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NATIONAL UNIVERSITY OF LIFE AND ENVIRONMENTAL SCIENCES OF UKRAINE
Department of Analytical and Bioinorganic Chemistry & Water Quality

WORKBOOK
in CHEMISTRY (I) (Inorganic & Bioinorganic)

of student_____
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Branch of knowledge – 10 Natural Sciences
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CONTENT

CHAPTER 1 INTRODUCTION

1.1 General chemistry safety and laboratory rules

Chemistry laboratories can be hazardous if the rules are not followed. During a chemistry course a student may handle materials which are carcinogenic, poisonous, flammable, and explosive. Some of these materials and equipment may also cause severe burns, cuts, or bruises if handled improperly or carelessly. Most accidents that occur in the chemistry laboratory are a result of carelessness, impatience, improper or unauthorized experimentation, and disregard for safety rules or proper operating procedures. In order to minimize the chances of an accident in the laboratory certain rules and regulations must be obeyed at all times when one is working or observing in a chemical laboratory. Therefore, it is not advisable for anyone to work in a laboratory without proper knowledge of the dangers involved. Due to the inherent dangers present in a chemical laboratory exercise, it should be understood that the following rules must be obeyed to minimize the chance of an accident. The student is expected to exercise proper judgment and extreme caution at all times when working in the laboratory.

1. DO NOT perform unauthorized experiments or work in a laboratory alone.

2. Approved eye protection must be worn at all times in the laboratory. If you do get a chemical in your eye rinse immediately with large quantities of water using the eye-wash stations.

3. Long hair and loose clothing must be confined while in a laboratory.

4. Appropriate clothing must be worn at all times while in the laboratory. Your legs must be completely covered below the knee by your choice of clothing. If your clothing does not meet the requirement you may choose to wear an approved laboratory coat or apron which does cover your legs to your knees.

5. Closed shoes with socks must be worn.

6. Know the location and proper use of fire extinguishers, fire blankets, eye wash devices, and first aid kits.

7. Before obtaining any chemicals carefully read the label on the reagent bottles.

8. Eating, smoking, and drinking are not allowed in a chemistry laboratory.

9. Thoroughly wash your hands after leaving the laboratory.

10. Use the fume hoods when toxic or irritating vapors are involved.

11. Mouth suction is never used to fill a pipette.

13. Never direct the open end of test tube toward yourself or anyone else.

14. Never pour water into concentrated acid (**especially H₂SO₄**).

15. Learn the proper procedure for igniting and operating a laboratory burner. Always extinguish the flame when the burner is not being used. Make sure that all flammable reagents are well removed before lighting the burner.

16. Liquid and solid waste containers must be properly used at all times.

17. Never place chemicals directly on the balance pan. Always use a proper weighing container when using a balance to weigh a chemical. Never pour chemicals directly over the balance.

18. Never return unused chemicals to their original container (unless directed to do so by the instructor).

19. Securely replace lids, caps, and stoppers after removing reagents from containers.

20. Always wipe spatulas clean before and after inserting into reagent bottles.

21. Report any accident and/or injury, however minor, to your instructor immediately.

22. Never place anything that is not directly required for the experiment on laboratory desks; other items may interfere with the experiment.

23. All personal belongings should be placed in the bookcases as you enter the laboratory.

24. Clean up any spill immediately.

25. Before leaving the laboratory, make sure your work area is clean and dry.

26. Your instructor is available for any assistance you may need. Never hesitate to ask questions especially if there is any question concerning proper operating procedure. Be sure that you understand every instruction before proceeding.

1.2 Chemical lab glassware

All chemical glassware is divided into several groups according to their use (Fig. 1.1):

> *Of general usage* (is used to carry out different chemical operations): test tubes, beakers, flat-bottom, round-bottom and conical flasks, Wurtz flasks (round-bottom with bleeder), crystallizer tanks, funnels, clock glass, weighing bottles;

> *Measuring glassware*: graduated cylinders, measuring tubes,

measuring pipettes, volumetric flasks;

➢ *Of special use*: flasks, Kipp gas generator, vacuum filtering apparatus, consisting of Bunsen flask, Buchner funnel, trap flask, and water-jet pump;

➢ *Porcelain ware and ware made from other materials*: spreading rods, mortars, evaporating dishes, crucibles and boats.
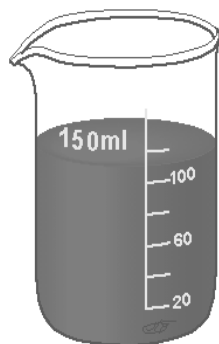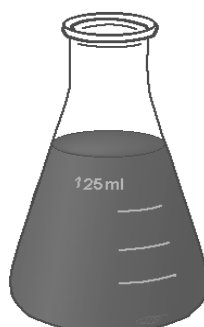
Test tube	Beaker	Erlenmeyer Flask	Florence Flask
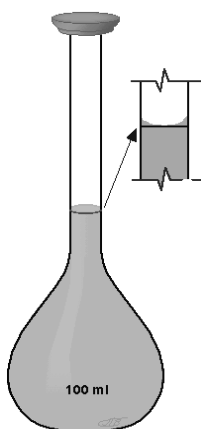
Volumetric Flask	Dropper Bottle	Glass Jar	Filtering Funnel
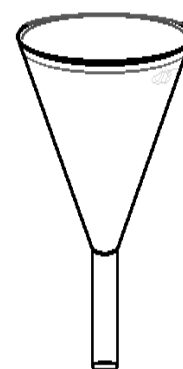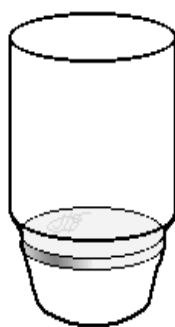
Buchner's Funnel	Gooch's Crucible	Walter's Crucible Holder	Pi-Pump
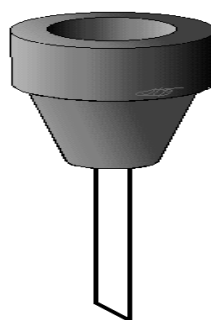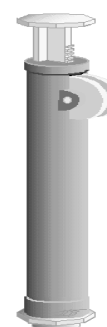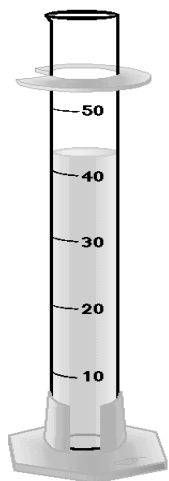
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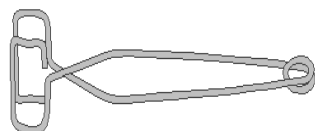
Test tube clamp
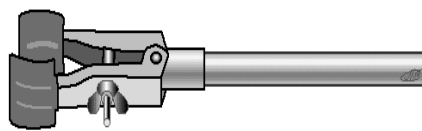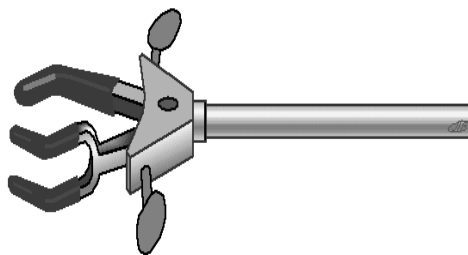
Clamps

Watch glass

Thermometers

Spatulas

5

4   3   2   1   0

Volumetric pipettes
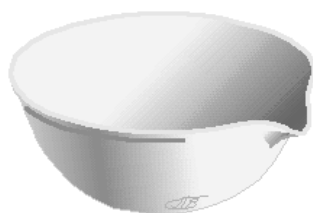
Evaporation dish
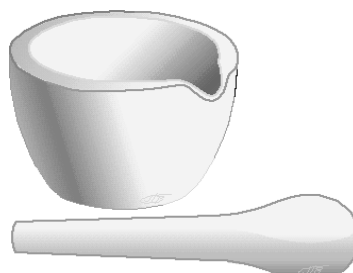
Pestle and mortar

Forceps

Crystallizing Dish as sand bath   Dessicator

Figure 1.1. Separate varieties of laboratory glassware

1.3 Cleaning of lab glassware

In the analysis of samples the preparation of scrupulously clean glassware is mandatory. Lab glassware cleaning procedures must follow specific method requirements. If procedures are not listed then the method of cleaning should be adapted to both the substances that are to be removed, and the determinations (tests) to be performed. Recommendations for such cleaning procedures are listed below.

Analysis/Parameter	Cleaning Procedure *(In order specified)*
ORGANICS	
Semi-Volatile:	
(Pesticides, Herbicides, Oil & Grease)	Solvents: 5, 1-4, 5 or 6, 13, 15 or Muffle: 5, 1-4, 12, 13, 15 or Oxidizer: 5, 1-3, 14,
INORGANICS	
Trace Metals:	1-4, 9, 8 (optional), 4
Nutrients, Minerals:	1-4, 8, 4
Solids:	1-4, 11 (Volatile Solids 16)
Non-Metals, Physical Properties: (Cyanide)	1-4, 14
MICROBIOLOGY	1-4 (Sterilize per approved method)
BIOASSAY	
Freshwater:	18, 2, 3, 9 or 8, 4, 5, 4, 20
Marine & Estuarine:	19, 2, 3, 9 or 8, 4, 5, 4, 20
RADIONUCLIDES	17, 3, 8, 4

Cleaning Procedures:

1. Remove all labels using sponge or acetone.

2. Wash with hot tap water and a brush to scrub inside of glassware, stopcocks, and other small pieces, if possible, using a suitable laboratory-grade detergent. Organics – Liquinox®, Alconox® (phosphate-free liquid detergents, mild and completely soluble in water), or equivalents.

Inorganic anions – Liquinox® or equivalents.

Inorganic cations – Liquinox®, Micro® or equivalents.

Microbiology – must pass inhibitory residue test.

3. Rinse thoroughly with hot tap water.

4. Rinse thoroughly with distilled water (DW).

5. Rinse thoroughly with pesticide grade Acetone.

6. Rinse thoroughly with pesticide grade Methanol.

7. Rinse thoroughly with pesticide grade Hexane.

8. Rinse or soak with 1:1 HCl (Hydrochloric Acid).

9. Rinse or soak with >10% HNO_3 (Nitrate Acid).

10. Bake at 105 °C for 1 hour.

11. Bake at 180 °C (prior to use as per method).

12. Drain, then heat in muffle furnace for 30-60 minutes at 400 °C.

13. Clean, dry glassware should be sealed and stored in dust-free environment.

14. Soak in oxidizing agent (Chromic acid or equivalent); preferably hot (40-50 °C).

15. Last step (prior to use) should be a rinse with the solvent used in analysis.

16. Drain, then heat in muffle furnace for 1 hour at 550 °C.

17. Heat 1 hour in EDTA solution at 90-100 °C.

18. New glassware must be soaked overnight in 10 % HNO_3 or HCl.

19. New glassware must be soaked overnight in seawater.

20. Rinse thoroughly with DW.

1.4 Chemical reagents and their storage

Reagents are individual substances, their solutions or mixtures of strictly determined composition, destined for laboratory works, scientific researches and chemical analysis.

Chemical reagents can be used in solid, liquid and gaseous state (as vapors). They are divided into several qualifications with characteristics, given in the Table 1.1, depending on the degree of purity.

Solid reagents are stored in glass and polyethylene boxes, liquids – in flasks. Depending on substance property boxes and flasks are closed with glass, polyethylene, and rubber or cork stoppers.

Hygroscopic substances are stored in weighing bottles, desiccators, soldered ampoules, and flasks with Calcium Chloride tubes and in boxes

with rubbed stoppers. Boxes stoppers can be covered with paraffin embedded. Reagents changing on light are stored only in dark-glass flasks.

Table 1.1. Analytical classification of chemicals

Qualification of reagent	Symbol	Contents of main substances, % (by mass)	Contents of separate admixtures, % (by mass)
Pure	p.	98	0,01- 0,5
Analytically pure	a.p.	Not less than 99	to 0,1
Chemically pure	c.p.	More than 99	to 0,1
Specially pure	s.p.	About 100	10^{-5}- 10^{-10}

The **desiccator** is used to store dried samples in a dry atmosphere. It should not be used to dry an object, but to maintain an already dried object indefinitely in a dry condition.

Usage:

1. To open – slide lid horizontally across the top to one side until it comes off. Use one hand to hold the bottom of the desiccator while using the other hand to grasp the knob;

2. To close – place lid partly on the top and slide across until desiccator is completely closed and then rotate lid gently in both directions;

3. Do not attempt to lift lid off vertically;

4. Make sure the lid has enough grease around the ground glass rim – if necessary, spread Vaseline uniformly on the rim. When the lid is properly seated, the greased rim will appear as shown in Fig. 1.2;
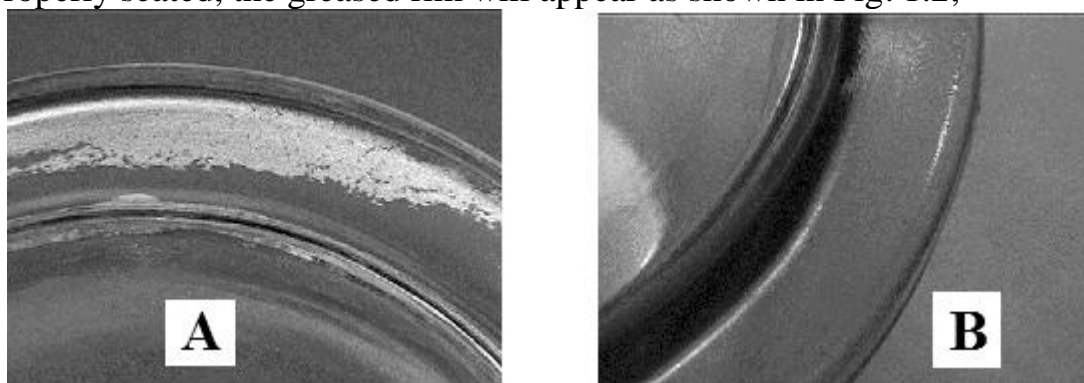
Figure 1.2. A – Improperly sealed desiccator (Note the cloudiness along the rim): **B** – Properly sealed desiccator. (Note that the rim is clear).

5. If the desiccant appears wet or clumpy, it probably needs to be replaced with new dessicant. It is helpful to have a small amount of indicating desiccant present. Is is a granulated silicagel coated of dry

Cobalt(II) sulfate, having blue color When the color changes to pink, the desiccant should be replaced.

6. Desiccants should be handled in the hood and added carefully, wearing goggles and lab coat. Desiccant should not coat the sides or plate of the desiccator.

Great amounts of gases are stored in gas storage tanks, small amounts – in gas burettes or gasometers.

1.5 Elementary operations carrying out

Balances and weighing

Chemical, pharmaceutical and analytical balances are usually used in chemical laboratories.

Chemical and pharmaceutical balances allow to determine the mass to a precision of 0,01 g and analytical one – that of 0,0001 g. Balances are equipped with the set of weights called the set of fractional weights. Weights from the set are taken with pincers.

For weighing the object put it on the left scale pan and put the weight on the right one. Chemical balances have the device called arrester supporting the scale pans in the non-working state. To bring the balances in the working state the arrester has to be put down. Take and put objects and fractional weights only when the arrester is lowered (non-working state). Weighing can be considered as completed if the deviation of pointer to the right and to the left from medium line becomes equal. After weighing put immediately the fractional weights back to the set.

Keep the following rules when weighing:

1. Do not put hot or wet objects on the scale pans. Work with liquids; avoid spilling of liquid on balances and fractional weights.
2. Do not put the substance being weighed directly on the scale pans, use special glassware (clock glass or weighing bottle) or filter paper.
3. Take fractional weights only with pincers and do not use the weights of another set of fractional weights.
4. After weighing put balances in the non-working state and do not leave anything on the balances.

Measurement of liquid reagents volume

Measurement of liquid reagents volume is carried out with the measuring vessels. Measuring graduates, measuring tubes, and volumetric flasks are used for the relatively rough measurement of liquid volume.

Burettes allow to measure the volume of flowing out liquid or the evolving gas to a precision of 0,1 %. Volumetric flasks are used for

preparation of solutions with necessary concentration or for diluting of solution to given extent. The precision of volume measurement is 0,12-0,20 %.

Measuring (Mohr's pipettes) and transfer pipettes are used in order to take precisely the volume. Measuring pipettes can be used to measure the total volume or its part.

Separation of solid components from liquids

For separation of solid components from liquid ones the filtering and decantation are used. Filtering is the process of liquid separation from solid matter through the filtering material with the simultaneous detaining of the sediment on its surface.

When the aim of filtering is the obtaining of solid precipitate the plain filter is used. If it is necessary to get pure liquid the folded filter is used. For separation of fine-crystalline precipitate and for the acceleration of filtering the vacuum filtering or filtering with removal by suction is used. For the separation of heavy precipitate the decantation – pouring the liquid off the precipitate – is used.

If it is necessary to filter a hot solution, the special double-wall funnel with electric heating is used. It is the metal funnel with double wall, the heating element inserted between them. Ordinary funnel is inserted in this double-wall funnel and is heated. The filtering with heating by vapor is widespread operation in chemical laboratory. The funnel for such filtering is the glass double-wall one. The jet of steam is passed between its walls at filtering.

Filtering materials are: paper, cotton wool, glass wool, and fabric. Paper filters can be ordinary and quantitative (ashless). Filter is quantitative if the weight of ashes forming when it burns is less than 0,0001 g. Funnels and Shott's crucibles (funnels with soldered pore glass partition) are used for aggressive liquids filtering.

Characteristics of paper filters are given in the Table 1.2.

Table 1.2. Characteristics of paper filters

Band color	Pore diameter, nm	Characteristic of paper and type of precipitate
Red or black	10	Wide pores, fast filtering, for rough precipitate
White	About 3	Medium pores, for large precipitate
Blue	1–2,5	Small pores, for fine precipitate
Green	Less than 1	High-density, for very fine precipitate
Yellow	3	Degreased paper

Rules of filtering

1. Correctly chosen filter must be 3-4 mm lower than the edge of

funnel and fit closely to its walls.

2. Filter is moistened with small amount of distilled water.

3. Let the precipitate settle on the bottom of glassware and carefully, not disturbing it, pour off the liquid along the glass rod on the filter. Only the last portion of liquid is to be mixed with the precipitate.

4. Fill the funnel with liquid so that its level is 2-3 mm lower than the edge of filter.

5. When all the liquid flows down, wash the precipitate with washing liquid.

6. Vacuum filtering is carried out with the installation consisting of Bunsen flask, Buchner's funnel, trap flask and water-jet pump. Filter must cover the whole perforated bottom of Buchner's funnel and its edge must not rise up. Then turn on the pump and, when the air begins to penetrate through the bottom of funnel, pour off the liquid. Filtering is considered as completed if the drop does not hang from the spout of funnel. The mixture on the filter must not be mixed! The precipitate on the filter is distributed evenly and is concentrated with flat glass stopper. After the operation is finished pass the air in the flask and only then close the water-supply tap. It is necessary to take the substance from the Buchner's funnel in the following way: disconnect the funnel from the flask, overturn it and knock out (blow out) the substance on the sheet of filter paper by light knocks.

Grinding

For solid substances grinding various mortars: porcelain, metal, agate is used most frequently. Metal mortars are used for rough grinding, porcelain – for finer grinding and agate – for very hard materials.

The very big pieces are firstly broken with hammer. The pieces of the walnut size can be ground in the mortar, filled with the substance to ¼ of its height. Grind carefully so that the substance does not throw out from the mortar. The size of the mortar must be chosen in accordance with the amount of substance. Mortars cannot be used for heating.

Dissolving of solid substances

Preparation of solutions is one of the most important operations of the inorganic synthesis. At preparing solutions the following rules are to be observed.

1. Solutions must be prepared using distilled water.

2. Usually the dissolving is carried out in glass or porcelain beakers, Erlenmeyer (conical) flasks, and other flasks. For the preparation of solutions with certain concentration measuring flasks are used. If the substance dissolves with the great heat production, the solution is prepared in thin-wall porcelain or thermally sound glassware.

The capacity of glassware where solution is prepared must be a little

greater than the given volume. Each flask with solution must be provided with an etiquette or inscription.

3. Pour out small quantity of solvent in the glassware then pour the substance, mix and add the solvent in the amount, slightly less then necessary to prepare solution. Add the solvent to the given volume only after solid substance is completely dissolved. After all solvent is added, mix the solution thoroughly and, if necessary, filter before use it.

4. If the substance is hydrolyzed easily, add firstly the substance preventing from the hydrolysis and then dissolve.

Obtaining and drying of gases

In the laboratory conditions gas can be obtained by the solid substance and solution interaction, by thermal decomposition of substances and from the gas storage tank with pressed gas.

The form and design of device for gas obtaining depends on the gas properties.

If the gas is obtained by solid substance decomposition, the latter is placed into the test tube, fixed horizontally so that the emitting moisture does not flow down to the place of heating.

If the gas is evolving when liquid reacts with solid substance, test tubes, Wurtz flasks, Kipp gas generator (Fig. 1.3) are used. In this case test tube or Wurtz flask is fixed vertically. Kipp gas generator (apparatus) is the device of non-stop action; it is used for obtaining of great amounts of gas.
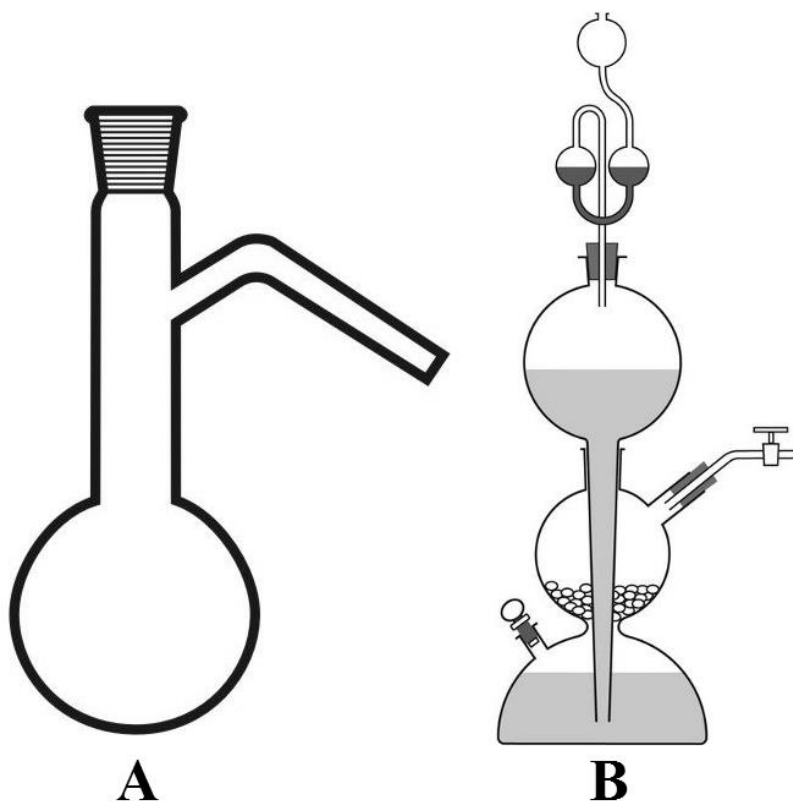
Figure 1.3. A – Wurtz flask; **B** – Kipp gas generator.

Methods of gas collecting depend on gas properties. Gases, heavier than air, are collected in the open glassware. If the gas and the air are similar by mass, the gas is collected

A   **B**

using the water displacement method. The possibility of gas interaction with water must be taken into account. If it reacts with water, other liquid, for example, the saturated solution of salt, must substitute water. Gases, lighter than air, are collected in open, overturned glassware.

The accompanying substances contaminated gases, industrial as well as obtained in laboratory, and gases, evolved from the water solutions, contain water. The purifying and drying of gases is carried out in special glassware: Tyshchenko's, Wulf's, Drexel's flasks (Fig. 1.4), etc.

A   B   C   D
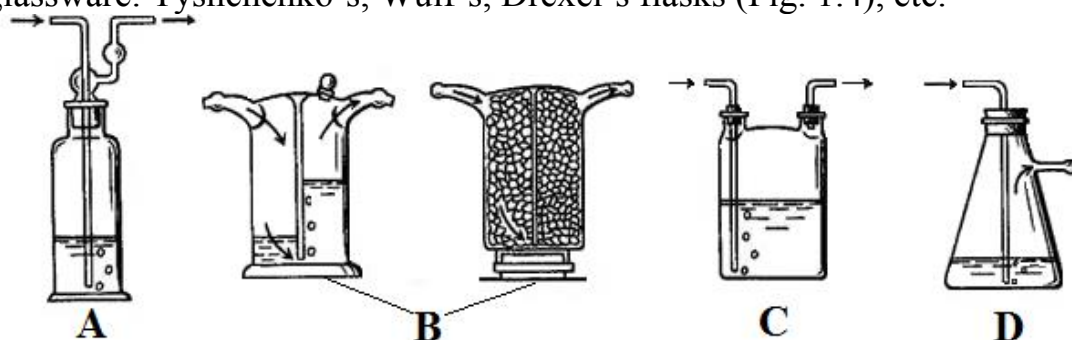
Figure 1.4. Wash bottles: Drexler's; Tishenko's - for liquid (left) and solid substances (right); C – Woulf's; D – Bunzen's.

Cooling

For substances, cooling in dry air after the incineration or melting, desiccators are used. The flowing water, ice, cooling mixtures are used for cooling in order to crystallize the solid substance. Pea-size pieces of ice (snow) are mixed with water to obtain the mess-like mass. To obtain the lower temperatures ice is mixed with Sodium Chloride: 1 part of ice to 0,3 parts of Sodium Chloride (temperature decreases to -21 °C) or 1 part of ice to 1,43 parts of five-watered calcium Chloride.

Heating

Heating is often used in laboratories at conducting the chemical reactions; incineration, dehydration, melting of solid substances; evaporation and boiling of solutions.

For heating different devices are used: electrical plates, drying chambers, electrical furnaces (muffles), spirit burners, bathes (Fig. 1.5). Depending on the substance properties and the purpose of heating, the different methods are used.

1. When substances are heated in test tubes, porcelain and metal crucibles (Fig. 1.6) for short time, and the open fire is used. Heating is done in the upper part of flame, fixing the test tube in the wooden holder. Liquids in the thermally sound glass or porcelain ware are heated on spirit burners through the asbestos net.

2. If the long-term heating at high temperature is necessary (incineration, melting etc.) the electrical plates (temperature up to 300 °C)

and electrical furnaces (temperature 300-1000 °C) are used. Incinerated substances are put to the porcelain, metal or graphite crucibles (Fig. 1.6).
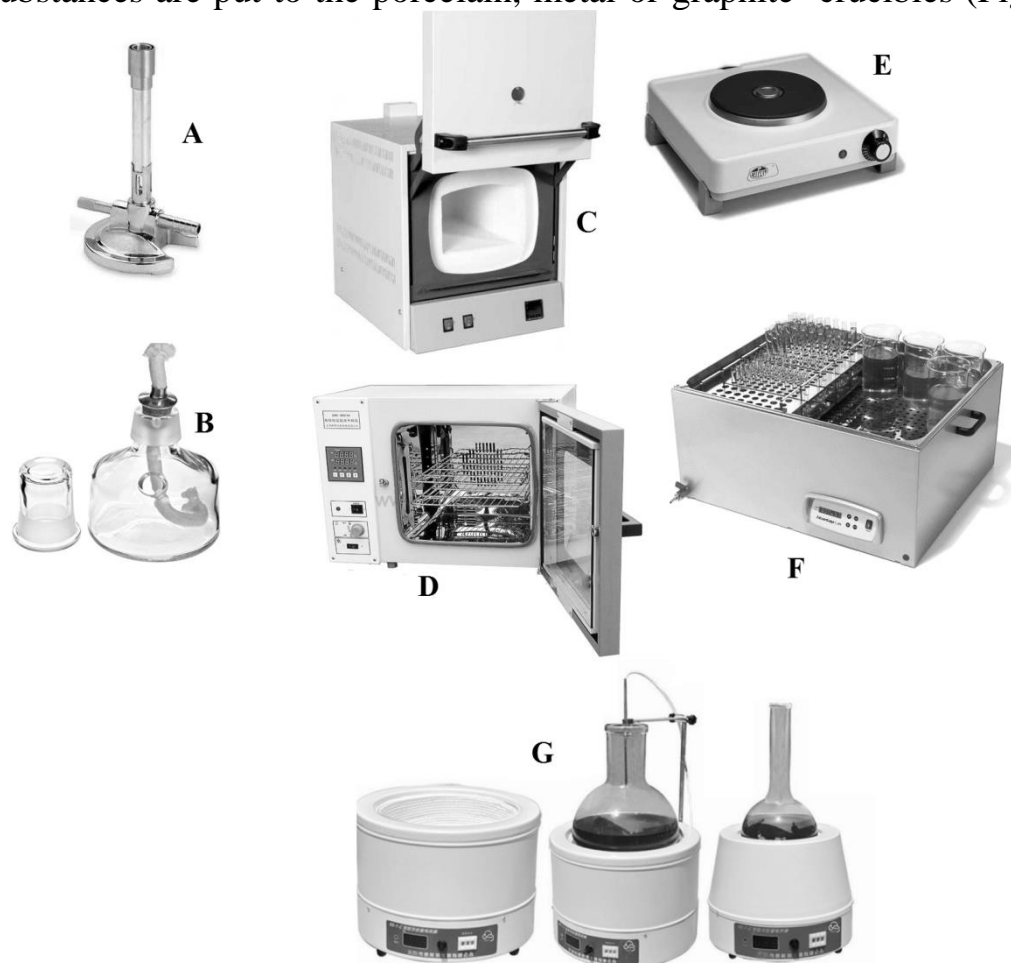
Figure 1.5. Lab heating equipment: A – Bunzen's gas burner; B – spirit burner; C - electrical furnace (muffle); D – drying chamber (oven); E – electrical plate; F – water bath; G – heating mantles.

Figure 1.6. Lab crucibles: A – metal; B – porcelain; D – graphite.

3. If the heating of solutions (evaporating) is to be done in the narrow temperature interval, the bathes (water – Fig. 1.6F, sand, glycerine, oil or silicon) filled with liquid (sand) to 2/3 its volume are used. The vapors of boiling water produce heating; if glycerin or oil is used, the liquid produces the heating itself. Sand bath is used for long heating. Bathes allow getting the temperature up to 300 °C.

4. Drying and the heating in order to remove hygroscopic moisture at temperature to 110 °C are made in the drying chambers. Hygroscopic substances and substances decomposed at heating are dried in desiccators (see Fig. 1.2) with the help of certain substances, taking water.

Drying is considered as completed if the crystals of substance taken with glass rod are poured from it when knocked slightly.

Ovens. Electrically heated ovens (Fig. 1.5D) are commonly used in the laboratory to remove water or other solvents from chemical samples and to dry laboratory glassware. *Never use laboratory ovens to prepare food for human consumption.*

Purchase or construct laboratory ovens with their heating elements and their temperature controls physically separated from their interior atmospheres. Small household ovens and similar heating devices usually do not meet these requirements and, consequently, should not be used in laboratories. With the exception of vacuum drying ovens, laboratory ovens rarely prevent the discharge of the substances volatilized in them into the laboratory atmosphere. The volatilized substances may also be present in sufficient concentration to form explosive mixtures with the air inside the oven. This hazard can be reduced by connecting the oven vent directly to an exhaust system.

Muffle furnace fire. A laboratory specializing in the analysis of soils was asked to analyze SOM (soil organic matter) content. The first step of the analytical protocol called for ashing the sample in a muffle furnace (Fig. 1.5C). The technician loaded the furnace.

Do not use ovens to dry any chemical sample that has even moderate volatility and might pose a hazard because of acute or chronic toxicity unless special precautions have been taken to ensure continuous venting of the atmosphere inside the oven. Thus, do not dry most organic compounds in a conventional unvented laboratory oven.

To avoid explosion, do not dry glassware that has been rinsed with an organic solvent in an oven until it has been rinsed again with distilled water. Potentially explosive mixtures can be formed from volatile substances and the air inside an oven.

Bimetallic strip thermometers are preferred for monitoring oven temperatures. Do not mount mercury thermometers through holes in the tops of ovens with the bulb hanging into the oven. If a mercury thermometer is broken in an oven of any type, close the oven and turn it off immediately to avoid mercury exposure. Keep it closed until cool. Remove all mercury from the cold oven with the use of appropriate cleaning equipment and procedures. After removal of all visible mercury, monitor the heated oven in a laboratory chemical hood until the mercury vapor concentration drops below the threshold limit value.

Hot plates. Laboratory hot plates (Fig. 1.5E) are often used when solutions are to be heated to 100 °C or higher and the inherently safer steam baths cannot be used as the source of heat. As previously noted, use only hot plates that have completely enclosed heating elements in laboratories. Although almost all laboratory hot plates currently sold meet this criterion, many older ones pose an electrical spark hazard arising from either the on/off switch located on the hot plate, the bimetallic thermostat used to regulate the temperature, or both. Normally, these two spark sources are located in the lower part of the hot plate in a region where any heavier-than-air and possibly flammable vapors evolving from a boiling liquid on the hot plate would tend to accumulate. In principle, these spark hazards are alleviated by enclosing all mechanical contacts in a sealed container or by using solid-state circuitry for switching and temperature control. However, in practice, such modifications are difficult to incorporate into many of the hot plates now in use. Warn laboratory personnel of the spark hazard associated with these hot plates. Set up any newly purchased hot plates to avoid electrical sparks. In addition to the spark hazard, old and corroded bimetallic thermostats in these devices can eventually fuse shut and deliver full continuous current to a hot plate. This risk can be avoided by wiring a fusible coupling into the line inside the hot plate. If the device does overheat, the coupling will melt and interrupt the current. For many brands of combined stirrer/hot plates, the controls for the stirrer and temperature control are not easily differentiated. Care must be taken to distinguish their functions. A fire or explosion may occur if the temperature rather than the stirrer speed is increased inadvertently.

Heating mantles are commonly used to heat round-bottom flasks, reaction kettles, and related reaction vessels (Fig. 1.5G). These mantles enclose a heating element in layers of fiberglass cloth. As long as the fiberglass coating is not worn or broken and no water or other chemicals are spilled into the mantle, heating mantles pose minimal shock hazard. They are normally fitted with a male plug that fits into a female receptacle

on an output line from a variable autotransformer. This plug combination provides a mechanically and electrically secure connection.

Always use heating mantles with a variable autotransformer to control the input voltage. Trained laboratory personnel should be careful not to exceed the input voltage recommended by the mantle manufacturer. Higher voltages will cause a mantle to overheat, melting the fiberglass insulation and exposing the bare heating element.

Some heating mantles are constructed by encasing the fiberglass mantle in an outer metal case that provides physical protection against damage to the fiberglass. If such metal-enclosed mantles are used, good practice is to ground the outer metal case either by using a grounded three-conductor cord from the variable autotransformer or by securely affixing one end of a heavy braided conductor to the mantle case and the other end to a known electrical ground. This practice protects the laboratory personnel against an electric shock if the heating element inside the mantle short-circuits against the metal case. Placing the heating mantle on a laboratory jack and holding the flask or container being heated by clamps attached to a separate ring stand or grid work is the recommended procedure. This allows for rapid removal of heat in the case of overheating or exothermicity.

When using *oil, salt, or sand baths*, take care not to spill water and other volatile substances into the baths. Such an accident can splatter hot material over a wide area and cause serious injuries.

Electrically heated oil baths are often used to heat small or irregularly shaped vessels or to maintain a constant temperature with a stable heat source. For temperatures below 200 °C, a saturated paraffin oil is often used; for temperatures up to 300 °C, a silicone oil should be used. Care must be taken with hot oil baths not to generate smoke or have the oil burst into flames from overheating. Always monitor an oil bath by using a thermometer or other thermal sensing device to ensure that its temperature does not exceed the flash point of the oil being used. For the same reason, fit oil baths left unattended with thermal-sensing devices that turn off the electric power if the bath overheats. Heat these baths by an enclosed heating element, such as a knife heater, a tubular immersion heater such as a calrod, or its equivalent. The input connection for this heating element is a male plug that fits a female receptacle from a variable autotransformer (e.g., Variac) output line. Alternatively, a temperature controller can be used to control the temperature of the bath precisely. Temperature controllers are available that provide a variety of heating and cooling options. **Thermocouples used by controlling devices must be clamped**

securely in place to maintain contact with the medium or object being heated at all times.

Oil baths must be well mixed to ensure that there are no hot spots around the elements that take the surrounding oil to unacceptable temperatures. This problem can be minimized by placing the thermoregulator fairly close to the heater. Contain heated oil in either a metal pan or a heavy-walled porcelain dish; a Pyrex dish or beaker can break and spill hot oil if struck accidentally with a hard object. Mount the oil bath carefully on a stable horizontal support such as a laboratory jack that can be raised or lowered easily without danger of the bath tipping over. Always clamp equipment high enough above a hot plate or oil bath that if the reaction begins to overheat, the heater can be lowered immediately and replaced with a cooling bath without having to readjust the clamps holding the equipment setup. Never support a bath on an iron ring because of the greater likelihood of accidentally tipping the bath over. Provide secondary containment in the event of a spill of hot oil. Wear proper protective gloves when handling a hot bath.

Molten salt baths, like hot oil baths, offer the advantages of good heat transfer, commonly have a higher operating range (e. g., 200…425 °C), and may have a high thermal stability (e.g., 540 °C). The reaction container used in a molten salt bath must be able to withstand a very rapid heat rise to a temperature above the melting point of the salt. Care must be taken to keep salt baths dry, because they are hygroscopic, a property that can cause hazardous popping and splattering if the absorbed water vaporizes during heating.

Hot air baths can be useful heating devices. Nitrogen is preferred for reactions in which flammable materials are used. Electrically heated air baths are frequently used to heat small or irregularly shaped vessels. Because of their inherently low heat capacity, such baths normally must be heated considerably above the desired temperature (≥100 °C) of the vessel being heated. Purchase or construct these baths so that the heating element is completely enclosed and the connection to the air bath from the variable autotransformer is both mechanically and electrically secure. These baths can be constructed from metal, ceramic, or, less desirably, glass vessels. If a glass vessel is used, wrap it thoroughly with heat-resistant tape so that if the vessel breaks accidentally, the glass will be contained and the bare heating element will not be exposed. Fluidized sand baths are usually preferred over air baths.

Tube furnaces (Fig. 1.7A) are often used for high-temperature reactions under reduced pressure. The proper choice of glassware or metal

tubes and joints is required, and the procedures should conform to safe practice with electrical equipment and evacuated apparatus.
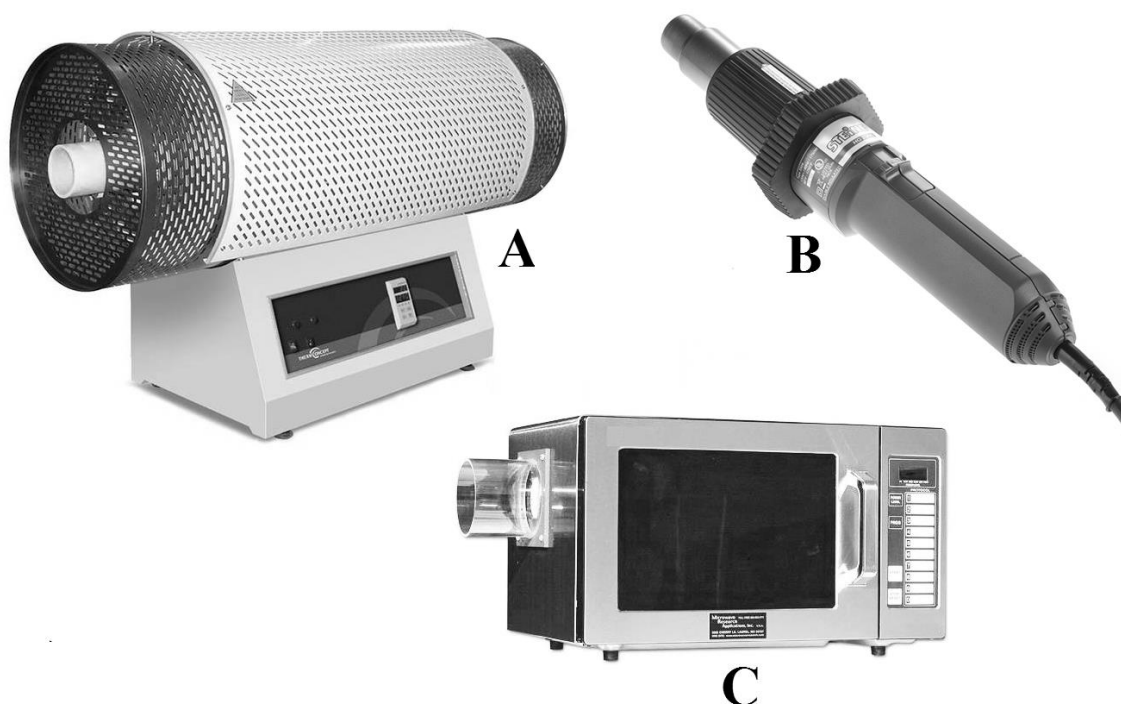
Figure 1.7. Special heat tools: A – tube furnace; B – heat gun; C – microwave lab oven.

Laboratory *heat guns* (Fig. 1.7B) are constructed with a motor-driven fan that blows air over an electrically heated filament. They are frequently used to dry glassware or to heat the upper parts of a distillation apparatus during distillation of high-boiling point materials. The heating element in a heat gun typically becomes red-hot during use and, necessarily cannot be enclosed. Also, the on/off switches and fan motors are not usually spark-free. Furthermore, heat guns are designed to pull lab air into and across the red-hot heating elements, thereby increasing the ignition risk. For these reasons, heat guns almost always pose a serious spark hazard. Never use them near open containers of flammable liquids, in environments where appreciable concentrations of flammable vapors may be present, or in laboratory chemical hoods used to remove flammable vapors. Household hair dryers may be substituted for laboratory heat guns only if they have three-conductor line cords or are double-insulated. Any handheld heating device of this type that will be used in a laboratory should have GFCI protection to ensure against electric shock.

Use *microwave ovens* (Fig. 1.7C) specifically designed for laboratory use. Domestic microwave ovens are not appropriate.

Microwave heating presents several potential hazards not commonly encountered with other heating methods: extremely rapid temperature and

pressure rise, liquid superheating, arcing, and microwave leakage. Microwave ovens designed for the laboratory have built-in safety features and operation procedures to mitigate or eliminate these hazards. Users of such equipment must be thoroughly knowledgeable of operation procedures and safety devices and protocols before beginning experiments, especially when there is a possibility of fire (flammable solvents), overpressurization, or arcing. To avoid exposure to microwaves, never operate ovens with the doors open. Do not place wires and other objects between the sealing surface and the door on the oven's front face. Keep the sealing surfaces absolutely clean. To avoid electrical hazards, the oven must be grounded. If use of an extension cord is necessary, use only a three-wire cord with a rating equal to or greater than that for the oven. To reduce the risk of fire in the oven, do not overheat samples. The oven must be closely watched when combustible materials are in it. Do not use metal containers or metal-containing objects (e.g., stir bars) in the microwave, because they can cause arcing.

In general, do not heat sealed containers in a microwave oven, because of the danger of explosion. If sealed containers must be used, select their materials carefully and the containers properly designed. Commercially available microwave acid digestion bombs, for example, incorporate a Teflon sample cup, a self-sealing Teflon O-ring, and a compressible pressure-relief valve. Do not exceed the manufacturer's loading limits. For such applications, properly vent the microwave oven using an exhaust system. Placing a large item, such as a laboratory microwave or an oven, inside a chemical fume hood is not recommended.

Heating a container with a loosened cap or lid poses a significant risk. Microwave ovens can heat material (e.g., solidified agar) so quickly that, even though the container lid is loosened to accommodate expansion, the lid can seat upward against the threads and the container can explode. Screw caps must be removed from containers being microwaved. If the sterility of the contents must be preserved, screw caps may be replaced with cotton or foam plugs.

CHAPTER 2 GENERAL NOTIONS OF ATOMIC-MOLECULAR STUDY

Chemists are interested in different kinds of matter (air, water, sand, salt, steel, petrol, sugar, aspirin, etc.). Matter occupies space, has mass, and so can be weighed. This distinguishes it from light and similar radiation.

Substances can be divided into **elements** and **compounds** on the basis of the chemical changes they are involved in. Compounds decompose into other substances, elements do not. Likewise, compounds can be made by combination of other substances, elements cannot. Compounds ultimately decompose into, and can be made from, elements. These considerations are helped by weighing the substances involved. When a compound decomposes, the masses of the products sum to the mass of the compound (an instance of the law of conservation of mass). Masses likewise balance when a compound is made by the combination of other substances.

Some elements exist as more than one substance. For example, carbon C exists as *graphite, diamond, buckminsterfullerene*, etc (**Fig. 2.1**).

Diamond   **Graphite**   **Buckminsterfullerene**
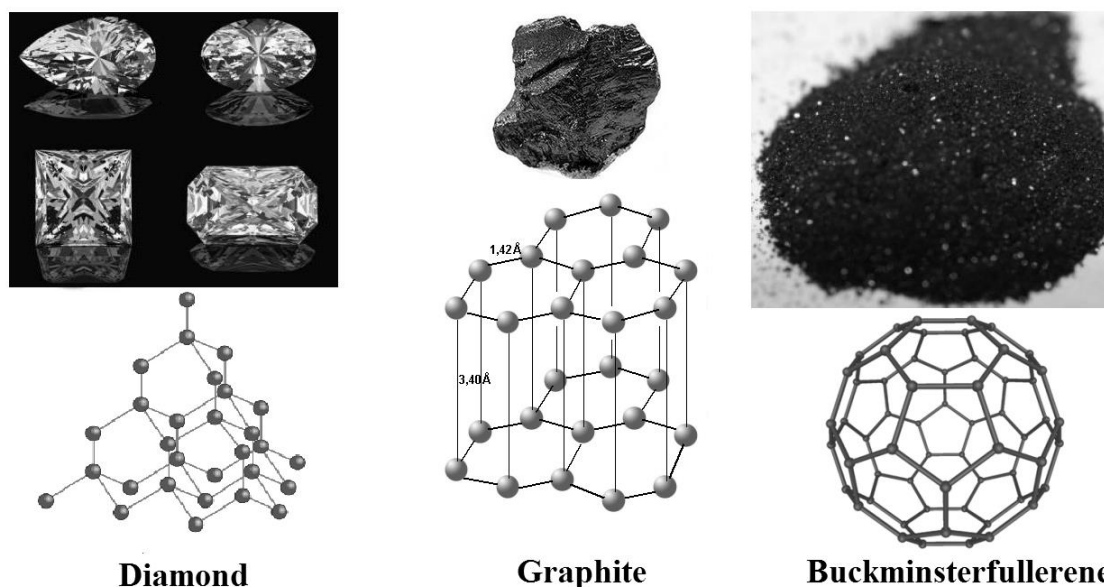
Figure 2.1. Allotropy of carbon

This phenomenon is called allotropy, and the different substances are called **allotropes.** They can be interconverted without change in mass, and combine with other substances to give the same compounds (e.g., the allotropes of carbon all burn in oxygen to give carbon dioxide). Different crystalline forms of an elementary substance (e.g. α- and β-sulfur) are also called allotropes. With all of the compounds of all of the elements (see **Appendix 1**, presented their English and Ukrainian names) to be identified,

systematic methods for writing formulas and naming compounds are necessary. In this section you will be introduced to the rules that apply to simple chemical compounds. **Appendix 2** lists the common and systematic names for a number of well-known substances. Certain common names such as "milk of magnesia" or "lime" remain in everyday use. As you can see, common names usually give no information about chemical composition.

2.1 Chemical formulas

A correctly written chemical formula must represent the known facts about the analytically determined composition of a compound. Care must be taken that subscripts are correct. The two formulas below represent different compounds with very different characteristic properties:

$$H_2O \qquad\qquad H_2O_2$$
Water *Hydrogen peroxide*

But practically chemical formulas are compiled basing on the ideas of **valency** and **oxidation numbers** of the elements.

For example, aluminium sulfate $Al_2(SO_4)_3$ contains the Aluminium cation Al^{3+} and Sulfate anion SO_4^{3-} and is clearly an ionic compound. Ionic compounds consist of huge numbers of positive and negative ions held together by mutual attraction. The formula therefore represents one formula unit - not just a molecule.

One formula unit of aluminium sulfate consists of 2 aluminium ions and 3 sulfate ions. Note in the fire below how the parentheses are used. They surround the polyatomic ion as a unit. The subscript 3 applies to the entire unit within the parentheses.

One formula unit of aluminium sulfate is therefore composed of 2 aluminium atoms, 3 sulfur atoms and 12 oxygen atoms.

How to compile chemical formula, basing on the systematic name of compound.

Example 1. Write the formula for tin(IV) sulfate.

Solution.

Step 1. Write the symbol of tin (see **Appendix 1**, The elements - their symbols, atomic numbers and atomic masses) – **Sn**;

Step 2. Word "sulfate" means an acidic residue of sulfate acid – **$(SO_4)^{2-}$** (see **Appendix 3**, Formulas of the some acids and names of their anions);

Step 3. Write the symbols for the particles side by side, with the positive charged atom of metal (Sn^{4+}) first:

Sn^{4+} $(SO_4)^{2-}$;
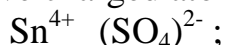
Step 4. Cross over the charge values to give subscripts:

$Sn^{4+}_2 (SO_4)^{2-}_4$;
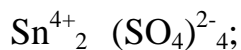
Step 5. Check the subscripts and write the formula.

The total positive charge is 2 x 4+ = 8+. The total negative charge is 4 x 2- = 8-. The charges are equal. Because ionic compounds are represented in the smallest possible whole-number ratio, the ratio 1:2 should be used instead of 2:4. The correct formula is therefore

$Sn(SO_4)_2$.

Symbol of Aluminium   Symbol of Sulfur
Symbol of Oxygen

$$Al_2(SO_4)_3$$

Subscript figures - **indexes**

✔ Subscript 2 refers to 2 aluminium atoms

✔ Subscript 4 refers to 4 oxygen atoms in sulfate ion

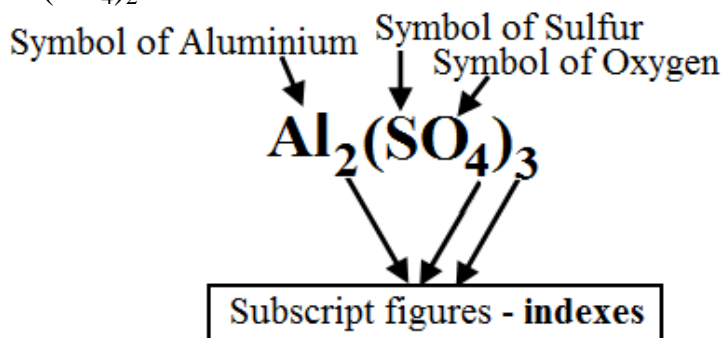✔ Subscript 3 refers to everything inside parenthesis giving 3 sulfate ions, with a total of 3 sulfur atoms and 12 oxygen atoms

Structure of the one simplest unit of aluminium sulfate

Using of oxidation numbers. Oxidation numbers, also called **oxidation states**, are assigned to the atoms in molecules, including molecular ions, to show the general distribution of electrons among the bonded atoms.

The next simple rules may be used for calculation of oxidation numbers of the most atoms in molecules of inorganic and organic substances:

1.   The algebraic sum of the oxidation numbers of all atoms in a neutral compound is **zero**;

2.   The algebraic sum of the oxidation numbers of all atoms in polyatomic ion is equal to the charge of the ion;

3.   An **uncombined element** (in the free state) has an oxidation number of zero. Thus, the atoms of Na, O_2, O_3, P_4, and S_8 all have oxidation number of zero;

4.   A monoatomic ion has an oxidation number equal to the charge of ion. Thus, ion Na^+, Ca^{2+}, Cl^- have oxidation numbers of +1, +2, and -1, respectively;

5.   **Fluorine F** has an oxidation number of -1 in all of its compounds, because it is the most electronegative element;

6. **Oxygen O** has an oxidation number of -2 in. almost all compounds (except in peroxides such as H_2O_2, where it is -1, in superoxides such KO_2, where it is -½; and in compounds with halogens, such as OF_2, where it is +2;

7. **Hydrogen H** has an oxidation number of +1 in all compounds with more electronegative elements, and an oxidation number of -1 in compounds with metals known as hydrides, such as NaH and CaH_2;

8. **Silver Ag** has an oxidation number of +1 in all compounds;

9. **Alkali metals** in the form of ions (**Li, Na, K, Cs, Rb, Fr**) have an oxidation number of +1 in all their compounds;

10. **Alkali-earth metals** in the form of ions (**Ca, Ba, Sr, Ra**) have an oxidation number of +2 in all their compounds;

11. **Magnesium Mg** and **Zinc Zn** in the form of ions have an oxidation number of +2 in all their compounds;

12. **Aluminium Al** in the form of ion has an oxidation number of +3 in all their compounds practically.

Rules 1 and 2 make it possible to assign oxidation numbers where they are not known. The total of the known and unknown oxidation numbers must satisfy rule 1 and 2, as illustrated in the samples below.

Example 2. Assign oxidation numbers to each atom in the following compounds or ions: a) UF_6; b) $GeCl_2$; c) ClO_3^-; d) $Na_2S_4O_6$; e) C_6H_6.

Solution.

a) In **UF_6**, fluorine has oxidation number -1 as it does in all compounds in which it is presented. Therefore, uranium U has oxidation number +6:

$\overset{+6}{U}\overset{-1}{F}_6$ Oxidation no. total = (+6) + (6 x -1) = 0.

b) In **$GeCl_2$**, chlorine is assigned the oxidation number it would have as an ion, -1 (see **Appendix 3**). Therefore, germanium in this compound has oxidation number +2.

$\overset{+2}{Ge}\overset{-1}{Cl}_2$ Oxidation no. total = (+2) + (2 x - 1) = 0.

c) In **ClO_3^-**, oxygen has oxidation number -2. the total oxidation number due to the three oxygen atoms is therefore -6. For the chlorate ion to have a 1- charge, chlorine must be assigned an oxidation number of +5.

$(\overset{+5}{Cl}\overset{-2}{O}_3)^{1-}$ Oxidation no. total = (+5) + (3 x -2) = -1.

**d)** In **Na₂S₄O₆,** according to the rules, sodium has oxidation number +1 and oxygen has oxidation number -2 with a total positive oxidation number of +2 for the two sodium atoms, and a total negative oxidation number of   -2 x 6   = -12 for the six oxygen atoms, sulfur must have an oxidation number of +10 : 4 = + 2½.

$$\overset{+1}{Na_2}\ \overset{+2,5}{S}_4\overset{-2}{O_6}$$
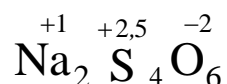
Oxidation no. total = (+1 x 2) + (4 x +2,5) + (6 x -2) = 0.

e) In **C₆H₆,** according to rule 7 (see above), hydrogen has oxidation number +1, because it connects with carbon having more electronegativity (2,1 and 2,5 correspondently) (see **Appendix 4**). So, total positive charge for six hydrogen atoms is +1 x 6 = + 6. Therefore, six atoms of carbon C have total oxidation number -6, one carbon C has oxidation number -1.

$$\overset{-1}{C_6}\overset{+1}{H_6}$$ Oxidation no. total = (6 x +1) + (6 x -1) = 0.
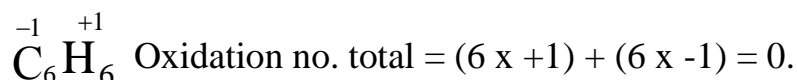
2.2 Basic notions

Relative atomic mass

Atomic weight is the average mass of atoms of an element, calculated using the relative abundance of isotopes in a naturally-occurring element. It is the weighted average of the masses of naturally-occurring isotopes.

Basis for atomic weight unit

Prior to 1961, a unit of atomic weight was based on $1/16^{th}$ (0,0625) of the weight of an oxygen atom. After this point, the standard was changed to be 1/12th the weight of a carbon-12 atom in its ground state.

A carbon-12 atom is assigned 12 atomic mass units. The unit is dimensionless.

Terms related to atomic weight

Relative atomic mass A_r is the mass of an atom or other particle, expressed in unified atomic mass units (amu).

An atomic mass unit is defined as $1/12^{th}$ the mass of a carbon-12 atom. Since the mass of electrons is much smaller than that of protons and neutrons, the atomic mass is nearly identical to the mass number. Atomic mass is denoted with the symbol m_a.

Relative Isotopic Mass. This is the ratio of the mass of a single atom to the mass of a unified atomic mass unit. This is synonymous with atomic mass.

Standard Atomic Weight. This is the expected atomic weight or relative atomic mass of an element sample in the Earth's crust and atmosphere. It is an average of relative isotope masses for an element from

samples collected all over the Earth, so this value is subject to change as new element sources are discovered. ***The standard atomic weight of an element is the value cited for atomic weight on the periodic table.***

> **The molecular mass (weight)** of a substance is the sum of the average masses of the atoms (expressed in atomic mass units or amu) in one molecule of a substance.
> **The formula weight** of an ionic compound is calculated by adding its atomic masses (weights) according to its empirical formula.

Three very important concepts – the mole, Avogadro's number and molar mass - provide the basis for relating masses in grams to numbers of atoms. The first, the mole, is the SI unit for amount of substance.

> **The mole** is the amount of a substance that contains the same number of particles as the number of atoms in exactly 12 g of ^{12}C.

The abbreviation for the mole is **mol**. The mole is a counting unit, like one dozen. In writing, a chemist might refer to 1 mol of Carbon, or 2 mol of Iron, or 2,567 mol of calcium. Amount of substance (in mol) is indicated as Greek letter υ.

The number of particles in a mole has been experimentally determinated in a number of ways. The best modern value is $6,022137 \cdot 10^{23}$ particles. This number is of such importance to chemistry that it is named in honor of the Italian scientist Amedeo Avogadro (1776-1856), whose ideas were crucial in the early understanding of chemistry.

> **Avogadro's number N_A** - $6,022137 \cdot 10^{23}$ – is the number of particles in exactly one mole of each pure substance. In most cases, Avogadro's number is rounded to $6,02 \cdot 10^{23} \; \dfrac{1}{mol}$ (or mol^{-1}).
> **Molar mass (M_m)** is the mass in grams of one mole of pure substance (g/mol).

Molar masses of elements contain equal numbers of atoms. One mole of a substance is one molar mass of this substance. An alternative definition of the mole is the amount of a substance that contains an Avogadro's number of particles of chemical units.

The molar mass is used as the conversion factor in chemical calculations. For a specific substance, a known number of grams can be converted into moles or a known number of moles can be converted into grams. Fig. 2.2 shows the conversions of molar mass, moles, and Avogadro's number.

In general, mass of any chemical substance (in grams) is connected with amount of this substance by the next ratio:
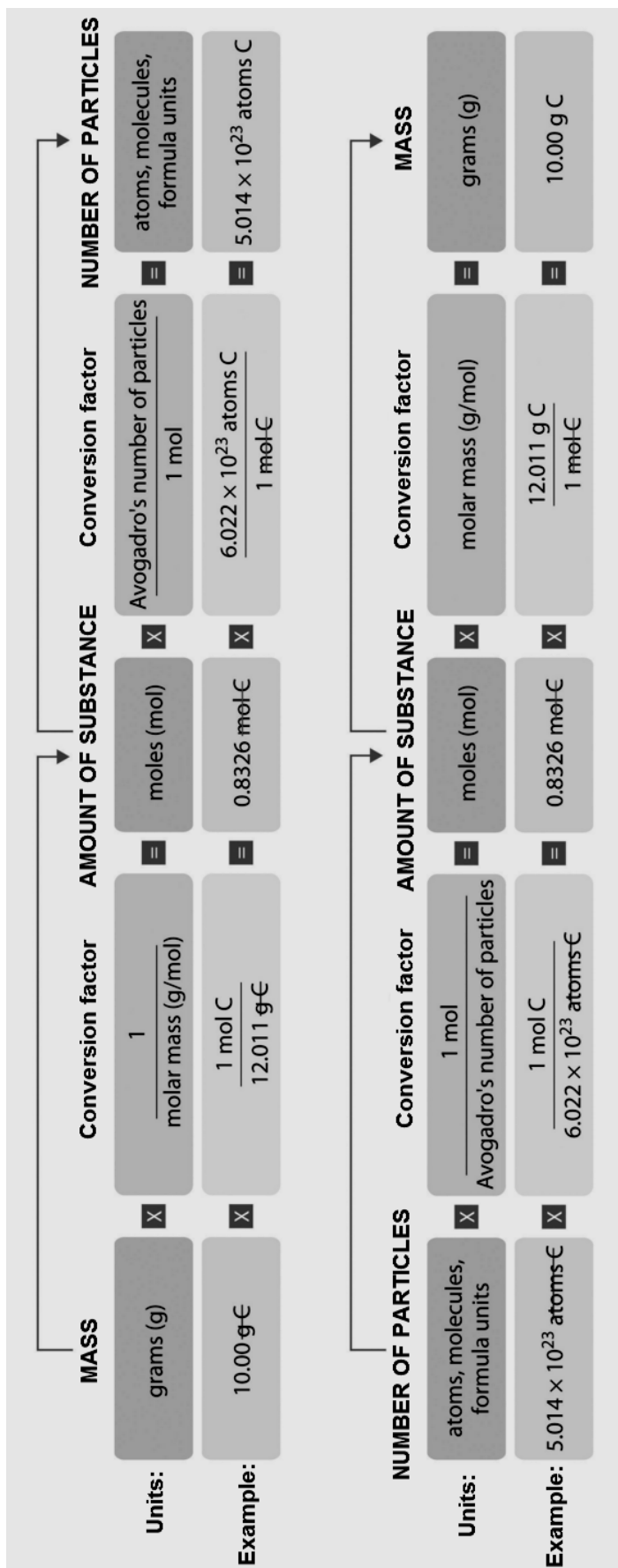
Figure 2.2. A Flowchart for Converting between Mass; the Number of Moles; and the Number of Atoms, Molecules, or Formula Units

$$\upsilon = \frac{m}{M_m}, \qquad\qquad (1)$$

where υ - amount of any pure substance (mol or kmol);

m - mass of any pure substance (g or kg);

M_m - molar mass (g/mol or kg/kmol).

Mass of a single atom of molecule is calculated as follows:

$$m(\text{single atom}) = \frac{A_r}{N_A},$$

where A_r – relative atomis mass of a definite chemical element;

N_A – Avogadro's number.

EXAMPLES OF CALCULATION

1. Determine a relative molecular mass of Sodium Sulfate Na_2SO_4.

Relative molecular mass M_r is determined as sum of relative atomic masses A_r of elements in this compound:

$M_r(Na_2SO_4)=2Ar(Na)+A_r(S)+4A_r(O)=2\cdot23+32+4\cdot16=142$ amu.

2. Caclucate molar mass of Calcium Nitrite $Ca(NO_3)_2$.

Molar mass of substance, expressed in grams, is numerically equal to relative molecular mass expressed in a.m.u. So, calculating relative molecular mass of $Ca(NO_3)_2$, we obtain:

$M_r(Ca(NO_3)_2)=A_r(Ca)+2A_r(N)+6A_r(O)=40+2\cdot14+6\cdot16=164$ c.u.

And molar mass of Calcium Nitrite is equal to 164 g/mol.

3. How many atoms and moles are contained in 60 g of Carbon ^{12}C? Calculate mass of one Carbon atom in grams.

If mass of substance m and its molar mass M_m are known, we could determine the amount of substance (number of moles) in this mass:

M_m is equal to 1 mol;

$$m \quad -\text{``-}\quad x \text{ mol; and } \upsilon = x = \frac{m}{M_m}.$$

Since m=60 g, M_m (C)=12 g/mol, then $\upsilon = x = \dfrac{60\,g}{12\,g/mol} = 5\,mol$.

Multiplying number of moles (5 moles) by Avogadro's number N_A we determine the number of atoms in given mass of substance:

$N=\upsilon \cdot N_A=5\cdot6,02\cdot10^{23}=3,01\cdot10^{24}$ atoms.

Next step - to be divisible molar mass of Carbon M_m (C)=12 g/mol by Avogadro's number N_A for calculation of mass of Carbon one atom in grams:

$$m(C) = \frac{M_m(C)}{N_A} = \frac{12\,g/mol}{6,02\cdot10^{23}\,1/mol} = 2,0\cdot10^{-23}\,g.$$

4. How many moles of Hydrobromide HBr are contained in 0,162 grams of this compound?

Determine a relative molecular mass of HBr:

$M_r(HBr)=A_r(H)+A_r(Br)=1+80=81$.

So, molar mass of HBr is equal to 81 g/mol. Calculate the number of moles in 0,162 g of HBr:

$$\upsilon = \frac{m}{M_m} = \frac{0,162\ g}{81\ g/mol} = 0,002\ mol.$$

5. For neutralization of acid it was used 6 moles of Calcium Hydroxide Ca(OH)₂. How many grams of Ca(OH)₂ are equal to such number of moles?

Calculate a molar mass of $Ca(OH)_2$:

$M_r(Ca(OH)_2)=40+2\cdot16+2\cdot1=74$ g/mol.

Mass of 6 moles: $m=\upsilon\cdot M_r = 6$ g$\cdot74$ g/mol $=444$ g.

6. Calculate a mass part of Sodium in Sodium Sulfate Na₂SO₄.

Calculate a molar mass of Sodium Sulfate $M_r(Na_2SO_4) = 142$ g/mol. 1 mole of Sodium Sulfate contains 2 moles of Sodium atoms. Its mass is equal to: $m = 2\ A_r\ (Na) = 2\cdot23 = 46$ g.

Mass part ω (Na) is the ratio of Sodium mass to total mass of substance:

$$\omega\ (Na) = \frac{m\ (Na)}{m\ (Na_2SO_4)} = \frac{46\ g}{142\ g} = 0,324.$$

7. Determine a mass part of waterless salt in crystalline hydrate.

Molar mass of crystalline hydrate of blue vitriol $M_r(CuSO_4\cdot5H_2O)=M_r(CuSO_4)+5M_r(H_2O)=160+90=250$ g/mol. One mole of hydrate (250 g) contains 160 g of waterless salt. We calculate Mass part ω (CuSO₄) as ratio of Copper Sulfate mass to mass of hydrate:

$$\omega\ (CuSO_4) = \frac{m(CuSO_4)}{m(CuSO_4\cdot5H_2O)} = \frac{160\ g/mol}{250\ g/mol} = 0,64\ (64\%).$$

### 2.3 The laws and concepts of Stoichiometry

Stoichiometry is the branch of chemistry dealing with mass relationships of elements in compounds and among reactants and products in chemical reactions. Accordingly, the calculations of the quantitative relationships between elements in compounds or between substances in chemical reactions are called *stoichiometric calculations*. They are based on the laws of:

- Conservation of mass;

- Definite proportions;
- Multiple proportions,
- and also the gas laws - Gay-Lussac's law of combining volumes and the Avogadro's law.

The law of conservation of mass refers to the total mass in chemical reactions. When we study the combining mass ratios in chemical reactions other interesting relationships emerge. The laws concerning these ratios are called "**stoihiometric laws**" (stoicheion" in the Greek word for "basic material"; "metron" is Greek for "measure".

Law of Constant Proportions. Water is a chemical compound; it can be decomposed into gaseous hydrogen aned gaseous oxygen by adding energy (e. g. thermal or electrical energy):

Water + Energy → Hydrogen + Oxygen.
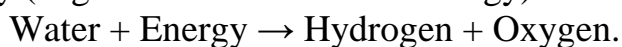
Hydrogen, like oxygen, cannot be separates into simpler substances by ordinary physical and chemical methods, and is therefore an element.

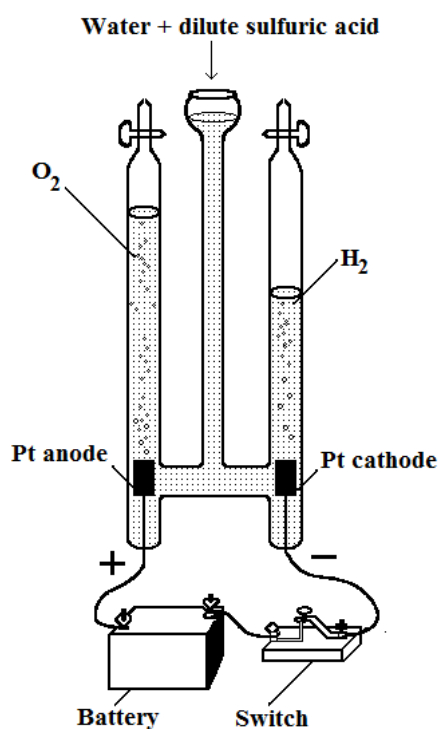Water can be decomposed into its elemental compounds in a Hofmann apparatus (Fig. 2.3).

Figure 2.3. Hofmann apparatus for electrolytic decomposition of water

It consists of three tubes, connected at the bottom. Water is poured in through the funnel on the middle tube until the two outer tubes are filled up to the stopcocks, which are then closed. In the lower part of each of the two outer tubes, there is a small piece of platinum foil with a platinum connecting wire. As soon as the platinum wires are connected to a direct current source of sufficiently high voltage, small bubbles begin to form on the platinum plates (electrodes). The water is being electrolytically decomposed into hydrogen and oxygen; this process is kown as electrolysis. Hydrogen, a gas which burns but does not support combustion, forms at the electrode connected to the negative terminal of the voltage source (cathode), while oxygen, a gas, which supports combustion but eill not burn, forms on the positive electrode (anode). Since pure water conducts electric current very poorly, a little sulfuric acid added to the water to increase its conductivity. If the masses

of the oxygen and hydrogen produced are not now determined, it is found that the mass ratio Oxygen : Hydrogen is always 7,936:1. This ratio is independent of the method used to split the water, and does not depend on the experimental conditions, such as the amount of the water decomposed, temperature, pressure, current density, etc.

The same conclusion is reached when water is synthesized from hydrogen and oxygen:

Hydrogen + Oxygen → Water + Energy.
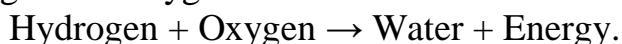
This process may be carried out in calibrated side of the merculy-filled apparatus sketched in Fig. 2.4. This unit is called an eudiometer tube, and was inverted by A. Volta.
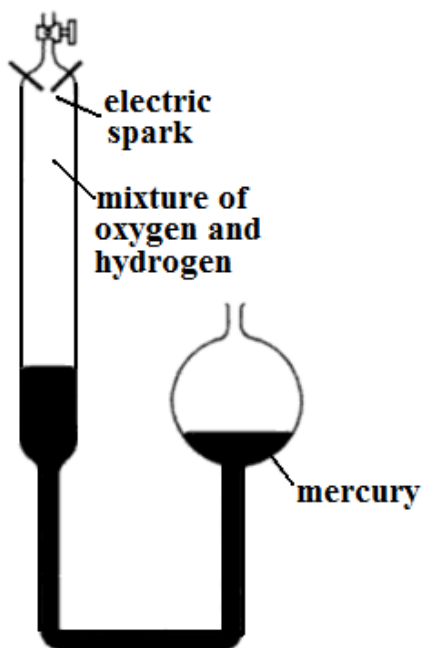
Figure 2.4. Synthesis of water

A mixture of hydrogen and oxygen is introduced into the eudiometer above the mercury and and the reaction is initiated by a small electric spark. The hydrogen and oxygen combine axplosively, releasing as heat the same amount of energy as that needed to decompose water. The water is deposited as extremely fine droplets on the inner wall of the tube. Here again, the combining mass ration of Oxygen : Hydrogen = 7,936:1. If one of the gases is present in excess of this mass ratio, that same amount of excess gas remains unchanged at the end of the reaction.

Similar results are found for other chemical reactions. If, for example, gaseous HCl is decomposed into its constituent gaseous elements, Hydrogwn and Chloride, the mass ration of Chlorine:Hydrogwn is always 35,175:1. Ammonia always contains nitrogen and hydrogen in the ratio 4,632:1. Methane consists of carbon and hydrogwn, always in the ration 2,979:1. The same ratios are found when HCl, NH_3 and CH_4 are synthesized from hydrogen and chlorine, hydrogen and nitrogen, or hydrogwn and carbon.

These and many other experiments illuctrate a general law, called the **Law of constant portions**: *The mass ratio of two elements which combine to form a particular chemical compound is constant.* The law was formulates in 1799 by the French chemist Joseph Louis Proust (1754-1826).

Law of Multiple Proportions. Tqo elements often combine with each other in more than one ratioo, forming several different compounds. For example, nitrogen and oxygen combine to form five different compounds. If the mass ratios of these elements in their various compounds are compared, it is seen that they are not arbitrary, independent numbers. Instead this is a simple relationship between them. The amounts of oxygen which combine with a given amount of nitrogen in these compounds are in the ratios 1:2:3:4:5.

Table 2.1. Mass ratio between elements in Nitrogen oxides

# Compound	Formula	Composition, % (mass)		Mass ratio of Oxygen on one part of Nitrogen	Ratio between quantity of Oxygen and Nitrogen
		Nitrogen	Oxygen		
1	N_2O	63,7	36,3	1: 0,571	1
2	NO	46,7	53,3	1: 1,142	2
3	N_2O_3	36,9	63,1	1: 1,713	3
4	NO_2	30,5	69,5	1: 2,284	4
5	N_2O_5	25,9	74,1	1: 2,855	5

Thorough investigation has shown that this too is a general law. It was discovered in 1803 by the English scientist John Dalton (1766-1844), and named the **Law of multiple proportions.** The mass ratios of two elements which combine to form different chemical compounds are related to each other as simple whole numbers. This law extends ans incorporates the law of constant proportions.

Law of Equivalent Proportions. If the mass ratios of oxygen and nitrogen in the compounds they form with each other are compared to the mass ratios between oxygen and hydrogen in water H_2O (1:7,936) and nitrogen and hydrogen in ammonia NH_3 (1:4,632), other interesting fact emerges.

Similar relationships are seen in many other cases: if two elements A and B each form one compound with a any other third element C, then the mass ratio in a compound cosnisting of A and B is never totally unrelated. But is a combination of two numbers which are multiples of the mass ratios in the first two compounds. This law, which was recognized is essence in 1791 by the German chemist Jeremias Benjamin Richter, is called **the Law of equivalent proportions**: *Elements always combine with one other to form chemical compounds in a ratio of definite combining masses or integral multiples of these masses.* This law goes beyond the scope of both the preceding laws, and included them as well.

The concept of equivalent mass (weight). **Equivalent weight** E (also used term **gram-equivalent – E, units of measure – g-eq**) is the mass of a given chemical element or substance which combine or displace directly or indirectly with 1,008 g of hydrogen or 8 g of oxygen. Other way of definition: such mass of element or substance, which supply or react with one mole of hydrogen ions (H^+) in an acid-base reactions. In RedOx processes equivalent mass (weight) of a reducing or oxiding agents is equal to their atomic or molecular weight divided into quantity of lost or attracted electrons e^- correspondently.

Equivalent weight has the dimensions and units of mass, unlike atomic weight, which is dimensionless. Equivalent weights were originally determined by experiment, but (insofar as they are still used) are now derived from molar masses. Additionally, the equivalent weight of a compound can be calculated by dividing the molecular weight by the number of positive or negative electrical charges that result from the dissolution of the compound.
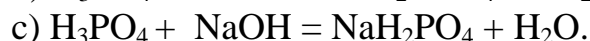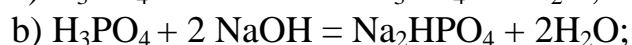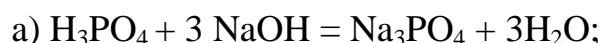
EXAMPLES OF CALCULATION

1. Calculate equivalent mass of Aluminium in Al_2O_3.
Two atoms of Aluminium ($2 \cdot A_r(Al)=2 \cdot 26,98=53,96$ amu) is combined with three atoms of Oxygen ($3 \cdot A_r(O)=2 \cdot 16,00=48,00$ amu).
So, x g of Al combines with 8 g of Oxygen.
$$E(Al) = x = \frac{53,96 \, \text{amu} \cdot 8 \, \text{g}}{48,00 \, \text{amu}} = 9,00 \, \text{g/g-eq.}$$

2. Calculate equivalent mass of Orthophosphate acid H_3PO_4 in reactions:
a) $H_3PO_4 + 3 \, NaOH = Na_3PO_4 + 3H_2O$;
b) $H_3PO_4 + 2 \, NaOH = Na_2HPO_4 + 2H_2O$;
c) $H_3PO_4 + NaOH = NaH_2PO_4 + H_2O$.
These reactions are acid-base interaction of neutralization processes. So, equivalent mass of acid may be determined as such its quantity that reacts by one hydrogen ion H^+.
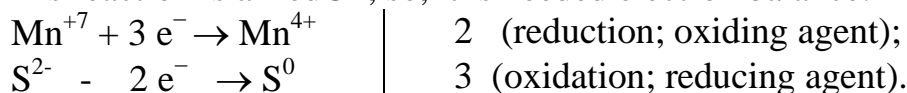Reaction (a): equivalent mass E of acid is its molecular wight divided 3, because acid reacts of its three hydrogen ions replaced of three Sodium ions:
$$E(H_3PO_4) = \frac{M(H_3PO_4)}{3} = \frac{97,99}{3} = 32,66 \, \text{g/g-eq.}$$

Reaction (b): equivalent mass E of acid is its molecular wight divided 2, because acid reacts of its three hydrogen ions replaced of two Sodium ions:

$$E\,(H_3PO_4) = \frac{M(H_3PO_4)}{2} = \frac{97,99}{2} = 49,00\,g/g\text{-}eq.$$

Reaction (c): equivalent mass E of acid is its molecular wight divided 1, because acid reacts of its three hydrogen ions replaced of one Sodium ions:

$$E\,(H_3PO_4) = \frac{M(H_3PO_4)}{1} = \frac{97,99}{1} = 97,99\,g/g\text{-}eq.$$

2. Calculate equivalent masses (weights) of reducing and oxidizing agents in reaction:

$3Na_2S + 2KMnO_4 + 4H_2O = 2MnO_2 + 3S + 6NaOH + 2KOH.$

This reaction is a RedOx, so, it is needed electron balance:

$$Mn^{+7} + 3\,e^- \rightarrow Mn^{4+} \qquad 2 \quad \text{(reduction; oxiding agent);}$$
$$S^{2-} - 2\,e^- \rightarrow S^0 \qquad 3 \quad \text{(oxidation; reducing agent).}$$

Equivalent weight of a substance (oxidant or reductant) is equal to molecular weight divided by number of electrons lost or gained by one molecule of the substance in a RedOx reaction.

So,

$$E\,(Na_sS) = \frac{M(Na_2S)}{2} = \frac{78,05}{2} = 39,03\,g/g\text{-}eq;$$

$$E\,(KMnO_4) = \frac{M(KMnO_4)}{3} = \frac{158,04}{3} = 52,68\,g/g\text{-}eq.$$

There is a scientific law called **the Law of Conservation of Mass,** discovered by outstanding Russian scientist M. Lomonosov in 1760. In its most compact form, it states: *matter is neither created nor destroyed*. This conclusion was confirmed experimentally by quantitative experiments on metals calcination and their transformation into oxides in closed vessels.

