current multidisciplinary collaborations, involving the fields of, among others, agronomy, biochemical engineering, biotechnology, chemistry, microbiology, physics, toxicology, or engineering. These collaborations result in the development of next-generation fuels, polymers, and other materials pivotal for our today's society based on renewable resources and characterized by low impact on health and environment. The current global dynamic of these developments indeed gives reason to optimism for the future. Finding a method to convert raw wastes such as spinney waste fibers into a mortar composite stabilized material could be an excellent application of this principal of green chemistry. Whenever switching from fossil feedstocks to renewables, one has to consider that using renewable resources enlarges the process concept by incorporating resource provision, transportation, storage, and other aspects of logistics into the process design. Such a switch in feedstock provision, however, results in a fundamental change in the structure of processes, used technologies, and the economical concepts of industry and society.

11.9.1.8. Reduce Derivatives

Many processes could be designed in such a way to reduce the use of additional reagents and the resulting wastes. It is commonly necessary to synthesize a derivative of a compound containing groups which are not needed in the final product, but which allow the synthesis or purification steps to proceed more easily. However, these derivatives result in lower atom economy, since they introduce atoms that are not incorporated into the final product, but finally end up as waste; this is in conflict with the atom efficiency principle according to [Table 11.1](#). For many reactions that have traditionally required protecting groups, chemists are currently devoting research efforts to finding alternatives that do without them.

11.9.1.9. Catalysis

Catalysis is the chemical reaction enabled or accelerated by a catalyst. According to Ostwald, catalysts are substances that speed up a reaction by enabling an energetically favored transition state between reactants, but which are not consumed by it and do not appear in the net reaction equation. Catalysts play an essential role in our modern industrial economy, in our stewardship of the environment, and in all biological processes. Saleh and others found that iron and copper sulfate as catalysts improved the mechanism of oxidative degradation of cellulosic wastes using 35% hydrogen peroxide. High weight reduction up to 95.2% in the presence of copper sulfate and 87.8% in the presence of ferrous sulfate was reported. Recently, synthesis of nano-catalysts of specific size and shape was developed to allow facile movement of materials in the reacting phase and the control over morphology of nanostructures to tailor their physical and chemical properties. Nano-catalyst systems encompassing a paramagnetic core allow rapid and selective chemical transformations with excellent product yield coupled with the ease of catalyst separation and recovery.

Talking about catalysis, it is nowadays indispensable to spend some words on the topic biocatalysis; hence, the application of enzymes as highly selective and active catalysts produced by Mother Nature. Not only do enzymes carry out the desired reactions under mild conditions of temperature and pressure, which is analogous to the above-discussed energy efficiency principle. Moreover, they are predestined to drive reactions of renewable materials (analogy to the renewable feedstock principle) and, in some cases, even enable reactions that are not accessible by using traditional catalysts, such as the generation of some enantio-pure products. In addition, biocatalysts in a free or immobilized form are to an increasing extent applied for bioremediation, hence, the mitigation of pollutants from the ecosphere. In the context of catalysis, microwave-driven chemical reaction for organic chemistry is an emerging field to drastically reduce reaction times from days to only seconds. During the last decades, this technique has matured from a laboratory shenanigan to a well-established technology, now already industrially applied.

11.9.1.10. Design for Degradation

One of the most important objectives of green chemistry is maximizing the production with minimizing unwanted by-products. Designing of products and processes that display reduced impact on humans and the environment, such as creating sustainable mortar composite that could be considered as an value-added product suitable for various applications as inert matrix for immobilization of some low and intermediate levels of radioactive wastes, decorative tiles, building bricks, and light concrete, is reported. In this case, highly reactive hydroxyl radicals react with the organic moieties of the spinning fiber

wastes either by subtracting ions of hydrogen or by addition to the unsaturated site to yield organic radicals, which are readily oxidized by oxygen. Therefore, the end products of the degradation process were only carbon dioxide and water.

11.9.1.11. Real-time Analysis for Pollution Prevention

With advancements in chemistry, the production of numerous toxic chemicals is a serious problem for the environment. One of the basic concepts of green chemistry is familiar to pollution prevention practitioners. Less hazardous materials in chemical formulations and reducing waste formation have been sounded for many years. Consequently, green chemistry aims at eliminating the usage and generation of hazardous substances by designing better manufacturing processes for chemical materials with minimum waste production by real-time monitoring of running processes. This consequently enables a timely intervention right before waste or toxins are generated.

11.9.1.12. Inherently safer chemistry for accident prevention

It is of outstanding importance to avoid highly reactive chemicals that could potentially cause accidents during the reaction. Substance and the form of a substance used in a chemical process should be chosen in such a way to minimize the potential for chemical accidents, including toxin releases, explosions, and fire formation. For example, the most abundant solution medium, water, could accidentally cause an explosion by flowing into a tank containing methyl isocyanate gas, releasing a large amount of methyl isocyanate into the surrounding area. Other well-known materials, which undergo reactions of often disastrous outcome with water, are found among alkali metals. If an alternative reaction had been developed that did not use this reagent, the risk of explosion even causing death would have been minimized.

Intrinsically, safe chemistry can also be carried out in flow mode, using tubular microreactors with reaction channels of tiny diameter. Such flow chemistry approaches drastically reduce the reaction volume, the reaction time, and catalyst requirement, intensifies the processes by boosting the space/time yield, opens new process windows in terms of extreme temperature and pressure conditions to be applied, and, moreover, even allows to carry out highly dangerous reactions in a safe way. In addition, the application of flow chemistry in microreactors also displays a strategy to overcome classical drawbacks of microwave-driven processes, such as the restricted penetration depth of microwaves into absorbing media.

PROGRESS CHECK

11.1. The bond energy of O₂ is 498 kJ / mol. What is the maximum wavelength of the photon that has enough energy to break the O=O bond of oxygen?

11.2. Find the number : a). CCl₂F₂ is CFC-12 b). C₂Cl₃F₃ is CFC-113

- 11.3 a). What is the unit used for measuring ozone layers?
- b). What is the wavelength range of the UV radiation?
- c). How is ozone different from oxygen?
- d). When CFCs are exposed to UV or sun light, what species are produced?
- e). What is the role of chlorine radical in the ozone formation or reactions.

f). What in the polar zone makes the depletion of ozone more serious?

- 11.4. a). Which layer contains the most ozone?
- b). How thick is the troposphere?
- c). What type of gas is present in the thermosphere?
- d). How is the ionosphere different from other layers?
- e). What causes the gas molecules in the ionosphere to ionize and become charged particles?
- f). If ozone is a beneficial gas in the atmosphere, why is ozone also a gaseous pollutant?
- g). Why are chlorofluorocarbons a gases pollutant?
- h). Why is warming up of the Earth a bad thing?

11.5. a). Why do oxygen atoms exist longer at 120-km altitude than at 50-km altitude? b). What is the biological significance of the stratospheric ozone layer at Earth's surface?

11.6. Why is rainwater always acidic, even in the absence of polluting gases such as SO₃?

11.7. What is a greenhouse gas? Give the chemical formulas of two compounds that function as greenhouse gases

11.8. a). Explain why the concentration of dissolved oxygen in fresh water is an important indicator of the quality of the water. b). How is the solubility of oxygen in water affected by increasing temperature?

11.9. Which of the following is a challenge for green chemists? a) Awareness of the benefits of green chemistry b) Developing chemicals that are recyclable c) Training for cleaning up chemical spills d) Knowing when to reduce and eliminate hazardous waste

11.10. The following is often referred to as the universal solvent and is a preferred green solvent? a) Water b) Methanol c) Ethyl Acetate d) Benzene

11.11. Used to indicate the level of contaminants present, the term 'PPM' means? a) Parts-per-micron b) Parts-per-million c) Parts-per-mass d) Parts-per-molecule

11.12. _____, or VOCs, have been replaced and were banned in some paints? a) Versatile Organic Chemicals b) Volatile Organic Compounds c) Volatile Organic Components d) Versatile Odorless Components

11.13 Soybean is used to replace traditional inks in printer cartridges, highlighting which of the Green chemistry principles? a) Atom economy b) Use of Renewable Feedstock's c) Reduce derivatives d) Prevent waste

11.14 Benzene, a _____ substance, is an important industrial solvent used in the production of pharmaceuticals, plastics, and dyes? a) Odorless b) Non-flammable c) Biodegradable d) Carcinogenic

11.15. An example of green chemistry is? a) Recycled carpet b) A product made on Earth Day c) A sublimation reaction d) Bio-plastic

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TOPIC/S: CHEMISTRY OF MODERN MATERIALS

- 12.1. Classification of Materials
- 12.2. Liquid Crystals
 - 12.2.1. Types of Liquid-Crystalline Phases
- 12.3. Polymers
 - 12.3.1. Writing Formulas for Polymeric Macromolecules
 - 12.3.2. Properties of Macromolecules
 - 12.3.3. Regio and Stereo-isomerization in Macromolecules
 - 12.3.4. Synthesis of Addition Polymers
 - 12.3.4.1. Radical Chain-Growth Polymerization
 - 12.3.4.2. Cationic Chain-Growth Polymerization
 - 12.3.4.3. Anionic Chain-Growth Polymerization
 - 12.3.4.4. Ziegler-Natta Catalytic Polymerization
 - 12.3.5. Copolymers
 - 12.3.5.1. Addition Copolymerization
 - 12.3.5.2. Block Configuration
 - 12.3.6. Condensation Polymerization
 - 12.3.6.1. Characteristics of Condensation Polymers
 - 12.3.7. Thermoset Versus Thermoplastic Polymers
 - 12.3.8. The Age of Plastics
 - 12.3.8.1. Recycling and Disposal
 - 12.3.8.2. Biodegradable Polymers
- 12.4. Biomaterials
 - 12.4.1. Classes of Biomaterials
 - 12.4.2. Applications
 - 12.4.3. Characteristics of Biomaterials
- 12.5. Ceramics
 - 12.5.1. Main Categories of Ceramics
 - 12.5.2. Composition
 - 12.5.3. Manufacturing of Advanced Ceramics
 - 12.5.4. Properties and Uses
 - 12.5.5. Ceramics Matrix Composite (CMC)
- 12.6. Thin Films
 - 12.6.1. Physical Deposition Techniques
 - 12.6.1.1. Evaporation Techniques
 - 12.6.1.2. Vacuum Thermal Evaporation Technique
 - 12.6.1.3. Electron Beam Evaporation
 - 12.6.1.4. Laser Beam Evaporation (Pulsed-laser Deposition)
 - 12.6.1.5. Sputtering Technique
 - 12.6.1.6. Chemical Deposition Technique
 - 12.6.1.7. Sol-Gel Technique
 - 12.6.1.7.1. Alkoxide Precursors in Organic Solvents
 - 12.6.1.8. Dip-Coating Technique
 - 12.6.1.9. Spin-Coating Technique
 - 12.6.1.10. Chemical Bath Deposition Technique
- 12.7. Nanomaterials
 - 12.7.1. Different aspects and Roles of Nanotechnology in the Food Industry

- 12.7.2. Application as Food Additives and Food Ingredients
- 12.7.3. Nanomaterials in Food Processing
- 12.7.4. Nanomaterials in Improving the Texture, Appearance, Taste and Nutritional Values of Foods
- 12.7.5. Nanomaterials in Food Processing
- 12.7.6. Nanomaterials in the Preservation of Foods
- 12.7.7. Nanomaterials in Emerging Devices in the Food Industry
- 12.7.8. Nanomaterials in the Detection of Toxins
- 12.7.9. Nanomaterials in the Detection of Pathogens
- 12.7.10. Nanomaterials in Sensing Chemicals and Pesticides in Foods
- 12.7.11. Nanomaterials in Sensing the Quality of Key Food Ingredients
- 12.7.12. Naomaterials and Devices in Food Safety
- 12.7.13. Nanobarcodes for Product Authenticity
- 12.7.14. Nanomaterials for Protection from Allergens
- 12.7.15. Nanomaterials for the Inhibition Biofilm Formation
- 12.7.16. Safety Issues of Nanomaterials in the Food
- 12.8. Carbon Nanotubes
 - 12.8.1. Properties of MWNTs
 - 12.8.2. Challenges in the Commercialization of MNWTs
 - 12.8.3. Applications of MWNTs

EXPECTED COMPETENCIES

At the end of the lesson, you must have:

1. enumerated the different modern materials,
2. described the different modern materials,
3. classified materials,
4. described polymers,
5. written the formulas for polymers,
6. described the properties of different materials,
7. described and explained polymers and copolymers, and their respective polymerization processes,
8. differentiated thermoset plastics from thermoplastics,
9. classified ceramics,
10. enumerated the applications of ceramics,
11. described thin films and the different techniques,
12. described and explained nanomaterials, their applications to food safety; and
13. described and explained carbon nanotubes.

CONTENTS

Functional materials are building blocks of modern society and play a critical role in the evolution of technology. **Materials chemistry** is unique in providing the intellectual foundation to design, create, and understand new forms of matter, let it be organic, inorganic, or hybrid materials. From nanomaterials and molecular devices to polymers and extended solids, chemistry is creating a world of new materials as catalysts, sensors, molecular transporters, artificial scaffolds, molecular filters, and light-emitting or electron-conducting ensembles, with the potential for broad scientific and societal impact.

12.1. CLASSIFICATION OF MATERIALS

Solid materials have been conveniently grouped into three basic classifications: metals, ceramics, and polymers. This scheme is based primarily on chemical makeup and atomic structure, and most materials fall into one distinct grouping or another, although there are some intermediates. In addition, there are three other groups of important engineering materials—composites, semiconductors, and biomaterials. Composites consist of combinations of two or more different materials, whereas semiconductors are utilized because of their unusual electrical characteristics; biomaterials are implanted into the human body in addition to advanced materials such as nanomaterials, LCD, thin films, biomedicine, organic electronics, fiber optics, etc. A brief explanation of the material types and representative characteristics will be discussed.

12.2. Liquid Crystals

When cooled, most liquids undergo a simple phase transition to an ordered crystalline solid, a relatively rigid substance that has a fixed shape and volume. In the phase diagrams for these liquids, there are no regions between the liquid and solid phases. Thousands of substances are known, however, that exhibit one or more phases intermediate between the liquid state, in which the molecules are free to tumble and move past one another, and the solid state, in which the molecules or ions are rigidly locked into place. In these intermediate phases, the molecules have an ordered arrangement and yet can still flow like a liquid. Hence they are called liquid crystals, and their unusual properties have found a wide range of commercial applications. They are used, for example, in the liquid crystal displays (LCDs) in digital watches, calculators, and computer and video displays.

The first documented example of a liquid crystal was reported by the Austrian Frederick Reinitzer in 1888. Reinitzer was studying the properties of a cholesterol derivative, cholestryl benzoate, and noticed that it behaved strangely as it melted. The white solid first formed a cloudy white liquid phase at 145°C, which reproducibly transformed into a clear liquid at 179°C. The transitions were completely reversible: cooling molten cholestryl benzoate below 179°C caused the clear liquid to revert to a milky one, which then crystallized at the melting point of 145°C.

12.2.1. Types of Liquid-Crystalline Phases

Substances that form liquid crystals are often composed of long, rodlike molecules. In the normal liquid phase, these molecules are oriented in random directions Figure 18.1(a). Liquid-crystalline phases, by contrast, exhibit some ordering of the molecules. Depending on the nature of the ordering, liquid crystals can be divided into three categories: nematic, smectic, and cholesteric.

In the nematic liquid-crystalline phase, the molecules are aligned along their long axes, but there is no ordering with respect to the ends of the molecules 181.(b). The arrangement of the molecules is like that of a handful of pencils whose ends are not aligned.

In the smectic liquid-crystalline phases the molecules exhibit additional ordering beyond that of the nematic phase. The smectic phases resemble a handful of pencils whose ends are more nearly aligned. There are different kinds of smectic phases, designated by the letters A, B, C, and so forth. In the smectic A phase the molecules are arranged in layers, with their long axes perpendicular to the layers Figure 18.1 (c). Other smectic phases display different types of alignments. For example, in the smectic C phase the molecules are aligned

with their long axes tilted relative to the layers in which the molecules are stacked Figure 18.1(d).

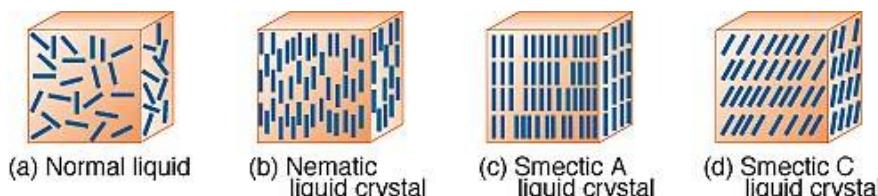


Figure 12.1. Ordering in liquid-crystalline phases, as compared with a normal (nonliquid-crystalline) liquid.

In a normal liquid, the molecules possess enough thermal energy to overcome the intermolecular attractive forces and tumble freely. This arrangement of the molecules is described as **isotropic**, which means that it is equally disordered in all directions. Liquid crystals, in contrast, are **anisotropic**: their properties depend on the direction in which they are viewed. Hence liquid crystals are not as disordered as a liquid because the molecules have some degree of alignment.

Most substances that exhibit the properties of liquid crystals consist of long, rigid rod- or disk-shaped molecules that are easily polarizable and can orient themselves in one of three different ways, as shown in Figure 8.1. In the nematic phase, the molecules are not layered but are pointed in the same direction. As a result, the molecules are free to rotate or slide past one another. In the **smectic phase**, the molecules maintain the general order of the **nematic phase** but are also aligned in layers. Several variants of the smectic phase are known, depending on the angle formed between the molecular axes and the planes of molecules. The simplest such structure is the so-called smectic A phase, in which the molecules can rotate about their long axes within a given plane, but they cannot readily slide past one another. In the cholesteric phase, the molecules are directionally oriented and stacked in a helical pattern, with each layer rotated at a slight angle to the ones above and below it. As the degree of molecular ordering increases from the nematic phase to the **cholesteric phase**, the liquid becomes more opaque, although direct comparisons are somewhat difficult because most compounds form only one of these liquid crystal phases when the solid is melted or the liquid is cooled.

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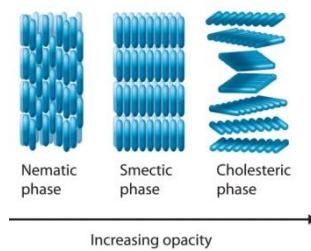


Figure 12.2. The Arrangement of Molecules in the Nematic, Smectic, and Cholesteric Liquid Crystal Phases

In the *nematic* phase, only the long axes of the molecules are parallel, and the ends are staggered at random intervals. In the *smectic* phase, the long axes of the molecules are parallel, and the molecules are also arranged in planes. Finally, in the *cholesteric* phase, the molecules are arranged in layers; each layer is rotated with respect to the ones above and below it to give a spiral structure. The molecular order increases from the nematic phase to the smectic phase to the cholesteric phase, and the phases become increasingly opaque.

Liquid crystals tend to form from long, rigid molecules with polar groups.

Molecules that form liquid crystals tend to be rigid molecules with polar groups that exhibit relatively strong dipole–dipole or dipole–induced dipole interactions, hydrogen bonds, or some combination of both. Some examples of substances that form liquid crystals are listed in Figure 12.2 along with their characteristic phase transition temperature ranges. In most cases, the intermolecular interactions are due to the presence of polar or polarizable groups. Aromatic rings and multiple bonds between carbon and nitrogen or oxygen are especially common. Moreover, many liquid crystals are composed of molecules with two similar halves connected by a unit having a multiple bond.

| Structure | Liquid Crystal Phase | Liquid Crystalline Temperature Range (°C) |
|--|----------------------|---|
| <chem>CC(C)C1=CC=C2C(C)=CC=C2C=C1Cc3ccc(cc3)C#N</chem> | Nematic | 14–28 |
| <chem>CC(=O)OC2=CC=CC=C2Cc3ccc(cc3)C#N</chem> | Smectic | 121–131 |
| <chem>CCCC(C)c1ccccc1C[C@H]2C[C@H]3[C@H]2CC[C@H]3C[C@H]4[C@H]3[C@H]4C[C@H]5[C@H]4[C@H]5C[C@H]6[C@H]5[C@H]6C[C@H]7[C@H]6[C@H]7C[C@H]8[C@H]7[C@H]8C[C@H]9[C@H]8[C@H]9C[C@H]10[C@H]9[C@H]10C</chem> | Cholesteric | 78–90 |

Figure 12.3. Structures of Typical Molecules That Form Liquid Crystals*. *Polar or polarizable groups are indicated in blue.

Because of their anisotropic structures, liquid crystals exhibit unusual optical and electrical properties. The intermolecular forces are rather weak and can be perturbed by an applied electric field. Because the molecules are polar, they interact with an electric field, which causes them to change their orientation slightly. Nematic liquid crystals, for example, tend to be relatively translucent, but many of them become opaque when an electric field is

applied and the molecular orientation changes. This behavior is ideal for producing dark images on a light or an opalescent background, and it is used in the LCDs in digital watches; handheld calculators; flat-screen monitors; and car, ship, and aircraft instrumentation. Although each application differs in the details of its construction and operation, the basic principles are similar, as illustrated in Figure 8.4.

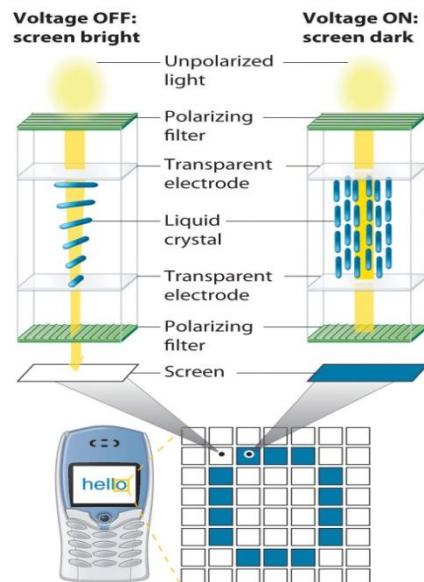


Figure 12.4. Schematic Drawing of an LCD Device, Showing the Various Layers

Applying a voltage to selected segments of the device will produce any of the numbers. The device is a sandwich that contains several very thin layers, consisting of (from top to bottom) a sheet of polarizer to produce polarized light, a transparent electrode, a thin layer of a liquid crystalline substance, a second transparent electrode, a second polarizer, and a screen. Applying an electrical voltage to the liquid crystal changes its orientation slightly, which rotates the plane of the polarized light and makes the area appear dark.

Changes in molecular orientation that are dependent on temperature result in an alteration of the wavelength of reflected light. Changes in reflected light produce a change in color, which can be customized by using either a single type of liquid crystalline material or mixtures. It is therefore possible to build a liquid crystal thermometer that indicates temperature by color (Figure 12.4) and to use liquid crystals in heat-sensitive films to detect flaws in electronic board connections where overheating can occur.

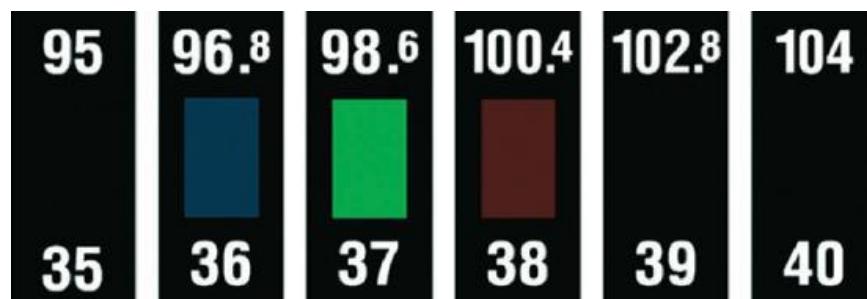


Figure 12.5 An Inexpensive Fever Thermometer That Uses Liquid Crystals. Each section contains a liquid crystal sample with a different liquid crystalline range. The section whose liquid crystalline range corresponds to the temperature of the body becomes translucent (here shown in green), indicating the temperature.

We also see the effect of liquid crystals in nature. Iridescent green beetles, known as jewel beetles, change color because of the light-reflecting properties of the cells that make up their external skeletons, not because of light absorption from their pigment. The cells form helices with a structure like those found in cholesteric liquid crystals. When the pitch of the helix is close to the wavelength of visible light, the cells reflect light with wavelengths that lead to brilliant metallic colors. Because a color change occurs depending on a person's angle of view, researchers in New Zealand are studying the beetles to develop a thin material that can be used as a currency security measure. The automobile industry is also interested in exploring such materials for use in paints that would change color at different viewing angles.

With only molecular structure as a guide, one cannot precisely predict which of the various liquid crystalline phases a given compound will actually form. One can, however, identify molecules containing the kinds of structural features that tend to result in liquid crystalline behavior.

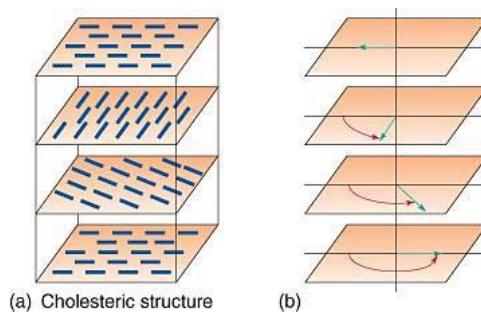


Figure 12.6. (a) Ordering in a cholesteric liquid crystal. The molecules in successive layers are oriented at a characteristic angle with respect to those in adjacent layers, to avoid unfavorable interactions. The result is a screwlike axis, as shown in (b).

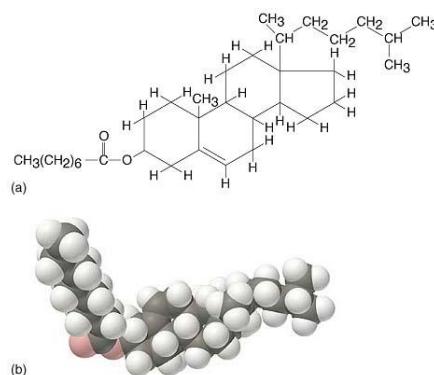
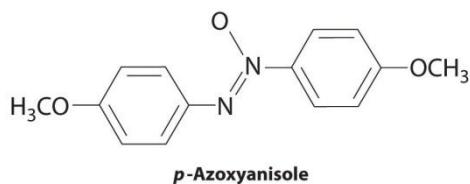


Figure 12.7. (a) Molecular structure of cholesteryl octanoate. Note that the rings in this molecule are not benzene rings. Each corner of the rings has a carbon atom and as many hydrogen atoms or other bonds as is needed to satisfy the carbon valency of four. (b) A three-dimensional molecular model of cholesteryl octanoate.

Sample Problem 12.1. Which molecule is most likely to form a liquid crystalline phase as the isotropic liquid is cooled?

- isooctane (2,2,4-trimethylpentane)
- ammonium thiocyanate $[\text{NH}_4(\text{SCN})]$
- p*-azoxyanisole



d). sodium decanoate {Na[CH₃(CH₂)₈CO₂]}

Solution:

- a). Isooctane is not long and rigid and contains no polar groups, so it is unlikely to exhibit liquid crystal behavior.
- b). Ammonium thiocyanate is ionic, and ionic compounds tend to have high melting points, so it should not form a liquid crystalline phase. In fact, ionic compounds that form liquid crystals are very rare indeed.
- c). *p*-Azoxyanisole combines two planar phenyl rings linked through a multiply bonded unit, and it contains polar groups. The combination of a long, rigid shape and polar groups makes it a reasonable candidate for a liquid crystal.
- d). Sodium decanoate is the sodium salt of a straight-chain carboxylic acid. The *n*-alkyl chain is long, but it is flexible rather than rigid, so the compound is probably not a liquid crystal.

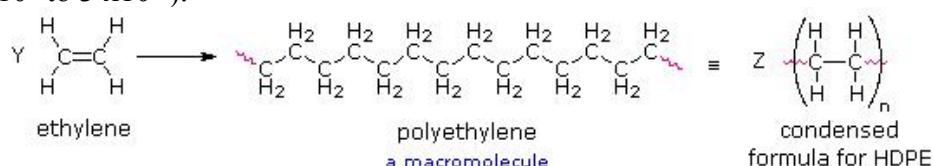
12.3. Polymers

Prior to the early 1920's, chemists doubted the existence of molecules having molecular weights greater than a few thousand. This limiting view was challenged by Hermann Staudinger, a German chemist with experience in studying natural compounds such as rubber and cellulose. In contrast to the prevailing rationalization of these substances as aggregates of small molecules, Staudinger proposed they were made up of **macromolecules** composed of 10,000 or more atoms. He formulated a **polymeric** structure for rubber, based on a repeating isoprene unit (referred to as a monomer). For his contributions to chemistry, Staudinger received the 1953 Nobel Prize. The terms **polymer** and **monomer** were derived from the Greek roots poly (many), mono (one) and meros (part).

Recognition that polymeric macromolecules make up many important natural materials was followed by the creation of synthetic analogs having a variety of properties. Indeed, applications of these materials as fibers, flexible films, adhesives, resistant paints and tough but light solids have transformed modern society. Some important examples of these substances are discussed in the following sections.

12.3.1. Writing Formulas for Polymeric Macromolecules

The repeating structural unit of most simple polymers not only reflects the monomer(s) from which the polymers are constructed, but also provides a concise means for drawing structures to represent these macromolecules. For polyethylene, arguably the simplest polymer, this is demonstrated by the following equation. Here ethylene (ethene) is the monomer, and the corresponding linear polymer is called high-density polyethylene (HDPE). HDPE is composed of macromolecules in which n ranges from 10,000 to 100,000 (molecular weight 2×10^5 to 3×10^6).



If Y and Z represent moles of monomer and polymer respectively, Z is approximately 10^{-5} Y. This polymer is called polyethylene rather than polymethylene, $(-\text{CH}_2-)_n$, because ethylene is a stable compound (methylene is not), and it also serves as the synthetic precursor of the polymer. The two open bonds remaining at the ends of the long chain of carbons (colored magenta) are normally not specified, because the atoms or groups found there depend on the chemical process used for polymerization. The synthetic methods used to prepare this and other polymers will be described later in this chapter.

Many polymeric materials having chain-like structures similar to polyethylene are known. Polymers formed by a straightforward linking together of monomer units, with no loss or gain of material, are called **addition polymers** or **chain-growth polymers**. A listing of some important addition polymers and their monomer precursors is presented in the following table.

Table 12.1 Some Common Addition Polymers

| Name(s) | Formula | Monomer | Properties | Uses |
|--|---|--|---|---|
| Polyethylene low density (LDPE) | $-(\text{CH}_2-\text{CH}_2)_n-$ | ethylene $\text{CH}_2=\text{CH}_2$ | soft, waxy solid | film wrap, plastic bags |
| Polyethylene high density (HDPE) | $-(\text{CH}_2-\text{CH}_2)_n-$ | ethylene $\text{CH}_2=\text{CH}_2$ | rigid, translucent solid | electrical insulation bottles, toys |
| Polypropylene (PP) different grades | $-[\text{CH}_2-\text{CH}(\text{CH}_3)]_n-$ | propylene $\text{CH}_2=\text{CHCH}_3$ | <u>atactic</u> : soft, elastic solid <u>isotactic</u> : hard, strong solid | similar to LDPE carpet, upholstery |
| Poly(vinyl chloride) (PVC) | $-(\text{CH}_2-\text{CHCl})_n-$ | vinyl chloride $\text{CH}_2=\text{CHCl}$ | strong rigid solid | pipes, siding, flooring |
| Poly(vinylidene chloride) (Saran A) | $-(\text{CH}_2-\text{CCl}_2)_n-$ | vinylidene chloride $\text{CH}_2=\text{CCl}_2$ | dense, high-melting solid | seat covers, films |
| Polystyrene (PS) | $-[\text{CH}_2-\text{CH}(\text{C}_6\text{H}_5)]_n-$ | styrene $\text{CH}_2=\text{CHC}_6\text{H}_5$ | hard, rigid, clear solid soluble in organic solvents | toys, cabinets packaging (foamed) |
| Polyacrylonitrile (PAN, Orlon, Acrilan) | $-(\text{CH}_2-\text{CHCN})_n-$ | acrylonitrile $\text{CH}_2=\text{CHCN}$ | high-melting solid soluble in organic solvents | rugs, blankets clothing |
| Polytetrafluoroethylene (PTFE, Teflon) | $-(\text{CF}_2-\text{CF}_2)_n-$ | tetrafluoroethylene $\text{CF}_2=\text{CF}_2$ | resistant, smooth solid | non-stick surfaces electrical insulation |
| Poly(methyl methacrylate) (PMMA, Lucite, Plexiglas) | $-[\text{CH}_2-\text{C}(\text{CH}_3)\text{CO}_2\text{CH}_3]_n-$ | methyl methacrylate $\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}_2\text{CH}_3$ | hard, transparent solid | lighting covers, signs skylights |
| Poly(vinyl acetate) (PVAc) | $-(\text{CH}_2-\text{CHOCOCH}_3)_n-$ | vinyl acetate $\text{CH}_2=\text{CHOCOCH}_3$ | soft, sticky solid | latex paints, adhesives |
| cis-Polyisoprene natural rubber | $-[\text{CH}_2-\text{CH}=\text{C}(\text{CH}_3)-\text{CH}_2]_n-$ | isoprene $\text{CH}_2=\text{CH}-\text{C}(\text{CH}_3)=\text{CH}_2$ | soft, sticky solid | requires vulcanization for practical use |
| Polychloroprene (cis + trans) (Neoprene) | $-[\text{CH}_2-\text{CH}=\text{CCI}-\text{CH}_2]_n-$ | chloroprene $\text{CH}_2=\text{CH}-\text{CCI}=\text{CH}_2$ | tough, rubbery solid | synthetic rubber oil resistant |

12.3.2. Properties of Macromolecules

A comparison of the properties of polyethylene (both LDPE & HDPE) with the natural polymers rubber and cellulose is instructive. As noted above, synthetic HDPE macromolecules have masses ranging from 10^5 to 10^6 amu (LDPE molecules are more than a hundred times smaller). Rubber and cellulose molecules have similar mass ranges, but fewer monomer units because of the monomer's larger size. The physical properties of these three polymeric substances differ from each other, and of course from their monomers.