In 1842, Julius Robert von Mayer (German physician, chemist and physicist) discovered **the Law of Conservation of Energy**. In its most compact form, it it now called the *First Law of Thermodynamics*: energy is neither created nor destroyed.

The **Law of conservation of mass** states that in a closed system, the mass of the system cannot change over time: *The mass of the reactants must equal the mass of the products.*

Sadly for fans of magic, anything that has mass, including matter and energy, cannot be created or destroyed. That means, mass cannot simply appear out of nowhere and equally it cannot disappear. Matter may change forms however, giving the illusion of nothing out of something or vice versa, but the mass of the matter is always the same before and after the

change. If 22 grams of reactants go into a chemical reaction, then 22 grams of products must be produced.

Importance

Discovery of the law of conservation of mass helped to turn chemistry into the respectable science it is today. Chemistry has its foundations in alchemy, a protoscience that put much stock into magic and mysticism. With the advent of the law of conservation of mass, chemists took the mystery and illusion of alchemy and brought predictability and reliability to the science of chemistry.

The law of conservation of mass is very important to the study and production of chemical reactions. If scientists know the quantities and identities of reactants for a particular reaction, they can predict the amounts of products that will be made. Chemical manufacturers can increase efficiency by applying the law of conservation of mass to their laboratory practices.

In 1905, famous German-born theoretical physicist A. Einstein showed that the mass of a body (m) and its energy (E) are related as follows (**Laws of conservation of mass-energy**):

$$E = mc^2 \qquad (2.1)$$

where **c** is the speed of light in vacuum, **c**=$2,997925 \cdot 10^8$ m·s^{-1} (or approximately 300000 km·s^{-1}).

In general, *the total amount of mass and energy in the universe is constant.*

The Law of Conservation of Mass is still a useful idea in chemistry. This is because the energy changes in a chemical reaction are so tiny that they did not affect any measurements. 100 kJ is a typical value for the energy involved in a chemical reaction and it is only about 10^{-9} gram. Only recently has such a small amount been able to be accurately measured. The mass loss or gain due to energy loss or gain in a chemical reaction may someday be something that is routinely measured. This is why the mass defect in chemical reactions may be disregarded.

Situation differs in the case of nuclear reactions. Nuclear reactions involve changes in the nuclei of atoms whereas chemical reactions involve only the outermost electrons of atoms. Another significant difference between the two types of reactions is in the amount of energy liberated. Nuclear reactions involve energies a million times greater than those of chemical reactions. Due to this a significant amounts of matter are transformed into energy in a nuclear explosion or reaction.

The quantitative composition of many substances was studied from the end of the 18th century. This led to the establishment of **the Law of definite proportions** (also called **the law of constant composition**) by a

French chemist Joseph Proust, in 1797: *The masses of the elements forming a given compound are always in a definite proportion that does not depend on how this compound was prepared.*

Unlike the law of conservation of mass, whose correctness was completely confirmed by the discoveries made after its establishment, the laws of definite proportions and multiple proportions were found to be not so universal. In connection with the discovery of isotopes, it was found that the ratio of the masses of the elements forming a given substance is constant only provided that the isotopic composition of these elements is constant. A change in the isotopic composition of an element is attended by a change in the mass composition of the compound.

The laws of definite proportions (the law of constant composition) and multiple proportions were found to be not realizing also for the compounds of varying composition **(berthollides)** vise versa **daltonides -** compounds with a fixed proportion of atoms. These terms were introduced by Russian chemist N.S.Kurnakov in 1912-1914 to designate chemical compounds of constant composition (daltonides) and variable composition (berthollides). The term "daltonide" was proposed in memory of J. Dalton (outstanding English chemist and physicist, 1766-1844), and the term "berthollide", in memory of C. L. Berthollet (famous French chemist, 1748-1822). Most ordinary chemical compounds are daltonides; their compositions satisfy **the law of definite proportions** and the **law of multiple proportions**. Numerous instances o the formation of berthollides have been discovered inmetallic systems and also among oxides, sulfides, carbides, hydride and others.

In these compounds, for each unit of mass of a given element there may be a varying mass of another element. For example, in a compound formed by Bismuth with Thallium (metal alloy), there may be from 1,24 to 1,82 units of mass of Bismuth per unit of mass of Thallium ($TlBi_{1,24-1,82}$). Compounds of varying composition are encountered also among other solids, for example oxides ($UO_{2,5-3,0}$, $FeO_{0,85-0,95}$), compounds of metals with Sulfur, Nitrogen, Carbon and Hydrogen ($TiH_{0,88-1,00}$).

Compounds of varying composition have an atomic structure instead of a molecular one, the formula only reflect the limits of the composition of the relevant substance. It has been found that for many compounds of varying composition, the limits within their composition may change. Non-stoichiometrical composition, i.e. variable indexes is pervasive for metal oxides, especially when the metal is not in its highest oxidation state (Fe^{2+}, $Mn^{3+,4+}$, Ti^{2+}, V^{3+}. For example, although wüstite (ferrous oxide) has an ideal (stoichiometric) formula FeO, but the actual (real) stoichiometry is closer to $Fe_{0,95}O$ (Fig. 2.5). The non-stoichiometry reflects the ease of

oxidation of Fe^{2+} to Fe^{3+} effectively replacing a small portion of Fe^{2+} with two thirds their number of Fe^{3+}. Thus for every three "missing" Fe^{2+} ions, the crystal contains two Fe^{3+} ions to balance the charge.
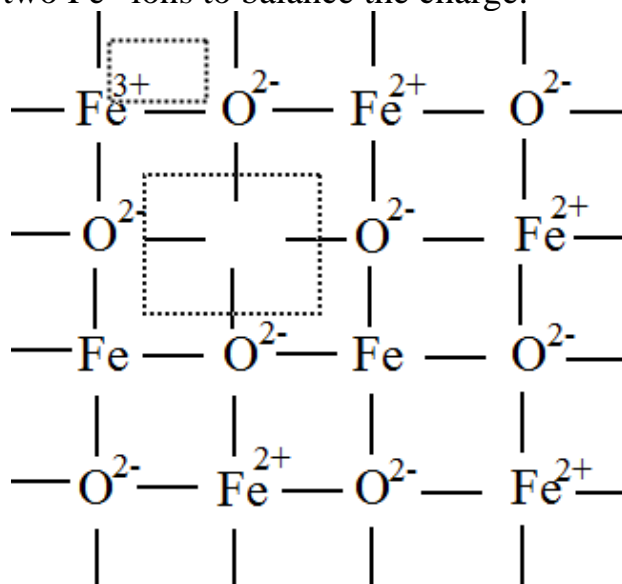

Figure 2.5. Crystalline structure of non-stoichiometrical iron(II) oxide Fe_xO (dot figures are shown to defect places in lattice – or replacing of Fe^{2+} cation into Fe^{3+}, or absence of cation in fixed position).

It is sometimes difficult to determine if a material is non-stoichiometric or if the formula is best represented by large numbers. The oxides of tungsten illustrate this situation. Starting from the idealized material tungsten trioxide, one can generate a series of related materials that are slightly deficient in oxygen. These oxygen-deficient species can be described as WO_{3-x} but in fact they are stoichiometric species with large unit cells with the formulas $W_nO_{(3n-2)}$ where n = 20, 24, 25, 40. Thus, the last species can be described with the stoichiometric formula $W_{40}O_{118}$, whereas the non-stoichiometric description $WO_{2.95}$ implies a more random distribution of oxide vacancies.

Nonstoichiometry is especially important in solid, three-dimensional polymers. For practical purposes, the term describes materials where the non-stoichiometry is measurable, usually at least 1% of the ideal composition.

Practical application of non-stoichiometrical compounds is descibed their using as *catalysts,* expesially oxides. The process operates via the transfer of "lattice" oxygen to the hydrocarbon substrate, a step that temporarily generates a vacancy (or defect). In a subsequent step, the missing oxygen is replenished by O_2. Such catalysts rely on the ability of the metal oxide to form phases that are not stoichiometric. An analogous sequence of events describes other kinds of atom-transfer reactions including hydrogenation and hydrodesulfurization catalysed by solid

catalysts. These considerations also highlight the fact that stoichiometry is determined by the interior of crystals: the surfaces of crystals often do not follow the stoichiometry of the bulk. The complex structures on surfaces are described by the term "surface reconstruction."

Ion conduction. The migration of atoms within a solid is strongly influenced by the defects associated with non-stoichiometry. These defect sites provide pathways for atoms and ions to migrate through the otherwise dense ensemble of atoms that form the crystals. Oxygen sensors and solid state batteries are two applications that rely on oxide vacancies. One example is the CeO_2-based sensor in automotive exhaust systems. At low partial pressures of O_2, the sensor allows the introduction of increased air to effect more thorough combustion.

Superconductivity. Many superconductors are non-stoichiometric. For example, Y-Ba-Cu oxide, arguably the most notable high-temperature superconductor, is a non-stoichiometric solid with the formula $Y_xBa_2Cu_3O_{7-x}$. The critical temperature of the superconductor depends on the exact value of *x*. The stoichiometric species has x = 0, but this value can be as great as 1.

So, a conclusion can be made that compounds with molecular structure always have constant composition, otherwise the composition of compounds may change in some range (homogeneity area) that depend on conditions of its obtaining.

2.4 Types of chemical reactions

Chemical reactions are processes by which atoms or molecules are redistributed, resulting in different substances with unique properties. Chemical reactions are classified into different categories according to the mechanics of the reactions. The original elements or compounds involved in a chemical reaction are called reactants, and the chemicals that result are called products. Usually the six types of chemical reactions are synthesis, decomposition, single-replacement, double-replacement, acid-base, and RedOx (one series of the last type is called combustion). Synthesis and decomposition reactions occur when chemical groups combine or separate. Single and double-replacement reactions are "shuffles" between either three (single replacement) or four (double replacement) distinct chemical groups. Acid-base and combustion are identified by distinct reactants and products.

Classification of types is presented in **Table 2.2.**

Table 2.2. Types of chemical reactions

Type	Scheme	Example
Synthesis (combination, construction, composition) reactions	X + Y = Z, where X, Y are elements or compounds; Z - new compound	$2 H_2 + O_2 = 2H_2O$; $H_2O + SO_3 = H_2SO_4$; $K_2O + CO_2 = K_2CO_3$
Decomposition (desythesis, decomposition, deconstruction) reactions	XZ = X + Z	$2KClO_3 \xrightarrow{t} 3 O_2\uparrow + 2 KCl$; $6NaHCO_3 \xrightarrow{t} 3 Na_2CO_3 + 3 CO_2\uparrow + 3H_2O$; $2 AgI \xrightarrow{t} 2 Ag + I_2$
Single replacement (single displacement, activity replacement) reactions	A + BX = B + AX	$2 Mg + TiCl_4 \xrightarrow{t} Ti + 2 MgCl_2$; $2Al + 6CaO \xrightarrow{t} Ca_3(AlO_3)_2 + 3Ca$;
Double replacement (double displacement or metathesis) reactions	AB + CD = AD + CB	$AgNO_3 + KCl = AgCl\downarrow + KNO_3$; $TiCl_4 + H_2O = 4 HCl\uparrow + TiO_2\downarrow$; $HCl + NaOH = NaCl + H_2O$
Oxidation-reduction reactions (Red-Ox)	$A^z + n\ e^- \rightarrow A^{(z-n)}$ $B^y - m\ e^- \rightarrow B^{(y+m)}$	$2Na + S \rightarrow Na_2S$; $2KMnO_4 \xrightarrow{t} K_2MnO_4 + MnO_2 + O_2$
Acid-Base reactions (neutralization)	$H^+ + OH^- \rightarrow H_2O$ (in net ionic form)	$H_2SO_4 + 2 NaOH = Na_2SO_4 + 2H_2O$

Review questions

1. What is an atomic mass unit?

2. What is the mass (in a.m.u.) of carbon-12 atom?

3. When we look up the atomic mass of carbon, we find that its value is 12,01 amu rather than 12,00 amu as defined. Why?

4. Define the term "mole". What is the unit for mole in calculations? What does the mole have in common with the pair, the dozen, and the gross?

5. What does Avogadro's number present?

6. Define molar mass. What are the common units for molar mass?

7. Calculate the charge (in coulumbs) and mass (in grams) of 1 mole of electrons.

8. Explain clearly what is meant the statement "The atomic mass of gold is 197,0 amu"?

9. The atomic massses of $^{35}_{17}Cl$ (75,53 %) and $^{37}_{17}Cl$ (24,47 %) are 34,968 amu and 36,956 amu, respectively. Calculate the average atomic mass of Chlorine. The percantages in parentheses denote the relative adundance.

10. Earth's population is about 7 000 000 000. Suppose thet every person on 4 per second. How many years would it take to count $6,02 \cdot 10^{23}$ particles? Assume that there are 365 days in a year.

11. What is the mass in grams of 13,2 amu?

12. What is the mass in grams of a single atom of earch of these elements: a) As; b) Ni?

13. Which of these has a greater mass: 2 atoms of lead Pb or $5,1 \cdot 10^{-23}$ mole of helium He?

14. Calculate the molecular mass (in amu) of each of these substances: a) CH_4; b) N_2O_4; c) $CaHPO_4$.

15. Calculate the molar mass of a compound if 0,372 mole of it has a mass of 152 g.

16. How many grams of ethane C_2H_6 are present in 0,334 g of C_2H_6?

17. Urea $(NH_2)_2CO$ is a compound used for fertilizer. Calculate the number of N, C, O, and H atoms in $1,68 \cdot 10^{-12}$ g of urea.

18. Pheromones are a special type of compound secreted by the females of many insect series to attract the males for mating. One pheromone has the molecular formula $C_{19}H_{38}O$. Normally, the amount of this pheromone secreted by a female insect is about $1 \cdot 10^{-12}$ g. How many molecules are there is in this quantity?

19. Allicin is a compound responsible for the characteristic smell of garlic. An analysis of the compound gives this persent composition by mass: C 44,4 %, H 6,21 %; S 39,5 %; O 9,86 %. Calculate its empirical formula. What is its molecular formula given (molar mass is about 162 g).

20. Monosodium glutamate (MSG), a food flavor enhancer, has been blamed for "Chinese restaurant syndrome", the symptoms of which are headaches and chest pains. MSG has the following composition by mass: 35,51 % C, 4,77 % H, 37,85 % O, 8,29 % N, and 13,60 % Na. What is its molecular formula if its molar mass is about 169 g?

21. On what law is stoichiometry based?

22. Define the following terms: chemical reaction; reactant; product.

23. What is the difference between a chemical reaction and a chemical equation?

24. Derermine a type of a chemical reaction: $6\ CO_2 + 6H_2O = C_6H_{12}O_6 + 6O_2$:

A	Single replacement	C	Oxidation-reduction reactions (Red-Ox)
B	Double replacement	D	Acid-Base reactions (neutralization)

25. All the substances listed here are fertilizers that contribute nitrogen to soil. Which of these is the richest source of nitrogen on a mass percentage basis?

A	Urea, $(NH_2)_2CO$ (M=60 g/mol)	C	Guanidine, $HNC(NH_2)_2$ (M=59 g/mol)
B	Ammonium nitrate, NH_4NO_3 (M=80 g/mol)	D	Liquid ammonia NH_3 (M=17 g/mol)

CHAPTER 3 STATE OF MATTER

Physical science, which includes chemistry and physics, is usually thought of as the study of the nature and properties of matter and energy in non-living systems. Matter is the "stuff" of the universe – the atoms, molecules and ions that make up all physical substances. Matter is anything that has mass and takes up space.

Energy is the capacity to cause change. Energy cannot be created or destroyed; it can only be conserved and converted from one form to another. "Potential energy" is the energy stored in an object due to its position – for example, a bucket of water balanced over a doorway has the *potential* to fall. "Kinetic energy" is energy that is in motion and causing changes. Any object or particle that is in motion has kinetic energy based on its mass and speed. Kinetic energy can be converted into other forms of energy, such as electrical energy and thermal energy.

3.1 Five phases

There are five known phases, or states, of matter: solids, liquids, gases, plasma and Bose-Einstein condensates. The main difference in the structures of each state is in the densities of the particles.

Solids

In a solid, particles are packed tightly together so they are unable to move about very much. Particles of a solid have very low kinetic energy. The electrons of each atom are in motion, so the atoms have a small vibration, but they are fixed in their position. Solids have a definite shape. They do not conform to the shape of the container in which they are placed. They also have a definite volume. The particles of a solid are already so tightly packed together that increasing pressure will not compress the solid to a smaller volume.

Liquids

In the liquid phase, the particles of a substance have more kinetic energy than those in a solid. The liquid particles are not held in a regular arrangement, but are still very close to each other so liquids have a definite volume. Liquids, like solids, cannot be compressed. Particles of a liquid have just enough room to flow around each other, so liquids have an indefinite shape. A liquid will change shape to conform to its container. Force is spread evenly throughout the liquid, so when an object is placed in a liquid, the liquid particles are displaced by the object.

The magnitude of the upward buoyant force is equal to the weight of the fluid displaced by the object. When the buoyant force is equal to the force of gravity pulling down on the object's mass, the object will float. This principle of buoyancy was discovered by the Greek mathematician.

Archimedes who, according to legend, sprang from his bath and ran naked through the streets shouting "Eureka!".

Particles of a liquid tend to be held by weak intermolecular attraction rather than moving freely as the particles of a gas will. This cohesive force pulls the particles together to form drops or streams.

Scientists reported in April 2016 they had created **a bizarre state of matter**, one that had been predicted to exist but never seen in real life. Though this type of matter could be held in one's hand as if it were a solid, a zoom-in on the material would reveal the disorderly interactions of its electrons, more characteristic of a liquid. In the new matter, called a Kitaev quantum spin liquid, the electrons enter into a sort of quantum dance in which they interact or "talk" to one another. Usually when matter cools down the spin of its electrons tends to line up. But in this quantum spin liquid, the electrons interact so that they affect how the others are spinning and never align no matter how cool the material gets. The material would behave as if its electrons, considered indivisible, had broken apart, the researchers reported April 4, 2016, in the journal "Nature Materials".

Gases

Gas particles have a great deal of space between them and have high kinetic energy. If unconfined, the particles of a gas will spread out indefinitely; if confined, the gas will expand to fill its container. When a gas is put under pressure by reducing the volume of the container, the space between particles is reduced, and the pressure exerted by their collisions increases. If the volume of the container is held constant, but the temperature of the gas increases, then the pressure will also increase. Gas particles have enough kinetic energy to overcome intermolecular forces that hold solids and liquids together, thus a gas has no definite volume and no definite shape (Fig. 3.1).
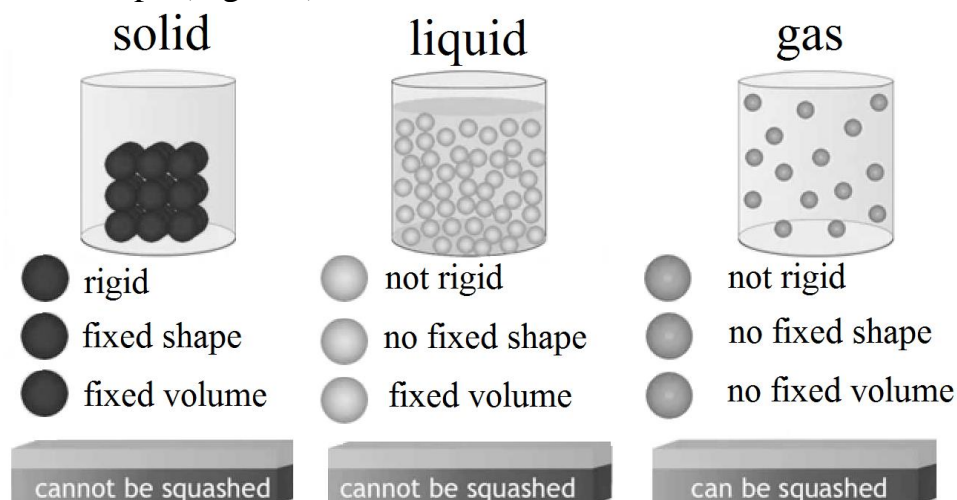
Figure 3.1. Comparing phases – solid, liquid and gas.

Plasma

Plasma is not a common state of matter here on Earth, but may be the most common state of matter in the universe. Plasma consists of highly charged particles with extremely high kinetic energy. The noble gases (He, Ne, Ar, Kr, Xe, and Rn) are often used to make glowing signs by using electricity to ionize them to the plasma state. Stars are essentially superheated balls of plasma.

Bose-Einstein condensates

In 1995, technology enabled scientists to create a new state of matter, the Bose-Einstein condensate (BEC). Using a combination of lasers and magnets, Eric Cornell and Carl Weiman cooled a sample of Rb – rubidium to within a few degrees of absolute zero. At this extremely low temperature, molecular motion comes very close to stopping altogether. Since there is almost no kinetic energy being transferred from one atom to another, the atoms begin to clump together. There are no longer thousands of separate atoms, just one "super atom". A BEC is used to study quantum mechanics on a macroscopic level. Light appears to slow down as it passes through a BEC, allowing study of the particle/wave paradox. A BEC also has many of the properties of a superfluid - flowing without friction. BECs are also used to simulate conditions that might apply in black holes.

3.2 Going through a phase

Adding energy to matter causes a physical change – matter moves from one state to another. For example, adding thermal energy – heat – to liquid water causes it to become steam or vapor – a gas. Taking away energy also causes physical change, such as when liquid water becomes ice – a solid – when heat is removed. Physical change also can be caused by motion and pressure (Fig. 3.2).
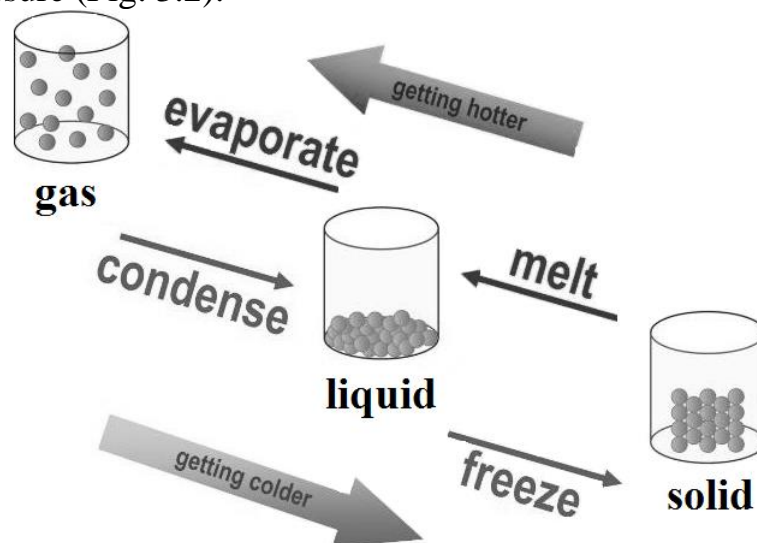
Figure 3.2. Transforming phases – solid, liquid and gas.

Melting and freezing

When heat is applied to a solid, its particles begin to vibrate faster and tend to move farther apart. When the substance, at standard pressure, reaches a certain point – called the melting point – the solid will begin to turn into a liquid. The melting point of a pure substance can often be determined to within 0,1 °C, the point at which the solid and liquid phases are in equilibrium. If you continue to apply heat to the sample, the temperature will not rise above the melting point until the entire sample has been liquefied. The heat energy is being used to convert the solid into the liquid form. Once the entire sample has become a liquid the temperature will begin to rise again.

Compounds that are otherwise very similar can have different melting points, so melting point can be a useful way to distinguish among them. For example, sucrose has a melting point of 186,1 °C while the melting point of glucose is 146 °C. A solid mixture, such as a metal alloy, can often be separated into its constituent parts by heating the mixture and extracting the liquids as they reach their different melting points.

The freezing point is the temperature at which a liquid substance is cooled enough to form a solid. As the liquid is cooled, particle motion slows. In many substances, the particles align in precise, geometric patterns to form crystalline solids. Most liquids contract as they freeze. One of the important characteristics of water is that it expands when it freezes, so ice floats. If ice didn't float, there would be no liquid water underneath a frozen body of water and many forms of aquatic life would be impossible.

The freezing point is often nearly the same temperature as the melting point, but is not considered to be characteristic of a substance, as several factors can alter it. For example, adding dissolved substances, or solutes, to a liquid will depress the freezing point. An example of this is using salt slurry to lower the temperature at which water freezes on our roads. Other liquids can be cooled to temperatures well below their melting point before they begin to solidify. Such liquids are said to be "super cooled" and often require the presence of a dust particle or "seed crystal" to start the process of crystallization.

Sublimation

When a solid is converted directly into a gas without going through a liquid phase, the process is known as sublimation. Sublimation occurs when kinetic energy of the particles is greater than atmospheric pressure surrounding the sample. This may occur when the temperature of the sample is rapidly increased beyond the boiling point (flash vaporization). More commonly, a substance can be "freeze dried" by cooling it under vacuum conditions so that the water in the substance undergoes

sublimation and is removed from the sample. A few volatile substances will undergo sublimation at normal temperature and pressure. The best known of these substances is CO_2 or "dry ice."

Vaporization

Vaporization is the conversion of a liquid to a gas. Vaporization can occur through either evaporation or boiling.

Because the particles of a liquid are in constant motion they frequently collide with each other, transferring energy when they do so. This energy transference has little net effect beneath the surface, but when enough energy is transferred to a particle near the surface; it may gain enough energy to be knocked completely away from the sample as a free gas particle. This process is called evaporation and it continues as long as liquid remains. It is interesting to note that a liquid cools as it evaporates. The energy transferred to surface molecules, which causes their escape, is carried away from the remaining liquid sample.

When enough heat is added to a liquid that vapor bubbles form below the surface of the liquid, we say that the liquid is boiling. The temperature at which a liquid boils is variable. Boiling point is dependent upon the pressure the substance is under. A liquid under higher pressure will require more heat before vapor bubbles can form within it. At high altitudes, there is less atmospheric pressure pressing down on the liquid, so it will boil at a lower temperature. The same amount of liquid at sea level is under a greater atmospheric pressure and will boil at a higher temperature.

Condensation and deposition

Condensation is when a gas transforms into a liquid. Condensation occurs when a gas has been cooled or compressed to the point where kinetic energy of the particles can no longer overcome the intermolecular forces. An initial cluster of particles initiates the process which tends to further cool the gas so that condensation continues. When the gas transforms directly into a solid, without going through the liquid phase, it is called deposition or desublimation. An example of this occurs when subfreezing temperatures convert water vapor in the atmosphere into frost or ice. Frost tends to outline solid blades of grass and twigs because the air touching these solids cools faster than air that is not touching a solid surface.

Physical changes do not cause a substance to become a fundamentally different substance. Chemical changes, on the other hand, cause a substance to change into something entirely new. Chemical changes are typically irreversible, but that is not always the case. It is easier to understand the difference between physical and chemical changes with examples.

State changes are physical.	Phase changes are when you melt, freeze, boil, condense, sublimate, or deposit a substance. They do not change the nature of the substance unless a chemical change occurs along with the physical change.
Cutting, tearing, shattering, and grinding are physical.	These may be irreversible, but the result is still composed of the same molecules. When you cut your hair, that is a physical change, even though you can't put the hair back on your head again.
Mixing together substances is physical.	For example, you could mix salt and pepper, dissolve salt in water, or mix molten metals together to produce an alloy.
Gas bubbles forming is chemical.	Not to be confused with bubbles from boiling, which would be physical (a phase change). Gas bubbles indicate that a chemical reaction has occurred.
Precipitates forming is chemical.	When dissolved substances are mixed, and a cloudy precipitate appears, there has been a chemical change.
Rotting, burning, cooking, and rusting (for example) are chemical.	The resulting substances are entirely new chemical compounds. For instance, wood becomes ash and heat; iron becomes rust; sugar ferments into alcohol.
Changes of color or release of odors (i.e. release of a gas) might be chemical.	As an example, the element chromium shows different colors when it is in different compounds, but a single chromium Cr compound will not change color on its own without some sort of reaction.
Release/absorption of energy (heat, light, sound) is generally not easily categorized.	Hot/cold packs involve dissolving a salt in water to change its temperature (more on that in later chapters); popping popcorn is mostly physical (but not completely).

3.3 Substances and Mixtures

A substance is matter that has a definite or constant composition and district properties. Examples are water, silver, ethanol, table salt (sodium chloride), and carbon dioxide. Substances differ from one other in composition and can be identified by their appearance, smell, taste, and other properties. At present, over 13 million substances are known, and the list is growing rapidly.

A mixture is a combination of two or more substances in which the substances retain their distinct identities. Some examples are air, soft drinks, milk, and cement. Mixtures do not have constant composition. Therefore, samples of air collected in different cities would probably differ in composition because of differences in altitude, pollution, and so on.

Mixtures are either *homogeneous* or *heterogeneous* (Fig. 3.3). When a spoonful of sugar dissolves in water, the composition of the mixture, after sufficient stirring, is the same throughout the solution. This solution is a *homogeneous mixture*.

If sand is mixed with iron filings, however, the sand grains asnd the iron filings remain visible and separate. This type of mixture, in which the composition is not uniform, is called a heterogeneous mixture. Adding oil to water creates another heterogeneous mixture because the liquid does not have a constant composition.
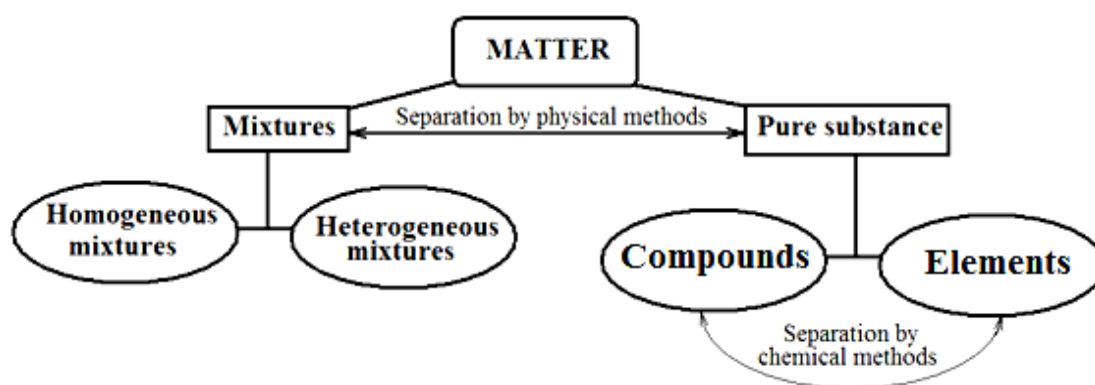
Figure 3.3. Classification of matter

Any mixture, whether homogeneous or heterogeneous, can be created and then separated by physical means into pure components without changing the identities of the components. Thus, sugar can be recovered form a water solution by heating the solution and evaporating it to dryness. Condensing the water vapor will give us back to the liquid water. To separate the iron-sand mixture, it can use a magnet. After separation, the components of the mixture will have the same composition and properties as they did to start with (Fig. 3.4).
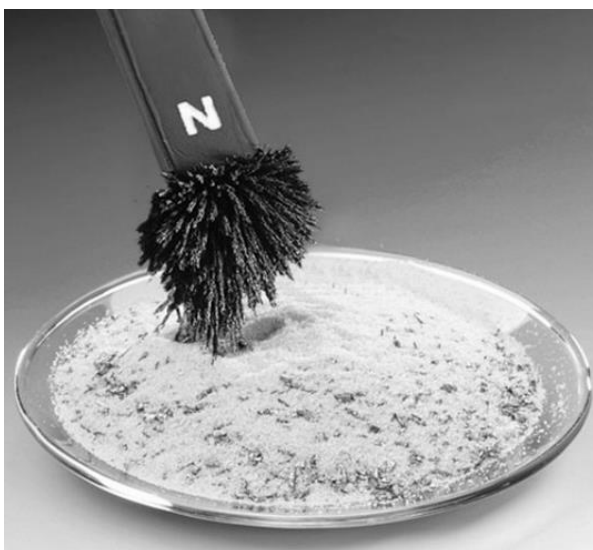
Figure 3.4. Separation mixture of the iron filings and sand by physical method

3.4 Elements and compounds

A substance can be either an element or a compound. An element is a substance that cannot be separated into simple substances by chemical means. At present, 118 elements have been positively identified (Appendix 1). 93 of tham occur naturally on Earth. The others have been created artificially by nuclear physicists.

Chemists use alphabetical symbols to represent the names of elements. The first letter of the symbol for an element is always capitalized, but the second letter is never capitalized. For example, Co is a symbol for the element cobalt, whereas CO is a formula for carbon monooxide, which is made up of the elements carbon and oxygen. The symbol for some elements are derived form their Latin names – for example, Au from aurum (gold), Fe from ferrum (iron), and Na from natrium (sodium) – althouth most of them are abbreviated forms of their English names.

Most elements can interact with one or more other elements to form compounds. **A compound** is a substance composed of atoms of two or more elements chemically united in fixed proportions. Hydrogen gas, for example, burns in oxygen gas to form water, a compound whose properties are distinctly different from those of the starting materials. Water is made up of two parts of hydrogen and one part of oxygen. This composition does not change, regardless of whether the water comed form a faucet in the United States, or river of Ukrainian Carpathians, or the ice caps on Mars. Unlike mixtures, compounds can be separated only by chemical means into their pure components (Fig. 3.4).

Elements

* consists of only one kind of atom

* can not be broken down into simpler substance

* can exist as either atoms (e.g. Argon Ar) or molecules (e.g., Nitrogen N_2)

* there are 118 chemical elements in the world now

* Compounds are made up of elements *

Compounds

* consists of two or more combined elements

* can be broken down into simpler types or matter (elements)

* has different properties that are different from its partner, elements

* always contain a different number of its components - atoms

Figure 3.4. Elements and compounds: comparing and contrast

Review questions

1. Define these terms: (a) matter; (b) substance; (c) mixture.

2. Give an example of a homogeneous mixture and an example of a heterogeneous mixture.

3. What is the difference between a physical proerty and a chemical property?

4. Define these terms: (a) element; (b) compounds.

5. Does each of these describe a physical change or a chemical change:

a) The helium gas inside a baloon tends to leak out;

b) Iron has a tendency to rust;

c) A flashlight beam slowly gets dimmer and finally goes out;

d) The growth of plants depends on the sun's energy in a process called photosynthesis;

e) Rainwater in industrialized regions tends to be acidic;

i) When a glass of water is left out in sun, the water gradually dissapears;

f) Carbon dioxide in air is converted to more complex molecules by plants during photosynthesis.

CHAPTER 4 ATOMIC STRUCTURE. CHEMICAL BONDING

4.1 The development of the model of the atom

Atomic theory is a scientific description of the nature of atoms and matter. Nowadays it combines physics, chemistry, and mathematics. According to the modern theory, matter is made of tiny particles called atoms, which are in turn made up of subatomic particles. Atoms of a given chemical element are identical and different from atoms of other elements. Atoms combine with other atoms in the definite ratios to form molecules and compounds.

The theory has evolved over time, from the philosophy of atomism to modern quantum mechanics (Table 4.1).

The atom and idea of atomism. The theory originated as a philosophical concept in ancient India and Greece. The word atom comes from the Ancient Greek word **atomos**, which means "indivisible". According to atomism, matter consisted of discrete particles. However, the theory was one of many explanation for matter and was not based on empirical data. In the fifth century B.C., Democritus proposed matter consisted of indestructible, indivisible units called atoms.

Dalton's atomic theory. It took until the end of the 18th century for science to provide concrete evidence of the existence of atoms. Antoine Lavoisier formulated the law of conservation of mass in 1789, which states the mass of the products of a reaction is the same as the mass of reactants. Joseph Louis Proust proposed the law of definite proportions in 1799, which states the masses of elements in a compound always occur in the same proportion. These theories did not reference atoms, yet John Dalton built upon them to develop the law of multiple proportions, which states the ratio of masses of elements in a compound are small whole numbers. Dalton's law of multiple proportions drew from experimental data. He proposed each chemical element consists of a single type of atoms that could not be destroyed by any chemical means. His oral presentation (1803) and publication (1805) marked the beginning of the scientific atomic theory.

In 1811, Amedeo Avogadro corrected a problem with Dalton's theory when he proposed equal volumes of gases at equal temperature and pressure contain the same number of particles. Avogadro's law made it possible to accurately estimate the atomic masses of element and made clear there was a distinction between atoms and molecules.

Plum Pudding Model and Rutherford Model. Up to this point, atoms were believed to be the smallest units of matter. In 1897, J.J. Thomson discovered the electron.

Table 4.1. Evolution of the idea of atomic structure

Who?	When?	What scientists thought and knew about the atom	A diagram to show what the atom would have looked like at that time in history
The ancient Greeks e.g. Democritus	400 B.C.	All matter could be divided and sub-divided into smaller and smaller units, and eventually there would be a tiny particle that could not be divided any further – an atom. Atoms were different shapes and sizes.	
John Dalton	1803	Substances were made of atoms that were like tiny hard spheres. Different substances were made of atoms that had a different mass.	
Joseph John Thomson	1897	The atom was made up of tiny electrons. Because atoms have no overall charge they must also have positive charges to balance out the negatively charged electrons. Atoms where likened to a plum pudding, with electrons (plums) embedded in a positively charged sphere (the pudding).	
Ernest Rutherford	1911	There was a positive charge in the centre of the atom that was concentrated into a tiny spot called the nucleus. The nucleus is orbited by negative electrons.	
Niels Bohr	1914	Electrons must orbit the nucleus at set distances, fixed energy levels called shells.	
Erwin Schrödinger	1926	Proposed mathematical equations to describe the likelihood of finding an electron in a certain position ('electron clouds'). This model is named the quantum mechanical one.	
James Chadwick	1932	There are neutral particles called neutrons in the nucleus of an atom.	

He believed atoms could be divided. Because the electron carried a negative charge, he proposed a plum pudding model of the atom, in which electrons were embedded in a mass of positive charge to yield an electrically neutral atom.

Ernest Rutherford, one of Thomson's students, disproved *"the plum pudding model"* in 1909. Rutherford found the positive charge of an atom and most of its mass was at the center or nucleus of an atom. He described a planetary model in which electrons orbited a small positive-charged nucleus.

Bohr Model of the Atom. Rutherford was on the right track, but his model could not explain the emission and absorption spectra of atoms nor why the electrons didn't crash into the nucleus. In 1913, Niels Bohr proposed the Bohr model, which states electrons only orbit the nucleus at specific distances from the nucleus. According to his model, electrons couldn't spiral into the nucleus, but could make quantum leaps between energy levels.

Quantum Atomic Theory. According to modern atomic theory, an electron could be anywhere in an atom, but it's most probable it is in an energy level. Bohr's model explained the spectral lines of hydrogen, but didn't extend to the behavior of atoms with multiple electrons.

Several discoveries expanded the understanding of atoms. In 1913, Frederick Soddy described isotopes, which were forms of an atom of one element that contained different numbers of neutrons. Neutrons were discovered in 1932.

Louis de Broglie proposed a wave-like behavior of moving particles, which Erwin Schrödinger described using Schrödinger's equation (1926). This, in turn, led to the Heisenberg uncertainty principle (1927), which states it's not possible to simultaneously know both the position and momentum of an electron.

Quantum mechanics led to an atomic theory in which atoms consist of smaller particles. The electron can potentially be found anywhere in the atom, but is found with greatest probability in an atomic orbital or energy level. Rather then the circular orbits of Rutherford's model, modern atomic theory describes orbitals that may be spherical, dumb bell shaped, etc. For atoms with a high number of electrons, relativistic effects come into play, since the particles are moving a speed that is a fraction of the speed of light.

Until 1932, the atom was believed to be composed of a positively charged nucleus surrounded by negatively charged electrons. In 1932, James Chadwick bombarded beryllium atoms with alpha particles. An unknown radiation was produced. Chadwick interpreted this radiation as

being composed of particles with a neutral electrical charge and the approximate mass of a proton. This particle became known as the *neutron*. With the discovery of the neutron, an adequate model of the atom became available to chemists.

Since 1932, through continued experimentation, many additional particles have been discovered in the atom. Also, new elements have been created by bombarding existing nuclei with various subatomic particles. The atomic theory has been further enhanced by the concept that protons and neutrons are made of even smaller units called *quarks*. The quarks themselves are in turn made of vibrating strings of energy. The theory of the composition of the atom continues to be an ongoing and exciting adventure.

4.2 Modern notions of the atom

Modern scientists have found smaller particles that make up the protons, neutrons, electrons, although the atom remains the smallest unit of matter that cannot be divided using any chemical means.

Atom is an electroneutral particle consisted of positive charged nucleus and negative charged electrons. Nucleus is a positive charged component of atom concentrated practically all its mass. Components of nucleus are s (*p*) and s (*n*). Sum of protons and neutrons is equal to relative atomic mass (*A$_r$*):

$A_r = \sum p^+ + n^0$

Nucleus charge of atom is equal to number of element in Periodical Table (Z).

Example: To consider structure of atom *Na:*

$$Z\ (Na) = 11$$

$$A_r\ (Na) = 23 \qquad {}^{23}_{11}Na$$

Positive charge of atomic nucleus – 11
Number of electrons   - 11

In nucleus: p$^+$-*11*
n^0 =*12 (* A$_r$ - p$^+$)

Motion of electrons around nucleus is described by energy and structure of atomic orbital. State of electron is described by values of 4 quantum figures (Tables 4.2, 4.3).
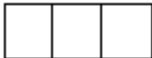
An atom consists of a nucleus of protons and neutrons, surrounded by electrons. Each of the elements in the periodic table is classified according to its atomic number, which is the number of protons in that element's nucleus. Protons have a charge of +1, electrons have a charge of -1, and neutrons have no charge. Neutral atoms have the same number of electrons and protons, but they can have a varying number of neutrons.

Within a given element, atoms with different numbers of neutrons are isotopes of that element. Isotopes typically exhibit similar chemical behavior to each other.

Table 4.2. Names and physical content of quantum figures

Names	Symbol	What's determined?	Possible values
Main (Principal)	N, n	Orbital energy (main energy level)	Algebraic integers from 0 to ∞ (infinity)
Secondary (Azimutal)	l	Orbital form (energy sub-level)	Algebraic integers from 0 to n-1
Magnetic	m_l	Spatial orientation of orbital	From $-l$ to $+l$ ($m_l=2l+1$)
Spin	m_s	Own magnetic moment of electrons	$+ \frac{1}{2}$ and $- \frac{1}{2}$

Table 4.3. Schematic description of atomic orbital

l		m_l	Quantity of orbitals	Schematic imagination
0	s	0	1	
1	p	-1 0 +1	3	
2	d	-2 –1 0 +1 +2	5	
3	f	-3 –2 –1 0 +1 +2 +3	7	

Electrons have such little mass that they exhibit properties of both particles and waves; in. We further know from Heisenberg's Uncertainty Principle that it is impossible to know the precise location of an electron. Despite this limitation, there are regions around the atom where the electron has a high probability of being found. Such regions are referred to as atomic orbitals.

4.3 Atomic Orbitals and Quantum Numbers

The relation of a particular electron to the nucleus can be described through a series of four numbers, called the Quantum Numbers. The first three of these numbers describe the energy (Principle quantum number), shape (Angular momentum quantum number), and orientation of the orbital (magnetic quantum number). The fourth number represents the "spin" of the electron (spin quantum number). The four quantum numbers are described below.

Principle quantum number (n) indicates how the distance of the orbital from the nucleus. Electrons are farther away for higher values of n. Electrons are negatively charged, so electrons that are closer to the

positively charged nucleus are more powerfully attracted and tightly bound than those that are farther away. Electrons that are closer to the nucleus are thus more stable, and less likely to be lost by the atom. In other words, as n increases, so does the energy of the electron and the likelihood of that electron being lost by the atom. In a given atom, all the atomic orbitals with the same n are collectively known as a shell. n can take on integer values of 1 or higher (ex. 1, 2, 3, etc.).

Angular momentum quantum number (l) describes the shape of the orbital. The angular momentum number (or subshell) can be represented either by a number (any integer from 0 up to n-1) or by a letter (*s, p, d, f, g*, and then up the alphabet), with 0 corresponding to s, 1 to p, 2 to d, and so on.

For example:

when $n = 1$, l can only equal 0; meaning that shell $n = 1$ has only an s orbital ($l = 0$).

when $n = 3$, l can equal 0, 1, or 2; meaning that shell $n = 3$ has s, p, and d orbitals. s orbitals are spherical, whereas p orbitals are dumbbell-shaped; d-orbitals and beyond are much harder to visually represent (Fig. 4.1).
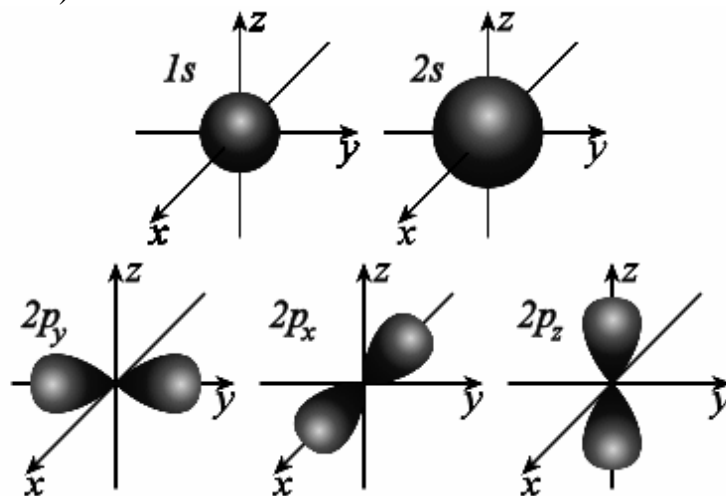
Figure 4.1. *s*- and *p*- atomic orbital shapes

Magnetic quantum number (m) gives the orientation of the orbital in space; in other words, the value of m describes whether an orbital lies along the x-, y-, or z-axis on a three-dimensional graph, with the nucleus of the atom at the origin. m can take on any value from -l to l. For our purposes, it is only important that this quantum number tells us that for each value of n there may be up to one *s*-orbital, three *p*-orbitals, five *d*-orbitals, and so on.

For example:

The *s*-orbital ($l = 0$) has one orbital, since *m* can only equal 0. That orbital is spherically symmetrical about the nucleus (Fig. 4.1).

The *p*-orbital ($l = 1$) has three orbitals, since $m = -1, 0$, and 1. These three orbitals lie along the *x*-, *y*-, and *z*-axes (Fig. 4.1).

The *d*-orbital ($l = 2$) has five orbitals, since $m = -2, -1, 0, 1$, and 2. It is far more difficult to describe the orientation of *d*-orbitals (Fig. 4.2).
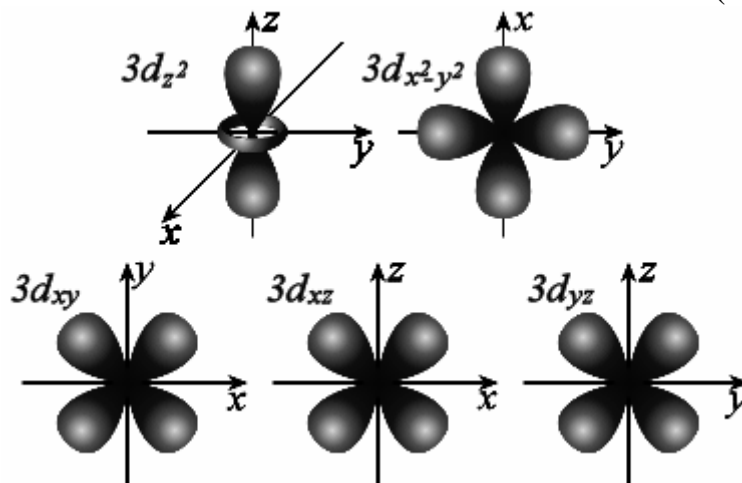
Figure 4.2. *d*-orbitals

4.4 Principles for distribution of electrons in atoms

Distributions of electrons in atoms on energy levels and sub-levels may be presented in the form of electronic formulas.

It may be compelled in the following way:

- Note Arabian figure, which indicates the main quantum figure (energy level);
- Note symbol of orbital, that determined electronic sub-level;
- Quantity of electrons on this sub-level is made by Arabian figure above it in the right upper corner.
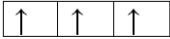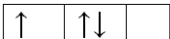
Example:

To show electronic formula of Nitrogen: $_7N$ $1s^2 2s^2 2p^3$. Atom of Nitrogen has 7 electrons, 2 – on the first level on *s*-sub-level, and 5 others – on the second level, *s* and *p*-sub-levels.

Principles, according to which the electrons are distributed in atoms, are shown in the Table 4.4.

Table 4.4. General rules for electronic formulas compilation

Name	Formulation	Using
Principle of energy minimum (Aufbau principle)	Minimum of energy responds to the most stable state of electrons in atom	Electron occupies a atomic orbital with minimum energy

Pauli's Principle	Atom may not have two electrons with the same values of all four quantum figures	$N=2n^2$ (quantity of e^- on the level) Max quantity of e^- on the sub-level is equal to $2 \cdot (2l+1)$ $s=2; p=6; d=10; f=14$
Rule of Klech-kovsky	Energy sub-levels are filled up according increasing of sum $n+l$	Indicate an order of sub-levels occupation
Rule of Hound	Summary spin value of electrons on sub-level must be maximum	Indicate an order of occupation of equal atomic orbitals:

4.5 Valence and Oxidation number as function of electrons distribution

Using electron formulas, possible values of valence and oxidation numbers for chemical elements may be predicted.

In general case valence is equal to the quantity of unpaired electrons on the last (for s- and p-elements) and next to last (for d-elements) sub-levels.

Example. $_{17}Cl$ $1s^2 2s^2 2p^6 3s^2 3p^5$
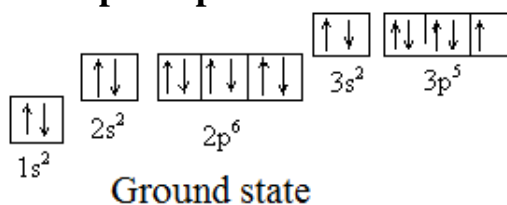
Electrons located on the last, third level, may go into free d-sublevel when atom was excited.
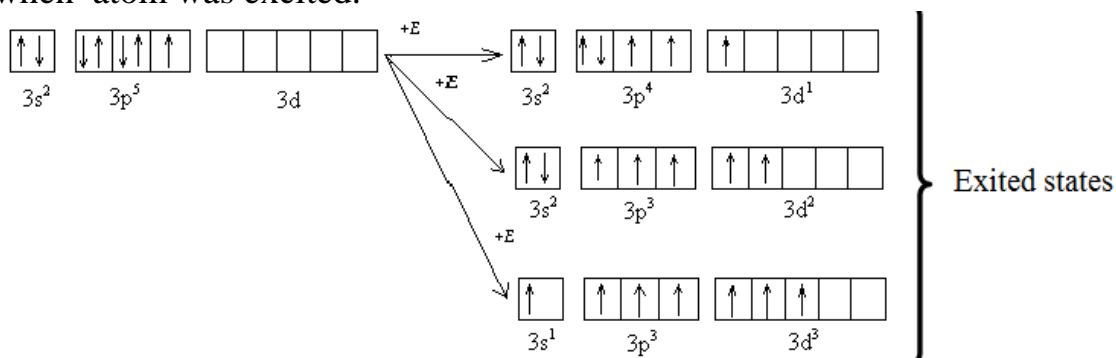
According to this idea, valence of Chlorine may be equal to **I** (normal state), **III** (the first excited state), **V** (the second excited state) and **VII** (the last, third excited state).

For estimation of oxidation number the theory of the "**octet configuration**" must be used. It says that all atoms pressing towards to obtain the same configuration of the last electron shell are similar to noble (indifferent) gases. Why? Because the noble gases are the most stable chemical elements and they have 8 (excluding He) electrons on the last electron shell (ns^2np^6). Chemical elements may form configuration like noble gases giving up unpaired electrons to other atoms or joining them from other atoms. If after such operation atom has structure of last or next to last electron shell absolutely like noble gas it will be stable. If its configuration is not "ideal", we may predict that such one is not stable and of course compounds included these atoms.

According to this theory, we may predict that in the first (normal) state atom of Chlorine may have three figures of oxidation number: −1 (when it joined one unpaired electron from any other atom); 0 (without interchange of electrons with other atoms) and +1 (when it lost one electron). Only the first figure of oxidation number will respond to an octet configuration of the last electron shell ($3s^23p^6$) and Cl^{-1} is a stable oxidation number for this chemical elements. Truly in nature this element exists only in the form of Chlorides where Chlorine has oxidation number −1.

Let's consider the first excited state of Chlorine atom. We see, that there are 3 unpaired electrons on the last electron shell. What can be said about possible degree of oxidation? The first possibility is to gain 3 electrons from other atom and to have oxidation number -3. This state is unstable, because atom has not octet configuration. If it lost 3 elections, its configuration is more stable, because atom has two pairs of electrons.

Analogously it may be shown that oxidation numbers of Chlorine in the second and third excited states will be equal to +5 and +7. Oxidation number +5 is more stable that +1 and +3, but the most stable compounds respond to oxidation number +7.

Note, that valence and oxidation number are the different notions. Oxidation is the virtual figure, mathematical value. For example, in molecules H_2 and O_2 oxidation numbers are equal to 0, but valence is equal to 1 and 2 correspondingly.

4.6 Ionic and covalent bonding

Chemical bonding, any of the interactions that account for the association of atoms into molecules, ions, crystals, and other stable species that make up the familiar substances of the everyday world. When atoms

approach one another, their nuclei and electrons interact and tend to distribute themselves in space in such a way that the total energy is lower than it would be in any alternative arrangement (Fig. 4.3). If the total energy of a group of atoms is lower than the sum of the energies of the component atoms, they then bond together and the energy lowering is the bonding energy.
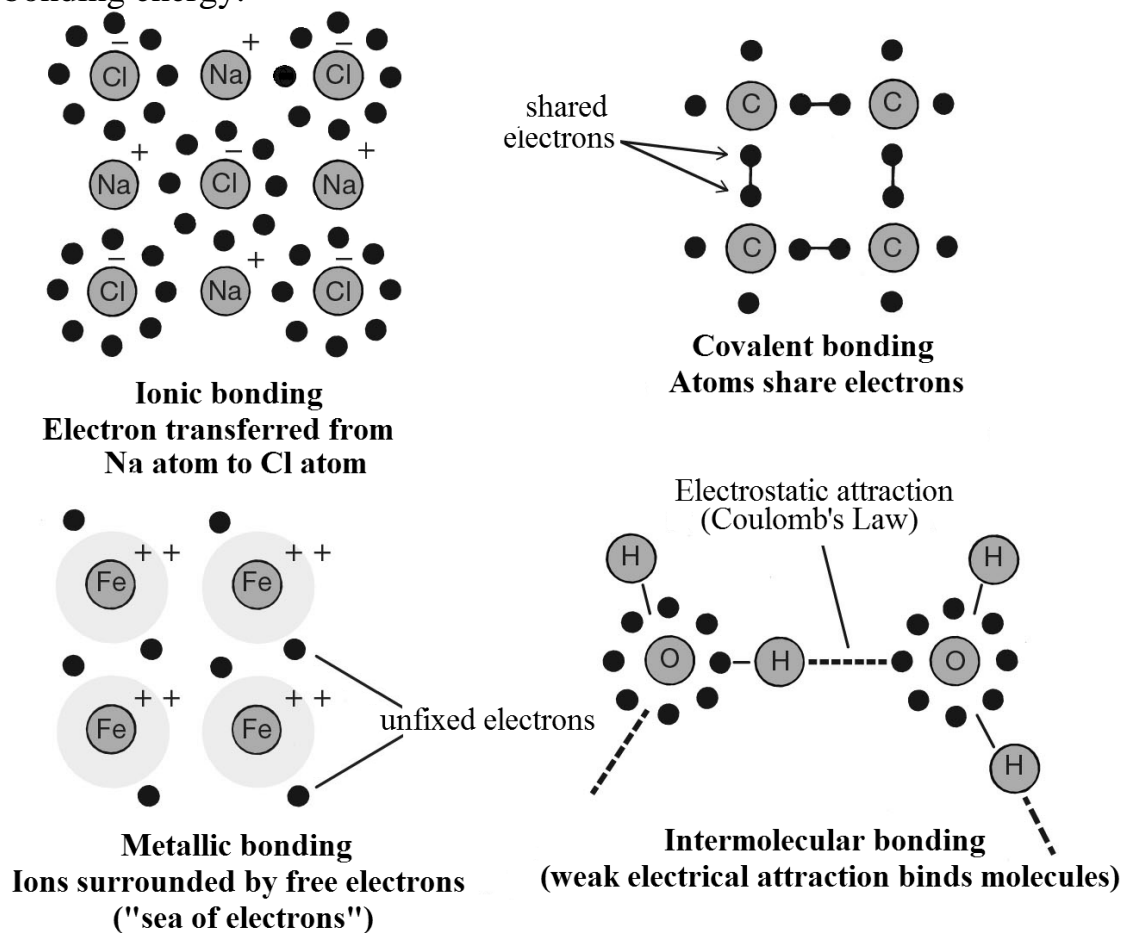
Figure 4.3. Ways of chemical bonding

An ionic bond is the *chemical bond resulting from electrostatic attraction between positive and negative ions*. If these is a **purely** ionic bond, one atom has completely given up one or more electrons, and another atom has gained them – as illustrated for two atoms that each have one unpaired electron at the top in Fig. 4.4.

In the second major type of chemical bond, called covalent bond, neither bonding atom completely loses or gains an electron or electrons. A **covalent bond** is a chemical bond resulting from the sharing of electrons between two atoms. A covalent bond in which two electrons are shared is represented by a pair of electron dots, as shown at the bottom right-hand corner in Fig. 4.4. In a purely covalent bond, the shared electrons are "owned" equally by the two atoms.
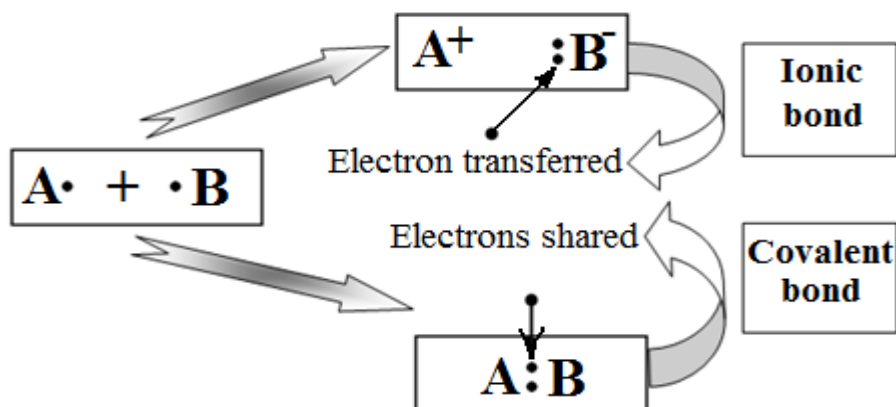
Figure 4.4. Two main types of chemical bond formation

Chemical bonds between unlike atoms are never completely ionic and rarely completely covalent. Bonds can be anywhere in the range between the bonded atoms attract electrons.

The degree to which bonds are ionic or covalent can be estimated by comparing of electronegativity of the bonded atoms. The more two atoms differ in electronegativity, the more ionic the bond is between them. In other words, the electrons spend more time close to the bonded atom that attracts them more strongly and hence cause that atom partially resemble an anion and the other atom, a cation.

Fig. 4.5 can be used to classify bonds according to electronegativity differences. The electronegativity (see **Appendix 3**) of one bonded atom is subtracted from that of the other.
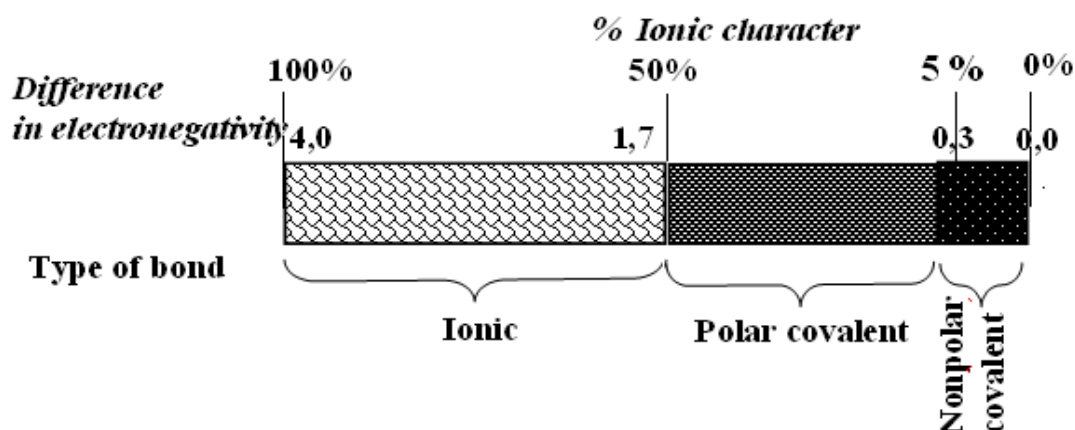
Figure 4.5. The variation of bond type with percent ionic character and the electronegativity difference between the bonded atoms

For example, the electronegativity difference between a Cesium (Cs) atom and a Fluorine (F) atom is 4,0-0,7 = 3,3. According to Fig. 4.5, a Cesium-Fluorine bond is an ionic one. In fact it is one of the most highly ionic bonds known.

Bonds that have an ionic character of 50% or less are classified as covalent bonds. A bond between identical atoms is completely covalent. Hydrogen, for example, exists in nature not as isolated atoms, but as pairs of atoms held together by covalent bonds, H:H. The Hydrogen-Hydrogen bond has 0% ionic character. It is **non-polar covalent bond,** *a covalent bond in which the bonding electrons are shared equally by the bonded atoms, with a resulting balanced distribution of electrical charge.* Bonds having 0%-5% ionic character, corresponding to electronegativity differences of roughly 0 to 0,3, are generally considered as non-polar covalent bonds. For example, because the electronegativity difference between Hydrogen (H) and Boron (B) is 0,1, they form a bond that is essentially non-polar.

In bonds with significantly different electronegativities, the electrons are more attracted to the more electronegative atom. Such bonds are **polar,** meaning that they have an uneven distribution of charge. Covalent bonds having 5%-50% ionic character are classified as polar. A **polar-covalent bond** *is a covalent bond in which the united atoms have an unequal attraction for the shared electrons.*

Nonpolar and polar-covalent bonds are compared in the sketches in Fig. 4.6 of the electron density.
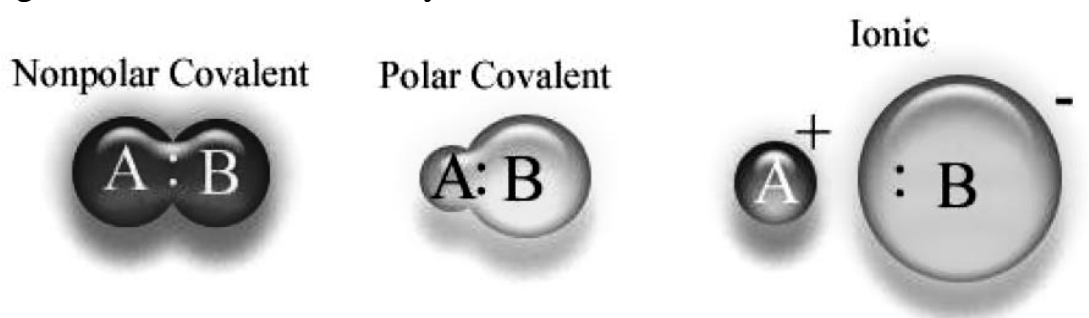
Figure 4.6. Comparison of the electron density in a non-polar, polar bonds and ionic bonds

In addition to ionic and covalent bond, there is a third major type of bond - **metallic** bond. In solid or liquid metals, metal atoms give up electrons, as in ionic compounds (Fig. 4.3). The liberated electrons however, are free to move throughout the material, rather than being held in place in negative ions.

In general, atoms of non-metals form covalent bonds with each other, atoms of metals form metallic bonds with each other, and atoms of metals form ionic bonds with atoms of non-metals. There are many exceptions, however. One common and important exception is the formation of polar-covalent bonds between metals and non-metals that do not differ greatly in electronegativity.

Sample

Use electronegativity differences and Fig. 4.5, to classify bonds between Sulfur and the following elements: Hydrogen, Cesium, Chlorine, Magnesium, and Oxygen. Which atom in each bond will be more negative?

The electronegativity of Sulfur is 2,5 (**Appendix 3**).

Bond from Sulfur to	Difference of electronegativitis	Bond type	More electronegative atom
Hydrogen H	2,5 - 2,1 = 0,4	Polar covalent	Sulfur
Cesium Cs	2,5 - 0,7 = 1,8	Ionic	Sulfur
Chlorine Cl	3,0 - 2,5 = 0,5	Polar covalent	Chlorine
Magnesium Mg	2,5 - 1,2 = 1,3	Polar covalent	Sulfur
Oxygen O	3,5 - 2,5 = 1,0	Polar covalent	Oxygen

4.7 Hydrogen Bonding

Hydrogen bonding differs from other uses of the word "bond" since it is a force of attraction a Hydrogen atom in one molecule and a small arom of high electronegativity (mostly Oxygen, Nitrogen, Fluorine) in another molecule. That is, it is an intermolecular force, not an intramolecular force as in the common use of the word "bond".

When Hydrogen atoms are joined in a polar covalent bond with a small atom of high electonegativity, the partial positive charge on the Hydrogen is highly concentrated because of its small size.

Hydrogen bonding has a very important effect on the properties of water. Consider two water molecules coming close together (see Fig. 4.7).

Polar molecules, such as water molecules, have a weak, partial negative charge at one region of the molecule (the Oxygen atom in water) and a partial positive charge elsewhere (the Hydrogen atoms in water). Thus when water molecules are close together, their positive and negative regions are attracted to the oppositely-charged regions of nearby molecules. The force of attraction, shown here as a dotted line, is a hydrogen bond. The $\delta+$ Hydrogen is so strongly attracted to the electron pair that it is almost as if you were beginning to form a co-ordinate (donor-acceptor covalent) bond. Notice that each water molecule can potentially form four Hydrogen bonds. It doesn't go that far, but the attraction is significantly stronger than an ordinary interaction. Hydrogen bonds have about a tenth of the strength of an average covalent bond, and are being constantly broken and reformed in liquid water.
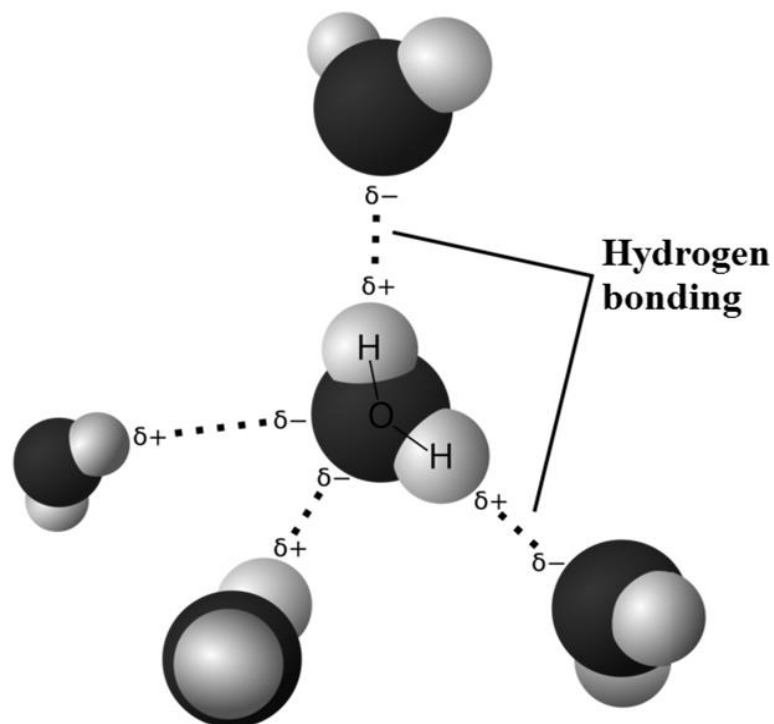
Figure 4.7. Formation of Hydrogen Bonding between water molecules

This is why the boiling point of water is higher than that of ammonia or Hydrogen Fluoride (see Fig. 4.8).
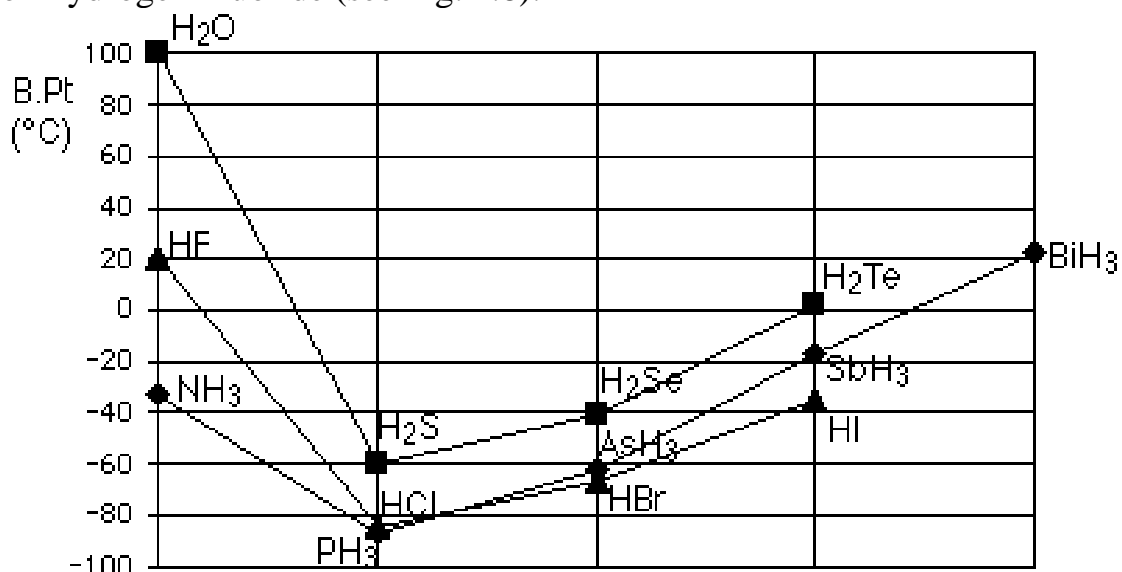
Figure 4.8. Depending of boiling-points (B.Pt) of double Hydrogen-contained compounds from nature of the second atom and presence of Hydrogen bonding

In the case of Ammonia NH_3, the amount of hydrogen bonding is limited by the fact that each Nitrogen only has one electron pair. In a group of Ammonia molecules, there aren't enough electron pairs to go around satisfying all the Hydrogens. In Hydrogen fluoride, the problem is a

shortage of hydrogens. In water, there are exactly the right number of each. Water could be considered as the "perfect" hydrogen bonded system. The hydrogen bonds that form between water molecules account for some of the essential and unique properties of water:

The attraction created by hydrogen bonds keeps water liquid over a wider range of temperature than is found for any other molecule its size.

The energy required to break multiple hydrogen bonds causes water to have a high heat of vaporization; that is a large amount of energy is needed to convert liquid water, where the molecules are attracted through their hydrogen bonds, to water vapor, where they are not.

Two outcomes of this:

The evaporation of sweat, used by many mammals to cool themselves, achieves this by the large amount of heat needed to break the hydrogen bonds between water molecules.

Moderating temperature shifts in the ecosystem (which is why the climate is more moderate near large bodies of water like the ocean).

Multiple hydrogen bonds in alive objects:

hold the two strands of the DNA double helix together:
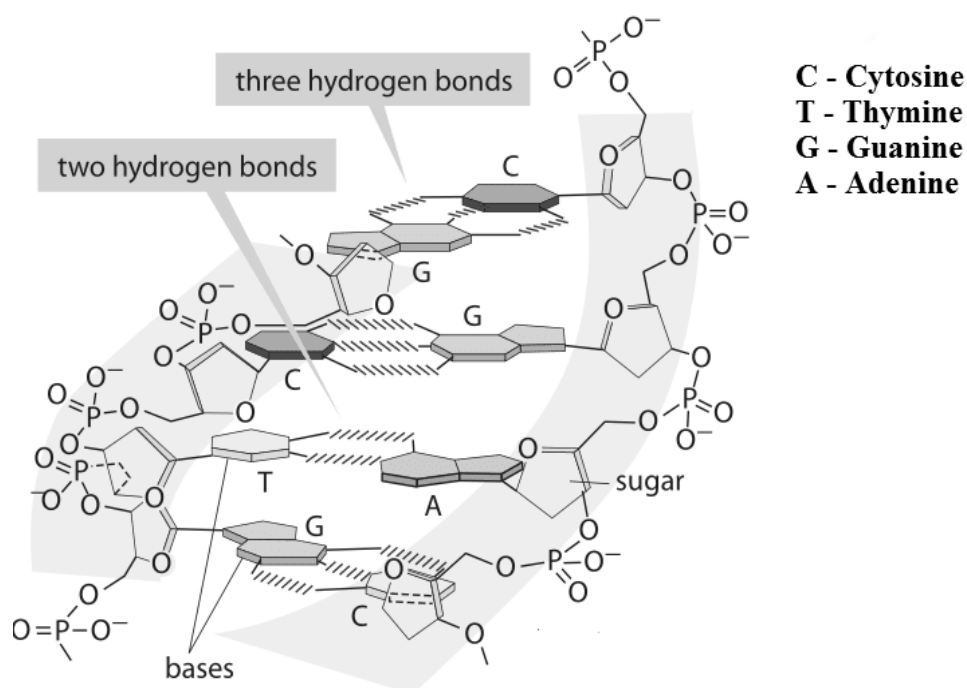
hold polypeptides together in such secondary structures as the alpha helix and the beta conformation;

help enzymes bind to their substrate;

help antibodies bind to their antigen

help transcription factors bind to each other;

help transcription factors bind to DNA.

4.8 Metallic Bonds

Metals have several qualities that are unique, such as the ability to conduct electricity, a low ionization energy, and a low electronegativity (so they will give up electrons easily, i.e., they are cations). Their physical properties include a lustrous (shiny) appearance, and they are malleable and ductile. Metals have a crystal structure. However, metals are also malleable and ductile. In the 1900's, Paul Drüde came up with "the sea of electrons" theory by modeling metals as a mixture of atomic cores (atomic cores = positive nuclei + inner shell of electrons) and valence electrons. In this model, the valence electrons are free, delocalized, mobile, and not associated with any particular atom. This model may account for:

−   Malleability and Ductility: The sea of electrons surrounding the protons act like a cushion, and so when the metal is hammered on, for instance, the over all composition of the structure of the metal is not harmed or changed. The protons may be rearranged but the sea of electrons with adjust to the new formation of protons and keep the metal intact.

−   Heat capacity: This is explained by the ability of free electrons to move about the solid.

−   Luster: The free electrons can absorb photons in the "sea," so metals are opaque-looking. Electrons on the surface can bounce back light at the same frequency that the light hits the surface, therefore the metal appears to be shiny.

−   Conductivity: Since the electrons are free, if electrons from an outside source were pushed into a metal wire at one end, the electrons would move through the wire and come out at the other end at the same rate (conductivity is the movement of charge).

However, these observations are only qualitative, and not quantitative, so they cannot be tested. The "Sea of Electrons" theory stands today only as an oversimplified model of how metallic bonding works.

Metals tend to have high melting points and boiling points suggesting strong bonds between the atoms. Even a metal like sodium (melting point 97,8 °C) melts at a considerably higher temperature than the element (neon Ne) which precedes it in the Periodic table. Sodium Na has the electronic structure $1s^2 2s^2 2p^6 3s^1$. When sodium atoms come together, the electron in the 3s atomic orbital of one sodium atom shares space with the corresponding electron on a neighboring atom to form a molecular orbital - in much the same sort of way that a covalent bond is formed.

The difference, however, is that each sodium atom is being touched by eight other sodium atoms - and the sharing occurs between the central atom and the 3s orbitals on all of the eight other atoms. And each of these eight is in turn being touched by eight sodium atoms, which in turn are

touched by eight atoms – and so on and so on, until you have taken in all the atoms in that lump of sodium.

All of the 3s orbitals on all of the atoms overlap to give a vast number of molecular orbitals which extend over the whole piece of metal. There have to be huge numbers of molecular orbitals, of course, because any orbital can only hold two electrons.

The electrons can move freely within these molecular orbitals, and so each electron becomes detached from its parent atom. The electrons are said to be delocalized. The metal is held together by the strong forces of attraction between the positive nuclei and the delocalized electrons.
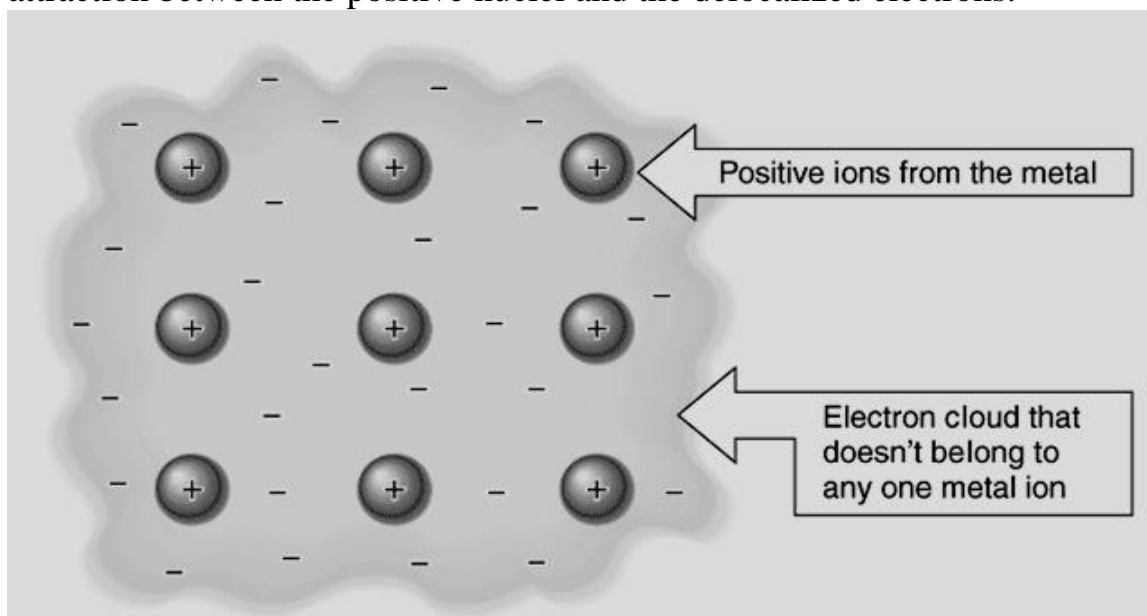
This is sometimes described as "an array of positive ions in a sea of electrons". If you are going to use this view, beware! Is a metal made up of atoms or ions? It is made of **atoms.** Each positive center in the diagram represents all the rest of the atom apart from the outer electron, but that electron hasn't been lost – it may no longer have an attachment to a particular atom, but it's still there in the structure. Sodium metal is therefore written as Na – not Na^+.

If you work through the same argument with magnesium Mg, you end up with stronger bonds and so a higher melting point. Magnesium has the outer electronic structure $3s^2$. Both of these electrons become delocalized, so the "sea" has twice the electron density as it does in sodium. The remaining "ions" also have twice the charge (if you are going to use this particular view of the metal bond) and so there will be more attraction between "ions" and "sea".

More realistically, each magnesium atom has 12 protons in the nucleus compared with sodium's 11. In both cases, the nucleus is screened

from the delocalized electrons by the same number of inner electrons - the 10 electrons in the $1s^2 2s^2 2p^6$ orbitals.

That means that there will be a net pull from the magnesium nucleus of 2+, but only 1+ from the sodium nucleus.

So not only will there be a greater number of delocalized electrons in magnesium, but there will also be a greater attraction for them from the magnesium nuclei. Magnesium atoms also have a slightly smaller radius than sodium atoms, and so the delocalized electrons are closer to the nuclei. Each magnesium atom also has twelve near neighbors rather than sodium's eight. Both of these factors increase the strength of the bond still further.

Metallic bonding in Transition Elements

Transition metals tend to have particularly high melting points and boiling points. The reason is that they can involve the 3d electrons in the delocalization as well as the 4s. The more electrons you can involve, the stronger the attractions tend to be.

The metallic bond in Molten Metals

In a molten metal, the metallic bond is still present, although the ordered structure has been broken down. The metallic bond is not fully broken until the metal boils. That means that boiling point is actually a better guide to the strength of the metallic bond than melting point is. On melting, the bond is loosened, not broken.

The strength of a metallic bond depends on three things:
- The number of electrons that become delocalized from the metal;
- The charge of the cation (metal);
- The size of the cation.

A **strong** metallic bond will be the result of more delocalized electrons, which causes the effective nuclear charge on electrons on the cation to increase, in effect making the size of the cation smaller. Metallic bonds are strong and require a great deal of energy to break, and therefore **metals have high melting and boiling points.** A metallic bonding theory must explain how so much bonding can occur with such few electrons (since metals are located on the left side of the periodic table and do not have many electrons in their valence shells). The theory must also account for all of a metal's unique chemical and physical properties.

4.9 Donor-acceptor covalent bonding

As indicated above, during the formation of the covalent bond, the bonding electrons enter the outermost shells of the atoms being bonded.

During covalent bond formation, both bonding electrons enter the outermost shells of both atoms being bonded. Respectively, the number of

electrons in the outermost shells of the atoms to be bonded is increased by one electron.

In the case of double and triple bond formation between the atoms, the number of electrons in the outermost shells of the atoms to be bonded is increased by two and three respectively.

If one atom, say, carbon (C), forms four bonds with hydrogen and chlorine atoms, the number of electrons in the outermost shell of a carbon atom increases by four electrons.

That is, the increase of the number of electrons in the outermost layer during chemical bond formation, is not limited by the number of electrons that enter the outermost layer during bond formation, but is limited only by the maximal number of electrons that can be situated in the outermost layer.

Recall that for elements of the 2nd and 3rd periods with fewer that 4 electrons, the number of covalent bonds, which the given element can form, is equal to the number of electrons in the outermost shell of the given element. Thus, for example, lithium (Li), beryllium (Be), and boron (B) can form 1, 2, and 3 covalent bonds respectively.

On the other hand, for elements of these periods with more than 4 electrons, the maximal number of electrons that can enter the outermost shell of the given element, when forming a covalent bond, defines the number of covalent bonds that the given element can form.

The total number of electrons that can be situated in the outermost shell of the elements of the 2nd and 3rd periods is equal to 8. Therefore, nitrogen (N), oxygen (O), fluorine (F), and neon (Ne) with 5, 6, 7, and 8 electrons in the outermost shell can form 3, 2, 1, 0 covalent chemical bonds respectively.

Atoms of sodium (Na), magnesium (Mg), and aluminum (Al), after forming the maximal number of covalent bonds, for example, after the formation of molecules of the NaF, MgF_2, AlF_3 type, contain 2, 4, and 6 electrons in the outermost shell respectively. This proves that the atoms' outermost shells contain fewer than 8 electrons, i.e., they remain non-saturated.

However, atoms of nitrogen (N), oxygen (O), and fluorine (F), after the formation of 3, 2, and 1 covalent bonds, contain 8 electrons in the outermost shell, of which the bonding ones are: nitrogen (N) – 6 electrons; oxygen (O) – 4 electrons; fluorine (F) – 2 electrons.

Atoms of nitrogen (N), oxygen (O), and fluorine (F), in compounds like ammonium (NH_3), water (H_2O), and hydrogen fluoride (HF) contain 2, 4, and 6 electrons relatively in the outermost shells and do not take part in chemical bond formation, i.e., they are regarded as being *free*. Since in

the formed compounds of NH_3, H_2O, and HF there are 8 electrons in the outermost shell of the N, O, and F atoms, the free, nonbonding electrons cannot take part in covalent bond formation because the outermost shell of these atoms is saturated with electrons.

These free (nonbonding) electrons do play the role of the electrons' donors in chemical bond formation. What can be a truly reliable helper for these electrons in the formation of such bonds? First of all, those atoms whose shells contain fewer than 8 electrons. The atoms in molecules, formed of elements of the 2^d and 3^d periods (with fewer than 4 electrons in the outermost layer), are of this kind; for example, recall the previously sighted Na, Mg, and Al in compounds NaF, MgF_2, and AlF_3. As already said, the outermost shells of Na, Mg, and Al in these molecules are unsaturated, i.e., capable of bonding electrons. Molecules like NaF, MgF_2 and AlF_3 are good partner-acceptors for such donor-electrons as atoms of N, O, and F in molecules that include these atoms.

The following stable compounds are well known:

$H_3B \leftarrow NH_3$; $H_3B \leftarrow N(CH_3)_2$; $F_3B \leftarrow NH_3$; $F_3B \leftarrow O(CH_3)_2$;

$Cl_2Be \leftarrow O(C_2H_5)_2$; $Cl_3Al \leftarrow NH_3$; etc.
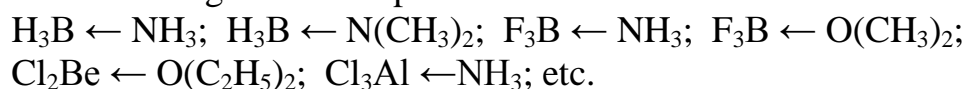
The arrows ($\leftarrow$) here indicate the donor-acceptor bonds.

Donors (N and O atoms) offer two electrons in these examples. The acceptors are B, Be and Al.

When forming donor-acceptor bonds the acceptor atoms increase the number of electrons in their outermost shells by 2.

According to donor-acceptor bonds formation rules, inert gases can form bonds as donors of electronic pairs with the atoms having 6 electrons. Thus the synthesis of XeO, XeO_2 and XeO_3 is an experimental confirmation of this theoretical supposition.

It is not only neutral atoms and molecules that can play the role of electrons' donors and acceptors, but also - the positively and negatively charged atoms and molecules, i.e., *cations* and *anions*.

Thus, for example, with the help of ammonia (NH_3) a hydrogen cation (H^+) forms the cation (NH_4^+) where one atom is bonded to the nitrogen at the expense of the nitrogen's electrons. In ammonia, the nitrogen atom has a lone pair of electrons after completing its octet. It donates this lone pair to the hydrogen ion.

Thus the nitrogen atom becomes the donor. The hydrogen atom becomes the acceptor. The linkage between N and H atoms is called coordinate bond. It is represented by an arrow $\rightarrow$.
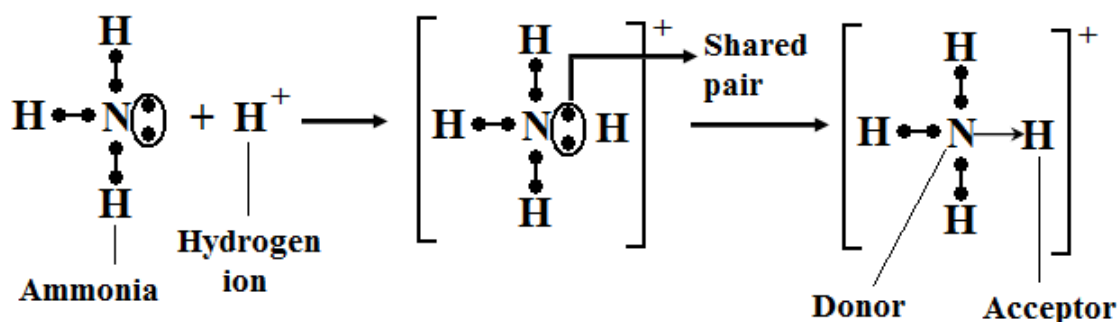
One of the main reasons for the comparatively weak donor-acceptor bonding is as follows. When calculating the bonding energy, the initial atoms' electronic energy, taking part in bond formation, is subtracted from the molecule's calculated energy. That is, the energy gain (difference between the electronic energies of the divided and bonded atoms via chemical bonding) in the case of the donor-acceptor bonding is smaller at the expense of the energy increase of the divided atoms.

4.10 Why does Chemical Bond occur?

The fascinating variety of materials in the world around us is possible because chemical bonds unite atoms of the elements in so many different combinations. Some elements are found in nature only in chemical compounds. Even the atoms of elements that can be found in nature in uncombined form - such as Oxygen and Nitrogen in the air, of Gold and Copper in the Earth's crust - do not exist as independent atoms. They are bonded together.

If their potential energy is lowered by the change, two atoms will form a chemical bond. Throughout nature, changes that decrease potential energy are favored. Books fall off desks, and the result is lower potential energy for the books. Most atoms have lower potential energy in bonds than as independent atoms.

Chemical-bond formation is often energy – releasing process. Experiments also show that the reverse - breaking chemical bonds – is often an energy-absorbing process. Atoms separated by breaking a chemical bond have a higher total potential energy than when they were bonded. Whether or not a given chemical reaction occurs spontaneously is partly dependent on whether or not forming new bonds in the products produced enough energy to break bonds in the reactants.

Covalent, ionic and metallic bond all decrease the potential energy of the combined atoms.

Review questions

1. *Define electronegativity, and explain the difference between electronegativity and electron affinity. Describe in general how electronegativities of elements charge according to pisition in the Periodical table.*

2. *Use the second member of main subgroups from Group 1 to Group 7 to show that the number of valence electrons on the atom of the element is the same as its group number.*

3. *Define these terms: lone pairs, electro structure, the octet rule, bond length.*

4. *Distinguish among single, double, and triple bonds in a molecule, and give an example of each.*

5. *List these bonds in order of increasing ionic character: carbon C to hydrogen H, fluorine F to hydrogen H, bromine Br to hydrogen H, sodium Na to chlorine Cl, potassium K to fluorine F, lithium Li to chlorine Cl.*

6. *What is a polar covalent bond? Name two compounds that contain one or more covalent bonds.*

7. *Classify the compounds and their chemical bonding (see Appendix 3 - Electronegativity Chart)*

A.	PH_3	1	Covalent non-polar
B.	Ca	2	Covalent polar
C.	CO_2	3	Ionic
D.	FeF_3	4	Metallic
E.	N_2H_4		

8. *Elements of the main sub-group of any group of the Mendeleev's Periodical Chart have the same:*

A.	Quantity of electron shells	C.	The charge of atomic nucleus
B.	Quantity of the electrons on the last shell	D.	The relative atomic weight

9. *Put in the sentence the missing word:Electronegativity estimates possibility of a neutral atom to _____ electron.*

10. *Sulfur S has such oxidation number and valence in the exited states (possible more than one true answer):*

A.	+6, VI	B.	-2, II	C.	+4, IV	D.	+2, II	E.	+6, IV

11. *Point the correctness of the statement: Multiple ionic bonds are motes the dots on the picture above.*

A.	True	B.	False

Adenine   Thymine
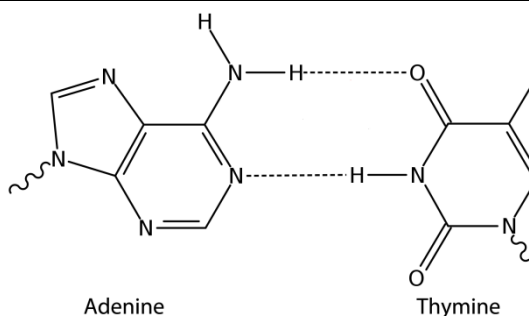
12. Write the electron configuration of the Silicon Si in the exited state.

13. The structure of the last energy (valence) level of the Noble gases is:

A.	ns^2np^6	B.	ns^2np^5	C.	ns^2np^4	D.	ns^2np^3

14. Quantum number characterizing electron state in atom is named
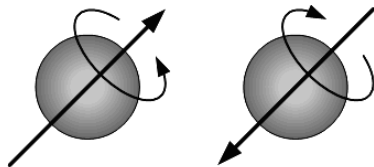
(see picture): +1/2   -1/2

A.	Azimuthal	B.	Spin	C.	Principal	D.	Magnetic

15. Why does the octet rule not hold for many compounds containing elements in the 3d period of Periodical table and beyond?

16. What is a donor-acceptor covalent bond? Is it different from a usual covalent bond?

17. The formulas of interholagenides are BrF_3, ClF_5, and IF_7. Identify those in which the octet ruke is not obeyed.

18. How many united pairs are of electron in the molecule N_2 (see figure)?
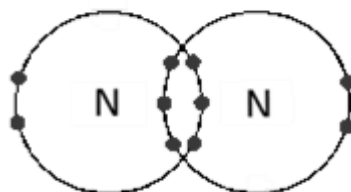
19. Note the type of atomic orbital having the next space forms:
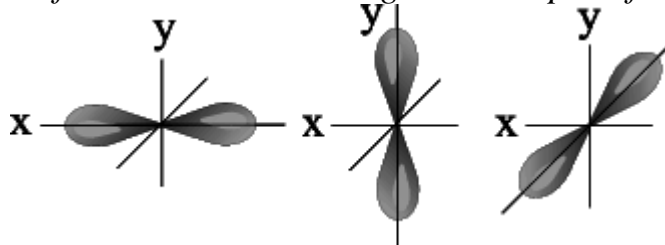
20. Point the correctness of the statement: Multiple _hydrogen_ bonds are motes the dots on the picture above.

A.	True	B.	False
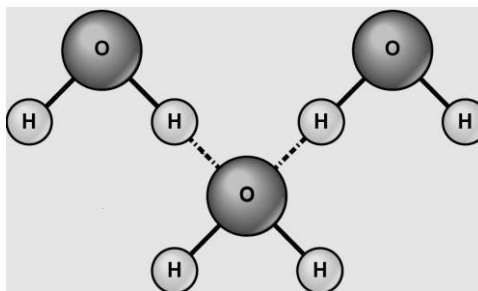
CHAPTER 5 THE PERIODIC LAW AND PERIODIC TABLE OF CHEMICAL ELEMENTS

5.1 General notions

The modern periodic table has evolved through a long history of attempts by chemists to arrange the elements according to their properties as an aid in predicting chemical behavior. One of the first to suggest such an arrangement was the German chemist Johannes Dobereiner (1780–1849), who noticed that many of the known elements could be grouped in triads (a set of three elements that have similar properties) – for example, chlorine Cl, bromine Br, and iodine I; or copper Cu, silver Ag, and gold Cu. Dobereiner proposed that all elements could be grouped in such triads, but subsequent attempts to expand his concept were unsuccessful. We now know that portions of the Periodic table – the d block in particular – contain triads of elements with substantial similarities. The middle three members of most of the other columns, such as sulfur S, selenium Se, and tellurium Te in the VIA group or aluminum Al, gallium Ga, and indium In in IIIA group, also have remarkably similar chemistry.

By the mid-19th century, the atomic masses of many of the elements had been determined. The English chemist John Newlands (1838-1898), hypothesizing that the chemistry of the elements might be related to their masses, arranged the known elements in order of increasing atomic mass and discovered that every seventh element had similar properties.

Newlands therefore suggested that the elements could be classified into octaves A group of seven elements, corresponding to the horizontal rows in the main group elements (not counting the noble gases, which were unknown at the time), corresponding to the *horizontal* rows in the main group elements. Unfortunately, Newlands's "law of octaves" did not seem to work for elements heavier than calcium, and his idea was publicly ridiculed. At one scientific meeting, Newlands was asked why he didn't arrange the elements in alphabetical order instead of by atomic mass, since that would make just as much sense. Actually, Newlands was on the right track– with only a few exceptions, atomic mass does increase with atomic number, and similar properties occur every time a set of ns^2np^6 subshells is filled. Despite the fact that Newlands's table had no logical place for the *d*-block elements, he was honore the Periodic table achieved its modern form through the work of the German chemist Julius Lothar Meyer (1830-1895) and the famous Russian chemist Dimitri Mendeleev (1834-1907), both of whom focused on the relationships between atomic mass and various physical and chemical properties. In 1869, they independently proposed essentially identical arrangements of the elements. Meyer aligned the

elements in his table according to periodic variations in simple atomic properties, such as "atomic volume", which he obtained by dividing the atomic mass (molar mass) in grams per mole by the density ($\rho\rho$) of the element in grams per cubic centimeter. This property is equivalent to what is today defined as molar volume, the molar mass of an element divided by its density, (measured in cubic centimeters per mole):

Molar mass (g/mol) density (g/cm^3) = molar volume (cm^3/mol)

Molar mass (g/mol) density (g/cm^3)=molar volume(cm^3/mol)

The alkali metals have the highest molar volumes of the solid elements. In Meyer's plot (Fig. 5.1) of atomic volume versus atomic mass, the nonmetals occur on the rising portion of the graph, and metals occur at the peaks, in the valleys, and on the downslopes.
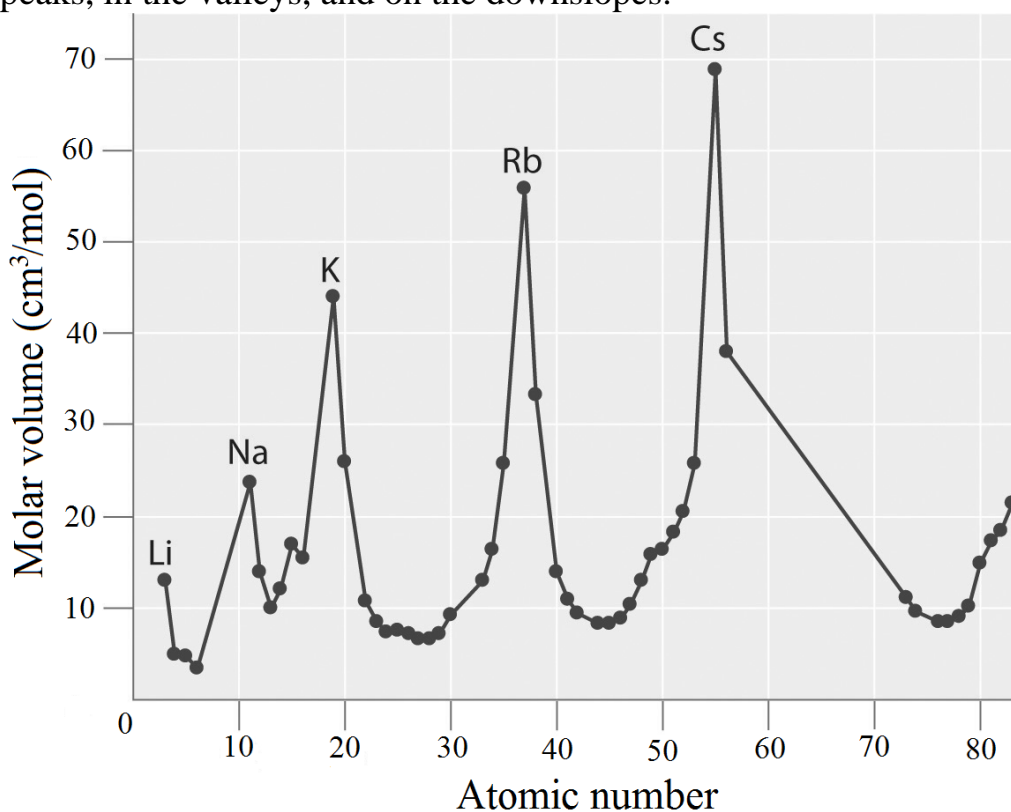
Figure 5.1. Variation of Atomic Volume with Atomic Number, Adapted from Meyer's Plot of 1870.

5.2 Mendeleev's Periodic Table

D.I. Mendeleev, who first published his periodic table in 1869 is usually credited with the origin of the modern Periodic table. The key difference between his arrangement of the elements and that of Meyer and others is that Mendeleev did not assume that all the elements had been discovered (actually, only about two-thirds of the naturally occurring elements were known at the time). Instead, he deliberately left blanks in his

table at atomic masses 44, 68, 72, and 100, in the expectation that elements with those atomic masses would be discovered. Those blanks correspond to the elements we now know as scandium Sc , gallium Ga , germanium Ge, and technetium Tc (Fig. 5.2).

Reihen	Gruppe I. — R^2O	Gruppe II. — RO	Gruppe III. — R^2O^3	Gruppe IV. RH^4 RO^2	Gruppe V. RH^3 R^2O^5	Gruppe VI. RH^2 RO^3	Gruppe VII. RH R^2O^7	Gruppe VIII. — RO^4
1	H=1							
2	Li=7	Be=9,4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27,3	Si=28	P=31	S=32	Cl=35,5	
4	K=39	Ca=40	— =44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63.
5	(Cu=63)	Zn=65	— =68	— =72	As=75	Se=78	Br=80	
6	Rb=85	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=96	— =100	Ru=104, Rh=104, Pd=106, Ag=108.
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	J=127	
8	Cs=133	Ba=137	?Di=138	?Ce= 40	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	
10	—	—	?Er=178	?La=180	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=199.
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	—	—	
12	—	—	—	Th=231	—	U=240	—	— — — —

Figure 5.2. Mendeleev's Periodic table, as Published in the German Journal "Annalen der Chemie und Pharmacie" in 1872. The column headings "Reihen" and "Gruppe" are German for "row" and "group". Formulas indicate the type of compounds formed by each group, with "R" standing for "any element" and superscripts used where we now use subscripts. Atomic masses are shown after equal signs and increase across each row from left to right.

The groups in Mendeleev's table are determined by how many oxygen O or hydrogen H atoms are needed to form compounds with each element. For example, in Group I, two atoms of hydrogen, lithium Li, sodium Na, and potassium K form compounds with one atom of oxygen O. In Group VII, one atom of fluorine F, chlorine Cl, and bromine, Br, react with one atom of hydrogen H. Notice how this approach has trouble with the transition metals. Until roughly 1960, a rectangular table developed from Mendeleev's table and based on reactivity was standard at the front of chemistry lecture halls.

The most convincing evidence in support of Mendeleev's arrangement of the elements was the discovery of two previously unknown elements whose properties closely corresponded with his predictions (Table 5.1). Two of the blanks Mendeleev had left in his original table were below aluminum and silicon, awaiting the discovery of two as-yet-unknown elements, *eka*-aluminum and *eka*-silicon (from the Sanskrit *eka*, meaning "one," as in "one beyond aluminum"). The observed properties of gallium

Ga and germanium Ge matched those of *eka*-aluminum and *eka*-silicon so well that once they were discovered, Mendeleev's periodic table rapidly gained acceptance.

Table 5.1. Comparison of the Properties Predicted by Mendeleev in 1869 for eka-Aluminum and eka-Silicon with the Properties of Gallium (Discovered in 1875) and Germanium (Discovered in 1886)

Property	*eka*-Aluminum (predicted)	Gallium (observed)	*eka*-Silicon (predicted)	Germanium (observed)
Atomic mass	68	69,723	72	72,64
Element	metal	metal	dirty-gray metal	gray-white metal
Melting point	low melting point	29,8 °C	high melting point	938 °C
Density	5,9 g/cm^3	5,91 g/cm^3	5,5 g/cm^3	5,323 g/cm^3
Oxide	E_2O_3	Ga_2O_3	EO_2	GeO_2
Chloride	ECl_3	$GaCl_3$	ECl_4	$GeCl_4$
	volatile	melting point = 78 °C; boiling point = 201 °C	boiling point < 100 °C	boiling point = 87 °C

When the chemical properties of an element suggested that it might have been assigned the wrong place in earlier tables, Mendeleev carefully reexamined its atomic mass. He discovered, for example, that the atomic masses previously reported for beryllium, indium, and uranium were incorrect. The atomic mass of indium had originally been reported as 75,6, based on an assumed stoichiometry of InO for its oxide. If this atomic mass were correct, then indium would have to be placed in the middle of the nonmetals, between arsenic (atomic mass 75) and selenium (atomic mass 78). Because elemental indium In is a silvery-white ***metal***, however, Mendeleev postulated that the stoichiometry of its oxide was really In_2O_3 rather than InO. This would mean that indium's atomic mass was actually 113, placing the element between two other metals, cadmium Cd and tin Sn.

One group of elements that absent from Mendeleev's table is the Noble gases, all of which were discovered more than 20 years later, between 1894 and 1898, by Sir William Ramsay (1852-1916; Nobel Prize in Chemistry 1904). Initially, Ramsay did not know where to place these elements in the Periodic table. Argon, the first to be discovered, had an atomic mass of 40. This was greater than chlorine's and comparable to that of potassium, so Ramsay, using the same kind of reasoning as Mendeleev, decided to place the Noble gases between the Halogens and the alkali metals.

After over a decade, four elements on the Periodic table have officially acquired new names. Elements 113, 115, 117 and 118 will now be called Nihonium, Moscovium, Tennessine and Oganesson.

Each of the elements were named for the location in which they were discovered or the researchers who helped locate them.

The name of element 113, Nihonium (Nh), comes from the Japanese word Nihon, which means Japan. The element was discovered in and named after the Asian country.

Russian researchers named element 115, Moscovium (Mc) after Moscow where experiments were conducted.

Tennessine (Ts), element 117 was named after the state of Tennessee. The state was recognized for research contributions from multiple universities including the University of Tennessee and Vanderbilt University.

Element 118, Oganesson (Og) got its name from Yuri Oganessian, a Russian team member and element hunter who helped discover it.

The scientific synthetization of these elements spanned from 2002-2010, and the discoveries were later recognized by the International Union of Pure and Applied Chemistry in 2015. Name suggestions were sent to IUPAC this summer and were eventually approved after a five-month waiting period during which the public could ask questions about the elements.

With the massive, highly-reactive elements named, the seventh row of the periodic table is now complete.

5.3 The Role of the Atomic Number in the Periodic table

Despite its usefulness, Mendeleev's Periodic table was based entirely on empirical observation supported by very little understanding. It was not until 1913, when British physicist H. G. J. Moseley (1887-1915), while analyzing the frequencies of X-rays emitted by the elements, discovered that the underlying foundation of the order of the elements was by the *atomic number*, not the atomic mass. Moseley hypothesized that the placement of each element in his series corresponded to its atomic number Z, which is the number of positive charges (protons) in its nucleus. Argon Ar, for example, although having an atomic mass greater than that of potassium K (39,9 amu versus 39,1 amu, respectively), was placed *before* potassium in the Periodic table. While analyzing the frequencies of the emitted X-rays, Moseley noticed that the atomic number of argon Ar is 18, whereas that of potassium K is 19, which indicated that they were indeed placed correctly. Moseley also noticed three gaps in his table of X-ray frequencies, so he predicted the existence of three unknown elements:

technetium Tc (Z=43), discovered in 1937; promethium Pm *(Z=61),* discovered in 1945; and rhenium Re (Z=75), discovered in 1925.

The elements in the Periodic table are arranged according to their properties, and the periodic table serves as an aid in predicting chemical behavior.
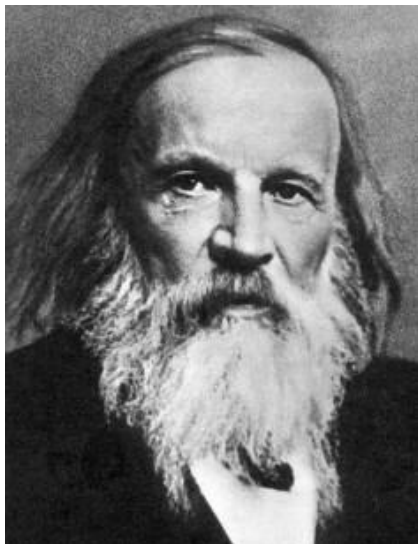
Figure 5.2. D.I. Mendeleev (1834-1907)

The Periodic table arranges the elements according to their electron configurations, such that elements in the same column have the same valence electron configurations. Periodic variations in size and chemical properties are important factors in dictating the types of chemical reactions the elements undergo and the kinds of chemical compounds they form. The modern Periodic table was based on empirical correlations of properties such as atomic mass; early models using limited data noted the existence of **triads** and **octaves** of elements with similar properties.

Mendeleev's principle of chemical periodicity is known as the periodic law: **"The physical and chemical properties of the elements are periodic function of their atomic mass".**

Modern formulation:

"The properties of chemical elements, as well as the forms and properties of the compounds of the elements are periodic function of the nuclear charge of atoms of the chemical elements".

5.3 Position of Hydrogen in Periodical table

Hydrogen is the first element of the periodic table. Its atomic number is 1, which indicates the presence of only one electron in the atom of hydrogen. This electron is present in its first shell. Due to the presence of only one electron in its 1s shell, hydrogen exhibits a dual behaviour, i.e., hydrogen resembles both The alkali metals (group I A) as well as the Halogens (group VII A). Therefore its position is said to be anomalous.

Properties of Hydrogen that Resemble the Alkali metals:

1. Like the Alkali metals, hydrogen contains one valence electron in its valency shell.

H : $1s^1$
Li : [He] $2s^1$
Na : [Ne] $3s^1$

Hence, it can lose one electron to form a unipositive ion.

2. Like alkali metals, hydrogen combines with electronegative elements to form oxides (H_2O), halides (HF), and sulphides (H_2S).

Properties of Hydrogen that Resemble with the Halogens:

1. Both Hydrogen and the Halogens require one electron to complete their octets.

H : $1s^1$

F : $1s^2 2s^2 2p^5$

Cl : $1s^2 2s^2 2p^6 3s^2 3p^5$

Hence, Hydrogen can gain one electron to form a uninegative ion.

2. Like the Halogens, it forms a diatomic molecule H_2 and several covalent compounds (i.e., PH_3, NH_3).

Though Hydrogen shows some similarity with both the Alkali metals and the Halogens, it differs from them on some grounds. Unlike the alkali metals, hydrogen does not possess metallic characteristics. On the other hand, it possesses a high ionization enthalpy. Also, it is less reactive than halogens.

Owing to these reasons, hydrogen cannot be placed with alkali metals (group I) or with halogens (group VII). In addition, it was also established that H^+ ions cannot exist freely as they are extremely small. H^+ ions are always associated with other atoms or molecules. Hence, hydrogen is best placed separately in the Periodic table.

Figure 5.3. Sculpture in honor of Mendeleev and the Periodic table, located in Bratislava (Slovakia)

5.5 Physical meaning of the chemical periodicity

Periodic changes of chemical properties of elements are stipulated by the correct repetition of electron configuration of external energy level (valency electrons) their atoms with nuclear charge increasing. Graphic inventing of a Periodic law is a periodic Table (see below). It is kept 7 periods and 8 groups.

Period – horizontal row of elements in the Periodic Table with similar maximum value of the main quantum number of electrons. Period number indicates the number of energy levels in the atom of element.

Period can consist of 2 (first), 8 (second and third), 18 (fourth and fifth) or 32 (sixth) electrons, depending on the amounts of electrons on the external energy level. Seventh period is not completed.

All periods (except the first) are begun with alkaline metal (s-element), but are finished by noble gas (ns^2np^6).

Metallic properties are considered as an ability of atoms of elements to loss electrons easily, but non-metallic – to accept electrons. Filling of external *s*-sublevel is pointed out to metallic properties of atom, but shaping an external *p*-sublevel (from 5) intensifies non-metallic properties of atom. Atoms with completely formed, energy firm configuration of the external electronic layer (ns^2np^6) are chemically inert.

At great periods change of the properties from the active metal to the noble gas occurs more smoothly, than at small periods, since a shaping an internal (n-1) *d*-sublevel occurs at the conservation external ns^2-layer. Great periods consist of even and odd rows.

At even row of elements on the external layer ns^2- electrons, such metallic properties are dominated and their weakening with the growing of nuclear charge is not great; in odd rows the *np*-sublevel is formed, that explains a significant weakening of metal properties.

Groups – vertical rows of elements with similar valency number electrons, which is equal to group number. Main and secondary sub-groups are distinguished.

Main sub-groups consist of elements of great periods; valency electrons are placed on the external *ns*- and *np*-sublevels.

Secondary groups consist of elements of great periods only. Their valency electrons are on the external ns-sublevel and internal (n-1) *d*-sublevel (or (n-2) *f*-sub-level).

Depending on the sub-level, which is filled by valency electrons, the periodic system of elements is subdivided into:

s-block (elements of main sub-group of I and II groups);

p-block (elements of sub-groups of III-IV groups);

d-block (elements of secondary sub-groups);

f-block (lanthanides and actinides).

In the main subgroups from top to bottom the metallic properties are intensified, but non-metallic are weakened.

The number of the group shows the highest valency of element (except N, O, F, elements of Copper sub-group and eighth group).

Formulas of the highest oxides are general for elements of main and secondary sub-groups (and their hydrates). At the highest oxides and hydrates – elements of I-III groups (except boron) the basic properties are dominated, but from IV till VII – acid.

For the elements of main sub-groups formulas of Hydrogen compounds are general. Elements of main sub-groups of I-III groups form hard substances – hydrides (Hydrogen has oxidation number –1), but IV-VII – gaseous. Hydrogen compounds of main sub-group of IV group (EH_4) are neutral, V group (EH_3) – base and VII groups (H_2E and HE) – acids (Table 5.2).

Table 5.2. General trends in periodicity

Group	I	II	III	IV	V	VI	VII	VIII (except noble gases)
Highest oxide	E_2O	EO	E_2O_3	EO_2	E_2O_5	EO_3	E_2O_7	EO_4
Hydrate of highest oxide	EOH	$E(OH)_2$	$E(OH)_3$	H_2EO_3	H_3EO_4	H_2EO_4	HEO_4	H_4EO_4

The properties of atom depend on the position of elements in the Periodic System, which is connected with structure of atoms.

Many characteristics of atoms are changed periodically, for example – electronegativity at the period is increased from left to right, but in sub-group is decreased; ionization energy – at the period increased, but in sub-group is decreased.

According to the position of element in the Periodic system it is possible to forecast its basic properties, as average of its neighbors:

Li		Be		B
Na		Mg		Al
K		Ca		Sc

The Periodic table is an arrangement of the elements according to their atomic numbers so that elements with similar properties fall in the same column.

The length of each period in the Periodic table determinates by the sublevel being filled with electrons as shown in Table 5.3. The first energy level holds only two electrons in its *1s* sublevel. Hydrogen and Helium are presented in the first period. The second main-energy level holds two electrons in *2s*-sublevel and six electrons in *2p*-sublevel. These eight electrons account for the eight elements presence in the second period. In eight elements of the third period, *3s-* and *3p*-sublevels are being filled.

Table 5.3. Relationship between quantity of elements in period and sublevels being filled in the Periodic Table

Period Number	Number of Elements in Period	Energy Sublevels in Order of Filling
1	2	*1s*
2	8	*2s 2p*
3	8	*3s 3p*
4	18	*4s 3d 4p*
5	18	*5s 4d 5p*
6	32	*6s 4f 5d 6p*
7	32	*7s 5f 6d* etc.

Filling *3d* and *4d*-sublevels in addition to *s* and *p* sublevels adds 10 elements to fourth and fifth periods, which therefore include totally 18 elements each. Filling *4f* sublevels in addition to *s*, *p*, *d* sublevels adds 14 elements to the sixth period, for totally of 32 elements in the sixth period. As new artificial elements are created, the 23 known elements in period 7 could be extended to 32.

The period of element can be determined from its electron configuration. For example, Arsenic (As) has the configuration [Ar]$3d^{10}4s^24p^3$. The "4" in "$4p^3$" indicates that the highest one occupied energy level is the fourth energy level. Arsenic is therefore in the fourth period in the Periodic table.

There are a lot of styles for presentation of the Periodical table of Chemical Elements (authors Stowe, Benfey, Zmaczynski, Gicuere - more details *http:/chemlab.pc.maricopa.edu/periodic/styles.html*). In Ukraine the most popular one is so-called "Short-Periodic" form, included 8 groups and 7 periods; the 3d and more periods include two rows. In foreign countries it is more popular so-called "Long-Periodic" table, included 18 groups and 7 periods.

A science exhibit designer, Roy Alexander, to eliminate the confusion and apparent inconsistencies in the flat table by arranging the elements contiguously and continuously according to the atomic number without disturbing the accepted group, originated the improvement for

learning and using the Periodic table and property interrelationships previously found in the periodic chart (see Fig. 5.4).
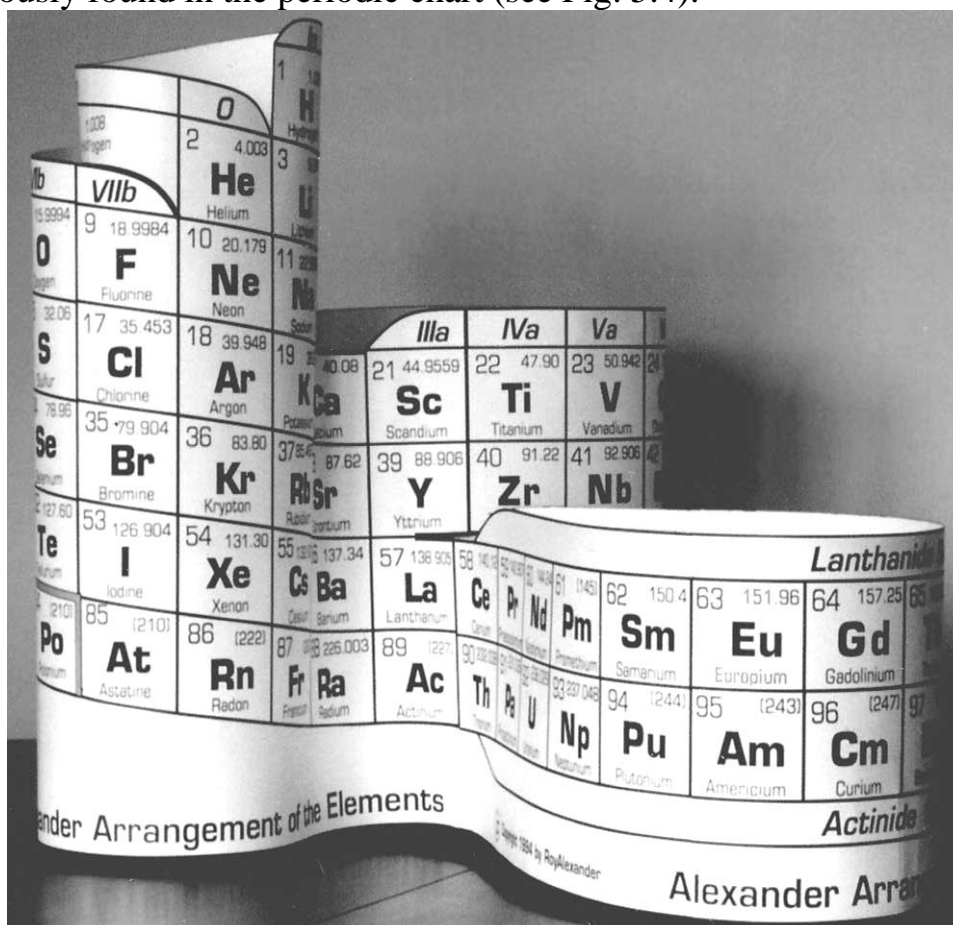
Figure 5.4. Roy Alexander Arrangement of the Elements

The resulting form has three parts looping outwards from a relatively central point. The elements in Groups 0 (VIII), IA, IIA, IIIB, IVB, VB, and VIIIB are in the narrowest and tallest part, which forms a tube in the upper part, topped by a "crown" of Hydrogen. From the lower part of this component the sides branch to a lengthier loop showing IIIA, IVA, VA, VIA, VIIA, VIIIB, IB, and IIB groups. From the lower half of this, the third, and longest loop protrudes the *f*-block.

Printed as a flat sheet, it can be easily assembled into a 3-D model by teacher or student. All printed element data, therefore, have a common plane so their electron numbers can trace the elements without changing direction or leaving the surface.

Review questions

1. Describe the general layout of a modern Periodical table.

2. What is the most important relationship amoung elements in the same group in the Periodical table?

3. Which of these elements are metals, nonmetals, and amphoteric metals (metalloids): As, Xe, Fe, Li, Cs, At, Ni, Ge, Al, Mn, Se?

4. Compate physical and chemical properties of metals and nonmetals.

5. Indicate whether these elements exist in atomic species, molecular species, or extensive three-dimensional structures in their most stable state at 25 °C and 1 atm, and write the molecular or empirical formula for elements: phosphorus P, Iodine I, Zinc Zn, Sulfur S, Carbon C, Oxygen O, and Clorine Cl.

6. Group these electron configurations in pairs that would represent similar chemical properties of their atoms:

a) $1s^2 2s^2 2p^6 3s^2$;

b) $1s^2 2s^2 2p^3$;

c) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$;

d) $1s^2 2s^2$;

e) $1s^2 2s^2 2p^6$;

f) $1s^2 2s^2 2p^6 3s^2 3p^3$.

7. Specify in what group of the Periodical table each of these elements is found: a) $[Ne]3s^1$; b) $[Ne]2s^2 sp^3$; c) $[Ne] 2s^2 sp^6$; d) $[Ar]4s^2 3d^8$.

8. State whether each of these properties of the representative elements generally increases, or decreases, or doesn't change:a) from left to right across a period, or b) from top to bottom in a group:

- metallic character;

- atomic size;

- ionization energy;

- acidity of oxides;

- the highest valencies;

- quanitity of electron shells;

- quantity of electrons;

- atomic mass.

9. Element M is a shiny and highly reactive metal (melting point 63 °C), and element X is a highly reactive nonmetal (melting point -7,2 °C). They react to form a compound with the empirical formula MX, a colorless, brittle solid that melts at 734 °C. When dissolved in water or when molten, the substance conducts electricity. When chlorine Cl gas is bubbled though an aqueous solution containing MX, a reddish-brown liquid appears and Cl^- are formed. From these observations, identify M and X.

10. In each of the followinf pairs, indicate which one of the two species is smaller: a) Cl or Cl^-; b) Na or Na^+; c) O^{2-} or S^{2-}; d) Mg^{2+} or Al^{3+}; e) Cu^+ or Cu^{2+}.

CHAPTER 6 THE MAIN CLASSES OF INORGANIC COMPOUNDS

6.1 Classification of inorganic substances

All inorganic substances are subdivided into simple and omplicates (conpounds) (Fig. 6.1).
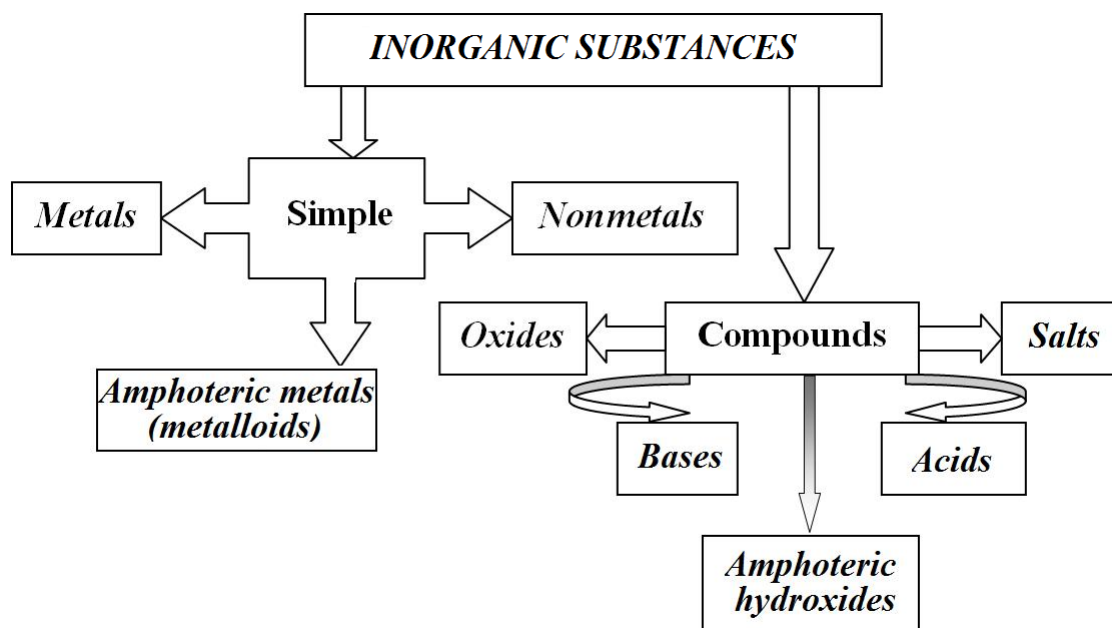
Figure 6.1. General classification of inorganic substances

Simple substances consist of one-type atoms (atoms of one chemical element). **Complex (complicated) substances (or chemical compounds)** consist of different type atoms (atoms of different chemical elements).

Chemical elements may be categorized according to element families. Knowing how to identify families, which elements are included, and their properties helps predict behavior of unknown elements and their chemical reactions.

What is an element family?

An element family is a set of elements sharing common properties. Elements are classified into families because the three main categories of elements (metals, nonmetals and amphoteric metals (also named semimetals, metalloids) are very broad. The characteristics of the elements in these families is determined primarily by the number of electrons in the outer energy shell. Element groups, on the other hand, are collections of elements categorized according to similar properties. Because element properties are largely determined by the behavior of valence electrons,

families and groups may be one and the same. However, there are different ways of categorizing elements into families. Many chemists and chemistry textbooks recognize five main families:

5 element families:
Alkali metals;
Alkaline-earth metals;
Transition metals;
Halogens;
Noble gases.

Another common method of categorization recognizes nine element families:

Alkali Metals – IA Group, having 1 valence electron;
Alkaline-Earth Metals – IIA Group, having 2 valence electrons;
Transition Metals – Groups I-VIII d- and f-block metals;
Boron Group or Earth Metals – IIIA Group, naving 3 valence electrons;
Carbon Group or Tetrels – IVA Group, having 4 valence electrons;
Nitrogen Group or Pnictogens – VA Group, having 5 valence electrons;
Oxygen Group or Chalcogens – VIA Group, having 6 valence electrons;
Halogens – VIIA Group, having 7 valence electrons;
Noble Gases – VIIIA Group, having 8 valence electrons.

A few classifications of elements include:
1. Iron family: Fe, Co, Ni;
2. Noble metals or Platinum Family: Ru, Rh, Pd, Os, Ir, Pt.

Recognizing families on the Periodic table
Columns of the Periodic table typically mark groups or families. Three systems have been used to number families and groups:
1. The older IUPAC system used Roman numerals together with letters to distinguish between the left (A) and right (B) side of the Periodic table.
2. The CAS system used letter to differentiate main group (A) and transition (B) elements.
3. The modern IUPAC system uses Arabic numbers 1-18, simply numbering the columns of the periodic table from left to right.

Many periodic tables include both Roman and Arabic numbers. The Arabic numbering system is the most widely accepted method used today.

So, nonmetals include the next groups of chemical elements with closely related properties:

The Noble (rare) gases – elements of VIIIA group of the Periodical table (He; Ne; Ar; Kr; Xe; Rn);

The Halogens – elements of VIIA group of the Periodical table (F, Cl, Br, I, At);

The Chalcogens – elements of VIA group of Periodical Table (O, S, Se, Te), except Po;

Elements of V, IV, III groups of Periodical Table – N, P, As, C, Si, B, H.

Metals are the most of chemical elements (near 70 % of known nowadays) included some groups of chemical elements with similar properties:

Alkali(ne) metals – elements of IA group of the Periodical table (Li, Na, K, Rb, Cs, Fr);

Alkaline-earth metals – some elements of IIA group of the Periodical table (Ca, Sr, Ba, Ra);

Iron Family – Fe, Co, Ni;

Noble metals Family (Platinum Family) – Ru, Rh, Pd, Os, Ir, Pt;

Lanthanide Series - elements of periodical table from № 58 till № 71, their properties are very similar to element La (Lanthanum);

Actinide Series - elements of periodical table from № 90 till № 103, their properties are very similar to element Ac (Actinium).

6.2 Relation between main classes of inorganic substances

In the very broadest sense, inorganic chemicals and compounds are defined by what they are not; they are not organic in nature, such that anything beyond biological, hydrocarbon, and other similar carbon-based chemicals may be considered inorganic. From a practical standpoint, inorganic chemicals are substances of mineral origin that do not contain carbon in their molecular structure and are typically based on the most abundant chemicals on earth: oxygen, silicon, aluminum, iron, calcium, sodium, potassium and magnesium.

The top 20 inorganic chemicals manufactured in Canada, China, Europe, India, Japan, and the US (2005 data) are:

1. *Aluminum sulfate $Al_2(SO_4)_3$* (coagulating agent in the purification of drinking water and waste water treatment plants, and also in paper manufacturing);

2. *Ammonia NH_3* (used for the nitria cid and nitrogen fertilizers syntheses, for organic syntheses);

3. *Ammonium nitrate NH_4NO_3* (mineral fertilizer and explosive);

4. *Ammonium sulfate $(NH_4)_2SO_4$* (mineral fertilizer);

5. *Carbon black C* (pure elemental carbon in the form of colloidal particles, pproximately 90% of carbon black is used in rubber applications, 9% as a pigment in printing inks etc.);

6. *Chlorine Cl_2* (commercial bleaches and desinfectants, chemical synthesis of organic derivates);

7. *Hydrochloric acid HCl* (a common chemical reagent for a wide variety of inorganic and organic syntheses);

8. *Hydrogen H_2* (used for ammonia production; an alternative ecologically pure fuel etc.);

9. *Hydrogen peroxide H_2O_2* (oxidizer, bleaching agent and antiseptic; propellant in rocketry);

10. *Nitric acid HNO_3* (a common chemical reagent for a wide variety of inorganic and organis syntheses);

11. *Nitrogen N_2* (used for ammonia production; inert atmospere agent);

12. *Oxygen O_2* (a common chemical reagent for a wide variety of inorganic and organis syntheses);

13. *Phosphoric acid H_3PO_4* (used in making fertilizers and detergents and in food processing);

14. *Sodium hydrocarbonate (bicarbonate, or baking soda) $NaHCO_3$* (is commonly used in a glass production, in cooking, as biopesticide, as a pH buffering agent, an electrolyte replenisher, systemic alkalizer and in topical cleansing solutions etc.);

15. *Sodium chlorate(V) $NaClO_3$* (the main commercial use for sodium chlorate is for making Chlorine Dioxide (ClO_2). The largest application of ClO_2, which accounts for about 95% of the use of chlorate, is in bleaching of pulp; used as chemical oxygen geterator; as non-selective herbicide, defoiant, desiccant etc);

16. *Sodium hydroxide NaOH* (a common chemical reagent for a wide variety of inorganic and organis syntheses, used as an alkaline electrolyte etc.);

17. *Sodium silicate $(Na_2SiO_2)_nO$* (used in cements, passive fire protection, textile and lumber processing, refractories, and automobiles);

18. *Sodium sulfate Na_2SO_4* (mainly used for the manufacture of detergents and in the kraft process of paper pulping);

19. *Sulfuric acid H_2SO_4* (a central substance in the chemical industry. Principal uses include mineral processing, fertilizer manufacturing, oil refining, wastewater processing, and chemical synthesis);

20. *Titanium dioxide TiO_2* (used as a pigment, has a wide range of applications, from paint to sunscreen to food coloring).

All of these chemicals and compounds have application in every aspect of the chemical industry-including catalysts, pigments, surfactants, coatings, medicine, fuel, and agriculture. The industry's products are used as basic chemicals for industrial processes (e.g., acids, bases, salts, oxidizing agents, gases, halogens), chemical additives (pigments, alkali metals, colors), and finished products (fertilizers, glass, construction materials).

General relationships of the main groups of inorganic substances are shown in Fig. 6.2.
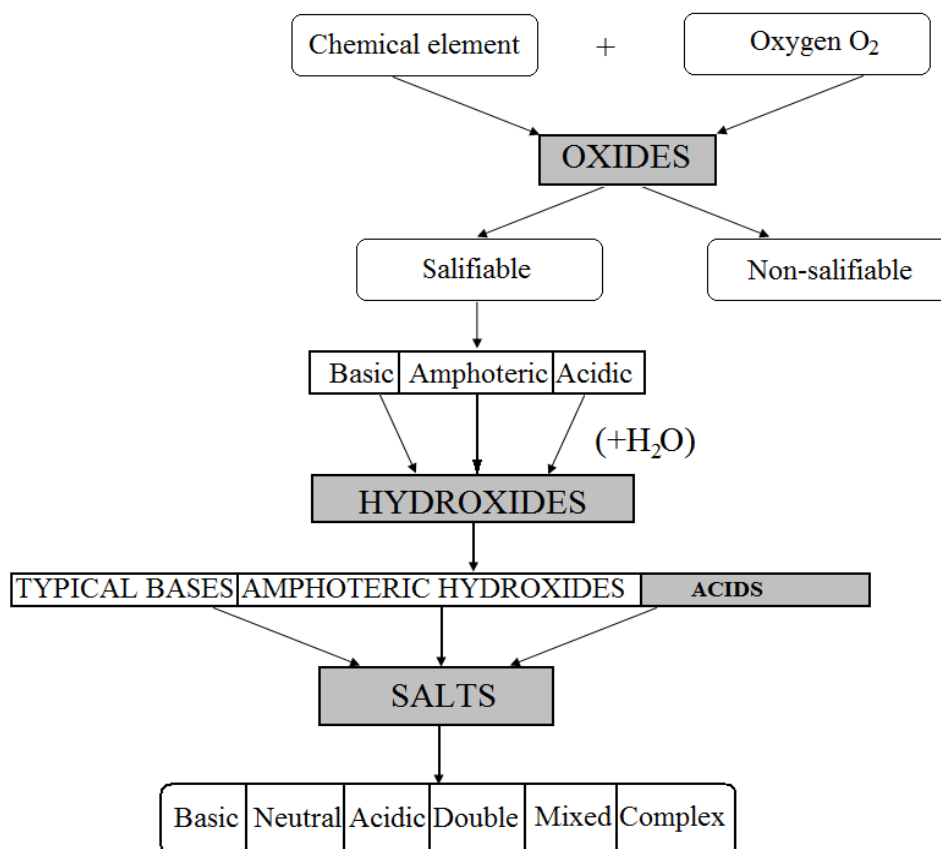
Figure 6.2. Scheme of genetically relationships of inorganic substances

6.2.1 Oxides

Oxides - complex substances, consisting of two elements, one of them is Oxygen. Practically all elements (excepting three noble gases - He, Ar and Ne) may form oxides.

Classification of oxides:

Non-Salifiable	- non-salts forming (CO, N_2O, NO)
Salifiable	- salts forming, subdivided into:
	Basic - it is a metal oxides in which metals display low oxidation number +1,

	+2 (Na_2O, MgO, CuO);
	Amphoteric (for some metals with oxidation number +3, +4, sometimes +2) - ZnO, Al_2O_3, Cr_2O_3, SnO, PbO, MnO_2;
	Acidic - it is oxides of non-metals and some metals with oxidation number from +5 to +7 (SO_2, SO_3, P_2O_5, Mn_2O_7, CrO_3).

Preparation

1. Interaction of simple and complex substances with Oxygen:

$2Mg + O_2 = 2MgO$;

$4Al + 3O_2 = 2Al_2O_3$;

$S + O_2 = SO_2$;

$2H_2S + 3O_2 = 2SO_2 + 2H_2O$;

$2C_2H_2 + 5O_2 = 4CO_2 + 2H_2O$;

$4FeS + 7O_2 = 2Fe_2O_3 + 4SO_2$.
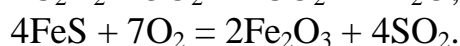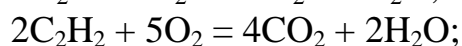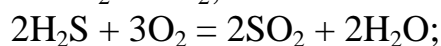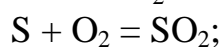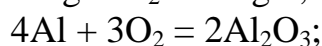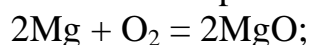
2. Decomposition of some substances containing Oxygen (oxides, bases, acids, salts) on heating:

$4CrO_3 \xrightarrow{t} 2Cr_2O_3 + 3O_2$;

$Cu(OH)_2 \xrightarrow{t} CuO + H_2O$;

$2Fe(OH)_3 \xrightarrow{t} Fe_2O_3 + 3H_2O$;

$H_2CO_3 \xrightarrow{t} CO_2 + H_2O$;

$H_2SiO_3 \xrightarrow{t} SiO_2 + H_2O$;

$CaCO_3 \xrightarrow{t} CaO + CO_2$;

$2AgNO_3 \xrightarrow{t} 2Ag + 2NO_2 + O_2$.
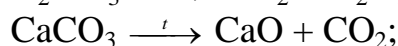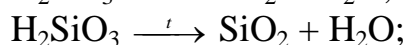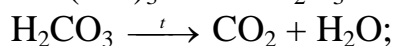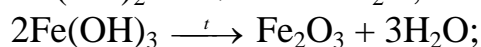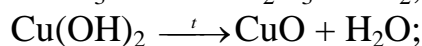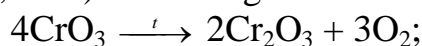
Chemical properties

Basic oxides

1. Interaction with water. Oxides of alkaline (Li_2O, Na_2O, K_2O, Rb_2O, Cs_2O) and alkaline-earth (CaO, SrO, BaO) metals form soluble bases - **alkalis**:
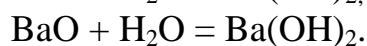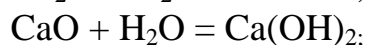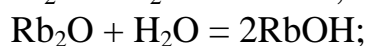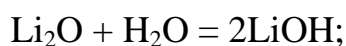
$Li_2O + H_2O = 2LiOH$;

$Rb_2O + H_2O = 2RbOH$;

$CaO + H_2O = Ca(OH)_2$;

$BaO + H_2O = Ba(OH)_2$.

2. Interaction with acidic oxides forming the salts:

$K_2O + SO_2 = K_2SO_3$;

$SrO + N_2O_5 = Sr(NO_3)_2$;

$CuO + SO_3 = CuSO_4$;

$3BaO + P_2O_5 = Ba_3(PO_4)_2$.

3. Interaction with acids forming the salts and water:

$Na_2O + 2HNO_3 = 2NaNO_3 + H_2O$

$NiO + H_2SO_4 = NiSO_4 + H_2O$

$3MgO + 2H_3PO_4 = Mg_3(PO_4)_2 + 3H_2O.$
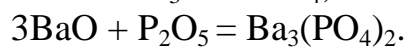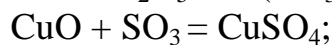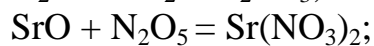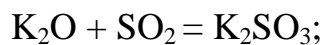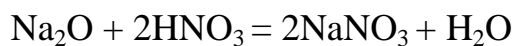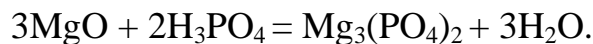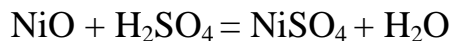
Other basic oxides do not react with water directly.

Acidic oxides

1. The most of acidic oxides reacts with water forming the acids (except a few oxides like SiO_2, MoO_3, WO_3):

$SO_3 + H_2O = H_2SO_4;$

$N_2O_5 + H_2O = 2HNO_3;$

$P_2O_5 + 3H_2O = 2H_3PO_4;$

$4NO_2 + O_2 + 2H_2O = 4HNO_3.$

2. Interaction with basic acids with forming the salts:

$N_2O_3 + Na_2O = 2NaNO_2;$

$P_2O_5 + 3CaO = 2Ca_3(PO_4)_2;$

$SO_3 + BaO = BaSO_4.$
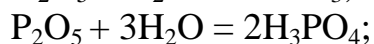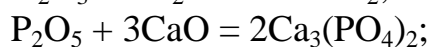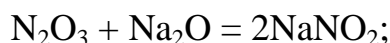
3. Interaction with bases forming the salts and water:

$SO_3 + Ba(OH)_2 = BaSO_4 + H_2O;$

$N_2O_5 + 2KOH = 2KNO_3 + H_2O;$

$SiO_2 + 2NaOH = Na_2SiO_3 + H_2O.$
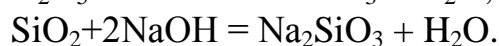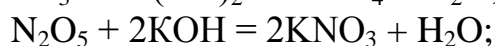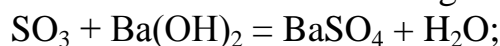
Amphoteric oxides

Term Amphoteric (from Greek) means *double-sided, mutual*. Therefore amphoteric oxides occupy a position between basic and acidic oxides and display corresponding chemical properties.

1. Interaction with basic and acidic oxides forming the salts:

$PbO + SO_3 = PbSO_4;$

$PbO + N_2O_5 = Pb(NO_3)_2;$

$Cr_2O_3 + 3SO_3 = Cr_2(SO_4)_3;$

$Cr_2O_3 + 3N_2O_5 = 2Cr(NO_3)_3;$

$Li_2O + PbO = Li_2PbO_2;$

$CaO + PbO = CaPbO_2;$

$3Li_2O + Cr_2O_3 = 2Li_3CrO_3;$

$Li_2O + Cr_2O_3 = 2LiCrO_2;$

$CaO + Cr_2O_3 = Ca_3(CrO_3)_2;$

$CaO + Cr_2O_3 = Ca(CrO_2)_2.$

2. Interaction with acids forming the salts and water:

$PbO + 2HCl = PbCl_2 + H_2O;$

$Al_2O_3 + 2H_3PO_4 = 2AlPO_4 + 3H_2O.$
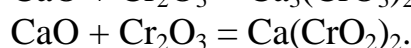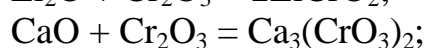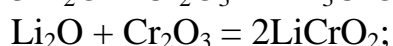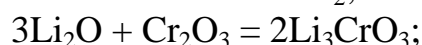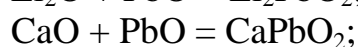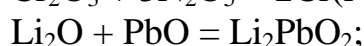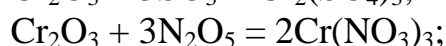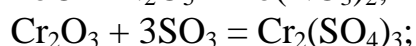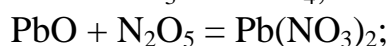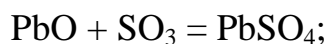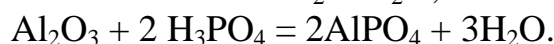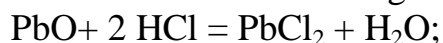
3. Interaction with alkalis forming the salts and water:

$Cr_2O_3 + 6KOH = 2K_3CrO_3 + 3H_2O;$

$MnO_2 + 2NaOH = Na_2MnO_3 + H_2O.$
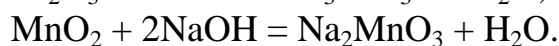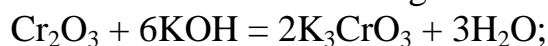
Peroxides may be shown as a peculiar group of Oxygen-contained compounds. Frequently peroxides are considered as salts of Hydrogen peroxide H_2O_2, where O_2^{-2} (-O-O-) is an analogue of acid residue. For example, BaO_2 - Barium peroxide includes Ba^{2+} and formally O^-.

6.2.2 Bases

Bases are complex substances, in which atoms of metals or ionic groups (for example, NH_4^+) are bonded with one or several hydroxyl groups.

Classification of bases: they are divided into two groups - soluble in waters (alkalis - LiOH, NaOH, KOH, RbOH, CsOH, FrOH, $Ca(OH)_2$, $Ba(OH)_2$, $Sr(OH)_2$) and insoluble (for example, $Fe(OH)_2$, $Cu(OH)_2$ etc.). Insoluble bases include amphoteric ones too ($Al(OH)_3$, $Cr(OH)_3$, $Zn(OH)_2$ etc.).

According to quantity of OH^- bases may be divided into:
One-acidic (NaOH);
Two-acidic ($Ca(OH)_2$);
Three-acidic ($Cr(OH)_3$) and so on.

Preparation

1. Interaction of alkaline and alkaline-earth metals and water forming alkalis and free Hydrogen (See **Appendix 5**):

$2K + 2H_2O = 2KOH + H_2$;
$Ba + 2H_2O = Ba(OH)_2 + H_2$;
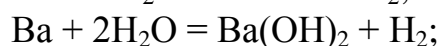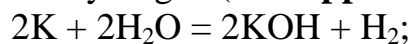
2. Direct interaction of alkaline and alkaline-earth metals oxides and water forming the alkalis:

$Na_2O + H_2O = 2NaOH$;
$CaO + H_2O = Ca(OH)_2$;
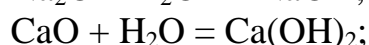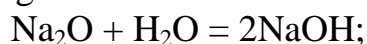
3. Insoluble bases may be prepared by interaction between soluble salts of corresponding metals and alkali solution:
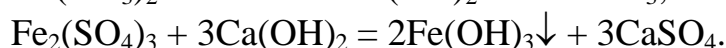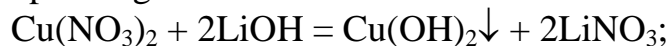
$Cu(NO_3)_2 + 2LiOH = Cu(OH)_2\downarrow + 2LiNO_3$;
$Fe_2(SO_4)_3 + 3Ca(OH)_2 = 2Fe(OH)_3\downarrow + 3CaSO_4$.

Chemical properties

1. Interaction with acidic oxides forming the salts and water:

$2LiOH + SO_3 = Li_2SO_4 + H_2O$;
$Ca(OH)_2 + N_2O_5 = Ca(NO_3)_2 + H_2O$;

2. Interaction with acids forming the salts and water:

$2LiOH + H_2SO_4 = Li_2SO_4 + 2H_2O$;
$Ca(OH)_2 + 2HNO_3 = Ca(NO_3)_2 + 2H_2O$;
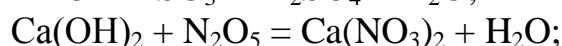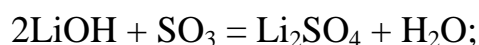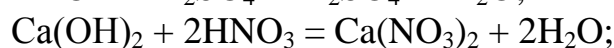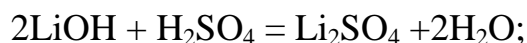
3. Interaction with amphoteric oxides forming the salts and water:

$2KOH + ZnO = K_2ZnO_2 + H_2O$;

$3Ba(OH)_2 + Al_2O_3 = Ba_3(AlO_3)_2 + 3H_2O$;
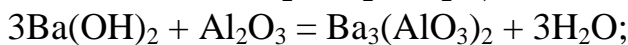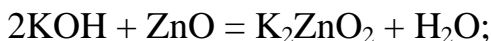
4. Interaction with amphoteric hydroxides forming the salts and water:

$3NaOH + Cr(OH)_3 = Na_3CrO_3 + 3H_2O$;

$Ca(OH)_2 + Sn(OH)_2 = CaSnO_2 + 2H_2O$;
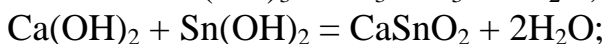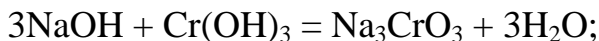
5. Alkalis react with some salts:

$2NH_4Cl + Sr(OH)_2 = 2NH_4OH + SrCl_2$;

$Fe_2(SO_4)_3 + 6LiOH = 2Fe(OH)_3 + 3Li_2SO_4$.
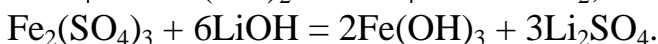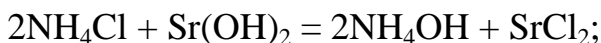
6.2.3 Acids

Acids are the complex substances, consisting from Hydrogen atoms and acid radical (residue).

According to quantity of H^+ *(basicity)* acids may be divided into:

One-basic (HCl, HNO_3, $HClO_4$, $CH_3–COOH$ etc.);

Two-basic (H_2CO_3, H_2SO_3, H_2SO_4 etc.);

Three-basic (H_3BO_3, H_3PO_4, H_3AsO_4 etc.);

Four-basic (H_4SiO_4, $H_4P_2O_7$ etc.).

There are two types of acids depending on their chemical composition: *Oxyacids* - contain Oxygen (the most of acids - H_2CO_3, H_2SiO_3, HNO_3, H_3PO_4, H_2SO_3, H_2SO_4, $HClO_4$ etc.) and *Oxygen-free acids* (HF, HCl, HBr, HI, H_2S, H_2Se, HCN, $HSCN$ etc.).

Oxyacids are hydrated forms of acidic oxides (anhydrides). The most of such oxides may react with water directly forming hydrates - acids. For example, Sulfuric acid is a hydrate of Sulfur (VI) oxide.

Preparation

1. Oxygen-free acids may be prepared by interaction between corresponding non-metals and free Hydrogen and following dissolution of gaseous products in water:

$$H_2 + Cl_2 = 2HCl;$$
$$H_2 + S = H_2S;$$
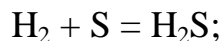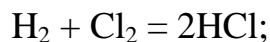
2. Oxygen-free acids are synthesized by action of strong acids **to** corresponding salts of Oxygen-free acids:

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF;$$
$$FeS + 2HCl = FeCl_2 + H_2S;$$
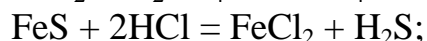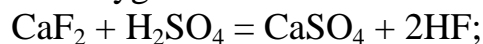
3. Interaction of acidic oxides (anhydrides) with water:

$$SO_3 + H_2O = H_2SO_4;$$
$$Cl_2O_7 + H_2O = 2HClO_4;$$
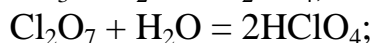
4. If anhydrides do not react with water directly, the corresponding acids may be prepared by action of strong acids to responding soluble salt of needed acid:
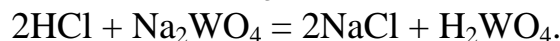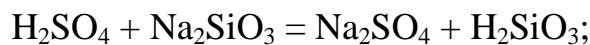
$$H_2SO_4 + Na_2SiO_3 = Na_2SO_4 + H_2SiO_3;$$
$$2HCl + Na_2WO_4 = 2NaCl + H_2WO_4.$$

Chemical properties

1. Interaction with basic oxides with formation of salts and water:
$$2HNO_3 + CuO = Cu(NO_3)_2 + H_2O;$$
$$3H_2SO_4 + Fe_2O_3 = Fe_2(SO_4)_3 + 3H_2O;$$

2. Interaction with amphoteric oxides with formation of salts and water:
$$2HCl + ZnO = ZnCl_2 + H_2O;$$
$$6HClO_4 + Al_2O_3 = 2Al(ClO_4)_3 + 3H_2O;$$

3. Interaction with bases with formation of salts and water:
$$H_2CO_3 + Ca(OH)_2 = CaCO_3 + 2H_2O;$$
$$2H_3PO_4 + 3Mg(OH)_2 = Mg_3(PO_4)_2 + 6H_2O;$$
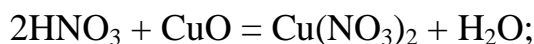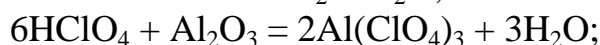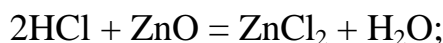
4. Interaction with amphoteric hydroxides with formation of salts and water:
$$2HNO_3 + Pb(OH)_2 = Pb(NO_3)_2 + 2H_2O;$$
$$3H_2SO_4 + 2Cr(OH)_3 = Cr_2(SO_4)_3 + 6H_2O;$$
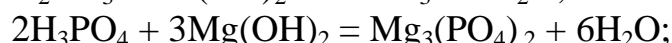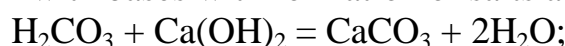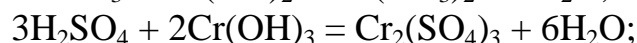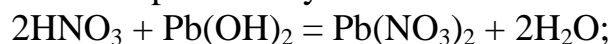
5. Interaction with metals (Red Ox reactions):
$$Zn + 2HCl = ZnCl_2 + H_2\uparrow;$$
$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO\uparrow + 4H_2O;$$
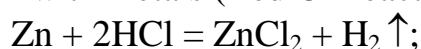
6. Interaction of weaker acid salts (metathesis or exchange reaction):
$$FePO_4 + 3HNO_3 = Fe(NO_3)_3 + H_3PO_4;$$
$$H_2SO_4 + BaCl_2 = BaSO_4 + 2HCl.$$
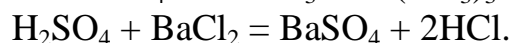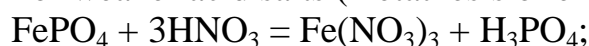
6.2.4 Amphoteric hydroxides

Amphoteric hydroxides are the hydrated forms of amphoteric oxides having weak basic and acidic properties.

Preparation

1. Interaction with acidic oxides forming **salts** and water (amphoteric hydroxides show properties of bases):
$$Zn(OH)_2 + N_2O_5 = Zn(NO_3)_2 + H_2O;$$
$$2Cr(OH)_3 + 3SO_3 = Cr_2(SO_4)_3 + 3H_2O.$$
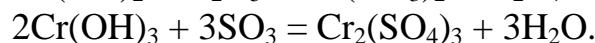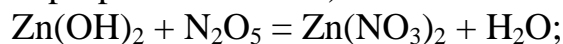
2. Interaction with acids forming salts and water (amphoteric hydroxides show properties of bases):
$$Zn(OH)_2 + 2HNO_3 = Zn(NO_3)_2 + 2H_2O;$$
$$2Cr(OH)_3 + 3H_2SO_4 = Cr_2(SO_4)_3 + 6H_2O.$$
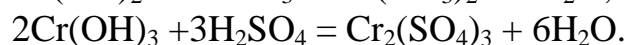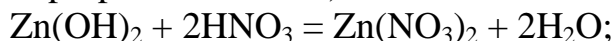
3. Interaction with basic oxides forming salts and water (amphoteric hydroxides show properties of acids):

for $Zn(OH)_2$: $H_2ZnO_2 + Li_2O = Li_2ZnO_2 + H_2O$

for $Cr(OH)_3$: $2HCrO_2 + BaO = Ba(CrO_2)_2 + H_2O$ or

$2H_3CrO_3 + 3BaO = Ba_3(CrO_3)_2 + 3H_2O$;
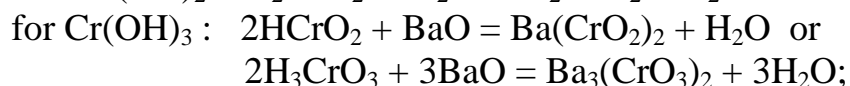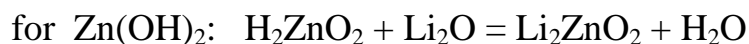
4. Interaction with bases forming salts and water (amphoteric hydroxides show properties of acids):

for $Zn(OH)_2$: $H_2ZnO_2 + 2LiOH = Li_2ZnO_2 + 2H_2O$

for $Cr(OH)_3$: $2HCrO_2 + Ba(OH)_2 = Ba(CrO_2)_2 + 2H_2O$ or

$2H_3CrO_3 + 3Ba(OH)_2 = Ba_3(CrO_3)_2 + 6H_2O$.
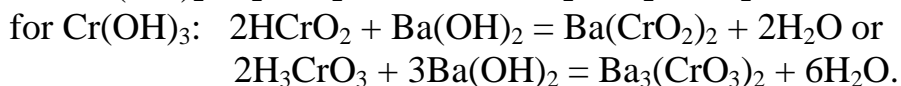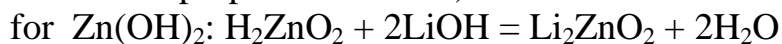
Depending on series of chemical reaction, names of amphoteric hydroxides are changed. For example, $Zn(OH)_2$ in reactions with acidic oxides and acids must be referred to "Zinc hydroxide", while in reactions with basic oxides and alkalis - "Zinc acid" (see **Appendix 4**).

6.2.5 Salts

Salts - complex substances, which consist of metal atoms and acid residuals. This is a most multiple class of inorganic compounds. Sometimes salts may include positive charged group of atoms (for example, NH_4^+).

Classification of salts:

Varieties	Characteristics	Examples
Neutral (normal)	Include atoms of metal (or ionic group NH_4^+) and acid residue. Products of full substitution of Hydrogen atoms in acids to metal atoms	$NaCl$, $Ca_3(PO_4)_2$, K_3AlO_3
Basic	Include atoms of metal (or ionic group NH_4^+), hydroxyl OH^- and acid residue. Products of incomplete substitution of OH-groups of multi-acidic bases into acid residue	$ZnOHCl$, $(MgOH)_2SO_4$, $(MgOH)_3PO_4$, $FeOHBr_2$
Acidic	Include atoms of metal (or ionic group NH_4^+), ion H^+ and acid residue. Products of incomplete substitution of H^+ of multi-basic acids into atoms of metal or NH_4^+	$NaHCO_3$, $NH_4H_2PO_4$, $Ca(H_2PO_4)_2$, $KHSO_4$
Double	Include atoms of two different metals and acid residue	$NaKSO_4$, $KAl(SO_4)_2$, $NH_4Cr(SO_4)_2$.
Mixed	Include atoms of metal and two different acid residues	$CaCl(ClO)$
Complex	Contain complex cations or anions	$[Ag(NH_3)_2]Cl$, $Na_3[Co(NO_2)_6]$

Salts are entitled starting from the name of corresponding metal and acid residue (See **Appendix 4**). For example, $Ca_3(PO_4)_2$ - Calcium Orthophosphate, $NaNO_3$ - Sodium Nitrate, $KHSO_4$ - Potassium Hydrosulfate, $FeOHCl_2$ - Iron (III) Hydroxychloride etc.

A few salts and chemical compounds or mixes have common names as household (domestic) chemicals or technical reactants. Sometimes names of such chemicals were given by Alchemists in great antiquity (for example, $BaSO_4$ (Barium Sulfate) - Heavy Spar, Aqua-regia - Mixture of conc. HNO_3 (1 volume) and conc. HCl (3 volumes) etc. (See **Appendix 2**).