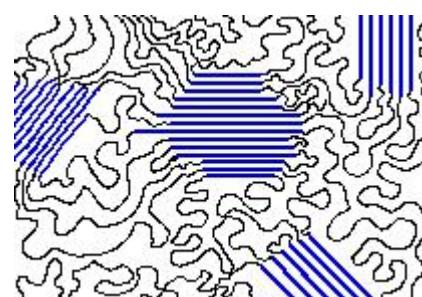
- HDPE is a rigid translucent solid which softens on heating above 100° C , and can be fashioned into various forms including films. It is not as easily stretched and deformed as is LDPE. HDPE is insoluble in water and most organic solvents, although some swelling may occur on immersion in the latter. HDPE is an excellent electrical insulator.

- LDPE is a soft translucent solid which deforms badly above 75° C . Films made from LDPE stretch easily and are commonly used for wrapping. LDPE is insoluble in water, but softens and swells on exposure to hydrocarbon solvents. Both LDPE and HDPE become brittle at very low temperatures (below -80° C). Ethylene, the common monomer for these polymers, is a low boiling (-104° C) gas.

- Natural (latex) rubber is an opaque, soft, easily deformable solid that becomes sticky when heated (above 60° C), and brittle when cooled below -50° C . It swells to more than double its size in nonpolar organic solvents like toluene, eventually dissolving, but is impermeable to water. The C_5H_8 monomer isoprene is a volatile liquid (b.p. 34° C).

- Pure cellulose, in the form of cotton, is a soft flexible fiber, essentially unchanged by variations in temperature ranging from -70 to 80° C . Cotton absorbs water readily, but is unaffected by immersion in toluene or most other organic solvents. Cellulose fibers may be bent and twisted, but do not stretch much before breaking. The monomer of cellulose is the $\text{C}_6\text{H}_{12}\text{O}_6$ aldohexose D-glucose. Glucose is a water soluble solid melting below 150° C .

To account for the differences noted here we need to consider the nature of the aggregate macromolecular structure, or morphology, of each substance. Because polymer molecules are so large, they generally pack together in a non-uniform fashion, with ordered or crystalline-like regions mixed together with disordered or amorphous domains. In some cases the entire solid may be amorphous, composed entirely of coiled and tangled macromolecular chains. **Crystallinity** occurs when linear polymer chains are structurally oriented in a uniform three-dimensional matrix. In the diagram on the right, crystalline domains are colored blue. Increased crystallinity is associated with an increase in rigidity, tensile strength and opacity (due to light scattering). Amorphous polymers are usually less rigid, weaker and more easily deformed. They are often transparent.



Three factors that influence the degree of crystallinity are:

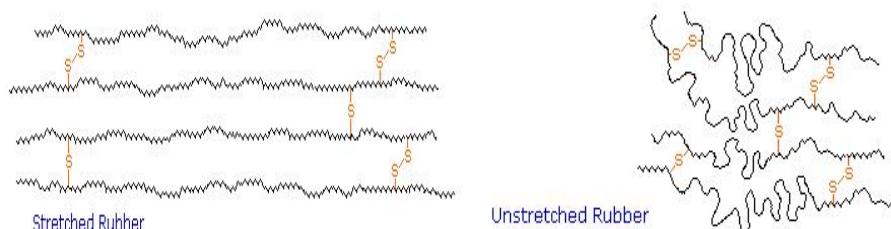
- i) Chain length
- ii) Chain branching
- iii) Inter-chain bonding

The importance of the first two factors is nicely illustrated by the differences between LDPE and HDPE. As noted earlier, HDPE is composed of very long unbranched hydrocarbon chains. These pack together easily in crystalline domains that alternate with amorphous segments, and the resulting material, while relatively strong and stiff, retains a degree of flexibility. In contrast, LDPE is composed of smaller and more highly branched chains which do not easily adopt crystalline structures. This material is therefore softer,

weaker, less dense and more easily deformed than HDPE. As a rule, mechanical properties such as ductility, tensile strength, and hardness rise and eventually level off with increasing chain length.

The nature of cellulose supports the above analysis and demonstrates the importance of the third factor (iii). To begin with, cellulose chains easily adopt a stable rod-like conformation. These molecules align themselves side by side into fibers that are stabilized by inter-chain hydrogen bonding between the three hydroxyl groups on each monomer unit. Consequently, crystallinity is high and the cellulose molecules do not move or slip relative to each other. The high concentration of hydroxyl groups also accounts for the facile absorption of water that is characteristic of cotton.

Natural rubber is a completely amorphous polymer. Unfortunately, the potentially useful properties of raw latex rubber are limited by temperature dependence; however, these properties can be modified by chemical change. The cis-double bonds in the hydrocarbon chain provide planar segments that stiffen, but do not straighten the chain. If these rigid segments are completely removed by hydrogenation (H_2 & Pt catalyst), the chains lose all constraint, and the product is a low melting paraffin-like semisolid of little value. If instead, the chains of rubber molecules are slightly cross-linked by sulfur atoms, a process called vulcanization which was discovered by Charles Goodyear in 1839, the desirable elastomeric properties of rubber are substantially improved. At 2 to 3% crosslinking a useful soft rubber, that no longer suffers stickiness and brittleness problems on heating and cooling, is obtained. At 25 to 35% crosslinking a rigid hard rubber product is formed. The following illustration shows a cross-linked section of amorphous rubber. By clicking on the diagram it will change to a display of the corresponding stretched section. The more highly-ordered chains in the stretched conformation are entropically unstable and return to their original coiled state when allowed to relax (click a second time).



On heating or cooling most polymers undergo thermal transitions that provide insight into their morphology. These are defined as the **melt transition**, T_m , and the **glass transition**, T_g .

T_m is the temperature at which crystalline domains lose their structure, or melt. As crystallinity increases, so does T_m .

T_g is the temperature below which amorphous domains lose the structural mobility of the polymer chains and become rigid glasses.

T_g often depends on the history of the sample, particularly previous heat treatment, mechanical manipulation and annealing. It is sometimes interpreted as the temperature above which significant portions of polymer chains are able to slide past each other in response to an applied force. The introduction of relatively large and stiff substituents (such as benzene rings) will interfere with this chain movement, thus increasing T_g (note polystyrene below). The introduction of small molecular compounds called plasticizers into the polymer matrix increases the interchain spacing, allowing chain movement at lower temperatures. with a resulting decrease in T_g . The outgassing of plasticizers used to modify interior plastic components of automobiles produces the "new-car smell" to which we are accustomed.

T_m and T_g values for some common addition polymers are listed below. Note that cellulose has neither a T_m nor a T_g .

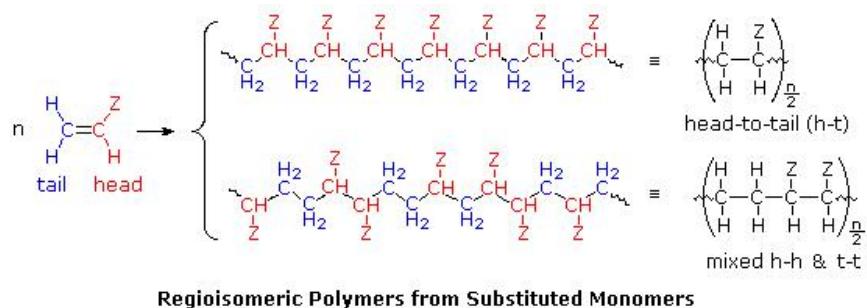
Table 12.2. T_m and T_g Values for Some Common Addition Polymers

| Polymer | LDPE | HDPE | PP | PVC | PS | PAN | PTFE | PMMA | Rubber |
|------------|------|------|-----|-----|-----|------|------|------|--------|
| T_m (°C) | 110 | 130 | 175 | 180 | 175 | >200 | 330 | 180 | 30 |
| T_g (°C) | -110 | -100 | -10 | 80 | 90 | 95 | -110 | 105 | -70 |

Rubber is a member of an important group of polymers called **elastomers**. **Elastomers** are amorphous polymers that have the ability to stretch and then return to their original shape at temperatures above T_g . This property is important in applications such as gaskets and O-rings, so the development of synthetic elastomers that can function under harsh or demanding conditions remains a practical goal. At temperatures below T_g elastomers become rigid glassy solids and lose all elasticity. A tragic example of this caused the space shuttle Challenger disaster. The heat and chemical resistant O-rings used to seal sections of the solid booster rockets had an unfortunately high T_g near 0 °C. The unexpectedly low temperatures on the morning of the launch were below this T_g , allowing hot rocket gases to escape the seals.

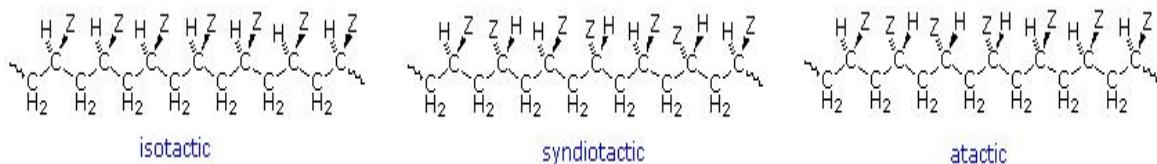
12.3.3. Regio and Stereoisomerization in Macromolecules

Symmetrical monomers such as ethylene and tetrafluoroethylene can join together in only one way. Monosubstituted monomers, on the other hand, may join together in two organized ways, described in the following diagram, or in a third random manner. Most monomers of this kind, including propylene, vinyl chloride, styrene, acrylonitrile and acrylic esters, prefer to join in a head-to-tail fashion, with some randomness occurring from time to time. The reasons for this regioselectivity will be discussed in the synthetic methods section.



Regioisomeric Polymers from Substituted Monomers

If the polymer chain is drawn in a zig-zag fashion, as shown above, each of the substituent groups (Z) will necessarily be located above or below the plane defined by the carbon chain. Consequently we can identify three configurational isomers of such polymers. If all the substituents lie on one side of the chain the configuration is called **isotactic**. If the substituents alternate from one side to another in a regular manner the configuration is termed **syndiotactic**. Finally, a random arrangement of substituent groups is referred to as **atactic**. Examples of these configurations are shown here.



Many common and useful polymers, such as polystyrene, polyacrylonitrile and poly(vinyl chloride) are atactic as normally prepared. Customized catalysts that effect stereoregular polymerization of polypropylene and some other monomers have been developed, and the improved properties associated with the increased crystallinity of these products has made this an important field of investigation. The following values of T_g have been reported.

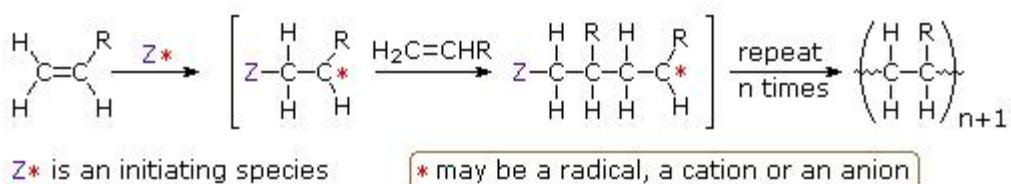
Table 12.3. Tg Values

| Polymer | T _g atactic | T _g isotactic | T _g syndiotactic |
|---------|------------------------|--------------------------|-----------------------------|
| PP | -20 °C | 0 °C | -8 °C |
| PMMA | 100 °C | 130 °C | 120 °C |

The properties of a given polymer will vary considerably with its tacticity. Thus, atactic polypropylene is useless as a solid construction material, and is employed mainly as a component of adhesives or as a soft matrix for composite materials. In contrast, isotactic polypropylene is a high-melting solid (ca. 170 °C) which can be molded or machined into structural components.

12.3.4. Synthesis of Addition Polymers

All the monomers from which addition polymers are made are alkenes or functionally substituted alkenes. The most common and thermodynamically favored chemical transformations of alkenes are addition reactions. Many of these addition reactions are known to proceed in a stepwise fashion by way of reactive intermediates, and this is the mechanism followed by most polymerizations. A general diagram illustrating this assembly of linear macromolecules, which supports the name **chain growth polymers**, is presented here. Since a pi-bond in the monomer is converted to a sigma-bond in the polymer, the polymerization reaction is usually exothermic by 8 to 20 kcal/mol. Indeed, cases of explosively uncontrolled polymerizations have been reported.



It is useful to distinguish four polymerization procedures fitting this general description.

- **Radical Polymerization**

The initiator is a radical, and the propagating site of reactivity (*) is a carbon radical.

- **Cationic Polymerization**

The initiator is an acid, and the propagating site of reactivity (*) is a carbocation.

- **Anionic Polymerization**

The initiator is a nucleophile, and the propagating site of reactivity (*) is a carbanion.

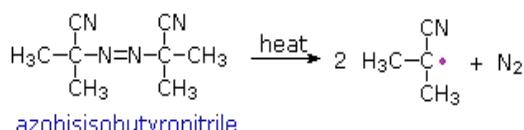
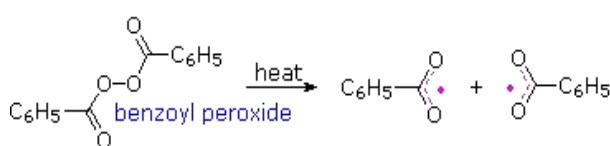
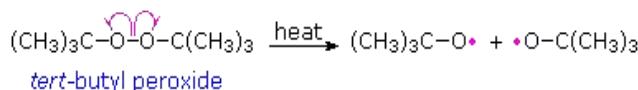
- **Coordination Catalytic Polymerization**

The initiator is a transition metal complex, and the propagating site of reactivity (*) is a terminal catalytic complex.

12.3.4 1. Radical Chain-Growth Polymerization

Virtually all of the monomers described above are subject to radical polymerization. Since this can be initiated by traces of oxygen or other minor impurities, pure samples of these compounds are often "stabilized" by small amounts of radical inhibitors to avoid unwanted reaction. When radical polymerization is desired, it must be started by using a **radical initiator**, such as a peroxide or certain azo compounds. The formulas of some common initiators, and equations showing the formation of radical species from these initiators are presented below.

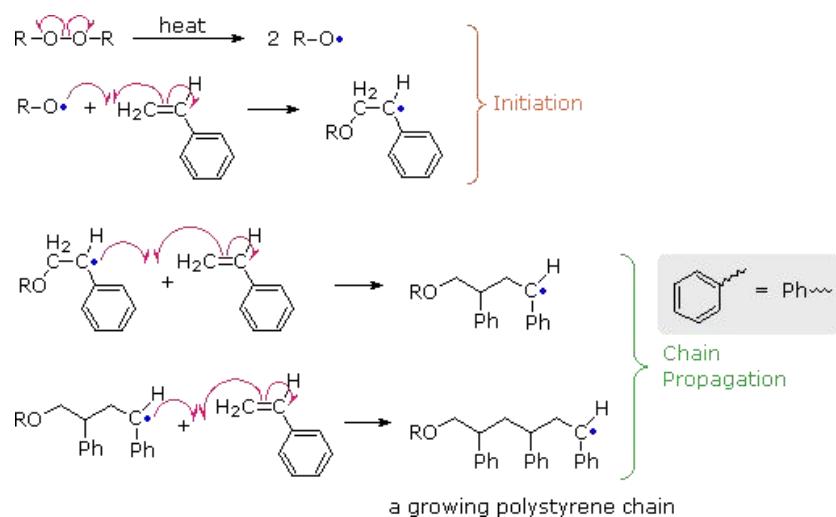
Some Radical Initiators



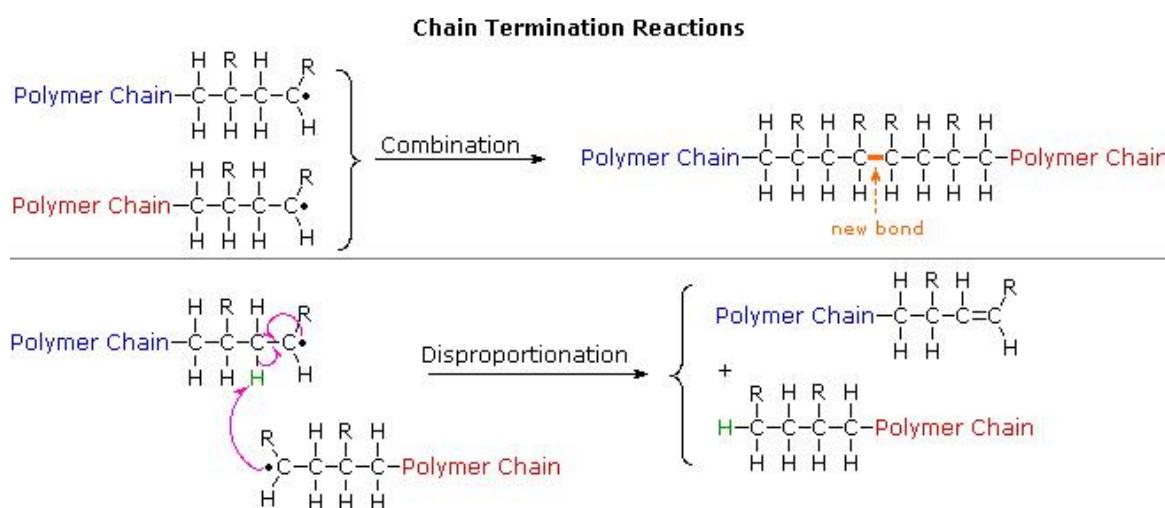
Subsequent Reactions



By using small amounts of initiators, a wide variety of monomers can be polymerized. One example of this radical polymerization is the conversion of styrene to polystyrene, shown in the following diagram. The first two equations illustrate the **initiation** process, and the last two equations are examples of **chain propagation**. Each monomer unit adds to the growing chain in a manner that generates the most stable radical. Since carbon radicals are stabilized by substituents of many kinds, the preference for head-to-tail regioselectivity in most addition polymerizations is understandable. Because radicals are tolerant of many functional groups and solvents (including water), radical polymerizations are widely used in the chemical industry.

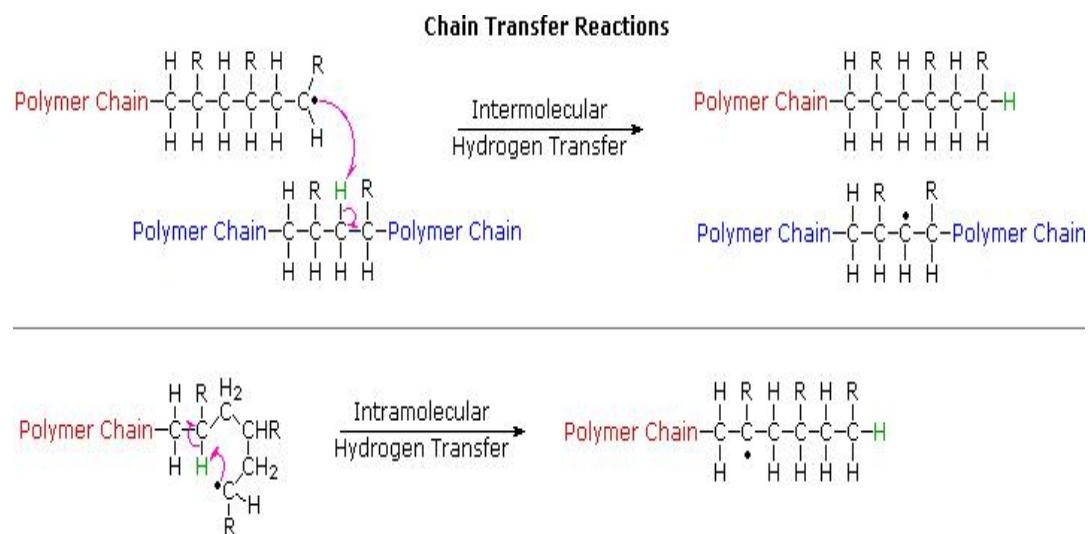


In principle, once started a radical polymerization might be expected to continue unchecked, producing a few extremely long chain polymers. In practice, larger numbers of moderately sized chains are formed, indicating that chain-terminating reactions must be taking place. The most common termination processes are **Radical Combination** and **Disproportionation**. These reactions are illustrated by the following equations. The growing polymer chains are colored blue and red, and the hydrogen atom transferred in disproportionation is colored green. Note that in both types of termination two reactive radical sites are removed by simultaneous conversion to stable product(s). Since the concentration of radical species in a polymerization reaction is small relative to other reactants (e.g. monomers, solvents and terminated chains), the rate at which these radical-radical termination reactions occurs is very small, and most growing chains achieve moderate length before termination.



The relative importance of these terminations varies with the nature of the monomer undergoing polymerization. For acrylonitrile and styrene combination is the major process. However, methyl methacrylate and vinyl acetate are terminated chiefly by disproportionation.

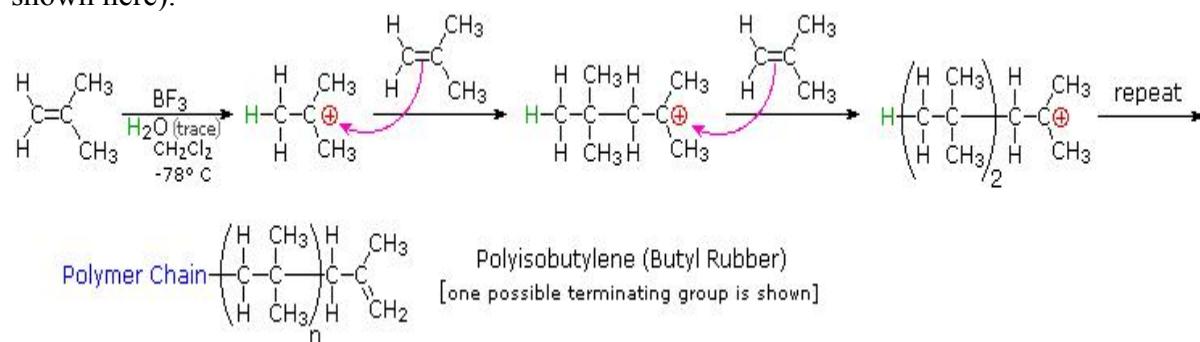
Another reaction that diverts radical chain-growth polymerizations from producing linear macromolecules is called **chain transfer**. As the name implies, this reaction moves a carbon radical from one location to another by an intermolecular or intramolecular hydrogen atom transfer (colored green). These possibilities are demonstrated by the following equations



Chain transfer reactions are especially prevalent in the high pressure radical polymerization of ethylene, which is the method used to make LDPE (low density polyethylene). The 1°-radical at the end of a growing chain is converted to a more stable 2°-radical by hydrogen atom transfer. Further polymerization at the new radical site generates a side chain radical, and this may in turn lead to creation of other side chains by chain transfer reactions. As a result, the morphology of LDPE is an amorphous network of highly branched macromolecules.

12.3.4.2. Cationic Chain-Growth Polymerization

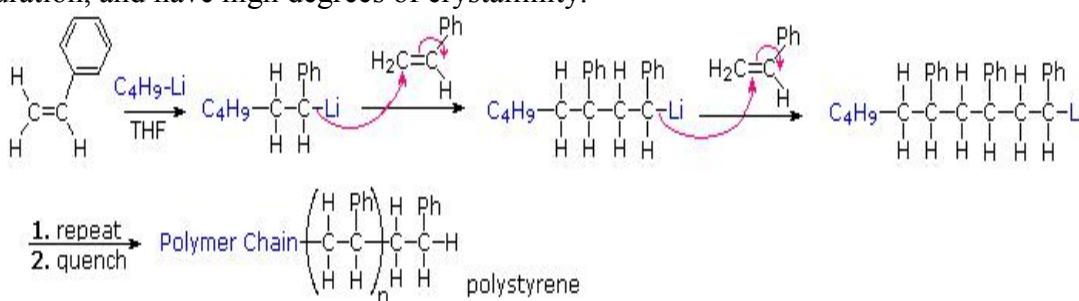
Polymerization of isobutylene (2-methylpropene) by traces of strong acids is an example of cationic polymerization. The polyisobutylene product is a soft rubbery solid, $T_g = -70^\circ \text{ C}$, which is used for inner tubes. This process is similar to radical polymerization, as demonstrated by the following equations. Chain growth ceases when the terminal carbocation combines with a nucleophile or loses a proton, giving a terminal alkene (as shown here).



Monomers bearing cation stabilizing groups, such as alkyl, phenyl or vinyl can be polymerized by cationic processes. These are normally initiated at low temperature in methylene chloride solution. Strong acids, such as HClO_4 , or Lewis acids containing traces of water (as shown above) serve as initiating reagents. At low temperatures, chain transfer reactions are rare in such polymerizations, so the resulting polymers are cleanly linear (unbranched).

12.3.4.3. Anionic Chain-Growth Polymerization

Treatment of a cold THF solution of styrene with 0.001 equivalents of n-butyllithium causes an immediate polymerization. This is an example of anionic polymerization, the course of which is described by the following equations. Chain growth may be terminated by water or carbon dioxide, and chain transfer seldom occurs. Only monomers having anion stabilizing substituents, such as phenyl, cyano or carbonyl are good substrates for this polymerization technique. Many of the resulting polymers are largely isotactic in configuration, and have high degrees of crystallinity.

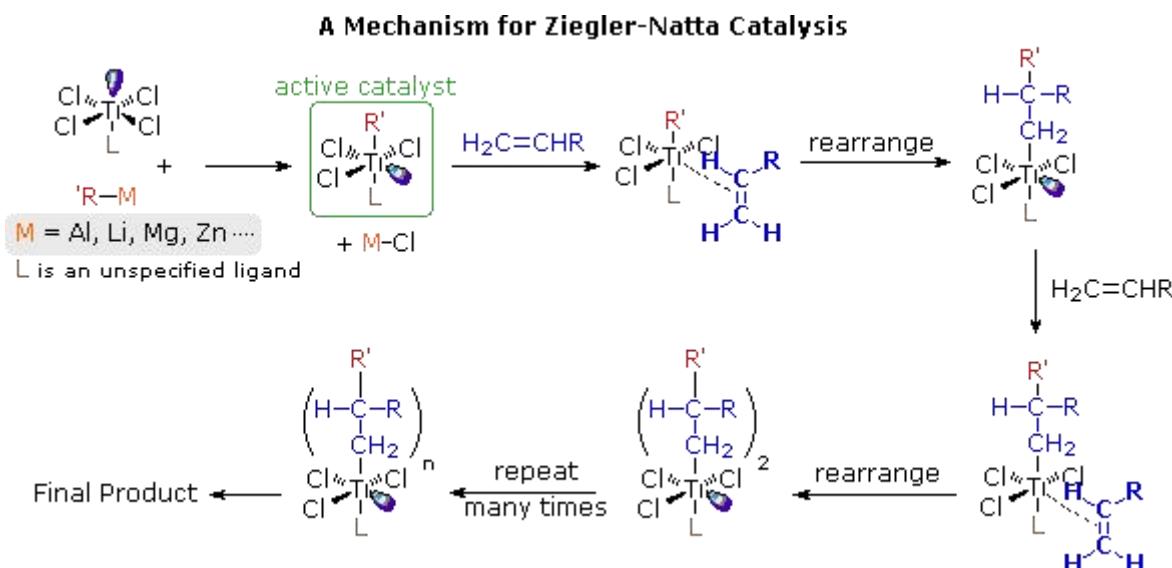


Species that have been used to initiate anionic polymerization include alkali metals, alkali amides, alkyl lithiums and various electron sources. A practical application of anionic polymerization occurs in the use of superglue. This material is methyl 2-cyanoacrylate, $CH_2=C(CN)CO_2CH_3$. When exposed to water, amines or other nucleophiles, a rapid polymerization of this monomer takes place.

12.3.4.4. Ziegler-Natta Catalytic Polymerization

An efficient and stereospecific catalytic polymerization procedure was developed by Karl Ziegler (Germany) and Giulio Natta (Italy) in the 1950's. Their findings permitted, for the first time, the synthesis of unbranched, high molecular weight polyethylene (HDPE), laboratory synthesis of natural rubber from isoprene, and configurational control of polymers from terminal alkenes like propene (e.g. pure isotactic and syndiotactic polymers). In the case of ethylene, rapid polymerization occurred at atmospheric pressure and moderate to low temperature, giving a stronger (more crystalline) product (HDPE) than that from radical polymerization (LDPE). For this important discovery these chemists received the 1963 Nobel Prize in chemistry.

Ziegler-Natta catalysts are prepared by reacting certain transition metal halides with organometallic reagents such as alkyl aluminum, lithium and zinc reagents. The catalyst formed by reaction of triethylaluminum with titanium tetrachloride has been widely studied, but other metals (e.g. V & Zr) have also proven effective. The following diagram presents one mechanism for this useful reaction. Others have been suggested, with changes to accommodate the heterogeneity or homogeneity of the catalyst. Polymerization of propylene through action of the titanium catalyst gives an isotactic product; whereas, a vanadium based catalyst gives a syndiotactic product.



12.3.5. Copolymers

The synthesis of macromolecules composed of more than one monomeric repeating unit has been explored as a means of controlling the properties of the resulting material. In this respect, it is useful to distinguish several ways in which different monomeric units might be incorporated in a polymeric molecule. The following examples refer to a two component system, in which one monomer is designated **A** and the other **B**.

Statistical Copolymers Also called random copolymers. Here the monomeric units are distributed randomly, and sometimes unevenly, in the polymer chain: ~ABBAABABAABBBAABA~.

Alternating Copolymers

Here the monomeric units are distributed in a regular alternating fashion, with nearly equimolar amounts of each in the chain: ~ABABABABABABABAB~.

Block Copolymers

Instead of a mixed distribution of monomeric units, a long sequence or block of one monomer is joined to a block of the second monomer: ~AAAAA-BBBBBB~AAAAAAA~BBB~.

Graft Copolymers

As the name suggests, side chains of a given monomer are attached to the main chain of the second monomer: ~AAAAAAA(BBBBBB~)AAAAAAA(BBBB~)AA~.

12.3.5.1. Addition Copolymerization

Most direct copolymerizations of equimolar mixtures of different monomers give statistical copolymers, or if one monomer is much more reactive a nearly homopolymer of that monomer. The copolymerization of styrene with methyl methacrylate, for example, proceeds differently depending on the mechanism. Radical polymerization gives a statistical copolymer. However, the product of cationic polymerization is largely polystyrene, and anionic polymerization favors formation of poly(methyl methacrylate). In cases where the

relative reactivities are different, the copolymer composition can sometimes be controlled by continuous introduction of a biased mixture of monomers into the reaction. Formation of alternating copolymers is favored when the monomers have different polar substituents (e.g. one electron withdrawing and the other electron donating), and both have similar reactivities toward radicals. For example, styrene and acrylonitrile copolymerize in a largely alternating fashion.