Preparation

There are known a lot of methods for salts' preparations. The typical ones are mentioned below:

1. Interaction between metals and non-metals (Sulfur, Halogens):
   $$Zn + S = ZnS$$
   $$2Bi + 3Cl_2 = 2BiCl_3;$$
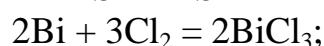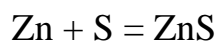
2. Interaction between salts and metals (according to relative activity of Metals):
   $$CuSO_4 + Fe = FeSO_4 + Cu;$$
   $$Pb(NO_3)_2 + Zn = Zn(NO_3)_2 + Pb;$$
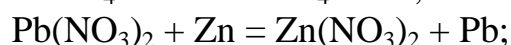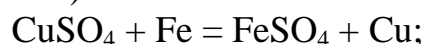
3. Interaction between some salts and non-metals:
   $$2FeCl_2 + Cl_2 = 2FeCl_3;$$
   $$2Na_2SO_3 + O_2 = 2Na_2SO_4;$$
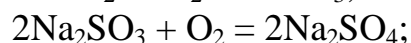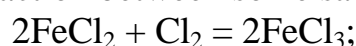
4. Interaction between basic oxides and acidic oxides:
   $$CaO + CO_2 = CaCO_3;$$
   $$3Na_2O + P_2O_5 = 2Na_3PO_4;$$
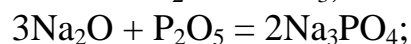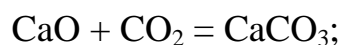
5. Interaction between acids and basic oxides:
   $$H_2SO_4 + MgO = MgSO_4 + H_2O;$$
   $$6HCl + Fe_2O_3 = 2FeCl_3 + 3H_2O;$$
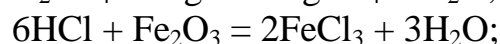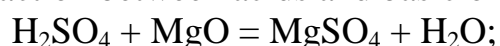
6. Interaction between bases and acidic oxides:
   $$Ba(OH)_2 + SO_2 = BaSO_3 + H_2O;$$
   $$2Fe(OH)_3 + 3N_2O_5 = 2Fe(NO_3)_3 + 3H_2O;$$

7. Interaction between acids and bases:
   $$HNO_3 + NaOH = NaNO_3 + H_2O;$$
   $$H_3PO_4 + 3KOH = K_3PO_4 + 3H_2O;$$
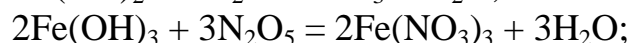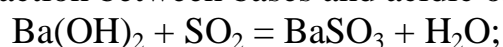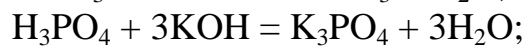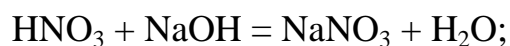
8. Interaction between stronger acids and salts of weaker acids:
   $$H_2SO_4 + K_2SiO_3 = K_2SO_4 + H_2SiO_3;$$
   $$HBr + AgNO_3 = AgBr + HNO_3;$$
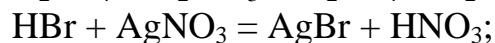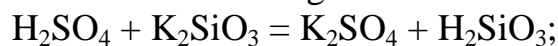
9. Interaction between alkalis and salts:
   $$2LiOH + CuCl_2 = Cu(OH)_2 + 2LiCl;$$
   $$Ca(OH)_2 + NiSO_4 = CaSO_4 + Ni(OH)_2;$$
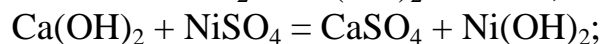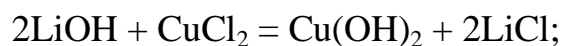
10. Interaction between two different salts (metathesis reaction):

$$2AgNO_3 + CaI_2 = 2AgI + Ca(NO_3)_2;$$
$$Cr_2(SO_4)_3 + 3BaCl_2 = 2CrCl_3 + 3BaSO_4.$$
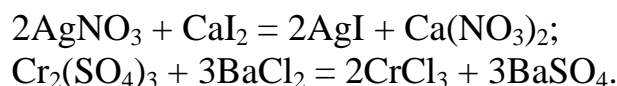
Chemical properties

1. Interaction with some of the acids with the formation of other salt and acid:
$$BaCl_2 + H_2SO_4 = BaSO_4 + 2HCl;$$
$$Na_2S + H_2SO_4 = Na_2SO_4 + H_2S;$$
2. Interaction with alkalis with the formation of other salt and base:
$$NiSO_4 + 2KOH = Ni(OH)_2 + K_2SO_4;$$
$$2FeCl_3 + 3Ba(OH)_2 = 2Fe(OH)_3 + 3BaCl_2;$$
3. Interaction with more active metals:
$$Zn + CuSO_4 = ZnSO_4 + Cu;$$
$$Cu + Hg(NO_3)_2 = Cu(NO_3)_2 + Hg;$$
4. **Some** salts may react with each other forming two new salts:
$$Ba(NO_3)_2 + K_2CO_3 = BaCO_3 + 2KNO_3; AlCl_3 + 3AgNO_3 = Al(NO_3)_3 + 3AgCl.$$
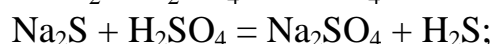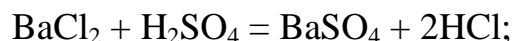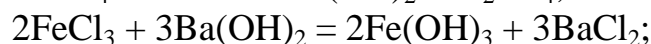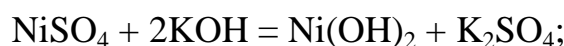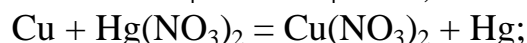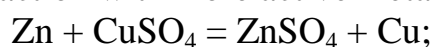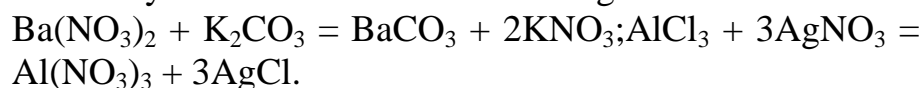
Basic salts

Basic salts may form only such bases that have two and more groups OH-. They are products of incomplete substitution of OH--groups of corresponding bases to acid residues.

Preparation

1. Hydrolysis of neutral salts formed by weak base and strong acid:
$$ZnCl_2 + HOH \leftrightarrow ZnOHCl + HCl;$$
$$2\,CuSO_4 + 2\,HOH \leftrightarrow (CuOH)_2SO_4 + H_2SO_4.$$
2. By addition (by drops) of small quantities of alkalis to solutions of neutral salts of metals:
$$AlCl_3 + 2NaOH = Al(OH)_2Cl + 2NaCl;$$
$$Ca(NO_3)_2 + NaOH = CaOHNO_3 + NaNO_3.$$
3. Interaction with salts formed weak acids with medium salts:
$$2MgCl_2 + 2Na_2CO_3 + H_2O = (MgOH)_2CO_3\downarrow + CO_2\uparrow + 4NaCl;$$
$$2CuSO_4 + 2(NH_4)_2SO_3 + H_2O = CuOH)_2SO_3\downarrow + SO_2\uparrow + (NH_4)_2SO_4.$$
4. In a few cases by interaction of neutral salts with bases of the same name:
$$CaCl_2 + Ca(OH)_2 = 2Ca(OH)Cl;$$
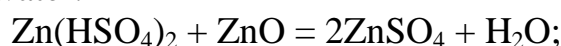$$Ba(NO_3)_2 + Ba(OH)_2 = 2BaOHNO_3.$$
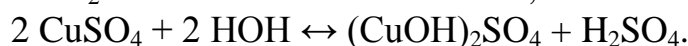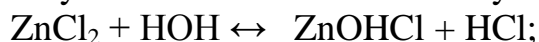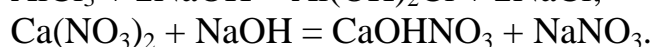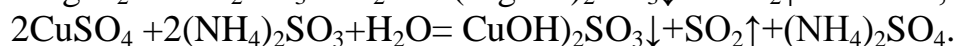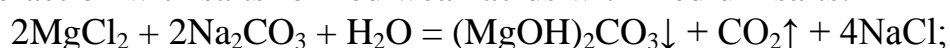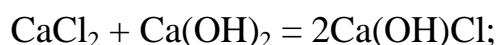
Chemical properties

1. Interaction with acids or acidic oxides forming neutral salts and water (likewise bases):

$$2Mg(OH)NO_3 + N_2O_5 = 2Mg(NO_3)_2 + H_2O;$$
$$Mg(OH)NO_3 + HNO_3 = Mg(NO_3)_2 + H_2O.$$

2. Thermal decomposition:
$$(CuOH)_2CO_3 \xrightarrow{t} 2 CuO + CO_2 + H_2O;$$
$$2 CaOHCl \xrightarrow{t} CaCl_2 + H_2O + CaO.$$
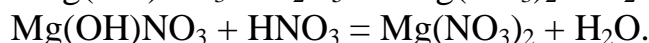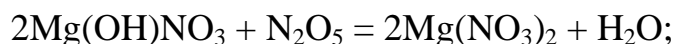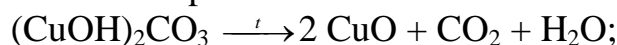
3. Some salts may (weaken) loose water with the formation of so-called oxysalts with time or on heating:
$$Bi(OH)_2Br \rightarrow BiOBr + H_2O.$$

Acidic salts

Acid salts are the products of partial replacement of Hydrogen in acids for atoms of metals or ionic groups. Acid salts may form only such acids that have two and more atoms of Hydrogen.

Preparation

1. Interaction of acid with the deficit of base:
$$NaOH + H2SO4 = NaHSO4 + H2O;$$
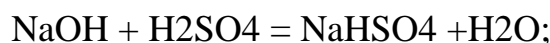
2. Interaction of bases with acid oxides in large excess:
$$Ca(OH)_2 + 2 CO_2 = Ca(HCO_3)_2;$$

3. Interaction of medium salts with acid (more with the same anion):
$$Ca_3(PO_4)_2 + 4H_3PO_4 = 3 Ca(H_2PO_4)_2.$$

Chemical properties

1. Interaction with basic oxides with forming of neutral salts and water:
$$2NaHSO_4 + Na_2O = 2Na_2SO_4 + H_2O;$$

2. Interaction with amphoteric oxides with forming of neutral salts and water:
$$Zn(HSO_4)_2 + ZnO = 2ZnSO_4 + H_2O;$$
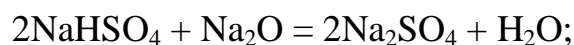
3. Interaction with bases with forming of neutral salts and water:
$$NaHSO_4 + NaOH = Na_2SO_4 + H_2O;$$
$$Ca(H_2PO_4)_2 + 2 Ca(OH)_2 = Ca_3(PO_4)_2\downarrow + 3 H_2O.$$
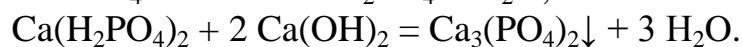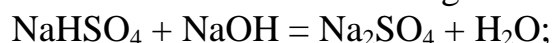
4. Interaction with amphoteric hydroxides with forming of salts and water:
$$Zn(HSO_4)_2 + Zn(OH)_2 = 2ZnSO_4 + 2H_2O;$$
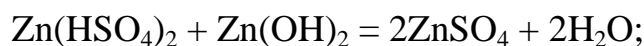
5. Interaction with active metals with forming of neutral salts and free Hydrogen isolation:
$$2NaHSO_4 + 2Na = Na2SO_4 + H_2\uparrow$$
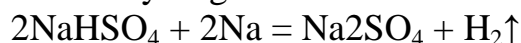
6. Thermal decomposition with medium salts formation:
$$Ca(HCO_3)_2 \rightarrow CaCO_3\downarrow + CO_2\uparrow + H_2O.$$

Double and mixed salts may be considered as the sort of neutral salts. Double salts may be prepared by interaction **between** any multi-basic acid and different bases:

$H_2SO_4 + KOH + NaOH = NaKSO_4 + 2H_2O$.

or during synchronous crystallization of different salts:

$K_2SO_4 + Al_2(SO_4)_3 + 24H_2O = 2KAl(SO_4)_2 \cdot 24H_2O$.
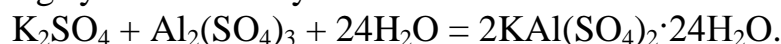
Mixed salts may be prepared by interaction of multi-acidic bases and different acids. For example, preparation of bleaching powder:
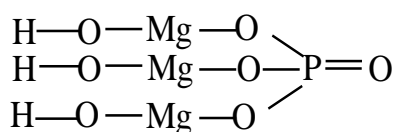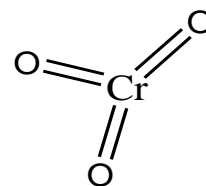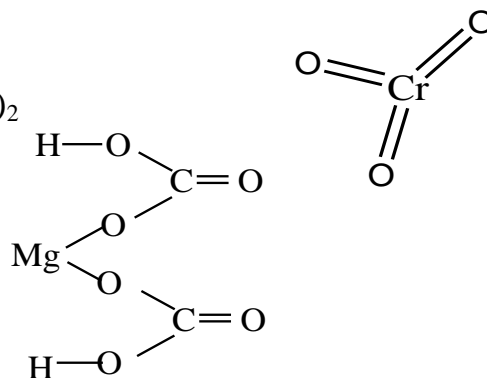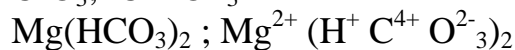
$Ca(OH)_2 + HCl + HClO = CaCl(ClO) + H_2O$.
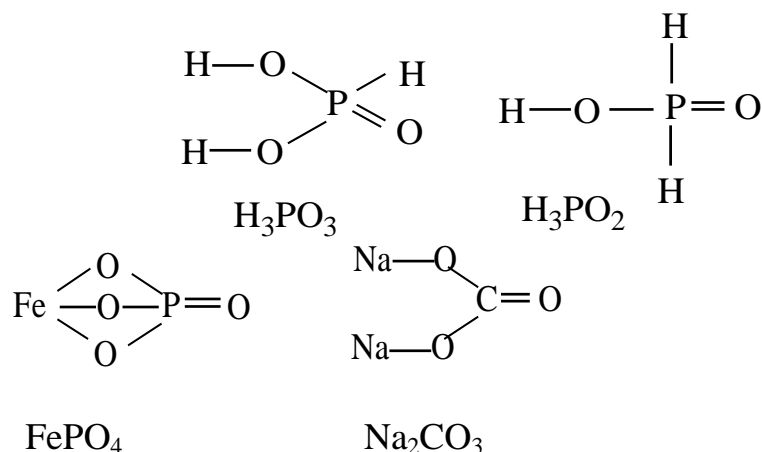
6.2.6 Structural formulas

These schemes show the order of atom combination in molecules of substance.

The rules for graphic formula's compilation are the following:

➢ It may directly connect ions to opposite charges only;
➢ Quantity of chemical bonds for each atom is equal to its charges (modulo) in most cases.
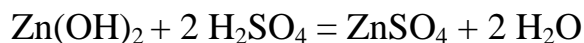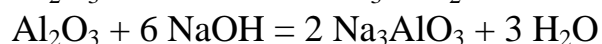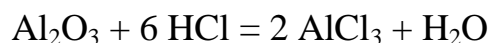
For example:

H_2SO_4; $H^+_2 S^{6+} O^{2-}_4$

H_2SO_4

H_2CO_3

$Al(OH)_3$; $Al^{3+}(O^{2-}H^+)_3$ or $H^+_3 Al^{3+} O^{2-}_3$

CrO_3; $Cr^{6+}O^{2-}_3$

$Mg(HCO_3)_2$; $Mg^{2+} (H^+ C^{4+} O^{2-}_3)_2$

(MgOH)$_3$PO$_4$

H_3PO_3 H_3PO_2
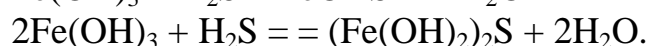
$FePO_4$ Na_2CO_3
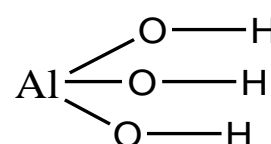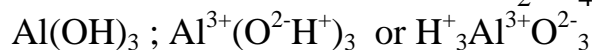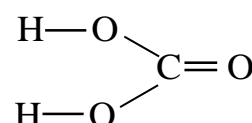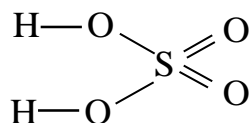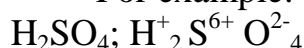
Examples of problems:

1. To write chemical reactions, demonstrated the amphoteric properties of Al_2O_3; $Zn(OH)_2$

Solution

$Al_2O_3 + 6\ HCl = 2\ AlCl_3 + H_2O$

$Al_2O_3 + 6\ NaOH = 2\ Na_3AlO_3 + 3\ H_2O$

$Zn(OH)_2 + 2\ H_2SO_4 = ZnSO_4 + 2\ H_2O$

$Zn(OH)_2 + 2\ NaOH = Na_2[Zn(OH)_4]$

2. To write all possible reactions of $Fe(OH)_3$ and H_2S.

Solution

$2Fe(OH)_3 + 3H_2S = Fe_2S_3 + 6\ H_2O$

$Fe(OH)_3 + 3H_2S = Fe(HS)_3 + 3\ H_2O$

$Fe(OH)_3 + H_2S = FeOHS + 2\ H_2O$

$2Fe(OH)_3 + H_2S = = (Fe(OH)_2)_2S + 2H_2O.$
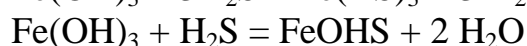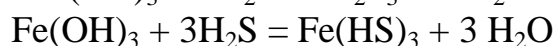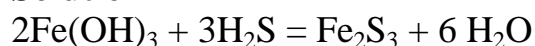
3. Write possible reactions between the next substances (by pairs):

BeO, $HClO_4$, KOH; P_2O_5

Solution
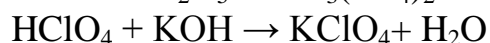
$BeO + 2\ HClO_4 = Be(ClO_4)_2 + H_2O$

$BeO + 2\ KOH \rightarrow K_2BeO_2 + H_2O$

$3\ BeO + P_2O_5 \rightarrow Be_3(PO_4)_2$

$HClO_4 + KOH \rightarrow KClO_4 + H_2O$

$6\ KOH + P_2O_5 \rightarrow 2\ K_3PO_4 + 3\ H_2O.$
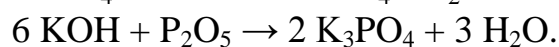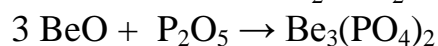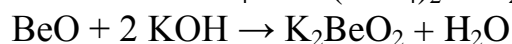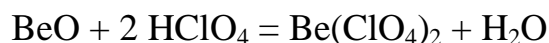
Review questions

1. Write equations, that demonstrate the amphoterism of BeO, MnO$_2$; Al(OH)$_3$.

2. Point the correspondence of the oxide formulas and their chemical nature:

A.	Basic	1	NO
B.	Non-salting	2	SrO
C.	Acidic	3	Cl$_2$O$_7$
D.	Amphoteric	4	PbO

3. Point the correspondence of the oxide formulas and their chemical nature:

A.	Non-salting	1	MnO
B.	Acidic	2	Mn$_2$O$_7$
C.	Basic	3	MnO$_2$
D.	Amphoteric	4	NO

4. To write all possible reactions between (by pairs):Zn(OH)$_2$; H$_2$S; H$_2$O; N$_2$O$_5$; Na; KOH; B$_2$O$_3$.
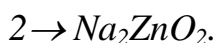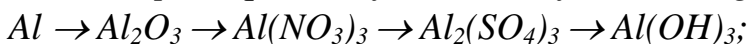
5.   Write reactions:

- *Fe$_2$(SO$_4$)$_3$ + CaCl$_2$ →*
- *Al$_2$O$_3$ + KOH   →*
- *FeSO$_4$ + Zn   →*
- *CoCl$_3$ + Na$_3$PO$_4$ →*
- *Cr(OH)$_3$ + KOH   →*
- *NO$_2$ + H$_2$O   →*
- *Ca(OH)$_2$ + SO$_2$ →*
- *Zn(OH)$_2$ + K$_2$O →*
- *CaCO$_3$ + HCl   →*
- *Sr(OH)$_2$ + CO$_2$ →*

6. To determine the oxidation numbers of elements in compounds: Fe$_2$O$_3$, H$_2$S, FeS, HNO$_2$, H$_4$P$_2$O$_7$, Ca$_3$(PO$_4$)$_2$, Fe$_2$(SO$_4$)$_3$, Ni(NO$_3$)$_3$, Na$_3$AlO$_3$, KAlO$_2$, LiFe(SO$_4$)$_2$, CaHAsO$_4$, Na$_2$O$_2$, MnSO$_3$, (NH$_4$)H$_2$PO$_4$.

7. Which oxides may react with water directly: BaO, Cu$_2$O, P$_2$O$_5$, SO$_3$, SO$_2$, K$_2$O, N$_2$O$_3$, CoO, Cl$_2$O$_7$, ZnO, NO$_2$, SiO$_2$, MnO$_2$, FeO, SrO? To write the corresponding equations of the chemical reactions.

8. Which oxides do correspond to the next compounds: H$_2$SO$_3$, Ca(OH)$_2$, NaOH, Fe(OH)$_3$, HNO$_3$, Co(OH)$_3$, H$_4$P$_2$O$_7$, CuOH, NAOH, CaBeO$_2$, HMnO$_4$, H$_2$CrO$_4$, K$_2$MnO$_4$?

9. To compile equations for the transformations given below:

Al →Al$_2$O$_3$ →Al(NO$_3$)$_3$ →Al$_2$(SO$_4$)$_3$ →Al(OH)$_3$;

2→Na$_2$ZnO$_2$.

10. To compile structural-graphic formulas of chemical compounds given below:

Cr_2O_3, $Ni(OH)_3$, H_3PO_4, $Al_2(SO_4)_3$, $Ca_3(PO_4)_2$.
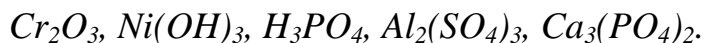
11. What oxides may react with each other (by pairs): Na_2O, CaO, SO_2, H_2O, P_2O_3, ZnO?

12. To write reactions for conversing of Iron (III) Dihydroxychloride and Calcium Dihydrophosphate in neutral salts.

13. To write all possible reactions between (taking into account the possibility of neutral, acidic and basic salts forming):

a) Aluminium Hydroxide and Orthophosphoric Acid;

b) Barium Oxide and Sulfuric Acid.

14. To present grafic formula of componds:

$Ca_3(PO_4)_2$; MnO_2; $KalO_2$; $Na_5P_3O_{10}$; HPO_3; N_2O_5; $Fe(OH)_3$.
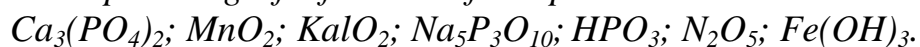
CHAPTER 7 REACTIONS IN AQUEOUS SOLUTIONS

Many chemical and almost all biological reactions occur in the aqueous medium. Substances (solutes) that are dissolved in water (solvent) can be subdivided into two categories: electrolytes and non-electrolytes, depending on the ability to conduct electricity.

Suppose a lump of sugar is dropped into a glass of water. You know from experience that the sugar will be dissolved. Sugar is described as "soluble in water". By "soluble" we mean the capability of being dissolved. Examination of sugar-water mixture, even under a microscope, would not reveal any particles of sugar. Such a mixture is called **"solution"**. Solution is a homogenous mixture of two or more substances in a single phase. In solution, atoms, and molecules of charged particles - ions are thoroughly mixed, with the result that the mixture has the same composition and properties throughout.

In the simplest type of solution, such as sugar-water solution, the molecules of one substance are distributed around the molecules of another one. The dissolving medium in a solution is called **solvent**, and the substance dissolved in a solution is called **solute**. In general, the solute is the substance, which mass is less than 50% of total mass of solution.

Three major types of reactions

In the precipitation reaction, the product, an insoluble substance, separates from solution. Acid-base reactions involve the transfer of a proton (H^+) from an acid to a base. In a oxidation-reduction reaction, or redox reaction, electrons are transferred from a reducing agent to an oxidizing agent. These three types of reactions represent the majority of reactions in chemical and biological systems.

7.1 Solution Stoichiometry

Quantitative studies of reactions in solution require that we know the concentration of the solution, which is usually represented by the molarity unit. These studies include **gravimetric analysis**, which involves the measurement of mass, and **titrations** in which the unknown concentration of a solution is determined by reaction with a solution of known concentration.

Table 7.1. Common Units for reporting concentrations

| Name	Units*	Symbol
1	2	3
Molarity (molar concentration)	$\dfrac{\text{moles solute}}{\text{liters solution}}$	M (for example, 2 M NaOH)

1	2	3
Normality (equivalent concentration)	$\dfrac{\text{numbers EWs solute}}{\text{liters solution}}$	N (for example, 0,05 N EDTA)
Molality	$\dfrac{\text{moles solute}}{\text{kg solvent}}$	m (for example, 1 m glucose)
Mass concentration (weight %)	$\dfrac{\text{g solute}}{\text{100 g solution}}$	% (w/w) (for example, 5% HCl)
Bulk concentration (volume %)	$\dfrac{\text{g solute}}{\text{100 mL solution}}$	% (v/v) (for example, 40% vol C_2H_5OH)
Parts per thousand	$\dfrac{\text{g solute}}{10^3 \text{ g solution}}$	ppt (for example, 5 ppt carbamide)
Parts per million	$\dfrac{\text{g solute}}{10^6 \text{ g solution}}$	ppm (for example, 10 ppm benzene)
Parts per billion	$\dfrac{\text{g solute}}{10^9 \text{ g solution}}$	ppb (for example, 20 ppb thyroxin)
*EW – equivalent weight		

The most useful unit in analytical practice and pharmacology are normality and molarity.

So, remember:

MOLARITY – the number of moles of solute per liter of solution	**NORMALITY – the number of equivalents of solute per liter of solution**
EQUIVALENT – the moles of a species that can donate one reaction unit	**EQUIVALENT WEIGHT – the mass of a compound containing one equivalent (EW)**

The numbers of equivalents, ν_E, is based into reaction unit, which is that part of a chemical species involved in a reaction. In a precipitation reaction, for example, the reaction unit is the charge of the cation or anion involved in the reaction; thus for the reaction

Pb^{2+} (aq) + $2I^-$ (aq) → PbI_2 (solid)
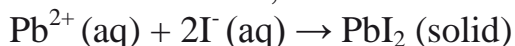
n = 2 for Pb^{2+} and n = 1 for I^-.

In an acid-base reaction, the reaction unit is the number of H^+ ions donated by an acid or accepted by a base. For the reaction between sulfate acid and ammonia

H_2SO_4 (aq) + $2NH_3$ (aq) → $2NH_4^+$ (aq) + SO_4^{2-} (aq)
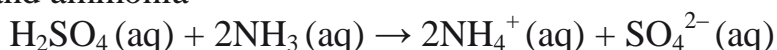
we find that n = 2 for H_2SO_4 and n = 1 for NH_3.

For a complexation reaction, the reaction unit is the number of electron pairs that can be accepted by the metal or donated by the ligand. In the reaction between Ag^+ and NH_3

Ag^+ (aq) + $2NH_3$ (aq) → $[Ag(NH_3)_2]^+$ (aq)
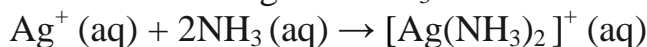
the value of n for Ag^+ is 2 and that for NH_3 is 1.

Finally, in an oxidation-reduction reaction the reaction unit is the number of electrons released by the reducing agent or accepted by the oxidizing agent; thus, for the reaction

$2Fe^{3+}$ (aq) + Sn^{2+} (aq) → Sn^{4+} (aq) + $2Fe^{2+}$ (aq)
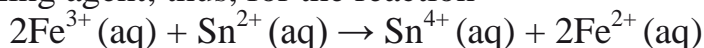
$n = 1$ for Fe^{3+} and $n = 2$ for Sn^{2+}. Clearly, determining the number of equivalents for a chemical species requires an understanding of how it reacts.

Normality is the number of **equivalent weights** (EW) per unit volume and is independent of speciation. An equivalent weight is defined as the ratio of a chemical species' **formula weight** (FW) **or molar mass** (M_m) to the number of its equivalents:
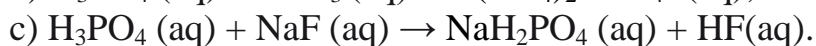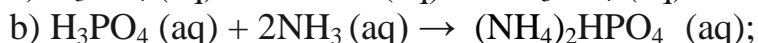
$$EW = \frac{M_m}{n} \qquad (7.1)$$

Consequently, the following simple relationship exists between normality and molarity:

$$N = n \cdot M \qquad (7.2)$$

Example 1 illustrates the relationship among chemical reactivity, equivalent weight, and normality

Calculate the equivalent weight and normality for a solution of 6.0 M H_3PO_4 given the following reactions:

    a) H_3PO_4 (aq) + $3NaOH$ (aq) → Na_3PO_4 (aq) + $3H_2O$ (liquid);

    b) H_3PO_4 (aq) + $2NH_3$ (aq) → $(NH_4)_2HPO_4$ (aq);

    c) H_3PO_4 (aq) + NaF (aq) → NaH_2PO_4 (aq) + HF(aq).

Solution

For phosphoric acid, the number of equivalents is the number of H^+ ions donated to the base. For the reactions in (a), (b), and (c) the number of equivalents are 3, 2, and 1, respectively. Thus, the calculated equivalent weights and normalities are:

$$EW = \frac{M_m}{n} = \frac{97,994}{3} = 32,665; \qquad N = n \cdot M = 3 \cdot 6,0 = 18 \text{ N};$$

$$EW = \frac{M_m}{n} = \frac{97,994}{2} = 48,997; \qquad N = n \cdot M = 2 \cdot 6,0 = 12 \text{ N};$$

$$EW = \frac{M_m}{n} = \frac{97,994}{1} = 97,994; \qquad N = n \cdot M = 1 \cdot 6,0 = 6 \text{ N}.$$

Molality is used in thermodynamic calculations where a temperature independent unit of concentration is needed. Molarity and normality are based on the volume of solution in which the solute is dissolved. Since density is a temperature depended property a solution's volume, and thus its molar and normal concentrations, will change as a function of its temperature. By using the solvent's mass in place of its volume, the resulting becomes independent of temperature.

Converting between concentration units

The units of concentration most frequently encountered in analytical chemistry and pharmacology, are Molarity, mass (weight) concentration, volume percent, ppm and ppb. By recognizing the general definition of concentration, it is easy to convert between concentration units.

Example 2. A concentrated solution of aqueous ammonia is 28% NH_3 and has a density of 0,899 g/mL. What is the molar concentration of NH_3 in this solution?

Solution

$$\frac{28\,g\,NH_3}{100\,g\,solution} \; x \; \frac{0,899\,g\,solution}{mL\,solution} \; x \; \frac{1\,mole\,NH_3}{17,04\,g\,NH_3} \; x \; \frac{1000\,mL}{liter} = 14,8\,M.$$

Example 3. The maximum allowed concentration of chloride in a municipal drinking water supply is $2,5 \cdot 10^2$ ppm Cl^-. When the supply of water exceeds this limit, it often has a distinctive salty taste. What is this concentration in moles Cl^- per liter?

Solution

$$\frac{2,5 \cdot 10^2 \; mg\,Cl^-}{L} \; x \; \frac{1\,g}{1000\,mg} \; x \; \frac{1\,mole\,Cl^-}{35,453\,g\,Cl^-} = 7,05 \cdot 10^{-3}\,M.$$

Table 7.2. Solubility Rules for Ionic Compounds in Water

Soluble Salts
1. The Na^+, K^+, and NH_4^+ ions form *soluble salts*. Thus, NaCl, KNO_3, $(NH_4)_2SO_4$, Na_2S, and $(NH_4)_2CO_3$ are soluble.
2. The nitrate (NO_3^-) ion forms *soluble salts*. Thus, $Cu(NO_3)_2$ and $Fe(NO_3)_3$ are soluble.
3. The chloride (Cl^-), bromide (Br^-), and iodide (I^-) ions generally form *soluble salts*. Exceptions to this rule include salts of the Pb^{2+}, Hg_2^{2+}, Ag^+, and Cu^+ ions. $ZnCl_2$ is soluble, but CuBr is not.
4. The sulfate (SO_4^{2-}) ion generally forms *soluble salts*. Exceptions include $BaSO_4$, $SrSO_4$, and $PbSO_4$, which are insoluble, and Ag_2SO_4, $CaSO_4$, and Hg_2SO_4, which are slightly soluble.
Insoluble Salts
1. Sulfides (S^{2-}) are usually *insoluble*. Exceptions include Na_2S, K_2S, $(NH_4)_2S$, MgS, CaS, SrS, and BaS.

2. Oxides (O^{2-}) are usually *insoluble*. Exceptions include Na_2O, K_2O, SrO, and BaO, which are soluble, and CaO, which is slightly soluble.	
3. Hydroxides (OH^-) are usually *insoluble*. Exceptions include NaOH, KOH, $Sr(OH)_2$, and $Ba(OH)_2$, which are soluble, and $Ca(OH)_2$, which is slightly soluble.	
4. Chromates (CrO_4^{2-}) are usually *insoluble*. Exceptions include Na_2CrO_4, K_2CrO_4, $(NH_4)_2CrO_4$, and $MgCrO_4$.	
5. Phosphates (PO_4^{3-}) and carbonates (CO_3^{2-}) are usually *insoluble*. Exceptions include salts of the Na^+, K^+, and NH_4^+ ions.	

Suppose a lump of sugar is dropped into a glass of water. You know from experience that the sugar will dissolve. Sugar is described as "soluble in water". By "soluble" we mean the capability of being dissolved. Examination of sugar-water mixture, even under a microscope, would not reveal any particles of sugar. Such a mixture is called **"solution"**. Solution is a homogenous mixture of two or more substances in a single phase. In solution, atoms, and molecules of charged particles - ions are thoroughly mixed, with the result that the mixture has the same composition and properties throughout.

In the simplest type of solution, such as sugar-water solution, the molecules of one substance are distributed around the molecules of another one. The dissolving medium in a solution is called **solvent**, and the substance dissolved in a solution is called **solute**. In general, the solute is the substance, which mass is less than 50% of total mass of solution.

Types of solutions. Solutions are formed in all three states - gaseous, liquid, and solid. Nine possible combinations of gases, liquids, and solids in solutions are summarized in Table 7.3.

Table 7.3. Types of solutions

Solute	Solvent	Example
Gas	Gas	Air
Gas	Liquid	Soda Water
Gas	Solid	Hydrogen in platinum
Liquid	Gas	Water vapor in air (mist, fog)
Liquid	Liquid	Alcohol in water
Liquid	Solid	Mercury in Copper (amalgam)
Solid	Gas	Sulfur vapor in air
Solid	Liquid	Sugar in water
Solid	Solid	Copper in nickel (different types of alloys)

The concentration of solution is the measurement of the amount of solute in a given amount of solvent or solution. Some medications are solutions of drugs - one-teaspoonful dose at correct concentration might

cure the condition; the same dose in the wrong concentration might kill the patient.

Sometimes solutions are referred as "concentrated" or "diluted". These are relative terms. "Diluted" means that there is relatively small amount of solute in solvent. "Concentrated", on the other hand, means that these terms are unrelated to the degree in which the solution is saturated. Saturated solution of substance that is not very soluble might be very diluted.

Percent by Mass (mass concentration, percent concentration)

Percent by Mass (P) of a solute in solution is the number of grams of solute dissolved in 100 g of solution. For example, the percent by mass of a solution made from 10 g of Sodium Hydroxide (NaOH) dissolved in 90 g of water is found as follows:

$$P = \frac{\text{Mass of solute m}_s}{\text{mass of solute m}_s + \text{mass of solvent m}_{solv}} \times 100\% =$$

$$= \frac{10\,\text{g NaOH}}{10\,\text{g NaOH} + 90\,\text{g H}_2\text{O}} \times 100\% = 10\,\%\ \text{NaOH (by mass)}.$$

Note that the mass of solution is the sum of the masses of the solute and solvent. Percent concentration is common for solutions used for practical purposes - household or industrial cleaning, killing pests in the garden, medical applications. Percent-by-mass concentration is based only on the mass of solute and is unrelated to its chemical formula of molar mass.

$$P = \frac{m_{solute}}{m_{solution}} \times 100\% \qquad (7.3)$$

Molarity (molar concentration)

Molarity (M) is the number of moles of solute in one litre of solution. To find the molarity of a solution one must know the molar mass of the solute. For example, "one-molar" solution of Sodium hydroxide (NaOH) contains one mole of NaOH in each litre of solution. The concentration of the proceeding solution is written as 1 M NaOH.

One mole of Sodium hydroxide (NaOH) has a mass of 40 g/mol (see Chapter 1.2). This quantity of NaOH dissolved in enough water to make exactly 1,00 L of solution gives a 1 M solution. If 20,0 g of NaOH, which is 0,500 mol, is dissolved in 1,00 L of solution, 0,500 M NaOH solution is produced:

$$\textbf{Molarity} = \frac{\text{Number of moles of solute}}{\text{Number of Litres of Solution}} = \frac{v}{V} = \frac{0,500 \, \text{mol NaOH}}{1,00 \, \text{L}} =$$

$= 0,500$ M NaOH.

Note that one molar solution is not made by adding 1 mol of solute to 1 L of solvent. In such case, the final total volume would be slightly different from 1 L. Instead of this 1 mol of salute is firstly dissolved in less than 1 L of solvent. Then, the resulting solution is carefully diluted with more solvent to bring the total volume to 1 L, using volumetric flask.

Molarity is useful when the quantity of solute participating in a chemical reaction taking place in solution is of interest. Any required molar quantity of the solute can be selected by measuring out the appropriate volume of the solution of known molarity.

$$M = \frac{v}{V} = \frac{\text{mass of solute}}{\text{Molar mass of solute} \times \text{Volume of solution in Litres}} \quad \text{or}$$

$$M = \frac{m_{solute}}{M_{solute} \times V} \tag{7.4}$$

Normality (normal concentration)

The concentration of solutions can be expressed by stating the quantity of the solute in equivalents rather than in moles. This measurement of concentration is called Normality (N). The normality of solution is the number of equivalents (v_E) of solute per litre (V) of solution:

$$\textbf{Normality} = \frac{\text{Number of equivalents of solute}}{\text{Number of Litres of Solution}} = \frac{v_E}{V}.$$

The normality of an acid or base solution is commonly expressed using the number of H^+ or OH^- ions available for a complete neutralization. Therefore:

$$E_{acid} = \frac{M_{acid}}{\text{number of hydrogen atoms in acid}},$$

$$E_{base} = \frac{M_{base}}{\text{number of OH groups in base}}.$$

For neutral salts equivalent mass may be expressed as:

$$E_{neutral\ salt} = \frac{M_{neutral\ salt}}{\text{number of atoms of metals in salt} \times \text{Valency of metals}},$$

where E_{acid}, E_{base}, $E_{neutral\ salt}$ - equivalent mass of acid, base or neutral salt respectively, g/g-eq;

M_{acid}, M_{base}, $M_{neutral\ salt}$ - molar mass of acid, base or neutral salt respectively, g/mol.

So, $\upsilon_E = \dfrac{m_{solute}}{E_{solute}}$ and

$$N = \frac{m_{solute}}{E_{solute} \times V} \qquad (7.5)$$

Titre

Titre (T) is a special unit for measuring of concentration connected with chemical quantitative analysis. Titre is the number of grams of solute in 1 millilitre of solution. For example, the titre of a solution made from 0,3 g of Silver Nitrate ($AgNO_3$) dissolved in 150 mL of solution is found as follows:

$$T = \frac{\text{Mass of solute } m_s \text{ in grams}}{\text{Volume of solution in mililiters}} =$$

$$= \frac{0,3\,\text{g AgNO}_3}{1150\,\text{mL of soution}} = 0,002\,\text{g/mL}.$$

So,

$$T = \frac{m_{solute\ in\ g}}{V_{solution\ in\ mL}} \qquad (7.6)$$

Table 7.3. Interconnection of concentration units

Measuring unit		Formulas for re-calculation			
Name	Symbol	**M**	**N**	**T**	**P**
Molarity (molar concentration)	**M**	-	$\dfrac{N \cdot E}{M_r}$	$\dfrac{T \cdot 1000}{M_r}$	$\dfrac{P \cdot 10d}{M_r}$
Normality (normal concentration)	**N**	$\dfrac{M \cdot M_r}{E}$	-	$\dfrac{T \cdot 1000}{E}$	$\dfrac{P \cdot 10d}{E}$
Titre	**T**	$\dfrac{M \cdot M_r}{1000}$	$\dfrac{N \cdot E}{1000}$	-	$\dfrac{P \cdot d}{100}$
Percent by Mass (mass concentration)	**P**	$\dfrac{M \cdot M_r}{10d}$	$\dfrac{N \cdot E}{10d}$	$\dfrac{T \cdot 100}{d}$	-

M_r - relative molar mass of solute, g/mol;

E - equivalent mass of solute, g/g-eq;

d - dencity of solution, g/L.

7.2 Theory of dissociation

It is experimentally established that solutions of certain substances in water may conduct an electric current (for example, solution of table salt in water) while the solution of sugar may not. The first group of substances was named **electrolytes**, the second one - **non-electrolytes**.

In order to understand the unique properties of electrolyte solutions, we will look briefly at the theory of Svante Arrhenius (1859-1927). His work forms the basis of the modern theory of ions in aqueous solutions, the solutions in which water is the solvent. Arrhenius considered the ions to be electrically charged. As a whole the solution contains equal numbers of positive and negative charges. He concluded that ions were produced by "ionization" of molecules in aqueous solution.

Water - solvent in aqueous solution - is not inert component. The polarity of water molecules plays an important role in the formation of solutions of ionic compounds in water. Molecule of H_2O is a polar particle called **"doublet" (dipole)** (Fig. 7.1):
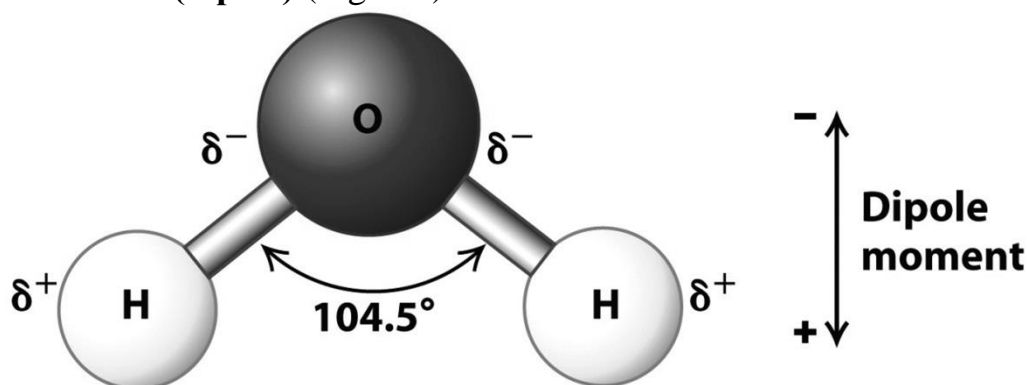
Figure 7.1. Polar structure of water molecule

The charged ends of water molecules attract the ions in the ionic compounds and bring them into solution. The energy released when an ion is attracted to a water molecule also affects the heat of solution of the ionic compound in water.

The solution process for ionic compounds. Suppose we drop a few crystals of Sodium Chloride into a beaker of water. At the crystal surface, water molecules come into contact with Na^+ and Cl^- ions. The positive ends of the water molecules are attracted to Cl^- ions; the negative ends are attracted to Na^+ ions. The attraction between water molecules and the ions is strong enough to draw the ions away from the crystal surface and into solution, as illustrated in Fig. 7.2.

This solution process with water as the solvent is referred to as **hydration**. The ions are said to be **hydrated**. The attraction between ions and water molecules is strong enough that each ion in solution remains surrounded by water molecules.

The separation of ions that occurs when an ionic compound dissolves is called **dissociation** (means disintegration, decay, decomposition). The equations representing the dissociation of Sodium Chloride in water are:

$$NaCl\ (s) \xleftrightarrow{H_2O} Na^+\ (aq) + Cl^-\ (aq)$$
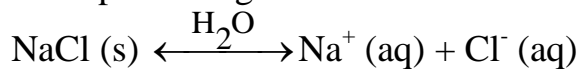
where (s) - solid phase;
(aq) - aqueous solution
or in simplified form
$$NaCl \longleftrightarrow Na^+ + Cl^-.$$
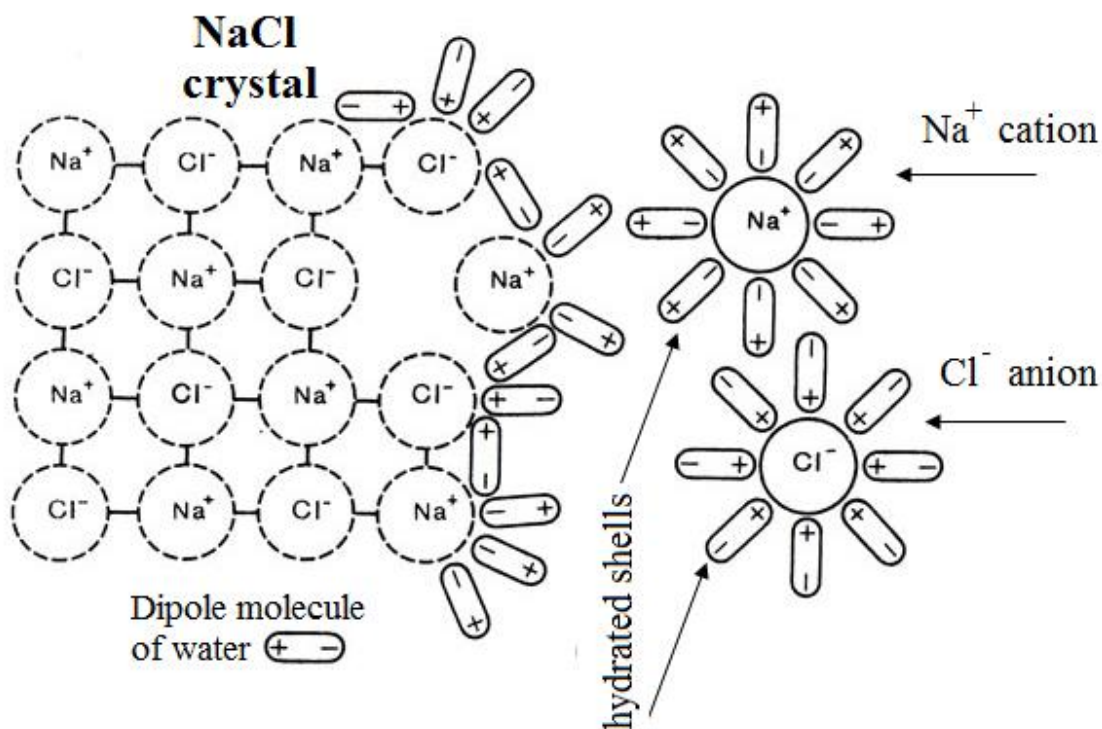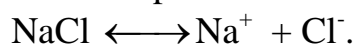
Figure 7.2. Table salt (Sodium Chloride) dissolves in water forming hydrated Sodium and Chloride ions

7.2.1 Degree of dissociation

Degree of dissociation (α) of electrolyte is the ratio:

$$\alpha = \frac{\text{Number of dissociated molecules of electrolyte}}{\text{Total number of dissolved molecules of electrolyte in solution}}.$$

α measures in percents (0…100%) or per unit (0…1). Degree of dissociation depends on:
➢ nature of chemical bonds in solute and solvent;

➢ concentration of solute;

➢ temperature of solution.

The main trends of these interdependences are:

1. Degree of dissociation is rising with decreasing of concentration of electrolyte;

2. Degree of dissociation is rising with rise in temperature.

Depending on degree of dissociation, all electrolytes are subdivided into three types: strong, medium and weak. This subdivision is relative, though.
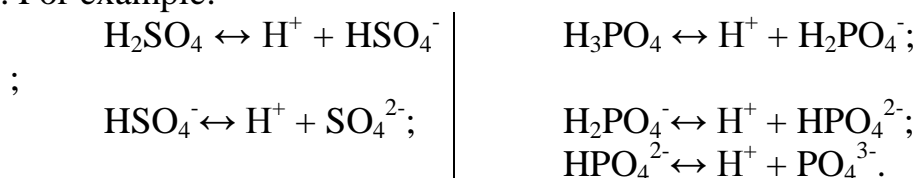
Degree of dissociation of **strong electrolytes** is more than 30%, **medium** - from 3% till 30%, **weak** - less or equal than 3%. In **Appendix 6, 7** it is presented the division of main classes of inorganic substances as electrolytes.

7.2.2 Main classes of inorganic substances from viewpoint of theory of electrolytic dissociation

Traditional definition of **an acid** according Arrhenius's theory: a chemical compound that contains Hydrogen and ionizes in aqueous solution to form Hydrogen ions:

$HCl \leftrightarrow H^+ + Cl^-$;

$HNO_3 \leftrightarrow H^+ + NO_3^-$.
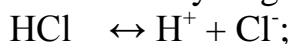
An acid that can donate one proton (Hydrogen ion) per molecule is known as a monoprotic acid (like foregoing ones). Acids contained more than one proton per molecule are polyprotic and ionize in more than one stage. For example:

$$H_2SO_4 \leftrightarrow H^+ + HSO_4^- \quad ; \qquad H_3PO_4 \leftrightarrow H^+ + H_2PO_4^-;$$

$$HSO_4^- \leftrightarrow H^+ + SO_4^{2-}; \qquad H_2PO_4^- \leftrightarrow H^+ + HPO_4^{2-};$$

$$HPO_4^{2-} \leftrightarrow H^+ + PO_4^{3-}.$$

Traditional definition of **a base** according Arrhenius's theory: this is a substance that contains hydroxide ions (OH^-) and dissociates to give hydroxide ions in aqueous solutions:

$NaOH \leftrightarrow Na^+ + OH^-$;
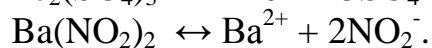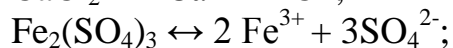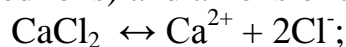
$KOH \leftrightarrow K^+ + OH^-$.
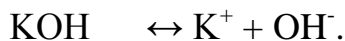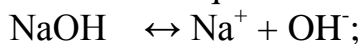
A base that can donate one hydroxyl OH^- per molecule is known as a monohydroxyl base (alkalis) (like foregoing ones). Bases contained more than one OH^--group per molecule are polyhydroxyl and ionize in more than one stages. For example:

$$Ca(OH)_2 \leftrightarrow CaOH^+ + OH^-;$$

$$CaOH^+ \leftrightarrow Ca^{2+} +$$
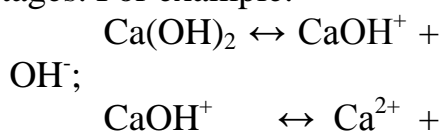
OH^-.

Neutral salts are dissociated with forming of metal cations (positive charged ions) and anions of acidic residues:

$CaCl_2 \leftrightarrow Ca^{2+} + 2Cl^-$;

$Fe_2(SO_4)_3 \leftrightarrow 2\,Fe^{3+} + 3SO_4^{2-}$;

$Ba(NO_2)_2 \leftrightarrow Ba^{2+} + 2NO_2^-$.

Acidic and basic salts are ionized in some steps as salts and corresponding acids or bases. For example:

Acidic salt NH_4HSO_4:

      1 step - like $NH_4HSO_4 \leftrightarrow NH_4^+ + HSO_4^-$;
neutral salt:

      2 step - like acid: $HSO_4^- \leftrightarrow H^+ + SO_4^{2-}$.

Basic salt BaOHCl:

      1 step - like $BaOHCl \leftrightarrow BaOH^+ + Cl^-$;
neutral salt:

      2 step - like base: $BaOH^+ \leftrightarrow Ba^{2+} + OH^-$.
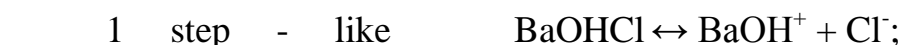
All simple substances and oxides are weak electrolytes and do not dissociate in aqueous solutions.

7.2.3 Ionic equations

Double replacement reactions and other reactions of ions in aqueous solution are usually represented by that are known as "net ionic equations". To write a net ionic equation, one firstly writes an equation in which all strong electrolytes are shown as dissociated ions in solution (without steps, of course). For example:
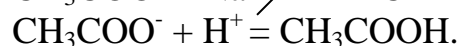
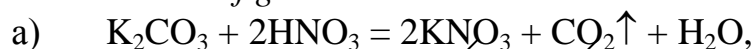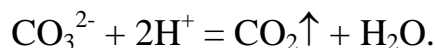*1. Formation of slightly soluble substance:*

$CuSO_4 + 2NaOH = Cu(OH)_2\downarrow + Na_2SO_4$

$Cu^{2+} + SO_4^{2-} + 2Na^+ + 2OH^- = Cu(OH)_2\downarrow + 2Na^+ + SO_4^{2-}$ -
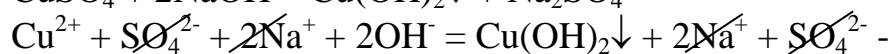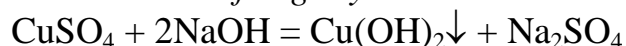
this is a complete ionic equation.

$Cu^{2+} + 2OH^- = Cu(OH)_2\downarrow$ - this is net ionic equation.
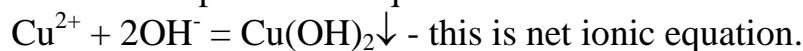
2. Formation of weak electrolyte:

a) $HCl + KOH = KCl + H_2O$,

      $H^+ + Cl^- + K^+ + OH^- = K^+ + Cl^- + H_2O$,

      $H^+ + OH^- = H_2O$.

b) $CH_3COONa + HCl = CH_3COOH + NaCl$,

      $CH_3COO^- + Na^+ + H^+ + Cl^- = CH_3COOH + Na^+ + Cl^-$,

      $CH_3COO^- + H^+ = CH_3COOH$.

3. Formation of gas:

a) $K_2CO_3 + 2HNO_3 = 2KNO_3 + CO_2\uparrow + H_2O$,

      $2K^+ + CO_3^{2-} + 2H^+ + 2NO_3^- = 2K^+ + 2NO_3^- + CO_2\uparrow +$

H_2O,

$$CO_3^{2-} + 2H^+ = CO_2\uparrow + H_2O.$$

b) $FeS + 2HCl = FeCl_2 + H_2S\uparrow$.
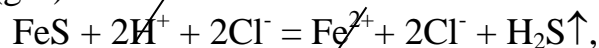
Iron (II) Sulfide is slightly soluble and Hydrogen Sulfide is a weak electrolyte (gas). Therefore:

$$FeS + 2H^+ + 2Cl^- = Fe^{2+} + 2Cl^- + H_2S\uparrow,$$
$$FeS + 2H^+ = Fe^{2+} + H_2S\uparrow.$$
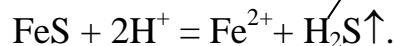
Interactions in the solutions of electrolytes are realized completely if in the result the following will be formed:

а) weak electrolyte;

б) sediments;

в) gases.

7.3 Ionic product of water. Notion of pH. Hydrolysis of salts

Pure water conducts an electric current very poorly, but nevertheless it has a measurable electrical conductivity that is explained by the slight dissociation of water into hydrogen and hydroxide ions:

$$HOH \rightleftharpoons H^+ + OH^-$$
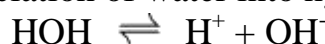
The concentration of hydrogen and hydroxide ions in water at 25°C is 10^{-7} mol/l. Let us write an expression for the dissociation constant of water:

$$K = \frac{[H^+]\cdot[OH^-]}{[H_2O]}.$$

We can rewrite this equation as follows:

$K[H_2O] = [H^+][OH^-]$.

Since the degree of dissociation of water is very low, the concentration of undissociated molecules of H_2O in water virtually equals the total concentration of water, i.e. 55.55 mol/1 (1 litre contains 1000 grams of water, i.e. 100:18.02 = 55.55 moles). Therefore, replacing the product $[H_2O]$ *K* in the last equation with the new constant K_w, we have:

$[H^+][OH^-] = K_w$

The obtained equation shows that for water and dilute aqueous solutions at a constant temperature, the product of the hydrogen ion and hydroxide ion concentrations is a constant quantify. The latter is called the **ion product** of water.

It is not difficult to obtain its numerical value by introducing into the last equation the concentrations of the hydrogen and hydroxide ions. For pure water at 25 °C, we have $[H+] = [OH-] = 1\cdot10^{-7}$ mol/L.

Solutions in which the concentrations of the hydrogen ions and hydroxide ions are the same are called **neutral solutions**.

At 25°C, as we have already indicated, the concentration of both hydrogen ions and hydroxide ions in neutral solutions is 10^{-7} mol/L. If, for

instance, we add so much acid to pure water that the hydrogen ion concentration grows to 10^{-3} mol/L, then the hydroxide ion concentration will diminish so that the product $[H^+][OH^-]$ remains equal to 10^{-14}. Consequently, in this solution, the hydroxide ion concentration will be:

$$10^{-14} = 10^{-3} \cdot x;$$

$$x = [OH^-] = \frac{10^{-14}}{10^{-3}} = 10^{-11}.$$

These examples show that both the degree of acidity and the degree of alkalinity of a solution can be characterised quantitatively by the hydrogen ion concentration.

The acidity or alkalinity of a solution can be expressed in another, more convenient way: instead of the hydrogen ion concentration, its common logarithm is taken with the reverse sign. The latter quantity is named the hydrogen ion index, but most chemists call it the pH-value or simply the pH:

pH = - lg $[H^+]$.

Analogically pOH = - lg $[OH^-]$.

For all water solutions it is realized such ratio:

pH + pOH = 14.

For instance, if $[H^+] = 10^{-5}$ mol/L, then pH = 5, if $[H^+] = 10^{-9}$ mol/L, then pH = 9, and so on.

It is thus clear that for a neutral solution ($[H^+] = 10^{-7}$ mol/L), pH = 7 (at a temperature of 25°C). For acid solutions, pH < 7, and diminishes with an increasing acidity of the solution. Conversely, for alkaline solutions, pH > 7, and grows with an increasing alkalinity of the solution.

The pH is of great significance for many processes. For example, plants can grow normally only when the pH of the soil solution is within a definite interval characteristic of a given species of plant.

For example, *Hydrangea macrophylla* blossoms in pink or blue, depending on soil pH. In acidic soils, the flowers are blue; in alkaline soils, the flowers are pink.

7.3.1 Measuring pH

Measuring pH is essential not only in finding the chemical characteristics of a substance but also as the first step toward managing chemical reactions. Currently, pH measurement is used in various fields, including nearly all industries that deal with water, not only the chemical industry, but public organizations, agriculture and fishery-related industries and biological industries, as well.

Textiles, Dyeing. In the textile industry, measuring pH is important in product testing, such as how a fabric reacts to things like perspiration,

especially when developing synthetics, to ensure safety and durability. Of course, pH measurement is indispensable in the process of dyeing, because permanence and processing speed depend on the pH of the dye bath, which is automatically adjusted to maintain proper pH. Also, pH measurement is applied when creating artificial perspiration to be used in color-change testing.

Paper, Pulp. Measurement of pH is carried out in the manufacturing processes of paper and pulp more often and continuously than any other industry. To reduce the consumption of chemicals and prevent corrosion of equipment, pH is controlled in the process of digestion, bleaching, creating of pulp to the manufacture of finished paper material products. Also, the durability and drying speed depends on the pH of the paper itself. Therefore, pH is strictly checked and adjusted as a vital part of quality control.

Chemistry. As pH measurement is essential for control of chemical reactions, it is carried out in the course of nearly all production of chemical products, be it plastics, fertilizers, electronic industrial materials such as semiconductors, cements, or glass. In order to optimize the desired reaction and to prevent unwanted reactions, controlling the pH of solutions is very important.

For example, in the manufacturing process for plastics, pH is strictly managed in the processes of producing long-chain molecular products, especially the processes of polymerization and condensation. Also, pH is controlled for efficient production of chemical fertilizers such as nitrogen fertilizers, potash fertilizers and phosphate fertilizers. Also, pH measurement is very important both in the mixing process of silicate in the case of cement and in combining processes at high temperature in the case of glass manufacturing. The transparency of finished glass is also influenced by pH.

Oil Refining. In oil refining, measurement of pH is carried out in the desulfurization process.

Metals and Minerals. Each metal tends to dissolve in solution of a certain pH by nature. Based on this characteristic, when extracting a particular material from crude ore or mixed metal, pH is controlled so as to extract only the desired metal without dissolving the slag. For example, if you place a mixture of copper and zinc in acid electrolytic solution and electrolyze it, only copper is separated out at the negative electrode.

Electricity, Electrochemistry. In this field, pH measurement is applied to plating, etching of metal surfaces and the manufacture of batteries. Control of the pH of a plating solution greatly affects the finish. Without proper control of the pH of a plating solution, the finished plating

will be likely to peel and will not have the optimum color and luster. Anodic oxidation processing is used in coating cooking utensils to produce a coating like the film that forms on aluminum objects, and controlling the pH of the processing solution is critical to achieving the desired finish. In advanced factory painting processes, pH is a vital factor in achieving paint finishes of the quality required for manufactured goods.

Ways of Measuring pH

The methods for measuring pH fall roughly into the following three categories:

- Indicator methods;
- Metal-electrode methods (including the hydrogen-electrode method, quinhydron-electrode method and antimony-electrode method);
- Glass-electrode methods.

Measuring pH using an indicator. This category basically includes two methods: one involves comparing the standard color corresponding to a known pH with the color of an indicator immersed in the test liquid using buffer solution. The other method involves preparing pH test paper which is soaked in the indicator, then immersing the paper in the test liquid and comparing its color with the standard color. This method is simple, but prone to error. A high degree of accuracy cannot be expected. :

Various errors include:
- Error due to high salt concentration in the test liquid;
- Error due to the temperature of the test liquid;
- Error due to organic substances in the test liquid.

Hydrogen-electrode method. A hydrogen electrode is made by adding platinum black to platinum wire or a platinum plate (fig. 7.4). It is immersed in the test solution and an electric charge is applied to the solution and platinum black with hydrogen gas.

The hydrogen-electrode method is a standard among the various methods for measuring pH. The values derived using other methods become trustworthy only when they match those measured using hydrogen electrode method.
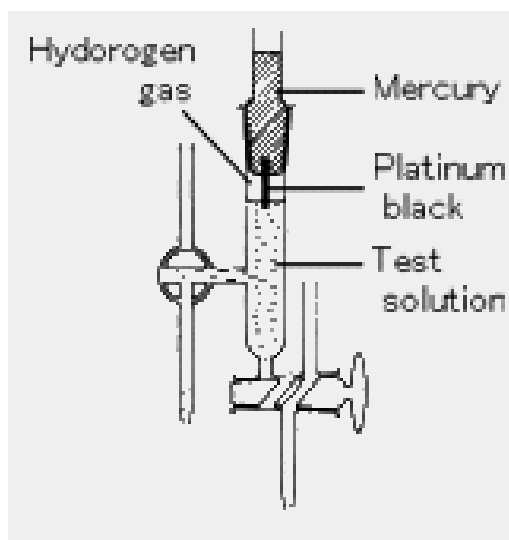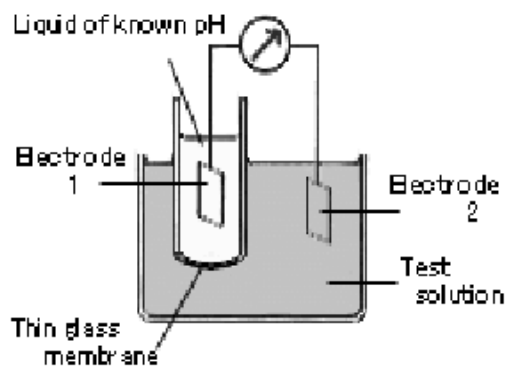

Figure 7.3. Hydrogen electrode

However, this method is not appropriate for daily use because of the effort and expense involved, with the inconvenience of handling hydrogen gas and great influence of highly

oxidizing or reducing substances in the test solution.

Glass-Electrode Method

In this field, pH measurement is applied to plating, etching of metal surfaces and the manufacture of batteries. This method is most widely used for pH measurement because the balancing time of electrical potential is short, it has high reproducibility, it is rarely affected by oxidizing and reducing agents, and it can measure pH of various solutions. This method is used not only in industry but in a wide variety of fields.

Principles of the Glass-Electrode Method. In the glass-electrode method, the known pH of a reference solution is determined by using two electrodes, a glass electrode and a reference electrode, and measuring the voltage (difference in potential) generated between the two electrodes. The difference in pH between solutions inside and outside the thin glass membrane creates electromotive force in proportion to this difference in pH.

Figure 11. Operating Principle of the glass-electrode method

This thin membrane is called the electrode membrane. Normally, when the temperature of the solution is 30 C, if the pH inside is different from that of outside by 1, it will create approximately 60 mV of electromotive force.

The liquid inside the glass electrode usually has a pH of 7. Thus, if one measures the electromotive force generated at the electrode membrane, the pH of the test solution can be found by calculation. A second electrode is necessary when measuring the electromotive force generated at the electrode membrane of a glass electrode. This other electrode, paired with the glass electrode, is called the reference electrode. The reference electrode must have extremely stable potential. Therefore, it is provided with a pinhole or a ceramic material at the liquid junction. In other words, a glass electrode is devised to generate accurate electromotive force due to the difference in pH. And a reference electrode is devised not to cause electromotive force due to a difference in pH.

7.3.2 Hydrolysis as replacement process

Hydrolysis occurs when an ion reacts with, or we could say "rips apart" a water molecule. This can only happen with ions capable of entering into an equilibrium situation with the molecules that are then formed. Those molecules capable of equilibrating are weak acid and base molecules while molecules not capable of equilibrating are strong acid and base molecules. A salt can be analyzed for hydrolysis by:

1. Dissociating it into ions.
2. Combining the positive ion from the salt with OH^- to form a base.
3. Judge this base to be strong or weak.
4. If the base is strong , no hydrolysis occurs, but if the base is weak hydrolysis does occur.

Now repeat steps 2 to 4 for the negative ion

5. Combining the negative ion from the salt with H^+ to form an acid.
6. Judge this acid to be strong or weak.
7. If the acid is strong, no hydrolysis occurs, but if the acid is weak hydrolysis does occur.

Write the equilibrium reaction for the hydrolysis by following the pattern:

Hydrolyzing ion + water $\rightleftharpoons$ weak acid molecule +
+ remaining fragment of water
or
Hydrolyzing ion + water $\rightleftharpoons$ weak base molecule +
+ remaining fragment of water

Example:

Do KBr, Cs_2SiO_3, $AlCl_3$, NH_4NO_2 alter the pH of (that is cause the hydrolysis of) water and if so, is the solution acidic or basic?

Following the above steps gives:	
K^+	Br^-
KOH	HBr
strong base	strong acid
no hydrolysis	no hydrolysis
Since no hydrolysis occurs, the salt is neutral and the pH of water is unaffected.	
Cs^+	SiO_3^{2-}
CsOH	$HSiO_3^-$
strong base	weak acid
no hydrolysis	hydrolysing ion

Since hydrolysis occurs due to anion of weak acid, the salt in water solution has alkali medium and the pH of solution is more than 7. $$SiO_3^{2-} + HOH \rightleftharpoons HSiO_3^- + OH^-$$ $$2Cs^+ + SiO_3^{2-} + HOH \rightleftharpoons 2Cs^+ + HSiO_3^- + OH^-$$ $$Cs_2SiO_3 + HOH \rightleftharpoons CsHSiO_3 + CsOH$$	
Al^{3+}	Cl^-
$Al(OH)_3$	HCl
weak base	strong acid
hydrolysing ion	no hydrolysis
Since hydrolysis occurs due to cation of weak base, the salt in water solution has acidic medium and the pH of solution is less than 7. $$Al^{3+} + HOH \rightleftharpoons AlOH^{2+} + H^+$$ $$Al^{3+} + 3Cl^- + HOH \rightleftharpoons AlOH^{2+} + H^+ + 3Cl^-$$ $$AlCl_3 + HOH \rightleftharpoons AlOHCl_2 + HCl$$	

NH_4^+	NO_2^-
NH_4OH	HNO_2
Weak base	Weak acid
hydrolysing ion	hydrolysing ion
Since hydrolysis occurs due to cation of weak base and anion of weak acid, the salt in water solution has neutral medium and the pH of solution is nearly 7. $$NH_4^+ + NO_2^- + HOH \rightleftharpoons NH_4OH + HNO_2$$ $$NH_4NO_2 + HOH \rightleftharpoons NH_4OH + HNO_2$$	

7.3.3 Types of hydrolysis

Individual possible cases of hydrolysis of salts are compared below (from the point of view of the acidity or alkalinity of the solution and the nature of the product obtained). The basis for the comparison is, on one hand, the strength of the corresponding acids and bases, and, on the other hand, the type of salt with regard to valency of the cation and the anion.

I. Strong base, weak acid. The solution is **alkaline**. The following cases are possible, depending on the valency of the cation or the anion.

a) Cation and anion monovalent. The hydrolysis products are free acid and free base, e.g.:

$NaCN + HOH \leftrightarrow NaOH + HCN$
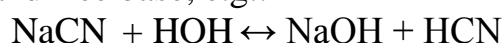
or, in net ionic form, $CN^- + HOH \leftrightarrow HCN + OH^-$ (pH>7).

b) Cation monovalent, anion multivalent. This is the most typical case. Hydrolysis gives acid salts and free alkali, e.g.:

$Na_3PO_4 + HOH \leftrightarrow Na_2HPO_4 + NaOH$
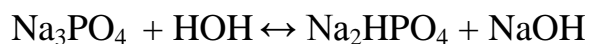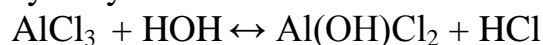
or, in net ionic form, $PO_4^{3-} + HOH \leftrightarrow HPO_4^{2-} + OH^-$ (pH>7).

In a large volume of water hydrolysis proceeds further:

$Na_2HPO_4 + HOH \leftrightarrow NaH_2PO_4 + NaOH$
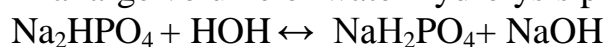
or, in net ionic form, $HPO_4^{2-} + HOH \leftrightarrow H_2PO_4^- + OH^-$.

However, it does not reach the stage of formation of free weak acid owing to the accumulation of free alkali (OH^- ions) in the solution.

c) Cation multivalent, anion monovalent. This case is rather rare. Hydrolysis results in basic salt and free acid. But the solution is alkaline since it contains more OH^- ions from the basic salt (formed by the strong base) than H^+ ions from the weak acid, e.g.:

$Ba(CN)_2 + HOH \leftrightarrow BaOHCN + HCN$
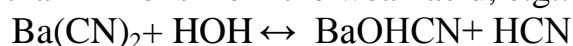
or, in ionic form, $CN^- + HOH \leftrightarrow HCN + OH^-$.

d) Cation and anion multivalent. This case is never encountered in practice, as the compounds of this group are all insoluble in water.

II. Weak base, strong acid. The solution is **acid**. The following cases are possible, depending on the valency of the cation or the anion.

a) Cation and anion monovalent. The hydrolysis gives free acid and free base, e.g.:

$NH_4NO_3 + HOH \leftrightarrow NH_4OH + HNO_3$
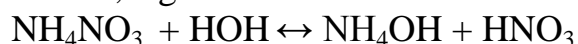
or, in ionic form, $NH_4^+ + HOH \leftrightarrow NH_4OH + H^+$.

b) Cation multivalent, anion monovalent. This is the most typical case. Hydrolysis results in basic salts and free acid, e.g.:

$AlCl_3 + HOH \leftrightarrow Al(OH)Cl_2 + HCl$

or, in net ionic form, $Al^{3+} + HOH \leftrightarrow Al(OH)^{2+} + H^+$ (pH<7).

In a large volume of water hydrolysis proceeds further:

$Al(OH)Cl_2 + HOH \leftrightarrow Al(OH)_2Cl + HCl$
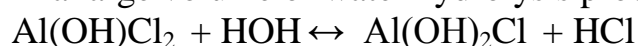
or, in ionic form, $Al(OH)^{2+} + HOH \leftrightarrow Al(OH)_2^+ + H^+$.

However, it does not reach the stage of formation of free weak base owing to the accumulation of free acid (H^+ ions) in the solution.

c) Cation monovalent, anion multivalent. This is very rare case. The result of hydrolysis is an acid salt and free base. In this case, the solution contains more H^+ ions from the acid salt (formed by the strong acid) than OH^- ions from the weak base, e.g.:

$(NH_4)_2SO_4 + HOH \leftrightarrow NH_4OH + NH_4HSO_4$
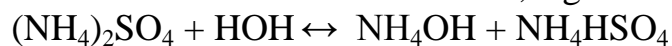
or, in net ionic form, $NH_4^+ + HOH \leftrightarrow NH_4OH + H^+$ (pH<7).

d) Cation and anion multivalent. Hydrolysis results in basic salt and free acid, e.g.:

$Fe_2(SO_4)_3 + 2 HOH \leftrightarrow 2 Fe(OH)SO_4 + H_2SO_4$
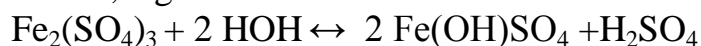
or in net ionic form, $Fe^{3+} + HOH \leftrightarrow Fe(OH)^{2+} + H^+$ (pH<7).

III. Weak base, weak acid. In this case the alkalinity or acidity of the solution depends on the relative strengths of the acid and the base. The nature of the hydrolysis products depends on the strengths of the acid and the base as well as on the valences of the cation and the anion. For example, Aluminum Acetate hydrolyses bring to forming of basic salts, according to the equations:

$Al(CH_3COO)_3 + HOH \leftrightarrow Al(OH)(CH_3COO)_2 + CH_3COOH$
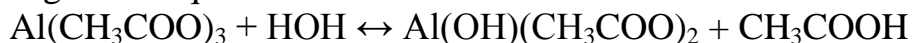
$Al(OH)(CH_3COO)_2 + HOH \leftrightarrow Al(OH)_2(CH_3COO) + CH_3COOH$ (pH≈7).

While Aluminium Sulfide, a salt of a much weaker acid, is hydrolyzed to free base and the free acid:

$Al_2S_3 + 6HOH \leftrightarrow 2 Al(OH)_3 + 3H_2S$.
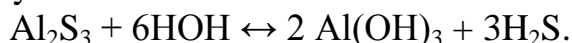
The last case concerns to the salts marked as symbol - (dash) in Table of salts and bases Solubility in water **(Appendix 5).**

IV. Strong base, strong acid. Solutions of such salts have neutral medium, since they are practically unhydrolyzed. This group includes NaCl, Na_2SO_4, $BaCl_2$ etc.

CHAPTER 8 CHEMICAL KINETICS AND EQUILIBRIUM

8.1 General concepts

Chemical kinetics, also known as reaction kinetics, is the study of **rates** of chemical processes. Chemical kinetics includes investigations of how different experimental conditions can influence the speed of a chemical reaction and yield information about the **reaction's mechanism** and **transition states**, as well as the construction of mathematical models that can describe the characteristics of a chemical reaction.

The **rate** of the chemical reaction is defined as (see fig. 1):

$$\frac{\text{change in concentration, } \Delta c, \text{ in time } \Delta t}{\Delta t}$$
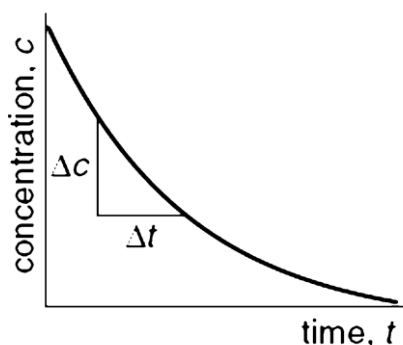
Fig. 1. Notion of rate of chemical reaction
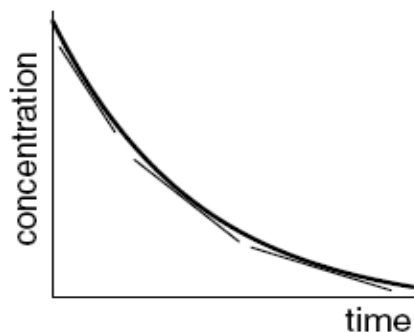
Fig. 2. The rate is the instantaneous slope, and this varies with time

We can talk about the rate of formation or loss of any species – reactant, intermediate or product. It is, however, important to specify which species we are talking about. The rate can be positive or negative: a positive rate means that the concentration is increasing with time *e.g.* a product; a negative rate means that the concentration is falling with time *e.g.* a reactant.

The rate may vary with time (and concentration), so it is usual to define the rate over a very small time, Δt. We think of the rate as the *derivative* of concentration *with respect to time* (see fig. 2):

$$\text{rate} = \frac{d[\text{concentration}]}{dt}$$

This derivative is the slope of a graph of concentration against time, taken at a particular time.

Consider a typical chemical reaction:

aA + bB → pP + qQ
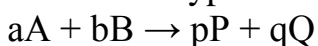
The lowercase letters (a, b, p, and q) represent stoichiometric coefficients, while the capital letters represent the **reactants** (A and B) and the **products** (P and Q).

According to the IUPAC's Gold Book definition, the **reaction rate *v*** (also *r* or *R*) for a chemical reaction occurring in a closed system under constant-volume conditions, without a build-up of reaction intermediates, is defined as:

$$v = k[A]^a \cdot [B]^b,$$

 where k – rate constant;

[A], [B] – molar concentrations of reactants.

This law is named **"law of mass action"** (discovered by Guldberg and Waage (Norway), 1864)**.**

The constant of proportionality, k, is called the ***rate constant***.

Physical essence of k – this is a experimentally determined rate of reaction when [A]=[B]=…=1 mol/L.

Factors affecting rate constant:

      1. Nature of reactants (type of bonding at el);

      2. Temperature.

NOTE: Reaction rate usually has the units of $mol \cdot L^{-1} \cdot s^{-1}$. It is important to bear in mind that the previous definition is only valid for a *single reaction*, in a *closed system* of *constant volume*. This most usually implicit assumption must be stated explicitly, otherwise the definition is incorrect: If water is added to a pot containing salty water, the concentration of salt decreases, although there is no chemical reaction.

8.2 Factors affecting reaction rate

8.2.1 Nature of the reactants

Depending upon what substances are reacting, the time varies. Acid reactions, the formation of salts, and ion exchange are **fast** reactions. When covalent bond formation takes place between the molecules and when large molecules are formed, the reactions tend to be very **slow**. Nature and strength of bonds in reactant molecules greatly influences the rate of its transformation into products. The reactions which involve lesser bond rearrangement proceed faster than the reactions which involve larger bond rearrangement.

8.2.2 Physical state

The physical state (solid, liquid, or gas) of a reactant is also an important factor of the rate of change. When reactants are in the same phase (**homogeneous systems**), as in aqueous solution, thermal motion brings them into contact. However, when they are in different phases

(**heterogeneous systems**), the reaction is limited to the interface between the reactants. Reaction can only occur at their area of contact, in the case of a liquid and a gas, at the surface of the liquid. Vigorous shaking and stirring may be needed to bring the reaction to completion. This means that the more finely divided a solid or liquid reactant, the greater its surface area per unit volume, and the more contact it makes with the other reactant, thus the faster the reaction. To make an analogy, for example, when one starts a fire, one uses wood chips and small branches - one doesn't start with large logs right away. On water reactions are the exception to the rule that homogeneous reactions take place faster than heterogeneous reactions.

Example. To describe the expression of the rate for the next reactions (in forward direction):

1. $C_8H_{18\,(gas)} + 25\,O_{2\,(gas)} \leftrightarrow 16\,CO_{2\,(gas)} + 18\,H_2O_{\,(gas)}$

and

2. $C_{\,(solid)} + O_{2\,(gas)} \leftrightarrow CO_{2\,(gas)}$
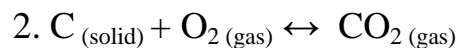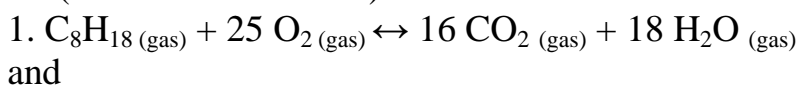
Solution. According to the low of mass action, rate of direct reaction is equal to product of concentrations of gas phases, excluding solids. So, for reaction 1:

$v = k\,[C_8H_{18}] \cdot [O_2]^{25}$ (homogeneous system);

and for reaction 2:

$v = k\,[O_2]$ (heterogeneous system, no solid phase concentration).

8.2.3 Concentration

Concentration plays a very important role in reactions according to the collision theory of chemical reactions, because molecules must collide in order to react together. As the concentration of the reactants increases, the frequency of the molecules colliding increases, striking each other more frequently by being in closer contact at any given point in time. Think of two reactants being in a closed container. All the molecules contained within are colliding constantly. By increasing the amount of one or more of the reactants it causes these collisions to happen more often, increasing the reaction rate (Fig. 3).

Mathematically influence of concentration is described by "law of mass action", but real rate is depends on so-called "order of reaction". A first-order reaction depends on the concentration of only one reactant (a unimolecular reaction). Other reactants can be present, but each will be zero-order. A second-order reaction depends on the concentrations of one second-order reactant, or two first-order reactants.
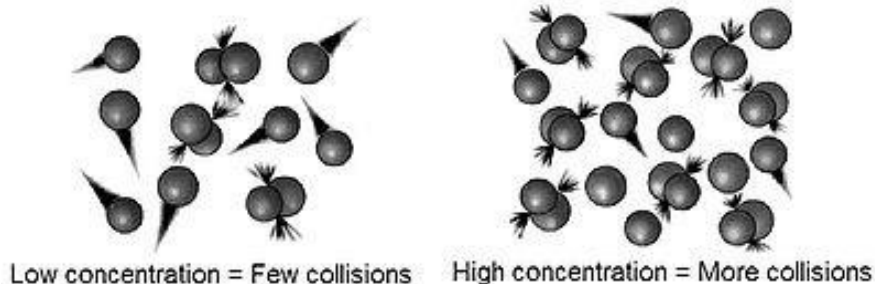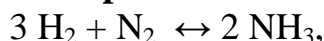
Low concentration = Few collisions   High concentration = More collisions

Fig. 3. Reaction rate tends to increase with concentration - a phenomenon explained by collision theory

Example. To determine the change of rate for direct reaction
$3 H_2 + N_2 \leftrightarrow 2 NH_3$,
if H_2 concentration was increased in two times.
Solution. According to the low of mass action, initial rate of direct reaction is equal to:
$v = k [H_2]^3 \cdot [N_2]$.
After increasing of hydrogen concentration in two times:
$v' = k [2 \cdot H_2]^3 \cdot [N_2] = k [H_2]^3 \cdot 2^3 \cdot [N_2] = k \cdot 8 \cdot [H_2]^3 \cdot [N_2]$.
So,
$v'/v = k \cdot 8 \cdot [H_2]^3 \cdot [N_2] / k [H_2]^3 \cdot [N_2] = 8$ times.
Answer:

The rate of reaction $3 H_2 + N_2 \leftrightharpoons 2 NH_3$ increased in 8 times after increasing of hydrogen concentration in two times.

8.2.4 Temperature

Temperature usually has a major effect on the rate of a chemical reaction. Molecules at a higher temperature have more thermal energy. Although collision frequency is greater at higher temperatures, this alone contributes only a very small proportion to the increase in rate of reaction. Much more important is the fact that the proportion of reactant molecules with sufficient energy to react (energy greater than **activation energy E_a**: $E > E_a$) (fig. 4) is significantly higher and is explained in detail by the Maxwell–Boltzmann distribution of molecular energies. The excess energy that molecules must have for their collision to be effective is called the **activation energy** of the given reaction. The activation energy is expressed in kJ/mol. Molecules having such an energy are called **active molecules.**
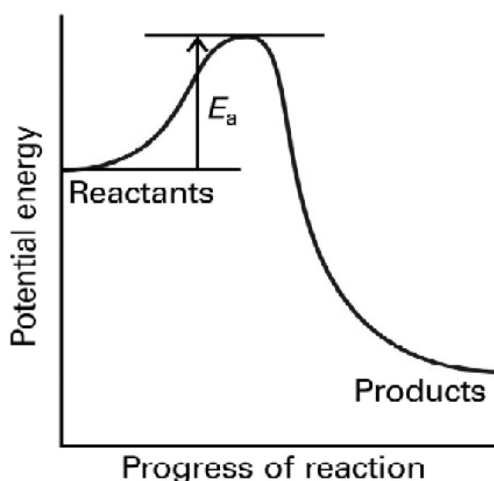
Fig. 4. Notion of activation energy

The influence of temperature is described by the Arrhenius equation:

$$k = A \exp\left(\frac{-E_a}{RT}\right),$$

where A is the frequency factor for the reaction, R is the universal gas constant, and T is the temperature (in Kelvin). While this equation suggests that the activation energy is dependent on temperature, in regimes in which the Arrhenius equation is valid this is cancelled by the temperature dependence of k. Thus E_a can be evaluated from the rate constant at any temperature (within the validity of the Arrhenius equation).

The "rule of thumb" (емпіричне правило, встановлене на основі практичних приблизних досліджень) that the rate of chemical reactions doubles for every 10 °C temperature rise is a common misconception. This may have been generalized from the special case of biological systems, where the Q_{10} (temperature coefficient) is often between 1.5 and 2.5.

The **temperature coefficient of the reaction rate (γ)** is a number showing how many times the rate of a given reaction grows when the temperature of the system increases by 10 degrees. This relation quantitatively describes **van't Hoff's** equation:

$$v_{t_2} = v_{t_1} \cdot \gamma^{\frac{t_2 - t_1}{10}}$$

where v_{t_2}, v_{t_1} – rate of reaction at temperature t_1 and t_2 correspondently;

γ - temperature coefficient.

For example, coal burns in a fireplace in the presence of oxygen but it doesn't when it is stored at room temperature. The reaction is spontaneous at low and high temperatures but at room temperature its rate is so slow that it is negligible. The increase in temperature, as created by a match, allows the reaction to start and then it heats itself, because it is exothermic. That is valid for many other fuels, such as methane, butane, hydrogen...

Reaction rates can be independent of temperature (*no-Arrhenius*) or decrease with increasing temperature (*anti-Arrhenius*). Reactions without an activation barrier (e.g. some radical reactions), tend to have anti Arrhenius temperature dependence: the rate constant decreases with increasing temperature.

Example. To determine the change of rate for direct reaction

$3 H_2 + N_2 \leftrightarrow 2 NH_3$,
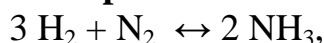
if temperature of reaction medium was increased from 200 till 250ºC and temperature coefficient $\gamma=2$.

Solution. According to the van't Hoff's equation, the rates of reaction are expressed as:

$$v_{t_2} = v_{t_1} \cdot \gamma^{\frac{t_2 - t_1}{10}} = v_{t_1} \cdot \gamma^{\frac{250 - 200}{10}} = v_{t_1} \cdot 2^5;$$

$$v_{t_2} / v_{t_1} = 2^5 = 32 \text{ times.}$$

Answer:

The rate of reaction $3 H_2 + N_2 \leftrightarrow 2 NH_3$ increased in 32 times after increasing of the temperature from 200 till 250ºC at temperature coefficient $\gamma=2$.

8.2.5 Catalysts

A **catalyst** is a substance that accelerates the rate of a chemical reaction but remains chemically unchanged afterwards. The catalyst increases rate reaction by providing a different reaction mechanism to occur with lower activation energy. Generic potential energy diagram shows the effect of a catalyst in a hypothetical endothermic chemical reaction. The presence of the catalyst opens a different reaction pathway (shown as dot line, fig. 5) with lower activation energy. The final result and the overall thermodynamics are the same.

A catalyst lowers the activation energy of the forward and the reverse reaction by the same amount. A catalyst does not affect the position of the equilibrium, as the catalyst speeds up the backward and forward

reactions equally. Hence, it follows that a catalyst accelerates both the forward and the reverse reaction the same number of times.
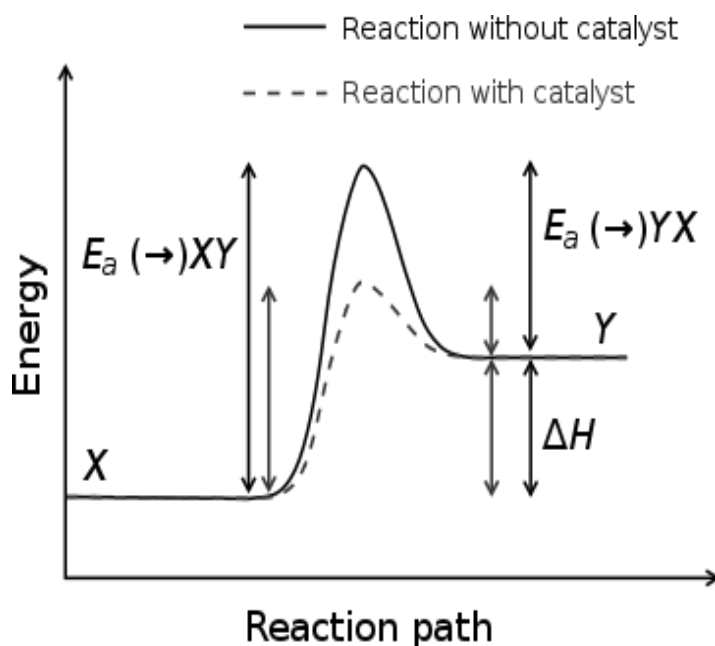

Fig. 5. Potential energy diagram

In autocatalysis a reaction product is itself a catalyst for that reaction leading to positive feedback. Proteins that act as catalysts in biochemical reactions are called **enzymes**. In certain organic molecules specific substituents can have an influence on reaction rate in neighboring group participation.

Homogeneous catalysis and **heterogeneous** catalysis are distinguished.

In homogeneous catalysis, the catalyst and the reactants form a single phase (a gas or solution). In heterogeneous catalysis, the catalyst forms an independent phase.

Heterogeneous catalysis is in great favor in the chemical industry. Examples of heterogeneous catalytic reactions are the oxidation of sulfur dioxide into the trioxide in the contact method of producing sulfuric acid, the synthesis of ammonia, and the oxidation of ammonia in the production of nitric acid. In heterogeneous catalysis, the reaction proceeds on the surface of the catalyst. It thus follows that the activity of a catalyst depends on the size and properties of its surface. As in homogeneous catalysis, in heterogeneous catalysis a reaction proceeds via active intermediate compounds (intermediates). But here, these intermediates are surface compounds of the catalyst with the reactants.

Example of the homogeneous catalytic reaction is the transformation of ozone in molecular oxygen:

Uncatalyzed Reaction:
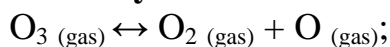
$O_{3\ (gas)} \leftrightarrow O_{2\ (gas)} + O_{(gas)}$;

$O_{(gas)} + O_{3\ (gas)} \leftrightarrow 2\ O_{2\ (gas)}$. The catalyst of this reaction is chlorine Cl_2. In presence of this gas (the same phase as reactants) the mechanism of interaction includes two stages (fig. 6):
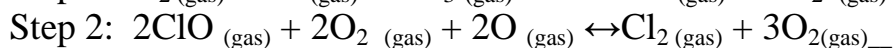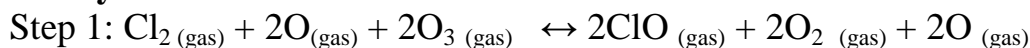
Catalyzed Reaction:

Step 1: $Cl_{2\ (gas)} + 2O_{(gas)} + 2O_{3\ (gas)} \leftrightarrow 2ClO_{(gas)} + 2O_{2\ (gas)} + 2O_{(gas)}$

Step 2: $2ClO_{(gas)} + 2O_{2\ (gas)} + 2O_{(gas)} \leftrightarrow Cl_{2\ (gas)} + 3O_{2(gas)}$

_____

Overall reaction: $2\ O_{3\ (gas)} + O_{(gas)} \leftrightarrow 2\ O_{2\ (gas)}$
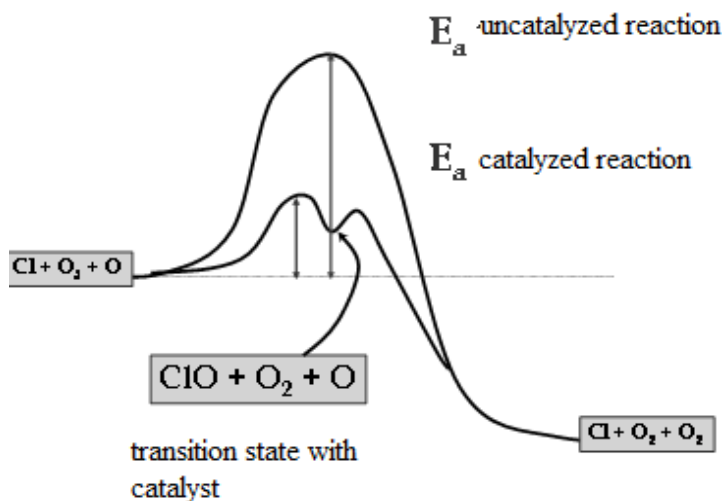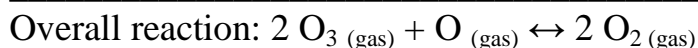
Fig. 6. Pathway of uncatalized and catalyzed reactions with formation of transition compounds with the catalyst

8.2.6 Pressure

Increasing the pressure in a gaseous reaction will increase the number of collisions between reactants, increasing the rate of reaction. This is because the activity (or, in general, concentration) of a gas is directly proportional to the partial pressure of the gas. This is similar to the effect of increasing the concentration of a solution. The rate of gaseous reactions increases with pressure, which is, in fact, equivalent to an increase in concentration of the gas. For condensed-phase reactions, the pressure dependence is weak.

Example. To determine the change of rate for direct reaction

$3\ H_2 + N_2 \leftrightarrow 2\ NH_3$,
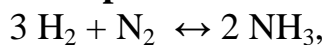
if pressure in this system was increased in 3 times.

Solution. According to the previous concept of collision, change of pressure for gaseous system is equal to change of concentration. So, starting rate was expressed as:

$v = k [H_2]^3 \cdot [N_2]$.

After increasing of pressure in three times:

$v' = k [3 \cdot H_2]^3 \cdot [3 \cdot N_2] = k \ 3^3 \cdot [H_2]^3 \cdot 3 \cdot [N_2] = k \cdot 3^4 \cdot [H_2]^3 \cdot [N_2] = k \cdot 81 \cdot [H_2]^3 \cdot [N_2]$.

So,

$v'/v = k \cdot 81 \cdot [H_2]^3 \cdot [N_2]/ k [H_2]^3 \cdot [N_2] = 81$ times.

Answer:

The rate of reaction $3 H_2 + N_2 \leftrightarrow 2 NH_3$ increased in 81 times after increasing of pressure in three times.

8.2.7 Other factors

Solvent: Many reactions take place in solution and the properties of the solvent affect the reaction rate. The ionic strength also has an effect on reaction rate.

Electromagnetic Radiation and *Intensity of light*: Electromagnetic radiation is a form of energy. As such, it may speed up the rate or even make a reaction spontaneous as it provides the particles of the reactants with more energy. This energy is in one way or another stored in the reacting particles (it may break bonds, promote molecules to electronically or vibrationally excited states...) creating intermediate species that react easily. As the intensity of light increases, the particles absorb more energy and hence the rate of reaction increases.

Isotopes: The kinetic isotope effect consists in a different reaction rate for the same molecule if it has different isotopes, usually hydrogen isotopes, because of the mass difference between hydrogen and deuterium.

Surface Area: In reactions on surfaces, which take place for example during heterogeneous catalysis, the rate of reaction increases as the surface area does increased. That is due to the fact that more particles of the solid are exposed and can be hit by reactant molecules.

Stirring: Stirring can have a strong effect on the rate of reaction for heterogeneous reactions. Agitating or mixing a solution will also accelerate the rate of a chemical reaction, as this gives the particles greater kinetic energy, increasing the number of collisions between reactants and therefore the possibility of successful collisions.

8.3 Chemical equilibrium

8.3.1 Irreversible and Reversible Reactions

Irreversible reaction proceeds to the end - until one of the reactants is completely used up. A good example of this might be burning some organic compounds or, for example, paper. The reaction proceeds until all of either one of the reactants is used up and then it stops. You cannot make the reaction run in reverse. Reversible reactions do not proceed to the end. In these reactions, none of the reactants is used up completely. Let us consider example. The synthesis of ammonia proceeds according to the equation: $N_2 + 3H_2 \leftrightarrow 2NH_3$. If we mix one mole of nitrogen with three moles of hydrogen, provide conditions favorable for the reaction to proceed in the system, and analyze the gas mixture after sufficient time elapses, the results of the analysis will show that the system contains not only the product (ammonia), but also the reactants (nitrogen and hydrogen). Thus, the synthesis of ammonia is a reversible reaction.

In equations of reversible reactions, the **equal** sign may be replaced with **arrows**. They indicate that the reaction proceeds both in the forward and in the reverse direction.

Fig. 7 shows how the rates of the forward and reverse reactions change with time. First, when the reactants are mixed, the rate of the forward reaction is high, while that of the reverse reaction is zero. As the reaction goes on, the reactants are used up, and their concentrations diminish. Simultaneously, the products appear, and their concentration grows. This causes the reverse reaction to begin, its rate gradually increasing. When the rates of the forward and reverse reactions become the same, **chemical equilibrium** sets in.
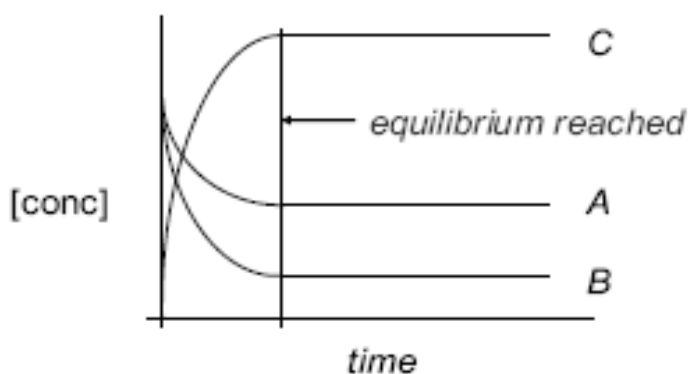
Fig. 7. Chemical equilibrium in progress

8.3.2 Equilibrium constant

Chemical equilibrium is characterized quantitatively by a change in rate of the forward (v_1) and reverse (v_2) reactions with time (t) quantity known as the **chemical equilibrium constant K.**

Let us consider it taking as an example the synthesis of hydrogen iodide: According to the law of mass action, the rates of the forward (v_1) and reverse (v_2) reactions are expressed by the equations:

$$H_{2(gas)} + I_{2(gas)} \leftrightarrow 2\ HI_{(gas)}$$
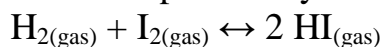
$v_1 = k_1[H_2][I_2]$

$v_2 = k_2[HI]^2$

At equilibrium, the rates of the forward and reverse reactions are equal, whence

$k_1[H_2][I_2] = k_2[HI]^2$

The ratio of the rate constants of the forward and reverse reactions is also a constant. It is called the **equilibrium constant** (**K**) of a given reaction:

$[HI]^2/[H_2][I_2] = k_2/k_1 = K$

The left-hand side of this equation contains the concentrations of the reacting substances that set in at equilibrium—the **equilibrium concentrations**. The right-hand side of the equation is a constant (at a constant temperature) quantity.

It can be shown that in the general case of a reversible reaction:

$A + B \leftrightarrow Y + Z$
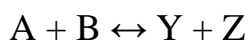
the equilibrium constant will be expressed by the equation:

$$K_{eq} = \frac{[Y]^y \cdot [Z]^z}{[A]^a \cdot [B]^b},$$

There the capital letters stand for the formulas of substances, and the small ones for the coefficients in the equation. Note, that the quantities [Y], [Z], [A], [B] in the expression for K_{eq} represent concentrations (e.g., number of moles/L, ppm, g/L, etc), not masses (e.g., grams, liters, etc).

Example. Using the following equation, calculate the equilibrium constant,

$3\ H_{2\ (gas)} + N_{2\ (gas)} \leftrightarrow 2\ NH_{3\ (gas)}$,
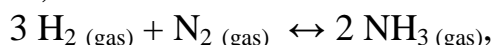
if a one-liter vessel contains 1,60 moles NH_3, 0,800 moles N_2, and 1,20 moles of H_2.

Solution:

$$K_{eq} = \frac{[1,60]^2}{[0,800]^2 \cdot [1,20]^3} = 1,85.$$

Answer: $K_{eq} = 1,85$.

Example "Start, change, equilibrium" problem:

Reaction of interaction: $C_2H_{6\ (gas)} + Cl_{2\ (gas)} \leftrightarrow C_2H_5Cl_{(solid)} + HCl_{(gas)}$
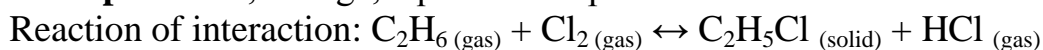
If we had six moles of $C_2H_{6\ (gas)}$ and six (6) moles of $Cl_{2\ (gas)}$ originally in a three (3) liter container at 10°C, determine the equilibrium concentration. K for this reaction at 10° C is 0.10.

Answer:

1. We must first convert our values to molarity: 6 moles/3 L= 2 M.

2. Fill in the "start, change, equilibrium" chart:

	C_2H_6 (gas)	Cl_{2} (gas)	C_2H_2Cl (solid)	HCl (gas)
Start:	2 M	2 M	-	0 M
Change:	- x	- x	-	+ x
Equilibrium:	2 - x	2 - x	-	x

3. Now substitute what we know into the equilibrium constant expression and solve for x:

$$K_{eq} = \frac{[HCl]}{[C_2H_2] \cdot [Cl_2]} = 0{,}10 = \frac{(x)}{(2 - x) \cdot (2 - x)} = \frac{x}{4 - 4x + x^2} \; ;$$

$$0{,}40 - 0{,}40x + 0{,}1x^2 = x;$$

$$0{,}10x^2 - 1{,}4x + 0{,}4 = 0;$$

$$x = \frac{0{,}40 \pm \sqrt{1{,}96 - 0{,}16}}{0{,}20} = 0{,}29.$$

4. Using the above table, we can find the equilibrium concentrations:

$$[C_2H_6] = 2 - 0{,}29 = 1{,}71 \text{ M};$$

$$[Cl_2] = 2 - 0{,}29 = 1{,}71 \text{ M};$$

$$[HCl] = 0{,}29 \text{ M}.$$

The equation of the equilibrium constant shows that in conditions of equilibrium, the concentrations of all the substances, participating in a reaction, are related to one another. A change in the concentration of any of these substances leads to changes in the concentrations of all the other substances. As a result, new concentrations are established, but the relationship between them again corresponds to the equilibrium constant.

The equilibrium constant depends on two factors:

- The nature of the reacting substances;
- On the temperature.

It doesn't depend on the presence of catalysts. We have already mentioned that the equilibrium constant equals the ratio of the rate constants of the forward and reverse reactions. Since a catalyst changes the activation energy of both the forward and reverse reactions by the same amount, it does not affect the ratio of their rate constants. Therefore, a catalyst doesn't affect the value of the equilibrium constant.

8.3.3 Displacement of Chemical Equilibrium. Henri Le Châtelier's Principle

In 1888, Le Châtelier gave a statement of the principle that bears his name now. Two examples of modern definitions are:

If any change of conditions is imposed on a system in equilibrium, the system will alter in such a way to counteract the imposed change.

Or:

If a system at equilibrium is subjected to stress, the equilibrium will shift in attempt to reduce the stress.

Of the greatest significance are cases of shifting of equilibrium owing to a change in the concentration of any of the substances participating in equilibrium, in the pressure or temperature.

- *Displacement of equilibrium Owing to a Change in the Concentration of One of the Substances Participating in the Reaction.*

When the concentration of one of the substances participating in equilibrium increases, the equilibrium shifts in the direction of consumption of this substance, when the concentration of one of the substances decreases, the equilibrium shifts in the direction of the formation of this substance.

The following table contains several examples showing how changing the quantity of a reaction component can shift an established equilibrium.

System	Change	Result
$CO_{2 (gas)} + H_{2 (gas)} \leftrightarrow H_2O_{(gas)} + CO_{(gas)}$	A drying agent is added to absorb H_2O	Shift to the right. Continuous removal of a product will force any reaction to the right
$H_{2(gas)} + I_{2(gas)} \leftrightarrow 2HI_{(gas)}$	Some nitrogen gas is added	No change; N_2 is not a component of this reaction system.

$NaCl_{(solid)} + H_2SO_{4(liquid)} \leftrightarrow Na_2SO_{4(solid)}+HCl_{(gas)}$	Reaction is carried out in an open container	Because HCl is a gas that can escape from the system, the reaction is forced to the right. This is the basis for the commercial production of hydrochloric acid.
$H_2O_{(liquid)} \leftrightarrow H_2O_{(gas)}$	Water evaporates from an open container	Continuous removal of water vapor forces the reaction to the right, so equilibrium is never achieved.
$HCN_{(aq)} \leftrightarrow H^+_{(aq)}+CN^-_{(aq)}$	The solution is diluted	Shift to right; the product $[H^+][CN^-]$ diminishes more rapidly than does [HCN].
$AgCl_{(solid)} \leftrightarrow Ag^+_{(aq)} + Cl^-_{(aq)}$	some NaCl is added to the solution	Shift to left due to increase in Cl^- concentration. This is known as the common ion effect on solubility.
$N_{2(gas)}+3H_{2(gas)} \leftrightarrow 2NH_{3(gas)}$	a catalyst is added to speed up this reaction	No change. Catalysts affect only the rate of a reaction; the have no effect at all on the composition of the equilibrium state.

Example involving change of concentration - in the equation

$$2NO_{(gas)} + O_{2(gas)} \leftrightarrow 2NO_{2(gas)}$$
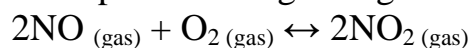
If you add more $NO_{(gas)}$ the equilibrium shifts to the right producing more $NO_{2(gas)}$;

If you add more $O_{2(gas)}$ the equilibrium shifts to the right producing more $NO_{2(gas)}$;

If you add more $NO_{2(gas)}$ the equilibrium shifts to the left producing more $NO_{(gas)}$ and $O_{2(gas)}$.

Example. To determine the direction of equilibrium shifting in reaction

$$CH_{4(gas)} + H_2O_{(vapor)} \leftrightarrow CO_{(gas)} + 3H_{2(gas)},$$
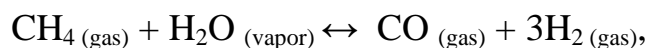
If:

- Increasing of CH_4 concentration – to right;
- Decreasing of H_2O concentration – to left;

- Increasing of H_2 concentration – to left;
- Decreasing of CO concentration – to right.

- **_Displacement of equilibrium owing to a change in pressure._**

When the pressure is increased by compressing a system, equilibrium shifts in the direction of a reduction in the number of molecules of the gases, i.e. in the direction of lowering of the pressure; when the pressure is lowered, equilibrium shifts in the direction of growth in the number of molecules of the gases, i.e. in the direction of an increase in the pressure. In the equation

$$2SO_{2\,(gas)} + O_{2\,(gas)} \leftrightarrow 2SO_{3(\,gas)},$$
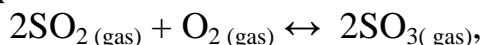
an increase in pressure will cause the reaction to shift in the direction that reduces pressure, that is the side with the fewer number of gas molecules. Therefore an increase in pressure will cause a shift to the right, producing more products (a decrease in volume is one way of increasing pressure).

Example. To determine the direction of equilibrium shifting in reaction

$$CH_{4\,(gas)} + H_2O_{\,(vapor)} \leftrightarrow CO_{\,(gas)} + 3H_{2\,(gas)},$$
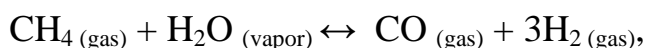
if pressure in this system increased.

Solution. Direct reaction accompanies by the increasing of system volume, because 2 moles of gases (1 mol CH_4 + 1 mol H_2O) transforms in 4 moles of gases (1 mol CO + 3 moles H_2). So, forward reaction results to increasing of pressure in this system, while reverse reaction – to decreasing of one. If outer pressure was increased, the equilibrium of this reaction shifted to left, because reverse reaction accompanies by the decreasing of pressure in this system.

- **_Displacement of equilibrium Owing to a Change in Temperature._**

The equilibrium of the overwhelming majority of chemical reactions shifts when the temperature changes. The factor determining the direction of equilibrium displacement is the sign of the heat effect of the reaction. It can be shown that upon elevation of the temperature, equilibrium shifts in the direction of the endothermic (+Q), and upon its lowering—in the direction of the exothermic reaction (-Q).

Indeed, when one of the substances participating in a reaction is introduced into the system, equilibrium shifts in the direction of consuming this substance. If the pressure is increased, it shifts so as to lower the pressure in the system; if the temperature is elevated, equilibrium shifts in the direction of the endothermic reaction— the temperature in the system drops. In the equation

$N_{2 (gas)} + 3H_{2 (gas)} \leftrightarrow 2NH_{3 (gas)} + 91,8$ kJ,
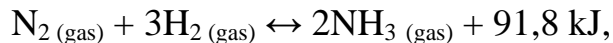
an increase in temperature will cause a shift to the left because the reverse reaction uses the excess heat. An increase in forward reaction would produce even more heat since the forward reaction is exothermic. Therefore the shift caused by a change in temperature depends upon whether the reaction is exothermic or endothermic.

The synthesis of ammonia, for instance, is an exothermic reaction. Hence, upon elevation of the temperature, equilibrium in the system H_2-N_2-NH_3 shifts to the left - in the direction of decomposition of ammonia, because this process goes on with the absorption of heat.

Conversely, the synthesis of nitrogen monoxide NO is an endothermic reaction:

$N_{2 (gas)} + O_{2 (gas)} \leftrightarrow 2$ NO $_{(gas)} - 45,8$ kJ.
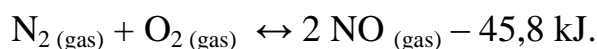
Therefore, decreasing of the temperature is attended by shifting of equilibrium in the system N_2-O_2-NO to the right, in the direction of formation of NO.

- ***The le Châtelier principle in physiology: oxygen transport and carbon monoxide poisoning.***

Many of the chemical reactions that occur in living organisms are regulated through the le Châtelier principle. Few of these are more important to warm-blooded organisms than those that relate to aerobic respiration, in which oxygen is transported to the cells where it is combined with glucose and metabolized to carbon dioxide, which then moves back to the lungs from which it is expelled.

hemoglobin + $O_2 \leftrightarrow$ oxyhemoglobin
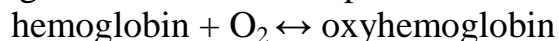
The partial pressure of O_2 in the air is 0,2 atm, sufficient to allow these molecules to be taken up by hemoglobin (the red pigment of blood) in which it becomes loosely bound in a complex known as oxyhemoglobin. At the ends of the capillaries which deliver the blood to the tissues, the O_2 concentration is reduced by about 50% owing to its consumption by the cells. This shifts the equilibrium to the left, releasing the oxygen so it can diffuse into the cells.

Carbon dioxide reacts with water to form a weak acid H_2CO_3 which would cause the blood pH to fall to dangerous levels if it were not promptly removed as it is excreted by the cells. This is accomplished by combining it with carbonate ion through the reaction

$H_2CO_3 + CO_3^{2-} \leftrightarrow 2$ HCO$_3^-$
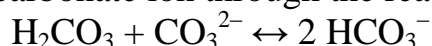
which is forced to the right by the high local CO_2 concentration within the tissues. Once the hydrogen carbonate (bicarbonate) ions reach the lung tissues where the CO_2 partial pressure is much smaller, the reaction reverses and the CO_2 is expelled.

Carbon monoxide poisoning. Carbon monoxide, a product of incomplete combustion that is present in automotive exhaust and cigarette smoke, binds to hemoglobin 200 times more tightly than does O_2. This blocks the uptake and transport of oxygen by setting up a competing equilibrium

O_2-hemoglobin ↔ hemoglobin ↔ CO-hemoglobin.

Air that contains as little as 0,1 percent carbon monoxide can tie up about half of the hemoglobin binding sites, reducing the amount of O_2 reaching the tissues to fatal levels. Carbon monoxide poisoning is treated by administration of pure O_2 which promotes the shift of the above equilibrium to the left. This can be made even more effective by placing the victim in a hyperbaric chamber in which the pressure of O_2 can be made greater than 1 atm.

CHAPTER 9 REDUCTION-OXIDATION PROCESSES

9.1 Oxidation numbers

Charges are either real in ions or "imaginary" in covalent compounds (molecules):

LiF Li $^{+1}$ F $^{-1}$ real charge Li$^+$ F$^-$

HF H $^{+1}$ F $^{-1}$ "imaginary" charge

Oxidation number provides a way of keeping track of transfer or unequal sharing of electrons. More electronegative atom in bonded pair has the negative oxidation number as if it has an extra electron.

Rules to assign Oxidation number:

1. *Sum of oxidation numbers add up to charge of species (ion or molecule):*

For example, $H_2S = 2(H) + (S) = 0$ Na+ = (+1) Al = (0) Al^{3+} = (+3)

2. Neutral uncombined atom or atom in pure element is assigned 0.

For example, Cl_2 (0) and Na (0), but in ion with actual charge that is the oxidation number: for example, NaCl made of ions Cl$^-$ and Na$^+$ then Cl (-1) Na (+1)

3. *Oxidation number of more electronegative is negative and equal to common charge of monatomic ion.*

For example, PCl_3 – where (P) + 3 (Cl) = 0 and (Cl) = -1 since it is more electronegative and its charge is -1.

Note: The electronegative (EN) trend of the periodic table is greater EN as you go up and to the right on the periodic table with fluorine having the highest EN. Ignore the noble gases completely – no EN (see Appendix 1).

Order of Selection (when dealing with a compound)

1. Range of oxidation number possible for an atom;
2. Highest oxidation number for family is Roman numeral group number (or second digit of modern group number);
3. Lowest oxidation number for a family is charge of monatomic ion. For example, Sulfur group **VI**A or 1**6** so highest is +6 and lowest oxidation number is charge on S^{-2}. Sodium in group IA so highest is +1 and charge is +1 so lowest and highest same +1.

Valency and oxidation number are different notions. Valency bases into physical concept – quantity of chemical bonds formed by one atom with others, when oxidation number is abstract value, introduced for mathematical approach to balancing of Redox processes. For example, valency of Oxygen is II in water H_2O and Hydrogen peroxide H_2O_2

(according to quantity of bonds: H-O-H and H-O-O-H), but oxidations numbers are -2 and -1 correspondently.

Table 1. Guidelines for assigning Oxidation Numbers

	Oxidation number	Examples	Exceptions
Free element	0	The oxidation number for each atom is Zn, H_2 and S_8 is zero.	none
Monatomic ions	Charge on ion	Cd in $CdCl_2$ is +2; Cl in $CdCl_2$ is -1; H is LiH is -1.	none
Fluorine in the combined form	-1	F in AlF_3 is -1; F in CF_4 is -1;	none
Oxygen in the combined form	-2	O in ZnO is -2; O in H_2O is -2.	O is -1 in peroxides, such as H_2O_2
Hydrogen in the combined form	+1	H in H_2O is +1.	H is -1 when combined with metals – LiH, KH.

9.2 Basic concepts of redox processes
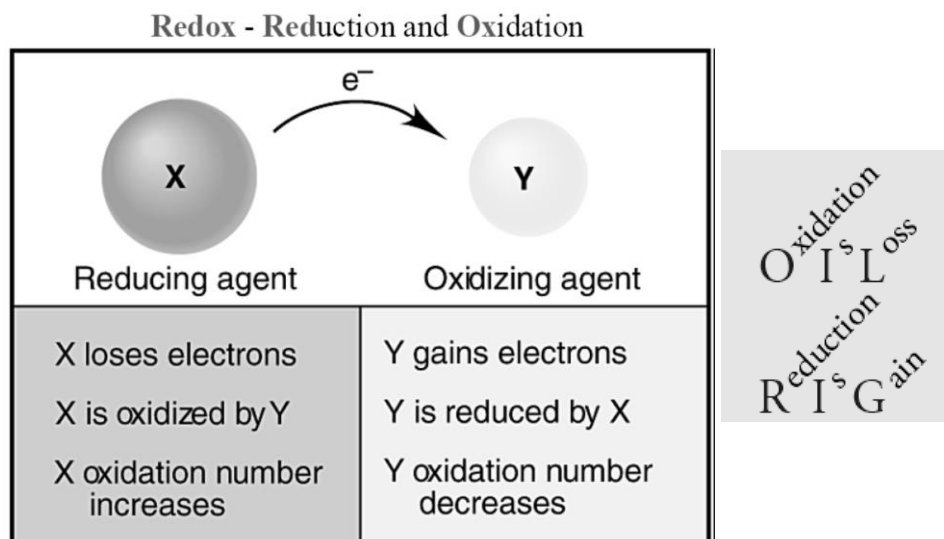
Fig. 8. Concepts of Redox processes

Reactions as a result of which the oxidation numbers of elements change are called *oxidation-reduction (Redox) reactions*.

Reduction: atom decreases oxidation number.

Oxidation: atom increases oxidation number.

Reduction is gain of electrons (real or "imaginary"); gain make oxidation numbers decrease since gaining negative electrons with -1 charge.

Oxidation is loss of electrons, losing make oxidation numbers increase since electron loss is equals to adding +1charge.

In engineering, the significance of Redox reactions is also very great. For example, the entire metallurgical industry is based on oxidation-reduction processes during which metals are recovered from natural compounds.

Oxidation-reduction reactions are of very great importance in biological systems. Photosynthesis, breathing, digestion - all these are chains of oxidation-reduction reactions. For example, a diverse variety of copper-containing metalloenzymes occur in plants and animals. They are utilized for electron transfer (azurin, plastocyanin, laccase), for oxygenation reactions (tyrosinase, ascorbate oxidase), and for oxygen transport (hemocyanin). Most biologically active copper centers are found in proteins outside cells or in vesicles. The enzyme superoxide dismutase is found in the cytosol as well as within cells. Copper ions normally are ligated by nitrogen ligands or by a combination of nitrogen and sulfur donors. Copper-containing metalloproteins and enzymes may contain Cu(I) (the last occupied electron sublevel has structure d^{10}), Cu(II) (d^9), and Cu(III) (d^8) ions. In aqueous solution, copper ions disproportionate according to reactions:

$$Cu^+_{(aq)} + e^- \rightarrow Cu^0;$$
$$Cu^{2+}_{(aq)} + e^- \rightarrow Cu^+;$$
$$2Cu^+_{(aq)} \rightarrow Cu^0_{(solid)} + Cu^{2+}_{(aq)}.$$
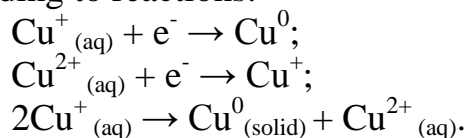
Azurin is a small, 128-residue, copper-containing metalloenzyme involved in electron transfer in photosynthetic pathways and respiratory systems of biological organisms. Its physiological Redox partners are cytochrome c55 and nitrite reductase. As a blue copper protein, it exhibits a large extinction coefficient in the visible spectrum around 600 nm. To facilitate electron transfer and cycling between Cu(II) and Cu(I), the copper coordination environment exists as a compromise between those preferred by the two oxidation states.

A simple example of an Redox process is the reaction of formation of an ionic compound from elementary substances, for example, the reaction of sodium with chlorine: $2Na + Cl_2 = 2NaCl$. This reaction, like any heterogeneous one, proceeds in several steps. In one of them, the sodium atoms transform into positively charged ions; the oxidation number of sodium changes from 0 to +1. Hence, in the reaction considered above, the sodium is oxidized, and the chlorine is reduced. Consequently, in the

above example, sodium is a reducing agent, and chlorine an oxidizing one. Inspection of the Redox equations shows that one molecule of chlorine when reduced gains two electrons, while the oxidation of one sodium atom is attended by the loss of one electron. The total number of electrons in a system in chemical reactions doesn't change: *the number of electrons lost by the molecules (atoms, ions) of the reducing agent equals the number of electrons gained by the molecules (atoms, ions) of the oxidizing agent.* Therefore, one molecule of chlorine can oxidize two sodium atoms.

9.3 Compiling equations of redox processes

When faced with a Redox reaction, sadly, you can't rely on the atoms and molecules alone to guide you in balancing. There will often be multiple solutions that appear to be right, yet don't reflect chemical reality. To make sure that you get the balancing right, you have to look at the electrons as well. That makes sense, as a Redox reaction is one where electrons are transferred as a part of the reaction.

The simplest example of Redox reaction balancing is presented by equations with known products.

Example 1.
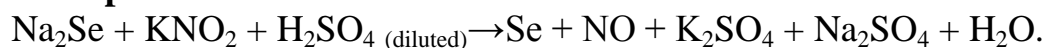
$Na_2Se + KNO_2 + H_2SO_4$ (diluted)$\rightarrow Se + NO + K_2SO_4 + Na_2SO_4 + H_2O$.

The 1st step: to determine oxidation numbers of every atom of compounds separately, using rules presented in the previous section:

Na$_2$Se: Na – an alkali metal, in compounds has only +1 oxidation number. Basing into principle of neutrality, two atoms of sodium have sum charge +2, so Se is -2.

KNO$_2$: K – alkali metal, in compounds, like Na, has only +1 oxidation number; oxygen O in the most compounds (excluding OF$_2$ and peroxides H$_2$O$_2$, Na$_2$O$_2$ etc) has -2 oxidation number. So, one atom of potassium has +1 charge, two atoms of oxygen – in sum -4, nitrogen N is +3.

H$_2$SO$_4$: In much the same way, hydrogen H has +1 charge in compounds (excluded hydrides – compounds with alkali and alkali-earth metals LiH^{-1}, CaH$_2^{-1}$ etc), oxygen is -2 charge, and sulfur S must be +6.

Se: any chemical element in the free state has 0 oxidation number.

NO: This compound is oxide, and oxygen has -2, therefore nitrogen is +2 oxidation number.

K$_2$SO$_4$: In much the same way, K^+, O^{-2}, S^{+6};

Na$_2$SO$_4$: By analogy, Na^+, O^{-2}, S^{+6};

H$_2$O: Similarly to previous compounds, hydrogen H has +1 charge, oxygen has -2.

So, in general:

$$Na^+_2Se^{-2} + K^+N^{+3}O^{-2}_2 + H^+_2S^{+6}O^{-2}_{4 \text{ (diluted)}} \rightarrow$$
$$\rightarrow Se^0 + N^{+2}O^{-2} + K^+_2S^{+6}O^{-2}_4 + Na^+_2S^{+6}O^{-2}_4 + H^+_2O^{-2}.$$
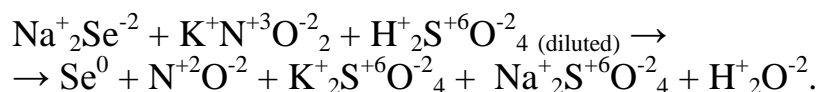
The 2-d step: to determine atoms of chemical elements changed oxidations numbers during the reaction:

Chemical element	Before reaction	After reaction	Conclusion
Na	+1	+1	No change
Se	-2	0	Changed
K	+1	+1	No change
N	+3	+ 2	Changed
O	-2	-2	No change
H	+1	+1	No change
S	+6	+6	No change

So, the next atoms changed their oxidation numbers:

$Se^{-2} \rightarrow Se^0$;

$N^{+3} \rightarrow N^{+2}$.
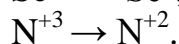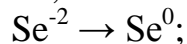
The 3-d step: to determine the quantity of electrons transferred in Redox processes. The next scale (see Fig. 9) may be useful for this purpose:
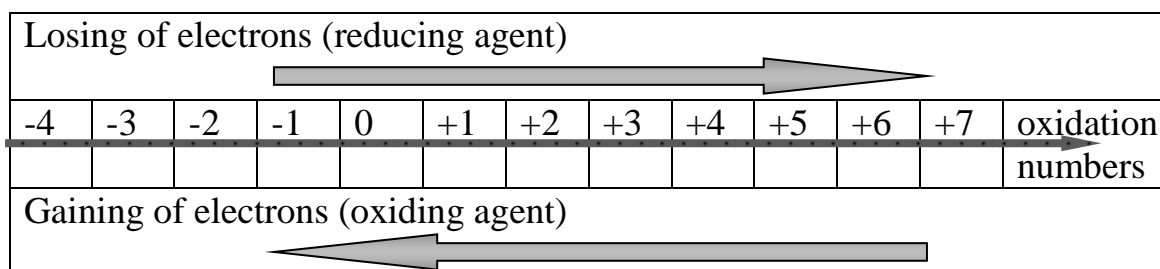
Fig. 9. Scale of oxidation numbers and direction of oxiding and reducing processes

According to this scale, atom of sulfur lost 2 electrons, while nitrogen gained 1 electron:

$Se^{-2} - 2\,\overline{e} \rightarrow Se^0$;

$N^{+3} + 1\,\overline{e} \rightarrow N^{+2}$.
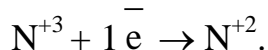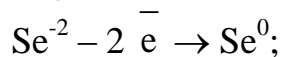
According to the Law of mass conservation, the quantities of electrons, transferring in the Redox processes, must be balanced, using coefficients. Such procedure is named "electron balance":

$Se^{-2} - 2\,\overline{e} \rightarrow Se^0$	1	(oxidation, reducing agent)
$N^{+3} + 1\,\overline{e} \rightarrow N^{+2}$	2	(reduction, oxiding agent)
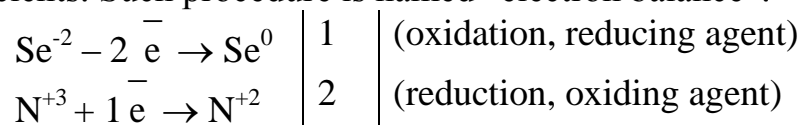
Figures 1 and 2 in the second column mean that it is needed to use 1 atom of Selenium, losing 2 electrons, and 2 atoms of Nitrogen, gaining together 2 electrons.

The 4-th step: to balance quantities of atoms changed oxidation numbers, transports coefficients from electron balance to the equation:

$Na_2Se + $ **2** $KNO_2 + H_2SO_{4 \text{ (diluted)}} \rightarrow$

$\rightarrow Se + $ **2** $NO + K_2SO_4 + Na_2SO_4 + H_2O.$
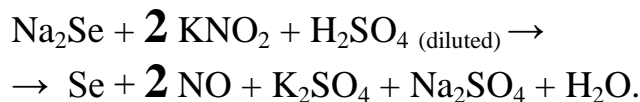
The 5-th step: to balance quantities of elements, don't changed oxidation numbers in the next order:

- Metal ions;
- Acidic residues;
- Hydrogen;
- Control of balancing is made calculating quantities of oxygen before and after reaction. If all previous stages were made correct, oxygen is balanced automatically in the most cases.

So, for proposed above equation:

$Na_2Se + 2 KNO_2 + H_2SO_{4 \text{ (diluted)}} \rightarrow$

$\rightarrow Se + 2 NO + K_2SO_4 + Na_2SO_4 + H_2O.$
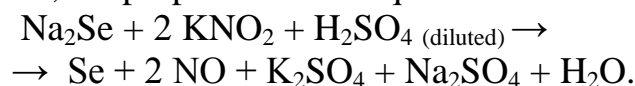
Metal ions: two atoms of sodium Na before and after reaction; two atoms of potassium K before and after reaction, it's OK;

Acidic residues: one SO_4 group – before reaction in the composition of H_2SO_4, but two SO_4 groups – after reaction in the salts K_2SO_4 and Na_2SO_4. So, it is needed coefficient 2 before H_2SO_4:

$Na_2Se + 2KNO_2 + $ **2** $H_2SO_{4 \text{ (diluted)}} \rightarrow Se + 2 NO + K_2SO_4 + Na_2SO_4 + H_2O.$
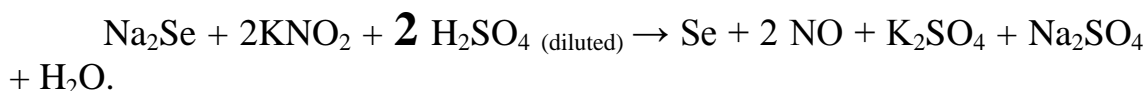
Hydrogen: four atoms of H before reaction (in composition of H_2SO_4), whereas only two atoms – after in one molecule of water. Thereby it is needed coefficient 2 near water formula:

$Na_2Se + 2KNO_2 + 2H_2SO_{4 \text{ (diluted)}} \rightarrow Se + 2NO + K_2SO_4 + Na_2SO_4 + $ **2**$H_2O.$
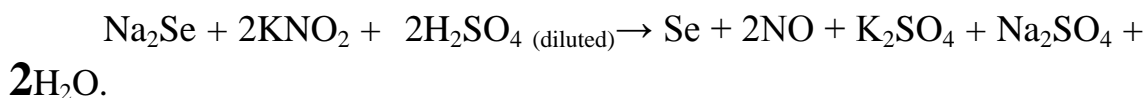
Oxygen balancing:

Before reaction: 4 atoms in 2 molecules of KNO_2 + 8 atoms in 2 molecules of H_2SO_4; overall: 12 atoms;

After reaction: 2 atoms in 2 molecules of NO + 4 atoms in molecule of K_2SO_4 + 4 atoms in molecule of Na_2SO_4 + 2 atoms in 2 molecules of H_2O; overall: 12 atoms; it's OK.

You ran into a little snag with Redox reactions without products. The mechanism of a lot reactions accompanied by change of oxidation numbers determines by a different factors, for example:

- Concentration of acids;

- Relative activity of free metals;
- Nature of acids (oxidizing or non- oxidizing character);
- Medium of reaction (alkali, neutral or acidic);
- Pressure, temperature, radiation etc.

Now it is proposed the simplest method for prediction of products for Redox processes.

Example 2. To compile the products of the next reaction and to balance it: $H_2SO_4 + HI \rightarrow$

The 1st step: to determine oxidation numbers of every atom of compounds separately, using rules presented in the previous section:

$H^+_2 S^{+6} O^{-2}_4 + H^+ I^- \rightarrow$
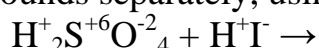
The 2-d step: to determine possible oxidation or reduction functions of every atom, basing into such principle:

Atom in **minimum** oxidation state may be only reducing agent;

Atom in **maximum** oxidation state may be only oxiding agent;

Atom in **intermediate** oxidation state may be oxiding or reducing agents depends on conditions. This step presents in the form of chart:

Atom	Possible oxidation numbers (states)*	Reducing agent	Oxiding agent	EN**
H^+	-1; 0; +1	no	yes	2,1
S^{+6}	-2, -1, 0, +2, +4, +6	no	yes	2,5
O^{-2}	-2, -1, 0, +2	yes	no	3,5
I^-	-1; 0; +1; +5	yes	no	2,5

* See Appendix 2.

** See Appendix 1.

The 3-d step: to determine oxiding and reducing agents and to compile electron balance. The basic ideas are:

- Real oxiding agent is atom with maximum EN among all possible oxiding agents;
- Real reducing agent is atom with minimum EN among all possible reducing agents.

So,

$S^{+6} + n\ \overline{e} \rightarrow$ | (reduction, oxiding agent)

$I^- - m\overline{e} \rightarrow$ | (oxidation, reducing agent)
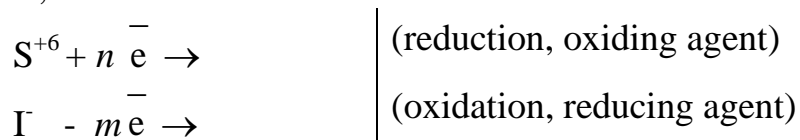
Quantities of transferring electrons (*n* and *m* in our example) are determined according to the next principles:

- Oxiding agent tends to gain maximum electrons;
- Reducing agent tends to lose minimum electrons;

- It might be well for the products are the most stable compounds of corresponded elements.

On the assumption of above-stated, the most likely outcome of this Redox processes are: sulfur transforms in S^{-2} (the lowest oxidation number, stable state) and iodine changes in free iodine I_2^0, lost the minimum electrons:

$S^{+6} + 8\,\bar{e} \rightarrow S^{-2}$	2	1	(reduction, oxiding agent)
$2\,I^- - 2\,\bar{e} \rightarrow I_2^0$	8	4	(oxidation, reducing agent)
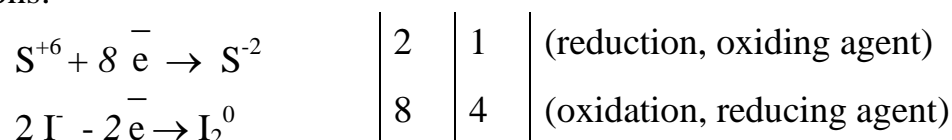
The 4-th step: to determine the chemical formulas of the products of Redox processes and elements didn't changed oxidation number.

The next principles are used:

- Element in the negative oxidation number (only non-metals) forms compound with hydrogen (general formula H_kE^{-k}) or with metals presented in starting compound or of alkali as medium;
- Element in the positive oxidation number (both non-metals and metals) forms oxides in presence of oxygen, hydroxides (only metals) or acids (only non-metals) in presence of water and salts (non-metals in the form of acidic residue – with metals presented in starting compound or in alkali as medium and metals in the form of ions – with acidic residues presented in the initial salts or of acids as medium).
- Elements in oxidation number 0 are presented in free state (for example, S^0, Cl_2, Na, O_2 etc).

According to these ideas, in our example:

S^{-2} forms compound with hydrogen H_2S; I^0 is presented in free state I_2; Oxygen O forms water H_2O.

So, general form of equation with product is:

$H_2SO_4 + HI \rightarrow I_2 + H_2S + H_2O$.
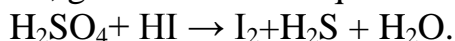
The 5-th step: to balance reaction as in example 1:

$H_2SO_4 + 8\,HI = 4\,I_2 + H_2S + 4\,H_2O$.
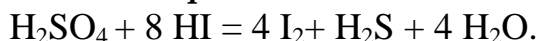
Example 3. To compile the products of the next reaction and to balance it: $Zn + KClO_3 + H_2SO_4 \rightarrow$

Like in previous example:

$Zn^0 + K^+Cl^{+5}O_3^{-2} + H_2^+S^{+6}O_4^{-2} \rightarrow$
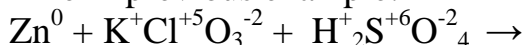
Atom	Possible oxidation numbers (states)	Reducing agent	Oxiding agent	EN
Zn^0	+0, +2	yes	no	1,6
K^+	0, +1	no	yes	0,8

Cl^{+5}	-1, 0, +1, +3, +5, +7	yes	yes	3,0
O^{-2}	-2, -1, 0, +2	yes	no	3,5
H^{+}	-1; 0; +1	no	yes	2,1
S^{+6}	-2, -1, 0, +2, +4, +6	no	yes	2,5

$$Cl^{+5} + m\overline{e} \rightarrow$$ (reduction, oxiding agent)

$$Zn^{0} - n\overline{e} \rightarrow$$ (oxidation, reducing agent)
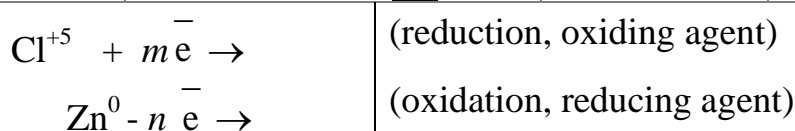
The most stable oxidation number for chlorine is -1, because this state corresponds to filled last energy level ("octet configuration" $3s^2 3p^6$). So, the most likely variant that chlorine gained 6 electrons, transforming in Cl^-. Zn being reducing agent is only +2 oxidation state after reaction:

$$Cl^{+5} + 6\overline{e} \rightarrow Cl^-$$ | 2 | 1 | (reduction, oxiding agent)

$$Zn^{0} - 2\overline{e} \rightarrow Zn^{+2}$$ | 6 | 3 | (oxidation, reducing agent)
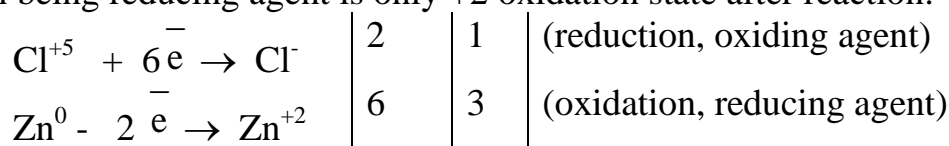
Chemical formulas of products:

Cl^- may forms hydrogen compound HCl or salt in presence of metal ions. More probably in our case that salt KCl will be formed because initial form of chlorine was presented by salt with potassium ion K^+;

Zn^{+2} is metal ion and it may forms oxide ZnO, hydroxide $Zn(OH)_2$ or salt in presence of acid or base (because zinc is amphoteric metal). More likely, Zn^{+2}, reacting with acidic medium of this mixture - H_2SO_4, forms $ZnSO_4$:

$$3\ Zn + KClO_3 + 3\ H_2SO_4 = 3\ ZnSO_4 + KCl + 3\ H_2O.$$
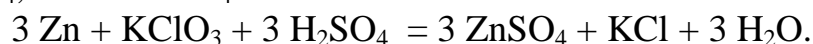
9.4 Typical oxidizing ans reduction agents

What substances can display the properties of oxidizing agents, and what - of reducing agents? We have already mentioned that an oxidizing agent contains an element whose oxidation number decreases, while a reducing agent contains an element whose oxidation number grows. Consequently, oxidizing agents will include first of all compounds with the higher, and reducing agents will include compounds with the lower oxidation numbers featuring a given element.

Metals display only a positive oxidation state in their compounds, and their minimum oxidation number is zero. In other words, they have the minimum oxidation number only in the free state. Indeed, all free metals, although to a different extent, are capable of exhibiting only reducing properties. The reducing agents used in practice include aluminium, magnesium, sodium, potassium, and zinc:

$$8\ \mathbf{Al^0} + 3\ Fe^{+8/3}_3 O_4 \xrightarrow{\ t, °C\ } 4\ \mathbf{Al^{+3}}_2 O_3 + 9\ Fe^0$$
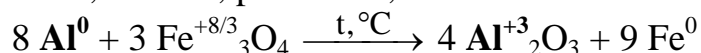
(aluminothermy method − based on reduction of metals from their oxides by free aluminium).

$$3Fe^{+8/3} + 8\,\overline{e} \rightarrow 3\,Fe^0$$

| | 6 | 3 | (reduction, oxiding agent) |

$$2\,Al^0 - 6\,\overline{e} \rightarrow 2\,Al^{+3}$$

| | 8 | 4 | (oxidation, reducing agent) |
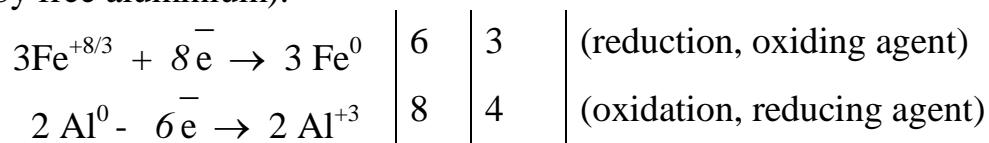
If a metal can have several oxidation numbers, those of its compounds in which it displays the lowest of them are also reducing agents, as a rule.

Examples are the compounds of iron(II), tin(II), chromium(II), and copper(I):

$$4\,\mathbf{Fe^{+2}}(OH)_2 + O^0_2 + 2H_2O = 4\,\mathbf{Fe^{+3}}(O^{-2}H)_3$$

$$O^0_2 + 4\,\overline{e} \rightarrow 2\,O^{-2}$$

| | 1 | (reduction, oxiding agent) |

$$Fe^{+2} - 1\,\overline{e} \rightarrow Fe^{+3}$$

| | 4 | (oxidation, reducing agent) |

$$\mathbf{Sn^{+2}}Cl_2 + 2\,FeCl_3 = \mathbf{Sn^{+4}}Cl_4 + 2\,FeCl_2$$

$$Fe^{+3} + 1\,\overline{e} \rightarrow Fe^{+2}$$

| | 2 | (reduction, oxiding agent) |

$$Sn^{+2} - 2\,\overline{e} \rightarrow Sn^{+4}$$

| | 1 | (oxidation, reducing agent) |
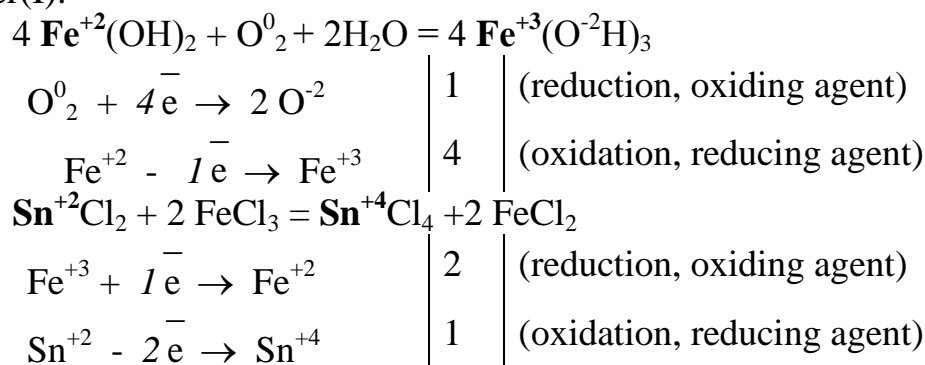
Those compounds of metals can be oxidizing agents in which the oxidation number is high and either equals the number of the group which the metal belongs to or is close to it. Practical use has been found, in particular, by an ammonia solution of silver oxide, an ammonia solution of copper(II) sulfate, mercury(II) chloride, lead (IV) oxide PbO_2, iron(III) chloride, potassium chromate and dichromate (K_2CrO_4 and $K_2Cr_2O_7$), potassium permanganate $KMnO_4$, and manganese dioxide MnO_2:

$$2\,\mathbf{Fe^{+3}}Cl_3 + Cu^0 = 2\,\mathbf{Fe^{+2}}Cl_2 + Cu^{+2}Cl_2$$

$$Fe^{+3} + 1\,\overline{e} \rightarrow Fe^{+2}$$

| | 2 | (reduction, oxiding agent) |

$$Cu^0 - 2\,\overline{e} \rightarrow Cu^{+2}$$

| | 1 | (oxidation, reducing agent) |

$$\mathbf{Mn^{+4}}O_2 + 4\,HCl = Cl^0_2 + \mathbf{Mn^{+2}}Cl_2 + 2\,H_2O$$

$$Mn^{+4} + 2\,\overline{e} \rightarrow Mn^{+2}$$

| | 2 | 1 | (reduction, oxiding agent) |

$$2\,Cl^- - 2\,\overline{e} \rightarrow Cl^0_2$$

| | 2 | 1 | (oxidation, reducing agent) |
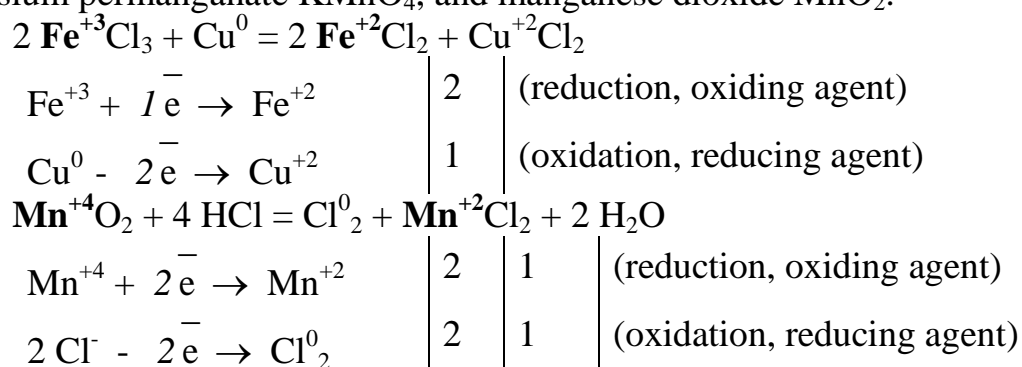
Non-metals exhibit both positive and negative oxidation states. It is natural that compounds containing non-metals in their higher positive oxidation states can be oxidizing agents, and compounds in which a non-metal displays a negative oxidation state can be reducing agents.

The most important reducing agents are hydrogen H_2, carbon C, and carbon monoxide CO.

Non-metals of the upper part of groups VI and VII of the periodic table are strong oxidizing agents. The strong oxidizing properties of these substances are explained by the high electronegativity of their atoms. Fluorine has the strongest oxidizing properties, but in practice oxygen, chlorine, and bromine are used most frequently as oxidizing agents.

The compounds used as oxidizing agents also include acids. Hydrochloric, sulfate, and nitrate acids have the greatest practical significance. The oxidizing element in hydrochloric acid is hydrogen, in nitrate acid it is nitrogen, in dilute sulfate acid - hydrogen, and in the concentrated acid - sulfur.

Nitrate acid, depending on its concentration, temperature, and the nature of the reducing agent, can be reduced to different oxidation numbers of the oxygen. Other compounds of non-metals used as oxidizing agents are hydrogen peroxide H_2O_2, the salts of acids in which the acid-forming element exhibits a high oxidation number - chlorates ($KClO_3$), perchlorates ($KClO_4$).

9.5 Applied problems connected with RedOx reactions

9.5.1 Oxiding agents and aging

In some of the normal chemical reactions that take place in the human body, strong oxidizing agents, such as hydrogen peroxide H_2O_2, are formed. These highly reactive substances cause chemical changes in cell DNA (*deoxyribonucleic acid; a nucleic acid that is the main constituent of the chromosomes of all organisms (except some viruses). The DNA molecule consists of two polynucleotide chains in the form of a double helix, containing phosphate and the sugar deoxyribose and linked by hydrogen bonds between the complementary bases adenine and thymine or cytosine and guanine. DNA is self-replicating, plays a central role in protein synthesis, and is responsible for the transmission of hereditary characteristics from parents to offspring*) that can be damaging unless the changes are reversed. Fortunately, in healthy cells, normal repair reactions occur that convert the altered DNA back to its normal form:

$$\text{Normal DNA} \xleftarrow[\text{Normal repair}]{\text{Oxiding agents (such as } H_2O_2)} \text{Altered DNA}$$
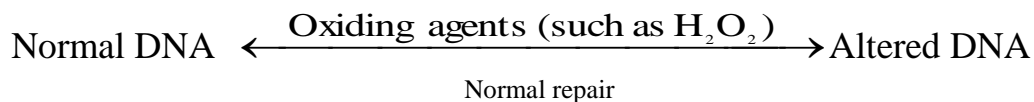
The repair mechanisms are thought to slow down with age, some medical researchers believe that this slowing down of DNA repair is connected to certain diseases associated with aging, such as cancer, heart disease, cataracts, and brain dysfunction.

$$\text{Normal DNA} \xleftrightarrow[\text{Normal repair slowed with aging}]{\text{Oxiding agents (such as } H_2O_2)} \text{Altered DNA}$$
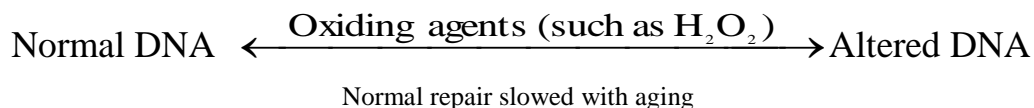
Substances called **antioxidants** that are found in food react with oxidizing agents (such as H_2O_2) and thus remove them from our system. This is believed to slow the alteration of DNA, so the slower rate of normal repair can balance it.

$$\text{Normal DNA} \xleftrightarrow[\text{Normal repair slowed with aging}]{\text{Fewer oxiding agents}} \text{Altered DNA}$$
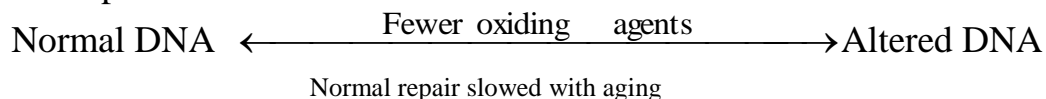
Vitamin C (or *ascorbic acid* - a white crystalline vitamin present in plants, esp. citrus fruits, tomatoes, and green vegetables; a deficiency in the diet of man leads to scurvy (*цинга, скорбут, хвороба Барлоу);* formula: $C_6H_8O_6$) and E (or *tocopherol* - any of a group of fat-soluble alcohols that occur in wheat-germ oil, watercress, lettuce, egg yolk, etc.) They are thought to be necessary for healthy human reproduction) are antioxidants, and foods that contain relatively high amounts of them are considered important in slowing some of the medical problems that come from aging. Five servings (portions of food) and vegetables per day are thought to supply enough antioxidants to provide reasonable protection from the damage done by oxiding agents.

9.5.2 Chemical current sources

We're people on the go… with laptop computers, mobile phones, e-books et al. To keep all of these tools and toys working, we need batteries, and because the newer electronic devices require more power in smaller packages. The goal of this part – to help you understand how batteries work, because all ones use Redox reactions – reversible or irreversible.

A battery is a device that converts chemical energy using Redox reactions. To discover what this means and how batteries work, let's examine a simple system that generates an electric current using reaction between zinc metal and copper(II) ions described in Fig. 10. In this Redox reaction, uncharged zinc atoms are oxidized to zinc ions, and copper(II) ions are reduced to uncharged copper atoms (see Fig. 10).

This reaction takes place when zinc metal is added to a solution of copper(II) sulfate. When a Cu^{2+} ion collides with zinc metal, two electrons are transferred from a zinc atom directly to the copper(II) ion.

A clever arrangement of the reaction components allows to harness this reaction to produce electrical energy. The setup, shown in Fig. 11, keeps the two half-reactions separated; causing the electrons released in the

oxidation half of the reaction to pass through a wire connecting the two halves of the apparatus. The proper name for a set-up of this type is a *voltaic cell*. Strictly speaking, a battery is a series of voltaic cells jointed in such a way that they work together.
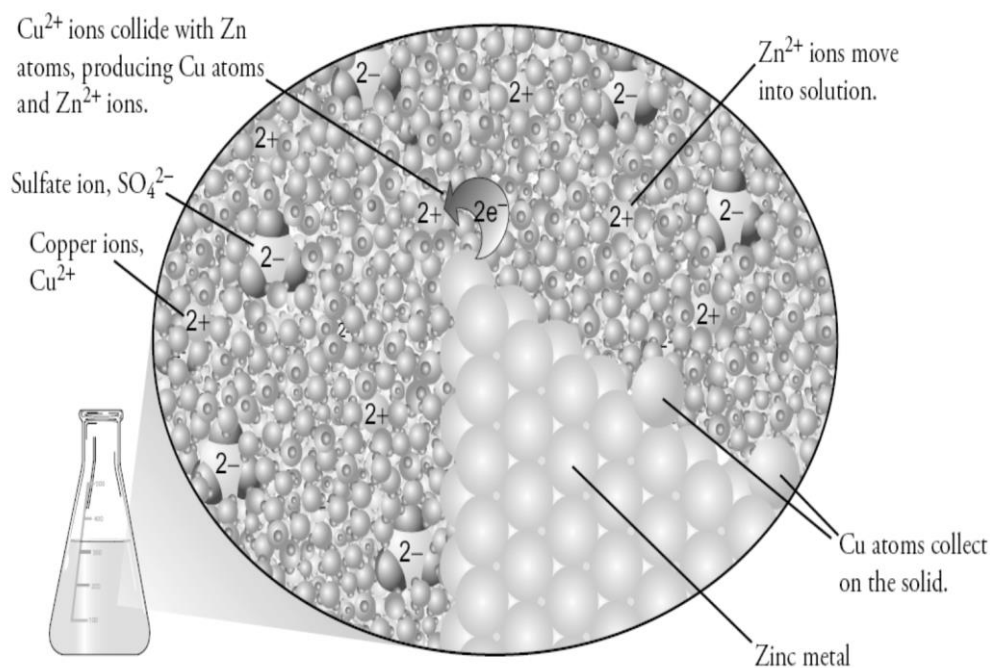
Fig. 10. Single-replacement reaction between free zinc and copper(II) sulfate solution

$$Zn_{solid} + Cu^{2+}{}_{(aqua)} \rightarrow Zn^{2+}{}_{(aqua)} + Cu_{solid}$$

$$\text{oxidation}: Zn_{solid} \rightarrow Zn^{2+}{}_{(aqua)} + 2\,\bar{e}$$

$$\text{reduction}: Cu^{2+}{}_{(aqua)} + 2\,\bar{e} \rightarrow Cu_{solid}.$$
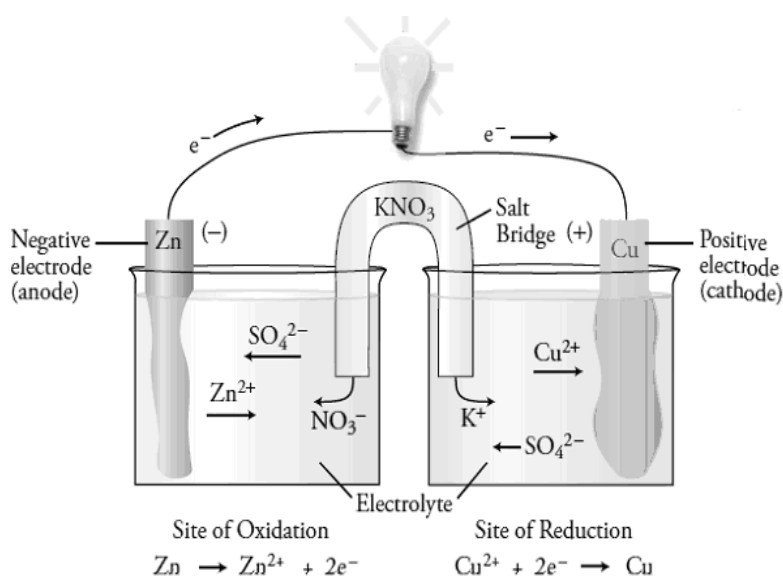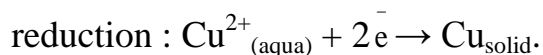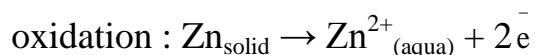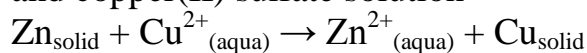
Fig. 11. Composition of the simplest voltaic cell

A voltaic cell, then, is composed of two separate half-cells. In the case of the zinc and copper(II) Redox reaction, the first half-cell consists of a strip of zinc metal in a solution of zinc sulfate. The second half-cell consists of a strip of copper metal in a solution of copper(II) sulfate. In the Zn/Zn^{2+} half-cell, zinc atoms lose two electrons and are converted to zinc ions. The two electrons pass through the wire to the Cu/Cu^{2+} half-cell, where Cu^{2+} ions gain the two electrons to form uncharged copper atoms. The zinc metal and copper metal strips are called *electrodes*, the general name for electrical conductors placed in half-cells of voltaic cells.

The electrode at which oxidation occurs in a voltaic cell is called the *anode*. Because electrons are lost in oxidation, the anode is the source of electrons. For this reason, the anode of as voltaic cell is designated the negative electrode. Because electrons are lost, forming more positive (or less negative) species at the anode, the anode surroundings tend to become more positive. Thus anions are attracted to the anode. In our voltaic cell, Zn is oxidized to Zn^{2+} at the zinc electrode, so this electrode is the anode. The solution around the zinc metal becomes positive due to excess Zn^{2+} ions, so anions are attracted to the zinc electrode.

The *cathode* is the electrode is a voltaic cell at which reduction occurs. By convention, the cathode is designated the positive electrode. Because electrons flow along the wire to the cathode, and substances gain those electrons to become more negative (or less positive), the cathode surroundings tend to become more negative. Thus cations are attracted to the cathode. In our voltaic cell, Cu^{2+} ions are reduced to uncharged copper atoms at the copper strip, so metallic copper in the cathode. Because cations are removed from the solution there and anions are not, the solution around the copper cathode tends to become negative and attracts cations.

The component of the voltaic cell through which ions are able to flow is called the electrolyte (see part I, Chapter 4). For the described voltaic cell, the zinc sulfate solution is the electrolyte in the anode half-cell, and the copper(II) sulfate solution is the electrolyte in the cathode half-cell. Exchange of free electrons formed in cathode and anode parts is realized to introduce a device called a *salt bridge*.

Dry cells

Although a voltaic cell of the kind described above, using zinc and a solution of copper ions, was used in early systems, there are problems with this sort of cell. The greatest problem in that the cell can't be easily moved because the electrolyte solutions are likely to spill. The Leclanché cell, or *dry cell*, was developed in the 1860s to solve this problem. It

contained a paste, or semisolid, electrolyte. The reactions in the dry cell can be thought of as consisting of the following half-reactions (although they are a bit more complicated than described here):

Anode oxidation : $Zn_{(solid)} \rightarrow Zn^{2+}_{(aqua)} + 2\bar{e}$

Cathode reduction : $2MnO_{2\ (solid)} + 2NH_4^{+}_{(aqua)} + 2\bar{e}$
$\rightarrow Mn_2O_{3\ (solid)} + 2NH_{3(aqua)} + H_2O_{(liquid)}$.

Overall reaction : $Zn_{solid} + 2MnO_{2\ (solid)} + 2NH_4^{+}_{(aqua)}$
$\rightarrow Zn^{2+}_{(aqua)} + Mn_2O_{3\ (solid)} + 2NH_{3\ (aqua)} + H_2O_{(liquid)}$.
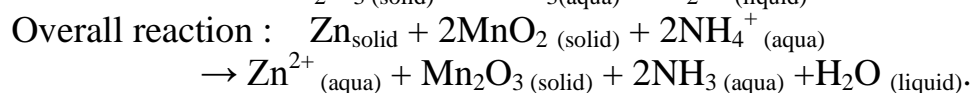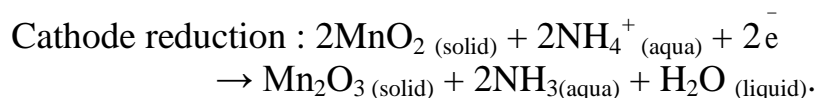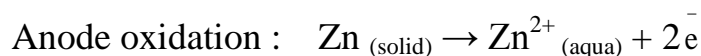
These inexpensive and reliable cells have served as the typical "flashlight battery" for many years. Their outer wrap surrounds a zinc metal cylinder that acts as the anode (see Fig. 12).
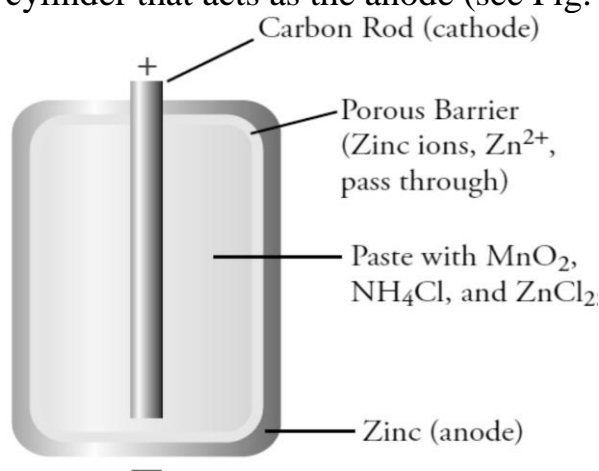
Fig. 12. The Leclanché cell

Inside the zinc cylinder is a porous barrier that separates the zinc metal from a paste containing NH_4Cl, $ZnCl_2$, and MnO_2. The porous barrier allows Zn^{2+} ions to pass through, but it keeps the MnO_2 from coming into direct with the zinc metal. In the center of the cell, a carbon rod that can conduct an electric current acts as the cathode.