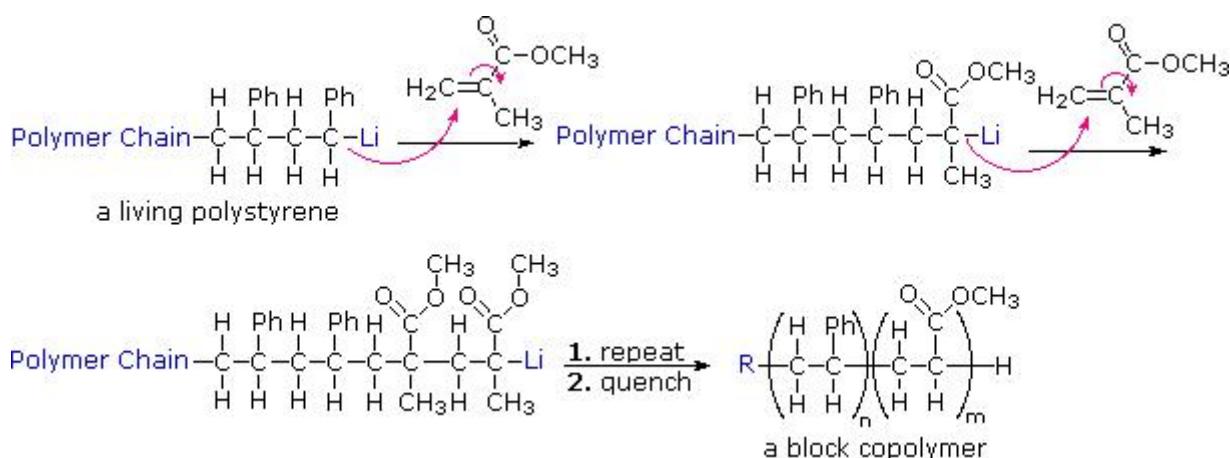
Table 12.4. Some Useful Copolymers

| Monomer A | Monomer B | Copolymer | Uses |
|---|---------------------------------------|---------------------------------|--------------------|
| H ₂ C=CHCl | H ₂ C=CCl ₂ | Saran | films & fibers |
| H ₂ C=CHC ₆ H ₅ | H ₂ C=C-CH=CH ₂ | SBR styrene butadiene rubber | tires |
| H ₂ C=CHCN | H ₂ C=C-CH=CH ₂ | Nitrile Rubber | adhesives hoses |
| H ₂ C=C(CH ₃) ₂ | H ₂ C=C-CH=CH ₂ | Butyl Rubber | inner tubes |
| F ₂ C=CF(CF ₃) | H ₂ C=CHF | Viton | gaskets |

A terpolymer of acrylonitrile, butadiene and styrene, called ABS rubber, is used for high-impact containers, pipes and gaskets.

12.3.5.2. Block Copolymerization

Several different techniques for preparing block copolymers have been developed, many of which use condensation reactions (next section). At this point, our discussion will be limited to an application of anionic polymerization. In the anionic polymerization of styrene described above, a reactive site remains at the end of the chain until it is quenched. The unquenched polymer has been termed a **living polymer**, and if additional styrene or a different suitable monomer is added a block polymer will form. This is illustrated for methyl methacrylate in the following diagram.



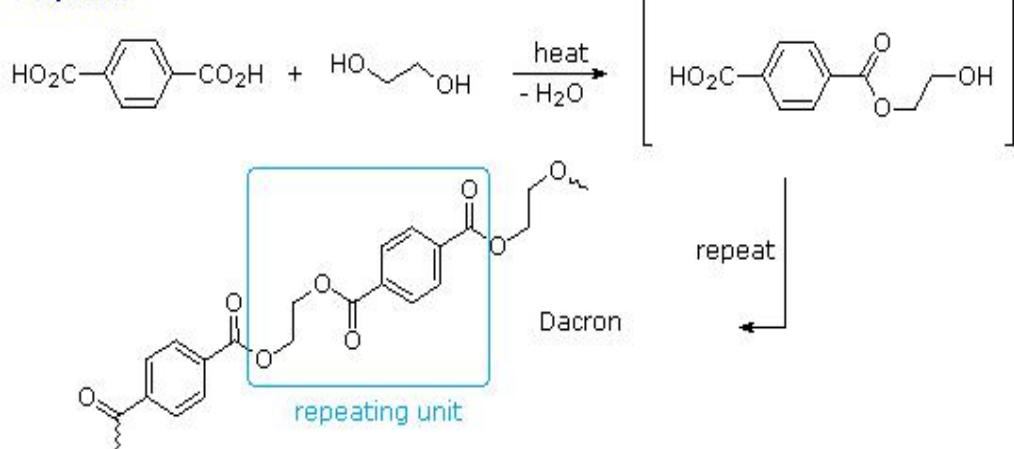
12.3.6. Condensation Polymers

A large number of important and useful polymeric materials are not formed by chain-growth processes involving reactive species such as radicals, but proceed instead by

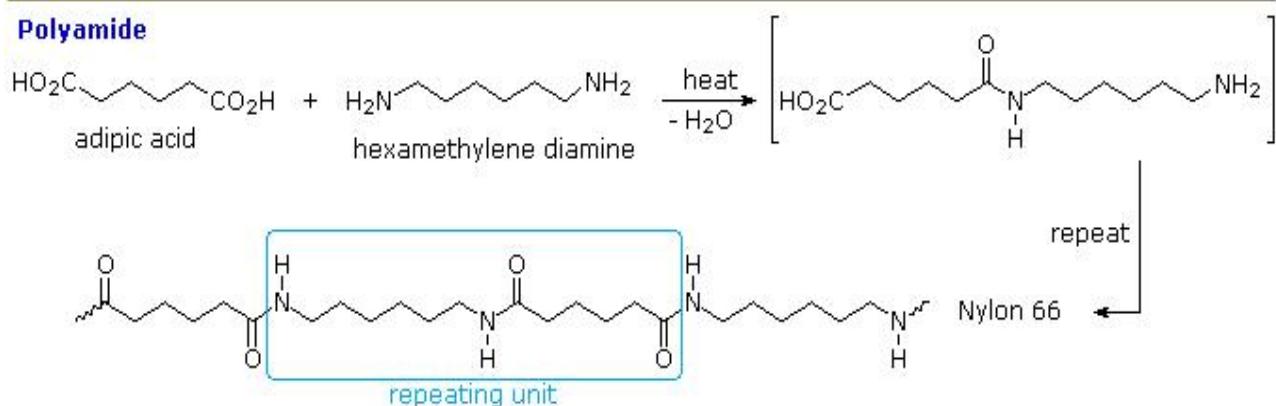
conventional functional group transformations of polyfunctional reactants. These polymerizations often (but not always) occur with loss of a small byproduct, such as water, and generally (but not always) combine two different components in an alternating structure. The polyester Dacron and the polyamide Nylon 66, shown here, are two examples of synthetic condensation polymers, also known as **step-growth** polymers. In contrast to chain-growth polymers, most of which grow by carbon-carbon bond formation, step-growth polymers generally grow by carbon-heteroatom bond formation (C-O & C-N in Dacron & Nylon respectively). Although polymers of this kind might be considered to be alternating copolymers, the repeating monomeric unit is usually defined as a combined moiety. Examples of naturally occurring condensation polymers are cellulose, the polypeptide chains of proteins, and poly(β -hydroxybutyric acid), a polyester synthesized in large quantity by certain soil and water bacteria. Formulas for these will be displayed below by clicking on the diagram.

Examples of Condensation Polymers

Polyester



Polyamide

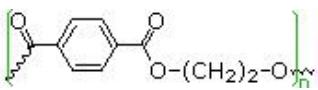
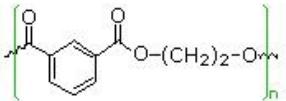
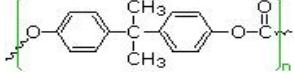
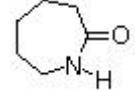
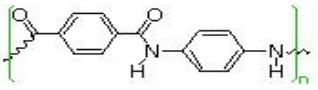
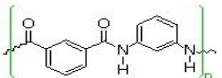
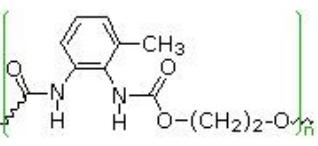
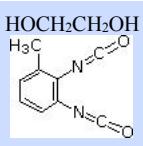


12.3.6.1. Characteristics of Condensation Polymers

Condensation polymers form more slowly than addition polymers, often requiring heat, and they are generally lower in molecular weight. The terminal functional groups on a chain remain active, so that groups of shorter chains combine into longer chains in the late stages of polymerization. The presence of polar functional groups on the chains often enhances chain-chain attractions, particularly if these involve hydrogen bonding, and thereby crystallinity and tensile strength. The following examples of condensation polymers are illustrative.

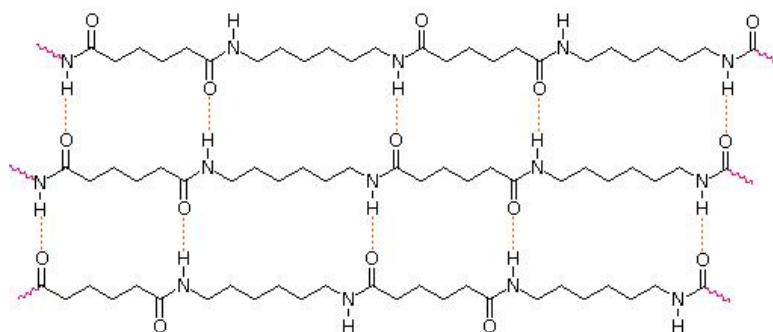
Note that for commercial synthesis the carboxylic acid components may actually be employed in the form of derivatives such as simple esters. Also, the polymerization reactions for Nylon 6 and Spandex do not proceed by elimination of water or other small molecules. Nevertheless, the polymer clearly forms by a step-growth process.

Table 12.5. Some Condensation Polymers

| Formula | Type | Components | T _g °C | T _m °C |
|---|--------------------------------|--|-------------------|-------------------|
| $\sim [CO(CH_2)_4CO-OCH_2CH_2O]_n \sim$ | polyester | HO ₂ C-(CH ₂) ₄ -CO ₂ H HO-CH ₂ CH ₂ -OH | < 0 | 50 |
|  | polyester Dacron Mylar | para HO ₂ C-C ₆ H ₄ -CO ₂ H HO-CH ₂ CH ₂ -OH | 70 | 265 |
|  | polyester | meta HO ₂ C-C ₆ H ₄ -CO ₂ H HO-CH ₂ CH ₂ -OH | 50 | 240 |
|  | polycarbonate Lexan | (HO-C ₆ H ₄ -) ₂ C(CH ₃) ₂ (Bisphenol A) X ₂ C=O (X = OCH ₃ or Cl) | 150 | 267 |
| $\sim [CO(CH_2)_4CO-NH(CH_2)_6NH]_n \sim$ | polyamide Nylon 66 | HO ₂ C-(CH ₂) ₄ -CO ₂ H H ₂ N-(CH ₂) ₆ -NH ₂ | 45 | 265 |
| $\sim [CO(CH_2)_5NH]_n \sim$ | polyamide Nylon 6 Perlon |  | 53 | 223 |
|  | polyamide Kevlar | para HO ₂ C-C ₆ H ₄ -CO ₂ H para H ₂ N-C ₆ H ₄ -NH ₂ | --- | 500 |
|  | polyamide Nomex | meta HO ₂ C-C ₆ H ₄ -CO ₂ H meta H ₂ N-C ₆ H ₄ -NH ₂ | 273 | 390 |
|  | polyurethane Spandex |  | | |

The difference in T_g and T_m between the first polyester (completely aliphatic) and the two nylon polyamides (5th & 6th entries) shows the effect of intra-chain hydrogen bonding on crystallinity. The replacement of flexible alkylidene links with rigid benzene rings also stiffens the polymer chain, leading to increased crystalline character, as demonstrated for polyesters (entries 1, 2 & 3) and polyamides (entries 5, 6, 7 & 8). The high T_g and

Interchain Hydrogen Bonding Enhances Crystallinity

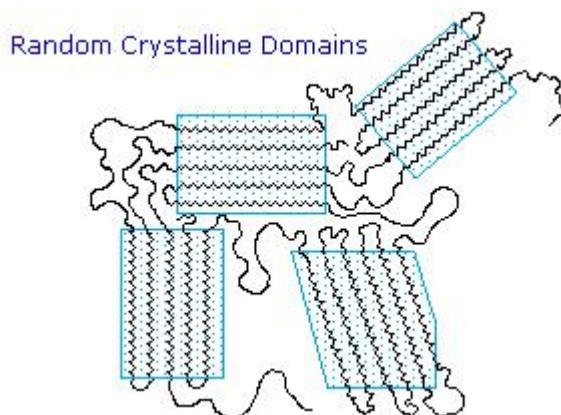


T_m values for the amorphous polymer Lexan are consistent with its brilliant transparency and glass-like rigidity. Kevlar and Nomex are extremely tough and resistant materials, which find use in bullet-proof vests and fire resistant clothing.

This cold-drawing procedure organizes randomly oriented amorphous domains so they become more crystalline. In these cases, the physically oriented morphology is stabilized and retained in the final product. This contrasts with elastomeric polymers, for which the stretched or aligned morphology is unstable relative to the amorphous random coil morphology.

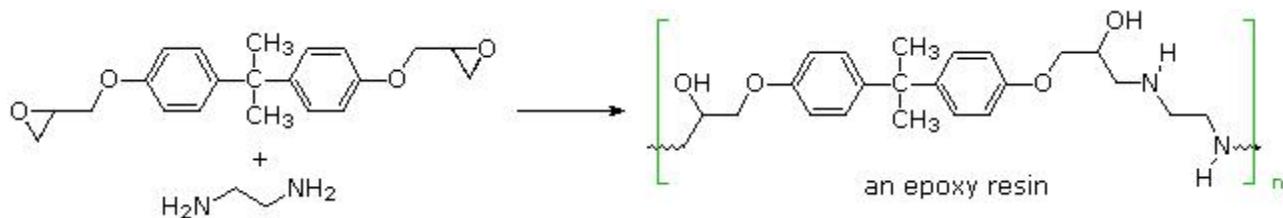
Many polymers, both addition and condensation, are used as fibers. The chief methods of spinning synthetic polymers into fibers are from melts or viscous solutions. Polyesters, polyamides and polyolefins are usually spun from melts, provided the T_m is not too high. Polyacrylates suffer thermal degradation and are therefore spun from solution in a volatile solvent. **Cold-drawing** is an important physical treatment that improves the strength and appearance of these polymer fibers. At temperatures above T_g , a thicker than desired fiber can be forcibly stretched to many times its length; and in so doing the polymer chains become untangled, and tend to align in a parallel fashion.

crystalline domains, and also
In these cases, the physically
oriented morphology is stabilized and retained in the final product. This contrasts with
elastomeric polymers, for which the stretched or aligned morphology is unstable relative to
the amorphous random coil morphology.



Step-growth polymerization is also used for preparing a class of adhesives and amorphous solids called epoxy resins. Here the covalent bonding occurs by an S_N2 reaction between a nucleophile, usually an amine, and a terminal epoxide. In the following example,

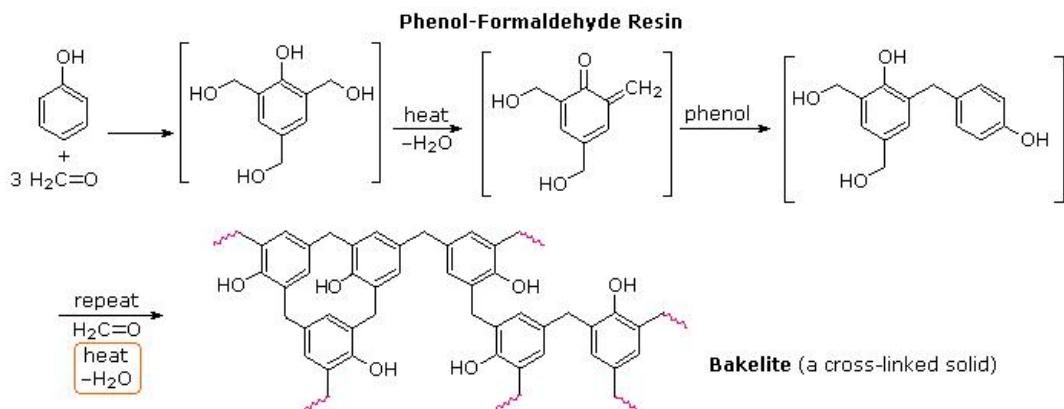
the same bisphenol A intermediate used as a monomer for Lexan serves as a difunctional scaffold to which the epoxide rings are attached. Bisphenol A is prepared by the acid-catalyzed condensation of acetone with phenol.



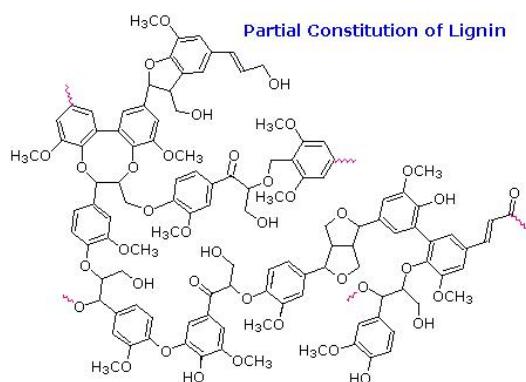
12.3.7. Thermosetting vs. Thermoplastic Polymers

Most of the polymers described above are classified as **thermoplastic**. This reflects the fact that above T_g they may be shaped or pressed into molds, spun or cast from melts or dissolved in suitable solvents for later fashioning. Because of their high melting point and poor solubility in most solvents, Kevlar and Nomex proved to be a challenge, but this was eventually solved.

Another group of polymers, characterized by a high degree of cross-linking, resist deformation and solution once their final morphology is achieved. Such polymers are usually prepared in molds that yield the desired object. Because these polymers, once formed, cannot be reshaped by heating, they are called **thermosets**. The initial display is of Bakelite, one of the first completely synthetic plastics to see commercial use (circa 1910).



A natural resinous polymer called lignin has a cross-linked structure similar to bakelite. Lignin is the amorphous matrix in which the cellulose fibers of wood are oriented. Wood is a natural composite material, nature's equivalent of fiberglass and carbon fiber composites. A partial structure for lignin is shown here

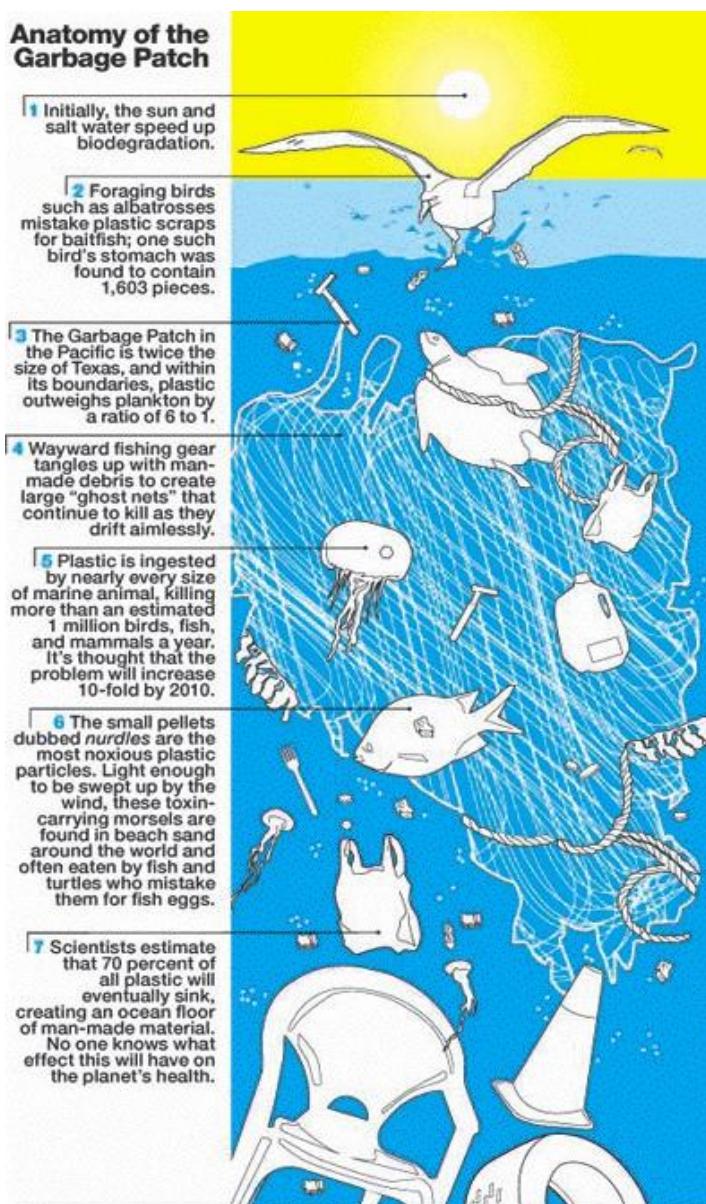


12.3.8. The Age of Plastics

Historically, many eras were characterized by the materials that were then important to human society (e.g. stone age, bronze age and iron age). The 20th century has acquired several labels of this sort, including the **nuclear age** and the **oil age**; however, the best name is likely the **plastic age**. During this period no technological advancement, other than the delivery of electrical power to every home, has impacted our lives more than the widespread use of synthetic plastics in our clothes, dishes, construction materials, automobiles, packaging, and toys, to name a few. The development of materials that we now call plastics began with rayon in 1891, continuing with Bakelite in 1907, polyethylene in 1933, Nylon and Teflon in 1938, polypropylene in 1954, Kevlar in 1965, and is continuing.

The many types of polymers that we lump together as plastics are, in general, inexpensive, light weight, strong, durable and, when desired, flexible. Plastics may be processed by extrusion, injection-moulding, vacuum-forming, and compression, emerging as fibers, thin sheets or objects of a specific shape. They may be colored as desired and reinforced by glass or carbon fibers, and some may be expanded into low density foams. Many modern adhesives involve the formation of a plastic bonding substance. Plastics have replaced an increasing number of natural substances. In the manufacture of piano keys and billiard balls plastics have replaced ivory, assisting the survival of the elephant. It is noteworthy that a synthetic fiber manufacturing facility occupies a much smaller area of ground than would be needed to produce an equal quantity of natural fibers, such as cotton, wool or silk. With all these advantages it is not surprising that much of what you see around you is plastic. Indeed, the low cost, light weight, strength and design adaptability of plastics to meet a variety of applications have resulted in strong year after year growth in their production and use, which is likely to continue. Indeed, many plastics are employed in disposable products meant only for a single use.

The Law of Unintended Consequences



Heather Jones

Successful solutions to technological projects are often achieved by focusing on a limited set of variables that are directly linked to a desired outcome. However, nature often has a way of rewarding such success by exposing unexpected problems generated "outside the box" of the defined project. In the case of plastics, their advantageous durability and relative low cost have resulted in serious environmental pollution as used items and wrappings are casually discarded and replaced in a never ending cycle. We see this every day on the streets and fields of our neighborhoods, but the problem is far more dire. Charles Moore, an American oceanographer, in 1997 discovered an enormous stew of trash, estimated at nearly 100 million tons, floating in the Pacific Ocean between San Francisco and Hawaii. Named the "Great Pacific Garbage Patch", this stew of trash is composed largely (80%) of bits and pieces of plastic that outweigh the plankton 6 : 1, in a region over twice the size of Texas. Although some of this flotsam originates from ships at sea, at least 80% comes from land generated trash. The information provided here, and the illustration on the left, come from an article by Susan Casey in Best Life.

Clock-wise circulation of currents driven by the global wind system and constrained by surrounding continents form a vortex or gyre comparable to a large whirlpool. Each major ocean basin has a large gyre in the subtropical region, centered around 30° north and south latitude. The North Atlantic Subtropical Gyre is known as the Sargasso Sea. The larger North Pacific Subtropical Gyre, referred to as the doldrums, is the convergence zone where plastic and other waste mixes together. There are similar areas in the South Pacific, the North and South Atlantic, and the Indian Ocean.

Aside from its disgusting aesthetic presence, the garbage patch is representative of serious environmental and health problems. No one knows how long it will take for some of these plastics to biodegrade, or return to their component molecules. Persistent objects such as six-pack rings and discarded nets trap sea animals. Smaller plastic scraps are mistaken for food by sea birds; and are often found undigested in the gut of dead birds. Nurdles, lentil-size pellets of plastic, found in abundance where plastics are manufactured and distributed, are

dispersed by wind throughout the biosphere. They're light enough to blow around like dust and to wash into harbors, storm drains, and creeks. Escaped nurdles and other plastic litter migrate to the ocean gyre largely from land. At places as remote as Rarotonga, in the Cook Islands they're commonly found mixed with beach sand. Once in the ocean, nurdles may absorb up to a million times the level of any organic pollutants found in surrounding waters. Nurdles in the sea are easily mistaken for fish eggs by creatures that would very much like to have such a snack. Once inside the body of a big eye tuna or a king salmon, they become part of our food chain.

12.3.8.1. Recycling and Disposal

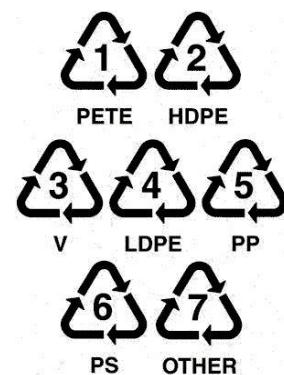
Most plastics crumble into ever-tinier fragments as they are exposed to sunlight and the elements. Except for the small amount that's been incinerated—and it's a very small amount—every bit of plastic ever made still exists, unless the material's molecular structure is designed to favor biodegradation. Unfortunately, cleaning up the garbage patch is not a realistic option, and unless we change our disposal and recycling habits, it will undoubtedly get bigger. One sensible solution would require manufacturers to use natural biodegradable packaging materials whenever possible, and consumers to conscientiously dispose of their plastic waste. Thus, instead of consigning all plastic trash to a land fill, some of it may provide energy by direct combustion, and some converted for reuse as a substitute for virgin plastics. The latter is particularly attractive since a majority of plastics are made from petroleum, a diminishing resource with a volatile price.

The energy potential of plastic waste is relatively significant, ranging from 10.2 to 30.7MJkg⁻¹, suggesting application as an energy source and temperature stabilizer in municipal incinerators, thermal power plants and cement kilns. The use of plastic waste as a fuel source would be an effective means of reducing landfill requirements while recovering energy. This, however, depends on using appropriate materials. Inadequate control of combustion, especially for plastics containing chlorine, fluorine and bromine, constitutes a risk of emitting toxic pollutants.

Whether used as fuels or a source of recycled plastic, plastic waste must be separated into different categories. To this end, an identification coding system was developed by the Society of the Plastics Industry (SPI) in 1988, and is used internationally. This code, shown on the right, is a set of symbols placed on plastics to identify the polymer type, for the purpose of allowing efficient separation of different polymer types for recycling. The abbreviations of the code are explained in the following table.

Table 12.6. Polymer Codes and Names

| PETE | HDPE | V | LDPE |
|----------------------------|---------------------------|---|--------------------------|
| polyethylene terephthalate | high density polyethylene | polyvinyl chloride | low density polyethylene |
| PP | PS | OTHER | |
| polypropylene | polystyrene | polyesters, acrylics polyamides, teflon etc. | |



Despite use of the recycling symbol in the coding of plastics, there is consumer confusion about which plastics are readily recyclable. In most communities throughout the United States, PETE and HDPE are the only plastics collected in municipal recycling programs. However, some regions are expanding the range of plastics collected as markets become available. (Los Angeles, for example, recycles all clean plastics numbered 1 through 7) In theory, most plastics are recyclable and some types can be used in combination with others. In many instances, however, there is an incompatibility between different types that necessitates their effective separation. Since the plastics utilized in a given manufacturing sector (e.g. electronics, automotive, etc.) is generally limited to a few types, effective recycling is often best achieved with targeted waste streams.

The plastic trash from most households, even with some user separation, is a mixture of unidentified pieces. Recycling of such mixtures is a challenging problem. A float/sink process has proven useful as a first step. When placed in a medium of intermediate density, particles of different densities separate—lower density particles float while those of higher density sink. Various separation media have been used, including water or water solutions of known density (alcohol, NaCl, CaCl₂ or ZnCl₂). As shown in the following table, the densities of common plastics differ sufficiently to permit them to be discriminated in this fashion. The cylindroconical cyclone device, shown on the right, provides a continuous feed procedure in which the material to be separated is pumped into the vessel at the same time as the separating media. Some polymers, such as polystyrene and polyurethane, are commonly formed into foamed solids that have a much lower density than the solid material.

Table 12.7. Densities of Typical Plastics

| Densities of Typical Plastics | | | |
|-------------------------------|-----------------------|------------------------------------|--------------------------|
| PE & PP | ABS & SAN & nylons | PMM & acrylics & polycarbonates | PETE & PVC & Bakelite |
| 0.90-0.99 | 1.05-1.09 | 1.10-1.25 | 1.3-1.6 |

PE = polyethylene & PP = polypropylene

ABS = acrylonitrile-butadiene-styrene copolymer

SAN = acrylonitrile-styrene copolymer

PMM = polymethyl methacrylate

PETE = polyethylene terephthalate

PVC = polyvinylchloride (rigid)

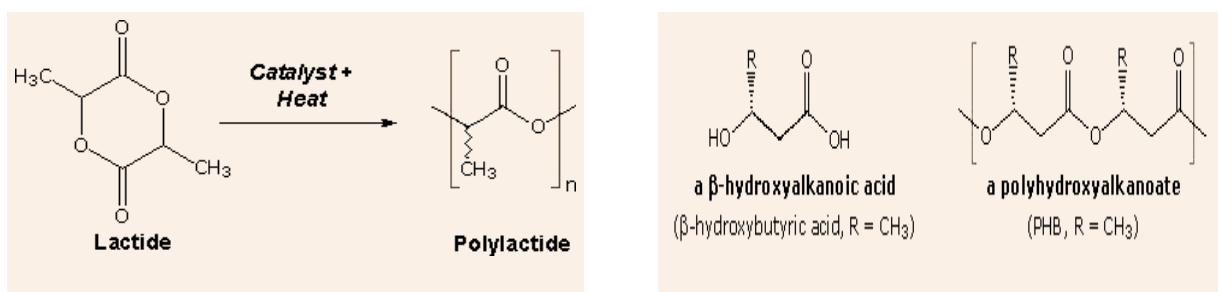
One serious problem in recycling is posed by the many additives found in plastic waste. These include pigments for coloring, solid fibers in composites, stabilizers and plasticizers. In the case of PETE (or PET), which is commonly used for bottles, some waste may be mechanically and thermally treated to produce low grade packaging materials and fibers. To increase the value of recovered PETE it may be depolymerized by superheated methanol into dimethyl terephthalate and ethylene glycol. These chemicals are then purified and used to make virgin PETE. Hydrocarbon polymers such as polyethylene and polypropylene may be melted and extruded into pellets for reuse. However, the presence of dyes or pigments limits the value of this product.

12.3.8.2. Biodegradable Polymers

Plastics derived from natural materials, such as cellulose, starch and hydroxycarboxylic acids are more easily decomposed when exposed to oxygen, water, soil organisms and sunlight than are most petroleum based polymers. The glycoside linkages in polysaccharides and the ester groups in polyesters represent points of attack by the enzymes of microorganisms that facilitate their decomposition. Such biodegradable materials can be composted, broken down and returned to the earth as useful nutrients. However, it is important to recognize that proper composting is necessary. Placing such materials in a landfill results in a slower anaerobic decomposition, which produces methane, a greenhouse gas.

Derivatives of cellulose, such as cellulose acetate, have long served for the manufacture of films and fibers. The most useful acetate material is the diacetate, in which two thirds of the cellulose hydroxyl groups have been esterified. Acetate fibers lose strength when wet, and acetate clothing must be dry cleaned. The other major polysaccharide, starch, is less robust than cellulose, but in pelletized form it is now replacing polystyrene as a packing material.

The two natural polyesters that are finding increasing use as replacements for petroleum based plastics are polylactide (PLA) and polyhydroxyalkanoates (PHA), the latter most commonly as copolymers with polyhydroxybutyrate (PHB). Structures for these polymers and their monomer precursors are shown below.



PLA is actually a polymer of lactic acid, but the dimeric lactide is used as the precursor to avoid the water that would be formed in a direct poly-esterification. Bacterial fermentation is used to produce lactic acid from corn starch or cane sugar. After dimerization to the lactide, ring-opening polymerization of the purified lactide is effected using stannous compounds as catalysts. PLA can be processed like most thermoplastics into fibers and films. In situations that require a high level of impact strength, the toughness of PLA in its pristine state is often insufficient. Blends of PLA with polymers such as ABS have good form-stability and visual transparency, making them useful for low-end packaging applications. PLA materials are currently used in a number of biomedical applications, such as sutures, stents, dialysis media and drug delivery devices. However, one of the drawbacks of polylactides for biomedical applications is their brittleness.

Lactic acid has a chiral center, the (S)(+)-enantiomer being the abundant natural form (L-lactic acid). Due to the chiral nature of lactic acid, several distinct forms of polylactide exist. Poly-L-lactide (PLLA) is the product resulting from polymerization of (S,S)-lactide. PLLA has a crystallinity of around 37%, a glass transition temperature between 50-80 °C and a melting temperature between 173-178 °C. The melting temperature of PLLA can be increased 40-50 °C and its heat deformation temperature can be increased from approximately 60 °C to up to 190 °C by physically blending the polymer with PDLA (poly-D-lactide). PDLA and PLLA form a highly regular stereocomplex with increased crystallinity.

PHA (polyhydroxyalkanoates) are synthesized by microorganisms such as *Alcaligenes eutrophus*, grown in a suitable medium and fed appropriate nutrients so that it multiplies rapidly. Once the population has increased, the nutrient composition is changed, forcing the micro-organism to synthesize PHA. Harvested amounts of PHA from the organism can be as high as 80% of the organism's dry weight. The simplest and most commonly occurring form of PHA is poly (R-3-hydroxybutyrate), PHB or P(3HB)). Pure PHB, consisting of 1000 to 30000 hydroxy acid units, is relatively brittle and stiff. Depending upon the microorganism, many of which are genetically engineered for this purpose, and the cultivation conditions, homo- or copolymers with different hydroxyalkanic acids may be generated. Such copolymers may have improved physical properties compared with homo P(3HB). Presently, these PHAs cost about twice as much as petroleum-based plastics. An engineered switch-grass that grows PHA inside its leaves and stems has also been created, offering the possibility of avoiding some of the costs associated with large scale bacterial fermentation.