The composition, structure, advantages and disadvantages of the typical modern dry cells are presented in the table 2.

Table 2. Common voltaic calls (batteries)

Voltaic cell	Anode reaction	Cathode reaction	Pros	Cons
Dry cell	$Zn_{solid} \rightarrow Zn^{2+}_{aqua} + 2\bar{e}$	$2MnO_{2\ solid} +2NH_4^{+}_{aqua} + 2\bar{e} \rightarrow Mn_2O_{3\ solid} + 2NH_{3\ aqua} + H_2O_{\ liquid}$	Inexpensive, reliable	Short shelf-life; large and heavy; not rechargeable
Alkaline	$Zn_{solid} + 2OH^{-}_{aqua} \rightarrow ZnO_{solid} + H_2O_{\ liquid} +$	$2MnO_{2\ solid} + H_2O$	Longer lasting	More

battery	$2\overset{-}{e}$	$\text{liquid} + 2\overset{-}{e} \rightarrow Mn_2O_3$ solid $+ 2OH^-$ aqua	and slightly higher energy than dry cells	expensive that
Nickel-cadmium battery	$Cd_{solid} + 2OH^-_{aqua} \rightarrow$ $Cd(OH)_{2\ solid} + 2\overset{-}{e}$	$NiO(OH)_{solid}$ + $H_2O_{liquid} + 2\overset{-}{e} \rightarrow$ $Ni(OH)_{2\ solid} + OH^-$ aqua	Rechargeable; lower price than other rechargeable batteries; long life	Relatively low energy density; less efficient with repeated use
Lead-Acid battery	$Pb_{solid} + HSO_4^-{}_{aqua} +$ $H_2O_{\ liquid} \rightarrow PbSO_4$ solid $+ H_3O^+{}_{aqua} + 2\overset{-}{e}$	$PbO_{2\ solid} + HSO_4^-$ aqua $+ H_3O^+{}_{aqua} + 2\overset{-}{e}$ $\rightarrow PbSO_{4\ solid} + 5H_2O$ liquid	Rechargeable; very reliable; inexpensive; durable	Very heavy; yielding a very low energy density
One type of lithium battery	$Li_nC_6 \rightarrow nLi^+ + 6C +$ $n\overset{-}{e}$	$CoO_2 + nLi^+ + n\overset{-}{e} \rightarrow$ Li_nCoO_2	Rechargeable; reliable; very high energy density	Expensive

9.5.3 Bleaching agents

Bleaching agents are compounds which are used to remove color from substances such as textiles. In earlier times textiles were bleached by exposure to the sun and air. Today most commercial bleaches are oxidizing agents, such as sodium hypochlorite ($NaOCl$) or hydrogen peroxide (H_2O_2) which are quite effective in "decolorizing" substances via oxidation. The action of these bleaches can be illustrated in the following simplified way (Fig. 13):
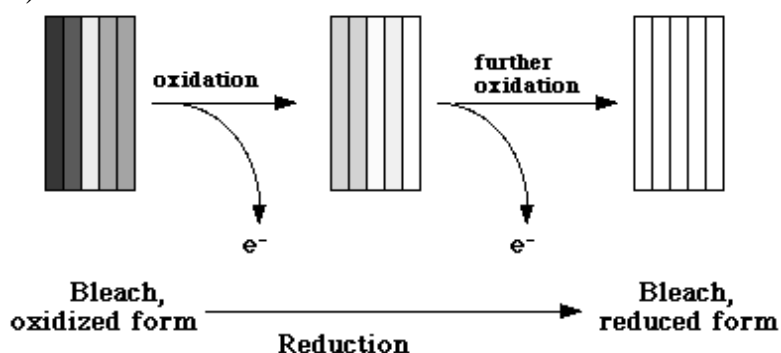
Fig. 13. Redox processes on bleaching

Recall that an oxidizing agent is any substance which causes another substance to lose one or more electrons. The decolorizing action of bleaches is due in part to their ability to remove these electrons which are activated by visible light to produce the various colors. The hypochlorite ion (OCl^-), found in many commercial preparations, is reduced to chloride

ions and hydroxide ions forming a basic solution as it accepts electrons from the colored material as shown below.

$$OCl^- + 2\,\overline{e} + HOH \rightarrow Cl^- + 2\,OH^-$$

Bleaches are often combined with "optical brighteners". These compounds are quite different from bleaches. They are capable of absorbing wavelengths of ultraviolet light invisible to the human eye, and converting these wavelengths to blue or blue-green light. The blue or blue-green light is then reflected by the substance making the fabric appear much "whiter and brighter" as more visible light is seen by the eye.

9.6 Redox reactions in biological processes

Many important biological processes involve Redox reactions. Cellular respiration, for instance, is the oxidation of glucose ($C_6H_{12}O_6$) to CO_2 and the reduction of oxygen to water. The summary equation for cell respiration is:

$$C_6H_{12}O_6 + 6\,O_2 \rightarrow 6\,CO_2 + 6\,H_2O$$
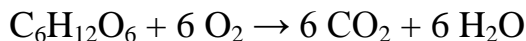
The process of cell respiration also depends heavily on the reduction of NAD^+ (Nicotinamide adenine dinucleotide) to NADH (Nicotinamide adenine dinucleotide and the reverse reaction (the oxidation of NADH to NAD^+NADH + H^+ + 2 monodehydroascorbate NAD^+ + 2 ascorbate). Photosynthesis is essentially the reverse of the Redox reaction in cell respiration:

$$6\,CO_2 + 6\,H_2O + \text{light energy} \rightarrow C_6H_{12}O_6 + 6\,O_2$$
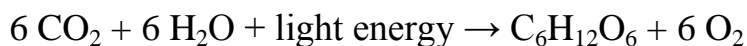
Biological energy is frequently stored and released by means of Redox reactions. Photosynthesis involves the reduction of carbon dioxide into sugars and the oxidation of water into molecular oxygen. The reverse reaction, respiration, oxidizes sugars to produce carbon dioxide and water. As intermediate steps, the reduced carbon compounds are used to reduce nicotinamide adenine dinucleotide (NAD^+), which then contributes to the creation of a proton gradient, which drives the synthesis of adenosine triphosphate (ATP) and is maintained by the reduction of oxygen. In animal cells, mitochondria perform similar functions.

The term **Redox state** is often used to describe the balance of NAD^+/NADH and $NADP^+$/NADPH in a biological system such *as a cell or organ*. The Redox state is reflected in the balance of several sets of metabolites (e.g., lactate and pyruvate, beta-hydroxybutyrate and acetoacetate), whose interconversion is dependent on these ratios. An abnormal Redox state can develop in a variety of deleterious situations, such as hypoxia, shock, and sepsis. Redox signaling involves the control of cellular processes by Redox processes.

Redox proteins and their genes must be co-located for Redox regulation according to the CoRR hypothesis for the function of DNA in mitochondria and chloroplasts.

Redox cycling

A wide variety of aromatic compounds are enzymatically reduced to form free radicals that contain one more electron than their parent compounds. In general, the electron donor is any of a wide variety of flavoenzymes and their coenzymes. Once formed, these anion free radicals reduce molecular oxygen to *superoxide*, and regenerate the unchanged parent compound. The net reaction is the oxidation of the flavoenzyme's coenzymes and the reduction of molecular oxygen to form superoxide. This catalytic behavior has been described as futile cycle or Redox cycling.

Examples of Redox cycling-inducing molecules are the herbicide paraquat and other viologens and quinones such as menadione.

CHAPTER 10 COMPLEX COMPOUNDS

10.1 General concepts

All the variety of inorganic compounds can be divided into two groups: 1) second order compounds or simple; 2) the highest order compounds.

The substances whose value of element oxidation number coincides with presented valency or with quantity of chemical bonds in molecule (NH_3, H_2O, SO_3, $AgCl$, etc.) are called simple compounds but the substances in which additional valence bonds occur are considered as compounds of the highest order and are called coordinate or complex.

The simple compounds are structured at the account of ionic, covalent polar or covalent non-polar bond. In contrast to this the additional covalent bond is formed in complex compounds on the basis of donor-acceptor interaction. Owing to this bond the complex bond is formed. Donor-acceptor interaction between central ion-complexing agent and ligands takes place. At the same time ion-complexing agent takes part in formation of the bonds, giving free orbitals of their external and pre-external energy levels but ligands - giving electron pairs of one of the atoms. For example, the following stages can be presented in case of $[Co(NH_3)_6]^{3+}$ complex ion formation:

1) Co^{3+} ion formation from cobalt atom:

$$_{27}Co^0\ 1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2 4p^0 \quad \xrightarrow{-3\bar{e}} \quad Co^{3+}\ 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^0 4p^0$$
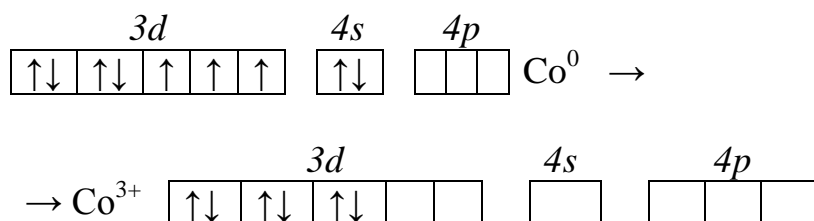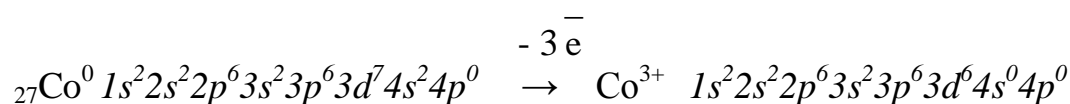
2) ammonia molecule formation:

$$_7N^0\ 1s^2 2s^2 2p^3 \quad \xrightarrow{+3\bar{e}} \quad N^{3-}\ 1s^2 2s^2 2p^6;\quad _1H^0\ 1s^1 \xrightarrow{-1\bar{e}} H^{1+}\ 1s^0\ \text{or}$$
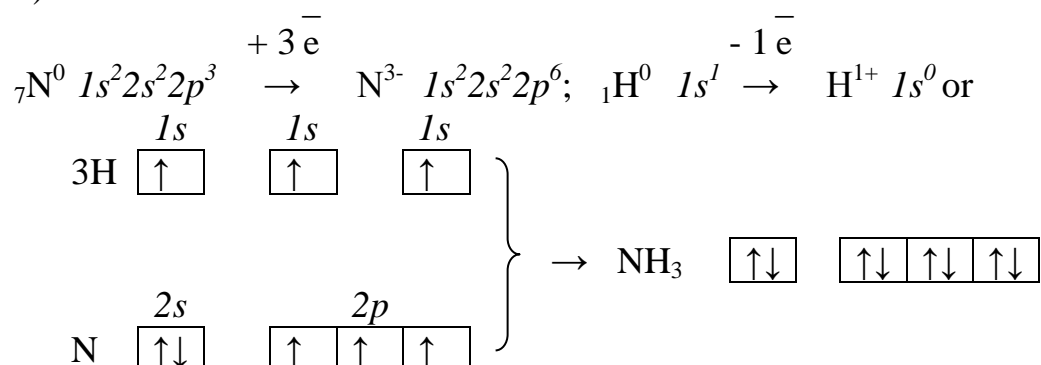
3) formation of $[Co(NH_3)_6]^{+3}$ complex ion at the account of six free orbitals 3d, 4s and 4p of Co^{+3} sublevels and paired Nitrogen 2s electrons which is the part of ammonia six molecules:
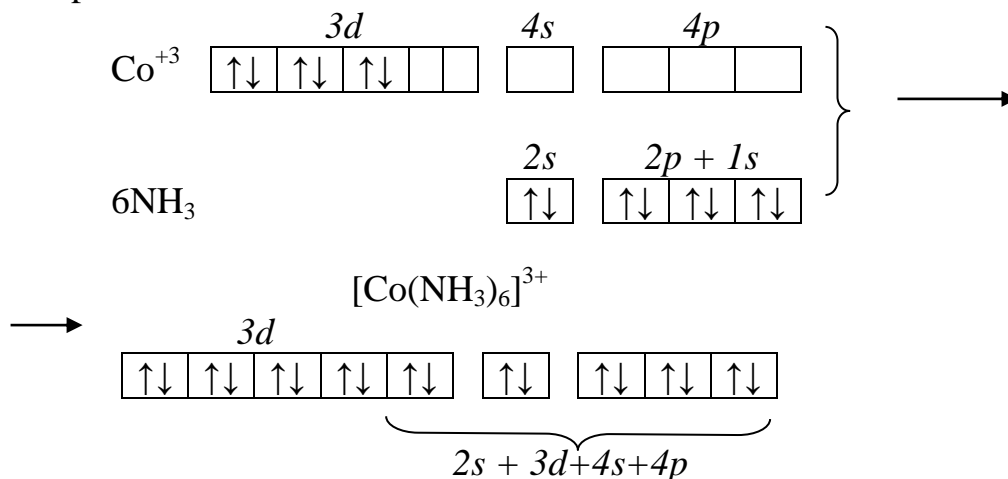
The main principles of complex compound formation were presented in 1893 by Swiss chemist Alfred Werner as **coordination theory**:

1. In the molecule of any complex compound one of the ions takes the central place and is called complexing agent or central ion;

2. Some quantity of ions or neutral molecules with opposite charges is placed close enough around the central ion and is called ligands.

Central ion with ligands placed around it forms so-called inner coordination sphere of compound (complex ion);

3. Ions, which are located far from central ion, make outer coordination sphere of complex compound;

4. Number, which shows how many ligands are located around complexing agent in the inner sphere, is called coordinating.

Structure of complex compound may be presented as:
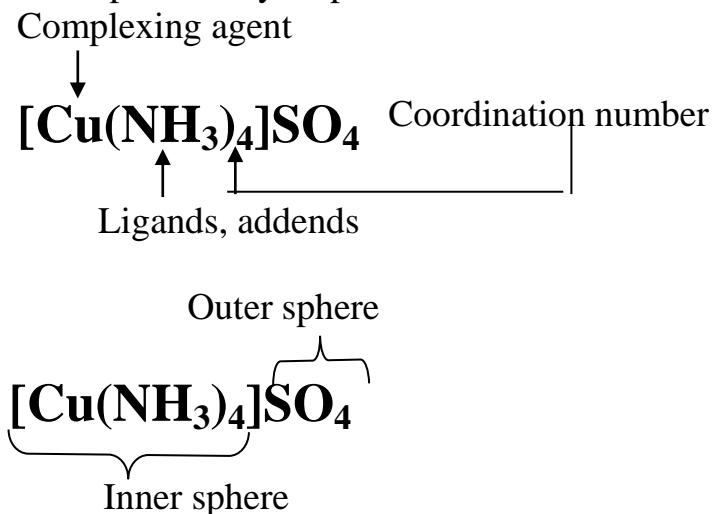
10.2 Nomenclature

Because of the large number of complicated coordination compounds, it has been necessary to develop a systematic method for naming them. Complex species may be a *cation* such as $[Cu(H_2O)_4]^{2+}$, an anion such as $[Fe(CN)_6]^{4-}$, or a *neutral* molecule such as $[Cr(NH_3)_3Cl_3]$. Many different electronically satisfied entities may act as electron-pair donor ligands. The names of some common ligands are given in the margin. It may be seen that the names of negatively-charged ligands end in *o*. The name of the molecule is generally used for neutral ligands. Water and ammonia are the two important exceptions. The rules listed below enable you to name a large number of common complex substances. The rules for naming chemical compounds are established by nomenclature committees of the International Union of Pure and Applied Chemistry (IUPAC).

The following rules should be taken into account while drawing the formulas of complex compounds:

1. Complex ion charge is numerically equal to algebraic sum of ion-complexing agent and ligands charges;

2. Total ion charges, located in outer sphere, are numerically equal and opposite in sign to the charge of inner coordinating sphere. For example, for $K_4[Fe(CN)_6]$ inner sphere charge is $(2+) + (6-) = 4-$, outer sphere charge is $4 \cdot (1+) = 4+$, complex compound charge is $(4-) + (4+) = 0$.

Multicharged ions of heavy metals, which have 18-electronic or transient from 8- to 18-electrinic outer configuration and have free orbitals show the ability to complex formation. Ions of some non-metals may be complexing agents. Generally the charge of complexing agent corresponds to the charge of given atom in simple compound composition. Therefore the process of complex compound may be easily presented as the composition of simple substance molecules:

$4KCN + Fe(CN)_2 = K_4[Fe(CN)_6]$;

$NiSO_4 + 6NH_3 = [Ni(NH_3)_6]SO_4$;

$2NaOH + Zn(OH)_2 = Na_2[Zn(OH)_4]$.
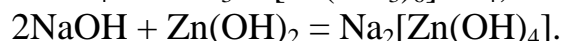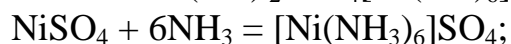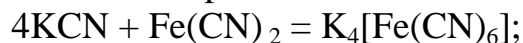
The prevailing coordination numbers are 2, 4, and 6. It can be pointed out that coordination number mostly is equal to doubled or triple charge of ion-complexing agent (see Table 14).

The ability of ligands to coordination depends on atoms presented in them or groups with undivided electron pairs owing to which the link with the central atom takes place. The prevalent electron donors are the atoms of N, O, C, Cl, Br, I.

The name of the positive ion is written before the name of the negative ion.

The name of the ligands is written before the name of the metal to which it is coordinated.

The Greek prefixes *mono-*, *di-*, *tri-*, *tetra-*, *penta-*, *hexa-*, and so on are used to indicate the number of ligands when these ligands are relatively simple. The Greek prefixes *bis-*, *tris-*, and *tetrakis-* are used with more complicated ligands.

The names of negative ligands always end in *o*, as in *fluoro* (F^-), *chloro* (Cl^-), *bromo* (Br^-), *iodo* (I^-), *oxo* (O^{2-}), *hydroxo* (OH^-), and *cyano* (CN^-). A handful of neutral ligands are given common names, such as *aquo* (H_2O), *ammine* (NH_3), and *carbonyl* (CO).

Ligands are listed in the following order: negative ions, neutral molecules, and positive ions. Ligands with the same charge are listed in alphabetical order.

A Roman numeral in parentheses indicates the oxidation number of the metal atom after the name of the metal atom.

The names of complexes with a net negative charge end in *-ate*. $Co(SCN)_4^{2-}$, for example, is the Tetrathiocyanatocobaltate (II) ion. When the symbol for the metal is derived from its Latin name, *-ate* is added to the Latin name of the metal. Thus, negatively charged Iron complexes are ferrates and negatively charged Copper complexes are cuprates (see examples in Table 14).

Table 14. Characteristics of some complex compounds

Complexing agent	Coordination number	Formula	Name
Ag^+	2	$[Ag(NH_3)_2]Cl$	Diaminesilver (I) Chloride
Cu^{2+}	4	$[Cu(NH_3)_4](OH)_2$	TetramineCopper (II) Hydroxide
Hg^{2+}	4	$K_2[HgI_4]$	Potassium Tetraiodomercurate (II)
Zn^{2+}	4	$Na_2[Zn(OH)_4]$	Sodium Tetra-hydroxozincate
Co^{2+}	4	$(NH_4)_2[Co(SCN)_4]$	Ammonium Tetra-thiocyanocobaltate (II)
B^{3+}	4	$Na[BF_4]$	Sodium Tetrafluoroborate
Co^{3+}	6	$[Co(H_2O)_6]Cl_3$	Hexaquocobalt (III)

			Chloride
Al^{3+}	6	$Na_3[Al(OH)_6]$	Sodium Hexa-hydroxoaluminate

10.3 Transition metal complexes

Although many transition metal complexes and even organometallic compounds were first obtained in the pre-last century, the structure and bonding of these compounds was entirely unclear.

Especially puzzling to the early chemists was the fact that many of their compounds had identical formulae but different properties. The octahedral complexes of trivalent chromium and trivalent cobalt played a crucial role at this early stage of complex-chemistry. The compounds could easily be obtained, crystallized well and showed characteristic colors that were often used to distinguish them from each other.

Compound	Color	Historic name
$CoCl_3 \cdot 6\,NH_3$	Yellow	*Luteo*-complex
$CoCl_3 \cdot 5\,NH_3$	Purple	*Purpureo*-complex
$CoCl_3 \cdot 4\,NH_3$	Green	*Praseo*-complex
$CoCl_3 \cdot 4\,NH_3$	Violet	*Violeo*-complex

It is remarkable that much of the early complex chemistry was developed by only two researchers, A. Werner, who was professor for chemistry at Zürich (Switzerland) and S. M. Jørgensen who was professor of chemistry at Copenhagen (Denmark).

Werner recognized that some of the groups and anions of the complexes are not easily replaced and resembled the corresponding functional groups in organic compounds in their reactivity. Other groups are readily exchanged and give the characteristic precipitation or color tests of the free ions/compounds.

$[Co(NH_3)_5Br]SO_4 + Ba^{2+} \rightarrow BaSO_4$

$[Co(NH_3)_5SO_4]\,Br + Ba^{2+} \rightarrow$ no reaction

$[Co(NH_3)_5Br]SO_4 + Ag^+ \rightarrow$ no reaction

$[Co(NH_3)_5SO_4]\,Br + Ag^+ \rightarrow BaSO_4$
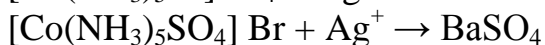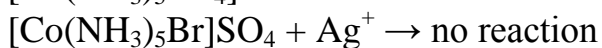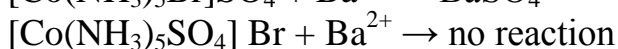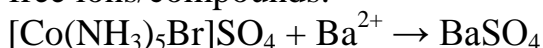
Werner correctly deduced the octahedral and tetrahedral geometry of the complexes investigated by him and Jørgensen, and correctly deduced the concepts of isomerism and chirality found in transition metal complexes. His work is documented in more than 120 publications and ultimately earned him the 1913 Nobel Prize in Chemistry, the first ever awarded for purely inorganic research.

10.4 Naming coordination compounds

A **complex** is a substance in which a metal atom or ion is associated with a group of neutral molecules or anions called **ligands**. **Coordination compounds** are neutral substances (i.e. uncharged) in which **at least** one ion is present as a complex.

The coordination compounds are named in the following way.

A. To name a coordination compound, no matter whether the complex ion is the cation or the anion, **always name the cation before the anion**. (This is just like naming an ionic compound.)

B. In naming the complex ion:

1. **Name the ligands first, in alphabetical order, then the metal atom or ion**. **Note:** The **metal atom or ion** is written **before** the **ligands** in the **chemical formula**.

2. The names of some common ligands are listed in Table 1.

- For anionic ligands end in "-o"; for anions that end in "-ide"(e.g. chloride), "-ate" (e.g. sulfate, nitrate), and "-ite" (e.g. nirite), change the endings as follows: -ide -o; -ate -ato; -ite -ito

*- For neutral ligands, the common name of the molecule is used e.g. $H_2NCH_2CH_2NH_2$ (ethylenediamine). **Important exceptions**: water is called 'aqua', ammonia is called 'ammine', carbon monoxide is called 'carbonyl', and the N_2 and O_2 are called 'dinitrogen' and 'dioxygen'.*

Table 3. Names of Some Common Ligands

Anionic Ligands	Names	Neutral Ligands	Names
Br^-	Bromo	NH_3	Ammine
F^-	Fluoro	H_2O	Aqua
O^{2-}	Oxo	NO	Nitrosyl
OH^-	Hydroxo	CO	Carbonyl
CN^-	Cyano	O_2	Dioxygen
$C_2O_4^{2-}$	Oxalato	N_2	Dinitrogen
CO_3^{2-}	Carbonato	C_5H_5N	Pyridine
CH_3COO^-	Acetato	$H_2NCH_2CH_2NH_2$	Ethylenediamine (*en*)

3. Greek prefixes are used to designate the number of each type of ligand in the complex ion, e.g. di-, tri- and tetra-. If the ligand already contains a Greek prefix (e.g. ethylene**di**amine) or if it is polydentate ligands (ie. can attach at more than one binding site) the prefixes bis-, tris-, tetrakis-, pentakis-, are used instead. (See examples 3 and 4.) The numerical prefixes are listed in Table below.

Table 4. Numerical Prefixes

Number	Prefix	Number	Prefix	Number	Prefix
1	mono	5	penta (pentakis)	9	nona (ennea)
2	di (bis)	6	hexa (hexakis)	10	deca
3	tri (tris)	7	hepta	11	undeca
4	tetra (tetrakis)	8	octa	12	dodeca

4. After naming the ligands, name the central metal. If the complex ion is a cation, the metal is named same as the element. For example, Co in a complex cation is call cobalt and Pt is called platinum. (See examples 1-4). If the complex ion is an anion, the name of the metal ends with the suffix –ate. For example, Co in a complex anion is called cobaltate and Pt is called platinate. For some metals, the Latin names are used in the complex anions e.g. Fe is called ferrate (not ironate).

Table 5. Name of Metals in Anionic Complexes

Name of Metal	Name in an Anionic Complex
Iron	Ferrate
Copper	Cuprate
Lead	Plumbate
Silver	Argenate
Gold	Aurate
Tin	Stannate

5. Following the name of the metal, the oxidation state of the metal in the complex is given as a Roman numeral in parentheses.

C. To name a neutral complex molecule, follow the rules of naming a complex cation. **Remember:** Name the (possibly complex) cation **BEFORE** the (possibly complex) anion.

For historic reasons, some coordination compounds are called by their common names. For example, $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ are named ferricyanide and ferrocyanide respectively, and $Fe(CO)_5$ is called iron carbonyl.

Examples.

Give the systematic names for the following coordination compounds:

1. $[Cr(NH_3)_3(H_2O)_3]Cl_3$
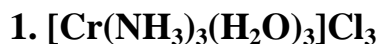
Answer: triamminetriaquachromium(III) chloride

Solution: The complex ion is inside the parentheses, which is a cation. The ammine ligands are named before the aqua ligands according to alphabetical order. Since there are three chlorides binding with the complex ion, the charge on the complex ion must be +3 (since the compound is electrically neutral). From the charge on the complex ion and the charge on

the ligands, we can calculate the oxidation number of the metal. In this example, all the ligands are neutral molecules. Therefore, the oxidation number of chromium must be same as the charge of the complex ion, +3.

2. $[Pt(NH_3)_5Cl]Br_3$

Answer: pentaamminechloroplatinum(IV) bromide

Solution: The complex ion is a cation, the counter anion is the 3 bromides. The charge of the complex ion must be +3 since it bonds with 3 bromides. The NH_3 are neutral molecules while the chloride carries -1 charge. Therefore, the oxidation number of platinum must be +4.

3. $[Pt(H_2NCH_2CH_2NH_2)_2Cl_2]Cl_2$

Answer: dichlorobis(ethylenediamine)platinum(IV) chloride

Solution: ethylenediamine is a bidentate ligand, the bis- prefix is used instead of di-.

4. $[Co(H_2NCH_2CH_2NH_2)_3]_2(SO_4)_3$

Answer: tris(ethylenediamine)cobalt(III) sulfate

Solution: The sulfate is the counter anion in this molecule. Since it takes 3 sulfates to bond with two complex cations, the charge on each complex cation must be +3.

Since ethylenediamine is a neutral molecule, the oxidation number of cobalt in the complex ion must be +3.

Again, remember that you never have to indicate the number of cations and anions in the name of an ionic compound.

5. $K_4[Fe(CN)_6]$

Answer: potassium hexacyanoferrate(II)

Solution: potassium is the cation and the complex ion is the anion.

Since there are 4 K^+ binding with a complex ion, the charge on the complex ion must be -4. Since each ligand carries -1 charge, the oxidation number of Fe must be +2. The common name of this compound is potassium ferrocyanide.

6. $Na_2[NiCl_4]$

Answer: sodium tetrachloronickelate(II)

Solution: The complex ion is the anion so we have to add the suffix – ate in the name of the metal.

7. $Pt(NH_3)_2Cl_4$

Answer: diamminetetrachloroplatinum(IV)

Solution: This is a neutral molecule because the charge on Pt^{+4} equals the negative charges on the four chloro ligands.

If the compound is $[Pt(NH_3)_2Cl_2]Cl_2$, eventhough the number of ions and atoms in the molecule are identical to the example, it should be named: diamminedichloroplatinum(II) chloride, a big difference.

8. $Fe(CO)_5$

Answer: pentacarbonyliron(0)

Solution: Since it is a neutral complex, it is named in the same way as a complex cation. The common name of this compound, iron carbonyl, is used more often.

9. $(NH_4)_2[Ni(C_2O_4)_2(H_2O)_2]$

Answer: ammonium diaquabis(oxalato)nickelate(II)

Solution: The oxalate ion is a bidentate ligand.

10. $[Ag(NH_3)_2][Ag(CN)_2]$

Answer: diamminesilver(I) dicyanoargentate(I)

Solution: You can have a compound where both the cation and the anion are complex ions. Notice how the name of the metal differs even though they are the same metal ions.

10.5 Bioinorganic systems as complex compounds

Coordination compounds play important roles in nature. *Chlorophyll,* which is involved in photosynthesis in plants, is a coordination complex of magnesium. Hemoglobin, the oxygen transporter in the human body, is a coordination complex of iron. Vitamin B_{12}, necessary for the prevention and cure of pernicious anaemia (a form of anaemia characterized by lesions of the spinal cord, weakness, sore tongue, numbness in the arms and legs, diarrhea *(перниціозна анемія, злоякісна анемія, хвороба Аддісона-Бірмера)*, is a coordination complex of cobalt.

In all three compounds, the metal ion is in an approximately octahedral environment, its coordination number is 6, and bonded to it are the four nitrogen atoms of a planar porphyrin - like ring (Fig. 14). The basic planar ring structure is closely related to that the extremely stable blue pigment, Cu(II)phthalocyanine.
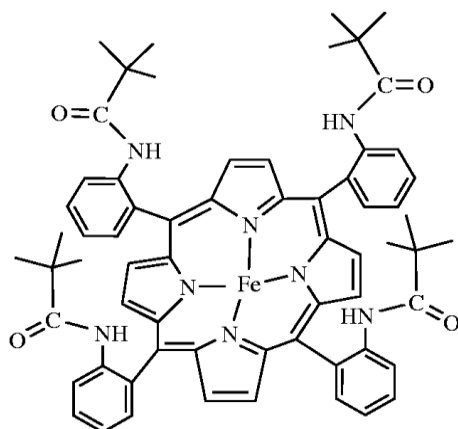
Fig.14. Structure of porhyrin

10.6 Isomerism of complex compounds

Linkage isomerism

Ligands that have more than one atom that can coordinate through to the metal give rise to linkage isomerism. Common examples are the nitrite and the thiocyanate ions.

nitro-complexes *nitrito-complexes* *S-thiocyanato complexes* *N-thiocyanato complexes*
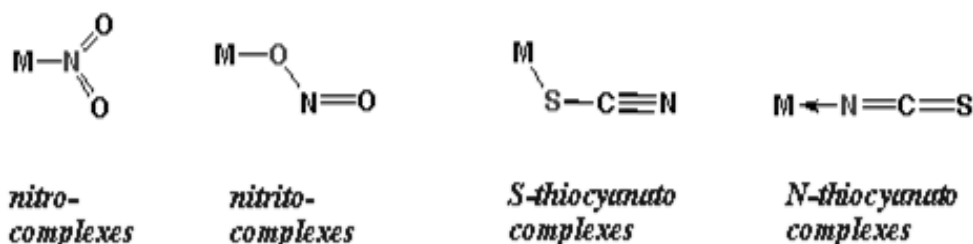
The concept of linkage isomerism was considered as questionable for many decades after it had first been proposed by Werner but there is now overwhelming evidence (including structural proof).

One of the first documented cases is the NO_2-ligand. In all documented cases, the O-bonded nitrito form is only metastable and reverts to the N-bound nitro-isomer.

" -nitrito "   " -nitro "
red   yellow
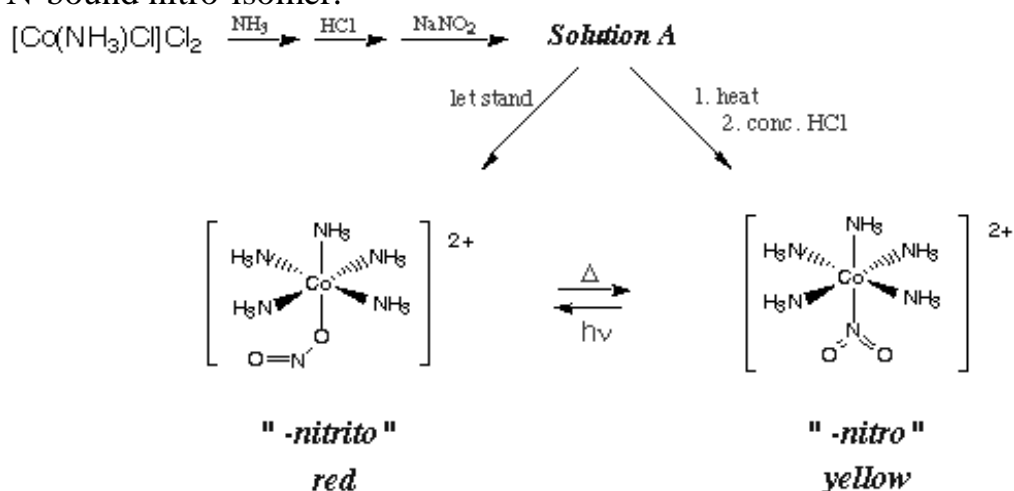
Ionization Isomerism

Ligands can be covalently bound to the metal or be simple counter ions. This is not obvious from the formula of the complex and gives rise to ionization isomerism. Ionization isomerism can only occur if the covalently bound ligand does not easily dissociate. This is generally the case for the inert octahedral complexes of octahedral Chromium(III) and Cobalt(III). Compared to a small number of inert complexes, the overwhelming majority of 3d-complexes are labile.

10.7 The concept of coordination numbers

The concept of coordination numbers was an important result of Werner's research. It clearly established the two most important aspects that are required to discuss chemical structure and change: oxidation state and coordination number.

The concept of oxidation state implies that we have knowledge who loses electrons and who gains electrons in a compound. This cannot be done unambiguously unless generally accepted rules are applied.

The concept of coordination number is a geometric concept and simply represents the number of next neighbors. It is important to realize that the concept of coordination numbers does not imply any specific type of bonding. Dative bonds, hydrogen bridge bonding, single, double or triple bonds indeed any type of bond (including those found in solids) is permissible. It is this generality of the concept that makes the concept so valuable.

Coordination Number 2

Stable compounds with coordination number 2 are restricted to the copper group (Cu, Ag, and Au) and to mercury.

$$\left[H_3N \rightarrow Cu \leftarrow NH_3 \right]^{\oplus} \qquad \left[H_3N \rightarrow Ag \leftarrow NH_3 \right]^{\oplus}$$

$$\left[Cl - Cu - Cl \right]^{\ominus} \qquad \left[NC \rightarrow Ag \leftarrow CN \right]^{\ominus}$$

$$\left[NC \rightarrow Au \leftarrow CN \right]^{\ominus} \qquad NC \rightarrow Hg \leftarrow CN$$

$$\left[Cl - Au - Cl \right]^{\ominus}$$
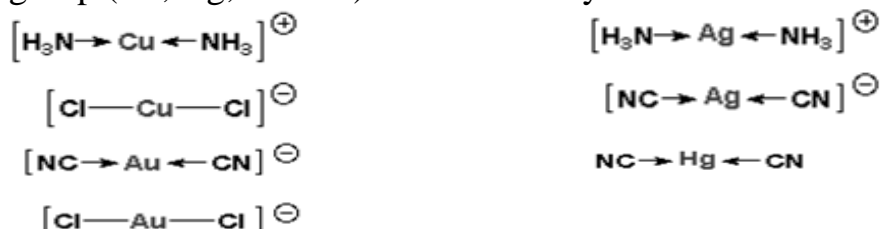
Some of these linear complexes can add further ligands to increase their coordination number to three or (more common) four.

Very few transition metal compounds have a preference for coordination number 2.

Coordination Number 3

Examples for coordination number 3 are exceedingly rare and include the anion HgI_3^-, the structure of $K[Cu(CN)_2]$ in the solid state.

The use of the very bulky bis(trimethylsilylamido) ligand has allowed D. C. Bradley's group in London to stabilize the elements titanium, vanadium and chromium in the coordination number 3.

M=Ti, V and Cr   M=Fe, Co, Ni
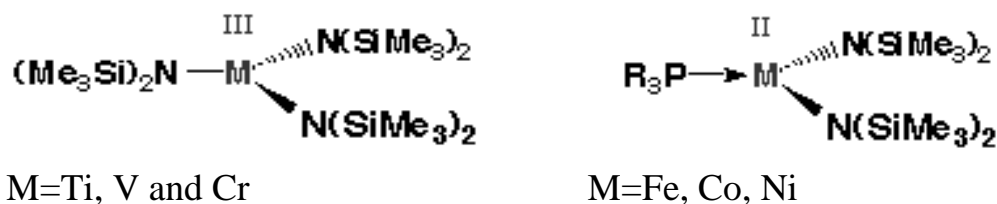
The complexes are covalent, soluble in hydrocarbons and can be sublimed under high vacuum conditions. Other members of the 3d series do not possess sufficient stability in the oxidation state +3 but form divalent complexes with coordination number 3.

Coordination number 4

The coordination number 4 is frequent and is represented by tetrahedral (point group T_d) and square planar complexes (point group D_{4h}).

Many complexes are not strictly tetrahedral or square planar but have an intermediate symmetry. This intermediate symmetry puts them in the point group D_{2d}.

cis / trans isomerism possible
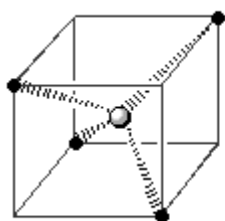
Point Group T_d Point Group D_{2d} Point Group D_{4h}
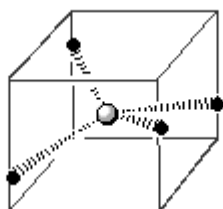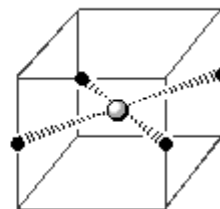
Square planar coordination is rare and found only for transition metals in the electron configuration d^8 and (less frequently) d^7 and d^9.

Square planar coordination is a common feature of two important homogeneous catalysts, Wilkinson's catalyst (catalyzes the hydrogenation of alkenes) and Vaska's catalyst (can undergo oxidative addition and is notable for its ability to bind to O_2 reversibly):
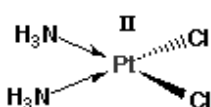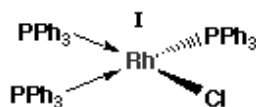
"Cis-Platin"   Wilkinson's Catalyst   Vaska's Catalyst
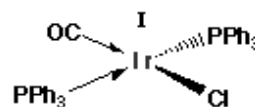
The square planar *cis*-diammineplatinum(II) chloride ("cis-platin") is an important **anti-cancer drug**.

Coordination Number 5

The coordination number 5 is not too common. Important examples include PF_5, and $Fe(CO)_5$, both of them with trigonal bipyramidal geometry.
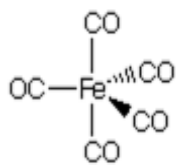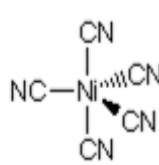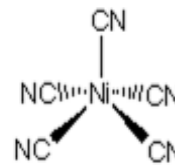
tbpy   *tbpy*   *tbpy*   *square pyramidal*

An example for the much rarer square pyramidal geometry is the anion $Ni(CN)_5^{3-}$ that occurs as square pyramidal and trigonal bipyramidal in the salt $[Cr(en)_3][Ni(CN)_5]$.

The energy difference between the two forms is very small so that the packing forces of the crystal lattice determine the geometry. For the larger cation $[Cr(1,3\text{-diaminopropane})_3]^{3+,}$ only the tbpy form is observed. With smaller cations like K^+, the tetracoordinate $Ni(CN)_4^{2-}$ is isolated.

10.8 Chelation

Many complexing agents exist that have more than one potential donor atom in molecule. If the molecular geometry is appropriate, then these can act as ligands that attach themselves to a metal ion through two or more separate points. Such ligands are called cheating agents (Fig. 15) (from the Greek *khele* meaning a claw - клешня), and the resulting complexes are known are known as *metal chelates*. If there are two points of attachment, we speak of *bidentate* chelation; if three – *terdentate*; if four, *quadridentate*, and so on (The preferred prefixes are Latin (to match the Latin stem dens – tooth – зуб), rather than the Greek di-, tri-, tetra-, etc., but either the Latin or the Greek system is acceptable.

Suppose, for example, we join two ammonia ligands together with a short hydrocarbon chain; we now have a bidentate chelating agent, for example,

$H_2N{-}CH_2{-}CH_2{-}NH_2$,
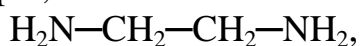
Which is commonly called *ethylendiamine* (abbreviated **en**), although it contains no double C=C double bond.
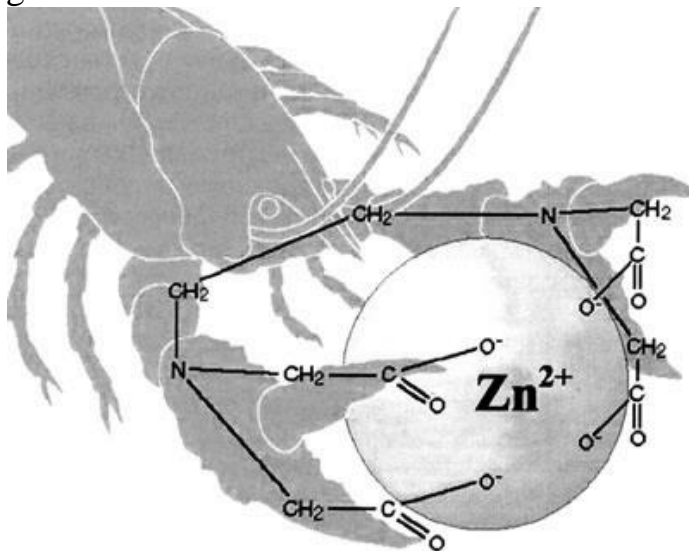
Fig. 15. Chelate complex

Optical isomerism

Fig. 16 shows the structure of $[Co(en)_3]^{3+}$. Note that there are two nonsuperposable (такі, що не накладаються один на одного, неконгруентні) ways in which $[Co(en)_3]^{3+}$ can be drawn, namely, as left-

handed and right-handed mirror images. There are known as *optical isomers* of $[Co(en)_3]^{3+}$ because a solution of one isomer will rotate the plane of polarization of light to left as it passes through, and a solution of the other will rotate it to the right. The two isomers will be present in equal amounts as $[Co(en)_3]^{3+}$ salts are usually prepared, but they can be resolved (i.e., separated from one another) by fractional crystallization of a salt of $[Co(en)_3]^{3+}$ from solution with an anion that is itself an optical isomer, for example, the *D*-tartrate anion.
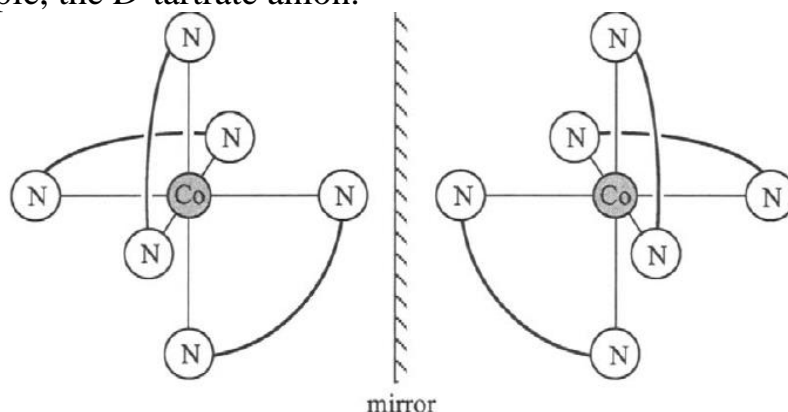
Fig. 16. Optical isomers of $[Co(en)_3]^{3+}$. N—N represents H_2N—CH_2—CH_2—NH_2. The two molecules shown are not superposable (cf. left and right hands).

The fact that optical isomers $Co(en)_3]^{3+}$ and other chelates do exist was used by Werner as incontrovertible proof of his theory of octahedral coordination in cobalt(III) and other complexes.

Chelate Complexes

Ligands can have more than one site that can bind to a central metal. From ammonia, a number of diamine ligands can be derived, but two of them, 1,2-diaminoethane ("ethylenediamine", "en") and 1,3-diaminopropane are special. They have the ability to replace two ammonia ligands under formation of very stable chelate complexes (Fig. 17).

$$K_{eq} = \frac{[L_nM(en)] \cdot [NH_3]^2}{[L_nM(NH_3)_2] \cdot [en]}$$
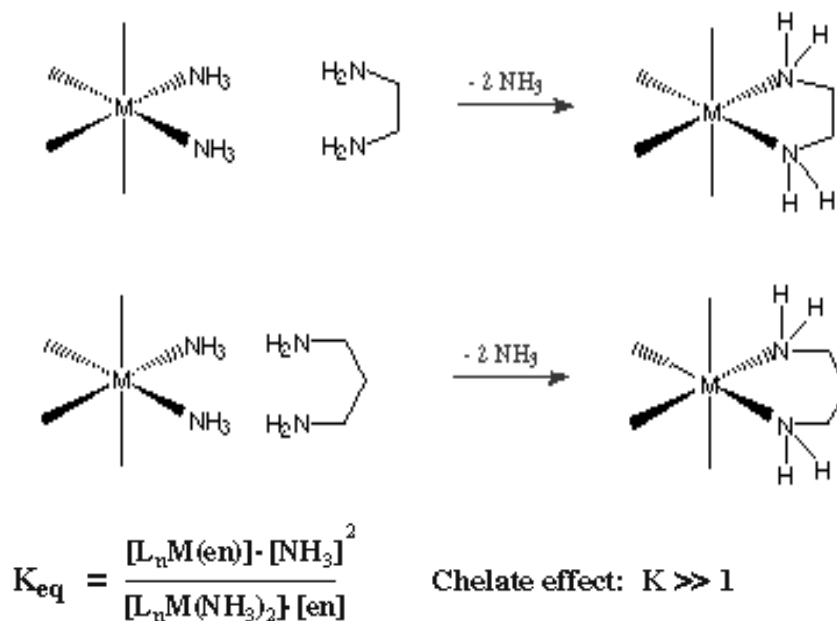
Chelate effect: $K \gg 1$

Fig. 17. Mechanism of chelate effect

The **chelate effect** is a thermodynamic effect and is best quantified by measuring formation constants K_{eq} of chelate complexes. The formation constants show the most dramatic increase for the replacement of two monodentate ligands with one bidentate ligand like in the example above. A further increase in stability is observed for tridentate or other multidentate ligands (see Fig. 18).

ethylenediamine   1,4-Diazadiene   1,1'-Bipyridine   1,10-Phenanthroline
"en"   "DAD"   "bipy"   "phen"

Ethylenediamine-   Acetylacetone
tetraacetate   "acac"

"EDTA"
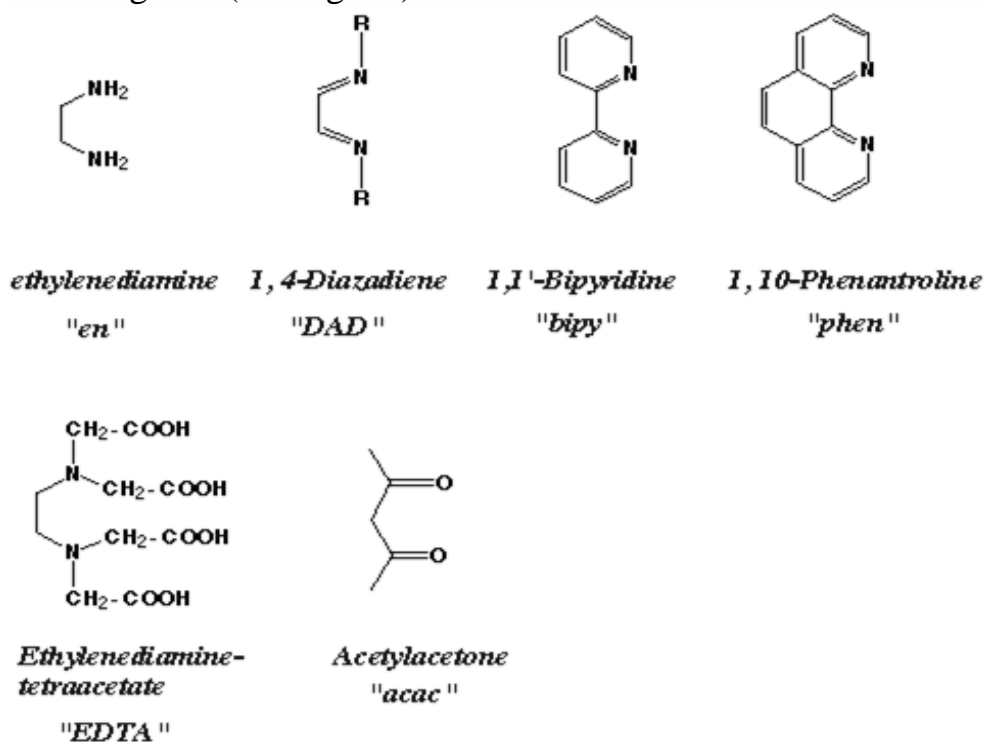
Fig. 18. Examples of multidentate ligands

Common Chelate ligands and their abbreviations

A particularly versatile chelate ligand is the anionic acetylacetone (See Fig. 16, last example) ligands. Acetylacetone ("acac") is a CH-acidic compound that exists as equilibrium between a keto- and an enol-form. The precise position of the equilibrium depends on the temperature and the solvent.

Nonpolar solvents favor the enol-form, polar solvents favor the keto-form. The enol form is stabilized by a intramolecular hydrogen bond (see Fig. 19).

keto-form   *enol-form*
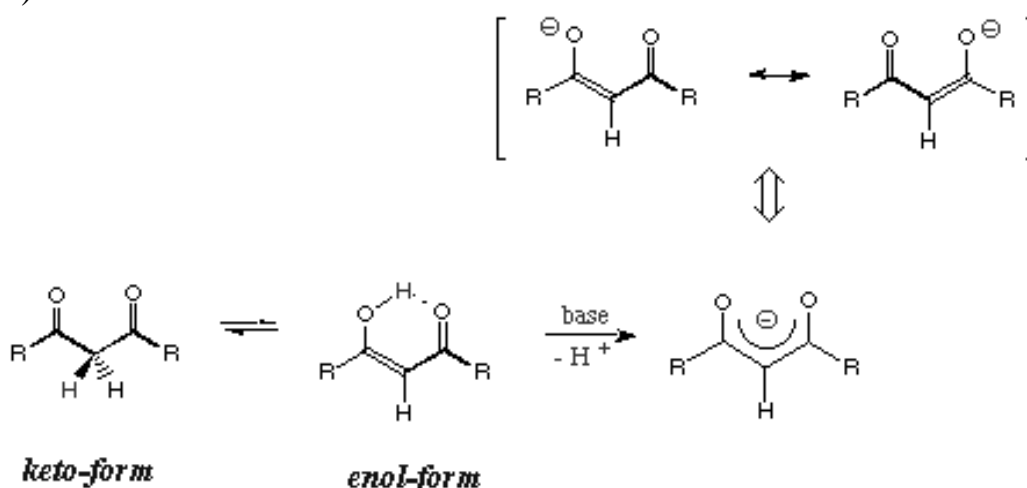
Fig. 19. Isomer forms of Acetylacetone ligand

Both forms are deprotonated to give the same resonance stabilized anion (acac⁻). The anion forms very stable chelate complexes with transition metals and main group elements, e.g. $Cr(acac)_3$, $Be(acac)_2$. These complexes are usually covalent, are soluble in hydrocarbons, can be sublimed and are usually quite stable against water and air. The standard procedure for their synthesis is the reaction of a metal salt, acetylacetone and ammonia (as deprotonation base).

Acetylacetone complexes are valuable staring materials for the synthesis of other transition metal compounds and are often better to handle than the usually very moisture sensitive anhydrous halides.

Crown ethers form a special class of multidentate chelate ligands with particularly high formation constants.

Polyaza-Macrocycles

Polyaza macrocycles are usually of the type N4-Ligand. They are common in nature and also form an important class of dyes, the so called "Phtalocyanines". Phtalocyanines were discovered by accident. An intense blue color was noticed whenever phtalodinitrile was handled in hot copper vessels. The compound that was ultimately isolated was copper(II) phtalocyanine (see Fig. 20).
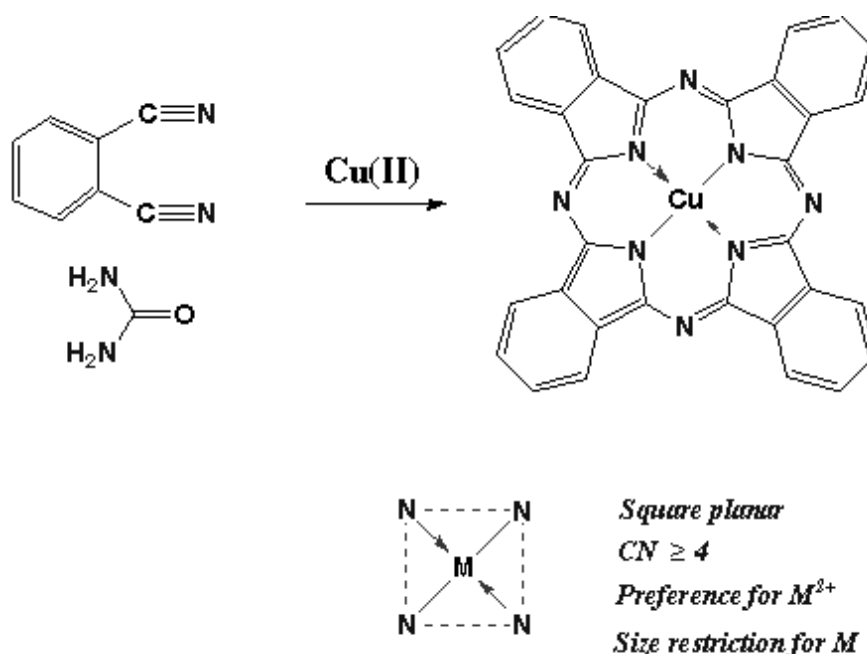
Fig. 20. Copper(II) phtalocyanine: a simple way to a complex molecule

Phtalocyanines are amongst the most stable "organic" molecules. They can be sublimed without decomposition between 400 and 600ºC.

Their very poor solubility in all solvents is a major obstacle for their widespread use but has been overcome in recent years by the introduction of alkylgroups or sulfonic acid groups (for watersolubility).

The phtalocyanines are related to three important N_4-macrocylces: Vitamin B_{12} (Co), Hemoglobin (Fe) and Chlorophyll (Mg) (see Fig. 21).
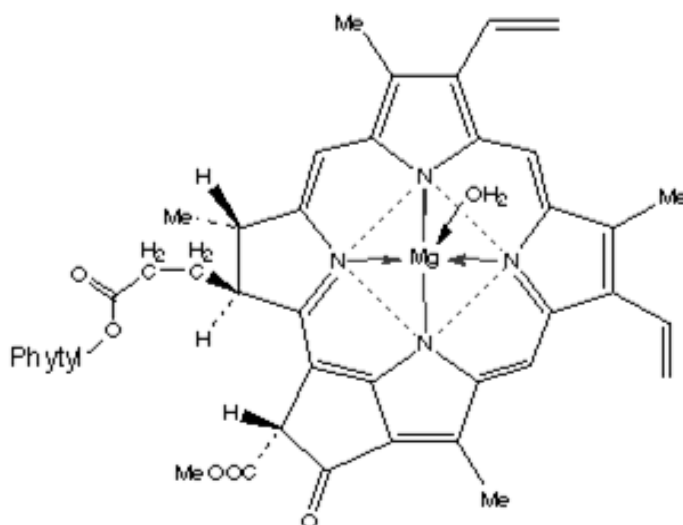
Fig. 21. Chlorophyll structure

The function of Magnesium in Chlorophyll has intrigued chemists since the pioneering studies of Richard Willstätter and Hans Fischer that led to the structure elucidation of chlorophyll (Nobel Prize for Chemistry 1915) and hemin (Nobel Prize for Chemistry 1930). It is now thought that Magnesium supports the special photophysics if the light harvest process. Heavier elements like Zn would damage this delicate process by facilitating the interconversion of singlet and triplet excited states.

CHAPTER 11 CHEMISTRY OF ELEMENTS

11.1 The Halogens

The elements of Group 7A (or the main sub-group of VII group), the Halogens, are:

Symbol	Electron configuration
Fluorine F	$[He]2s^2 2p^5$
Chlorine Cl	$[Ne]3s^2 3p^5$
Bromine Br	$[Ar]4s^2 4p^5$
Iodine I	$[Kr]5s^2 5p^5$
Astatine As	$[Xe]6s^2 6p^5$

All the isotopes of astatine are radioactive, and so this element will not be considered further here. The similarity of their properties is conditioned by similar electronic structure of the atoms where the external energy level is expressed by the electronic formula $ns^2 np^5$. Moreover only F has no d-sublevel and as the result it is exclusively one-valent. Taking into account that F is the most electronegative element it is characterized by two levels of oxidation in compounds (0 and 1-).

Appearance

Fluorine is a poisonous pale yellow gas, Chlorine is a poisonous pale green gas, Bromine is a toxic and caustic brown volatile liquid, and Iodine is a shiny black solid, which easily sublimes to form a violet vapor on heating.

General Reactivity

The elements of Group 17, the Halogens, are very similar set of non-metals. They all exist as diatomic molecules, X_2, and oxidize metals to form halides. The halogen oxides are acidic, and the hydrides HX are covalent. Fluorine is the most electronegative element of all. Generally, electronegativity and oxidizing ability decrease on descending the Group. The result of this decreasing electronegativity is increased covalent character in the compounds, so that AlF_3 is ionic whereas $AlCl_3$ is covalent.

Fluorine shows some anomalies because of the small size of its atom and ion. This allows several F atoms to pack around a different central atom, as in $[AlF_6]^{3-}$ compared with $[AlCl_4]^-$. The F-F bond is also unexpectedly weak because the small size of the F atom brings the lone pairs closer together than in other halogens, and repulsion weakens the bond.

Occurrence and Extraction

The Halogens are too reactive to occur free in nature. Fluorine is mined as fluorspar, calcium fluoride and cryolite. It is extracted by electrolysis as no oxidant will oxidize fluorides to Fluorine. Chlorine is

also found in minerals such as rock salt, and huge quantities of Chloride ions occur in seawater, inland lakes and subterranean brine wells. It is obtained by the electrolysis of molten Sodium Chloride or brine. Bromine is also found as the bromide ion in seawater, and in larger quantities in brine wells, from which it is extracted. Iodine is mined as Sodium Iodate (V) $NaIO_3$, which is present in Chile saltpetre. It is obtained by reaction with Sodium Hydrogen Sulfite.

Physical Properties

At room temperature all the Halogens exist as diatomic molecules. The melting points, boiling points, atomic radii and ionic radii all increase on descending the Group. More than 8 electrons never surround Fluorine, whereas the other halogens may be surrounded by up to 14 electrons.

Chemical Properties

The most characteristic chemical feature of the Halogens is their ability to oxidize. Fluorine has the strongest oxidizing ability, so other elements, which are combined with Fluorine, have their highest possible oxidation number:

$$2F_2 + H_2O = 2HF + OF_2$$

$$F_2^0 + 2\bar{e} \rightarrow 2F^- \quad \bigg| \quad 2 \text{ (reduction);}$$

$$O^{2-} - 4\bar{e} \rightarrow O^{2+} \quad \bigg| \quad 1 \text{ (oxidation).}$$

$$2F_2 + 2NaOH \rightarrow 2NaF + OF_2 + H_2O.$$
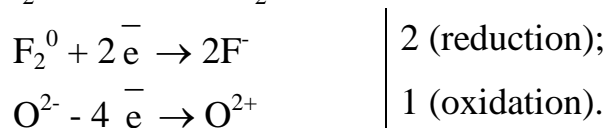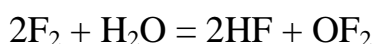
Fluorine is such a strong oxidizing agent that it must be prepared by electrolysis of solid salts:

$$2NaF_{solid} \xrightarrow{\text{electrolysis}} 2Na + F_2\uparrow.$$
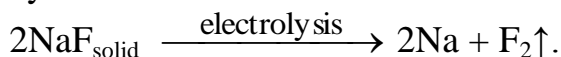
Chlorine is the next strongest oxidizing agent, but it can be prepared by chemical oxidation. Most elements react directly with Chlorine, Bromine and Iodine, with decreasing reactivity going down the Group, but often the reaction must be activated by heat or UV light. The oxidation of Thiosulfate ions, $S_2O_3^{2-}$, by the Halogens is quantitative.

This means that oxidizing agents can be estimated accurately; the oxidizing agent is reacted with excess I^- ions, and the liberated I_2 titrated with standard Thiosulfate solution. The end point is detected with starch as indicator, which forms a dark blue complex with Iodine.

Chlorine, Bromine and Iodine disproportionate in the presence of water and alkalis.

Oxides and Oxoacids

There are no Fluorine oxides as F is more electronegative than O. Chlorine, Bromine and Iodine each form several oxides, which are thermally unstable, such as Chlorine dioxide ClO_2. The only Fluorine oxoacid, HOF, is unstable at room temperature, but there are many

oxoacids of the other Halogens. The best-known salts of these are: Hypochlorite, Chlorate (I) ClO^-, Chlorite, Chlorate (III) ClO_2^-, Hypochlorate, Chlorate (V) ClO_3^-, and Perchlorate, Chlorate (VII) ClO_4^-. These are all powerful oxidizing agents.

Halides

The Halogens can be combined with each other to form interhalogens and polyhalide ions. Olyhalide ions have the general formula $[Y-X-Y]^-$. It is not possible for F to represent X in a polyhalide ion, as it cannot expand its octet.

Hydrides

Hydrogen halides have the general formula HX. HF is a colorless liquid, which boils at $19,5^0C$, and all the other Hydrogen halides are colorless gases. HF is a liquid due to the extensive Hydrogen bonding which occurs between molecules. All the Hydrogen halides are easily dissolved to give acidic solutions, the most widely used being hydrochloric acid, HCl. All except HF are typical acids; they liberate carbon dioxide from Carbonates and form salts with basic oxides. HF is a weak acid because the H-F bond is very strong, and because Hydrogen-bonding occurs between F- and HF in solution.

Oxidation States

Fluorine in all its compounds has an assigned oxidation number of -1, as it is the most electronegative of all the elements. The other halogens show a wide range of oxidation numbers, and the redox chemistry of these halogens is important. The oxidation numbers most commonly shown are odd; there are few compounds with even oxidation numbers and they are often thermally unstable. Chlorine is the third most electronegative element after F and O. The halide ions are readily formed by accepting one electron, as this completes an octet of valence electrons. The electron affinity decreases on descending the Group.

Industrial information

The Halogens are probably the most important Group of the Periodic Table used in industry. Fluorine is widely used as an oxidizing agent. HF is used to etch glass. Chlorine is used for chlorinating of drinking water, and in many organochlorine compounds. Some of these, such as the insecticide DDT, are effective but environmentally damaging, and much controversy surrounds their use. Chlorine dioxide ClO_2 is used to bleach wood pulp for paper making, as it gives a good whiteness without degrading the paper. Hypochlorites are used in domestic bleaches. Potassium chlorate (V) $KClO_3$ is used as an oxidant in fireworks and matches. The properties of the Halogens on the example of Chlorine will be presented below.

Chlorine

Being the third period element, Chlorine has the following electronic structure: $1s^2 2s^2 2p^6 3s^2 3p^5$. The following oxidation numbers are possible for Chlorine in the compounds on the basis of external energy level structure ($3s^2 3p^5$) (see Chapter 2.2-2.3):

Ground (nonexcited) state (1-, 0, 1+ oxidation number, for example, in HCl, Cl_2, HClO compounds):

3s		3p			3d				
↑↓		↑↓	↑↓	↑					
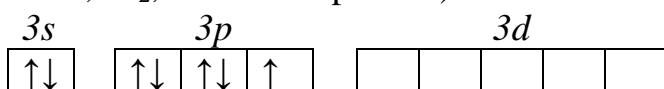
The first excited state (3+ oxidation number, for example, in $HClO_2$ compound);

3s		3p			3d				
↑↓		↑↓	↑	↑	↑				
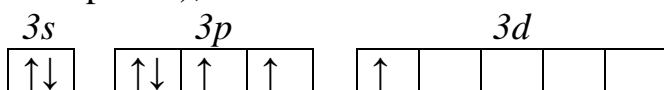
The second excited state (5+ oxidation number, for example, in $HClO_3$ compound);

3s		3p			3d				
↑↓		↑	↑	↑	↑	↑			
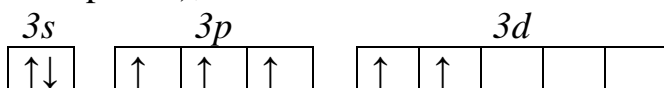
The third excited state (7+ oxidation number, for example, in $HClO_4$ compound).

3s		3p			3d				
↑		↑	↑	↑	↑	↑	↑		

The general characteristics of the most important Chlorine compounds are shown in Table 15.

Table 15. General characteristics of Chlorine compounds

Oxidation number	-1	0	+1	+3	+5	+7
Compounds	HCl, NaCl	Cl_2	Cl_2O, HClO, KClO	Cl_2O_3, $HClO_2$, $NaClO_2$	Cl_2O_5 $HClO_3$ $KClO_3$	Cl_2O_7 $HClO_4$ $NaClO_4$
Names of acids and salts	Hydrochloric, Chlorides	-	Hypochlorous, Hypochlorites, Chlorates (I)	Chlorous, Chlorites, Chlorates (III)	Chloric, Chlorates, Chlorates (V)	Perchloric, Perchlorates, Chlorates (VII)
Redox properties	Only reducing agent	Properties of oxidizing and reducing agent; oxidizing properties prevail	Properties of oxidizing and reducing agent; oxidizing properties prevail	Properties of oxidizing and reducing agent	Reducing properties surpasses oxidizing ones	Only oxidizing agent
Acid-Base properties	HCl - strong acid	-	HClO - weak acid; unstable in free state	$HClO_2$ - acid of medium strength; unstable in free state	$HClO_3$ - strong acid; unstable in free state	$HClO_4$ - extrastrong acid; stable in free state

Strengthening of acid properties

Chlorine (Cl_2) is the typical non-metal with brightly expressed features of oxidant. Due to high activity Chlorine in nature occurs only in bound state as Chlorides: NaCl - halite or rock salt, NaCl · KCl - sylvinite, KCl · MgCl_2 · 6H_2O - carnallite, $MgCl_2 · 5H_2O$ - bischofite, etc. Chlorides are abundant in sea water.

In industry Chlorine is prepared by the electrolysis of concentrated solution of NaCl:

$2NaCl + 2H_2O \leftrightarrow 2NaOH + Cl_2\uparrow + H_2\uparrow$

and in the laboratory - by influence of HCl on MnO_2 or $KMnO_4$:

$2KMnO_4 + 16HCl = 5Cl_2 + 2MnCl_2 + 2KCl + 8H_2O$

$Mn^{7+} + 5\overline{e} \rightarrow$ $\qquad$ 2 (reduction);
Mn^{2+}

$2Cl^- - 2\overline{e} \rightarrow$ $\qquad$ 5 (oxidation).
Cl_2
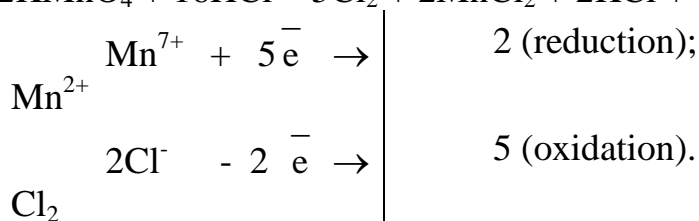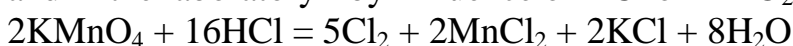
Chlorine actively reacts almost with all periodic system elements. With the metals it forms the salts and with non-metals - halogenous anhydrides:

$Mg + Cl_2 = MgCl_2$;

$2P + 3Cl_2 = 2PCl_3$.
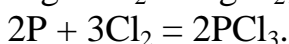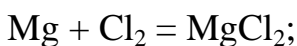
Halogenous anhydrides are hydrolyzed forming both nonmetal acids with the relevant oxidation numbers:

$PCl_5 + 4H_2O = H_3PO_4 + 5HCl$.
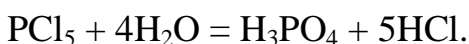
Chlorine does not react directly with Oxygen, Carbon and Nitrogen.

HCl (Hydrochloric aqua solution) is of practical value. In the reaction of the Halogens and Hydrogen composition there is the tendency of oxidative activity weakening from Fluorine and Iodine: Fluorine reacts with Hydrogen generating the explosion in the dark; Chlorine - in air or while heating with the explosion, Bromine and Iodine - in case of extensive heating, for example,

$Cl_2 + H_2 = 2HCl$.
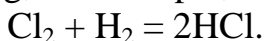
The intensity of HF, HCl, HBr, HI acids increases. It is characterized by number of reaction typical for acids:

$2HCl + 2Na = 2NaCl + H_2\uparrow$;

$2HCl + SrO = SrCl_2 + H_2O$;

$2HCl + Ca(OH)_2 = CaCl_2 + 2H_2O$.
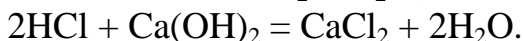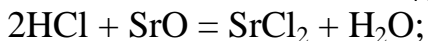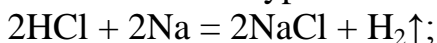
Halogens form Oxygen compounds as well, mainly: oxides, acids and salts.

The basis for preparation of halogens oxygen-contained compounds is their interaction with water and alkalis. In cold the reaction is carried out in case of dynamic balance:

$Cl_2 + H_2O \leftrightarrow HCl + HClO$

$Cl_2^0 + 2\overline{e} \rightarrow 2Cl^-$	1 (reduction);
$Cl_2^0 - 2\overline{e} \rightarrow 2Cl^+$	1 (oxidation).

$2Cl_2 + 2Ca(OH)_2 = CaCl_2 + Ca(ClO)_2 + 2H_2O$.
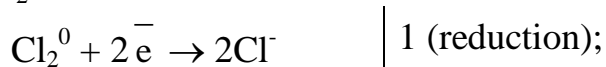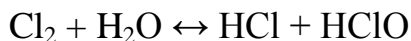
On heating such mixture reacts with the formation of Chlorates:

$3Cl_2 + 3H_2O \xleftrightarrow{\;t\;} 5HCl + HClO_3$;

$Cl_2^0 + 2\overline{e} \rightarrow 2Cl^-$	5 (reduction);
$Cl_2^0 - 10\overline{e} \rightarrow 2Cl^{+5}$	1 (oxidation).

$3Cl_2 + 6NaOH = 5NaCl + NaClO_3 + 3H_2O$.
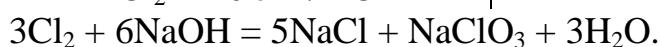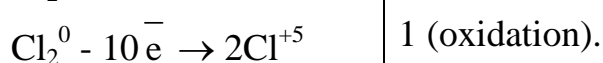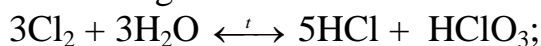
HClO, HBrO, HIO electrolytes are the less stable and the weakest among Chlorine oxyacids and other halogens.

Thus in air HClO is decayed with active (atomic) Oxygen:

$HClO = HCl + \overset{\bullet}{O}$.
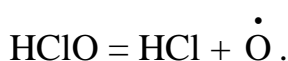
Active Oxygen discolors many colorants and that is why Chlorine (1+) oxyacid salts are called bleaching: $NaClO$ are used for bleach and wash; the mixture of $Ca(ClO)_2$ and $CaCl_2$ which is known as bleaching powder, is used in agriculture for disinfections of the facilities, warehouses, and animal corpses.

Sodium, Magnesium and Calcium chlorates are of great value for the agriculture. They are used as herbicides for wild grass control. In Redox reactions Cl^- is exclusively reducing agent, but Cl^{7+} - only the oxidizing one. Halogens with the medium oxidation numbers (Cl^0, Cl^+, Cl^{3+}, Cl^{5+}) may be mainly as the reducing agents, but also the oxidizing ones. Oxidative activity of the compounds is increased from Cl^{7+} to Cl^{1+}.

For example,

$2KI + NaClO + H_2SO_4 = I_2 + NaCl + K_2SO_4 + H_2O$

$Cl^+ + 2\overline{e} \rightarrow Cl^-$	1 (reduction);
$2I^- - 2\overline{e} \rightarrow I_2$	1 (oxidation).
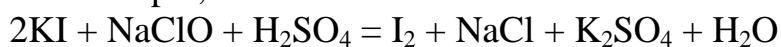
11.2 The Chalcogens

The elements of Group 6A (or the main sub-group of VI group) are:

Symbol	Electron configuration
Oxygen O	$[He]2s^2 2p^4$
Sulfur S	$[Ne]3s^2 3p^4$
Selenium Se	$[Ar]3d^{10} 4s^2 4p^4$
Tellurium Te	$[Kr]4d^{10} 5s^2 5p^4$

Polonium Po   [Xe]$4f^{14}5d^{10}6s^2\,6p^4$

Often this group of chemical elements (except the last Po) is named **the Chalcogens.**

Appearance

The first element of this sub-group, Oxygen, is the only gas, and is colorless and odorless. Sulfur is a pale yellow, brittle solid. Selenium can have either an amorphous or a crystalline structure; the amorphous form can be red or black, and the crystalline form can be red or gray. Tellurium is a silvery-white color with a metallic luster. Polonium is a naturally radioactive element.

Selenium and Tellurium are rare elements with few uses, and along with Polonium will not be considered further here.

General Reactivity

Oxygen and Sulfur are highly electronegative elements - the electronegativity of Oxygen is second only to that of Fluorine. Their general reactivity is therefore dominated by their ability to gain electrons.

There is a transition down the sub-group from non-metallic to more metallic properties, so that Oxygen is a non-metal and Tellurium a metalloid. All the elements except Polonium form M^{2-} ions.

There is a marked difference between Oxygen and the other members of the Group. This arises from:

> ➤ the small size of the O atom which enables it to form double bonds;
> ➤ its inability to expand its valence shell like the other elements as it has no accessible d-orbitals;
> ➤ its high electronegativity, which enables it to participate in Hydrogen-bonding.

Occurrence and Extraction

Oxygen occurs widely as the free element in the form of O_2, comprising 21% of the air by volume. It also occurs as O_3, ozone, at high altitudes in the ozone layer. In the combined form it is found in very many minerals, and also in water. Oxygen is obtained industrially by the fractional distillation of liquid air. It is stored under pressure in cylinders.

Sulfur is found as the free element and also as metal Sulfide ores and a number of Sulfates. Native sulfur is brought to the surface from underground deposits by the Frasch Process, which uses superheated water to melt the Sulfur and force it upwards.

Physical Properties

The covalent and ionic radii increase going down the sub-group, as electrons occupy shells with higher quantum numbers.

Oxygen occurs as two gaseous allotropes, O_2 (dioxygen or more commonly Oxygen) and O_3 (trioxygen or ozone). Oxygen is more common. It condenses to a pale blue paramagnetic liquid at -183^0C. Ozone is a pale blue, pungent gas, which condenses to an inky-blue liquid at -112^0C. The ozone layer in the upper atmosphere is an important shield against harmful UV radiation from the Sun.

Sulfur has several allotropes, the two main ones being rhombic and monoclinic sulfur. These both consist of S_8 molecules.

Industrial Information

Sulfuric acid is of immense industrial importance. Because it has three chemical functions and is very cheap to produce, Sulfuric acid is used at some stage of the manufacture of most products. It is said that the economic prosperity of a country can be assessed by its consumption of sulfuric acid. It is manufactured by the Contact Process.

Hydrogen peroxide H_2O_2 is used to bleach hair and textiles, as a mild disinfectant and in pollution control.

Sulfur hexafluoride SF_6 cannot be ionized by electric fields and so is widely used as a gaseous insulator in transformers and electrical switchgear.

Oxygen

Oxygen is the element of the second period, its formula is $1s^2 2s^2 2p^4$.

$$2p$$
$$2s \quad \boxed{\uparrow\downarrow}\,\boxed{\uparrow\downarrow}\,\boxed{\uparrow}$$
$$\boxed{\uparrow\downarrow}$$

$$1s$$
$$\boxed{\uparrow\downarrow}$$
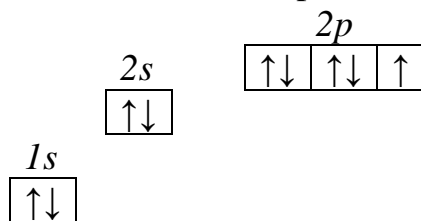
On the assumption of external electron shell structure (graphic presentation) and electronegativity of Oxygen, it is characterized by oxidation number equal to 2-, moreover, in composition with Fluorine the oxidation number of Oxygen will be 2+ (for example, OF_2) but in peroxides it will be 1- (for example, H_2O_2) or, sometimes, $-\frac{1}{2}$ (for example, superoxide KO_2).

Oxygen, like Fluorine, forms compounds with all elements except Helium, Neon and Argon. Atomic Oxygen is extremely active.

In elemental state Oxygen is mostly characterized as the oxidizing agent in the reactions:

1) $4FeS + 7O_2 = 2Fe_2O_3 + 4SO_2$

$$O_2^0 + 4\,\overline{e} \rightarrow 2O^{2-} \qquad 7 \text{ (reduction)};$$

$$S^{2-} \quad - \; 6\;\overline{e} \rightarrow S^{+4}$$

$$Fe^{2+} - 1\overline{e} \rightarrow Fe^{3+} \qquad \Big\} \; 4 \text{ (oxidation)}.$$

2) $2 KI + O_3 + H_2O = I_2 + 2 KOH + O_2$

$$O^0 + 2\bar{e} \rightarrow O^{2-} \quad \Big| \quad \text{1 (reduction);}$$

$$2I^- - 2\bar{e} \rightarrow I_2^0 \quad \Big| \quad \text{1 (oxidation).}$$
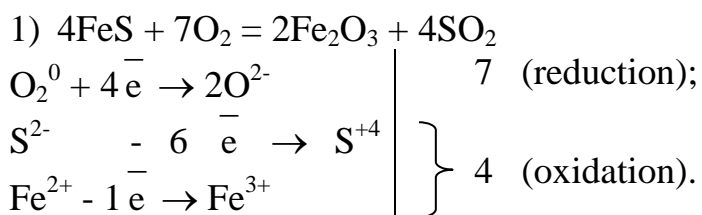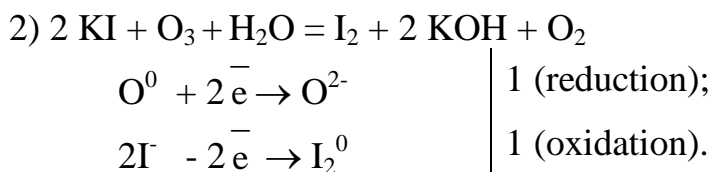
Oxygen compounds in which the oxidation number is equal to 1- are called **peroxides.** For example, Hydrogen peroxide H_2O_2, where covalent and non-polar bonds in molecule connect two atoms of Oxygen.

Water solution of Hydrogen peroxide (perhydrol) presents weak dibasic acid:

$H_2O_2 \leftrightarrow H^+ + HO_2^-$;
$HO_2^- \leftrightarrow H^+ + O_2^{2-}$.
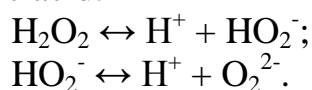
Medium of oxidation number of Oxygen in peroxides causes its oxidation-reduction duality in the reactions. H_2O_2 is the reducing agent:

$H_2O_2 + 2KMnO_4 + 2KOH = 2K_2MnO_4 + 2H_2O + O_2$

$$Mn^{7+} + \bar{e} \rightarrow Mn^{6+} \quad \Big| \quad \text{2 (reduction);}$$

$$2O^- - 2\bar{e} \rightarrow O_2^0 \quad \Big| \quad \text{1 (oxidation).}$$
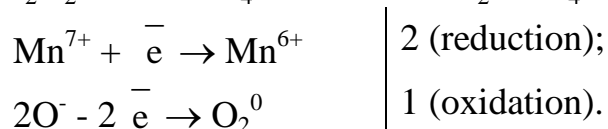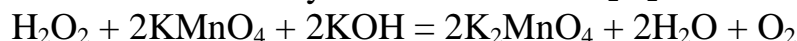
but in presence of strong reducing agent it is oxidizing agent:

$H_2O_2 + 2KI + H_2SO_4 = I_2 + K_2SO_4 + 2H_2O$

$$2O^- + 2\bar{e} \rightarrow 2O^{2-} \quad \Big| \quad \text{1 (reduction);}$$

$$2I^- - 2\bar{e} \rightarrow I_2^0 \quad \Big| \quad \text{1 (oxidation).}$$
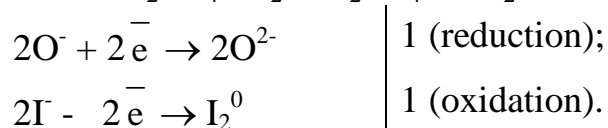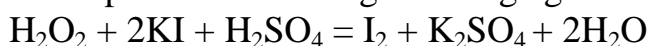
Ozone is also a highly reactive and powerful oxidizing agent which can cleave the C=C double bond.

Sulfur

In contrast to Oxygen, Sulfur atom has free *d*-sublevel in the external electronic shell: *$1s^2 2s^2 2p^6 3s^2 3p^4 3d^0$*.

Accordingly, Sulfur can form the compounds due to two, four and six unpaired electrons, showing such oxidation levels: 2-, 0, 2+, 4+, 6+:

Ground (nonexcited) state (2-, 0, 2+ oxidation number, for example, in H_2S, S, SO compounds):

3s	*3p*	*3d*
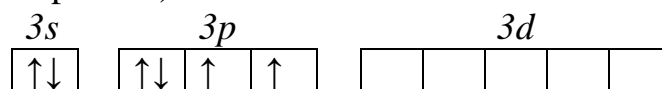
The first excited state (4+ oxidation number, for example, in SO_2 compound):

s	*3p*	*3d*
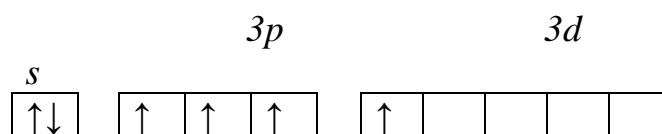
The second excited state (6+ oxidation number, for example, in H_2SO_4 compound):

3s   *3p*   *3d*

| ↑ | | ↑ | ↑ | ↑ | | ↑ | ↑ | | | |
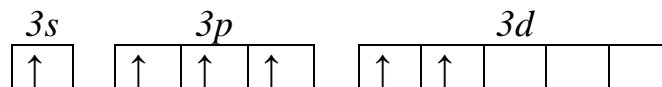
Characteristic of the most important sulfur compounds is shown in Table 16.

Sulfur is the typical non-metal, which is inferior to Halogens, Oxygen and Nitrogen in electroactivity and thus is oxidized by them:

$S + O_2 = SO_2$;

$S + 2Cl_2 = SCl_4$.
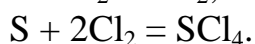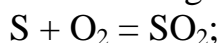
As oxidizing agent, Sulfur reacts with the metals and Hydrogen at high temperature. For example,

$Zn + S = ZnS$;

$S + H_2 = H_2S$.
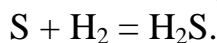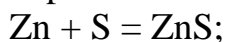
Hydrogen sulphide (H_2S) is the gas and occurs in nature as the result of putrescent bacteria action to proteins containing sulfur so it can be detected by its characteristic odor ("bad eggs gas"). Inhalation of pure Hydrogen sulphide can bring about to immediate death; even 0,01% of its concentration in the air is extremely dangerous for human being.

Aqueous solution of H_2S is the weak dibasic acid; therefore there are acid and neutral salts (sulphides and hydrosulphides):

$H_2S \leftrightarrow H^+ + HS^-$;

$HS^- \leftrightarrow H^+ + S^{2-}$.

H_2S is strong reducing agent. In air it burns with the generation of SO_2 or S (in case of Oxygen deficit):

$$2 H_2S + 3 O_2 = 2 H_2O + 2 SO_3$$

$$O_2^0 + 4 \overline{e} \rightarrow 2O^{2-} \qquad 3 \quad \text{(reduction)};$$

$$S^{2-} - 6 \overline{e} \rightarrow S^{4+} \qquad 2 \quad \text{(oxidation)}.$$

or $2 H_2S + O_2$ (in deficit) $= 2 H_2O + 2 S$

$$O_2^0 + 4 \overline{e} \rightarrow 2O^{2-} \qquad 1 \quad \text{(reduction)};$$

$$S^{2-} - 2 \overline{e} \rightarrow S^0 \qquad 2 \quad \text{(oxidation)}.$$
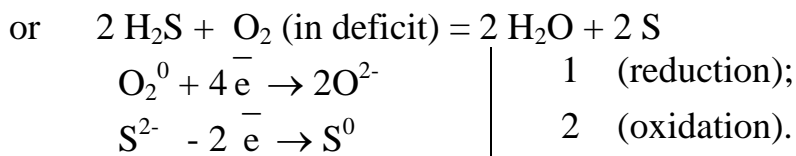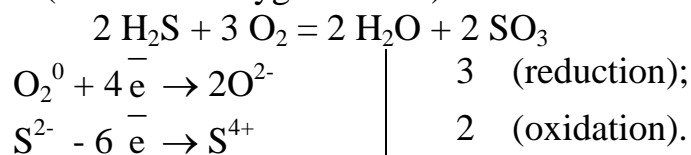
Table 16. Characteristic of the most important Sulfur compounds

Oxidation numbers	2-	1-	0	2+	4+	6+
Compounds	H_2S, CuS	H_2S_2; FeS_2 (pyrite)	S	SO	SO_2, H_2SO_3	SO_3, H_2SO_4
Name of corresponding acids and salts	Hydrosulfuric acid, sulfides	Persulfides	Free Sulfur	Sulfur (II) Oxide	Sulfur acid, sulphites	Sulfuric acid, sulphates
Redox properties	Only reducing agent	Properties of oxidizing and reducing agent	Properties of oxidizing and reducing agent	-	Reducing properties surpasses oxidizing ones	Only oxidizing agent
Acid-base properties	H_2S - weak acid	-	-	Unstable non-Salifiable Oxide	H_2SO_3 - acid of medium strength, unstable in water solutions	H_2SO_4 - strong acid, stable in water solutions

Strengthening of acid properties

Sulfur dioxide (SO_2) is **sulfurous gas** (pungent, choking gas) formed when Sulfur or Sulfides are burnt in air or Oxygen, and as all fossil fuels contain Sulfur it is formed when they burn and contributes to the problem of *"acid rain"* :

$$S + O_2 \xrightarrow{t} SO_2 \uparrow;$$
$$2CuS + 3O_2 \xrightarrow{t} 2\,CuO + \ 2\,SO_2 \uparrow;$$
$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2\uparrow.$$
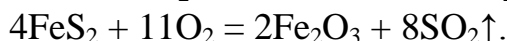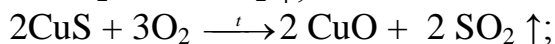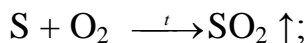
SO_2 may be prepared by Sulfuric acid reduction:

$$2H_2SO_4\ (conc) + Cu = CuSO_4 \ + SO_2 \uparrow + 2H_2O.$$

Aqueous solution of SO_2 is called Sulfurous acid, which is unknown in free state. H_2SO_3 is of medium strength and can produce acid and neutral salts. Sulfurous acid salts decay in case of strong acids action with SO_2 isolation. This is the base for getting of Sulfur dioxide in laboratory conditions:

$$Na_2SO_3 + 2HCl = 2NaCl + SO_2 \uparrow + H_2O.$$

The medium of oxidation number in Sulfur (IV) compounds causes their oxidation-reduction duality:

$$Na_2SO_3 + Cl_2 + H_2O = NaHSO_4 + HCl + NaCl$$

$Cl_2^0 \ + 2\ \overline{e} \rightarrow \ 2Cl^-$	1 (reduction);
$S^{4+} \ - \ 2\ \overline{e} \rightarrow S^{6+}$	1 (oxidation).

$$SO_2 + 2\,H_2S = 3\,S + 2H_2O$$

$S^{4+} + 4\ \overline{e} \rightarrow S^0$	1 (reduction);
$S^{2-} \ - 2\ \overline{e} \rightarrow S^0$	2 (oxidation).
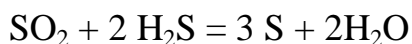
SO_2 is used for fumigation of basements, cellars in order to avoid funguses. Calcium hydroSulfite $Ca(HSO_3)_2$ with sulfurous acid is used for sulfitation - one of the methods for preserving of tender fruits and vegetables.

Sulfur trioxide (SO_3) or Sulfur (VI) oxide is the Sulfur acid anhydride. In industry it is produced by SO_2 oxidation in presence of catalyst (Pt) (in so-called Contact Process):

$$2\,SO_2 + O_2 = 2\,SO_3.$$
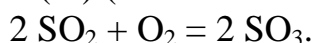
Sulfuric acid is manufactured as the result of SO_2 interaction with water or dilute sulfuric acid:

$$SO_3 + H_2O = H_2SO_4.$$

Strong acidic properties of H_2SO_4 solutions are the basis for their use in fertilizer production or mineral premixes for animals (simple and triple superphosphates, Ammonium Sulfate):

$$Ca_3(PO_4)_2 + 2H_2SO_4 + 5H_2O = \underbrace{Ca(H_2PO_4)_2 \cdot H_2O + 2[CaSO_4 \cdot 2H_2O]};$$

Simple superphosphate

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 2H_3PO_4 + 3CaSO_4;$$
$$Ca_3(PO_4)_2 + 4H_3PO_4 + 3H_2O = 3 \underbrace{Ca(H_2PO_4)_2 \cdot H_2O}.$$

Triple superphosphate

$$H_2SO_4 + 2NH_3 = (NH_4)_2SO_4.$$
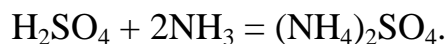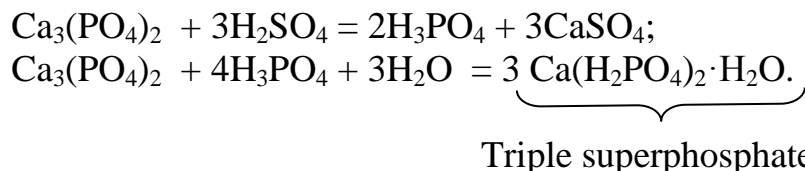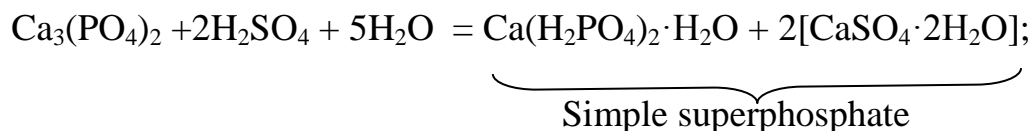
Concentrated H_2SO_4 is a fairly strong oxidizing agent. Non-metals are oxidized by it up to oxides and H_2SO_4 itself reduces to SO_2:

$$C + 2 H_2SO_4 \text{ (conc)} = CO_2 + SO_2 + 2 H_2O$$

$$
\begin{array}{c|c}
S^{6+} + 2 \, \overline{e} \rightarrow S^{4+} & 2 \\
& \text{(reduction)}; \\
\hline
C^0 - 4 \, \overline{e} \rightarrow C^{4+} & 1 \\
& \text{(oxidation).}
\end{array}
$$
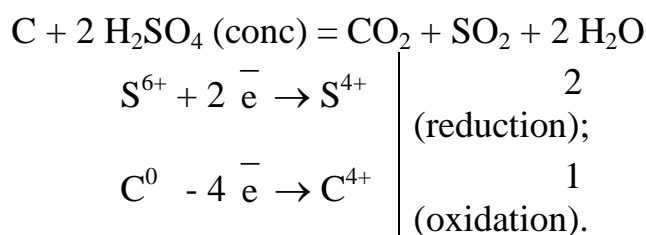
11.3 Nitrogen, Phosphorus

The elements of Group 5A (or the main sub-group of V group) are:

Symbol	Electron configuration
Nitrogen N	$[He]2s^2 2p^3$
Phosphorus P	$[Ne]3s^2 3p^3$
Arsenic As	$[Ar]3d^{10}4s^2 4p^3$
Antimony Sb	$[Kr]4d^{10}5s^2 5p^3$
Bismuth Bi	$[Xe]4f^{14}5d^{10}6s^2 6p^3$

The most important members of this sub-group are Nitrogen and Phosphorus. The other elements will mostly not be considered here.

Appearance

The appearance of the Group 5A elements varies widely. Nitrogen is a colorless, odorless gas; Phosphorus exists in white, red and black solid forms (allotropic modifications); Arsenic is found in yellow and gray solid forms; Antimony is found in a metallic or amorphous gray form; and finally Bismuth is a white, crystalline, brittle metal. These appearances reflect the changing nature of the elements as the sub-Group is descended, from non-metal to metal.

General Reactivity

The elements of Group 5A show a marked trend towards metallic character on descending the Group. This trend is reflected both in their

structures and in their chemical properties, as for example in the oxides, which become increasingly basic.

Occurrence

Nitrogen is found in the atmosphere, and makes up 78% of the air by volume. Phosphorus is not found free in nature, but occurs in several minerals and ores such as Phosphate rock (see **Appendix 12**). The other elements are all found in the elemental form in the Earth crust, but more frequently as minerals.

Physical Properties

The physical properties of this Group vary widely as Nitrogen is a gas, and the other elements are solids of increasingly metallic character.

Nitrogen exists as the diatomic molecule N_2. It is a colorless, odorless gas, which condenses to a colorless liquid at -196^0C. The strength of the bond and the short bond length provide evidence for the bond between the N atoms being a triple bond: $N \equiv N$.

Phosphorus has at least two allotropes, red and white one. White phosphorus is a solid composed of covalent tetrahedral P_4 molecules, and red phosphorus is an amorphous solid, which has an extended covalent structure.

The covalent radii of the atoms increase on descending the sub-Group. However, the N atom is anomalously small and so it can multiple-bond to other N, C and O atoms.

Chemical Properties

Both Nitrogen and phosphorus exist in oxidation states +3 and +5 in their compounds. Nitrogen is very unreactive. The only element to react with Nitrogen at room temperature is Lithium, to form the nitride Li_3N. Magnesium also reacts directly, but only when ignited. Some microorganisms, however, have developed a mechanism for reacting directly with Nitrogen gas and building it into protein - this is called Nitrogen fixation, and is an important early step in the food chain.

Phosphorus is more reactive than Nitrogen. It reacts with metals to form phosphides, with Sulfur to form Sulfides, with halogens to form halides, and ignites in air to form oxides. It also reacts with both alkalis and concentrated nitric acid.

Industrial Information

For industrial use Nitrogen is obtained by fractional distillation of the air. It is used for the manufacture of ammonia by the Haber-Bosch Process:

$N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g)$
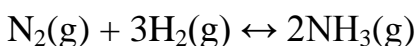
A catalyst of finely-divided Iron is required for this equilibrium reaction. The mixture is heated to 450°C at 250 atm of pressure. Working at high pressure increases the yield of ammonia, but this adds to the cost of

the plant, and a compromise between cost and yield is needed. The reaction is exothermic so low temperatures increase the yield of ammonia, but this slows up the reaction so again a compromise is needed. At the temperatures and pressures used in practice about 15% conversion is attained. The ammonia is condensed and removed from the plant and the unreacted gases are recycled.

Ammonia has numerous uses - approximately 100 megatonnes are produced worldwide each year. It is used as a fertilizer both directly and after conversion to other fertilizers such as Ammonium Nitrate. It is also a raw material for nitric acid manufacture and for the production of nylon. Gaseous Nitrogen is used to provide an inert atmosphere for reactions, which cannot be carried out in Oxygen. It is also used as a carrier gas in liquid-gas chromatography. Phosphorus is used in match-heads and on safety.

Nitrogen

Its electronic formula is $1s^2 2s^2 2p^3$. On the basis of graphic drawing of the external energy level ($2s^2 2p^3$) the following valency state and oxidation numbers are possible for Nitrogen:

$$
\begin{array}{c}
2p \\
2s \quad \boxed{\uparrow}\,\boxed{\uparrow}\,\boxed{\uparrow} \\
\boxed{\uparrow\downarrow} \\
1s \\
\boxed{\uparrow\downarrow}
\end{array}
$$
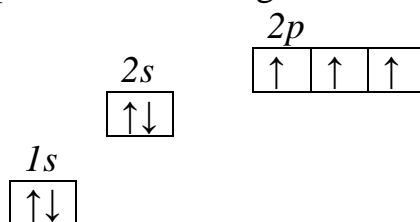
Valency is III (owing to three unpaired electrons of $2p$-sublevel). Valency is IV (three - owing to unpaired $2p$-electrons, the forth bond - after donor-acceptor mechanism using $2s$-electrons). Oxidation numbers are 3-, 2-, 1-, 0, 1+, 2+, 3+, 4+, 5+.

Nitrogen is the typical non-metal, only Fluorine and Oxygen have stronger electronegativity (3,0). The most widespread Nitrogen compounds of different oxidation levels (from 3- to 5+) are shown in Table 17.

Ammonia (NH_3) is colorless gas with purgen odor. In the laboratory heating of NH_4Cl with Calcium hydroxide or any strong alkalis can produce it:

$$2\,NH_4Cl + Ca(OH)_2 \xrightarrow{\;t\;} 2\,NH_3\uparrow + CaCl_2 + 2\,H_2O.$$
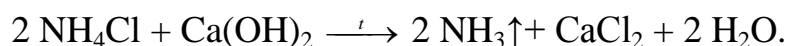
Ammonia can react with water and acids, showing the main properties in the reactions. Practically it does not make NH_4OH hydroxide well dissolved in water (31% at 20^0C), but reacts with H_2O by means of Hydrogen bond:

Table 17. General characteristic of Nitrogen compounds

Oxidation numbers	3-	2-	1-	0	1+	2+	3+	4+	5+
Nitrogen compounds	NH_3 (NH_4^+)	N_2H_4 - hydrazine	NH_2OH - hydroxyl-amine	N_2	N_2O - laughing gas	NO (N_2O_2)	N_2O_3	NO_2 (N_2O_4)	N_2O_5
Properties in reactions without oxidation number	Weak basic properties; Proton acceptor	Basic properties; Proton acceptor	Weak base	Low chemical activity	Indifferent oxides			Acid oxides	
							HNO_2	HNO_2 + HNO_3	HNO_3
Properties in reactions with oxidation number change	Reducing agent only	Reduction properties prevail over oxidation ones	Oxidizing agent; reducing agent relative to F_2 and O_2	Oxidizing and reducing agents (depending on reaction conditions)					Oxidizing agent only

$NH_3 + H_2O \leftrightarrow NH_3 \cdot H_2O$;

$NH_3 \cdot H_2O \leftrightarrow NH_4OH$.
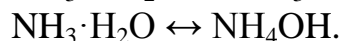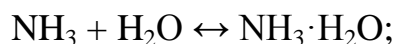
The following important fertilizers are produced by ammonia interaction with acids:

$NH_3 + HNO_3 = NH_4NO_3$ - Ammonia Nitrate;

$2NH_3 + H_2SO_4 = (NH_4)_2SO_4$ - Ammonia Sulfate;

$NH_3 + H_3PO_4 = NH_4H_2PO_4$ - Ammonia dihydrophosphate (**ammophos**);

$2NH_3 + H_3PO_4 = (NH_4)_2HPO_4$ - Ammonia hydrophosphate (**diammophos**).
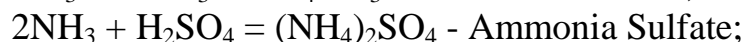
Nitric oxide (NO) is get by oxidation of Ammonia and it is used as the intermediate product in HNO_3 production:

$$4\ NH_3 + 5\ O_2 \xrightarrow{\ Kt\ } 4\ NO + 6\ H_2O$$

$O_2^0 + 4\ \bar{e} \rightarrow 2\ O^{2-}$	5 (reduction);
$N^{3-} - 5\ \bar{e} \rightarrow N^{2+}$	4 (oxidation).
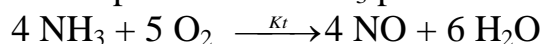
Nitrogen oxide (III) and nitrous acid

Nitrogen oxide (III) is nitrous acid anhydride:

$N_2O_3 + H_2O \leftrightarrow 2HNO_2$.
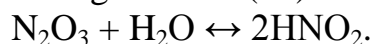
As acid oxide it reacts with alkalis:

$N_2O_3 + 2NaOH = 2NaNO_2 + H_2O$.
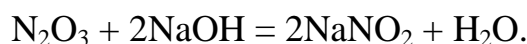
Nitrous acid (HNO_2) dissociates with Hydrogen ions formation:

$HNO_2 \leftrightarrow H^+ + NO_2^-$.

At it's heating and under the influence of strong acids the process of disproportion takes place:

$$3HNO_2 \leftrightarrow HNO_3 + 2NO + H_2O$$

$N^{3+} + \bar{e} \rightarrow N^{2+}$	2 (reduction);
$N^{3+} - 2\ \bar{e} \rightarrow N^{5+}$	1 (oxidation).
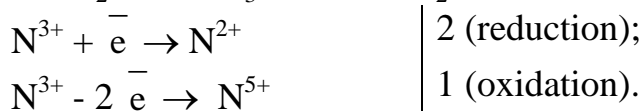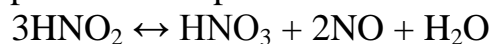
Nitrous acid and its salts can be both reducing and oxidizing agents:

$$2NaNO_2 + 2KI + 2H_2SO_4 = I_2 + 2NO + K_2SO_4 + Na_2SO_4 + 2H_2O$$

$N^{3+} + 1\ \bar{e} \rightarrow N^{2+}$	2 (reduction);
$2I^- - 2\ \bar{e} \rightarrow I_2^0$	1 (oxidation).

$$5KNO_2 + 2KMnO_4 + 3H_2SO_4 = 5KNO_3 + 2MnSO_4 + K_2SO_4 + 3H_2O$$

$Mn^{7+} + 5\ \bar{e} \rightarrow Mn^{2+}$	2 (reduction);
$N^{3+-} - 2\ \bar{e} \rightarrow N^{5+}$	5 (oxidation).
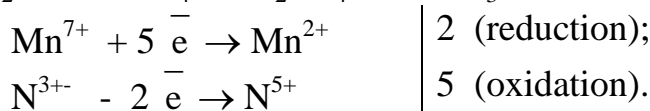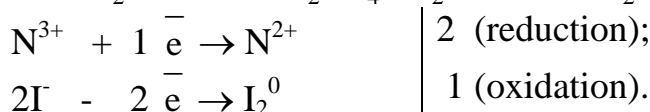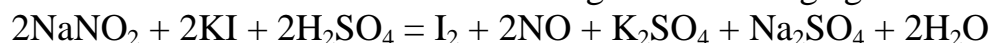
Nitric oxide (V) and nitric acid

Nitric acid and its salts (Nitrates) have the oxidizing properties:

$$3KNO_3 + 8Al + 5KOH + 2H_2O = 3NH_3 + 8KAlO_2$$

$N^{5+} + 8\ \bar{e} \rightarrow N^{3-}$	3 (reduction);
$Al^0 - 3\ \bar{e} \rightarrow Al^{3+}$	8 (oxidation).
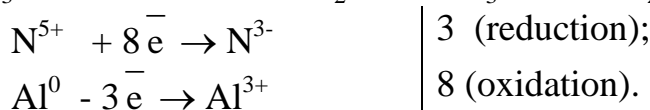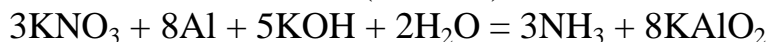
Particular feature of nitric acid is in interaction almost with all metals and non-metals, at the same time it oxidizes them. The reduction of N(5+) but not H(1+) as with acids-oxidizing agents always takes place. Generally NO and NO_2 prevail among reduction products. Active metals (Mg, Zn, Ca and others) reduce diluted HNO_3 up to N_2 and NH_4NO_3.

At the same time some N(5+) reduction products can be isolated. However, the equations of such reactions are relative and only one compound (NO_2, NO or N_2, NH_3), formed in quantity, is indicated in the products:

$$4\ Mg + 10HNO_3\ (diluted) = 4Mg(NO_3)_2 + NH_4NO_3 + 3H_2O;$$
$$Cu + 4HNO_3\ (conc) =\ Cu(NO_3)_2 + 2NO_2 + 2H_2O;$$
$$S + 6HNO_3\ (conc) =\ H_2SO_4 + 6NO_2 + 2H_2O;$$
$$3P + 5HNO_3\ (diluted) + 2H_2O = 3H_3PO_4 + 5NO.$$
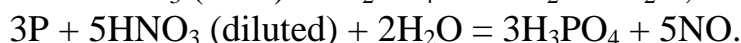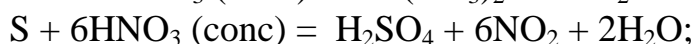
Nitric acid salts - Sodium, Potassium, ammonia, and calcium Nitrates are of great practical value. They are called saltpeters and are used in great quantity as fertililizers.

Phosphorus

The electronic formula of phosphorus is $1s^2 2s^2 2p^6 3s^2 3p^3 3d^0$. $3s^2 3p^3 3d^0$ is the configuration of external electronic shell of phosphorus atom. In contrast to Nitrogen atom the phosphorus atom has unoccupied d-orbitals, thus gives the possibility to pass into excited state at "pair break" of $3s$-electrons. According to current concept the following oxidation numbers are typical for phosphorus atom: 3-, 0, 3+, 5+:

Ground (nonexcited) state (3-, 0, 3+ oxidation number, for example, in PH_3, P, P_2O_3 compounds):

$3s$		$3p$			$3d$				
↑↓		↑	↑	↑					
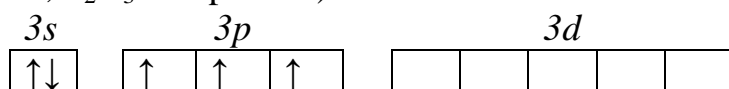
The excited state (5+ oxidation number, for example, in P_2O_5 compound):

$3s$		$3p$			$3d$				
↑		↑	↑	↑		↑	↑		
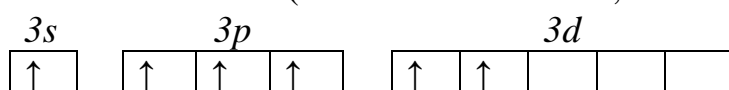
The most typical phosphorus compounds are given in Table 18.

Table 18. Compounds of Phosphorus

Oxidation numbers	3-	0	1+	3+	5+
Compound	PH_3	P (P_2, P_4, P_n)	H_3PO_2	P_2O_3, H_3PO_3	P_2O_5, H_3PO_4, HPO_3, $H_4P_2O_7$

Chemical properties	Reducing agent only	Oxidizing and reducing agents	Hypophosphorous acid, strong reducing agent	Phosphorus acid, reducing agent	Phosphoric anhydride and phosphoric acids, oxidizing agent only

Phosphorus is produced from natural Phosphates of P_2O_5 vapors reduction by coal, which is isolated from melt (at 1500^0C) according to the reaction:

$Ca_3(PO_4)_2 + 3SiO_2 \xrightarrow{\ t\ } 3CaSiO_3 + P_2O_5$;

$P_2O_5 + 5C \xrightarrow{\ t\ } 5CO + 2P$

$$P^{5+} + 5\bar{e} \to P^0 \qquad\qquad 2 \text{ (reduction)};$$

$$C^0 - 2\bar{e} \to C^{2+} \qquad\qquad 5 \text{ (oxidation)}.$$
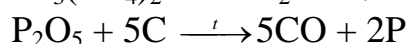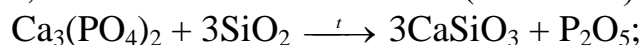
Phosphorus behaves as the typical non-metal. It reacts with Oxygen, formed acid oxides:

$4P + 3O_2 = 2P_2O_3$;

$4P + 5O_2 = 2P_2O_5$.
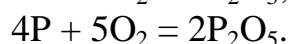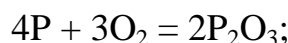
Phosphorus oxides (V), phosphoric acid, Phosphates

P_2O_5 (P_4O_{10}) is very hygroscopic white powder and the most effective agent for drying. Interacting with water it forms phosphoric (monophosphoric) acid:

$P_4O_{10} + 6H_2O \xrightarrow{\ t\ } 4H_3PO_4$.
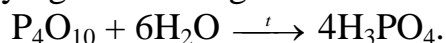
Acid properties of P_2O_5 are shown in its interaction with hydroxides and basic oxides:

$6KOH + P_2O_5 = 2K_3PO_4 + 3H_2O$;

$3CaO + P_2O_5 = Ca_3(PO_4)_2$.
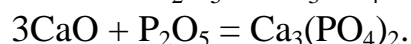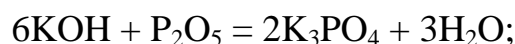
Orthophosphoric acid H_3PO_4 is threebasic acid:

$$\begin{array}{l} \text{H-O} \searrow \\ \text{H-O} \longrightarrow \text{P} = \text{O} \\ \text{H-O} \nearrow \end{array}$$
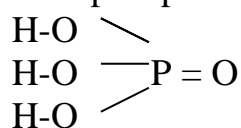
At heating monophosphoric acid dehydration and formation of cyclic or linear polyphosphoric acids take place and among them diphosphoric and metaphosphoric acids are of great value:

$2H_3PO_4 = H_2O + H_4P_2O_7$ (diphosphoric acid);

$H_4P_2O_7 = H_2O + 2HPO_3$ (metaphosphoric acid).
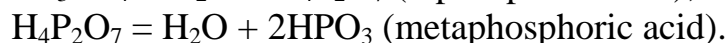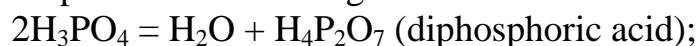
In fact, metaphosphoric acid is inorganic polymer of cyclic structure mostly with three and four chain rings: $(HPO_3)_3$ and $(HPO_3)_4$. Diphosphoric acid and other condensed phosphoric acids with the same structure are inorganic polymers:

$$\begin{array}{ccc} & O & O \\ & || & || \\ H-O- & P-O- & P-O-H \\ & | & | \\ & O-H & O-H \end{array}$$
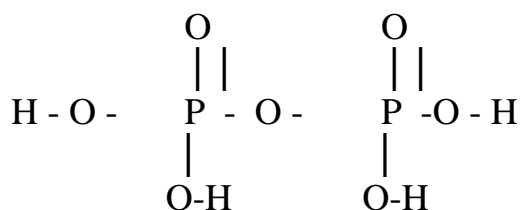
In Phosphate fertilizer production the extraction phosphoric acid is received by sulfuric acid action to $Ca_3(PO_4)_2$, which is the part of natural phosphorites and apatites:

$Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4$.
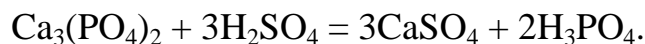
Phosphoric acid forms mono- , di- and triple-substituted salts. For example, NaH_2PO_4 - Sodium dihydroPhosphate, Na_2HPO_4 - Sodium hydroPhosphate, Na_3PO_4 - Sodium Phosphate.

The ability of phosphoric acid to react with metals, basic oxides, hydroxides and weak acid salts are used in industry for production of mineral fertilizers:

$CaHPO_4 \cdot 2H_2O$ (precipitate);

$Ca_3(PO_4)_2 + 4H_3PO_4 = 3Ca(H_2PO_4)_2$;
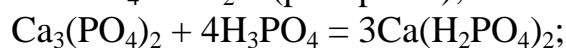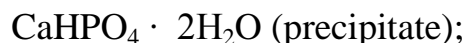
in fact $Ca(H_2PO_4)_2 \cdot H_2O$ - triple superphosphate is produced.

$Ca_3(PO_4)_2 + 2H_2SO_4 = Ca(H_2PO_4)_2 + 2CaSO_4$ - is the receipt of simple superPhosphate. The real composition of simple superphosphate is $Ca(H_2PO_4)_2 \cdot H_2O + 2[CaSO_4 \cdot 2H_2O]$.

11.4 Carbon, Silicon, Tin, Lead

In group IVA of the periodic table there are five chemical elements: carbon C, silicon Si, germanium Ge, tin Sn and lead Pb. The atoms of these elements have the following configurations:

$_6C$ — $1s^2 2s^2 2p^2$ $\qquad\qquad$ $[He]2s^2 2p^2$

$_{14}Si$ — $1s^2 2s^2 2p^6 3s^2 3p^2$ $\qquad\qquad$ $[Ne]3s^2 3p^2$

$_{32}Ge$ — $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$ $\qquad\qquad$ $[Ar]\ 4s^2 4p^2$

$_{50}Sn$ — $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^2$ $\qquad$ $[Kr]\ 5s^2 5p^2$

$_{82}Pb$ — $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^2$ $\quad$ $[Xe]6s^2 6p^2$

In IVA group in the middle of the periodic table there is a considerably greater change in properties from top to bottom than there is, for example, in the alkali metals group on the left and the halogen group on the right.

Carbon is a typical nonmetal, silicon and germanium are semimetals, and tin and lead are metals. However, the elements of group 4 have one important feature in common, namely each of them have four valence electrons. In its compounds carbon almost invariably completes its valence shell by forming four covalent bonds, which have a tetrahedral arrangement around the carbon atom. Silicon and germanium also usually form four covalent bonds with a tetrahedral arrangement, whereas tin and lead, which are larger and have smaller ionization energies than carbon and silicon, often, lose just two of their valence electrons to form the Sn^{2+} and Pb^{2+} ions.

Silicon, symbol Si, is a semimetallic element that is the second most common element on earth, after oxygen. The atomic number of silicon is 14. It was firstly isolated from its compounds in 1823 by the Swedish chemist *Baron Jцns Jakob Berzelius*.

Crystalline silicon has a hardness of 7, compared to 5 to 7 for glass. Silicon melts at about 1410 °C, boils at about 2900 °C, and has a specific gravity of 2.33. The atomic weight of silicon is 28.086.

Silicon constitutes about 28 percent of the earth's crust. It does not occur in the free elemental state, but it is found in the forms of silicon dioxide and complex silicates. Silicon-containing minerals constitute nearly 40 percent of all common minerals, including more than 90 percent of igneous-rock-forming minerals. The mineral *quartz* (composed of silicon dioxide, or silica, SiO_2), varieties of quartz (such as *carnelian*, *chrysoprase*, *onyx*, *flint*, and *jasper*), and the minerals *cristobalite* and *tridymite* are the naturally occurring crystal forms of silica. Silicon dioxide is the principal constituent of sand. The silicates (such as the complex aluminum, calcium, and magnesium silicates) are the main constituents of clays, soils, and rocks in the form of *feldspars*, *amphiboles*, *pyroxenes*, *micas*, and *zeolites*, and of semiprecious stones, such as *olivine*, *garnet*, *zircon*, *topaz*, and *tourmaline*.

Germanium, symbol Ge, is a hard, brittle, grayish-white, crystalline semimetallic element. The atomic number of germanium is 32. Germanium melts at about 937 °C, boils at about 2830 °C, and has a specific gravity of 5.3; its atomic weight is 72.59.

The Russian chemist *Dmitry Mendeleyev* predicted the existence and chemical properties of germanium in 1871; he called it ekasilicon because of its position under silicon in the periodic table. The element was actually discovered in the silver-sulfide ore argyrodite by the German chemist *Clemens Alexander Winkler* in 1886.

Germanium ranks 54th in order of abundance of the elements in the earth's crust. Germanium occurs in small quantities in the ores of silver, copper, and zinc, and in the mineral germanite, which contains 8 percent of germanium.

Tin, symbol Sn, is a metallic element which has been used by people since ancient times. The atomic number of tin is 50. Ordinarily a silver-white metal, at temperatures below 13 °C it often changes into an allotropic (distinctly different) form known as *gray tin*, which is an amorphous, grayish powder with a specific gravity of 5.75. Tin melts at about 232 °C, boils at about 2260 °C, and has a specific gravity of 7.31. The atomic weight of tin is 118.69.

Tin has been found in the tombs of ancient Egyptians and was exported to Europe in large quantities from Cornwall, England, during the Roman period. The ancient Egyptians considered tin and lead different forms of the same metal.

Tin ranks 49th in abundance of the elements in the earth's crust. The principal ore of tin is the mineral *cassiterite* (or *tinstone*), SnO_2, found abundantly in Cornwall, England, and in Germany, the Malay Peninsula, Bolivia, Brazil, and Australia.

Lead, symbol Pb (Latin *plumbum*, a lead weight), is a dense, bluish-gray metallic element which was the one of the first known metals. The atomic number of lead is 82. Lead melts at 327 °C, boils at 1745 °C, and has a specific gravity of 11.34; the atomic weight of lead is 207.20.

Lead was mentioned in the Old Testament. It was used by the Romans for making water pipes, soldered with an alloy of lead and tin.

Lead is widely distributed all over the world in the form of its sulfide, the ore *galena* (PbS). Lead ranks about 36th in natural abundance among elements in the earth's crust. Ores of the secondary importance are *cerussite* and *anglesite*.

Physical Properties of Carbon

Carbon occurs in several different solid forms, the most important of which are diamond and graphite.*The different forms of an element are called allotropes*. Thus diamond and graphite are allotropes of carbon.
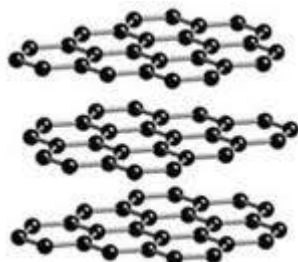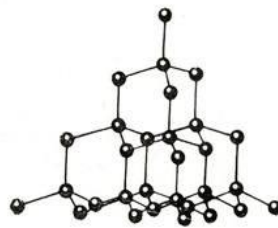
graphite   diamond

Diamond and graphite are so different that if we did not know that they both consist of carbon, and carbon only, we would find it difficult to believe that they are forms of the same element. Pure diamond forms beautiful, transparent, colorless, very hard, and highly refractive crystals. In contrast, graphite is a soft, black substance which is used as a lubricant, and as the "lead" in lead pencils when mixed with varying amounts of clay. Diamond has a much higher density (3.53 g/cm^3) than graphite (2.25 g/cm^3) and is an electrical insulator, whereas graphite is a fairly good conductor. Being a fairly good conductor of electricity graphite is exceptional among the nonmetals.

Carbon black is a pure form of soot which is deposited when hydrocarbons are burned in a very limited supply of air. For example,

$2C_2H_2 + O_2 \rightarrow 4C + 2H_2O$.
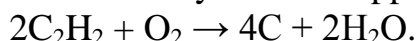
Ethyne

Carbon black has a very intense color and is used in large quantities as a pigment for paint, paper, and printer's ink, and to reinforce and color the rubber used in automobile tires.

Charcoal is made by heating wood and other organic materials to a high temperature in the absence of air. We are familiar with the fact that charcoal is much lighter than the wood from which it is made; in other words, it appears to have a very low density. The density is low because charcoal is extremely porous; it has a structure resembling a sponge but with holes that are too small to be visible to the eye. This porous structure means that it has a very large surface area relative to its volume. This large surface area can adsorb considerable quantities of other substances. Charcoal that has been thoroughly cleaned by heating with steam is known as *activated charcoal*. It has many applications, such as removing unburnt hydrocarbons from automobile exhaust, unpleasant and dangerous gases from the air, and impurities from water. Many municipal water treatment plants pass water through beds of activated charcoal.

Coke is made by heating coal in the absence of air. Coal is a very complex material consisting of many organic compounds. It contains 60%–90% C together with H, O, N, S, Al, Si, and some other elements. When coal is heated to a high temperature, it decomposes, producing a variety of gaseous and liquid products. The mixture of gases, methane and hydrogen mainly, is known as *coal gas.* The mixture of liquid products, which includes many hydrocarbons and other organic compounds, is called*coal tar.* The solid residue contains 90%–98% C and is known as coke. Coke is used in enormous quantities in industry as a reducing agent for the production of metals, phosphorus, and other substances.

In 1985, scientists vaporized graphite to produce a stable form of carbon molecule consisting of 60 carbon atoms (C_{60}) in a roughly spherical shape, looking like a soccer ball. The molecule was named*buckminsterfullerene* – "buckyball" for short – in honor of *R. Buckminster Fuller*, the inventor of the geodesic dome. The
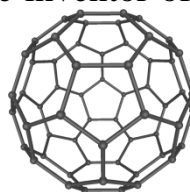
molecule may be common in interstellar dust.   *buckminsterfullerene*

Carbon is rather chemically passive while its reactivity increasing with the increasing of temperature. It reacts vigorously with oxygen when heated in the air. In the lack of oxygen carbon monoxide forms while carbon dioxide is formed in the excess of oxygen:

$2C + O_2 \rightarrow 2CO\uparrow$;

$C + O_2 \rightarrow CO_2\uparrow$.
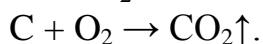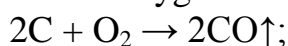
Carbon reacts with some metals giving the metals carbides under the high temperatures:

$2C + Ca \rightarrow CaC_2$.
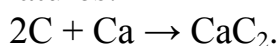
Carbon combines with hydrogen at the temperature of electric arc producing methane:

$C + 2H_2 \rightarrow CH_4\uparrow$.
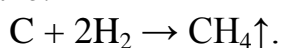
When water steam is passing through red heated charcoal or coke (at the temperature of 1200 °C) the mixture of carbon monoxide and hydrogen gasses forms:

$C + H_2O \rightarrow CO\uparrow + H_2\uparrow$.
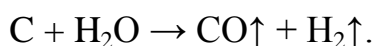
There are other products of this reaction at low temperatures (1000 °C):

$C + 2H_2O \rightarrow CO_2\uparrow + 2H_2\uparrow$.
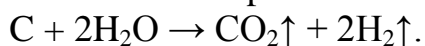
These reactions make the basis of conversion method of hydrogen preparation.

Concentrated sulfuric and nitric acids oxidize carbon to carbon dioxide when heated:

$C + 2H_2SO_4 \rightarrow CO_2\uparrow + 2SO_2\uparrow + 2H_2O$;

$3C + 4HNO_3 \rightarrow 3CO_2\uparrow + 4NO\uparrow + 2H_2O$.
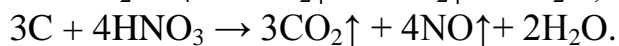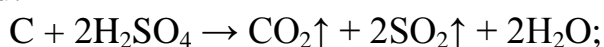
Chemical Properties of Carbon and its Compound

CARBON MONOXIDE

When carbon is burned in a limited supply of air, carbon monoxide, CO is obtained:

$$2C + O_2 \rightarrow 2CO.$$
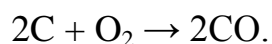
Industrially, carbon monoxide mixed with hydrogen is made on a large scale by passing water steam over red-hot coke:

$$C + H_2O \rightarrow CO + H_2.$$
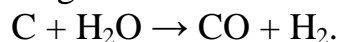
This mixture of hydrogen and carbon monoxide is called *water gas*.

Another increasingly important method of carbon monoxide preparation is the high-temperature reaction of methane (natural gas) with steam in the presence of a catalyst:

$$CH_4 + H_2O \xrightarrow{\text{Catalyst}} CO + 3H_2.$$
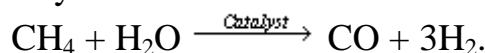
The mixture of carbon monoxide and hydrogen prepared in this way is known as *synthesis gas,* because of its importance as the basic material for synthesis of many organic compounds. It is also used as a fuel.

Carbon monoxide is a colorless, odorless, and tasteless gas that has only a slight solubility in water. It is very toxic because it combines with hemoglobin in the blood, thus preventing hemoglobin from carrying out its function as an oxygen carrier. It is particularly dangerous because it is odorless and therefore not easily detected. Carbon monoxide is produced when tobacco burns in cigarettes and it is present in the exhaust gases from automobiles.

Carbon monoxide is a reducing agent which can be oxidized to carbon dioxide. It burns in the air forming carbon dioxide:

$$2CO + O_2 \rightarrow 2CO_2.$$
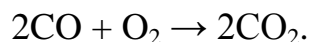
It reduces steam at high temperature, giving an equilibrium mixture of CO_2 and H_2:

$$CO + H_2O \rightleftarrows CO_2 + H_2.$$
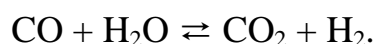
Carbon monoxide reduces metal oxides to metals. For example,

$$Fe_2O_3 + 3CO \xrightarrow{\Delta} 2Fe + 3CO_2\uparrow.$$
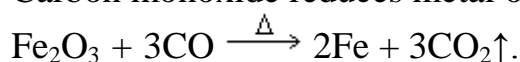
CARBON DIOXIDE AND CARBONIC ACID

The combustion of carbon and carbon-containing compounds in the excess of oxygen leads to the formation of carbon dioxide, CO_2. It is produced also by heating alkaline-earth metal carbonates, such as calcium carbonate:

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2\uparrow.$$
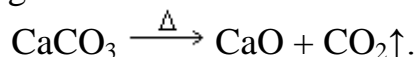
Beer and wine making also produce carbon dioxide as a by-product because the fermentation of a sugar such as glucose gives ethanol and carbon dioxide:

$$C_6H_{12}O_6 \xrightarrow{\text{fermentation}} 2C_2H_5OH + 2CO_2\uparrow.$$
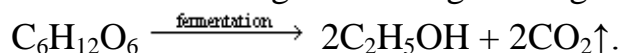
In the laboratory we can prepare small amounts of carbon dioxide by adding a dilute aqueous acid to a metal carbonate:

$$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + CO_2\uparrow + H_2O.$$

Carbon dioxide is a linear AX_2 molecule with two double bonds. It is a colorless gas with a very slight odor. When cooled, it forms a white solid (dry ice) that sublimes at $-78\ ^0C$ at 1 atm pressure. Liquid carbon dioxide can be obtained only under pressure.

Carbon dioxide dissolves readily in water giving a solution that contains a small equilibrium amount of carbonic acid, H_2CO_3:

$CO_2 + H_2O \rightleftarrows H_2CO_3$.

This solution is commonly called soda water; it has a slightly acidic taste. *Carbonic acid* is a weak acid that is partially ionized in two stages:

$H_2CO_3 + H_2O \rightleftarrows H_3O^+ + HCO_3^-$;

$HCO_3^- + H_2O \rightleftarrows H_3O^+ + CO_3^{2-}$.
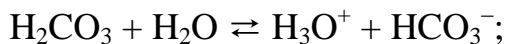
Carbonic acid and its two ions, HCO_3^- and CO_3^{2-}, are represented by the following structures:
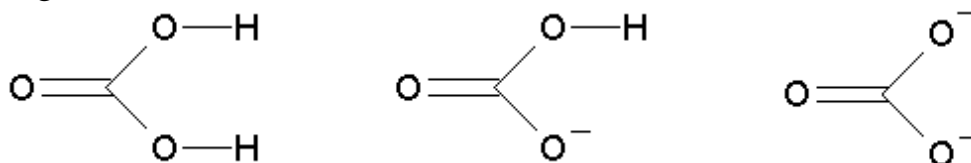
Carbonate ion, CO_3^{2-}, and hydrogen carbonate ion, HCO_3^-, being the anions of a weak acid, H_2CO_3, are weak bases. In the presence of an acid CO_3^{2-} adds a proton forming its conjugate acid HCO_3^-:

$CO_3^{2-} + H^+ \rightleftarrows HCO_3^-$.
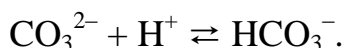
And in turn HCO_3^- adds a proton giving its conjugate acid H_2CO_3:

$HCO_3^- + H^+ \rightleftarrows H_2CO_3$.

But H_2CO_3 is not very stable and it almost completely decomposes to CO_2 and water:

$H_2CO_3 \rightleftarrows H_2O + CO_2$.

Carbon dioxide is used as a fire extinguisher because it does not burn or easily support combustion of other substances and because it has a higher density than air. It sinks down on the fire, forming a blanket of carbon dioxide that excludes air, extinguishing the fire. Only a few very reactive metals such as sodium, potassium, and magnesium will burn in carbon dioxide. For example, a previously ignited piece of magnesium will burn in carbon dioxide with a spluttering flame producing white magnesium oxide and black carbon particles:

$CO_2 + 2Mg \rightarrow 2MgO + C$.
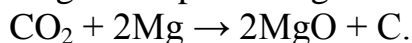
CARBON DISULFIDE

Carbon combines with sulfur at heating and gives carbon disulfide, CS_2:

$C + 2S \xrightarrow{\Delta} CS_2$.
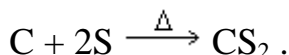
Carbon disulfide is a linear AX_2 molecule with double bonds, just like carbon dioxide:

:S=C=S:
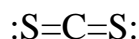
Carbon disulfide is a toxic, flammable liquid, but it is a useful solvent for sulfur and rubber.

TETRACHLOROMETHANE (CARBON TETRACHLORIDE)

When carbon disulfide is heated with chlorine, tetrachloromethane, CCl_4, and disulfur dichloride, S_2Cl_2, are formed:

$$CS_2 + 3Cl_2 \xrightarrow{\Delta} CCl_4 + S_2Cl_2 \ .$$
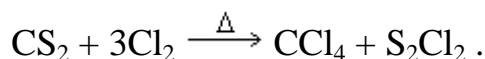
The two products can be separated by distillation. Tetrachloromethane is a useful solvent. Because it is a good solvent for oils and grease, it may be used as a cleaning agent. But it should be used with suitable precautions because it is toxic and the liquid can pass through the skin.

HYDROGEN CYANIDE

When heated to approximately 1000–1200 °C in the presence of a catalyst, a mixture of methane and ammonia burns in the air and gives hydrogen cyanide in an exothermic reaction:

$$2CH_4 + 2NH_3 + 3O_2 \xrightarrow{\Delta} 2HCN + 6H_2O.$$
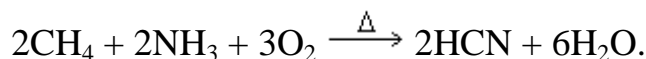
Ammonia and methane react also in the absence of air. The reaction is endothermic and requires a temperature of 1200–1300 °C and a platinum catalyst:

$$CH_4 + NH_3 \xrightarrow{Catalyst, \Delta} HCN + 3H_2.$$
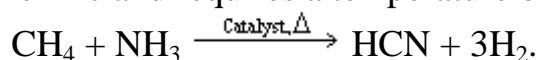
Hydrogen cyanide is a colorless liquid that boils just above room temperature (25.6 °C). It has the odor and taste of bitter almonds and is highly toxic. In the form of a gas it is used in execution chambers; a concentration of only 0.2 % by volume causes death within minutes.

HCN can be conveniently prepared in the laboratory by adding acid to a metal cyanide such as NaCN or KCN:

$$NaCN + HCl \rightarrow NaCl + HCN.$$
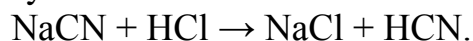
HCN is a weak acid and therefore the position of the equilibrium lies far to the right:

$$CN^- + H_3O^+ \rightleftharpoons HCN + H_2O.$$
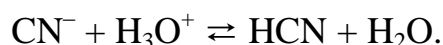
Because of its low boiling point HCN is evolved as a gas. For this reason acids should not be added to metal cyanide except in a fume hood. The HCN molecule has a triple C≡N bond. It has a linear geometry as expected for an AX_2 molecule.

Hydrogen cyanide behaves as a weak acid in water. An aqueous solution is called *hydrocyanic acid.*Its salts are the cyanides, such as sodium cyanide, NaCN. They contain the cyanide ion.

$$: \overset{\overline{}}{C} \equiv N :$$
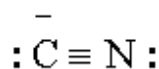
Hydrogen cyanide has many important applications in the plastics industry. Sodium cyanide is used for the extraction of gold and silver from their ores:

$$4Au + 8NaCN + O_2 + 2H_2O \rightarrow 4Na[Au(CN)_2] + 4NaOH \ .$$
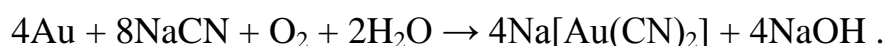
When an alkali metal cyanide is fused with sulfur, a *thiocyanate* is formed, for example:

$$S + NaCN \xrightarrow{\Delta} NaSCN.$$
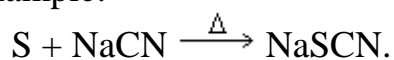
The thiocyanate ion, SCN^-, has the following structure:

$$\overline{} : \overset{..}{\underset{..}{S}} - C \equiv N :$$
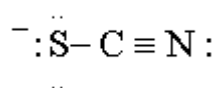
CARBIDES

In addition to its compounds with nonmetals such as oxygen, sulfur, and nitrogen, carbon reacts with many metals. The compounds of carbon with the alkali and alkaline earth metals contain the carbide ion, C_2^{2-}, for example, Na_2C_2 and CaC_2.

Commercially, calcium carbide is made by heating lime with coke in a furnace:

$CaO + 3C \quad\quad CaC_2 + CO\uparrow$.

Calcium carbide reacts with water giving ethyne (acetylene), C_2H_2:

$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2\uparrow$.

These carbides are salts of ethyne, which are too weak as acid to ionize in water. Therefore, the carbide ion, C_2^{2-}, is a strong base in water. It removes protons from water and gives C_2H_2, which bubbles off as a gas:

$C_2^{2-} + 2H_2O \rightarrow C_2H_2\uparrow + 2OH^-$.
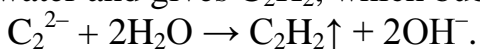
There are many other types of metal carbides that do not contain the C_2^{2-} ion, for example Al_4C_3:

$Al_4C_3 + 12H_2O \rightarrow 4Al(OH)_3 + 3CH_4$.
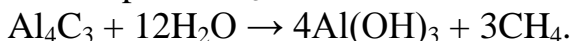
Often they have unexpected formulas, such as iron carbide, Fe_3C:

$Fe_3C + 6HCl \rightarrow 3FeCl_2 + CH_4 + H_2$,
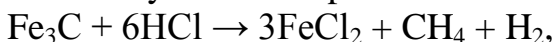
which is called *cementite* and is an important component of some steels.

With more electronegative elements such as silicon, carbon forms covalent rather than ionic carbide.*Silicon carbide,* SiC, is a covalent compound with the diamond structure, except that each alternate atom is a silicon atom rather than a carbon atom. Silicon carbide, commonly known as carborundum, is almost as hard as diamond and is used as an abrasive; for example, carbide sandpaper and grinding wheels are coated with silicon carbide.

Silicon and its Compounds

Silicon follows carbon in group IVA. Whereas carbon is a typical nonmetal, silicon and the next element germanium, are semimetals, and they are followed by tin and lead, which are metals. Unlike the elements in the groups on the left and right sides of the periodic table, those in the main groups in the middle of the table show a considerable variation in properties on descending the group. Silicon is a shiny, silvery solid that looks like a metal but has only a low electrical conductivity; moreover, its conductivity increases with increasing of temperature, whereas the conductivity of a metal decreases with increasing of temperature. Substances that have small electrical conductivity in the solid state which increases appreciably with increasing temperature are known as *semiconductors*.

Silicon occurs not only as silicates but also as *silicon dioxide,* SiO_2, which has been known for centuries as *silica,* which is familiar, in an impure form, as sand.

Preparation of Silicon

The element can be prepared from silica by it heating with coke to a temperature of about 3000 °C in an electric arc furnace:

$$SiO_2 + 2C \rightarrow Si + 2CO\uparrow.$$
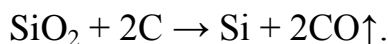
The reactants are added continuously at the top of the furnace. Carbon monoxide escapes from the furnace and burns giving carbon dioxide, while the molten silicon (T_m= 1414 °C) runs out from the bottom of the furnace and solidifies. This silicon is pure enough for many purposes, such as the manufacture of alloys with metals, but ultra pure silicon, needed in many electronic devices is obtained by preliminary converting impure silicon into silicon tetrachloride by heating it with chlorine:

$$Si + 2Cl_2 \rightarrow SiCl_4 \; (T_b= 57.6 \; °C) .$$

The obtained $SiCl_2$ is then purified by distillation and reduced to silicon by heating with hydrogen or magnesium:

$$SiCl_2 + H_2 \rightarrow Si + 2HCl \; ;$$
$$SiCl_4 + 2Mg \rightarrow Si + 2MgCl_2 \, .$$
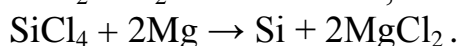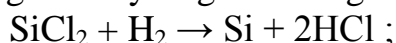
The magnesium chloride is removed from the silicon by washing it out with hot water. The silicon can be further purified by *zone refining*.

Chemical Properties of Silicon and its Compounds

Silicon is a rather uncreative element and is not attacked by acids. Amorphous silicon burns brilliantly in oxygen when heated to 450 °C. It reacts with fluorine at 400 °C, with chlorine at 450 °C and with bromine at 500 °C. It reacts at red heat with iodine:

$$Si + 2F_2 \qquad\qquad SiF_4;$$

$$Si + 2Cl_2 \qquad\qquad SiCl_4;$$

$$Si + 2Br_2 \qquad\qquad SiBr_4.$$

Silicon decomposes water at red heat:

$$Si + 2H_2O \rightarrow SiO_2 + 2H_2\uparrow.$$
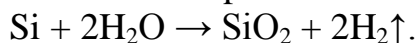
It reacts with hot, concentrated aqueous hydroxide solutions and with molten hydroxides forming silicates and evolving hydrogen:

$$Si + 2NaOH + H_2O \rightarrow Na_2SiO_3 + 2H_2.$$
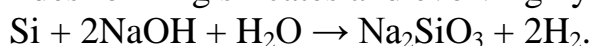
Silicon does not react with oxyacids, it may be dissolved in the mixture of nitric and hydrofluoric acids:

$$3Si + 4HNO_3 + 18HF \rightarrow 3H_2SiF_6 + 4NO\uparrow + 8H_2O.$$
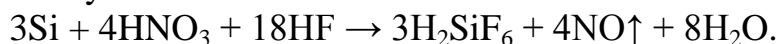
SILICON DIOXIDE

Silicon dioxide (SiO_2), or *silica,* occurs in several crystalline forms, including *quartz, cristobalite,* and *tridymite,* and in several amorphous forms, such as agate and flint. Quartz is the best known of the silica minerals. It is one of the commonest minerals in the earth's crust and is often found in the form of colorless, transparent crystals, which are sometimes beautifully formed and of enormous size. Quartz is a constituent of many rocks, which are often complex mixtures of different minerals. Granite, for example, is a mixture of the three silicon minerals, quartz, mica, and feldspar. Some forms of quartz that contain traces of impurities are beautifully colored and are often used as semiprecious gemstones. Amethyst, for example, is quartz that is colored violet by traces of Fe(III). Onyx, jasper, carnelian, and flint are colored forms of noncrystalline silicon dioxide.

Silicon dioxide is an acidic oxide that reacts with NaOH or Na_2CO_3 on heating giving silicates:

$SiO_2 + 4NaOH \rightarrow Na_4SiO_4 + 2H_2O$;

$SiO_2 + Na_2CO_3 \rightarrow Na_2SiO_3 + CO_2\uparrow$.
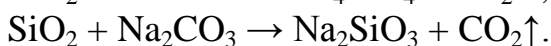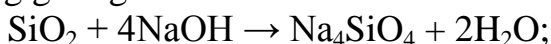
These are only simplified representations of the reactions; there are many silicates with complex structures, as we will see in the next section.

A concentrated solution of sodium silicate in water is called *wafer glass.* It is used for fireproofing wood and cloth, for adhesives, and for preserving eggs. It can be used to prepare other metal silicates.

SILICIC ACID AND SILICATES

Silicon dioxide is the anhydride of silicic acid. When finely powdered silicon dioxide is shaken with water for a long time, a very slightly acidic solution is obtained, due to the formation of a very small amount of silicic acid, $Si(OH)_4$:

$SiO_2 + 2H_2O \rightarrow Si(OH)_4$ or

$SiO_2 + 2H_2O \rightarrow H_2SiO_3$.
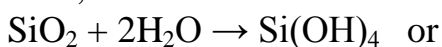
The very small solubility of silicon dioxide in water is increased at high pressure and temperature, which accounts for the deposits of silica found around many hot geysers. The silicon dioxide which is dissolved in water at high pressure below the surface precipitates from the solution when the water rises to the surface, where the pressure and temperature are much lower.

More concentrated solutions of silicic acid can be obtained by the reaction of silicon tetrachloride with water:

$SiCl_4 + 4H_2O \rightarrow Si(OH)_4 + 4HCl$
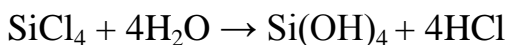
or by the reaction of an aqueous solution of sodium silicate with hydrochloric acid:

$Na_2SiO_3 + H_2O + 2HCl \rightarrow Si(OH)_4 + 2NaCl$.

However, the product of these reactions is not simply a solution of $Si(OH)_4$. A gelatinous solid is obtained that consists of polymeric silicic acids formed by condensation reactions such as:
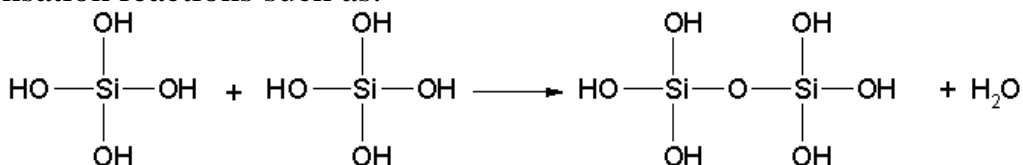
Continuation of such reactions leads to a complex mixture of many polymeric acids.

Silicic acid is very weak ($K_a = 1 \times 10^{-10}$). It is a member of very weak acids class such as HOCI and $B(OH)_3$ (or H_3BO_3), it has the general formula $X(OH)_n$. It is the first member of the third-period oxoacids series. These acids increase in strength from the very weak silicic acid to the very strong perchloric acid.

If the mixture of polymeric silicic acids is heated, causing further condensation reactions to occur, a hard, granular, translucent substance called *silica gel* is obtained. It has a large surface area and readily adsorbs water and other substances. It is widely used as a drying agent and as a catalyst. Small bags of silica gel are

frequently packed with delicate scientific apparatus, cameras, and electronic equipment to protect them from damage by moisture during transportation.

Over one thousand silicates occur naturally. Their number and complexity result from the great variety of ways in which SiO_4 tetrahedral can be linked together. The simplest silicates contain the anion SiO_4^{4-}, derived from the acid $Si(OH)_4$. *Olivine* is an important mineral of this type; it is the principal component of the earth's mantle, which lies between the core and the crust. Olivine is an iron magnesium silicate that is often represented by the formula $FeMgSiO_4$, although its composition may vary from Mg_2SiO_4 to Fe_2SiO_4. The SiO_4^{4-} tetrahedrals are packed together in a compact way in olivine, giving it a greater density compared with most other silicate minerals.

Many silicates are the salts of the many polymeric forms of silicic acid. The condensation of two silicic acid molecules gives the acid $H_6Si_2O_7$:

$$HO-\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{Si}}-OH \;+\; HO-\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{Si}}-OH \;\longrightarrow\; HO-\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{Si}}-O-\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{Si}}-OH \;+\; H_2O$$
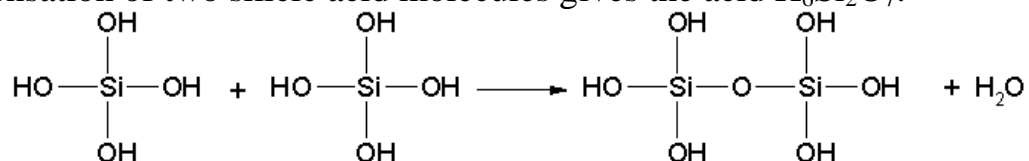
SILICONE POLYMERS

The wide range of applications of the mineral silicates depends on their great thermal stability and inertness toward other substances. These properties are caused by the great strength of the silicon–oxygen bond, which has an average bond energy (464 kJ/mol) that is much greater than the silicon–silicon bond energy (196 kJ/mol) or even the carbon–carbon, single-bond energy (348 kJ/mol). Chemists succeeded in combination of the strength and inertness of the silicon-oxygen bond with some of the useful properties of organic polymers in the synthetic polymers known as *silicones.*

The simplest silicones are chain polymers that have the general formula $(R_2SiO)_n$, where R is an alkyl or aryl group such as CH_3, C_2H_5, or C_6H_5. There are also cyclic polymers (see Figure 1) and cross-linked polymers in which chains are held together by sharing oxygen atoms.

Silicones are prepared by heating silicon with chloroalkanes such as chloromethane, CH_3Cl. The main product of the reaction with CH_3Cl is dimethyl silicon dichloride, $(CH_3)_2SiCl_2$:

$$Si(s) + 2CH_3Cl(g) \longrightarrow \underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{Si}}\underset{}{\overset{}{{}_{H_3C}}}{}^{,,,,Cl}$$
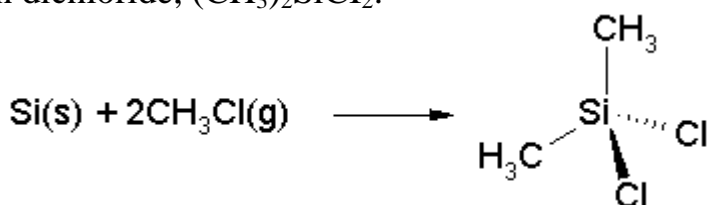
But small amounts of $(CH_3)_3SiCl$ and CH_3SiCl_3 are also formed.

a long-chain polymer   a cyclic polymer
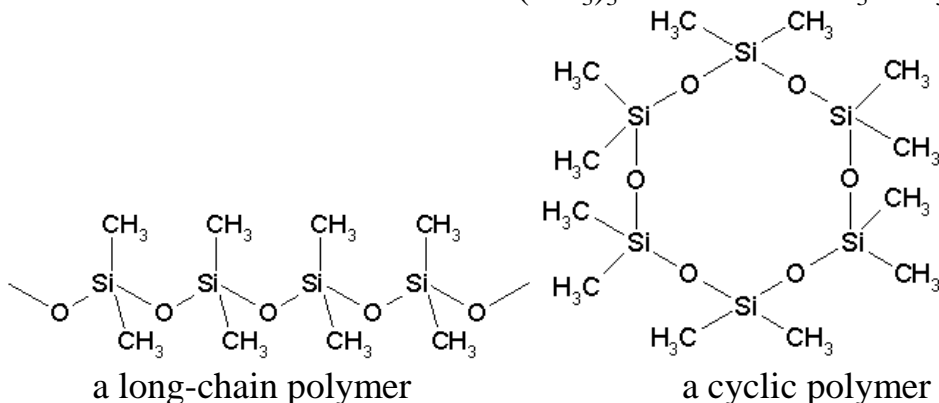
SILANES

The great difference between the chemistry of silicon and the chemistry of carbon is also illustrated by the hydrides of silicon, which are called *silanes.* In their general formula Si_nH_{2n+2}, the silanes are analogous to the alkanes, C_nH_{2n+2}, but only a few silanes are known. They are extremely reactive and are spontaneously flammable in the air:

$SiH_4 + 2O_2 \rightarrow SiO_2 + 2H_2O$.
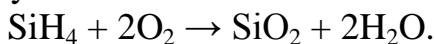
In contrast, the alkanes burn only when ignited. The silanes react rapidly with basic aqueous solutions evolving hydrogen:

$SiH_4 + OH^- + 3H_2O \rightarrow SiO(OH)_3^- + 4H_2\uparrow$.
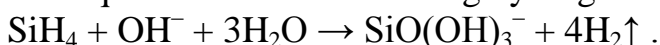
SILICON HALIDES

ilicon tetrachloride, which is a colorless liquid (T_b= 57 °C), can be made by passing chlorine through a red-hot mixture of sand and coke:

$SiO_2 + 2C + 2Cl_2 \rightarrow SiCl_4 + 2CO\uparrow$.
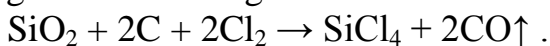
Silicon tetrafluoride, which is a colorless gas, can be made by the reaction of silicon with fluorine,

$Si + 2F_2 \rightarrow SiF_4$
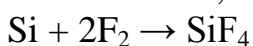
or by heating calcium fluoride with sand and concentrated sulfuric acid:

$2CaF_2 + SiO_2 + 2H_2SO_4(conc.) \rightarrow SiF_4\uparrow + 2CaSO_4 + 2H_2O$.
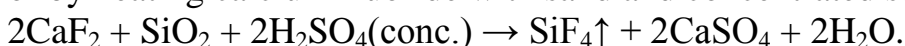
In this reaction hydrogen fluoride is produced by the reaction of calcium fluoride with concentrated sulfuric acid, and then HF reacts with silicon dioxide:

$CaF_2 + H_2SO_4(conc.) \rightarrow 2HF + CaSO_4$;

$SiO_2 + 4HF \rightarrow SiF_4\uparrow + 2H_2O$.
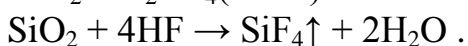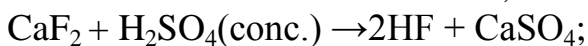
Both $SiCl_4$ and SiF_4 are covalent tetrahedral AX_4 molecules. In contrast to the carbon compounds CF_4 and CCl_4, which are stable in the presence of water, both $SiCl_4$ and SiF_4 react rapidly with water giving silicic acid, $Si(OH)_4$, and a hydrogen halide:

$SiCl_4 + 4H_2O \rightarrow Si(OH)_4 + 4HCl$;

$SiF_4 + 4H_2O \rightarrow Si(OH)_4 + 4HF$.
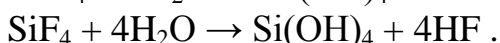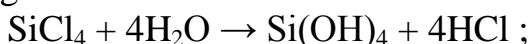
Compounds of Tin

Tin shows allotropy among its three allotropic forms:

α-tin (*gray tin*) $\xrightleftharpoons{18\ °C}$ β-tin (*white tin*)
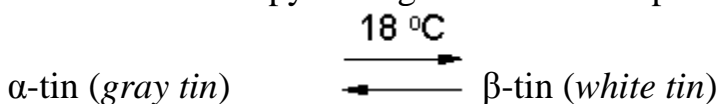
Specific gravity = 5.8   Specific gravity = 7.8

The common oxidation states of tin are +2 and +4, but Sn^{+4} compounds are a little more stable.

When tin metal is heated to whiteness (1500-1600°C) in presence of O_2 tin burns with a bright flame and forms SnO_2.

When Sn is heated in an atmosphere of Cl_2 or with sulfur, $SnCl_4$ and SnS_2 are formed:

$Sn + 2Cl_2 \rightarrow SnCl_4$;

$Sn + 2S \rightarrow SnS_2$.
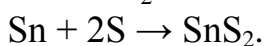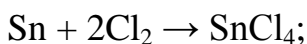
Sn is slowly attacked by dilute HCl and dilute H_2SO_4 and H_2 is evolved in both the cases. With concentrated HCl, H_2 is evolved and with concentrated H_2SO_4, SO_2 gas is obtained:

$Sn + 2HCl \rightarrow SnCl_2 + H_2\uparrow$;

$Sn + H_2SO_4(dil.) \rightarrow SnSO_4 + H_2\uparrow$;

$Sn + 4H_2SO_4(conc.) \rightarrow Sn(SO_4)_2 + 2SO_2\uparrow + 4H_2O$.
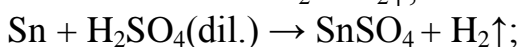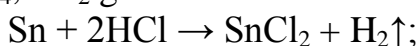
When very dilute HNO_3 (6%) reacts with metallic tin, the metal is oxidized to $Sn(NO_3)_2$ but HNO_3 reduces to NH_4NO_3:

$4Sn + 10HNO_3 \rightarrow 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O$.

When hot and concentrated HNO_3 reacts with the metal, it is oxidized to stannic acid (H_2SnO_3) while the acid gets reduced to NO_2:

$Sn + 4HNO_3 \rightarrow H_2SnO_3 + 4NO_2\uparrow + H_2O$.

When boiling with concentrated alkali solution, the metal dissolves, forming solution of stannate:

$Sn + 2KOH \rightarrow K_2SnO_3 + 4H_2\uparrow$.
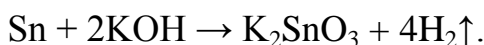
Dihydrated stannous chloride $SnCl_2 \times 2H_2O$ is prepared by dissolving Sn in hot and concentrated HCl:

$Sn + 2HCl \rightarrow SnCl_2 + H_2\uparrow$.
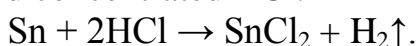
The solution after evaporation and cooling gives the transparent monoclinic crystals of the $SnCl_2 \times 2H_2O$ which is known as tin salt

Hydrated stannous chloride forms transparent monoclinic crystals which melt at 40 °C. At heating $SnCl_2 \times 2H_2O$ loses HCl and gives stannous oxochloride, Sn(OH)Cl. Hence anhydrous salt cannot be prepared by heating $SnCl_2 \times 2H_2O$.

$SnCl_2 + H_2O \qquad Sn(OH)Cl\downarrow + HCl$.

When treated with alkalies, a white precipitate of $Sn(OH)_2$ is obtained. This precipitate dissolves in the excess of the alkali and forms corresponding stannite. Na_2SnO_2 absorbs atmospheric O_2 forming sodium stannate, Na_2SnO_3:

$SnCl_2 + 2NaOH \rightarrow Sn(OH)_2\downarrow + 2NaCl$;

$Sn(OH)_2 + 2NaOH \rightarrow Na_2SnO_2 + 2H_2O$;

$2Na_2SnO_2 + O_2 \rightarrow 2Na_2SnO_3$.
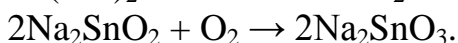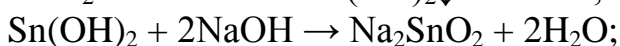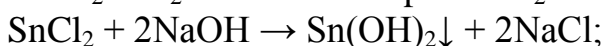
With H_2S a dark brown precipitate of SnS is obtained. This precipitate is soluble in yellow ammonium sulfide $(NH_4)_2S$ forming ammonium thiostannate, $(NH_4)_2SnS_3$:

$SnCl_2 + H_2S \rightarrow SnS\downarrow + 2HCl$;

$SnS + (NH_4)_2S_2 \rightarrow (NH_4)_2SnS_3$.
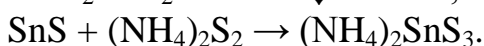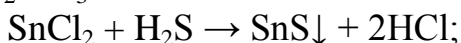
Stannous chloride is an active reducing agent and reduces a number of compounds:

$2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4$;

$2HgCl_2 + SnCl_2 \rightarrow Hg_2Cl_2\downarrow + SnCl_4$;

$Hg_2Cl_2 + SnCl_2 \rightarrow 2Hg\downarrow + SnCl_4$;

$2CuCl_2 + SnCl_2 \rightarrow 2CuCl\downarrow + SnCl_4$.
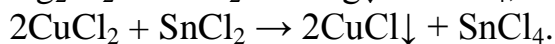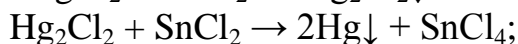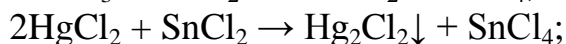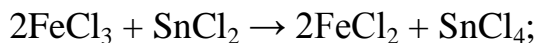
Anhydrous stannous chloride $SnCl_2$ is prepared by heating tin in a steam of dry HCl gas or by heating a mixture of metallic tin in excess with $HgCl_2$ when Hg volatilizes and $SnCl_2$ remains:

$Sn + 2Cl_2 \rightarrow SnCl_4$;

$Sn + 2HgCl_2$ (excess) $\rightarrow SnCl_4 + 2Hg$.
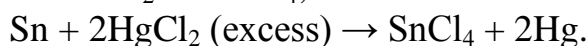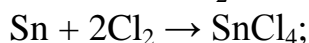
Anhydrous $SnCl_2$ is a glass-like transparent substance with the density of 3.95. It melts at 246 °C and boils at 603 °C, the vapour being associated with Sn_2Cl_4:

$Sn_2Cl_4 \rightarrow 2SnCl_2$.
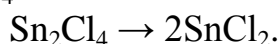
It is a covalent compound soluble in organic solvents like alcohol and ether. It combines with NH_3 forming various addition compounds like $SnCl_2 \times 2NH_3$, $SnCl_2\times2NH_3$ and $3SnCl_2\times2NH_3$ depending the temperature of the reaction.