In contrast to P(3HB), the polymer of 4-hydroxybutyrate, P(4HB), is elastic and flexible with a higher tensile strength. Copolymers of P(3HB) and P(4HB) are synthesized by *Comamonas acidovarans*. The molecular weight remains roughly the same (400,000-700,000 Da), but thermal properties correlate with the ratio of these monomer units. The mp decreases from 179 to 130 (or lower) with an increase in 4HB, and as 4HB increases from 0% to 100% the Tg decreases from 4 to -46. 4-Hydroxybutyrate (4HB) is produced from 1,4-butanediol by microorganisms such as *Aeromonas hydrophila*, *Escherichia coli*, or *Pseudomonas putida*. Fermentation broth containing 4HB has then been used for the production of the

homopolymer P(4HB), as well as coolymers with P(3HB), [P(3HB-4HB)]. The following table lists some of the properties of these homo-polymers and co-polymers.

Table 12.8. Properties of Some Polymers

| Polymer | T _m °C | T _g °C | %Crystallinity | Tensile Strength |
|--------------------------|-------------------|-------------------|----------------|------------------|
| P(3HB) | 179 | 4 | 70 | 40 MPa |
| P(4HB) | 53 | -47 | 53 | 100 |
| co-Polymer 3HB-20%3HV | 145 | -1 | 50 | 32 |
| co-Polymer 3HB-7%3HD | 133 | -8 | > 50 | 17 |
| isotactic-PP | 176 | 0 | > 50 | 40 |
| LDPE | 110 | -100 | < 50 | 10 |

3HV = 3-hydroxyvalerate, 3HD = 3-hydroxydecanoate

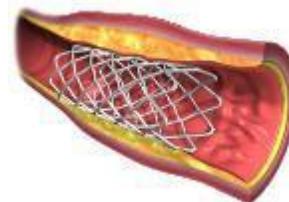
It remains an open question whether it's more energy and cost efficient to use biodegradable plastic or to recycle petroleum-based plastic. There is little doubt, however, that biodegradable materials lead to less environmental pollution when randomly discarded after use, as is often the case.

12.4. Biomaterials



Biomaterial is a nonviable material used in a medical device, intended to interact with biological systems. It is used to make devices as replacement part of a function of the body in a safe, reliable, economic, and physiological acceptable manner. A substance other than a drug, which is natural or synthetic that treats augments, or replaces any tissue, organ or body function. However, biomaterial has a particular lifespan in the human body.

Biomaterials stem from an inability to treat many diseases, injuries and conditions with other therapies or procedures such as replacement of body part that has lost function (total hip, heart), correct abnormalities (spinal rod), improve function (pacemaker, stent) and assist in healing (structural, pharmaceutical effects: sutures, drug release).



12.4.1. Classes of Biomaterials

Below are the different classes of biomaterials:

- Metals
 - stainless steel, cobalt alloys, titanium alloys
- Ceramics
 - aluminum oxide, zirconia, calcium phosphates

- Polymers
 - silicones, poly(ethylene), poly(vinyl chloride), polyurethanes, polylactides
- Natural polymers
 - collagen, gelatin, elastin, silk, polysaccharides.

12.4.2. Applications

Some examples of biomaterial applications include:

- Heart pacemaker, artificial valve and artificial heart.
- Eye - contact lens and intraocular lens.
- Ear - artificial stapes and cochlea implant.
- Bone - bone plate, intramedullary rod, joint prosthesis, bone cement and bone defect repair.
- Kidney - dialysis machine.
- Bladder - catheter and stent.
- Muscle – sutures and muscle stimulator.
- Circulation - artificial blood vessels.
- Skin - burn dressings and artificial skin.
- Endocrine - encapsulated pancreatic islet cells.

12.4.3. Characteristics of Biomaterials

The most important characteristics that influence the choice of biomaterials are: biocompatibility, sterilizability, physical characteristics and manufacturability.

Biocompatibility includes noncarcinogenic, nonpyrogenic, nontoxic, nonallergenic, blood compatible, non-inflammatory. The ability of a material to perform with an appropriate host response in a specific application. **Host response** is the reaction of a living system to the presence of a material

Sterilizability refers to the ability of biomaterial not destroyed by typical sterilizing techniques such as autoclaving, dry heat, radiation, ethylene oxide.

Physical characteristics refers to the physical requirement which includes strength, elasticity, and durability.

Manufacturability the characteristic of materials that are machinable, moldable, and extrudable.

Possible host reactions to biomaterials include: thrombosis (blot clot within the blood vessel), hemolysis (rupture of red blood cells), inflammation, infection, carcinogenesis, hypersensitivity and systemic effects (problems caused inside the body once a hazardous agent has entered).

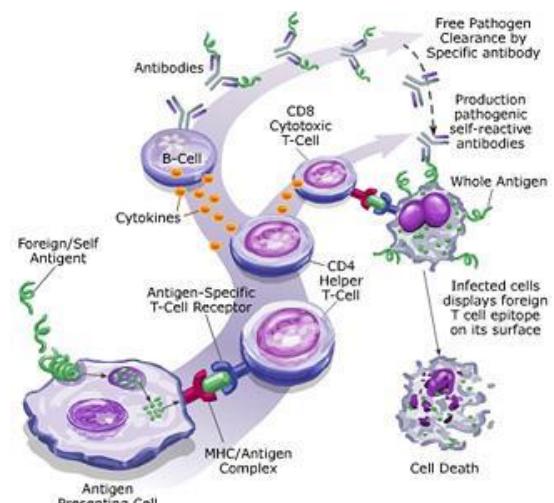


Figure 12.8. Steps in the Development of Biomaterial Devices

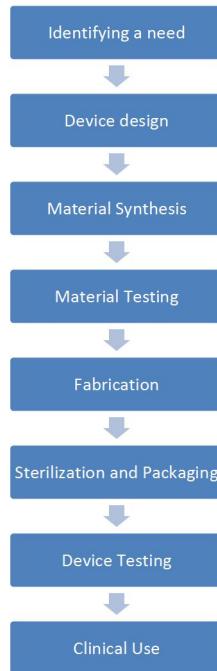


Figure 12.9. Dental Implants



Figure 12.10. Intraocular Lenses

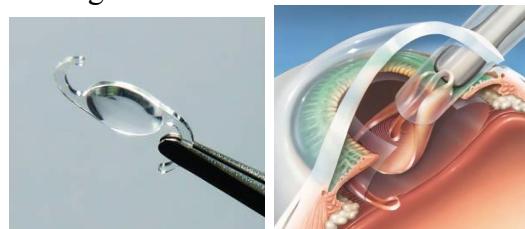


Figure 12.11. Vascular Grafts



Figure 12.12. Hip Replacements

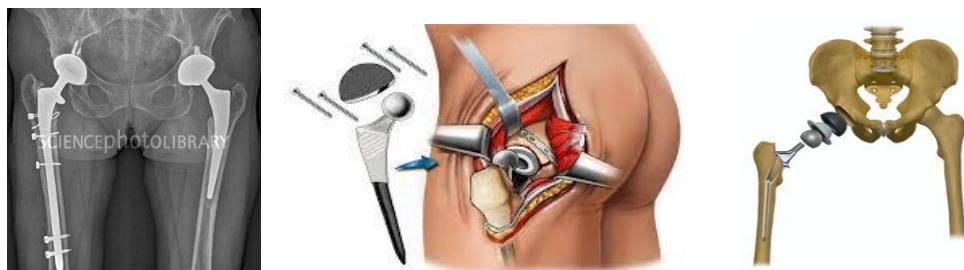
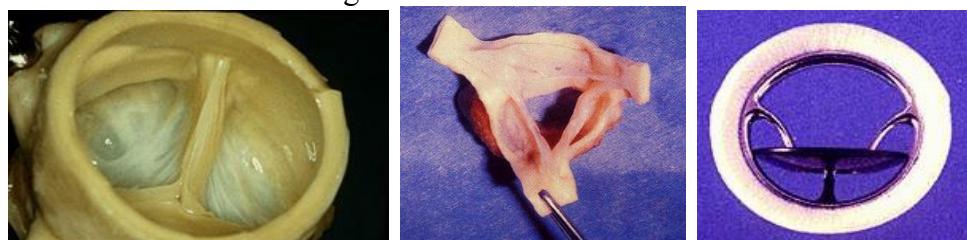


Figure 12.13. Face/Nose Lift



Figure 12.14. Heart Valves



12.5. Ceramics



Ceramics can be defined as heat-resistant, nonmetallic, inorganic solids that are (generally) made up of compounds formed from metallic and nonmetallic elements. Although different types of ceramics can have very different properties, in general ceramics are corrosion-resistant and hard, but brittle. Most ceramics are also good insulators and can withstand high temperatures. These properties have led to their use in virtually every aspect of modern life.

12.5.1. Main Categories of Ceramics

The two main categories of ceramics are **traditional** and **advanced**. **Traditional ceramics** include objects made of clay and cements that have been hardened by heating at high temperatures. Traditional ceramics are used in dishes, crockery, flowerpots, and roof and wall tiles. **Advanced ceramics** include carbides, such as silicon carbide, SiC; oxides, such as aluminum oxide, Al_2O_3 ; nitrides, such as silicon nitride, Si_3N_4 ; and many other materials, including the mixed oxide ceramics that can act as superconductors. Advanced ceramics require modern processing techniques, and the development of these techniques has led to advances in medicine and engineering.

Glass is sometimes considered a type of ceramic. However, glasses and ceramics differ in that ceramics have a crystalline structure while glasses contain impurities that prevent **crystallization**. The structure of glasses is amorphous, like that of liquids. Ceramics tend to have high, well-defined melting points, while glasses tend to soften over a range of temperatures before becoming liquids. In addition, most ceramics are opaque to visible light, and glasses tend to be translucent. Glass ceramics have a structure that consists of many tiny crystalline regions within a noncrystalline matrix. This structure gives them some properties of ceramics and some of glasses. In general, glass ceramics expand less when heated than most glasses, making them useful in windows, for wood stoves, or as radiant glass-ceramic cook top surfaces.

12.5.2. Composition

Some ceramics are composed of only two elements. For example, alumina is aluminum oxide, Al_2O_3 ; zirconia is zirconium oxide, ZrO_2 ; and quartz is silicon dioxide, SiO_2 . Other ceramic materials, including many minerals, have complex and even variable compositions. For example, the ceramic mineral feldspar, one of the components of granite, has the formula KAlSi_3O_8 .

The chemical bonds in ceramics can be covalent, ionic, or polar covalent, depending on the chemical composition of the ceramic. When the components of the ceramic are a **metal** and a nonmetal, the bonding is primarily ionic; examples are magnesium oxide (magnesia), MgO , and barium titanate, BaTiO_3 . In ceramics composed of a **metalloid** and a nonmetal, bonding is primarily covalent; examples are boron nitride, BN, and silicon carbide, SiC. Most ceramics have a highly crystalline structure, in which a three-dimensional unit, called a unit cell, is repeated throughout the material. For example, magnesium oxide crystallizes in the rock salt structure. In this structure, Mg^{2+} ions alternate with O^{2-} ions along each **perpendicular** axis.

12.5.3. Manufacture of Advanced Ceramics

The preparation of an advanced ceramic material usually begins with a finely divided powder that is mixed with an organic binder to help the powder consolidate, so that it can be molded into the desired shape. Before it is fired, the ceramic body is called "green." The green body is first heated at a low temperature in order to decompose or oxidize the binder. It is then heated to a high temperature until it is "sintered," or hardened, into a dense, strong ceramic. At this time, individual particles of the original powder fuse together as chemical bonds form between them. During sintering the ceramic may shrink by as much as 10 to 40 percent. Because shrinkage is not uniform, additional machining of the ceramic may be required in order to obtain a precise shape.

Sol-gel technology allows better mixing of the ceramic components at the molecular level, and hence yields more **homogeneous** ceramics, because the ions are mixed while in solution. In the sol-gel process, a solution of an **organometallic compound** is hydrolyzed to produce a "sol," a colloidal suspension of a solid in a liquid. Typically the solution is a metal alkoxide such as tetramethoxysilane in an alcohol solvent. The sol forms when the individual formula units polymerize (link together to form chains and networks). The sol can then be spread into a thin film, precipitated into tiny uniform spheres called microspheres, or further processed to form a gel inside a mold that will yield a final ceramic object in the desired shape. The many crosslinks between the formula units result in a ceramic that is less brittle than typical ceramics.

Although the sol-gel process is very expensive, it has many advantages, including low temperature requirements; the ceramist's ability to control porosity and to form films, spheres, and other structures that are difficult to form in molds; and the attainment of specialized ceramic compositions and high product purity.

Porous ceramics are made by the sol-gel process. These ceramics have spongelike structures, with many porelike lacunae, or openings, that can make up from 25 to 70 percent of the volume. The pore size can be large, or as small as 50 nanometers (2×10^{-6} inches) in diameter. Because of the large number of pores, porous ceramics have enormous surface areas (up to 500 square meters, or 5,382 square feet, per gram of ceramic), and so can make excellent catalysts. For example, zirconium oxide is a ceramic oxygen sensor that monitors the air-to-fuel ratio in the exhaust systems of automobiles.

Aerogels are solid foams prepared by removing the liquid from the gel during a sol-gel process at high temperatures and low pressures. Because aerogels are good insulators, have very low densities, and do not melt at high temperatures, they are attractive for use in spacecraft.

12.5.4. Properties and Uses

For centuries ceramics were used by those who had little knowledge of their structure. Today, understanding of the structure and properties of ceramics is making it possible to design and engineer new kinds of ceramics.

Most ceramics are hard, chemically **inert**, refractory (can withstand very high heat without deformation), and poor conductors of heat and electricity. Ceramics also have low densities. These properties make ceramics attractive for many applications. Ceramics are used as refractories in furnaces and as durable building materials (in the form of bricks, tiles, cinder blocks, and other hard, strong solids). They are also used as common electrical and thermal insulators in the manufacture of spark plugs, telephone poles, electronic devices, and the nose cones of spacecraft. However, ceramics also tend to be brittle. A major difficulty with the use of ceramics is their tendency to acquire tiny cracks that slowly become larger until the material falls apart. To prevent ceramic materials from cracking, they are often applied as coatings on inexpensive materials that are resistant to cracks. For example, engine parts are sometimes coated with ceramics to reduce heat transfer.

Composite materials that contain ceramic fibers embedded in polymer matrices possess many of the properties of ceramics; these materials have low densities and are resistant to corrosion, yet are tough and flexible rather than brittle. They are used in tennis rackets, bicycles, and automobiles. Ceramic composites may also be made from two distinct ceramic materials that exist as two separate ceramic phases in the composite material. Cracks generated in one phase will not be transferred to the other. As a result, the resistance of the composite material to cracking is considerable. Composite ceramics made from diborides and/or carbides of zirconium and hafnium mixed with silicon carbide are used to create the

nose cones of spacecraft. Break-resistant cookware (with outstanding thermal shock resistance) is also made from ceramic composites.

Although most ceramics are thermal and electrical insulators, some, such as cubic boron nitride, are good conductors of heat, and others, such as rhenium oxide, conduct electricity as well as metals. Indium tin oxide is a transparent ceramic that conducts electricity and is used to make liquid crystal calculator displays. Some ceramics are semiconductors, with conductivities that become enhanced as the temperature increases. For example, silicon carbide, SiC, is used as a semiconductor material in high temperature applications.

High temperature superconductors are ceramic materials consisting of complex ionic oxides that become superconducting when cooled by liquid nitrogen. That is, they lose all resistance to electrical current. One example is the material $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, which crystallizes to form "sheets" of copper and oxygen atoms that can carry electrical current in the planes of the sheets.

Some ceramics, such as barium ferrite or nickel zinc ferrites, are magnetic materials that provide stronger magnetic fields, weigh less, and cost less than metal magnets. They are made by heating powdered ferrite in a magnetic field under high pressure until it hardens. Ceramic magnets are brittle, but are often used in computers and microwave devices.

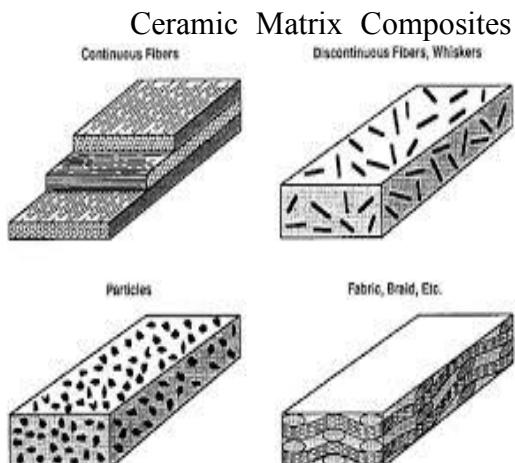
The properties of piezoelectric ceramics are modified when **voltage** is applied to them, making them useful as sensors and buzzers. For example, lead zirconium titanate is a piezoelectric ceramic used to provide "muscle action" in robot limbs in response to electrical signals.

Some ceramics are transparent to light of specific frequencies. These optical ceramics are used as windows for infrared and ultraviolet sensors and in radar installations. However, optical ceramics are not as widely used as glass materials in applications in which visible light must be transmitted. An electro-optic ceramic such as lead lanthanum zirconate titanate is a material whose ability to transmit light is altered by an applied voltage. These electro-optic materials are used in color filters and protective goggles, as well as in memory-storage devices.

Still other ceramics are important in medicine. For example, they are used to fabricate artificial bones and to crown damaged teeth. The fact that many ceramics can be easily sterilized and are chemically inert makes ceramic microspheres made of these materials useful as biosensors. Drugs and other chemicals can be carried within microsphere pores to desired sites in the body.

12.5.5. Ceramics Matrix Composite (CMC)

Ceramic Matrix Composite (CMC) is a material consisting of a ceramic matrix combined with a ceramic (oxides, carbides) dispersed phase.



Ceramic Matrix Composites are designed to improve toughness of conventional ceramics, the main disadvantage of which is brittleness. Ceramic Matrix Composites are reinforced by either continuous (long) fibers or discontinuous (short) fibers.

Short-fiber (discontinuous) composites are produced by conventional ceramic processes from an oxide (alumina) or non-oxide (silicon carbide) ceramic matrix reinforced by whiskers of silicon carbide (SiC), titanium boride (TiB_2), aluminum nitride (AlN), zirconium oxide (ZrO_2) and other ceramic

fibers. Most of CMC are reinforced by silicon carbide fibers due to their high strength and stiffness (modulus of elasticity).

Whiskers incorporated in a short-fiber Ceramic Matrix Composite improve its toughness resisting to cracks propagation. However a character of failure of short-fiber reinforced materials is catastrophic.

Long-fiber (continuous) composites are reinforced either by long monofilament or long multifilament fibers.

The best strengthening effect is provided by dispersed phase in form of continuous monofilament fibers, which are fabricated by chemical vapor deposition (CVD) of silicon carbide on a substrate made of tungsten (W) or carbon (C) fibers.

Monofilament fibers produce stronger interfacial bonding with the matrix material improving its toughness.

Failure of long-fiber Ceramic Matrix Composites is not catastrophic.



12.5.6. Ceramic Superconductors

Superconductivity is the complete disappearance of electric resistance in materials that are cooled to extremely low temperatures. The temperature at which resistance ceases is referred to as the transition temperature, or critical temperature (T_c). T_c is usually measured in degrees kelvin (K)—0 K being absolute zero, the temperature at which all atomic motion ceases. The best ceramic conductors are the so-called high T_c superconductors, materials that lose their resistance at much higher critical temperatures than their metal alloy counterparts. Most high T_c ceramics are layered structures, with two-dimensional copper-oxygen sheets along which superconduction takes place. The first of these was discovered in 1986 by the Swiss researchers J. Georg Bednorz and Karl Alex Müller. Within a year an yttrium barium copper oxide ceramic, $\text{YBa}_2\text{Cu}_3\text{O}_7$, had been discovered to have a T_c higher than 77 K, the boiling point of nitrogen (-195.8°C , or -320.4°F). This finding raised the possibility of practical superconductors being cooled by liquid nitrogen—as opposed to conventional superconducting materials, which have to be cooled by more expensive liquid helium. (The crystal structure of $\text{YBa}_2\text{Cu}_3\text{O}_7$ is described in the article ceramic composition and properties: Crystal structure, where it is illustrated in Figure 18.15.)

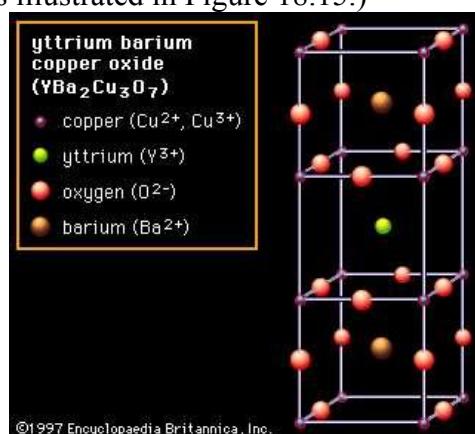


Figure 12.15. The arrangement of copper, yttrium, oxygen, and barium ions in yttrium barium copper oxide ($\text{YBa}_2\text{Cu}_3\text{O}_7$); an example of a superconducting ceramic crystal structure.

Although still higher transition temperatures have since been achieved, ceramic superconductors are difficult to process (in contrast to metal alloy superconductors), and they are notoriously brittle—properties that have limited their application. In hospitals and clinics small superconducting magnets are used in magnetic resonance imaging (MRI) apparatuses, where they generate the large magnetic fields necessary to excite and then image atomic nuclei in body tissues. Potential applications include wires for highly efficient superconducting magnets and low-loss electric power transmission lines, as well as advanced devices such as Josephson junctions and so-called SQUIDs (superconducting quantum interference devices). Josephson junctions, formed at contacts between two superconductors, can convert a direct voltage into an alternating current whose frequency rises with applied voltage. Frequencies in the superhigh frequency (SHF) range can be achieved. SQUIDs are highly sensitive magnetic-field sensors based on a superconducting ring with a weak link, a point where the material reverts to its normal, nonsuperconducting state at a small current relative to the rest of the ring. SQUIDs are widely used in geophysics for measuring magnetic field oscillations of the Earth. They also are used to record magnetograms of organs in the human body.

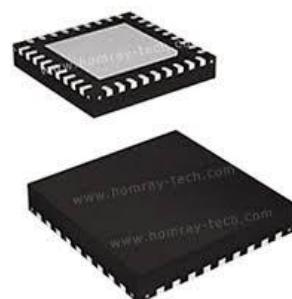


Figure 8.16. Gallium Arsenide Integrated Circuit Mounted on a Ceramic Support

12.6. Thin Films

Nowadays, most of the technologies are used for minimizing the materials into nano-size as well as nano-thickness leading to the emergence of new and unique behaviors of such materials in optical, electrical, optoelectronic, dielectric applications, and so on. Hence, a new branch of science/materials science is called thin films or coatings. Thin film can be defined as a thin layer of material, where the thickness is varied from several nanometers to few micrometers. Like all materials, the structure of thin films is divided into amorphous and polycrystalline structure depending on the preparation conditions as well as the material nature. Thin films comprise two parts: the layer and the substrate where the films are deposited on it. Also, thin films can be composed of different layers such as thin-film solar cells, electrochromic cells, and so on.

In order to obtain thin films with good quality, there are two common deposition techniques: physical and chemical depositions. It can be summarized as shown in Table 12.9.

Table 12.9. Methods of Thin Films Deposition

| | |
|-----------------------------|---------------------------|
| Physical deposition | Chemical deposition |
| Evaporation techniques | Sol-gel technique |
| Vacuum thermal evaporation. | Chemical bath deposition |
| Electron beam evaporation. | Spray pyrolysis technique |

| | |
|---|---------------------------------|
| Physical deposition | Chemical deposition |
| Laser beam evaporation. | Plating |
| Arc evaporation. | Electroplating technique. |
| Molecular beam epitaxy. | Electroless deposition. |
| Ion plating evaporation. | Chemical vapor deposition (CVD) |
| Sputtering techniques | Low pressure (LPCVD) |
| Direct current sputtering (DC sputtering). | Plasma enhanced (PECVD) |
| Radio frequency sputtering (RF sputtering). | Atomic layer deposition (ALD) |

12.6.1. Physical Deposition Techniques

12.6.1.1. Evaporation Techniques

Evaporation methods are considered as the common deposition of materials in the form of thin-layer films. The general mechanism of these methods is obtained by changing the phase of the material from solid phase to vapor phase and converting again to solid phase on the specific substrate. It takes place under vacuum or controlled atmospheric condition.

12.6.1.2. Vacuum Thermal Evaporation Techniques

Vacuum evaporation technique is the simplest technique used to prepare amorphous thin films especially chalcogenide films such as CdSSe, MnS, Ge-Te-Ga, and so on. In general, chalcogenide materials can be used for memory-switching applications, phase-change materials, and solar applications.

The technique of thermal evaporation is strongly dependent on two parameters: thermally vaporized material and applying a potential difference to the substrate under medium- or higher-vacuum level ranging from 10^{-5} to 10^{-9} mbar. The schematic diagram for thermal evaporation is shown in Figure 18.17 taken from elsewhere.

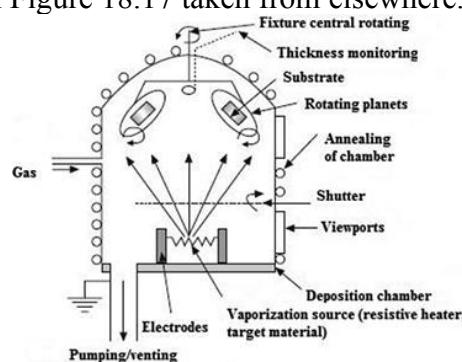


Figure 12.17. Schematic of thermal evaporation system with substrate holder (a) on a planetary rotation system and (b) directly above the evaporating source.

12.6.1.3. Electron Beam Evaporation

This type of evaporation is another method of physical deposition where the intensive beam of electrons is generated from a filament and steered through both electric and magnetic fields to hit the target and vaporize it under vacuum environment as shown in Figure 8.18. Thin films prepared by electron beam evaporation are of good quality and purity.

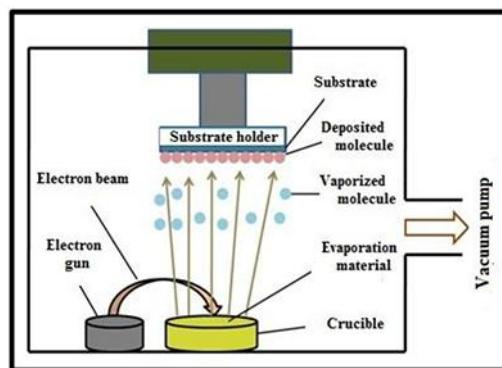


Figure 12.18. Schematic diagram of electron beam evaporation.

Large categories of materials can be prepared by electron beam evaporation technique such as amorphous and crystalline semiconductors, metals, oxides, and molecular materials.

12.6.1.4. Laser Beam Evaporation (Pulsed-laser Deposition)

Pulsed-laser deposition (PLD) is another physical deposition technique to deposit the thin-film-coating system. During the thin-film deposition process, the laser beam is used to ablate the material for depositing the thin films inside a vacuum chamber as shown in Figure 8.19.

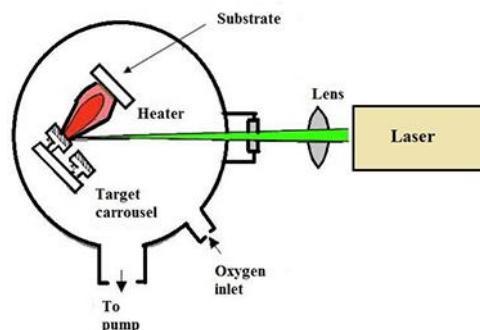


Figure 12.19. Schematic of pulsed-laser deposition

Different kinds of laser sources are being used to ablate the target. The most common sources are Nd-YAG laser, KrF (248 nm), and XeCl (308 nm). When the laser beam strikes the target material, it produces the plume which could deposit on the various substrates. The created plume may contain neutral- and ground-state atoms and ionized species. In the case of metal oxide thin films, oxygen is used to deposit the oxides of metals. The thin-film quality from the PLD depends on the various parameters such as wavelength of the laser, energy, ambient gas pressure, pulsed duration, and the distance of the target to the substrate. The ablation process during the deposition may control and monitor by using laser-induced fluorescence, laser ablation molecular isotopic spectroscopy, and optical emission spectroscopy. The morphology of the deposited thin films is also affected by the substrate temperature. The coating of thin films through PLD follows three modes: Frank--van der Merwe, Stranski--Krastanov, and Volmer--Weber. PLD has some advantages over other physical deposition systems because of its fast deposition time and its compatibility to oxygen and other inert gases.

12.6.1.5. Sputtering Technique

Sputtering technique is mostly used for depositing metal and oxide films by controlling the crystalline structure and surface roughness. The simple form of the sputtering system consists of an evacuated chamber containing metallic anode and cathode in order to obtain a glow discharge in the residual gas in the chamber. Also, an applied voltage in the order of several KeV with pressure more than 0.01 mbar is sufficient for film deposition. The sputtering process depends on the bombardment of the ions released from the discharge to the molecules in the cathode leading to the liberation of the molecules from the cathode with higher kinetic energy. The atomic weight of the bombarding ions should be nearly to that of the target material in order to maximize the momentum transfer. These molecules move in straight lines and strike on the anode or on the substrate to form a dense thin film. The diagram of the sputtering system is shown in Figure 8.20.

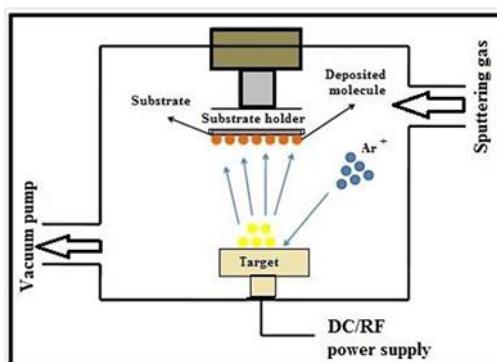


Figure 12.20. Sputtering System Diagram

The process of sputtering has several advantages. High-melting point materials can be easily formed by sputtering. The deposited films have composition similar to the composition of the starting materials. Sputtering technique is available to use for ultrahigh vacuum applications. The sputtering sources are compatible with reactive gases such as oxygen. Contrarily, thick coatings cannot be obtained and there is a difficulty to deposit uniformly on complex shapes.

There are two common types of sputtering process: direct current (DC) and radio frequency (RF) sputtering. The first one depends on DC power, which is generally used with electrically conductive target materials. It is easy to control with low-cost option. The RF sputtering uses RF power for most dielectric materials. A common example for sputtered films is aluminum nitride films. These films were prepared by both DC- and RF-sputtering technique, and their structure and optical properties were compared

12.6.1.6. Chemical Deposition Technique

Although the production of thin films via physical methods as previously described gives good quality and functionalizes properties, it is highly expensive and perhaps requires a large amount of material target. Since the need to produce good-quality thin films with low economical cost is necessary, chemical deposition techniques are widely used globally. These techniques are cheap producing good-quality films. Most of them do not require expensive equipment. The chemical deposition is strongly dependent on the chemistry of solutions, pH value, viscosity, and so on. The most common chemical deposition has been obtained via sol-gel route, chemical bath deposition, electrodeposition, chemical vapor deposition (CVD), and spray pyrolysis technique. This section is concerned only on sol-gel and chemical bath deposition techniques because they can form good film quality with low equipment requirement.

12.6.1.7. Sol-gel Technique

The sol-gel technique is broadly used for the synthesis of oxide materials. Sol-gel process is one of the famous wet-chemical methods. It works under lower-temperature processing and gives better homogeneity for multicomponent materials. The word “sol” means the formation of a colloidal suspension and ‘gel’ means the conversion of ‘sol’ to viscous gels or solid materials. Two routes are used to prepare transition metal oxides (TMOs) as follows:

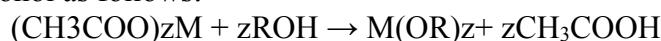
Preparing of inorganic precursors via inorganic salts in aqueous solution.

Preparing of metal alkoxide precursors via metal alkoxides in nonaqueous solvents.

In this section, we are concerned on the famous route “the metal alkoxide precursor solution by an alcoholic solution.”

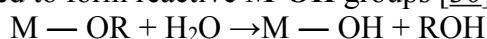
12.6.1.7.1. Alkoxide Precursors in Organic Solvents

The sol-gel technique is based on the polycondensation of metal alkoxides **M(OR)_z** in which **R** represents an alkyl group ($R = CH_3, C_2H_5, \dots$) and **z** is the oxidation state of the metal atom **M^{z+}**. It can be synthesized via the reaction of metal salt (chloride, acetate, nitrate, etc.) with alcohol as follows:



After this process, two important steps should be involved:

Hydrolysis: this step is aimed to form reactive **M-OH** groups [30]:



Condensation: condensation is the second step after hydrolysis leading to the departure of a water molecule. The process of condensation can be either olation process or oxolation process.

Olation: a hydroxyl bridge ("ol" bridge) is formed between two metal centers.

Oxolation: oxolation is a reaction in which an oxo bridge (—O—) is created between two metal centers. When the metal is coordinately unsaturated, oxolation with rapid kinetics leads to edge- or face-shared polyhedral as shown in Figure 8.21.

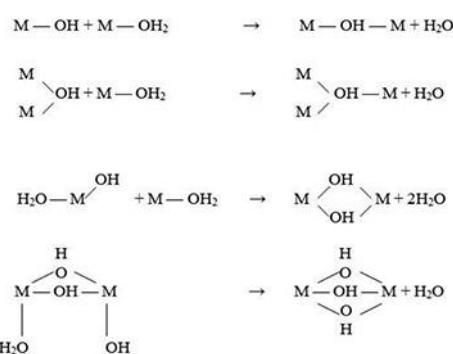


Figure 12.21. Several types of OH bridges can be formed by olation condensation process.

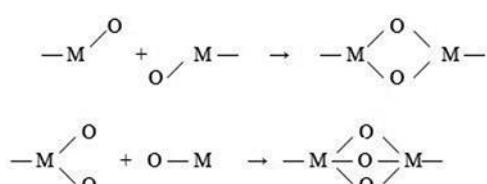


Figure 12.22. Formation of oxo-bridging links between two metal centers.

12.6.1.8. Dip-Coating Technique

Dip-coating technique is almost used to fabricate transparent layers of oxides on a transparent substrate with a high degree of planarity and surface quality. Other substrates are also possible to use. Well-defined film thicknesses up to 1 μm can be deposited. Several additive layers can be superimposed.

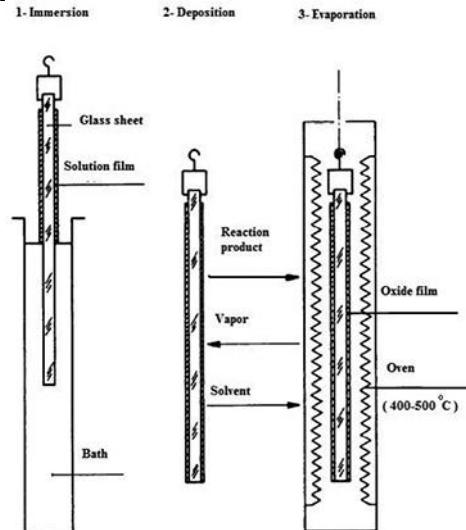
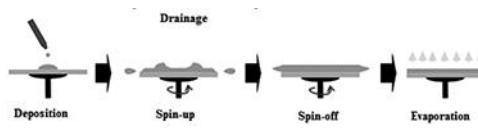


Figure 12.23. Dip-coating process levels.

Scriven described the dip-coating process in five stages: immersion, start-up, deposition, drainage, and evaporation. Hence, the evaporation normally accompanies the start-up, deposition, and drainage steps as shown in Figure 8.23.

12.6.1.9. Spin-coating Technique

Another technique is also available for usage after the precursor solution is prepared known as spin coating or spinning. The solution is dripped onto a spinning substrate and spreads evenly. The spinning process is most suitable for the coating of small disks or lenses but is not very economical. The process of spinning film can be described as shown in Figure 12.24.



2.24 Spin-coating process.

12.6.1.10. Chemical Bath Deposition Technique

Chemical bath deposition method is also known as solution growth technique or controlled precipitations. It is the oldest method to deposit films on a substrate. Solution growth technique is mostly used to prepare chalcogenide films as well as metal oxide films. Also, the deposition can be performed at lower temperatures. In the solution growth method, the precursor solution of metal ions must be complexed by ligands. The complex solution is almost obtained with ammonia solution, triethanol amine, ethylene-diamine-tetraacetic acid (EDTA), citric acid, and so on. When the complexation is completed, the addition of the

anions should take place. These anions come from the thiourea, thioacetamide, thiosulfate, and sodium Sulfide solutions as sources of sulfur anions or selenourea and sodium selenosulfate for selenium anions to deposit the chalcogenides. Substrates are put in vertical, horizontal, or specific position inside the solution and left until the desired film thickness is obtained. The deposition of oxide films is quite different than chalcogenides. After making the complexation by controlling the pH value, the substrate is immersed in the solution under the desired temperature varied in the range 60°–100 °C to deposit in most cases the metal hydroxide films. The hydroxide film can then be transferred to oxide by the annealing process. Figure 12.25 represents the simple chemical bath deposition method. Indeed, much reviews and literature, which describes the chemical bath deposition for both chalcogenide and oxide films, are found elsewhere.

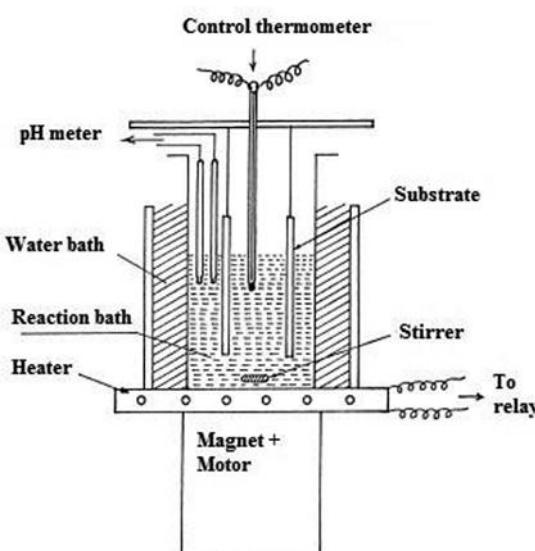


Figure 12.25. Home-made chemical bath deposition technique.

12.7. Nanomaterials

Nanotechnology offers attractive opportunities in the food industry such as for food safety and quality control as well as the production of new food additives/supplements and other flavors. In the food industry, nanotechnology can also be used for the production of packages with enhanced thermal and/or mechanical properties and safety. Indeed, nanosensors embedded in food packaging systems are used to alert consumers when foods have expired. Nanotechnology can also be used to make healthier foods. The variety of nanostructures with diverse properties makes them suitable for addition to foods as well as in packaging products that enhance the nutritional quality of foods. Out of 633 available nanomaterials, 55 are exploited in agriculture and food sciences. A recent report pointed out that food products linked to nanotechnology will account for around 50% of total food products in 2020.

Undoubtedly, nanotechnology is revolutionizing the food industry. Most of the reported applications of nanostructures in food include (i) the improvement of food quality, (ii) bioactive fortification, (iii) controlled release of bioactive compounds using nanocarrier encapsulation, (iv) modification of food structures and textures, and (v) the detection and neutralization of biochemical, microbiological and chemical alterations using intelligent packaging systems Figure 18.26. Different nanomaterials have vast applications in the formation of food products and the improvement of nutritional values. For example, protein nanoparticles are used in the manufacture of food products because protein solubility is

helpful in the assembly of protein nanoparticles with preferred functional properties in food substances

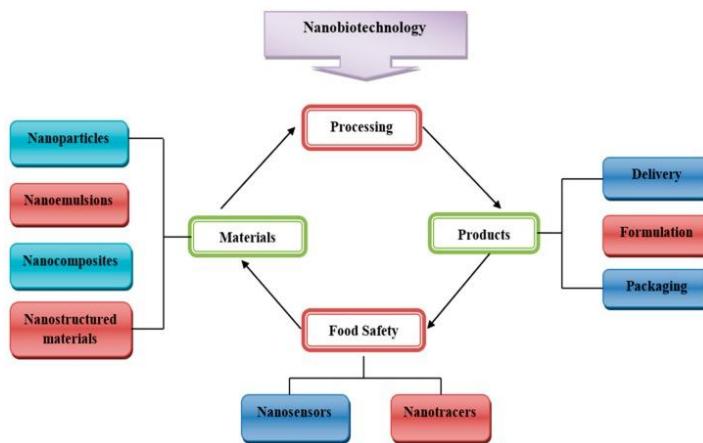


Figure 12.26. Role of nanotechnology in various sectors of the food industry.

Currently, the principle applications of nanotechnology in the food sector are mainly related to food nanosensing and nanostructured food ingredients. Nanostructured food ingredients include food formulation or food packaging. For a better assessment of quality and safety, food nanodetection is applied for better results. In food packaging, conventional materials are being replaced by nanopolymers. The modern characteristics of nanotechnology allow the development of new, functional foods in the food industry. New nanomaterial-based engineering approaches for the targeted distribution of nutrients and bioactive compounds in functional foods is another potential application of nanotechnology. The development of nanocapsules, nanocarriers, nanotubes, nanosensors and nanopackages are new opportunities for nanotechnology in the food industry. This review presents recent developments in nanobiotechnology to enhance food safety and/or quality, with a special focus on the toxicity and health issues related to the consumption of these nanoparticles in food. A concise overview from the regulatory point of view is also addressed.

12.7.1. Different Aspects and Roles of Nanotechnology in the Food Industry

There is an increasing interest in nanotechnology in the food industry. Several applications have been reported in various dimensions, such as the targeted delivery of nutrients and/or bioactive molecules through nanoencapsulation, the use of biosensors to detect and quantify pathogens and alteration of food composition, or fruit and vegetable preservation by edible films Table 8.10.

Table 12.10 An overview of various applications of nanomaterials in the food industry.

| Nanomaterials | Type of Nanomaterials | Applications in Food Industry | References |
|----------------|---|---|------------|
| Nanoparticles | Ag, ZnO, Mg, SiO ₂ | Food packaging, oxidation of contaminant, anti-bacterial | [12,13,14] |
| Nanosieves | Specific nanoparticles | Removal of pathogens or contaminants | [15,16] |
| Nanocapsules | Bioactive compounds | Increased efficacy and water solubility, local and controlled release | [17,18] |
| Nano-emulsions | Tweens or spans; gum arabica or modified starch, soy, caseinate | Food encapsulation, food processing, antimicrobial and storage, stability, colorant | [19,20,21] |
| Nanospheres | Starch nanosphere | Food encapsulation, synthetic adhesives | [22,23,24] |
| Nanosensors | Aptasensors | Detection of micro-organisms, food deterioration control | [25,26,27] |
| Nanocochleates | Coiled Nanoparticles | Enhanced nutritional value of food, antioxidant, food protection and stability | [28,29,30] |
| Nanocomposite | Fe-Cr/Al ₂ O ₃ Ni/Al ₂ O ₃ | Enhanced shelf life of food, food protection and food packaging | [31,32,33] |
| Nanomicelles | Aquanova, novasol | Liquid carrier, enhanced solubility | [34,35,36] |

Potential applications of nanotechnology in the food chain include food storage, food quality control, food formulation and food packaging Figure 18.27.

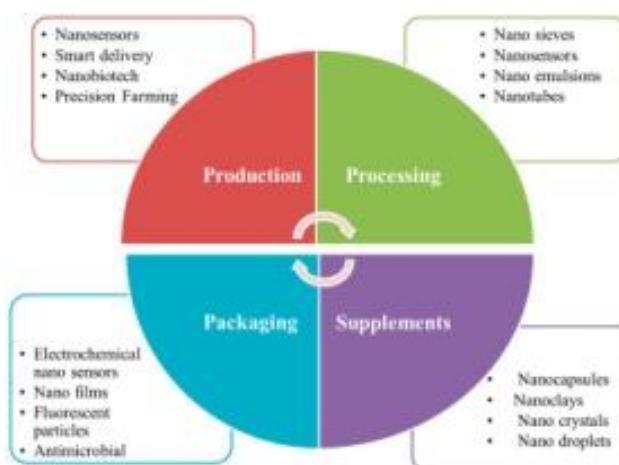


Figure 12.27. An overview of applications of nanomaterials in the food industry.

In the food industry, production processes are enhanced by nanotechnology, which provides products with better characteristics as well as with new functionalities.

The use of nanotechnologies can be considered from the production phase, which allows a technical innovation in precision agriculture to improve plant growth, but also the detection of and/or resistance to pests and allelopathy. The nanoencapsulation of conventional fertilizers, pesticides and herbicides allows (i) a slower and longer release of nutrients for more efficient use, allowing the optimal growth of plants; while, for agrochemical products, (ii) it allows safer handling, more efficient usage and a more precise dosage of these compounds with less exposure to the environment, thus guaranteeing the better protection of the environment. In addition, the rapid and early detection of plant diseases based on nanotechnology is also attracting attention. The potential uses and benefits

of nanotechnology in precision farming are discussed in detail by Anjum et al. and Duhan et al.

Nanotechnology is also used in food processing and preservation. This application offers a protective barrier to mask different tastes and flavors. Nanotechnology also provides food ingredients as well as water-insoluble food supplements with controlled release and improved dispersibility. The benefits of nanotechnology in food processing include the development of a complete texture for food components, the encapsulation of food additives, the development of new flavors and sensations, and the control of aroma release with increased bioavailability in dietary supplements.

Nanotechnology has revolutionized the food industry by designing innovative delivery systems for the production of nano-formulated agrochemicals, improving nutritional values and generating new products through bioactive encapsulation. Nanoencapsulation clearly improves the nutritional values of the product. Indeed, at the nanoscale, the processing of food ingredients allows an improvement of aromas, textures or new tastes, but also enhances nutritional values. Nanoparticles have improved characteristics for product encapsulation as well as a higher release efficiency than conventional encapsulation approaches. Nanomaterial encapsulations protect food products from heat or moisture while controlling the active release of food ingredients and their interaction with other materials in the food matrix. For example, liposomes are delivery vectors for hydrophobic molecules, and nano-emulsions improve oral bioavailability. Nanocochleates are used to deliver nutrients more efficiently to cells without disturbing the taste or color of food. However, self-assembled nanoscale liquid structures are used as vehicles and are called dilated micelles; their size is less than 30 nm. They have been used for the delivery of nutraceuticals and beverages. Potential applications containing lycopene, omega-3 fatty acids, β-carotene and isoflavones are targeted. The American company, Fresh Corporation, has launched an innovative nanoceramic that allows the nano-drying of food, which halves the use of oil in fast food and restaurants because of its immense surface. Therefore, nanoencapsulation allows a precise (bio) availability of the product with a specific rate for the target time.

Recently, industrial applications of food nanotechnology have ranged from intelligent packaging to the creation of interactive food. Active packaging is one of the modern terms used for packaging food items in which the packaged foodstuff status changes to improve the sensory quality as well as safety of food products, increasing shelf life by maintaining the quality of food products. Advanced food packaging and nano-based systems minimize food losses due to different microbial infections. Different nanoparticles such as titanium dioxide, magnesium oxide, zinc oxide, silver nanoparticles, carbon nanotubes, fullerene derivatives and zerovalent iron have shown great impacts as antimicrobial agents.

Furthermore, the use of specific nanomaterials to detect/eliminate harmful chemicals/pathogens in food products has recently been developed. In advanced food packaging, an integrated electronic tongue contains a collection of nanosensors that are particularly sensitive to the gases released from food waste; this gives a clear and visible signal indicating whether the food is fresh or not, using a sensor strip that changes color. For the rapid detection of food-borne pathogens, magnetic oxide nanoparticles are also used in the food industry. Nanosensors detect microorganisms, toxic substances and contaminants present in different foodstuffs because of their high detection capacity, which is useful for the safety of food products.

The applications of nanotechnology in the food industry promote innovations in different dimensions of food items, including texture, taste, sensory attributes, the color strength of products, and the stability/shelf life of products.

12.7.2. Applications as Food Additives and Food Ingredients

Basically, the ingested food components are carbohydrates, proteins and lipids. However, a common factor between them is the digestion of their components, which occurs at the nanoscale. On this basis, it could be argued that food processing at the nanoscale would only increase the efficiency or speed of digestion, bioavailability, metabolism and absorption in the human body. Obviously, within the food market, there are supplements available that have tri- and di-peptides and are thus further voluntarily digestible. On the contrary, it might be claimed that the processing of substances at this scale frequently changes their properties, rather than processing at the nanoscale level. This important issue needs additional research as it drives significant regulatory questions about modifications in properties.

12.7.3. Nanomaterial in Food Processing

Some food ingredients that work on the nanoscale or are termed as nanostructured have different properties as they improve texture, consistency and taste, etc. Various types of food nanotechnology have been involved in improving shelf life. Today, nanocarriers are used in the same way as delivery structures for different flavors of food in food yields without manipulating the morphology Figure 18.28. Particle sizes might openly influence the supply of bioactive complex to numerous sites inside the body; for example, it was observed that the submicron particles can only work on the nanoscale. A perfect delivery method is comprised of the following:

The ability to bring energetic material specifically to the target position;

Confirming the accessibility of the target period along with a definite rate;

Efficiency at keeping compounds that are active at appropriate levels for extended phases of time (storage state). Nanotechnology is functional in the development of emulsions, encapsulations, simple solutions, the association of colloids biopolymer matrices, and well-organized delivery organizations with the above-mentioned abilities.

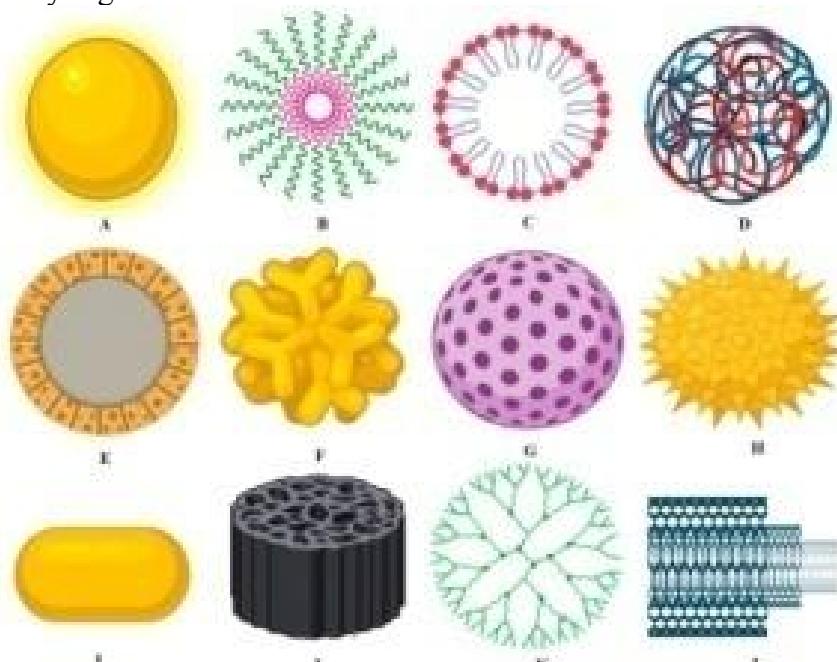


Figure 12.28. Graphical representation of different types of nanomaterials used in the food industry. (A) Metallic nanoparticles, (B) Polymeric micelle, (C) Liposomes nanoparticles, (D) Polymeric nanoparticles, (E) Solid-core mesoporous nanoparticles, (F) Branched gold

nanoparticles, (G) Mesoporous nanoparticles, (H) Surface functionalized nanoparticles, (I) Nanorod, (J) Porous silica nanoparticles, (K) Dendrimer, (L) Carbon

Nanoparticles have enhanced capabilities such as release efficiency and encapsulation properties when compared with traditional encapsulation methods. Nanoencapsulation covers tastes and the odor control connections of potent ingredients by means of the food matrix, release of active compounds, confirmation of the availability of the target time, and protection from different sources of contamination such as heat, moisture, biological and chemical degradation during storage, processing and utilization.

These nanoparticles also show compatibility when compared with other compounds in the system. Furthermore, these delivery classifications retain the capability to enter into tissues owing to their small size and thus permit the well-organized distribution of active complexes to mark sites in body. Various artificial and ordinary polymer-based encapsulation delivery classifications have been explained for better-quality bioavailability as well as the protection of active components of food. Moreover, the significance of nanotechnology such as in food processing can be estimated by seeing its role in the enhancement of food items.

12.7.4. Nanomaterials in Improving the Texture, Appearance, Taste and Nutritional Values of Food

Nanotechnology provides several opportunities for improvements in food value and taste. Nanoencapsulation methods are recycled largely for progressive taste release along with maintaining a culinary balance. Nanoencapsulation is used for extremely reactive plant pigments that are unstable, such as anthocyanins. Photostability and thermal stability can be improved by encapsulating such molecules as cyanidin-3-O-glucoside inside the middle cavity of recombinant soybean kernel. H-2 subunit ferritin (rH-2) enhances photostability and thermal stability. **Rutin** is considered to be a dietary flavonoid with abundant significant pharmacological properties, but owing to its reduced solubility, its utilization in the food industry is less common. The encapsulation of ferritin nanocages improved the thermal, UV radiation and firmness properties of ferritin-confined rutin as related to unattached rutin. The usage of nano-emulsions to create lipid-soluble compounds that are bioactive is much more common, as it has also found applications in improving bioavailability and water-dispersion.

The majority of bioactive complexes, such as carbohydrates, lipids, vitamins and proteins, are fragile in a highly acidic environment along with enzyme action in the duodenum and stomach. Bioactive multifarious encapsulation not only allows them to fight that difficult situation but permits them to adjust willingly into food goods. This phenomenon is quite difficult to attain by the usage of non-capsulated bioactive compounds that have less solubility. To enhance the delivery of vitamins, fragile micronutrients, and medicines, currently, small edible capsules coated with nanoparticles are used in daily foods to provide beneficial health effects.

12.7.5. Nanomaterials in Food Packaging

Packaging plays an essential role in the modern food industry. However, the most valuable process in the preservation of food products is the improvement in quality from production to consumption. Nanotechnology applications in the food packaging field offer novel promises for improvements in the efficiency of foodstuff packages Figure 12.29. Many nanoparticles are produced and used in the industry due to their encapsulation ability in active compounds and enhancement of functionality, stability, and bioavailability. Nanofillers are also used in food packaging due to their desired functions as well as applications in the packaging of food. In biosensors, nanofillers not only shelter food from environmental factors

but also integrate properties in packaging materials and permit numerous potential opportunities in the food packaging industry.

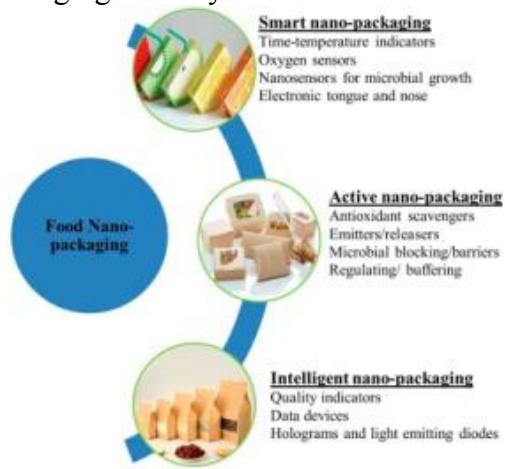


Figure 12.29. Classification of food nanopackaging

Zinc oxide is a nanocomposite material which is used in the active packaging of food materials as it has an antioxidant effect, which is important for the food industry. The main degradation reaction is the oxidation that occurs in food, limiting its preservation. Antioxidants are incorporated in the packaging material in the active packaging approach that maintains the preservation of food products. Not only are nanoparticles used in the antimicrobial packaging of food items, but nanocomposites along with nanolaminates also extensively used for the packaging of food. They are used to protect food from severe temperatures and mechanical stunning and to extend shelf life. The incorporation of nanoparticles into the packaging of food materials offers a longer shelf life and better quality of food.

The smart packaging of food constitutes active and intelligent packaging. Active packaging generally enhances the shelf life, and maintains and improves the packaged food. Bioactive packaging provides a positive impact for the health of consumers with the production of packaged foods which are good for health. A wide range of nanoparticles have antimicrobial effects and have attracted a great deal of attention in a series of applications in food packaging. Metal nanoparticles have been incorporated in polymer films of metal nanocomposites in a new generation of nano-food-packaging, which is based on the antimicrobial active packaging of food products; for example, silver nanoparticles are used for food packaging as an active system due to their antimicrobial activity. The most basic commercial applications of nanotechnology are in food packaging in the food industry. The incorporation of nanomaterials in food products improves the packaging properties including the flexibility as well as gas barrier properties, which is the most important application of nanotechnology in the food industry. Active packaging includes nanoparticles with antimicrobial and oxygen scavenging activities, smart packaging, and intelligent food packaging, including nanosensors which are intended to sense microbial as well as biochemical alterations and provide signals.

The packaging of numerous food items is improved through nanotechnology. New nanopackages for foodstuff acquire exclusive properties; i.e., they are capable of destroying microbes that are present in food substances. Nano materials used for the wrapping of food products enhance the existence of foodstuff products without causing any unwanted modification within the features of products. Nanoparticles are also used for the nanopackaging of food substances. This application of nanotechnology give solutions

intended for the packaging of food through modification in the penetration activities of foils, increasing the mechanical, chemical and microbial obstacle effects as well as resistant to heat.

Nanotechnology decreases environmental pollution by the production of biodegradable packaging. A silicate layer is a nanostructure that is used in the packaging of food products in the food industry. Improvements in the sensor technology present in the smart packaging of food material provide information on the quality and safety as well as the half-life of materials. Nanocomposites are also used in the packaging of food products. They have enhanced properties to resist thermal stress in food processing, as well as the transportation and storage of food products. Currently, nanocomposites are used in bottles of beer, enhancing their shelf life by up to 6 months. Carbon-based graphene nanoplates are resistant to heat and have potential applications in the packaging of food products in the food industry.

A technique is used by researchers known as sonochemical coating, which is a versatile and simple technique utilized for the creation of coating materials using ultrasonication. The coating has been verified to be fruitful against numerous bacterial strains (Gram positive *E. coli* or Gram negative *S. aureus* bacteria). The method has been verified to advance the production of materials which can help food to be conserved for an extended duration.

Silver nanoparticles are considered to be important particles for material packaging and are used for longer period of time. For example, substances that are covered by such particles are prevented from contamination. Many researchers have stated that silver nanoparticles have importance in research involving food packaging and in the food preservation industry, although only some methods of silver nanoparticles are certified by the EFSA (European Food Safety Authority) to be able to be recycled in food preservation and packaging. For everyday applications, zinc oxide is termed as a safe material, certified by FDA, and is considered as a food additive. Nanotechnology produces many antimicrobial agents with novel properties such as zinc oxide, magnesium oxide, nickel oxide and silver nanoparticles. These nanoparticles have shown potential applications and antimicrobial properties at the nanoscale. These nanoparticles are incorporated in matrices of polymers to provide good properties such as antimicrobial activity and enhance the properties of packaging.

12.7.6. Nanomaterials in the Preservation of Food

Different nanoparticles are used in the preservation of food. For example, zinc oxide exhibits antimicrobial activities along with inherent functions in the preservation of food. Nanotechnology is helpful in the preservation and maintenance of the quality of food products as well as improving the following characteristics: (1) product appearance, (2) the function of products, and (3) the nutritional and sensory attributes of products. Metallic nanoparticles such as silver nanoparticles are used not only for antimicrobial preservatives but have encouraging roles in preserving food products. Titanium dioxide is a white color enhancer in food products; for example, it is added in milk, cheeses, and other dairy products to enhance the white color appearance. The bioactive component becomes degraded and inactivated in functional foods, and the nanoencapsulation of bioactive constituents increases the shelf-life of food goods through a reduction in the process of degradation; otherwise, degradations are stopped until the product is brought to its intended place. Furthermore, edible nanocoatings for numerous foodstuff substances might produce an obstacle to gas interchange as well as creating flavors, colors, antioxidants, and anti-browning mediators as well as enzymes which also increase the shelf life of artificial foodstuffs. By changing the properties of the interfacial layer with the help of the encapsulation of nanoparticles, it is possible to decrease degradation.

12.7.7. Nanosensors as Emerging Devices in the Food Industry

Nanosensors are bioanalytical devices that are developed by using various nanostructured materials and biological receptors in an integrated system design. Nanosensors play an important role in the food industry and have attracted much attention in recent times due to their quick detection capacity, integrity and cost-effectiveness. Nanosensors have the potential to be integrated with an array of analytes due to their high sensitivity and specificity. These devices have a high surface-to-volume ratio and excellent optical and electric properties due to conjugation with various types of nanomaterials such as carbon nanotubes, nanoparticles (metallic, non-metallic and metal oxide), semiconductor nanoparticles, nanorods, nanowires, nanobiofilms, nanofibers, and quantum dots. Currently, nanosensors are being used in the detection of food-borne pathogens, adulterants, toxins, chemicals and pesticides which are present in different foodstuffs. They also used to monitor the freshness of food and food packaging integrity. Different types of techniques/methodologies such as cyclic voltammetry, surface plasmon resonance, differential pulse voltammetry, interdigitated array microelectrode-based impedance analysis, amperometry, flow injection analysis and bioluminescence are employed as nanobiosensing tools to rapidly and accurately detect different pathogens, toxins and adulterants present in foods. The potential applications of nanosensors in various sectors of the food industry are summarized in 18.10.

12.7.8. Nanosensors in the Detection of Toxins

The micro fluidic sensor is a type of nanosensor based on microfluidics along with liposomes, providing advantages in the detection of toxic substances in aqueous samples even within the micro liter range. Electrochemical sensors and biosensors based on novel nanomaterials such as carbon nanotubes (single and multi-walled), metallic nanoparticles (silver, gold, platinum, copper and zinc), and superparamagnetic nanoparticles are currently used in the detection of various toxins present in foodstuffs. A group of toxic and carcinogenic compounds known as aflatoxins have been found in food contaminated with *Aspergillus flavus* and *Aspergillus parasiticus*. Gold nanoparticles functionalized with anti-aflatoxin antibodies have been used for the detection of aflatoxin B1. Likewise, superparamagnetic beads containing anti-aflatoxin M1 antibodies and gold nanoprobe have also been used for the detection of aflatoxin M1 in milk samples. Similarly, gold nanoparticles acting as nanoprobe in enzyme-linked immunosorbent and immune-chromatographic assays have been used for the detection of botulinum neurotoxin type B and brevetoxins present in processed foods. Contaminated seafood generally contains marine toxin, namely palytoxin, which has also been detected by using carbon nanotube-based electrochemiluminescent sensors.

12.7.9. Nanosensors in the Detection of Food Pathogens

Foodborne pathogen detection in food materials is mainly achieved by identifying the bacterial genetic material or whole bacterial cell. The control of pathogens by using these conventional microbiological techniques is very reliable, but at the same time, it is very complicated. Nanotechnology allows the implementation of low-cost nanosensors in the packaging of food to detect different pathogenic microorganisms present in various food products. The nanobioluminescent spray, one of the most efficient nanobiosensors, produces a visual glow for the easy detection of pathogen strains in different food products. This spray is made up of different magnetic nanoparticles which react with pathogens present in food

substances and produce a visual color that can be easily detected. Magnetic iron oxide nanoparticles have been used to isolate the DNA of the milk pathogenic bacterium *Listeria monocytogenes*. Various nanosensors integrated with different types of nanomaterials have been documented for detecting pathogenic bacteria in standard bacterial culture samples as well as complex food samples see Table 12.10.

Surface-enhanced Raman spectroscopy coupled with silver nanosensors is one of the most efficient techniques in detecting pathogenic bacteria. Besides silver, nanosensors integrated with other nanomaterials such as nanorods, nanocolloids, graphene oxide, carbon nanotubes, plamonic gold and magnetic beads are also routinely used for the detection of foodborne pathogens. In recent years, an array-based immunosorbent assay coupled with liposomal nanovesicles has gained popularity due to its efficacy and specificity in detecting *E. coli*, *L. monocytogenes*, and *Salmonella* spp. Further, silicon-based nanosensors coupled with proteins that vibrate at different frequencies depending on their biomass have been used for pathogen detection in various mixed liquid food systems. In recent years, various new nanoparticle-based detection platforms such as lateral-flow immune test strips with palladium nanoparticles against *Klebsiella* and field effect transistors with graphene-based nanoparticles against *E. coli* have been developed.

12.7.10. Nanosensors in Sensing Chemicals and Pesticides in Food

Nanosensors composed of different nanomaterials have been used for the detection of pesticides, fertilizers and other toxic chemicals present in various foodstuffs see Table 18.10. Colorimetric and fluorometric nanosensors conjugated with gold nanoparticles have been used for the detection of organophosphorus and carbamate pesticides. Core-shell quantum dots made up of cadmium selenide and zinc sulfide have been explored for paraoxon sensing. Potentiometer sensors based on silica nanocomposites and multi-walled carbon nanotubes have been reported for the detection of toxic cadmium ions. Similarly, voltametric nanosensors based on nanocomposite biofilms (gold/zirconium dioxide) and fluorescent nanosensors (conjugated with gold nanoparticles) have been developed for the detection of parathion and melamine pesticides, respectively.