Stannic chloride $SnCl_4$ is prepared by passing dry Cl_2 over molten tin kept in a retort, or by heating tin with the excess of mercury (II) chloride:

$Sn + 2Cl_2 \rightarrow SnCl_4$;

$Sn + 2HgCl_2$ (excess) $\rightarrow SnCl_4 + 2Hg$.
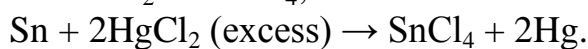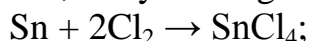
It is a colourless fuming liquid, density 2.229 (at 20°C), its boiling point is 114.1°C. It is a covalent compound, soluble in organic solvents like C_6H_6 and of very negligible electrical conductivity. It is miscible with CS_2 in all proportions and can dissolve phosphorus, sulfur, iodine etc. In small quantity of water $SnCl_4$ dissolves with the evolution of heat and forms a clear solution from which several soluble hydrates like $SnCl_4\times3H_2O$, $SnCl_4\times5H_2O$, $SnCl_4\times6H_2O$ etc., can be crystallized. With the excess of water, $SnCl_4$ is hydrolyzed and basic stannic chloride, $Sn(OH)Cl_3$ is precipitated. At further hydrolysis $Sn(OH)Cl_3$ gives a colloidal solution of stannic acid, H_4SnO_4:

$SnCl_4 + H_2O \rightleftarrows Sn(OH)Cl_3\downarrow + HCl$;

$Sn(OH)Cl_3 + 3H_2O \rightleftarrows H_4SnO_4 + 3HCl$.
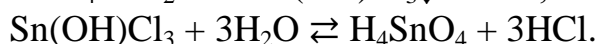
With NH_3, it gives double salt, $SnCl_4\times4NH_3$ which can be sublimed without decomposition.

Compounds of Lead

Lead is the element of IV group and has the electron configuration $[Xe]4f^{14}5d^{10}6s^26p^2$, with a valence shell consisting of the four $6s^26p^2$ electrons. Its valence-shell electron configuration is similar to that of carbon, $2s^22p^2$, and it forms a few compounds in which all four electrons are used to form four covalent bonds. In these compounds, which are predominately covalent and resemble the corresponding compounds of carbon and silicon, lead is in the +4 oxidation state. However, we have pointed out previously that elements in the central groups of the periodic table resemble each other less than those in the groups at either end. All

elements in group IV have a common valence of 4, but there is a distinct trend in the group from the typically nonmetallic element carbon at the top to the typically metallic element lead at the bottom. Because of the large size of the lead atom, its valence-shell electrons are much less strongly held than are those of carbon. Thus lead loses two electrons from its ground state configuration quite readily to form the Pb^{2+} ion in which lead is in the + 2 oxidation state:
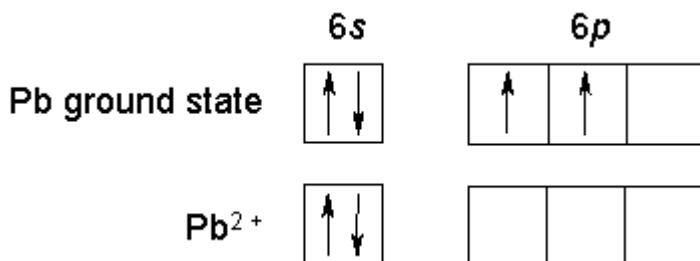
These Pb(II) compounds are typical ionic compounds like those formed by other metals and they are the most common compounds of lead. The less numerous Pb(IV) compounds are much less ionic and are best described as covalent.

Lead is readily obtained in crystalline state by the process of precipitation. If a zinc rod is suspended in a weak solution of lead acetate the metallic lead precipitates as a mass of carbonaceous crystals, (commonly known as the lead tree):

$(CH_3COO)_2Pb + Zn \rightarrow Pb + (CH_3COO)_2Zn$.
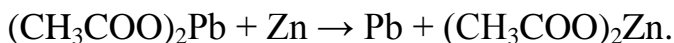
Lead is unaffected in dry air but in the presence of moisture it tarnishes due to the formation of a thin film of the hydroxide and finally carbonate. This layer protects the metal from further influence of air.

When heated in air or oxygen, it is slowly oxidized to lead monoxide, PbO, and at a high temperature (400-500°C) to red lead, Pb_3O_4.

$2Pb + O_2 \rightarrow 2PbO$;
$2PbO + O_2 \rightarrow 2PbO_2$;
$2PbO + PbO_2 \rightarrow Pb_3O_4$.
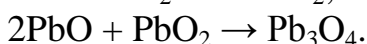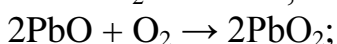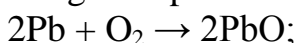
Lead is not attacked by pure water in the absence of air but water containing dissolved air has a solvent action on it due to the formation of lead hydroxide:

$2Pb + O_2 + 2H_2O \rightarrow 2Pb(OH)_2$.

Dilute hydrochloric and sulfuric acids have practically no action on lead. Hot concentrated hydrochloric acid forms lead chloride with the evolution of hydrogen:

$Pb + 2HCl(hot\ conc.) \rightarrow PbCl_2 + H_2\uparrow$.

Hot concentrated sulfuric acid liberates sulfur dioxide but the reaction is retarded by the formation of an insoluble layer of lead sulfate:

$Pb + 2H_2SO_4 \rightarrow PbSO_4 + SO_2\uparrow + 2H_2O$.

Dilute and concentrated nitric acid dissolves lead forming lead nitrate and the oxides of nitrogen:

$3Pb + 8HNO_3(dil.) \rightarrow 3Pb(NO_3)_2 + 2NO\uparrow + 4H_2O$;
$Pb + 4HNO_3(conc.) \rightarrow Pb(NO_3)_2 + 2NO_2\uparrow + 2H_2O$.
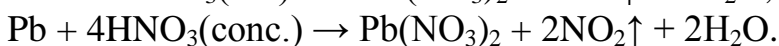
Lead combines with chlorine and sulfur on heating:

$Pb + S \rightarrow PbS$;

$Pb + 2Cl_2 \rightarrow PbCl_4$.
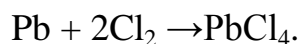
When lead is heated in air, the yellow oxide PbO is formed.

Lead dissolves slowly in boiling, concentrated hydrochloric acid to form $PbCl_2$:

$Pb(s) + 2HCl(aq) \rightarrow PbCl_2(aq) + H_2(g)$.
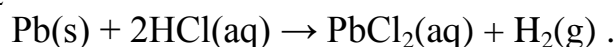
Lead(II) chloride is more easily prepared by addition of a soluble chloride to a solution of a lead(II) salt:

$Pb^{2+}(aq) + 2Cl^-(aq) \rightarrow PbCl_2(s)$.
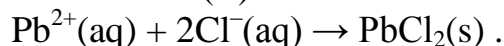
It is only sparingly soluble in cold water but is more soluble in hot water. When the hot solution is cooled, white crystals of $PbCl_2$ precipitate.

Lead(II) iodide can be precipitated from a solution of a Pb(II) salt. The precipitate is somewhat soluble in hot water. When the solution is cooled, sparkling golden yellow crystals are obtained:

$Pb^{2+}(aq) + 2I^-(aq) \rightarrow PbI_2(s)$.
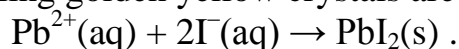
When NaOH(aq) is added to a solution of a soluble Pb(II) salt a white precipitate of $Pb(OH)_2$ is obtained:

$Pb^{2+}(aq) + 2OH^-(aq) \rightarrow Pb(OH)_2(s)$.
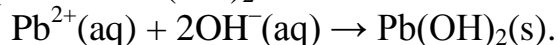
But this precipitate redissolves when the excess of OH^- ions is added because of the soluble $Na_2[Pb(OH)_4]$ formation, which contains the $[Pb(OH)_4]^{2-}$ ions:

$Pb(OH)_2(s) + 2OH^-(aq) \rightarrow [Pb(OH)_4]^{2-}(aq)$.
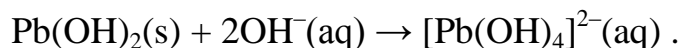
Lead hydroxide is amphoteric and soluble in aqueous acids:

$Pb(OH)_2(s) + 2HCl(aq) \rightarrow PbCl_2(aq) + 2H_2O(l)$.
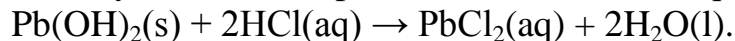
When lead is heated with sulfur PbS is obtained. When H_2S gas is passed through an aqueous solution of a lead(II) salt black precipitate of PbS is forming.

These salts can be prepared from PbO or $Pb(OH)_2$ and the appropriate acid. Lead(II) sulfate is not very soluble so it is conveniently prepared by addition of a soluble sulfate to a solution of a soluble Pb(II) salt such as $Pb(NO_3)_2$. Lead(II) nitrate decomposes at heating and gives nitrogen dioxide, NO_2, and oxygen:

$2Pb(NO_3)_2(s) \rightarrow 2PbO(s) + 4NO_2(g) + O_2(g)$.
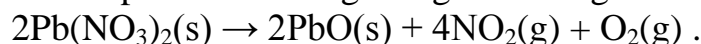
This reaction is used often to prepare small amounts of NO_2.

If lead is heated in oxygen, or if PbO is strongly heated in air, it is further oxidized to Pb_3O_4, *red lead:*

$6PbO(s) + O_2(g) \rightarrow 2Pb_3O_4(s)$.
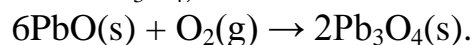
The oxide Pb_3O_4 is the basis of a red paint that is widely used for protecting iron and steel structures against rust; apparently, it forms an oxidized, unreactive layer on the surface of the iron. Red lead, Pb_3O_4, contains both Pb(II) and Pb(IV) and its formula may be written as $Pb(II)_2Pb(IV)O_4$.

Red lead reacts with concentrated nitric acid giving soluble lead(II) nitrate and lead dioxide, $Pb(IV)O_2$, a brown insoluble solid in which lead is in the +4 oxidation state:

$Pb_3O_4 + 4HNO_3(conc.) \rightarrow 2Pb(NO_3)_2 + PbO_2 + 2H_2O$.
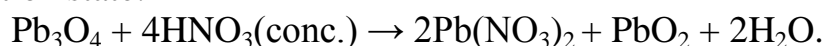
The reaction of Pb_3O_4 with HNO_3 is consistent with the formulation of this oxide as $Pb(II)_2Pb(IV)O_4$, because the Pb(II) atoms convert to soluble $Pb(NO_3)_2$, lead(II) nitrate, leaving the Pb(IV) as the insoluble oxide PbO_2.

Lead(IV) chloride (lead tetrachloride), $PbCl_4$, is a yellow liquid that decomposes when heated forming chlorine and $PbCl_2$:

$$PbCl_4(l) \rightarrow PbCl_2(s) + Cl_2(g) \ .$$

It is a covalent compound consisting of tetrahedral $PbCl_4$ molecules,
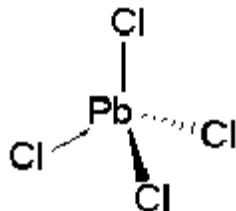
analogous to carbon tetrachloride, CCl_4, and silicon tetrachloride, $SiCl_4$.

Uses

Carbon is used as a fuel (coal) and as lubricant (graphite). C-14 isotope is used in archaeological dating. Carbon compounds are important in many branches of the chemical industry.

Silicon doped with boron, gallium, phosphorus, or arsenic, etc. is applied for production of silicon which is used in transistors, solar cells, rectifiers, and other electronic solid-state devices. Silica, as sand, is a principal ingredient of glass, a material with excellent mechanical, optical, thermal, and electrical properties. Silicon is used in manufacturing of computer chips and as a lubricant. It is used also in medicine for silicone implants.

Tin is used in the preparation of a number of alloys which are very useful. Tin alloys with lead are used in soldering, in making cups, mugs and other utensils. Its alloys with arsenic and copper are used for making bearings for machinery as well as for making crockery and table wares. Alloys of tin with copper, lead, bismuth, and arsenic are applied for making bells, gongs *etc.*, for electrical fuses, for printing types. Tin is used for tinning of household utensils and for plating of iron sheets. Tin amalgam is used for mirrors production.

Lead is used for making cable covering, protective sheets for roofs and drains, water pipes and for lining the chambers in sulfuric acid manufacturing. It is employed in production of accumulator plates, lead shots, fuse wire and such compounds as red lead, litharge, lead tetraethyl and white lead. It is an excellent protection from radiation in atomic work.

Compounds of tin and lead are poisonous.

11.5 Boron, Aluminum, Gallium, Indium, And Thallium

Physical Properties and Occurrence

Boron, symbol B, hard, brittle semimetallic element with an atomic number of 5. Pure boron, as usually prepared, is an amorphous powder. A crystalline form can be prepared, however, by dissolving boron in molten aluminum and cooling slowly. The atomic weight of boron is 10.81; the element melts at about 2076 °C, boils at about 3927 °C, and has a specific gravity of 2.46.

Compounds of boron, notably *borax*, have been known since early times, but the pure element was firstly prepared in 1808 by the French chemists *Joseph Gay-Lussac* and *Baron Louis Thinard*, and independently by the British chemist *Sir Humphry Davy*. Important boron ores are *ulexite* ($NaCaB_5O_9 \cdot 8H_2O$), *colemanite* ($Ca_2B_6O_{11} \cdot 5H_2O$), and *kernite* ($Na_2B_4O_7 \cdot 4H_2O$). Boron ranks about 38th in natural abundance among the elements in the earth's crust.

Aluminum (in Canada and Europe, *aluminium*), symbol Al, the most abundant metallic element in the earth's crust. The atomic number of aluminum is 13. It is a lightweight, silvery metal. The atomic weight of aluminum is 26.9815; the element melts at 660 °C, boils at 2519 °C, an*Hans Christian Oersted*, a Danish chemist, was the first who isolated aluminum in 1825, using a chemical process involving potassium amalgam. Between 1827 and 1845, *Friedrich Wohler*, a German chemist, improved Oersted's process by using metallic potassium. He was the first to measure the specific gravity of aluminum and show its lightness. In 1854 *Henri Sainte-Claire Deville*, in France, obtained the metal by reducing aluminum chloride with sodium. Aided by the financial backing of Napoleon III, Deville established a large-scale experimental plant and displayed pure aluminum at the Paris Exposition in 1855.

Aluminum is the most abundant metallic constituent in the earth's crust; only the nonmetals namely oxygen and silicon are more abundant. Aluminum is never found as a free metal; commonly as aluminum silicate or as a silicate of aluminum mixed with other metals such as sodium, potassium, iron, calcium, and magnesium. However, the extracting of aluminum from these silicates is chemically difficult and therefore an expensive process that is why they are not useful ores. *Bauxite* (consisting of aluminum oxide of various degrees of hydration) is the commercial source of aluminum and its compounds.

Gallium, symbol Ga, is a metallic element that remains in the liquid state over a wider range of temperatures than any other element. Gallium is blue-gray in color as a solid and silvery as a liquid. Its atomic number is 31. Gallium melts at 30 °C, boils at about 2204 °C, and has specific gravity of 5.9; the atomic weight of the element is 69.72.

d has a specific gravity of 2.7. Gallium was discovered spectroscopically by the French chemist *Paul Imile Lecoq de Boisbaudran* in 1875; a year later he isolated the element in its metallic state. The element is about 34th in order of abundance in the earth's crust. Gallium occurs in small quantities in some varieties of *zinc blende*,*bauxite*, *pyrite*, *magnetite* and *kaolin*.

Indium, symbol In, is a soft, malleable, silvery white metallic element. Its atomic number is 49. Indium melts at about 157 °C, boils at about 2072 °C, and has a specific gravity of 7.3. The atomic weight of indium is 114.82.

Indium was discovered spectroscopically in 1863 by the German chemists *Hieronymus Theodor Richter* and *Ferdinand Reich*. It ranks 63rd in order of abundance of the elements in the earth's surface. Indium never occurs as a free metal and is usually found as the sulfide In_2S_3; in certain *zinc blendes*; and in tungsten, tin, and iron ores.

Thallium (Greek *thallos,* "young shoot"), symbol Tl, soft, malleable metallic element that acquires a bluish-gray color upon exposure to the atmosphere. The atomic number of thallium is 81. Thallium melts at about 304 °C, boils at about 1473 °C, and has a specific gravity of 11.85. The atomic weight of thallium is 204.38.

Thallium was discovered spectroscopically in 1861 by the British chemist *Sir William Crookes*. It was isolated by Crookes and, independently, by the French chemist *Claude August Lamy* in 1862. Thallium ranks 60th in abundance among the elements in the earth's crust. Thallium occurs in combination with *pyrites*, *zinc blende*, and *hematite* and is often recovered from the flue dust produced by pyrites ovens in which sulfur and iron are separated.

Preparation of Elements

The most common sources of boron are *tourmaline*, *borax* ($Na_2B_4O_5(OH)_4.8H_2O$), and *kernite* [$Na_2B_4O_5(OH)_4.2H_2O$]. It is difficult to obtain pure boron. It can be made through the magnesium reduction of B_2O_3 oxide. The oxide is made by melting boric acid, $B(OH)_3$, which in turn is obtained from borax.

$$B_2O_3 + 3Mg \rightarrow 2B + 3MgO.$$
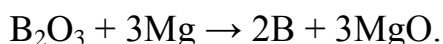
Some amounts of high purity boron are available through the thermal decomposition of such boron compounds as BBr_3 with hydrogen gas using a heated tantalum wire. Results are better when hot wires at temperatures over 1000 °C are used:

$$2BBr_3 + 3H_2 \rightarrow 2B + 6HBr.$$
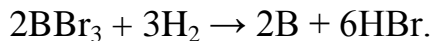
Aluminium is mined in huge scales as *bauxite* (typically $Al_2O_3 \cdot 2H_2O$). Bauxite contains Fe_2O_3, SiO_2, and other impurities. In order to isolate pure aluminium, these impurities must be removed from the bauxite. This is done by the *Bayer process*. It involves bauxite treatment with sodium hydroxide solution, which results in a solution of sodium aluminate and sodium silicate:

$$Al_2O_3 + 6NaOH + 3H_2O \rightarrow 2Na_3[Al(OH)_6];$$
$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O.$$
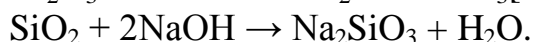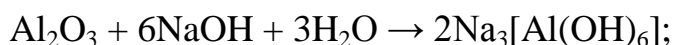
The iron remains behind as a solid. When CO_2 is blown through the resulting solution, the sodium silicate stays in solution while the aluminium is precipitated out as aluminium hydroxide:

$$2Na_3[Al(OH)_6] + 3CO_2 \rightarrow 2Al(OH)_3^- + 3Na_2CO_3 + 3H_2O.$$

The hydroxide can be filtered off, washed, and heated to form pure alumina, Al_2O_3:

$$2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O.$$
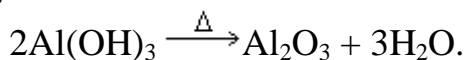
The next stage is formation of pure aluminium. It is obtained from the pure Al_2O_3 by an electrolytic method.

In aqueous solution aluminium oxide dissociates into ions:

$$Al_2O_3 \rightleftarrows Al^{3+} + AlO_3^{3-}.$$

On anode: **On cathode:**

$Al^{3+} + 3e^- \rightarrow Al$ $4AlO_3^{3-} - 12e^- \rightarrow 2Al_2O_3 + 3O_2\uparrow$

$$2Al_2O_3 \xrightarrow{\text{electrolysis, } \Delta} 4Al + 3O_2\uparrow.$$
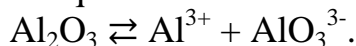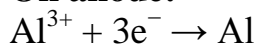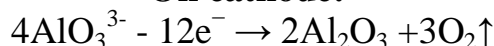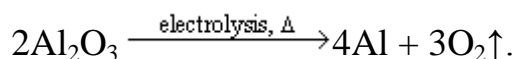
Electrolysis is necessary as aluminium is very electropositive. It seems these days that electrolysis of the hot oxide in a carbon lined steel cell acting as the cathode with carbon anodes is most common.

Gallium is normally a byproduct of the manufacture of aluminium. The purification of bauxite by the Bayer process results in concentration of gallium in its ratio from 5000 to 300 in the alkaline solutions from an aluminium. Electrolysis using a mercury electrode provides a further concentration and following electrolysis of the resulting sodium gallate using a stainless steel cathode affords liquid gallium metal.

Preparation of very pure gallium requires a number of further processes ending with zone refining to make very pure gallium metal.

Indium is a byproduct of the formation of lead and zinc. Indium metal is isolated by the electrolysis of indium salts in water. Further processes are required to make very pure indium for electronics purposes.

Crude thallium is present as a component in flue dust along with arsenic, cadmium, indium, germanium, lead, nickel, selenium, tellurium, and zinc. Thallium is prepared by dissolving of flue dust in diluted acid, precipitating out lead sulfate, and then adding HCl to precipitate thallium chloride, TlCl. Further purification can be achieved by electrolysis of soluble thallium salts.

Chemical Properties of Boron and its Compounds

Boron is the first element in group III. In many of its properties it differs from the next element in the group, aluminum, which is a metal. Although it is somewhat metallic in appearance, it is a very poor conductor of electricity. It is best regarded as a semimetal, like silicon. Boron shows trivalency in its compounds. It is difficult to get B^{3+} because large amount of energy is required and, therefore, boron forms tricovalent compounds. It shows common oxidation state of +3 in majority of its compounds. However boron shows also an oxidation state of –3 in the metal borides, *e.g.*, in Mg_3B_2 (magnesium boride) oxidation state of boron is –3.

Boron forms oxide B_2O_3 when heated in oxygen atmosphere at high temperature:

$$4B + 3O_2 \xrightarrow{T-700^0 C} 2B_2O_3 \text{ (Boron oxide or Boric anhydride)}.$$

Boron can form trichloride either by passing chlorine over the heated boron or by passing chlorine over the heated mixture of its oxide and charcoal:

$$2B + 3Cl_2 \xrightarrow{\Delta} 2BCl_3;$$

$$B_2O_3 + 3C + 3Cl_2 \xrightarrow{\Delta} 2BCl_3 + 3CO.$$
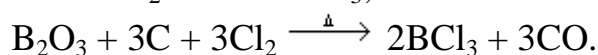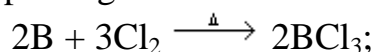
BCl_3 is hydrolyzed by water:

$$BCl_3 + 3H_2O \rightarrow H_3BO_3 + 3HCl.$$
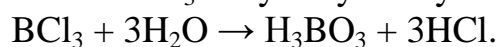
Boron forms also nitride BN when heated in the atmosphere of nitrogen or ammonia and sulfide B_2S_3 when heated with sulfur:

$$2B + N_2 \xrightarrow{\Delta} 2BN;$$

$$2B + 2NH_3 \xrightarrow{\Delta} 2BN + 3H_2;$$

$2B + 3S \xrightarrow{\text{t}} B_2S_3$.
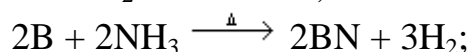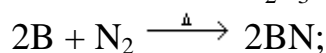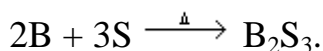
The nitride and sulfide undergo hydrolysis with steam:

$BN + 3H_2O \rightarrow H_3BO_3 + NH_3$;

Boric acid

$B_2S_3 + 6H_2O \rightarrow 2H_3BO_3 + 3H_2S$.
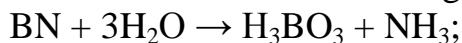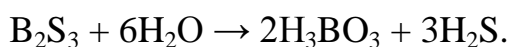
Boron reacts with steam at red heat liberating hydrogen:

$2B + 3H_2O \xrightarrow{\text{t}} B_2O_3 + 2H_2$.
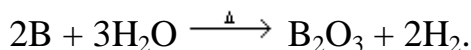
Boron reacts with concentrated H_2SO_4 and evolves sulfur dioxide, SO_2:

$2B + 3H_2SO_4(\text{conc.}) \rightarrow 2H_3BO_3 + 3SO_2\uparrow$.
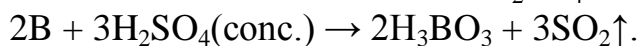
It can also dissolve in alkalies and evolve hydrogen:

$2B + 6NaOH \rightarrow 2Na_3BO_3 + 3H_2\uparrow$.
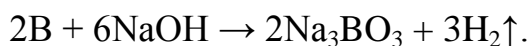
sodium orthoborate

Boron acts as powerful reducing agent:

$4B + 3CO_2 \rightarrow 2B_2O_3 + 3C$;

$4B + 3SiO_2 \rightarrow 2B_2O_3 + 3Si$.
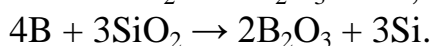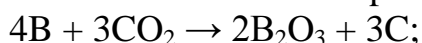
BORIC ACID AND BORATES

Boric acid and the borates are among the simplest and most important of the boron compounds. Boric acid, $B(OH)_3$, is a stable, colorless crystalline compound that forms thin, plate like crystals. It consists of planar molecules with an equilateral triangular $AHal_3$ geometry around boron. The molecules are held together in flat sheets by hydrogen bonds:
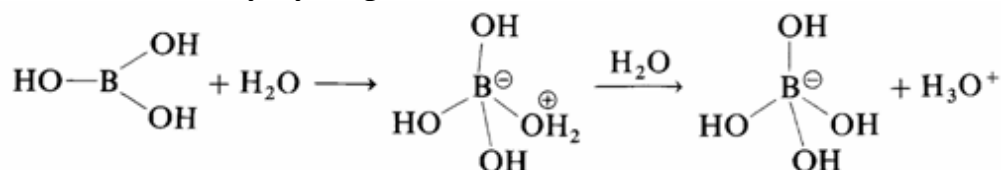
Boric acid is a very weak monoprotic acid $(K_a = 6.0 \times 10^{-10})$. It ionizes in water in an unusual way. Instead of donating one of its hydrogen atoms to a water molecule; it removes an OH^- from a water molecule, leaving an H^+ ion, which combines with another water molecule to give an H_3O^+ ion:

$H_3BO_3 + 2H_2O \rightarrow B(OH)_4^- + H_3O^+$.
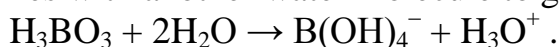
The boron atom has a vacant $2p$ orbital, which can accept an electron pair from a water molecule. This water molecule, simultaneously or in a subsequent step, gives a proton to another water molecule. In this way, boron completes its octet by forming the tetrahedral borate ion $B(OH)_4^-$. When it is heated, boric acid loses water to form various condensed boric acids, such as cyclic metaboric acid:
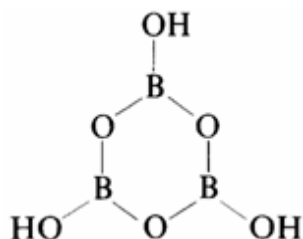
Further heating gives boric oxide, B_2O_3 which is often formed in an amorphous form, or glass. The crystalline form has a complex network structure

based on planar BO_3 groups. A few of the salts of boric acid, the borates, contain the simple anion BO_3^{3-} but most are derived from condensed forms of the acid. The most common and most important is sodium tetraborate, $Na_2[B_4O_5(OH)_4]\cdot 8H_2O$, which is commonly called *borax* and for which the formula is often written as $Na_2B_4O_7\cdot 10H_2O$. The structure of the tetraborate anion, $B_4O_5(OH)_4^{2-}$ is shown below:
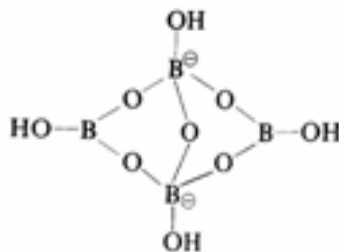
Borax and other borates are the only important boron minerals. They are found only in a very few places, for example, in California and Turkey, but the deposits in those places are extremely large.

Aqueous solutions of borax are basic, because tetraborate is the anion of a weak acid and, therefore, it is a weak base:

$$B_4O_5(OH)_4^{2-} + 5H_2O \rightarrow 4H_3BO_3 + 2OH^-.$$
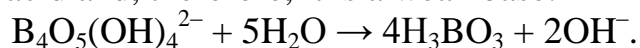
Since calcium and magnesium borates are insoluble, borax is used as a water softener and as a component of washing powders.

The boron halides are typical covalent nonmetal halides. Boron trifluoride, BF_3, and boron trichloride, BCl_3, are gases at room temperature; BBr_3 is a liquid, and BI_3 is a solid. They all consist of molecules with the expected AX_3 planar triangular structure. Although the electronegativity difference between boron and fluorine is 2.1, boron trifluoride is a covalent molecular compound with polar B–F bonds rather than an ionic crystal containing B^{3+} and F^- ions. The electronegativity difference between two elements is not always a reliable guide to finding out whether they will form an ionic crystal or a molecular compound.

Because of the presence of the vacant $2p$ orbital on the boron atom in the boron halides, they are rather reactive compounds. For example, BF_3 reacts with an F^- ion to form BF_4^- in which the valence shell of boron is completed

$$BF_3 + NaF \rightarrow NaBF_4.$$
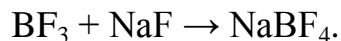
Boron trifluoride reacts in a similar way with many other molecules and ions which have unshared electron pairs that can be donated to its vacant $2p$ orbital. Thus it forms compounds with ammonia and other amines and with ethers and alcohols. In all these cases BF_3 is behaving as a Lewis acid, that is, as an electron pair acceptor:
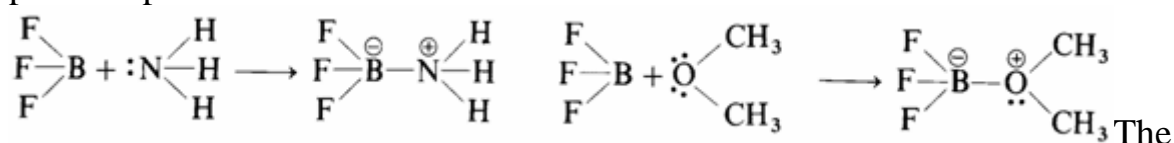
The boron halides react with water forming boric acid and the hydrogen halides. For example,

$$BCl_3 + 3H_2O \rightarrow H_3BO_3 + 3HCl.$$
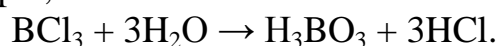
It occurs readily because the vacant $2p$ orbital of the boron atom can accept an electron pair from a water molecule. In contrast, the carbon tetrahalides have no vacant orbital and they do not react with water.

BORANES

At least twenty five compounds of boron and hydrogen have been prepared. They are known as the *boranes*. They all have unexpected formulas such as B_2H_6, B_4H_{10}, B_5H_9, and $B_{10}H_{14}$. We would expect the formula of the simplest borane to be BH_3, but this molecule is unknown as a stable species. The simplest borane that can be isolated is diborane, B_2H_6; its structure is
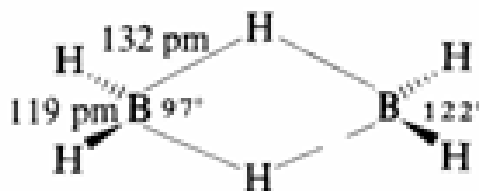
The unusual and unexpected feature of this structure is that there are two hydrogen atoms, called *bridging hydrogens,* shared between the two borons. However, there are not enough electrons for each of the lines shown in the structure to represent an electron pair. Each atom of boron contributes 3 electrons and each atom of hydrogen 1 electron, making a total of 12 electrons, or six pairs for the molecule. Thus there can be a maximum of only six ordinary covalent bonds, whereas the structure appears to have eight bonds. Because B_2H_6 has too few electrons for all the atoms to be held together by normal electron pair bonds between two nuclei, it is often described as an *electron-deficient molecule.* The bonding in diborane is best described as involving two *three-center bonds,* in which one electron pair holds together three rather than two nuclei. Each boron atom is surrounded by four electron pairs, which have the expected tetrahedral arrangement. But two of these electron pairs form three-center bonds in which one electron pair holds together two boron nuclei and a hydrogen nucleus. In the following diagram of the structure the two electron pairs forming the three-center bonds are denoted by ✸:

The following alternative but equivalent representation of the bonding in diborane emphasizes its close relationship to the bent-bond model of ethene:
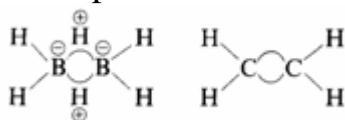
In this way each boron atom completes on octet in its valence shell, whereas in a BH_3 molecule the boron atom would have only six electrons in its valence shell and an empty $2p$ orbital. Another way to represent the structure of this molecule is by means of the two resonance structures.
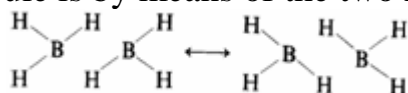
A molecule of diborane readily adds two hydride ions forming two borohydride ions, BH_4^-:

$B_2H_6 + 2H^- \rightarrow 2BH_4^-$;

$B_2H_6 + 2LiH \rightarrow 2LiBH_4$.
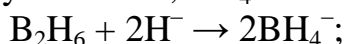
This ion has the expected tetrahedral AX_4 structure and ordinary two-center, electron pair bonds. Salts such as lithium borohydride, $LiBH_4$, and sodium borohydride, $NaBH_4$, are good reducing agents with wide application in organic chemistry. The higher boranes have unusual and fascinating structures (see Figure 1.1) that can not be explained in terms of simple bonding theories, so they are usually discussed in terms of the molecular orbital theory. There are also many anions derived from the boranes that are more complicated than BH_4^-. A particularly fascinating example is $B_{12}H_{12}^{2-}$ (Figure 1.2). It has the shape of an icosahedron, which has 12 equivalent vertices, 20 equilateral triangular faces, and 30 equivalent edges.

$B_4 H_{10}$　　　　　　　　　　$B_5 H_9$

$B_6 H_{10}$　　　　　　　　　　$B_{10} H_{14}$
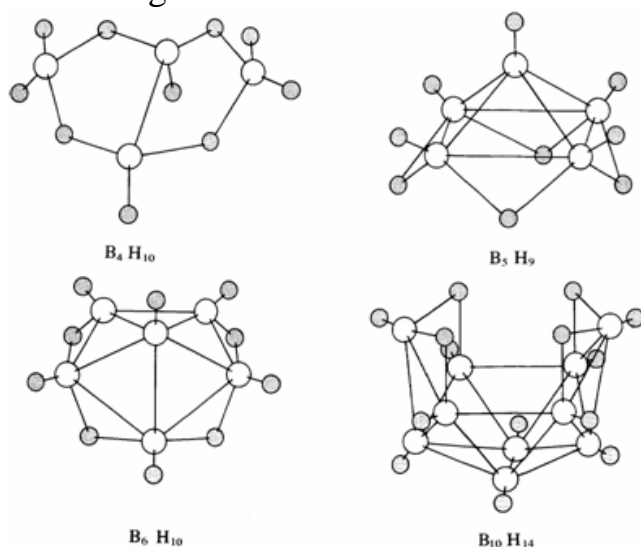
Figure 1.1 Structures of Some Higher Boranes

○ B　　○ H
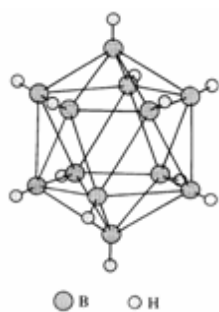
Figure 1.2 Structure of the $B_{12}H_{12}^{2-}$ Anion

The bonding in the electron-deficient $B_{12}H_{12}^{2-}$ can be satisfactorily described only by means of molecular orbital theory. The structures of these remarkable compounds serve to illustrate the fact that although the simple ideas of chemical bonding presented in this book enable us to understand the structures of many compounds, they are inadequate for many others. A more detailed interpretation of the chemical bond is necessary to enable the understanding of such compounds. Although our understanding of chemical bonding has progressed considerably

since Lewis first proposed the idea of the shared electron pair, many aspects of this subject are still not fully understood. Chemists continue to prepare new compounds, the structures of which present a challenge for even the most sophisticated theories.

Chemical Properties of Aluminum and its Compounds

Like Boron Aluminium shows trivalency. Aluminium also forms covalent compounds. However it can form electrovalent compounds when it combines with strong electron accepting atoms or groups. The size of Al^{3+} ion is very small. On account of small size and high charge, it has high polarizing power. These accounts for a covalent character even in the case of electrovalent compounds, for example, $AlCl_3$, $AlBr_3$, and AlI_3 have covalent nature. Aluminium shows common oxidation state of +3 in a majority of its compounds.

Aluminium is not affected by dry air but in moist air a thin film of oxide is formed over its surface. It burns in oxygen producing brilliant light:

$4Al + 3O_2 \rightarrow 2Al_2O_3 + \Delta Q$.
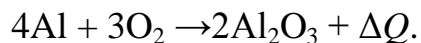
The reaction is highly exothermic.

Besides oxygen, aluminium reacts with nonmetals directly to form corresponding compounds. When heated in the atmosphere of nitrogen or ammonia it forms aluminium nitride:

$2Al + N_2 \qquad 2AlN$;

$2Al + 2NH_3 \qquad 2AlN + 3H_2$.

Aluminium powder when fused with sulfur forms aluminium sulfide:

$2Al + 3S \qquad Al_2S_3$.

Finely powdered heated aluminium combines with halogens or by passing halogens over heated mixture of its oxide and charcoal to form corresponding halides:

$2Al + 3Hal_2 \qquad 2AlHal_3$;

$Al_2O_3 + 3C + 3Hal_2 \qquad 2AlHal_3 + 3CO$.
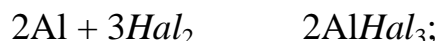
($Hal_2 = F_2$, Cl_2, Br_2, I_2)

All these compounds are hydrolysed with water:

$AlN + 3H_2O \rightarrow Al(OH)_3 + NH_3$;

$Al_2S_3 + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2S$;

$Al_2Hal_3 + 3H_2O \rightarrow 2Al(OH)_3 + 3HHal$.
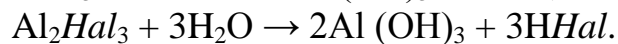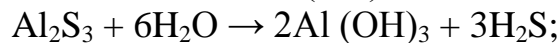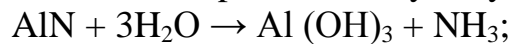
Pure aluminium is not affected by pure water. The impure aluminium is readily corroded by water containing salts (sea water). Aluminium decomposes boiling water evolving hydrogen:

$2Al + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2\uparrow$.
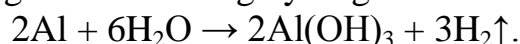
Aluminium does not interact with hydrogen directly. Aluminium hydride can be prepared by the reaction of LiH with aluminium chloride in the etheric solution:

$AlCl_3 + 3LiH \rightarrow AlH_3 + 3LiC$
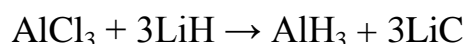
The oxidation potential of aluminium is 1.66 V. Thus, it is strongly electropositive, very reactive and a powerful reducing agent. It dissolves in HCl (dilute and concentrated) and dilute sulfuric acid, evolving hydrogen:
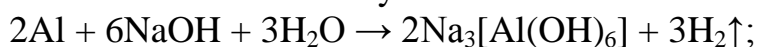
$2Al + 6HCl \rightarrow 2AlCl_3 + 3H_2\uparrow$;

$2Al + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2\uparrow$.
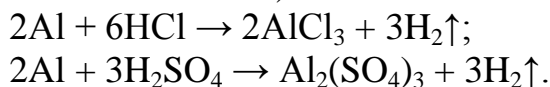
The reaction with dilute H_2SO_4 is very slow probably on account of the insolubility of the oxide film in this acid.

Hot concentrated sulfuric acid dissolves Al with the evolving of SO_2:

$2Al + 6H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3SO_2\uparrow + 6H_2O$
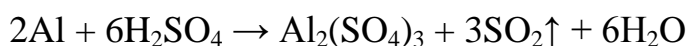
Dilute and concentrated HNO_3 has no effect on Al, i.e., Al is rendered passive by nitric acid due to surface oxidation and formation of a thin film of oxide on its surface.

Aluminium is attacked by caustic alkalies with the evolving of hydrogen:

$2Al + 6NaOH + 3H_2O \rightarrow 2Na_3[Al(OH)_6] + 3H_2\uparrow$;

Sodium hexahydroxoaluminate

$2Al + 6NaOH \qquad 2Na_3AlO_3 + 3H_2\uparrow$.

Sodium aluminate

It is a good reducing agent and reduces oxides of metals like Cr, Fe, Mn, etc.:

$Cr_2O_3 + 2Al \rightarrow 2Cr + Al_2O_3 + Q$;

$Fe_2O_3 + 2Al \rightarrow 2Fe + Al_2O_3 + Q$;

$3Mn_3O_4 + 8Al \rightarrow 9Mn + 4Al_2O_3 + Q$.
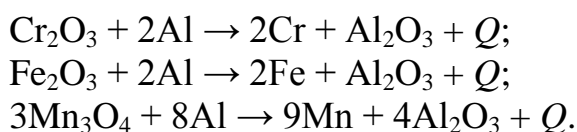
It reduces oxides of non-metals also:

$3CO_2 + 4Al \rightarrow 2Al_2O_3 + 3C$;

$3SiO_2 + 4Al \rightarrow 2Al_2O_3 + 3Si$.
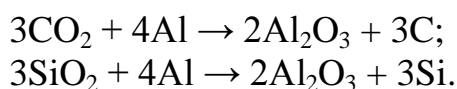
Being more electronegative it displaces copper, zinc and lead from the solutions of their salts:

$3ZnSO_4 + 2Al \rightarrow Al_2(SO_4)_3 + 3Zn$;

$3CuSO_4 + 2Al \rightarrow Al_2(SO_4)_3 + 3Cu$.
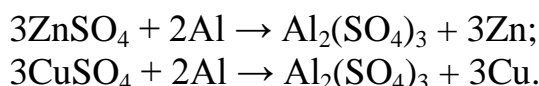
Aluminium oxide Al_2O_3 is a white amorphous powder, usually soluble in acids but when it's ignited above 850 ^0C, it becomes dense and insoluble in acids.

Pure Al_2O_3 is prepared by igniting $Al(OH)_3$, $Al_2(SO_4)_3$ or ammonium alum, $(NH_4)Al(SO_4)_2 \times 12H_2O$:

$2Al(OH)_3 \qquad Al_2O_3 + 3H_2O$;

$Al_2(SO_4)_3 \qquad Al_2O_3 + 3SO_3$;

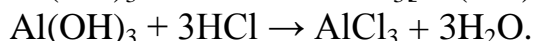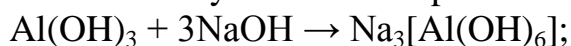$2(NH_4)Al(SO_4)_2 {'} 12H_2O \qquad Al_2O_3 + 2NH_3 + 4H_2SO_4 + 9H_2O$.
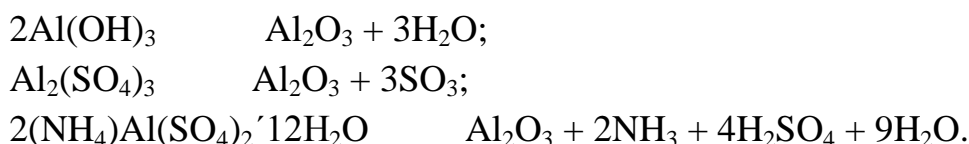
It is amphoteric oxide. Ignited Al_2O_3 is brought into solution as aluminate by fusion with alkali and carbonates or as sulfate by fusion with $KHSO_4$:
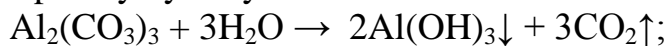
$Al_2O_3 + 3Na_2CO_3 \qquad 2Na_3AlO_3 + 3CO_2\uparrow$;

$Al_2O_3 + CaCO_3 \qquad Ca(AlO_2)_2 + CO_2\uparrow$;

$Al_2O_3 + 6KHSO_4 \qquad 3K_2SO_4 + Al_2(SO_4)_3 + 3H_2O$.
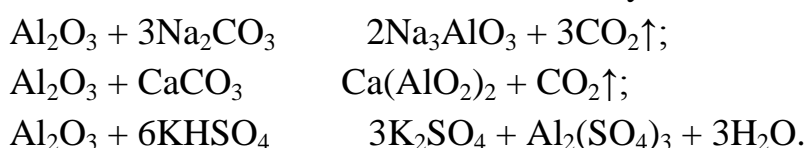
When ammonium hydroxide is added to any soluble aluminium salt, we get a gelatinous white precipitate of ***aluminium hydroxide***:

$Al_2(SO_4)_3 + 6NH_4OH \rightarrow 2Al(OH)_3\downarrow + 3(NH_4)_2SO_4$.
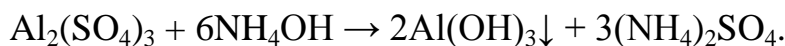
Aluminium hydroxide is amphoteric and dissolves both in alkalies and acids:

$Al(OH)_3 + 3NaOH \rightarrow Na_3[Al(OH)_6]$;

$Al(OH)_3 + 3HCl \rightarrow AlCl_3 + 3H_2O$.

Aluminium salts which are formed by weak acids (sulfide, carbonate, etc.) are completely hydrolysed:

$Al_2(CO_3)_3 + 3H_2O \rightarrow 2Al(OH)_3\downarrow + 3CO_2\uparrow$;

$Al_2S_3 + 6H_2O \rightarrow 2Al(OH)_3\downarrow + 3H_2S\uparrow$;

so when acting with $(NH_4)_2S$ of an aluminium salt in aqueous solution aluminium hydroxide $Al(OH)_3$ is formed instead of aluminium sulfide Al_2S_3:

$2AlCl_3 + 3(NH_4)_2S + 6H_2O \rightarrow 2Al(OH)_3\downarrow + 6NH_4Cl + 3H_2S\uparrow$.
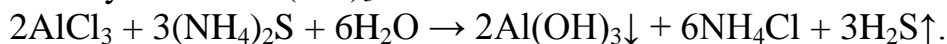
11.6 Beryllium, magnesium and alkaline earth metals

There are six chemical elements in group IIA of the periodic table: beryllium Be, magnesium Mg, calcium Ca, strontium Sr, barium Ba and radium Ra. Calcium, strontium and barium name alkaline earth metal.

The atoms of these elements have the following configurations:

Be	$1s^2 2s^2$	$[He]2s^2$
$_2$Mg	$1s^2 2s^2 2p^6 3s^2$	$[Ne]3s2$
$_0$Ca	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$	$[Ar]4s2$
$_8$Sr	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2$	$[Kr]5s2$
$_6$Ba	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^2$	$[Xe]6s2$
$_8$Ra	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^6 7s^2$	$[Rn]7s2$

Properties of Group IIA Elements

Beryllium, symbol Be, is a gray, brittle metallic element, with an atomic number of 4. It was discovered as an oxide, known as *beryllia* now, in 1797 by French chemist *Louis Nicolas Vauquelin*. The free element was firstly isolated in 1828 independently by *Friedrick Wöhler* and *Antoine Bussy*. Its atomic weight is 9.012. Beryllium melts at about 1287 °C, boils at about 3000 °C, and has a specific gravity of 1.85.

Magnesium, symbol Mg, is a silvery white metallic element. The atomic number of magnesium is 12. The metal was isolated firstly by the British chemist *Sir Humphry Davy* in 1808. Magnesium melts at about 649 °C, boils at about 1107 °C, and has a specific gravity of 1.74; the atomic mass of magnesium is 24.305.

Magnesium ranks sixth in natural abundance among elements in crustal rocks. It occurs in nature in chemical combination with other elements only, particularly as the minerals *carnallite* ($KMgCl_3 \cdot 6H_2O$), *dolomite* ($CaCO_3 \cdot MgCO_3$), and *magnesite* ($MgCO_3$); in many rock-forming silicates; and as salts,

such as magnesium chloride, in ocean and saline-lake waters. It is an essential constituent of animal and plant tissue.

Calcium, symbol Ca, is a silvery-white metallic element. The atomic number of calcium is 20. The British chemist *Sir Humphry Davy* isolated calcium in 1808 by means of electrolysis. Calcium melts at about 839 °C, boils at about 1484 °C, and has a specific gravity of 1.54; its atomic mass is 40.08.

Calcium is fifth in abundance among the elements in the earth's crust, but it is not found uncombined in nature. It occurs in many highly useful compounds, such as calcium carbonate ($CaCO_3$), of which *calcite*, *marble*, *limestone*, and *chalk* are composed; calcium sulfate ($CaSO_4$) in *alabaster* or *gypsum*; calcium fluoride (CaF_2) in *fluorite*; calcium phosphate ($Ca_3(PO_4)_2$) in rock phosphate; and in many silicates.

Strontium, symbol Sr, is a malleable, ductile metallic element. The atomic number of strontium is 38. Metallic strontium was isolated firstly by the British chemist *Sir Humphry Davy* in 1808. Strontium melts at about 769 °C boils at about 1384 °C, and has a specific gravity of 2.6. The atomic weight of strontium is 87.62.

Strontium is never found in the elemental state, occurring mainly as *strontianite* ($SrCO_3$), and *celestite* ($SrSO_4$). Strontium ranks about 15th among the elements in natural abundance in the earth's crust and is widely distributed in small quantities.

Barium, symbol Ba, is a soft, silvery, metallic element. The atomic number of barium is 56. Barium was recognized as an element firstly in 1808 by the English scientist *Sir Humphry Davy*. Barium is the 14th most common element, making up 1/2000th of the crust of the earth. The atomic weight of barium is 137.33. The element melts at about 725 °C, boils at about 1640 °C, and has a specific gravity of 3.5.

Barium occurs in nature in the form of its compounds only. Its most important compounds are the minerals barium sulfate and barium carbonate (*witherite*, $BaCO_3$).

PREPARATION

Metals of Group IIA, like the alkali metals, are prepared by electrolysis of the molten halides (usually the chlorides) or by chemical reduction of either the halides or the oxides.

Beryllium extraction from ores is complex. The mineral beryl, [$Be_3Al_2(SiO_3)_6$] is the most important source of beryllium. It is roasted with sodimu hexafluorosilicate, Na_2SiF_6, at 700 °C to form beryllium fluoride. This is water soluble and the beryllium can be precipitated as the hydroxide $Be(OH)_2$ by adjustment of the pH to 12.
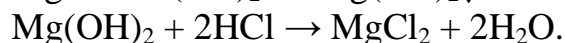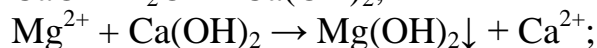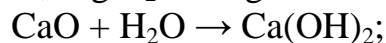
Pure beryllium can be obtained by electrolysis of beryllium chloride, $BeCl_2$, to which sodium chloride is added to increase the conductivity of the molten salt:

$$BeCl_2(l) \xrightarrow{electrolysis} Be + Cl_2\uparrow.$$
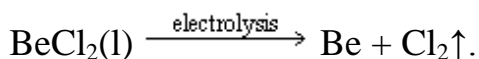
Another method involves the reduction of beryllium fluoride with magnesium at 1300°C:

$$BeF_2 + Mg \xrightarrow{\Delta} MgF_2 + Be.$$

Magnesium can be prepared commercially by several processes and normally is not made in the laboratory because of its ready availability. There are massive amounts of magnesium in seawater. It can be recovered as magnesium chloride, $MgCl_2$ through reaction with calcium oxide, CaO:

$$CaO + H_2O \rightarrow Ca(OH)_2;$$
$$Mg^{2+} + Ca(OH)_2 \rightarrow Mg(OH)_2\downarrow + Ca^{2+};$$
$$Mg(OH)_2 + 2HCl \rightarrow MgCl_2 + 2H_2O.$$

Electrolysis of hot molten $MgCl_2$ affords magnesium as a liquid which is poured off, and chlorine gas:

$$MgCl_2(l) \xrightarrow{electrolysis} Mg + Cl_2\uparrow.$$
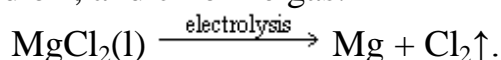
The other methods used to produce magnesium are non electrolytic and involve dolomite, $(MgCa(CO_3)_2)$, an important magnesium mineral. It is "calcined" by heating to form calcined dolomite, $MgO \cdot CaO$, which reacts with ferrosilicon alloy:

$$2[MgO \cdot CaO] + FeSi \xrightarrow{\Delta} 2Mg + Ca_2SiO_4 + Fe.$$
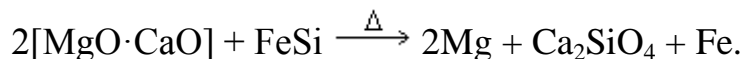
The magnesium can be distilled out from this mixture of products.

Calcium is prepared by electrolysis of molten calcium chloride and by reduction of calcium oxide by aluminum in a vacuum, where the calcium produced distills off:

$$3CaO + 2Al \xrightarrow{\Delta} 3Ca + Al_2O_3.$$
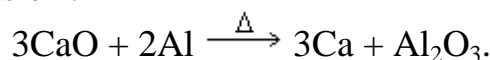
Barium is produced by reduction of the oxide by aluminum also, and although very small amounts of strontium are used commercially, it can be produced by a similar process.

Chemical Properties of Beryllium and its Compounds

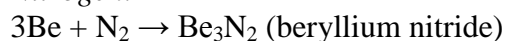Beryllium reacts directly with many nonmetals. For example, with:
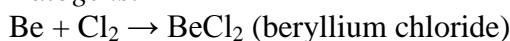
Oxygen:
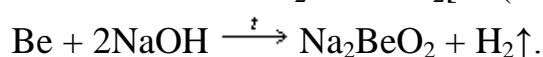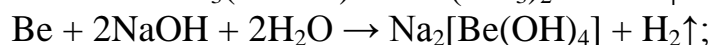$2Be + O_2 \rightarrow 2BeO$ (beryllium oxide)

Sulfur:
$Be + S \rightarrow BeS$ (beryllium sulfide)

Nitrogen:
$3Be + N_2 \rightarrow Be_3N_2$ (beryllium nitride)

Halogens:
$Be + Cl_2 \rightarrow BeCl_2$ (beryllium chloride)
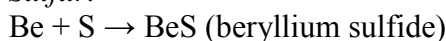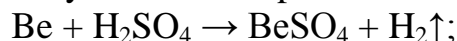
Beryllium is a amphoteric metal and reacts with strong acids and bases:

$$Be + H_2SO_4 \rightarrow BeSO_4 + H_2\uparrow;$$
$$3Be + 8HNO_3(diluted) \rightarrow Be(NO_3)_2 + 2NO\uparrow + 4H_2O;$$
$$Be + 2NaOH + 2H_2O \rightarrow Na_2[Be(OH)_4] + H_2\uparrow;$$
$$Be + 2NaOH \xrightarrow{t} Na_2BeO_2 + H_2\uparrow.$$
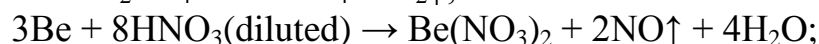
Concentrated nitric and sulfuric acids do not react with beryllium.

Beryllium oxide is a white, high-melting compound. It is prepared by decomposition of beryllium hydroxide or beryllium carbonate:
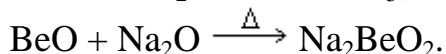
$$Be(OH)_2 \xrightarrow{\Delta} BeO + H_2O;$$
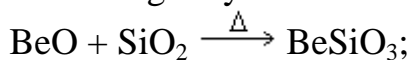$$BeCO_3 \xrightarrow{\Delta} BeO + CO_2.$$
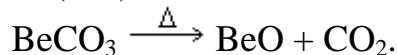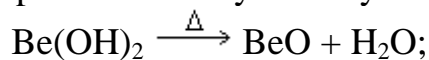
Beryllium oxide is a amphoteric oxide, which reacts with strong acids and bases:

$$BeO + H_2SO_4 \rightarrow BeSO_4 + H_2O;$$

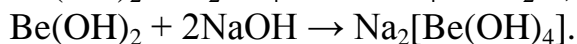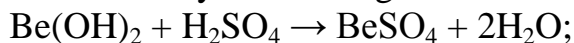$BeO + 2NaOH + H_2O \rightarrow Na_2[Be(OH)_4]$.
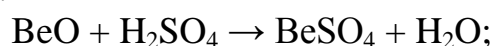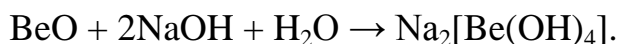
At heating beryllium oxide react with acidic and basic oxides:

$BeO + SiO_2 \xrightarrow{\Delta} BeSiO_3$;

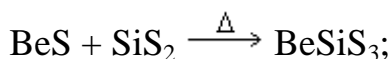$BeO + Na_2O \xrightarrow{\Delta} Na_2BeO_2$.

Beryllium hydroxide is insoluble in water. It is an amphoteric hydroxide which reacts readily with strong acids and bases:

$Be(OH)_2 + H_2SO_4 \rightarrow BeSO_4 + 2H_2O$;

$Be(OH)_2 + 2NaOH \rightarrow Na_2[Be(OH)_4]$.

Beryllium sulfide like its oxide has amphoteric properties, at heating it reacts with acidic and basic sulfides:

$BeS + SiS_2 \xrightarrow{\Delta} BeSiS_3$;

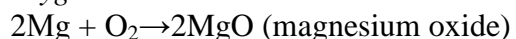$BeS + Na_2S \xrightarrow{\Delta} Na_2BeS_2$.
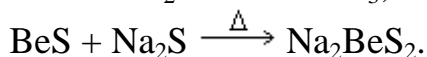
Be^{2+} has a tendency to accept electrons due to its small size. As a result, bonding in its compounds is highly covalent. For example, the melting point of beryllium chloride (450 °C) is low compared with that of the other chlorides of Group IIA elements ($MgCl_2$ melts at 714 °C). Also, the molten salt has a low electrical conductivity, so electrolysis of $BeCl_2$ requires the addition of a salt such as NaCl. In the solid phase, beryllium chloride has a polymeric structure (that is, covalent substance with an infinitely repeating unit), in which each chlorine atom "bridges" two beryllium atoms:
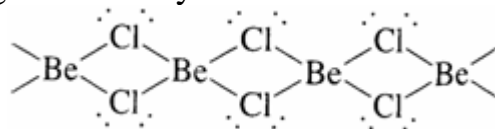
Chemical Properties of Magnesium and its Compounds

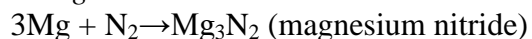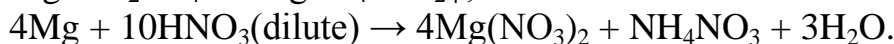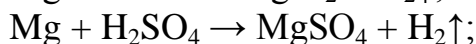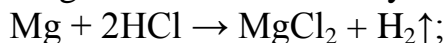Magnesium reacts with nonmetals. For example, with:

oxygen

$2Mg + O_2 \rightarrow 2MgO$ (magnesium_oxide)

nitrogen

$3Mg + N_2 \rightarrow Mg_3N_2$ (magnesium_nitride)

sulfur

$Mg + S \rightarrow MgS$ (magnesium sulfide)
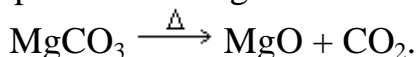
Halogens

$Mg + Cl_2 \rightarrow MgCl$ (magnesium_chloride)

Magnesium reacts directly with many acids:

$Mg + 2HCl \rightarrow MgCl_2 + H_2\uparrow$;

$Mg + H_2SO_4 \rightarrow MgSO_4 + H_2\uparrow$;

$4Mg + 10HNO_3(\text{dilute}) \rightarrow 4Mg(NO_3)_2 + NH_4NO_3 + 3H_2O$.

Magnesium oxide is a white, high-melting compound. It can be prepared by decomposition of magnesium carbonate:

$MgCO_3 \xrightarrow{\Delta} MgO + CO_2$.

Magnesium oxide is a basic oxide which reacts with acids and acidic oxides:

$MgO + H_2SO_4 \rightarrow MgSO_4 + H_2O$;

$MgO + CO_2 \xrightarrow{\Delta} MgCO_3$.
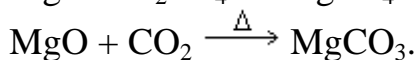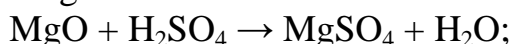
Magnesium hydroxide is insoluble in water, it is a basic hydroxide which reacts readily with acids and acidic oxides:

$Mg(OH)_2 + H_2SO_4 \rightarrow MgSO_4 + 2H_2O$;

$Mg(OH)_2 + SO_3 \rightarrow MgSO_4 + H_2O$.
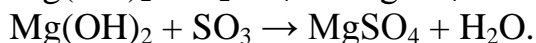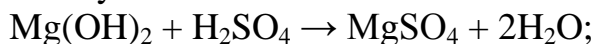
Chemical Properties of the Alkaline Earth Metals

The chemistry of the alkaline earth metals is relatively simple. Since two electrons can be easily removed from their atoms to form the M^{2+} ions, there is only one stable oxidation state +2 respectively. With the exception of a very few compounds, all compounds of alkaline earth metals are ionic.
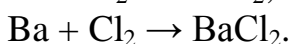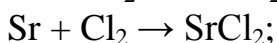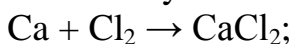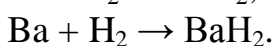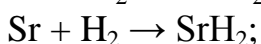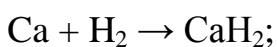
As we might expect from their low ionization energies, all these elements are very reactive. The metals react directly with many other elements and compounds. They react with the halogens giving ionic halides:

$Ca + Cl_2 \rightarrow CaCl_2$;
$Sr + Cl_2 \rightarrow SrCl_2$;
$Ba + Cl_2 \rightarrow BaCl_2$.

The alkaline earth metals react with hydrogen at heating giving ionic hydrides:

$Ca + H_2 \rightarrow CaH_2$;
$Sr + H_2 \rightarrow SrH_2$;
$Ba + H_2 \rightarrow BaH_2$.

Calcium, strontium, and barium react with nitrogen at heating, forming ionic nitrides containing the N^{3-}ion:

$3Ca + N_2 \xrightarrow{\Delta} Ca_3N_2$;

$3Sr + N_2 \xrightarrow{\Delta} Sr_3N_2$;

$3Ba + N_2 \xrightarrow{\Delta} Ba_3N_2$.
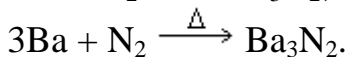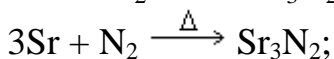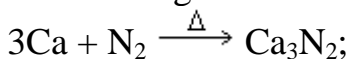
Since all alkaline earth metals react readily with oxygen, they must be stored out of contact with the atmosphere. The reactions with oxygen are more complicated than we might have expected. Calcium and strontium give the expected oxides, CaO and SrO, in a pure state when they react with excess of oxygen under ordinary conditions. Barium gives peroxide:

$Ba + O_2 \rightarrow BaO_2$.
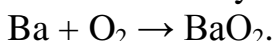
Oxides and Hydroxides of the Alkaline Earth Metals Oxides of the alkaline earth metals are basic oxides and have all properties of basic oxides.

1. Reactions with water are:
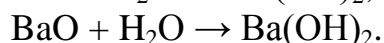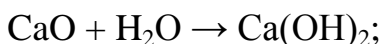
$CaO + H_2O \rightarrow Ca(OH)_2$;
$BaO + H_2O \rightarrow Ba(OH)_2$.

2. Reactions with acids are:

$SrO + 2HCl \rightarrow SrCl_2 + H_2O$;
$BaO + 2HNO_3 \rightarrow Ba(NO_3)_2 + H_2O$.

3. Reactions with acidic oxides are:

$CaO + CO_2 \rightarrow CaCO_3$;
$BaO + SO_3 \rightarrow BaSO_4$.
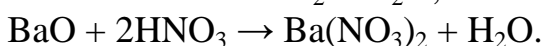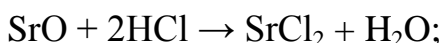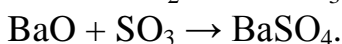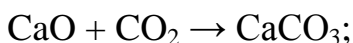
Hydroxides of the alkaline earth metals are strong bases. These react with:

— acids

$Ca(OH)_2 + 2HCl \rightarrow CaCl_2 + H_2O$;

— acidic oxides

$Sr(OH)_2 + CO_2 \rightarrow SrCO_3\downarrow$;

─s alts

$$Ca(OH)_2 + CuCl_2 \rightarrow CaCl_2 + Cu(OH)_2\downarrow.$$
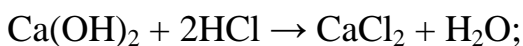
Carbonates of the alkaline earth metals are minerals and are the most important sources of these elements. Unlike the alkali metal carbonates (other than Li_2CO_3), they decompose when heated, giving the oxides and CO_2:

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2\uparrow .$$
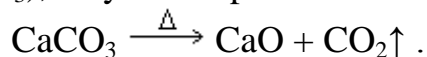
Uses and biological role

Although *beryllium* products are safe to use and handle, the fumes and dust released during fabrication are highly toxic. Extreme care must be taken to avoid breathing or ingesting even very small amounts. Specially designed exhaust hoods are used by persons working with beryllium oxide.

Beryllium and its oxide are being utilized more and more in industry. Besides its importance in aircraft and X-ray tubes, beryllium is used in computers, lasers, televisions, oceanographic instruments, and personal body armor.

Beryllium has no biological role. Beryllium metal dust can cause major lung damage and beryllium salts are very toxic. Compounds containing beryllium are very poisonous and should be handled by a professional under controlled conditions only. One route for beryllium into the biosphere is by way of industrial smoke.

Magnesium is an important element in both plant and animal life. Chlorophylls are porphyrins based upon magnesium. Magnesium is required for the activation of some enzymes. The adult daily requirement of magnesium is about 0.3 g·day-1. Magnesium is an essential component of bone, cartilage and the crustacean exoskeleton.

Magnesium is an activator of several key enzyme systems, including kinases, (i.e. enzymes that catalyse the transfer of the terminal phosphate of ATP to sugar or other acceptors), mutases (transphosphorylation reactions), muscle ATPases, and the enzymes cholinesterase, alkaline phosphatase, enolase, isocitric dehydrogenase, arginase (magnesium is a compone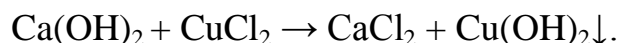nt of the arginase molecule), deoxyribonuclease, and glutaminase. Through its role in enzyme activation, magnesium (like calcium) stimulates muscle and nerve irritability (contraction), is involved in the regulation of intracellular acid-base balance, and plays an important role in carbohydrate, protein and lipid metabolism.

Magnesium hydroxide used in medicine as the laxative "milk of magnesia," and in sugar refining; magnesium sulfate ($MgSO_4·7H2O$), well known as *Epsom salt*; and magnesium oxide (MgO), called burnt magnesia, or magnesia are used as a heat-refractory and insulating material, in cosmetics, as a filler in paper manufacture, and as a mild, antacid laxative.

Calcium is present in the chemically combined state in lime (calcium hydroxide), cement and mortar (as calcium hydroxide or a variety of silicates of calcium), teeth and bones (as a calcium hydroxyphosphate), and in many body fluids (as complex proteinaceous compounds) essential to muscle contraction, the transmission of nerve impulses, and the clotting of blood.Calcium is an essential component of bone, cartilage and the crustacean exoskeleton. Calcium is essential

for the normal clotting of blood, by stimulating the release of thromboplastin from the blood platelets. It is an activator for several key enzymes, including pancreatic lipase, acid phosphatase, cholinesterase, ATPases, and succinic dehydrogenase. Through its role in enzyme activation, calcium stimulates muscle contraction (ie. promotes muscle tone and normal heart beat) and regulates the transmission of nerve impulses from one cell to another through its control over acetylcholine production. Calcium, in conjunction with phospholipids, plays a key role in the regulation of the permeability of cell membranes and consequently over the uptake of nutrients by the cell. It is believed to be essential for the absorption of vitamin B12 from the gastro-intestinal tract.

Strontia (strontium oxide), SrO, is used in recovering of sugar from beet-sugar molasses. A radioactive isotope of the element, strontium-85, is used in the detection of bone cancer. Strontium-90 is a dangerous radioactive isotope found in the fallout that results from the detonation of some nuclear weapons.

Strontium has no biological role. But chemically, strontium resembles calcium and the human body does a poor job of distinguishing the two. Therefore it is absorbed by the body and stored in the skeleton in places where calcium should be. This happens also with radioactive ^{90}Sr which was produced by above-ground nuclear explosions in the 1950s. Regrettably strontium-90 is widely spread in the environment.

Barium metal has few practical applications, although it is used sometimes in coating electrical conductors in electronic apparatus and in automobile ignition systems. Barium sulfate ($BaSO_4$) is used as a filler for rubber products, in paint, and in linoleum. Barium nitrate is used in fireworks, and barium carbonate in rat poisons. A form of barium sulfate, which is opaque to X-rays, is used for the X-ray examination of the gastrointestinal tract.

Barium has no biological role. The British Pharmaceutical Codex from 1907 indicates that barium chloride ("barii chloridum", $BaCl_2 \cdot 2H_2O$] has a stimulant action on the heart and other muscles. It was said that it "raises blood pressure by constricting the vessels and tends to empty the intestines, bladder, and gall bladder". Its poisonous nature was pointed out also. Barium sulfide (BaS) was used as a depilatory agent (removes hair). Barium sulfate ($BaSO_4$) is insoluble and used for body imaging (*barium meal*).

All dissolvable barium compounds should be regarded as highly toxic although initial evidence would appear to suggest the danger is limited. Barium salts can damage the liver. The metal dust presents a fire and explosion hazard.

11.7 The alkali metals

The elements of Group 1, the Alkali metals, are:

Symbol	Electron configuration
Lithium Li	[He]$2s^1$
Sodium Na	[Ne]$3s^1$
Potassium K	[Ar]4s^1
Rubidium Rb	[Kr]5s^1

| *Cesium Cs* | $[Xe]6s^1$ |
| *Francium Fr* | $[Rn]7s^1$ |

In each element the valency electron configuration is ns^1, where n is the period number. The last element, Francium, is radioactive and will not be considered here.

Appearance

All the Group 1A elements are silvery-colored metals. They are soft, and can be easily cut with a knife to expose a shiny surface, which dulls on oxidation.

General Reactivity

These elements are highly reactive metals. The reactivity increases on descending the Group from Lithium to Cesium. There is a closer similarity between the elements of this sub-Group than in any other Group of the Periodic Table.

Occurrence and Extraction

These elements are too reactive to be found free in nature. Sodium occurs mainly as NaCl (salt) in seawater and dried-up seabeds. Potassium is more widely distributed in minerals such as sylvite, KCl, but is also extracted from seawater. The alkali metals are so reactive that they cannot be displaced by another element, so are isolated by electrolysis of their molten salts.

Physical Properties

The alkali metals differ from other metals in several ways. They are soft, with low melting and boiling temperatures. They have low densities - Li, Na and K are less dense than water. They show relatively weak metallic bonding, as only one electron is available from each atom.

Alkali metals color flames. When the element is placed in a flame the heat provides sufficient energy to promote the outermost electron to a higher energy level. On returning to ground level, energy is emitted and this energy has a wavelength in the visible region: Li - red; Na - yellow; K - lilac; Rb - red; Cs - blue.

The ionic radii of the alkali metals are all much smaller than the corresponding atomic radii. This is because the atom contains one electron in an s-level relatively far from the nucleus in a new quantum shell, and when it is removed to form the ion the remaining electrons are in levels closer to the nucleus. In addition, the increased effective nuclear charge attracts the electrons towards the nucleus and decreases the size of the ion.

Chemical Properties

The alkali metals are strong reducing agents. The standard electrode potentials all lie between -2,7V and -3,0V, indicating a strong tendency to form cations in solution. They can reduce Oxygen, Chlorine, Ammonia and Hydrogen. The reaction with Oxygen tarnishes the metals in air, so they are stored under oil. They cannot be stored under water because they react with it to produce Hydrogen and alkali hydroxides:

$2M + 2H_2O = 2MOH + H_2$.
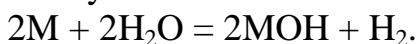
This reaction illustrates the increasing reactivity on descending the Group. Li reacts steadily with water, with effervescence; Sodium reacts more violently and can burn with an orange flame; K ignites on contact with water and burns with a lilac flame; Cs sinks in water, and the rapid generation of Hydrogen gas under water produces a shock wave that can shatter a glass container. Na dissolves in liquid Ammonia to give a deep blue solution of Sodium cations and solvated electrons. This solution is used as a reducing agent.

At higher concentrations the color of the solution changes to bronze and it conducts electricity like a metal.

The chemistry of Li shows some anomalies, as the cation Li^+ is so small it polarizes anions and so introduces a covalent character to its compounds. Li has a diagonal relationship with Magnesium.

Oxides

The Alkali metals form ionic solid oxides of composition M_2O when burnt in air. However, Na also forms the peroxide Na_2O_2 as the main product, and K forms the superoxide KO_2, also as the main product:

$$4Li + O_2 \xrightarrow{t} 2Li_2O;$$
$$2Na + O_2 \xrightarrow{t} Na_2O_2;$$
$$K + O_2 \xrightarrow{t} KO_2.$$
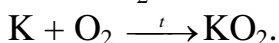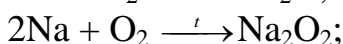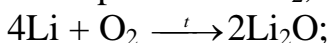
Hydroxides

Alkali metal hydroxides are white ionic crystalline solids of formula MOH, and are soluble in water. They are all deliquescent except LiOH. The aqueous solutions are all strongly alkaline (hence the name of this Group) and therefore dangerous to handle. They neutralize acids to form salts, eg: $NaOH + HCl = NaCl + H_2O$.

Halides

Alkali metal halides are white ionic crystalline solids. They are all soluble in water except LiF.

Oxidation States

Alkali metals have oxidation states of 0 and +1. All the common compounds are based on the M^+ ion. This is because the first ionization energy of these elements is low, and the second ionization energy is much higher. The outermost electron is well shielded from the attraction of the nucleus by filled inner electron levels and so is relatively easy to remove. The next electron is much more difficult to remove as it is part of a full level and is also closer to the nucleus.

Industrial Information

Sodium hydroxide, Chloride and Carbonate are among the most important industrial chemicals associated with this Group. Sodium hydroxide is produced by the electrolysis of saturated brine in a cell with steel cathodes and titanium anodes. Sodium Carbonateis made by the Solvay Process, in which soluble Sodium Chloride is converted into insoluble Sodium Hydrogen Carbonate and filtered off, then heated to produce the Carbonate. However, the principal by-product of this process is calcium Chloride, and its deposition in rivers causes environmental

concern. The Solvay Process is therefore gradually being replaced by the purification of Sodium Carbonate from minerals.

11.8 Other bioactive metals

Near 75% of all known chemical elements are metals. Among them there is a series of biologically active macro- and micronutrients (see Table 19).

Table 19. Characteristics of main bioactive metals

Element	Period	Group	Possible Oxidation numbers	Chemical properties
Mg	3	2A	0, +2	Weak amphoteric metal
K	4	1A	0, +1	Typical alkali metal
Ca	4	2A	0, +2	Alkali-Earth Metal
Mn	4	7B	0, +2, +3, +4, +5, +7	Transition metal
Fe	4	8B	0, +2, +3, +6	Transition metal
Co	4	8B	0, +2, +3, +6	Transition metal
Cu	4	1B	0, +1, +2	Transition metal
Zn	4	2B	0, +2	Transition metal
Al	3	3A	0, +1, +3	Amphoteric metal

All bioactive metals depending on its function for plant, animals or human body may be divided into macro-, micronutrients and toxicants (see Table 20).

Table 20. Characteristic of biological function

Element	Biological function
Mg	Included in Chlorophilium
K	Macronutrient for plant nutrition, needed for cell water balance and transparency of membranes
Ca	Macronutrient for plant and human nutrition, takes part in synthesis of proteins
Mn	Micronutrient, takes part in Redox processes. In excess - toxicant
Fe	Micronutrient, needed for processes of breathing and photosynthesis; includes in hemoglobin
Co	Micronutrient, included coferments (for example Vitamin B_{12} - cobalt ammine). In excess - toxicant
Cu	Irreplaceable micronutrient. In excess - toxicant
Zn	Micronutrient. In excess - toxicant

It is important to know the principles of interaction of metals with different types of acids (see Table 21).

Table 21. Interaction acids-oxidizing agents with metals

Formula of acid	Metals		Notes
	Active: The Alkali, The Alkali-Earth, Mg, Zn	Heavy with low activity	
	Scheme of products		
H_2SO_4 (conc.)	Sulfate + S + H_2O or	Sulfate + SO_2 + H_2O	Fe is immunized

	Sulfate + H_2S + H_2O		by acid
HNO_3 (conc.)	Nitrate + N_2O + H_2O	Nitrate + NO_2 + H_2O	Not reacts with Au, Pt, Rh, Ir, Ti, Ta; Al, Fe, Co, Ni, Cr are immunized by acid
HNO_3 (diluted)	Nitrate + N_2 + H_2O or Nitrate + NH_4NO_3 + H_2O	Nitrate + NO + H_2O	Fe and Sn forms NH_4NO_3

CHAPTER 12 MINERAL FERTILIZERS

The term fertilizer is defined in the Act. No. 156/1998 Coll., as amended. Fertilizers are considered substances containing nutrients for nutrition of crop plants and forest trees, to maintain or improve soil fertility and positive influence on yield or quality of production

Fertilizers are divided according to three basic aspects:
1. According to efficiency
    1. straight fertilizers
    2. auxiliary substances
2. According to origin
    1. mineral fertilizers
    2. manure
3. According to phase
    1. solid fertilizers
    2. liquid fertilizers

Staight fertilizers are substances that contain one or more plant nutrients, typically in large amounts, either mineral or in organic form. They provide plants with macro- or micronutrients, including mineral fertilizers and manure.

Auxiliary substances contain plant nutrients in larger quantities, thus not supply nutrients to plants, but allow improving nutrition by editing environment or affecting the metabolism of plants so that the plants can utilize larger quantities of nutrients to yield formation.

Devided into:
1. Auxiliary soil substances – substances without effective amount of nutrients which would biologically, chemically or physically affect the soil, improving soil state or increasing the efficiency of fertilizers
2. plant preparations – substances without effective amount of nutrients which otherwise favorably affect the development of cultivated plants or the quality of plant products.

Mineral fertilizers include all fertilising substances manufactured outside the agricultural plant. They are mainly chemical products, mining and construction industries. The main representatives of this group are concentrated mineral fertilizers, which are divided into
1. one-component (straight) fertilizers – contain one nutrient as a major. They may also comprise accompanying ions,

respectively microelements. They are divided into nitrogen, phosphoric acid, potassium, calcium and magnesium fertilizers.

2. multi-component (compound) fertilizers – fertilizers containing at least two or more major nutrients, may include accompanying ions and microelements.. According to the nutrient content they are divided into fertilizers – double ones containing 2 major nutrients (NP, NK, PK), triple (full), fertilizers with micronutrients and special group consists of fertilizers containing sulphur.

According to the process of manufacture we distinquish multi-component mixed fertilizers (manufactured by mechanical mixing of one-componenet fertilizers and are either in powder or granulated form) and combined (manufactured by chemical processes of the original raw material)

Livestock manure are fertilizers which are characterized by a large volume, are produced in agricultural production and are divided into:

1. stable
   1. farmyard manure,
   2. manure,
   3. slurry,
   4. dung water,
2. other
   1. compost,
   2. green fertilization,
   3. straw for fertilization,
   4. other organic matter.

solid fertilizers –mineral fertilizers straight or compound, which are divided according to particle size:

1. powder (prevalent particles smaller than 1 mm)
2. granular (particles typically 1-4 mm) and according to the method of manufacture may be crystalline or granulated

Liquid Fertilizers can again be straight or compound, are produced as clear solutions or suspensions and may be subdivided into inorganic fertilizers liquid - pressure-free, high and low pressure.

Similarly, it is possible to conduct distribution of manure into solid (manure) and liquid (liquid manure, dung water, slurry).