Food dyes and preservatives are also toxic when used above permissible limits. Ionic-liquid nanocomposites modified with multi-walled carbon nanotubes have been employed for the detection of food dyes such as sudan-I (a carcinogenic red dye used as an adulterant in chili powder tomato ketchup, strawberry and chili sauce), sunset yellow, and tartrazine. Likewise, nanocomposites in conjugation with zinc oxide nanoparticles and carbon nanotubes have been reported for the simultaneous detection of bisphenol A (a toxic organic compound released from plastic containers) and sudan I.

12.7.11. Nanosensors in Sensing the Quality of Key Food Ingredients

Vitamins and other key food ingredients such as antioxidant compounds are necessary for the normal function of various metabolic pathways in our body, and their deficiency can lead to serious health issues such as anemia, cardiovascular diseases, and carcinogenesis. These key food ingredients are easily degraded in different processed foods. To avoid their degradation, different types of nanosensors conjugated with various nanomaterials have been reported to date see Table 18.10. Ionic liquid nanocomposites based on carbon nanotubes and nickel oxide nanoparticles have been reported for the detection of ascorbic acid and folic acid in various fruit juices, wheat flour and milk samples. The level of succinic acid, citric acid, L-malic acid, fructose, D-sorbitol, sucrose, glucose, hydrogen peroxide and L-glutamic acid in stored food products is used as an indicator of food quality. Different types of nanosensors in

conjugation with silver, zirconium dioxide, iron, nickel–platinum, chitosan, gold, tin dioxide, prussian blue–gold and cuprous oxide nanoparticles have been used to monitor the quality of the above-mentioned food ingredients in various food components.

12.7.12. Nanomaterials and Devices in Food Safety

In the food industry, the safety of food products is an important issue. According to a recent survey, more than 45% of processed and packaged food items are prone to degradation and contamination. Nanotechnology has played a positive role in solving various issues related to the quality and safety of food products. Currently, different types of nanomaterials and nanodevices such as polymeric nanoparticles, liposomal nanovesicles, nanoloaded emulsions and temperature–time indicators are used for the improvement of the quality of food by increasing shelf life, sensing freshness, and detecting chemical, heavy metal, and allergen contamination in food items. Different nanosensors and nanotracers conjugated with various nanomaterials such as gold nanoparticles, silicon nanorods, magnetic beads, quantum dots, single-walled and multi-walled carbon nanotubes, immunomagnetic liposomes, aptamer conjugated gold, and palladium nanoparticles are also highly efficient in detecting various contaminants and degradants that influence the quality of food. Additionally, the newly developed radio frequency identification technique (RFID) is found to be well suited for numerous operations in food engineering and supply chain supervision due to its speed and effectiveness. RFID technology may also deliver safety and security improvements for food corporations by tracing the source of contaminants in various food products.

12.7.13. Nanobarcodes for Product Authenticity

Two-dimensional barcodes are used globally for the visual authentication of products; however, they can be easily altered, falsified, and damaged. To solve these issues, nanoparticle and nanodisk-based unique invisible barcodes have been developed in recent years to confirm the authenticity of various food products. The nanodisk barcode can be scanned with a Raman microscope, which could be in the form of a linear gold nanodisk array, silver–gold heterodimer nanodisk, or silver nanodisk codes. Nanodisks can be functionalized and amalgamated with metal composites to improve their properties further. Fluorescent-based barcode nanorods, invisible nanobarcodes, and fluorescent DNA dendrimer nanobarcodes have been reported for product labelling and pathogen detection in food and biological samples. Henceforth, nanotechnology will find use in developing efficient nanobarcodes systems to ensure food quality and safety.

12.7.14. Nanomaterials for Protection from Allergens

Nanotechnology also finds application in controlling and managing various food allergens. Conventional adjuvants such as aluminum hydroxide (alum) present several side effects including indurations, swelling, erythema, granulomas, and cutaneous nodules at the site of injection. In contrast to conventional adjuvants, nanomaterials such as polymer or protamine-based nanoparticles with Toll-like receptor 9 (TLR-9) ligand cytosine phosphate guanine-oligodeoxynucleotides are used as adjuvants and delivery systems due to their biodegradability, low toxicity, low dosage, reduced allergen exposure to IgE, and efficiency. These protamine-based nanoparticle adjuvants also act as a novel carrier system in allergen immunotherapy by counteracting Th2-type immune responses.

The development of aptamer-based gold nanorod and magnetic nanoparticle fluorescence assay has been reported to detect ochratoxin A in grape juice samples (a food mycotoxin

causing allergy) and allergens in different food matrices. Moreover, other nanomaterials such as polyanhydride nanoparticles, quantum dots, and dendrimers proved to be efficient oral vehicles for immunotherapy against experimental peanut allergies. Furthermore, the newly synthesized bioinspired nanostructured materials (green synthesized) can be potentially exploited in the food industry to overcome the issues of food allergens due to their low toxicity and cost-effectiveness.

12.7.15. Nanomaterials for the Inhibition of Biofilm Formation

Biofilms pose a problem in the food industry, as they are bacterial cells which adhere together very tightly and secrete a polymeric extracellular matrix which is impenetrable. They are formed by the adherence of free-floating microbes on a substrate surface through Van der Waals forces, leading to biofouling, biocorrosion, and interference in food processing. Various types of nanomaterials play a positive role in controlling the biofilm formation in food items, such as filter membranes made up of nanofibers, which have proved to be very efficient in the inhibition of the biofilm formation of many multi-drug resistant bacterial strains. Moreover, the use of different nanoparticles such as silver, nickel oxide, and zinc oxide in anti-bacterial, anti-fungal, anti-biofilm formation has been well documented in many scientific reports. The fermentation of *Bacillus subtilis* produces high-value products in an industrial setting, but on the other hand, it also hinders the processing of food products through biofilm formation. The efficacy of naked and coated superparamagnetic iron oxide nanoparticles against *B. subtilis* was evaluated by Ranmadugala et al. Both types of iron oxide nanoparticles significantly reduced the bacterial growth and biofilm formation without affecting the cell viability. Similarly, gold nanoparticles conjugated with chlorhexidine prevented the biofilm formation of *K. pneumonia* and *S. aureus*.

12.7.16. Safety Issues of Nanomaterials in the Food Industry

As is well known, the use of various nanomaterials in the food industry has numerous advantages; however, at the same time, they also pose serious threats to human health, the environment, and other ecosystems due to their cytotoxic effects. Some serious concerns have arisen recently regarding the use of nanomaterials, even those with no toxic element in their composition, but they have an inherent potential risk due to their small size and subcellular interaction with cells. For example, some nanoparticles have the ability to penetrate within skin and cause health problems in humans as well as in animals. Nanoparticles can cause genomic and proteomic changes even in plants and can affect their growth rate. Experimental studies have shown that single and multi-walled carbon nanotubes can induce fibrosis as well as oxidative stress in the lungs of models animals such as mice and rats.

To understand the mechanisms of toxicity of different nanomaterials to human health and the environment, we first have to define a clear description of the various exposure routes and entry pathways of nanomaterials from the food industry to human body. We purposely or accidentally consume several processed food items bearing numerous nanomaterials through intraoral, dermal and pulmonary pathways. Oral captivation is the main pathway by which we intake chemicals, water, and nutrients into our bodies. Certainly, numerous nanomaterials are involved in various food items today, and it is supposed that the digestive organs are exposed directly to these nanomaterials every day. Nanoparticles swallowed orally move from the mouth to stomach and then intestines, posing serious health-related risks to human.

To evaluate the toxicity of nanomaterials, zebrafish are used as a model organism to overcome the challenges including the development and maintenance of cell cultures for animals and human cells. This vertebrate fish has the ability to reproduce rapidly. The U.S.

Food and Drug Administration (FDA) and European Union (EU) gave approval for the use of zebrafish for the evaluation of toxicity of nanomaterials. The complete evaluation of various end points related to toxicity specifies that the nanomaterials do not cause developmental defects, mortality or alteration in the behavior of zebrafish. Furthermore, the uptake and biodistribution analysis of nanostructures reveals that they are present in specific locations within body. The recent cytotoxicity evaluation of green synthesized zinc oxide nanoparticles has been carried out in *in vitro* as well as *in vivo*, clearly indicating that the green hydrothermally synthesized nanoparticles are more biocompatible and less toxic compared to chemically synthesized nanoparticles. For biosafety and biokinetics assessments of metallic nanoparticles such as gold, silver, and platinum, murine is used as a model organism. This study confirmed the enhanced excretion of nanoparticles through the renal pathway due to their small size. Additionally, the biosafety of all metallic nanoparticles was fully assessed in zebrafish for the evaluation of toxicity within the whole body.

The bioaccumulation of nanomaterials derived from either nanopackaging or nanoprocessed items has been confirmed in food and human beings. Therefore, the risk assessment procedures must be strictly followed while processing food items. Even with the advent of nanotechnology, the challenges to the development of a healthy and sustainable food industry remain obscure. With the intervention of nanotechnology in the food industry, the public should be educated regarding the possible risks associated with nanomaterials to human health and the environment. Several EU and non-EU countries have designed several regulatory frameworks for dealing with nanomaterials to ensure the safety of nanoproducts in feed, agriculture and food sectors. Additionally, supervisory authorities such as the FDA and Environmental Protection Agency (EPA) have made several amendments to various criteria intended for marketable foodstuffs in terms of health and the quality and safety of products.

12.8 Carbon Nanotube

Carbon nanotubes (CNTs) are an allotrope of carbon. They take the form of cylindrical carbon molecules and have novel properties that make them potentially useful in a wide variety of applications in nanotechnology, electronics, optics and other fields of materials science. They exhibit extraordinary strength and unique electrical properties, and are efficient conductors of heat.

Inorganic nanotubes have also been synthesized. Nanotubes are members of the fullerene structural family, which also includes buckyballs. Whereas buckyballs are spherical in shape, a nanotube is cylindrical, with at least one end typically capped with a hemisphere of the buckyball structure. Their name is derived from their size, since the diameter of a nanotube is on the order of a few nanometers (approximately 50,000 times smaller than the width of a human hair), while they can be up to several millimeters in length.

There are two main types of nanotubes: single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs).

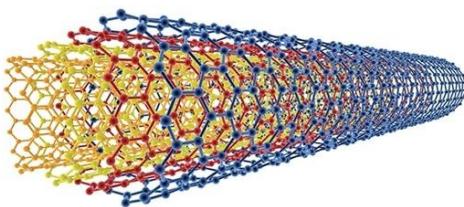


Figure 12.30. Multi-walled Carbon Nanotubes

Single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs) are similar in certain respects but they also have striking differences. SWNTs are an allotrope of sp₂ hybridized carbon similar to fullerenes. The structure is a cylindrical tube including six-membered carbon rings similar to graphite. Analogous MWNTs have several tubes in concentric cylinders.

The number of these concentric walls may vary from 6 to 25 or more. The diameter of MWNTs may be 30 nm when compared to 0.7–2.0 nm for typical SWNTs. The unique properties of carbon nanotubes enable a wide range of novel applications and improvements in the performance of existing ones.

This article offers a brief overview of the physico-chemical nature and characterization of MWNTs, with specific emphasis on recently introduced materials that signify the most recent advancement of the technology and the level of its commercialization.

12.8.1. Properties of MWNTs

MWNTs have excellent properties and are being employed in a large number of commercial applications. The properties of MWNTs are:

Electrical: MWNTs are highly conductive when properly integrated into a composite structure, however, the outer wall alone has conductive properties, but the inner walls are not instrumental to conductivity.

Morphology: MWNTs have a high aspect ratio with lengths typically more than 100 times the diameter, and in certain cases much higher. Their performance and application are based not just on their aspect ratio, but also on the degree of entanglement and the straightness of the tubes; which in turn is a function of both the degree and dimension of defects in the tubes.

Physical: Defect-free, individual, MWNTs have an excellent tensile strength and when integrated into a composite, such as a thermoplastic or thermoset compound can significantly increase its strength.

Thermal: MWNTs have a thermal stability above 600 °C, as a result of the level of defects - and to a certain extent on the purity; as a residual catalyst in the product can also accelerate decomposition.

Chemical: MWNTs are an allotrope of sp₂ hybridized carbon similar to graphite and fullerenes, and therefore have high chemical stability. However, the nanotubes can be functionalized to enhance both the strength and dispersibility of composites.

12.8.1.2. Challenges in Commercialization of MWNTs

The challenges in commercializing MWNTs include:

Dispersion: This property in MWNTs is better in solutions or polymers than SWNTs, however, the quality of the dispersion is a critical factor in the performance of the final product.

Purity: Many MWNTs processes cause a considerable residual metallic catalyst which can be detrimental to performance.

Defects: The number of defects is dependent on the number of layers within MWNTs. The high aspect ratio of MWNTs contributes significantly to its use.

12.8.1.3. Applications of MWNTs

There are a large number of present and evolving applications for MWNTs. These include:

Electrically Conductive Polymers: MWNTs are suitable for these applications – in particular as a result of their high conductivity and high aspect ratio. The required conductivity level can be achieved with much lesser loadings than for conventional solutions such as metal particulates or carbon black. Applications include electrostatic discharge protection in wafer processing fabrication, antistatic elastomeric and plastic components for automobile fuel line components, plastics rendered conductive to enable electrostatic spray painting of automobile body parts, RFI shielding materials, and more.

Battery Cathodes: Novel MWNT materials from SouthWest NanoTechnologies (SWeNT®) have shown considerable improvements when integrated into cathodes.

Improved Structural Composites: MWNTs in the form of non-woven or woven fabrics or resin infused buckypaper, when saturated with thermoset resins have shown considerable increases in the stiffness and strength of composite structures, such as structural laminates, golf club shafts and aerospace applications.

Water filtration membranes: High aspect ratio, high mechanical strength and large specific surface enable very efficient filtration media.

Other development applications include spray-coatable heater elements; thermal interface and other heat conduction materials and enhanced carbon fiber.

12.8.2. Single-walled Carbon Nanotubes (SWNTs, SWCNTs)

Most single-walled nanotubes (SWNT) have a diameter of close to 1 nanometer, with a tube length that can be many millions of times longer. The structure of a SWNT can be conceptualized by wrapping a one-atom-thick layer of graphite called graphene into a seamless cylinder.

Single-walled nanotubes are an important variety of carbon nanotube because they exhibit electric properties that are not shared by the multi-walled carbon nanotube (MWNT) variants. In particular, their band gap can vary from zero to about 2 eV and their electrical conductivity can show metallic or semiconducting behavior, whereas MWNTs are zero-gap metals. Single-walled nanotubes are the most likely candidate for miniaturizing electronics beyond the micro electromechanical scale currently used in electronics. The most basic building block of these systems is the electric wire, and SWNTs can be excellent conductors.

12.8.2.1. Single-walled Carbon Nanotubes (SWNTs, SWCNTs) Applications

Potential applications of carbon nanotubes are: (1) additives in polymers; (2) catalysts; (3) electron field emitters for cathode ray lighting elements; (4) flat panel display; (5) gas-discharge tubes in telecom networks; (6) electromagnetic-wave absorption and shielding; (7) energy conversion; (8) lithium-battery anodes; (9) hydrogen storage; (10) nanotube composites (by filling or coating); (11) nanoprobes for STM, AFM, and EFM tips; (12) nanolithography; (13) nanoelectrodes; (14) drug delivery; (15) sensors; (16) reinforcements in composites; (17) supercapacitor.

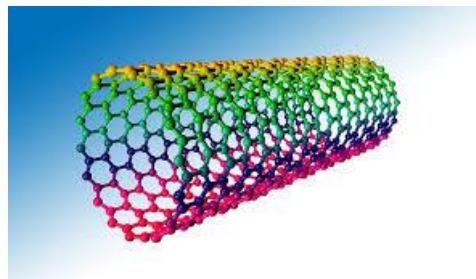
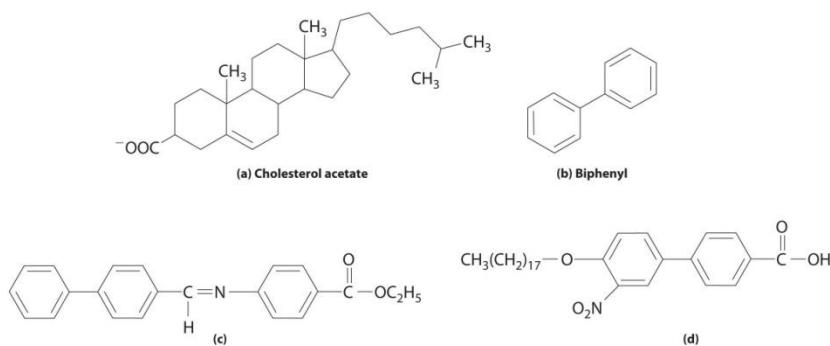


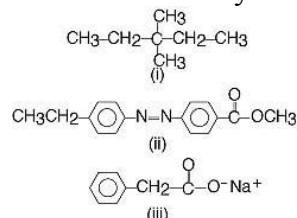
Figure 12.31. Single-Walled Nanotube

PROGRESS CHECK

12.1. Which compound is least likely to form a liquid crystal phase?



12.2. Which of the following substances is most likely to exhibit liquid-crystalline behavior?



12.3. Suggest a reason why the following molecule, decane, does not exhibit liquid-crystalline behavior:



12.4. Liquid-crystalline phase tend to be more viscous than the isotropic , or normal liquid phase of the same substance. Why?

12.5. The smectic liquid-crystalline phase can be said to be more highly ordered than the nematic. In what sense is this true?

12.6. Many polymers are formed through a condensation reaction. Write a chemical equation for formation of a polymer from the monomer HOCH₂CH₂OH, which is called ethylene glycol.

12.7. Several years ago a biomedical company produced and marketed a new, efficient design of heart valve implant. However, it was later withdrawn from the market because patients using it suffered from severe loss of red blood cells. Describe what properties of the valve could have been responsible for this result?

12.8. In what ways does a ceramic material differ from an organic polymer, both in terms of molecular structure and in terms of physical properties?

12.9. List the characteristics that a thin film should possess if it is to have useful application.

12.10. To what does the term superconductivity refer? Why might superconductive materials be of value?

12.11. Steel reinforcing rods are used when concrete is used as a highway bed or in a construction of a building. Describe the analogy between this practice and the formation of ceramic composites. What does this analogy suggest about the optimal shape and size of the added composite material? Why is this the optimal shape?

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www.sciencedirect.com/book/9780323512718/nanomaterials-for-food-packaging

TOPIC/S: CRYSTAL STRUCTURES

- 13.1. Introduction
- 13.2. Unit Cells
- 13.3. Packing of Spheres
 - 13.3.1. Simple Cubic Structure
 - 13.3.2. Body-Centered Cubic Structure
 - 13.3.3. Hexagonal Closed-Packed Structure and Cubic Closed-Packed Structure
- 13.4. Long and Short-Range Orders
- 13.5. Categories of Crystals
- 13.6. Structures of Metals
- 13.7. Structures of the Non-Metallic Elements
- 13.8. Structures of Binary Crystals
- 13.9. Alloys
- 13.10. Crystal Defects
- 13.11. Electrical Properties
 - 13.11.1. Resistivity
 - 13.11.2. Conduction Through Ion Hopping
 - 13.11.3. Conduction Electrons
 - 13.11.4. Electrical Insulators
 - 13.11.5. Conductivity of Metals
 - 13.11.6. Conducting Properties of semi-Conductors
- 13.12. Solving Density using a Unit Cell

EXPECTED COMPETENCIES

At the end of the lesson, you must have:

1. described the characteristic properties of crystalline and amorphous solids,
2. recognized the unit cell of a crystalline solid,
3. calculated the density of a solid given its unit cell,
4. described the different packing of spheres,
5. explained long and short-range orders,
6. categorized crystals,
7. described the structures of metals, non-metallic elements, binary crystals, and alloys,
8. explained crystal defects; and
9. enumerated and explained the electrical properties.

13.1. Introduction

Crystal, any solid material in which the component atoms are arranged in a definite pattern and whose surface regularity reflects its internal symmetry. A solid composed of atoms, ions, or molecules arranged in a pattern that is repeated in three dimensions. A material in which atoms are situated in a repeating or periodic array over large atomic distances

A crystalline solid can be represented by its unit cell, which is the smallest identical unit that when stacked together produces the characteristic three-dimensional structure. **Solids** are characterized by an extended three-dimensional arrangement of atoms, ions, or molecules in which the components are generally locked into their positions. The components can be arranged in a regular repeating three-dimensional array (a **crystal lattice**), which results in a **crystalline solid**, or more or less randomly to produce an **amorphous solid**. Crystalline solids have well-defined edges and faces, diffract x-rays, and tend to have sharp melting points. In contrast, amorphous solids have irregular or curved surfaces, do not give well-resolved x-ray diffraction patterns, and melt over a wide range of temperatures.

Crystalline solids have regular ordered arrays of components held together by uniform intermolecular forces, whereas the components of amorphous solids are not arranged in regular arrays. With few exceptions, the particles that compose a solid material, whether ionic, molecular, covalent, or metallic, are held in place by strong attractive forces between them. When we discuss solids, therefore, we consider the positions of the atoms, molecules, or ions, which are essentially fixed in space, rather than their motions (which are more important in liquids and gases). The constituents of a solid can be arranged in two general ways: they can form a regular repeating three-dimensional structure called a crystal lattice, thus producing a crystalline solid, or they can aggregate with no particular order, in which case they form an amorphous solid (from the Greek *ámorphos*, meaning “shapeless”).



Figure 13.1. (Left) Crystalline faces. The faces of crystals can intersect at right angles, as in galena (PbS) and pyrite (FeS_2), or at other angles, as in quartz. (Right) Cleavage surfaces of an amorphous solid. Obsidian, a volcanic glass with the same chemical composition as granite (typically KAlSi_3O_8), tends to have curved, irregular surfaces when cleaved.

Crystalline solids, or crystals, have distinctive internal structures that in turn lead to distinctive flat surfaces, or faces. The faces intersect at angles that are characteristic of the substance. When exposed to x-rays, each structure also produces a distinctive pattern that can be used to identify the material. The characteristic angles do not depend on the size of the crystal; they reflect the regular repeating arrangement of the component atoms, molecules, or ions in space.

When an ionic crystal is cleaved Figure 4.2, for example, repulsive interactions cause it to break along fixed planes to produce new faces that intersect at the same angles as those in the original crystal. In a covalent solid such as a cut diamond, the angles at which the faces

meet are also not arbitrary but are determined by the arrangement of the carbon atoms in the crystal.

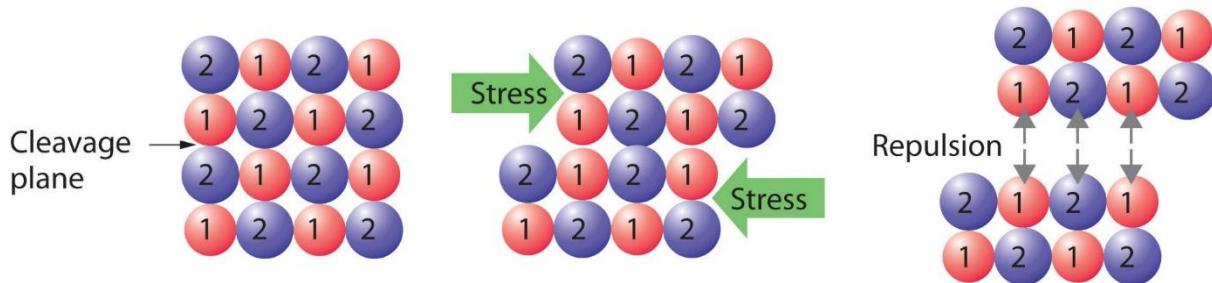


Figure 13.2. Cleaving a Crystal of an Ionic Compound along a Plane of Ions. Deformation of the ionic crystal causes one plane of atoms to slide along another. The resulting repulsive interactions between ions with like charges cause the layers to separate.

Crystals tend to have relatively sharp, well-defined melting points because all the component atoms, molecules, or ions are the same distance from the same number and type of neighbors; that is, the regularity of the crystalline lattice creates local environments that are the same. Thus the intermolecular forces holding the solid together are uniform, and the same amount of thermal energy is needed to break every interaction simultaneously.

Amorphous solids have two characteristic properties. When cleaved or broken, they produce fragments with irregular, often curved surfaces; and they have poorly defined patterns when exposed to x-rays because their components are not arranged in a regular array. An amorphous, translucent solid is called a **glass**. Almost any substance can solidify in amorphous form if the liquid phase is cooled rapidly enough. Some solids, however, are intrinsically amorphous, because either their components cannot fit together well enough to form a stable crystalline lattice or they contain impurities that disrupt the lattice. For example, although the chemical composition and the basic structural units of a quartz crystal and quartz glass are the same—both are SiO_2 and both consist of linked SiO_4 tetrahedra—the arrangements of the atoms in space are not. Crystalline quartz contains a highly ordered arrangement of silicon and oxygen atoms, but in quartz glass the atoms are arranged almost randomly. When molten SiO_2 is cooled rapidly (4 K/min), it forms quartz glass, whereas the large, perfect quartz crystals sold in mineral shops have had cooling times of thousands of years. In contrast, aluminum crystallizes much more rapidly. Amorphous aluminum forms only when the liquid is cooled at the extraordinary rate of $4 \times 10^{13}\text{ K/s}$, which prevents the atoms from arranging themselves into a regular array.

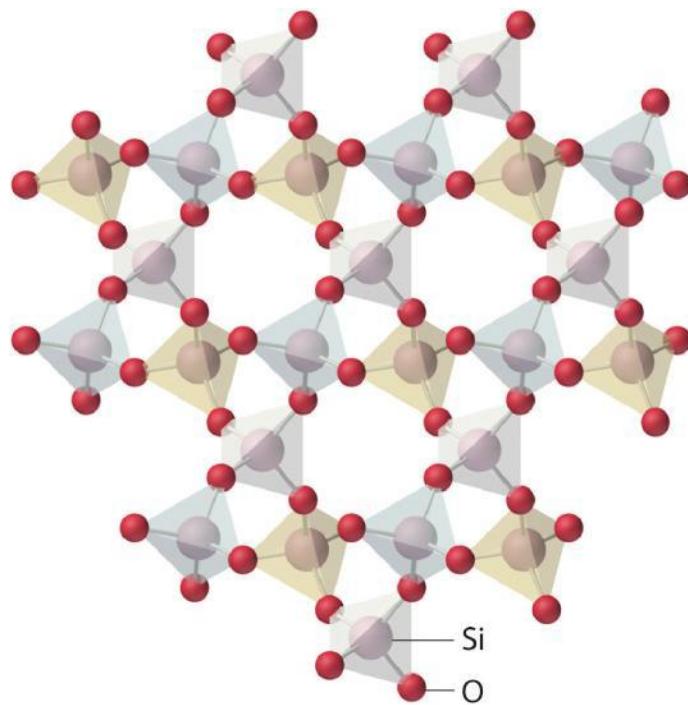


Figure 13.3. The lattice of crystalline quartz (SiO_2). The atoms form a regular arrangement in a structure that consists of linked tetrahedra.

In an amorphous solid, the local environment, including both the distances to neighboring units and the numbers of neighbors, varies throughout the material. Different amounts of thermal energy are needed to overcome these different interactions. Consequently, amorphous solids tend to soften slowly over a wide temperature range rather than having a well-defined melting point like a crystalline solid. If an amorphous solid is maintained at a temperature just below its melting point for long periods of time, the component molecules, atoms, or ions can gradually rearrange into a more highly ordered crystalline form.

Crystals have sharp, well-defined melting points; amorphous solids do not.

Because a crystalline solid consists of repeating patterns of its components in three dimensions (a crystal lattice), we can represent the entire crystal by drawing the structure of the smallest identical units that, when stacked together, form the crystal. This basic repeating unit is called a unit cell. For example, the unit cell of a sheet of identical postage stamps is a single stamp, and the unit cell of a stack of bricks is a single brick. In this section, we describe the arrangements of atoms in various unit cells.

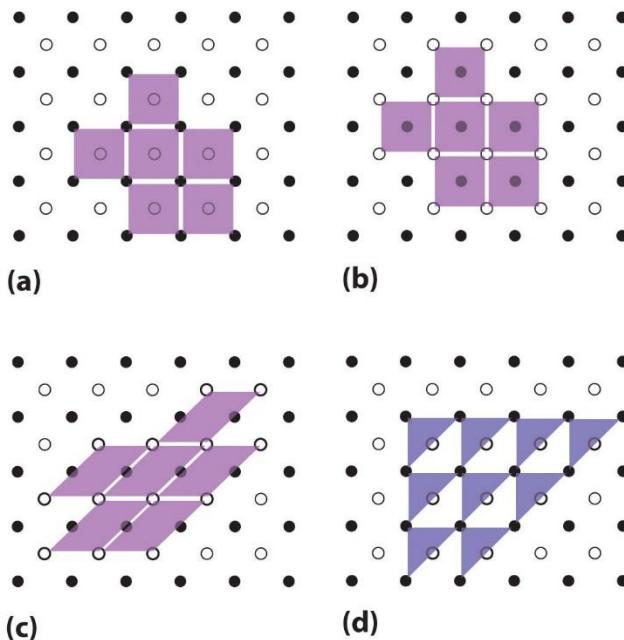


Figure 13.4. Unit Cells in Two Dimensions. (a–c) Three two-dimensional lattices illustrate the possible choices of the unit cell. The unit cells differ in their relative locations or orientations within the lattice, but they are all valid choices because repeating them in any direction fills the overall pattern of dots. (d) The triangle is not a valid unit cell because repeating it in space fills only half of the space in the pattern.

Unit cells are easiest to visualize in two dimensions. In many cases, more than one unit cell can be used to represent a given structure, as shown for the Escher drawing in the chapter opener and for a two-dimensional crystal lattice in Figure 4.4. Usually the smallest unit cell that completely describes the order is chosen. The only requirement for a valid unit cell is that repeating it in space must produce the regular lattice. Thus the unit cell in Figure 4.4d is not a valid choice because repeating it in space does not produce the desired lattice (there are triangular holes). The concept of unit cells is extended to a three-dimensional lattice in the schematic drawing in Figure 4.5.

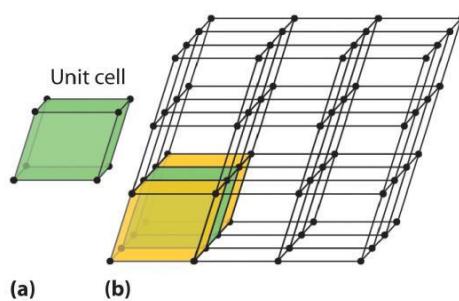


Figure 13.5. Unit Cells in Three Dimensions. These images show (a) a three-dimensional unit cell and (b) the resulting regular three-dimensional lattice.

13.2. The Unit Cell

The smallest repeating unit of a crystal lattice is the unit cell. The basic structural unit or building block of the crystal structure.

There are seven fundamentally different kinds of unit cells, which differ in the relative lengths of the edges and the angles between them (Figure 4.6). Each unit cell has six sides, and each side is a parallelogram. We focus primarily on the cubic unit cells, in which all sides have the same length and all angles are 90° , but the concepts that we introduce also apply to substances whose unit cells are not cubic.

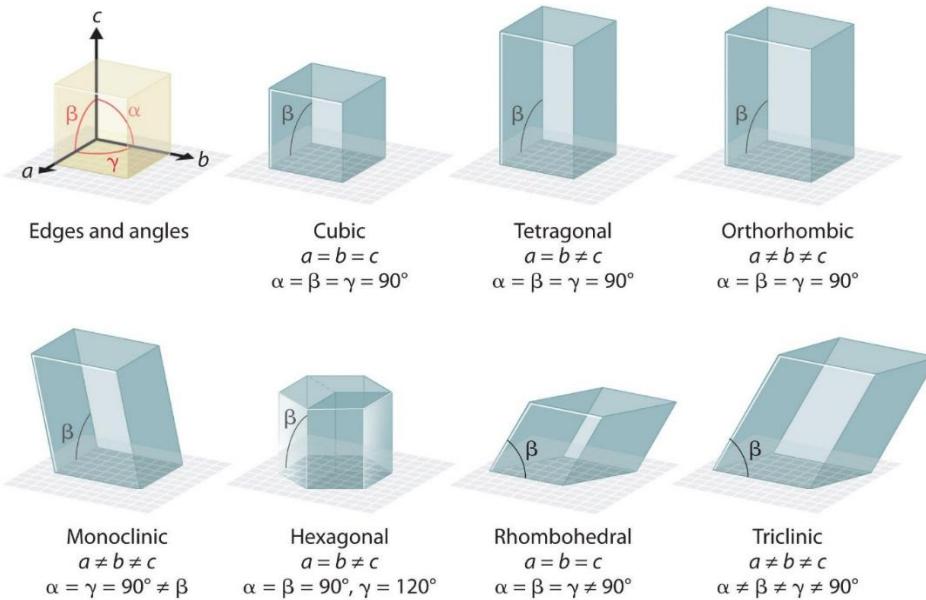


Figure 13.6. The General Features of the Seven Basic Unit Cells. The lengths of the edges of the unit cells are indicated by a , b , and c , and the angles are defined as follows: α , the angle between b and c ; β , the angle between a and c ; and γ , the angle between a and b .

If the cubic unit cell consists of eight component atoms, molecules, or ions located at the corners of the cube, then it is called simple cubic (Figure 4.7a). If the unit cell also contains an identical component in the center of the cube, then it is body-centered cubic (bcc) (Figure 4.7b). If there are components in the center of each face in addition to those at the corners of the cube, then the unit cell is face-centered cubic (fcc) (Figure 4.7c).

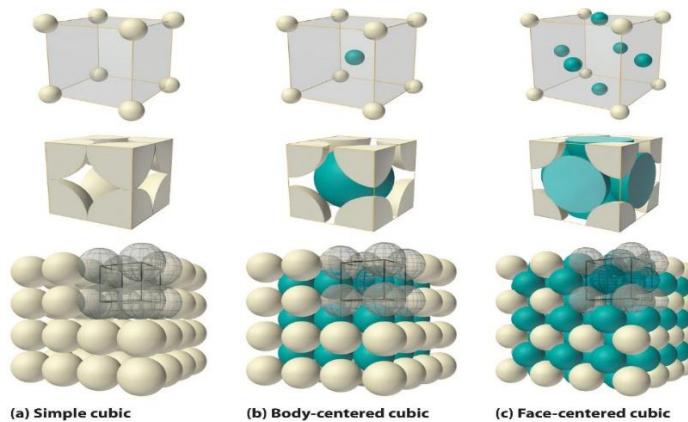


Figure 13.7. The Three Kinds of Cubic Unit Cell. For the three kinds of cubic unit cells, simple cubic (a), body-centered cubic (b), and face-centered cubic (c), there are three

representations for each: a ball-and-stick model, a space-filling cutaway model that shows the portion of each atom that lies within the unit cell, and an aggregate of several unit cells.

As indicated in Figure 13.7, a solid consists of a large number of unit cells arrayed in three dimensions. Any intensive property of the bulk material, such as its density, must therefore also be related to its unit cell. Because density is the mass of substance per unit volume, we can calculate the density of the bulk material from the density of a single unit cell. To do this, we need to know the size of the unit cell (to obtain its volume), the molar mass of its components, and the number of components per unit cell. When we count atoms or ions in a unit cell, however, those lying on a face, an edge, or a corner contribute to more than one unit cell, as shown in Figure 3.7. For example, an atom that lies on a face of a unit cell is shared by two adjacent unit cells and is therefore counted as 1/2 atom per unit cell. Similarly, an atom that lies on the edge of a unit cell is shared by four adjacent unit cells, so it contributes 1/4 atom to each. An atom at a corner of a unit cell is shared by all eight adjacent unit cells and therefore contributes 1/8 atom to each. The statement that atoms lying on an edge or a corner of a unit cell count as 1/4 or 1/8 atom per unit cell, respectively, is true for all unit cells except the hexagonal one, in which three unit cells share each vertical edge and six share each corner (Figure 3.7), leading to values of 1/3 and 1/6 atom per unit cell, respectively, for atoms in these positions. In contrast, atoms that lie entirely within a unit cell, such as the atom in the center of a body-centered cubic unit cell, belong to only that one unit cell.

For all unit cells except hexagonal, atoms on the faces contribute 1/2 atom to each unit cell, atoms on the edges contribute 1/4 atom to each unit cell, and atoms on the corners contribute 1/8 atom to each unit cell.

13.3. Packing of Spheres

Our discussion of the three-dimensional structures of solids has considered only substances in which all the components are identical. As we shall see, such substances can be viewed as consisting of identical spheres packed together in space; the way the components are packed together produces the different unit cells. Most of the substances with structures of this type are metals.

13.3.1. Simple Cubic Structure

The arrangement of the atoms in a solid that has a simple cubic unit cell was shown in Figure 4.8a. Each atom in the lattice has only six nearest neighbors in an octahedral arrangement. Consequently, the simple cubic lattice is an inefficient way to pack atoms together in space: only 52% of the total space is filled by the atoms. The only element that crystallizes in a simple cubic unit cell is polonium. Simple cubic unit cells are, however, common among binary ionic compounds, where each cation is surrounded by six anions and vice versa.

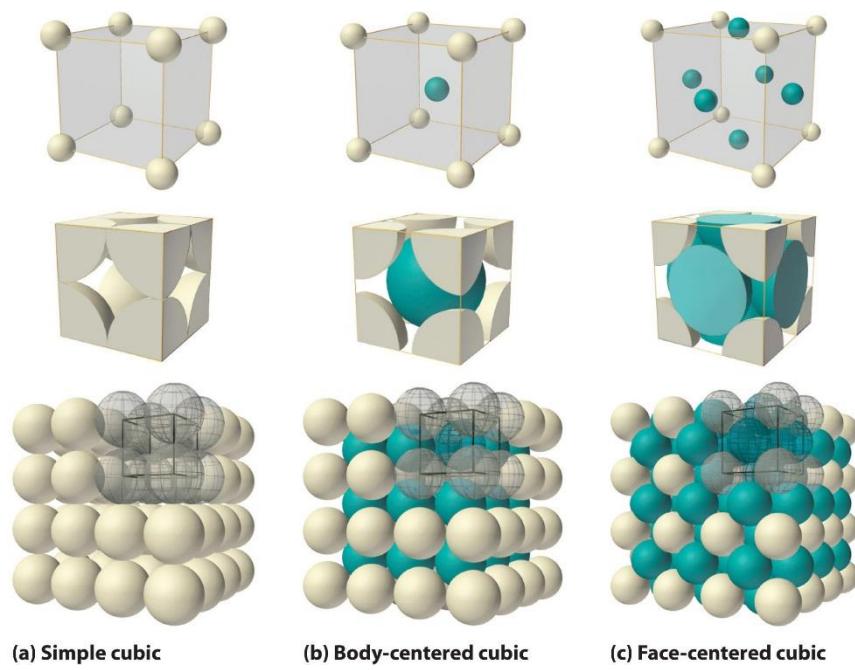


Figure 13.8. The arrangement of atoms in a simple cubic unit cell. Each atom in the lattice has six nearest neighbors in an octahedral arrangement.

13.3.2. Body-Centered Cubic Structure

The body-centered cubic unit cell is a more efficient way to pack spheres together and is much more common among pure elements. Each atom has eight nearest neighbors in the unit cell, and 68% of the volume is occupied by the atoms. As shown in Figure 3.8, the body-centered cubic structure consists of a single layer of spheres in contact with each other and aligned so that their centers are at the corners of a square; a second layer of spheres occupies the square-shaped “holes” above the spheres in the first layer. The third layer of spheres occupies the square holes formed by the second layer, so that each lies directly above a sphere in the first layer, and so forth. All the alkali metals, barium, radium, and several of the transition metals have body-centered cubic structures.

13.3.3. Hexagonal Close-Packed and Cubic Close-Packed Structures

The most efficient way to pack spheres is the close-packed arrangement, which has two variants. A single layer of close-packed spheres is shown in Figure 12.6.6a. Each sphere is surrounded by six others in the same plane to produce a hexagonal arrangement. Above any set of seven spheres are six depressions arranged in a hexagon. In principle, all six sites are the same, and any one of them could be occupied by an atom in the next layer. Actually, however, these six sites can be divided into two sets, labeled B and C in Figure 3.9a. Sites B and C differ because as soon as we place a sphere at a B position, we can no longer place a sphere in any of the three C positions adjacent to A and vice versa.

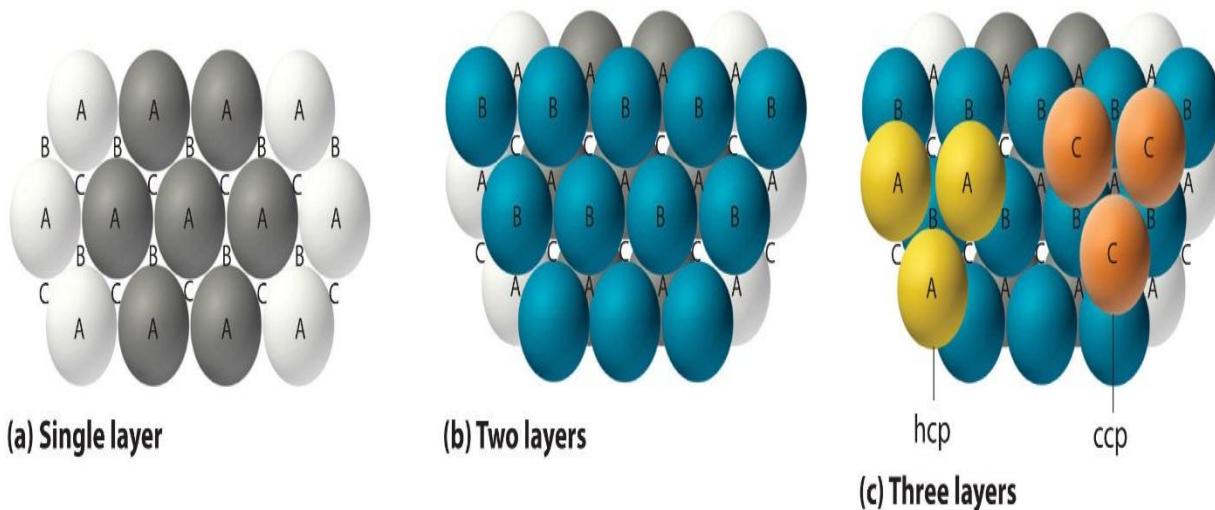


Figure 13.9. Close-Packed Layers of Spheres. (a) In this single layer of close-packed spheres, each sphere is surrounded by six others in a hexagonal arrangement. (b) Placing an atom at a B position prohibits placing an atom at any of the adjacent C positions and results in all the atoms in the second layer occupying the B positions. (c) Placing the atoms in the third layer over the atoms at A positions in the first layer gives the hexagonal close-packed structure. Placing the third-layer atoms over the C positions gives the cubic close-packed structure.

If we place the second layer of spheres at the B positions in Figure 3.9a, we obtain the two-layered structure shown in Figure 3.9b. There are now two alternatives for placing the first atom of the third layer: we can place it directly over one of the atoms in the first layer (an A position) or at one of the C positions, corresponding to the positions that we did not use for the atoms in the first or second layers (Figure 3.9c). If we choose the first arrangement and repeat the pattern in succeeding layers, the positions of the atoms alternate from layer to layer in the pattern ABABAB..., resulting in a hexagonal close-packed (hcp) structure (Figure 3.9a). If we choose the second arrangement and repeat the pattern indefinitely, the positions of the atoms alternate as ABCABC..., giving a cubic close-packed (ccp) structure not look particularly cubic. As shown in Figure 3.9b, however, simply rotating the structure reveals its cubic nature, which is identical to an fcc structure. The hcp and ccp structures differ only in the way their layers are stacked. Both structures have an overall packing efficiency of 74%, and in both each atom has 12 nearest neighbors (6 in the same plane plus 3 in each of the planes immediately above and below).

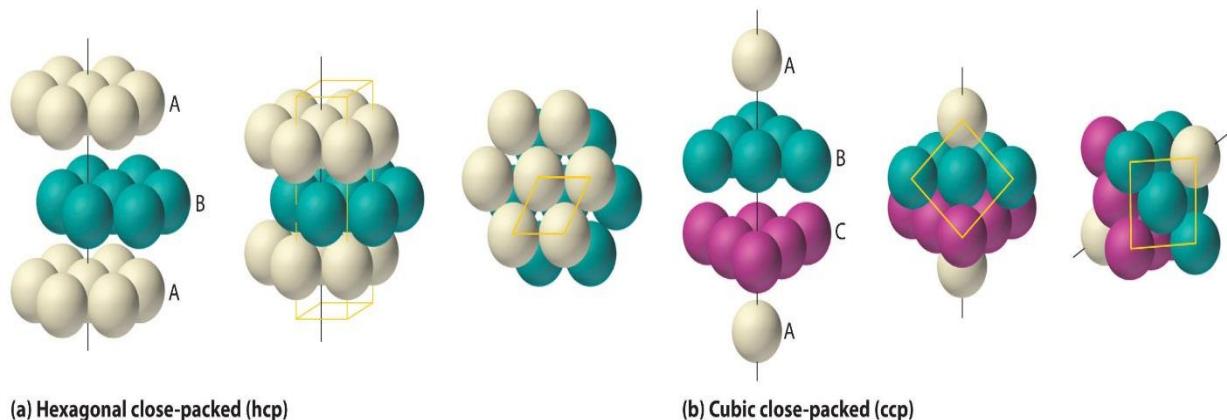


Figure 13.10. The ccp structure in (b) is shown in an exploded view, a side view, and a rotated view. The rotated view emphasizes the fcc nature of the unit cell (outlined). The line that connects the atoms in the first and fourth layers of the ccp structure is the body diagonal of the cube.

Table 13.1 compares the packing efficiency and the number of nearest neighbors for the different cubic and close-packed structures; the number of nearest neighbors is called the coordination number. Most metals have hcp, ccp, or bcc structures, although several metals exhibit both hcp and ccp structures, depending on temperature and pressure.

Table 13.1. Properties of the Common Structures of Metals

| Structure | Percentage of Space Occupied by Atoms | Coordination Number |
|---|---------------------------------------|---------------------|
| simple cubic | 52 | 6 |
| body-centered cubic | 68 | 8 |
| hexagonal close packed | 74 | 12 |
| cubic close packed (identical to face-centered cubic) | 74 | 12 |

13.4. Long- and Short-Range Orders

A solid is crystalline if it has long-range order. Once the positions of an atom and its neighbors are known at one point, the place of each atom is known precisely throughout the crystal. Most liquids lack long-range order, although many have short-range order. **Short range** is defined as the first- or second-nearest neighbors of an atom. In many liquids the first-neighbor atoms are arranged in the same structure as in the corresponding solid **phase**. At distances that are many atoms away, however, the positions of the atoms become uncorrelated. These fluids, such as water, have short-range order but lack long-range order. Certain liquids may have short-range order in one direction and long-range order in another direction; these special substances are called **liquid crystals**. **Solid crystals** have both short-range order and long-range order.

Solids that have short-range order but lack long-range order are called **amorphous**. Almost any material can be made **amorphous** by rapid solidification from the melt (molten state). This condition is unstable, and the solid will crystallize in time. If the timescale for crystallization is years, then the amorphous state appears stable. Glasses are an example of

amorphous solids. In crystalline silicon (Si) each atom is tetrahedrally bonded to four neighbors. In amorphous silicon (a-Si) the same short-range order exists, but the bond directions become changed at distances farther away from any atom. Amorphous silicon is a type of glass. **Quasi-crystals** are another type of solid that lack long-range order.

Most solid materials found in nature exist in **polycrystalline** form rather than as a **single crystal**. They are actually composed of millions of grains (small crystals) packed together to fill all space. Each individual **grain** has a different orientation than its neighbors. Although long-range order exists within one grain, at the boundary between grains, the ordering changes direction. A typical piece of iron or copper (Cu) is polycrystalline. Single crystals of metals are soft and malleable, while polycrystalline metals are harder and stronger and are more useful industrially. Most polycrystalline materials can be made into large single crystals after extended heat treatment. In the past blacksmiths would heat a piece of metal to make it malleable: heat makes a few grains grow large by incorporating smaller ones. The smiths would bend the softened metal into shape and then pound it awhile; the pounding would make it polycrystalline again, increasing its strength.

13.5. Categories of Crystals

Crystals are classified in general categories, such as insulators, metals, semiconductors, and molecular solids. A single crystal of an insulator is usually transparent and resembles a piece of glass. Metals are shiny unless they have rusted. Semiconductors are sometimes shiny and sometimes transparent but are never rusty. Many crystals can be classified as a single type of solid, while others have intermediate behavior. Cadmium sulfide (CdS) can be prepared in pure form and is an excellent insulator; when impurities are added to cadmium sulfide, it becomes an interesting semiconductor. Bismuth (Bi) appears to be a metal, but the number of electrons available for electrical conduction is similar to that of semiconductors. In fact, bismuth is called a semimetal. Molecular solids are usually crystals formed from molecules or polymers. They can be insulating, semiconducting, or metallic, depending on the type of molecules in the crystal. New molecules are continuously being synthesized, and many are made into crystals. The number of different crystals is enormous.

13.6. Structures of Metals

The elements are found in a variety of crystal packing arrangements. The most common lattice structures for metals are those obtained by stacking the atomic spheres into the most compact arrangement. There are two such possible periodic arrangements. In each, the first layer has the atoms packed into a plane-triangular lattice in which every atom has six immediate neighbors. Figure 3.11 shows this arrangement for the atoms labeled *A*. The second layer is shaded in the figure. It has the same plane-triangular structure; the atoms sit in the holes formed by the first layer. The first layer has two equivalent sets of holes, but the atoms of the second layer can occupy only one set. The third layer, labeled *C*, has the same structure, but there are two choices for selecting the holes that the atoms will occupy. The third layer can be placed over the atoms of the first layer, generating an alternate layer sequence *ABABAB* . . . , which is called the hexagonal- closest-packed (hcp) structure. Cadmium and zinc crystallize with this structure. The second possibility is to place the atoms of the third layer over those of neither of the first two but instead over the set of holes in the first layer that remains unoccupied. The fourth layer is placed over the first, and so there is a three-layer repetition *ABCABCABC* . . . , which is called the face-centered cubic (fcc), or cubic-closest-packed, lattice. Copper, silver (Ag), and gold (Au) crystallize in fcc lattices. In the hcp and the fcc structures the spheres fill 74 percent of the volume, which represents the

closest possible packing of spheres. Each atom has 12 neighbors. The number of atoms in a unit cell is two for hcp structures and one for fcc. There are 32 metals that have the hcp lattice and 26 with the fcc. Another possible arrangement is the body-centered cubic (bcc) lattice, in which each atom has eight neighbors arranged at the corners of a cube. Figure 3A shows the cesium chloride (CsCl) structure, which is a cubic arrangement. If all atoms in this structure are of the same species, it is a bcc lattice. The spheres occupy 68 percent of the volume. There are 23 metals with the bcc arrangement. The sum of these three numbers (32 + 26 + 23) exceeds the number of elements that form metals (63), since some elements are found in two or three of these structures.

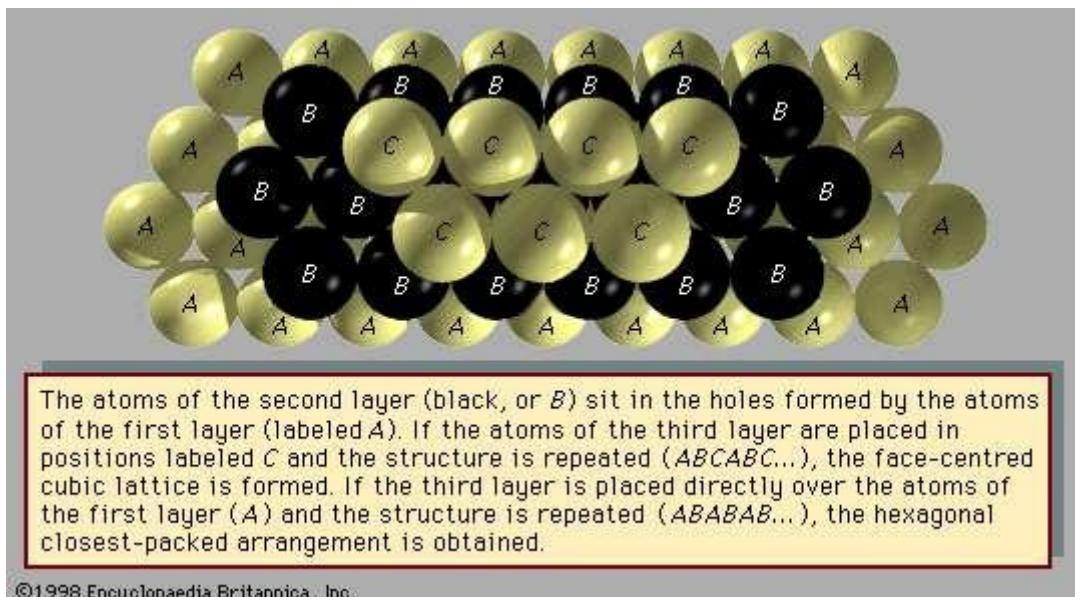


Figure 13.11. Stacking of Spheres in closed –packed arrangement

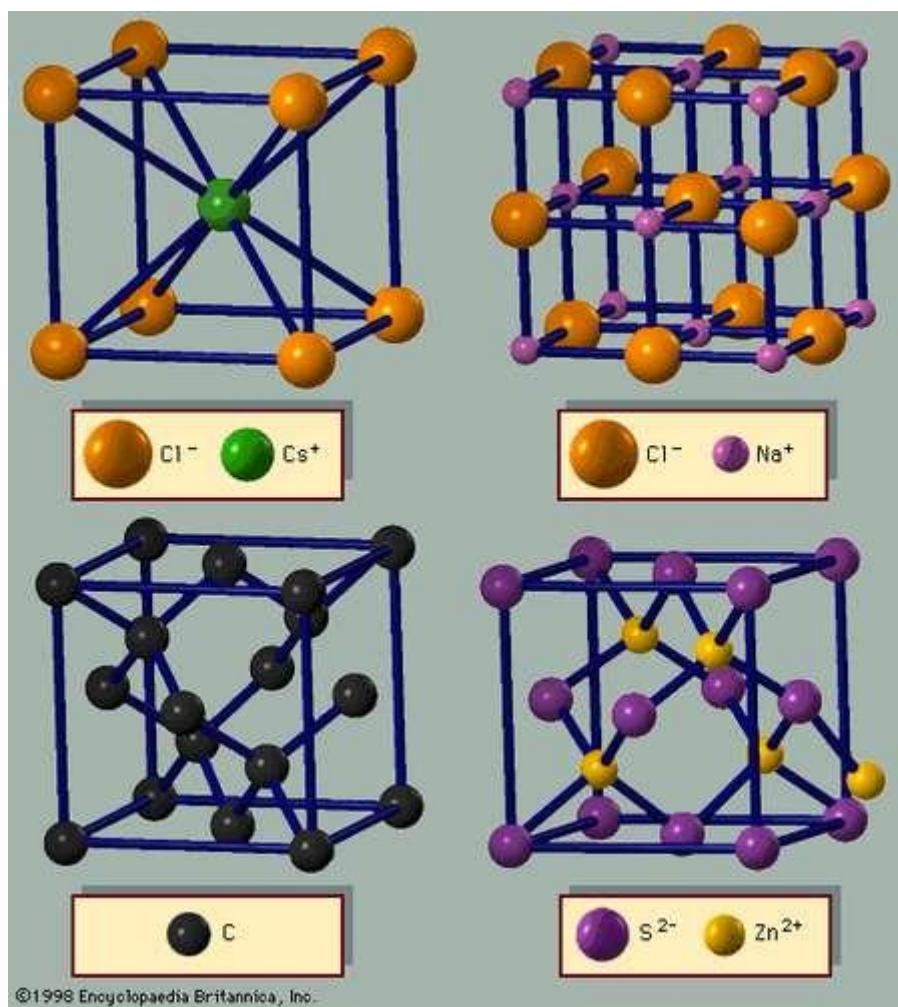


Figure 13.12. *Crystal structures*. There is an equal number of the two types of ions in the unit cell of the (A) cesium chloride, (B) sodium chloride, and (D) zinc blende arrangements. The diamond arrangement is shown in (C). If both atoms are identical in (A), the structure is body-centred cubic.

The fcc structure is also found for crystals of the rare gas solids neon (Ne), argon (Ar), krypton (Kr), and xenon (Xe). Their melting temperatures at atmospheric pressure are: Ne, 24.6 K; Ar, 83.8 K; Kr, 115.8 K; and Xe, 161.4 K.

13.7. Structures of Non-Metallic Elements

The elements in the fourth row of the periodic table—carbon, silicon, germanium (Ge), and α -tin (α -Sn)—prefer covalent bonding. Carbon has several possible crystal structures. Each atom in the covalent bond has four first-neighbors, which are at the corners of a tetrahedron. This arrangement is called the diamond lattice and is shown in Figure 3.12c. There are two atoms in a unit cell, which is fcc. Large crystals of diamond are valuable gemstones. The crystal has other interesting properties; it has the highest sound velocity of any solid and is the best conductor of heat. Besides diamond, the other common form of carbon is graphite, which is a layered material.

Each carbon atom has three coplanar near neighbors, forming an arrangement called the honeycomb lattice. Three-dimensional graphite crystals are obtained by stacking similar layers.

Another form of crystalline carbon is based on a molecule with 60 carbon atoms called buckminsterfullerene (C_{60}). The molecular shape is spherical. Each carbon is bonded to three neighbors, as in graphite, and the spherical shape is achieved by a mixture of 12 rings with five sides and 20 rings with six sides. Similar structures were first visualized by the American architect R. Buckminster Fuller for geodesic domes. The C_{60} molecules, also called buckyballs, are quite strong and almost incompressible. Crystals are formed such that the balls are arranged in an fcc lattice with a one-nanometer spacing between the centers of adjacent balls. The similar C_{70} molecule has the shape of a rugby ball; C_{70} molecules also form an fcc crystal when stacked together. The solid fullerenes form molecular crystals, with weak binding—provided by van der Waals interactions—between the molecules.

Many elements form diatomic gases: hydrogen (H), oxygen (O), nitrogen (N), fluorine (F), chlorine (Cl), bromine (Br), and iodine (I). When cooled to low temperature, they form solids of diatomic molecules. Nitrogen has the hcp structure, while oxygen has a more complex structure.

The most interesting crystal structures are those of elements that are neither metallic, covalent, nor diatomic. Although boron (B) and sulfur (S) have several different crystal structures, each has one arrangement in which it is usually found. Twelve boron atoms form a molecule in the shape of an icosahedron (Figure 4.13). Crystals are formed by stacking the molecules. The β -rhombohedral structure of boron has seven of these icosahedral molecules in each unit cell, giving a total of 84 atoms. Molecules of sulfur are usually arranged in rings; the most common ring has eight atoms. The typical structure is α -sulfur, which has 16 molecules per unit cell, or 128 atoms. In the common crystals of selenium (Se) and tellurium (Te), the atoms are arranged in helical chains, which stack like cordwood. However, selenium also makes eight-atom rings, similar to sulfur, and forms crystals from them. Sulfur also makes helical chains, similar to selenium, and stacks them together into crystals.

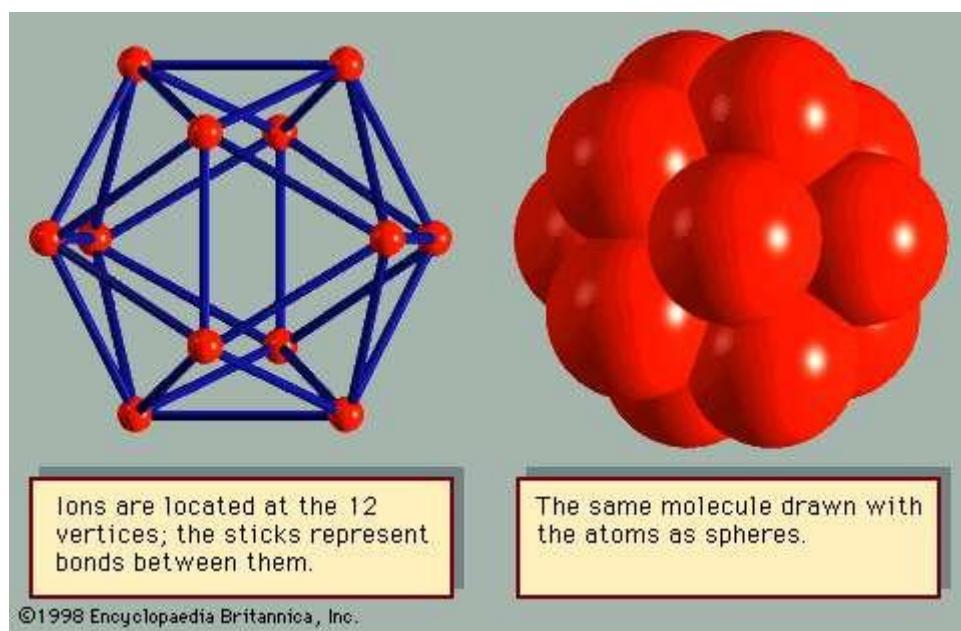


Figure 13.13. The icosahedral arrangement of boron molecules.

13.8. Structures of Binary Crystals

Binary crystals are found in many structures. Some pairs of elements form more than one structure. At room temperature, cadmium sulfide may crystallize either in the zinc blende or wurtzite structure. Alumina also has two possible structures at room temperature, α -alumina (corundum) and β -alumina. Other binary crystals exhibit different structures at different temperatures. Among the most complex crystals are those of silicon dioxide (SiO_2), which has seven different structures at various temperatures and pressures; the most common of these structures is quartz. Some pairs of elements form several different crystals in which the ions have different chemical valences. Cadmium (Cd) and phosphorus (P) form the crystals Cd_3P_2 , CdP_2 , CdP_4 , Cd_7P_{10} , and Cd_6P_7 . Only in the first case are the ions assigned the expected chemical valences of Cd^{2+} and P^{3-} .

Among the binary crystals, the easiest structures to visualize are those with equal numbers of the two types of atoms. The structure of sodium chloride is based on a cube. To construct the lattice, the sodium and chlorine atoms are placed on alternate corners of a cube, and the structure is repeated (Figure 3.12b). The structure of the sodium atoms alone, or the chlorine atoms alone, is fcc and defines the unit cell. The sodium chloride structure thus is made up of two interpenetrating fcc lattices. The cesium chloride lattice (Figure 4.12a) is based on the bcc structure; every other atom is cesium or chlorine. In this case, the unit cell is a cube. The third important structure for AB (binary) lattices is zinc blende (Figure 4.12d). It is based on the diamond structure, where every other atom is A or B . Many binary semiconductors have this structure, including those with one atom from the third (boron, aluminum, gallium [Ga], or indium [In]) and one from the fifth (nitrogen, phosphorus, arsenic [As], or antimony [Sb]) column of the periodic table (GaAs, InP, etc.). Most of the chalcogenides (O, S, Se, Te) of cadmium and zinc (CdTe , ZnSe , ZnTe , etc.) also have the zinc blende structure. The mineral zinc blende is ZnS ; its unit cell is also fcc. The wurtzite structure is based on the hcp lattice, where every other atom is A or B . These four structures comprise most of the binary crystals with equal numbers of cations and anions.

The fullerene molecule forms binary crystals $M_x\text{C}_{60}$ with alkali atoms, where M is potassium (K), rubidium (Rb), or cesium (Cs). The fullerene molecules retain their spherical shape, and the alkali atoms sit between them. The subscript x can take on several values. A compound with $x = 6$ (e.g., K_6C_{60}) is an insulator with the fullerenes in a bcc structure. The case $x = 4$ is an insulator with the body-centred tetragonal structure, while the case $x = 3$ is a metal with the fullerenes in an fcc structure. K_3C_{60} , Rb_3C_{60} , and Cs_3C_{60} are superconductors at low temperatures.

13.9. Alloys

Alloys are solid mixtures of atoms with metallic properties. The definition includes both amorphous and crystalline solids. Although many pairs of elements will mix together as solids, many pairs will not. Almost all chemical entities can be mixed in liquid form. But cooling a liquid to form a solid often results in phase separation; a polycrystalline material is obtained in which each grain is purely one atom or the other. Extremely rapid cooling can produce an amorphous alloy. Some pairs of elements form alloys that are metallic crystals. They have useful properties that differ from those exhibited by the pure elements. For example, alloying makes a metal stronger; for this reason alloys of gold, rather than the pure metal, are used in jewelry.

Atoms tend to form crystalline alloys when they are of similar size. The sizes of atoms are not easy to define, however, because atoms are not rigid objects with sharp boundaries. The outer part of an atom is composed of electrons in bound orbits; the average number of electrons decreases gradually with increasing distance from the nucleus. There is

no point that can be assigned as the precise radius of the atom. Scientists have discovered, however, that each atom in a solid has a characteristic radius that determines its preferred separation from neighboring atoms. For most types of atom this radius is constant, even in different solids. An empirical radius is assigned to each atom for bonding considerations, which leads to the concept of atomic size. Atoms readily make crystalline alloys when the radii of the two types of atoms agree to within roughly 15 percent.

Two kinds of ordering are found in crystalline alloys. Most alloys at low temperature are binary crystals with perfect ordering. An example is the alloy of copper and zinc. Copper is fcc, whereas zinc is hcp. A 50-percent-zinc–50-percent-copper alloy has a different structure— β -brass. At low temperatures it has the cesium chloride structure: a bcc lattice with alternating atoms of copper and zinc and a cubic unit cell. If the temperature is raised above 470° C, however, a phase transition to another crystalline state occurs. The ordering at high temperature is also bcc, but now each site has equal probability of having a copper or zinc atom. The two types of atoms randomly occupy each site, but there is still long-range order. At all temperatures, thousands of atoms away from a site, the location of the atom site can be predicted with certainty. At temperatures below 470° C one also knows whether that site will be occupied by a copper or zinc atom, while above 470° C there is an equal likelihood of finding either atom. The high-temperature phase is crystalline but disordered. The disorder phase is obtained through a partial melting, not into a liquid state but into a less ordered one. This behavior is typical of metal alloys. Other common alloys are steel, an alloy of iron and carbon; stainless steel, an alloy of iron, nickel (Ni), and chromium (Cr); pewter and solder, alloys of tin and lead (Pb); and britannia metal, an alloy of tin, antimony, and copper.

13.10. Crystal Defects

A crystal is never perfect; a variety of imperfections can mar the ordering. A **defect** is a small imperfection affecting a few atoms. The simplest type of defect is a missing atom and is called a **vacancy**. Since all atoms occupy space, extra atoms cannot be located at the lattice sites of other atoms, but they can be found between them; such atoms are called **interstitials**. Thermal vibrations may cause an atom to leave its original crystal site and move into a nearby interstitial site, creating a vacancy-interstitial pair. Vacancies and interstitials are the types of defects found in a pure crystal. In another defect, called an **impurity**, an atom is present that is different from the host crystal atoms. Impurities may either occupy interstitial spaces or substitute for a host atom in its lattice site.

There is no sharp distinction between an alloy and a crystal with many impurities. An alloy results when a sufficient number of impurities are added that are soluble in the host metal. However, most elements are not soluble in most crystals. Crystals generally can tolerate a few impurities per million host atoms. If too many impurities of the insoluble variety are added, they coalesce to form their own small crystallite. These inclusions are called precipitates and constitute a large defect.

Germanium is a common impurity in silicon. It prefers the same tetrahedral bonding as silicon and readily substitutes for silicon atoms. Similarly, silicon is a common impurity in germanium. No large crystal can be made without impurities; the purest large crystal ever grown was made of germanium. It had about 10^{10} impurities in each cubic centimeter of material, which is less than one impurity for each trillion atoms.

Impurities often make crystals more useful. In the absence of impurities, α -alumina is colorless. Iron and titanium impurities impart to it a blue color, and the resulting gem-quality mineral is known as sapphire. Chromium impurities are responsible for the red color characteristic of rubies, the other gem of α -alumina. Pure semiconductors rarely conduct

electricity well at room temperatures. Their ability to conduct electricity is caused by impurities. Such impurities are deliberately added to silicon in the manufacture of integrated circuits. In fluorescent lamps the visible light is emitted by impurities in the phosphors (luminescent materials).

Other imperfections in crystals involve many atoms. **Twinning** is a special type of grain boundary defect, in which a crystal is joined to its mirror image. Another kind of imperfection is a **dislocation**, which is a line defect that may run the length of the crystal. One of the many types of dislocations is due to an extra plane of atoms that is inserted somewhere in the crystal structure. Another type, called an **edge dislocation**, is shown in Figure 3.14. This line defect occurs when there is a missing row of atoms. In the figure the crystal arrangement is perfect on the top and on the bottom. The defect is the row of atoms missing from region *b*. This mistake runs in a line that is perpendicular to the page and places a strain on region *a*.

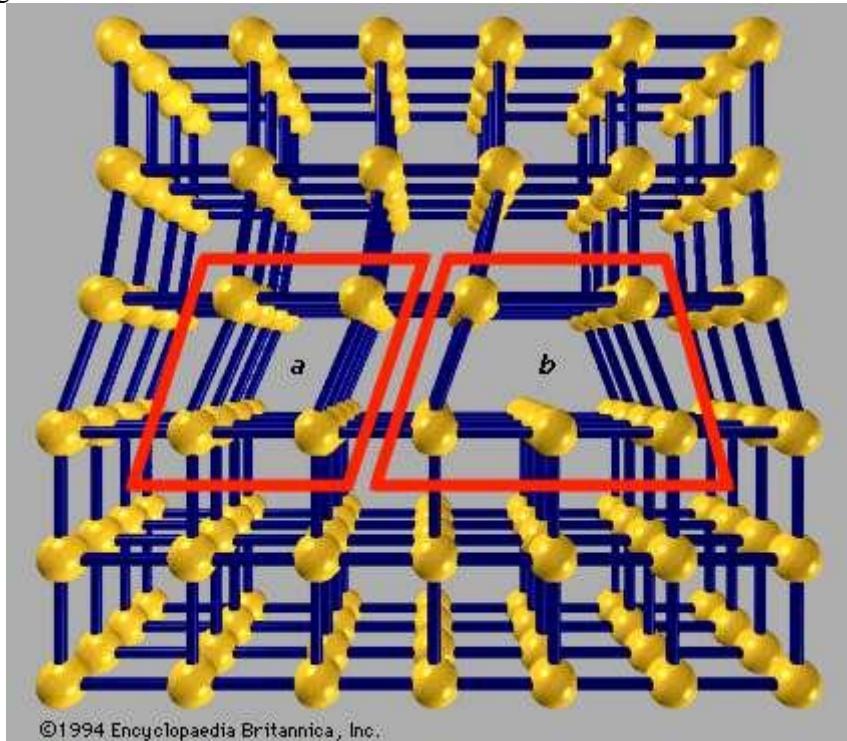


Figure 13.14. *Crystalline lattice defect.* An edge dislocation occurs when there is a missing row of atoms as shown in region *b*. Region *a* is strained.

Dislocations are formed when a crystal is grown, and great care must be taken to produce a crystal free of them. Dislocations are stable and will exist for years. They relieve mechanical stress. If one presses on a crystal, it will accommodate the induced stress by growing dislocations at the surface, which gradually move inward. Dislocations make a crystal mechanically harder. When a metal bar is cold-worked by rolling or hammering, dislocations and grain boundaries are introduced; this causes the hardening.

13.11. Electric Properties

13.11.1. Resistivity

The German physicist Georg Simon Ohm discovered the basic law of electric conduction, which is now called Ohm's law. His law relates the voltage (*V*, measured in volts), the current (*I*, in amperes), and the resistance (*R*, in ohms) according to

the formula $V = RI$. A current I through a solid induces a voltage V ; the resistance R is the constant of proportionality. The value of R is an important factor in the design of electrical circuits. It is determined by the shape of the resistor: a long narrow object has more resistance than a short wide one of the same material. For solids, the important parameter is the resistivity ρ , which is given in units of ohm-meters. It is the resistivity per volume unit and is independent of shape. The relationship between R and ρ is $R = \rho L/A$, where A is the area of the resistor and L is the length. These dimensions are measured in the direction of the current: L is the length of the current path, and A is the cross-sectional area. The resistance of a copper bar depends on its shape, but at a given temperature every piece of pure copper has the same resistivity. Thus the resistivity is a fundamental parameter of a material and is investigated by scientists. Resistivities of solids span a wide range of values. Certain metals have zero resistivity at low temperatures; they are called superconductors. At the other extreme, very good insulators such as sulfur and polystyrene have resistivities larger than one quadrillion ohm-meters. At room temperature, the metal with the lowest value of resistivity is silver, with $\rho = 1.6 \times 10^{-8}$ ohm-meter; the second best conductor is copper, with $\rho = 1.7 \times 10^{-8}$ ohm-meter. Copper, rather than silver, is used in household wires because of the high cost of silver.

13.11.2. Conduction through Ion Hopping

Electrical conductivity σ is the inverse of resistivity and is measured in units of ohm-meter⁻¹. Electrical current is produced by the motion of charges. In crystals, electrical current is due to the motion of both ions and electrons. Ions move by hopping occasionally from site to site; all solids can conduct electricity in this manner. When the voltage is zero, there is no net current because the ions hop randomly in all directions. The imposition of a small voltage causes the ions to slightly favor one direction of motion, which leads to a net flow of charge in that direction; this constitutes an electrical current. The electricity conducted by this process is quite small and is usually negligible compared with that carried by the electrons. When an ion hops, it must migrate to a vacant site, which could be either an interstitial or a vacancy. Ionic conductivity can occur because hopping ions cause vacancies to move through the solid. An ion hops to the vacant site, thereby filling the vacancy, while creating a new one at the ion's former site. Repeating this process causes the position of the vacancy to migrate through the crystal. The motion of the vacancy arises from the motion of ions, which carry charge and contribute to electrical conductivity.

Ion hops are induced by thermal fluctuations. Most of the ions move within their lattice site, vibrating around this point. **Temperature** is defined as the average energy of this vibrational motion; the more the ions move, the higher the temperature. An individual ion at times moves slowly and at times vibrates quite rapidly but usually has an energy near the average value. Each ion shares its vibrational energy with its neighboring ions. An ion typically has some neighbors with small vibrations and others with large ones. The average energy shared with the neighbors is close to the average energy of all the atoms. As a random process, however, it occasionally happens that all neighbors of an ion may have large vibrations, in which case the ion will acquire an unusually high energy. This energy may be high enough to cause it to leave its site and hop to a neighboring site. A thermal fluctuation is the rare process in which the energy at a local site may be much higher or lower than the average energy in the crystal. Probability theory shows that the higher the temperature, the more frequent are these thermal fluctuations. Ions therefore hop more often at high temperature.

A few solids conduct electricity better by ion motion than by electron motion. These unusual materials are technologically important in making batteries. All batteries have two

electrodes separated by an electrolyte, which is a material that conducts ions better than electrons. An example of a crystal electrolyte is β -alumina, which readily conducts monovalent cations such as silver (Ag^+) and sodium (Na^+). Among all ions, silver has the largest value of ionic conductivity in many different electronic insulators. The copper ion (Cu^+) forms the same type of chemical bonds as does the silver ion, but the copper ion, because of its smaller radius, does not migrate as well within an electrolyte. Silver ions fit perfectly into the interstitial sites of the crystal lattices of several electrolytes, while the smaller copper ions permit the neighboring ions to collapse around them, inhibiting further hopping. There are a few good conductors of the inexpensive copper ion that can be used as solid electrolytes in batteries. Silver is too costly and heavy to use in large-volume batteries such as those found in automobiles, but it is used in the smaller batteries that power devices such as hearing aids.

13.11.3. Conduction electrons

Electrons carry the basic unit of charge e , equal to 1.6022×10^{-19} coulomb. They have a small mass and move rapidly. Most electrons in solids are bound to the atoms in local orbits, but a small fraction of the electrons are available to move easily through the entire crystal. These so-called conduction electrons carry the electrical current. Solids with many conduction electrons are metals, while those with a few are semimetals or semiconductors. In insulators, nearly all the electrons are bound, and very few electrons are capable of carrying current. A typical metal has one or more conduction electrons in each atomic unit cell, a semiconductor may have only one conduction electron for each thousand unit cells, and an insulator may have one conduction electron per one million or one trillion unit cells.

The bonding properties of the individual atoms of a solid determine the behavior of the bulk solid. The electrical properties of a solid can usually be predicted from the valence and bonding preferences of its atoms. In the argon atom, for example, all atomic shells are filled with electrons. The electrons of solid argon remain in the atomic shells; none are conduction electrons, and the electrical resistivity is therefore high. Solid argon, like all the rare gas solids, is a good insulator. A few conduction electrons are contributed by impurities, and so the conductivity, though small, is not zero. These conduction electrons move quite readily through the solid. The term mobility is used to describe how well a conduction electron moves through the solid in response to a voltage. Conductivity is the product of mobility, the electrical charge e , and the number N of conduction electrons per unit volume: $\sigma = Ne\mu$, where σ is the conductivity and μ is the mobility. The mobility of the rare gas solids is high, but their conductivity is nonetheless low because there is a small number of conduction electrons.

13.11.4. Electrical Insulators

Like the rare gas solids, most ionic solids are electrical insulators. In sodium chloride, for example, each sodium atom donates its single valence electron to a chlorine atom, thus forming a solid composed of Na^+ and Cl^- ions. All electrons are in filled shells at low temperature, and in a perfect crystal there are no conduction electrons. Sodium chloride is thus an insulator with a very high resistivity. Some conduction electrons are provided by impurities or thermal excitations. At high temperatures large ion vibrations from thermal fluctuations may knock an electron out of a filled shell, upon which it becomes a conduction electron and contributes to the conductivity. The number of conduction electrons created by thermal excitations is small for most insulators.

Although defects can be responsible for producing conduction electrons, they can also destroy the conducting ability of electrons by trapping them. The defects have local orbitals

that provide a lower energy state for the electron than the one occupied in the conduction state. A conduction electron becomes bound at the defect, ceasing to contribute to the conductivity. This process is very efficient in insulators, so the few conduction electrons provided by impurities and thermal fluctuations are usually trapped at other defects. By definition, an **insulator** is a solid that does not provide a stable environment for conduction electrons.

13.11.5. Conductivity of Metals

Metals have a high density of conduction electrons. The aluminum atom has three valence electrons in a partially filled outer shell. In metallic aluminum the three valence electrons per atom become conduction electrons. The number of conduction electrons is constant, depending on neither temperature nor impurities. Metals conduct electricity at all temperatures, but for most metals the conductivity is best at low temperatures. Divalent atoms, such as magnesium or calcium, donate both valence electrons to become conduction electrons, while monovalent atoms, such as lithium or gold, donate one. As will be recalled, the number of conduction electrons alone does not determine conductivity; it depends on electron mobility as well. Silver, with only one conduction electron per atom, is a better conductor than aluminum with three, for the higher mobility of silver compensates for its fewer electrons.

In metals such as sodium and aluminum, the atoms donate all their valence electrons to the conduction band. The resulting ions are small, occupying only 10–15 percent of the volume of the crystal. The conduction electrons are free to roam through the remaining space. A simple model, which often describes well the properties of the conduction electrons, treats them as interacting neither with the ions nor with each other. The electrons are approximated as free particles wandering easily through the crystal. This concept was first proposed by the German scientist Arnold Johannes Wilhelm Sommerfeld. It works quite well for those metals, known as simple metals, whose conduction electrons are donated from *sp*-shells—for example, aluminum, magnesium, calcium, zinc, and lead. They are called simple because they are aptly described by the simple theory of Sommerfeld.

The transition metals are found in three rows of the periodic table: the first row consists of scandium through nickel, the second row is yttrium through palladium, and the third row is lanthanum plus hafnium through platinum. Within these rows, as the atomic number increases, the electrons fill *d*-states in the outer shell of the atom. In crystal form the transition metal atoms are metals with interesting properties. The *d*-electrons are more tightly bound to the ion centre than are *sp*-electrons. While the *sp*-valence electrons become conduction electrons that move freely through the crystal, the *d*-electrons tend to stay localized near the ion. Neighboring ions may covalently bond *d*-electrons. In most cases, these *d*-states are only partially filled. Electrons in these *d*-states can conduct as well as those in the *sp*-states, but the electron motion in the *d*-states is not well approximated by the Sommerfeld model of free particles. Instead, the electrons move from ion to ion through the shared covalent bonds of the *d*-electrons. These metals have some conduction electrons donated from *sp*-states and others from *d*-states; therefore, some electrons move freely according to the Sommerfeld model, while others move through the bonds. Each electron switches back and forth between these two modes of conduction, resulting in electron motion that is quite complicated.

An applied voltage causes the electrons of metals to accelerate and contribute to the electric current. The electrons scatter occasionally from imperfections in the crystal, and the rate of scattering determines the mobility. The electrons do not scatter from the ions in the crystal that are located at the expected site in the crystal lattice. The electrons move to

accommodate the host ions rather than scatter from them. If an ion is missing, misplaced, or of a different species, however, the electron will scatter from this defect. Ions vibrate around their lattice site, with the amplitude vibration increasing with temperature. The vibration may cause the ion to be displaced from its crystal site, providing a defect from which an electron will scatter. The resistivity of metals increases at high temperature, owing to the increase in vibrations of the ions in the crystal and the resulting increase in scattering.

13.11.6. Conducting Properties of Semiconductors

Semiconductors have conducting properties intermediate to those of insulators and metals. In some cases the semiconductors are insulators, while in others they are metals. Semiconductors share with insulators the property that they have no conduction electrons in a perfect crystal without thermal fluctuations. Conduction electrons are provided by electrons from impurities or by thermal fluctuation of electrons from atomic shells. The important difference between insulators and semiconductors is in the nature of the traps. A **trap** is a local electron energy state at a defect.

Although the traps in insulators bind conduction electrons tightly, those in semiconductors only weakly bind the electrons. A trapped conduction electron in a semiconductor can be kicked back to the conduction band by thermal fluctuations. At room temperature, the majority of extra electrons are found in the conduction band rather than in traps. The inability of traps to keep electrons is the main difference between semiconductors and insulators. A semiconductor at room temperature has a sufficient number of conduction electrons to provide good electrical conductivity. Since the mobility of electrons in many semiconductors is exceptionally high, even a small number of conduction electrons is generally sufficient to allow high conductivity.

Phosphorus has five valence electrons, while silicon has four. When a phosphorus atom substitutes for an atom in a silicon crystal lattice, four of its five valence electrons enter covalent bonds. The fifth one is extra, sitting in a shallow trap around the phosphorus site. It is easily excited, however, to the conduction band by thermal fluctuations. At room temperature, there is nearly one conduction electron in silicon for each phosphorus impurity. By controlling the number of impurities, it is possible to control the conductivity of silicon. Other substitutional atoms such as arsenic and antimony also serve as electron donors to the conduction band of silicon.

If a sufficient number of conduction electrons are added to a semiconductor through the introduction of impurities, the electrical properties become metallic. There is a critical concentration of impurities N_c , which depends on the type of impurity. For impurity concentrations less than the critical amount N_c , the conduction electrons become bound in traps at extremely low temperatures, and the semiconductor becomes an insulator. For a concentration of impurities higher than N_c , the conduction electrons are not bound in traps at low temperatures, and the semiconductor exhibits metallic conduction. For phosphorus impurities in silicon, $N_c = 2 \times 10^{18}$ impurities per cubic centimetre. Although this number seems large, it represents about one phosphorus atom for each 100,000 silicon atoms. On a percentage basis, a small number of phosphorus atoms will change silicon from an insulator to a metallic conductor. Other semiconductors have similar properties. In gallium arsenide the critical concentration of impurities for metallic conduction is 100 times smaller than in silicon.

Gallium atoms, like those of phosphorus, can be used as substitutional impurities in silicon. Each atom contributes three electrons to covalent bonds. Since four electrons are needed to complete a tetrahedral arrangement, there is one electron absent per gallium atom from a full set of covalent bonds. The missing electron is called a **hole**. Holes can move

around the crystal in a process similar to the motion of ion vacancies, except in this case there is an electron vacancy. An electron from a nearby covalent bond can jump over and fill the empty electron state, thereby moving the hole to the neighboring bond. The hole contributes a positive charge, since it is the absence of an electron. The mobility of holes in response to an external voltage is almost as high as the mobility of conduction electrons. A semiconductor may have a high density of impurities that cause holes, and a high electrical conductivity is created by their motion. A *p*-type semiconductor is one with a preponderance of holes; an *n*-type semiconductor has a preponderance of conduction electrons. The symbols *p* and *n* come from the sign of the charge of the particles: *positive* for holes and *negative* for electrons.

Movement of a hole

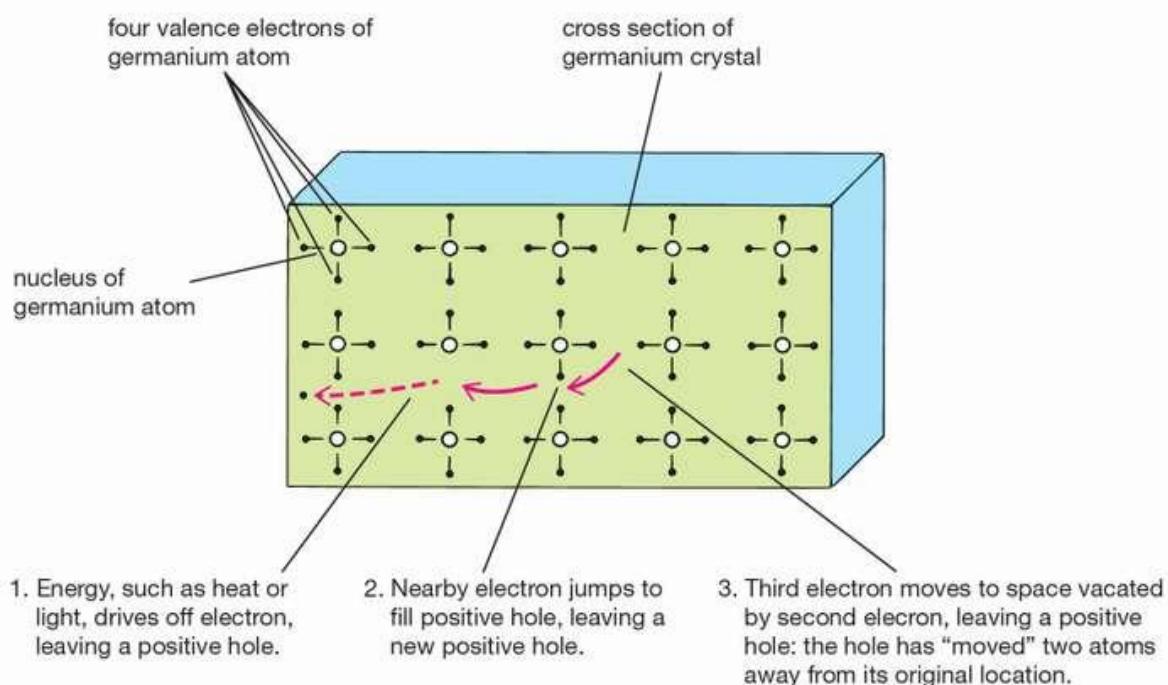


Figure 13.15. Movement of an electron hole in a crystal lattice.

Thermal fluctuations can excite an electron out of a covalent bond, making it a conduction electron. The bond is left with a missing electron, which constitutes a hole. Thermal fluctuations thus make electron-hole pairs. Usually the electron and hole separate in space, and each wanders away. The Swiss-American scientist Gregory Hugh Wannier first suggested that the electron and hole could bind together weakly. This bound state, called a **Wannier exciton**, does exist; the hole has a positive charge, the electron has a negative charge, and the opposites attract. The exciton is observed easily in experiments with electromagnetic radiation. It lives for only a short time—between a nanosecond and a microsecond—depending on the semiconductor. The short lifetime is due to the preference for the electron to reenter a covalent bond state, thereby eliminating both the hole and the conduction electron. This recombination of electron and hole is easily accomplished from the exciton state, since the two particles are spatially nearby. If the electron and hole escape the exciton state by thermal fluctuation, they travel away from each other. Recombination is then less probable, since it occurs only when the wandering particles pass close to one another again. Recombination also can occur at defect sites. First, one particle becomes bound to the

defect, followed by the second particle. The electron and hole are again close to one another, and the electron can reoccupy the covalent bond.

As in metals, the mobility of electrons in semiconductors is limited by electron scattering. For crystals with few defects, the mobility is limited by defect scattering at the lowest temperatures and by ion vibrations at moderate and high temperatures. Since semiconductors with few defects have a small number of conduction electrons, the resistivity is high. The number of conduction electrons is increased in semiconductors by adding impurities. Unfortunately, this also increases the scattering from impurities, which reduces the mobility. Figure 8 shows the resistivity of silicon at room temperature ($T = 300$ K) as a function of the concentration of impurities. The two curves represent conduction by electrons and by holes. Each grid mark on the graph is a factor of 10. The resistivity varies by a factor of one million from the lowest to the highest concentration of impurities.

Semiconductors with few impurities are good photoconductors. Photoconductivity is the phenomenon in which the electrical conductivity of a solid is increased by exposing it to light. Light is electromagnetic radiation within a specific narrow band of frequencies. The quanta of light are absorbed by the semiconductor, creating electron-hole pairs that provide the electrical conduction. More intense light produces more electron-hole pairs and gives rise to better conductivity. Each semiconductor absorbs light over a specific frequency range, so different semiconductors are used as photoconductors for different ranges of frequency.

Zinc oxide (ZnO) is an interesting material with respect to conductivity. It crystallizes in the wurtzite structure, and its bonding is a mix of ionic and covalent. High-purity single crystals are insulators. Zinc oxide is the most piezoelectric of all materials and is widely used as a transducer in electronic devices. (Piezoelectricity is the property of a crystal to become polarized when subjected to pressure.) Zinc oxide is a good semiconductor when aluminum impurities are included in the crystal. Polycrystalline ceramics of semiconducting zinc oxide conduct well and obey Ohm's law. The addition of small amounts of other oxides, such as those of barium and chromium, causes zinc oxide ceramics to have very nonohmic electrical properties; the electrical current in such ceramics is the most nonlinear of any known material. The current I becomes proportional to a power of the voltage V^n , where the exponent n has values of more than 100 in certain ranges of voltage. This material is called a varistor, which is a contraction of the words variable and resistor. Zinc oxide varistors are widely used as circuit elements to protect against voltage surges. There is little current until a critical voltage of about 330 volts is reached, at which point the current rises steeply in a nonlinear fashion. Another interesting application of zinc oxide was its former use as a white pigment in paint. It has been replaced by titanium dioxide (TiO_2), however, which is whiter.

13.12. Solving Density Using a Unit Cell

$$\rho = \frac{\text{mass of a unit cell (m)}}{\text{volume of a unit cell (v)}}$$

$$m = \frac{ZM}{N_a e^3}$$

where:

m = the mass of the unit cell

Z = effective number of atoms in a unit cell

M – Molar mass (atomic mass)

N_a = Avogadro's Number

e = edge length of a unit cell

Sample Problem 13.1. Many metals pack in cubic unit cells. The density of a metal and length of the unit cell can be used to determine the type for packing. For example, sodium has a density of 0.968 g/cm³ and a unit cell side length (e) of 4.29 Å

- a. How many sodium atoms are in 1 cm³?
- b. How many unit cells are in 1 cm³?
- c. How many sodium atoms are there per unit cell?

Solution: (Solve using dimensional analysis)

Given:

$$e = 4.29 \text{ \AA} \times \frac{1 \times 10^{-8} \text{ cm}}{1 \text{ \AA}} = 4.29 \times 10^{-8} \text{ cm}$$

$$v = (4.29 \times 10^{-8} \text{ cm})^3 = 7.90 \times 10^{-23} \text{ cm}^3 / \text{unit cell}$$

$$\rho = 0.968 \text{ g/cm}^3$$

$$Na = 23.0 \text{ g/mol}$$

- a. Solving for the average mass of Na atoms:

$$m_{ave} = \frac{23.00 \text{ g/mol}}{6.023 \times 10^{23} \text{ atoms/mol}} = 3.82 \times 10^{-23} \text{ g/atom in } 1.0 \text{ cm}^3$$

$$\text{Na atoms} = \frac{0.968 \text{ g/cm}^3}{3.82 \times 10^{-23} \text{ g/atom}} = 2.53 \times 10^{22} \text{ atom/cm}^3$$

- b. Solving for the unit cells in 1.0cm³:

$$\text{No. of unit cells} = \frac{1.0 \text{ cm}^3}{\frac{7.90 \times 10^{-23} \text{ cm}^3}{\text{unit}}} = 1.27 \times 10^{22} \text{ unit cells}$$

- c. Solving for Na atoms per unit cell:

$$\text{Na atoms/unit cell} = \frac{2.53 \times 10^{22} \text{ atoms/cm}^3}{1.27 \times 10^{22} \text{ units/cm}^3} = 2.0 \text{ atoms/unit cell}$$

Sample Problem 13.2. a) You are given a cube of silver metal that measures 1.015 cm on each edge. The density of silver is 10.49 g/cm³. How many atoms are in this cube? b) Because atoms are spherical, they cannot occupy all of the space of the cube. The silver atoms pack in the solid in such a way that 74% of the volume of the solid is actually filled with the silver atoms. Calculate the volume of a single silver atom.

Solution:

$$v = (1.015 \text{ cm})^3 = 1.046 \text{ cm}^3$$

$$e = 1.015 \text{ cm}$$

$$\rho = 10.49 \text{ g/cm}^3$$

$$Na = 6.023 \times 10^{23} \text{ atoms/mol}$$

$$M \text{ of Ag} = 107.9 \text{ g/mol}$$

a. No. of atoms in the cube of Ag = $\frac{10.97 \text{ g/cm}^3 (6.023 \times 10^{23} \text{ atoms/mol}) (1.015 \text{ cm})^3}{107.9 \text{ g/mol}} = 6.40 \times 10^{22}$ atoms

b. 74% volume filled = 0.74

$$\text{Volume filled by Ag atoms} = (1.046 \text{ cm}^3)(0.74) = 0.774 \text{ cm}^3$$

$$\text{Volume occupied per Ag atom} = \frac{0.774 \text{ cm}^3}{6.023 \times 10^{23} \text{ atoms}} = 1.29 \times 10^{-24} \text{ cm}^3/\text{atom}$$

Sample Problem 13.3. The edge length of the unit cell of Ta, is 330.6 pm; the unit cell is body-centered cubic. Tantalum has a density of 16.69 g/cm³.

a) calculate the mass of a tantalum atom.

b) Calculate the atomic weight of tantalum in g/mol.

Solution:

Given:

$$e = 330.6 \text{ pm} \times \frac{1.0 \text{ cm}}{1.0 \times 10^{10} \text{ pm}} = 3.3 \times 10^{-8} \text{ cm}$$

$$\text{volume of the unit cell} = (3.3 \times 10^{-8} \text{ cm})^3 = 3.59 \times 10^{-23} \text{ cm}^3$$

Sample Problem 13.4. The density of TlCl(s) is 7.00 g/cm³ and that the length of an edge of a unit cell is 385 pm, a) determine how many formula units of TlCl there are in a unit cell. Based on your answer for the number of formula units of TlCl(s) in a unit cell, b) how is the unit cell of TlCl(s) likely to be structured?

Solution:

Given:

$$\rho = 7.00 \text{ g/cm}^3$$

$$M = 204.4 + 35.5 = 239.9 \text{ g/mol}$$

$$e = 385 \text{ pm} \times \frac{1 \text{ cm}}{1 \times 10^{10} \text{ pm}} = 3.85 \times 10^{-8} \text{ cm}$$

$$v = (3.85 \times 10^{-8} \text{ cm})^3 = 5.71 \times 10^{-23} \text{ cm}^3$$

Mass of TlCl per unit cell:

$$m = (7.00 \text{ g/cm}^3)(5.71 \times 10^{-23} \text{ cm}^3) = 4.00 \times 10^{-22} \text{ g}$$

$$\text{mol} = \frac{4.00 \times 10^{-22} \text{ g}}{239.9 \text{ g/mol}} = 1.67 \times 10^{-24} \text{ mol}$$

∴ Formula units of TlCl in the unit cell is:

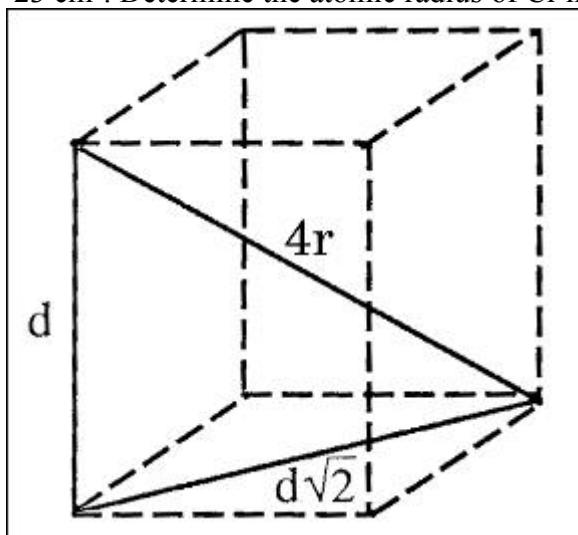
$$(1.67 \times 10^{-24} \text{ mol})(6.023 \times 10^{23} \text{ atoms/mol}) = 1.00$$

PROGRESS CHECK

13.1. Avogadro's number has been determined by about 20 different methods. In one approach, the spacing between ions in an ionic substance is determined by using X-ray diffraction. X-ray diffraction of sodium chloride have shown that the distance between adjacent Na^+ and Cl^- ions is 2.819×10^{-8} cm. The density of solid NaCl is 2.165 g/cm^3 . By calculating the molar mass to four significant figures, you can determine Avogadro's number. What value do you obtain?

13.2. Aluminum B is a solid phase of aluminum still unknown to science. The only difference between it and ordinary aluminum is that Aluminum B forms a crystal with a bcc unit cell and a lattice constant $a = 331 \text{ pm}$. Calculate the density of Aluminum B.

13.3. Chromium crystallizes in a body-centered cubic structure. The unit cell volume is $2.583 \times 10^{-23} \text{ cm}^3$. Determine the atomic radius of Cr in pm. Refer to the figure below:



The triangle we will use runs differently than the triangle used in fcc calculations. d is the edge of the unit cell, however $d\sqrt{2}$ is NOT an edge of the unit cell. It is a diagonal of a face of the unit cell. $4r$ is a body diagonal. Since it is a right triangle, the Pythagorean Theorem works just fine.

13.4. Calcium fluoride crystallizes with a cubic lattice. The unit cell has an edge of 546.26 pm and has a density of 3.180 g/cm^3 . How many formula units must there be per unit cell?

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