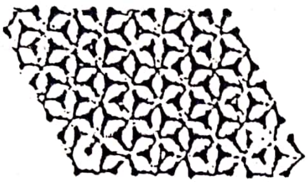
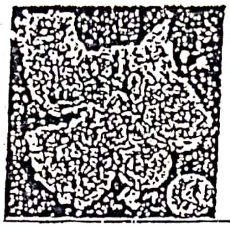
Aluminium oxide





Properties	
Molecular formula	Al_2O_3
Molar mass	101.96 g mol^{-1}
Appearance	white solid very hygroscopic
Odor	Odorless
Density	3.95-4.1 g/cm^3
Melting point	2072 °C [1]
Boiling point	2977 °C [2]
Solubility in water	Insoluble
Solubility	insoluble in diethyl ether practically insoluble in ethanol
Refractive index (n_D)	n_ω=1.768 - 1.772 n_ε=1.760 - 1.763 Birefringence 0.008

Structure	
Crystal structure	Trigonal, hR30, SpaceGroup = R-3c, No. 167
Coordination geometry	octahedral

Aluminium oxide is the family of inorganic compounds with the chemical formula Al_2O_3. It is an amphoteric oxide and is commonly referred to as alumina, corundum as well as many other names, reflecting its widespread occurrence in nature and industry. Its most significant use is in the production of aluminium metal, although it is also used as an abrasive due to its hardness and as a refractory material due to its high melting point.

Natural occurrence Corundum is the most common naturally occurring crystalline form of aluminium oxide. Rubies and sapphires are gem-quality forms of corundum, which owe their characteristic colors to trace impurities. Rubies are given their characteristic deep red color and their laser qualities by traces of chromium. Sapphires come in different colors given by various other impurities, such as iron and titanium.

Properties

- Aluminum oxide in its powdered form. Aluminium oxide is an electrical insulator but has a relatively high thermal conductivity (30 Wm^{-1}K^{-1}) for a ceramic material.

- In its most commonly occurring crystalline form, called corundum or α-aluminium oxide, its hardness makes it suitable for use as an abrasive and as a component in cutting tools.
- Aluminium oxide is responsible for resistance of metallic aluminium to weathering. Metallic aluminium is very reactive with atmospheric oxygen, and a thin passivation layer of alumina (4 nm thickness) forms in about 100 picoseconds on any exposed aluminium surface. This layer protects the metal from further oxidation. The thickness and properties of this oxide layer can be enhanced using a process called anodising.
- A number of alloys, such as aluminium bronzes, exploit this property by including a proportion of aluminium in the alloy to enhance corrosion resistance.

Structure

- The most common form of crystalline alumina is known as corundum.
- The oxygen ions nearly form a hexagonal close-packed structure with aluminium ions filling two-thirds of the octahedral interstices. Each Al3+ center is octahedral. In terms of its crystallography, corundum adopts a trigonal Bravais lattice with a space group of R-3c (number 167 in the International Tables). The primitive cell contains two formula units of aluminium oxide. Alumina also exists in other phases, namely η-, χ-, γ-, δ- and θ-aluminas. Each has a unique crystal structure and properties. The so-called β-alumina proved to be $NaAl_{11}O_{17}$.

Production Aluminium hydroxide minerals are the main component of bauxite, the principal ore of aluminium. A mixture of the minerals comprise bauxite ore, including gibbsite ($Al(OH)_3$), boehmite (γ-$AlO(OH)$), and diaspore (α-$AlO(OH)$), along with impurities of iron oxides and hydroxides, quartz and clay minerals. Bauxites are found in laterites. Bauxite is purified by the Bayer process: $Al_2O_3 + 3\,H_2O + 2\,OH^- \rightarrow 2\,Al(OH)_4^-$

Except for SiO_2, the other components of bauxite do not dissolve in base. Upon filtering the basic mixture, Fe_2O_3 is removed. When the Bayer liquor is cooled, $Al(OH)_3$ precipitates, leaving the silicates in solution. The solid is then calcined (heated strongly) to give aluminium oxide

$$2\,Al(OH)_3 \rightarrow Al_2O_3 + 3\,H_2O$$

The product alumina tends to be multi-phase, i.e., consisting of several phases of alumina rather than solely corundum. The production process can therefore be optimized to produce a tailored product.

Annual world production of alumina is approximately 45 million tonnes, over 90% of which is used in the manufacture of aluminium metal. The major uses of specialty aluminium oxides are in refractories, ceramics, and polishing and abrasive applications. Large tonnages are also used in the manufacture of zeolites, coating titania pigments, and as a fire retardant/smoke suppressant.

Applications The great majority of alumina is consumed for the production of aluminium, usually by the Hall process.

As a filler: - Being fairly chemically inert, relatively non-toxic, and white, alumina is a favored filler for plastics. Alumina is a common ingredient in sunscreen.

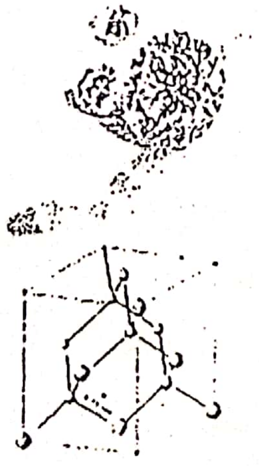
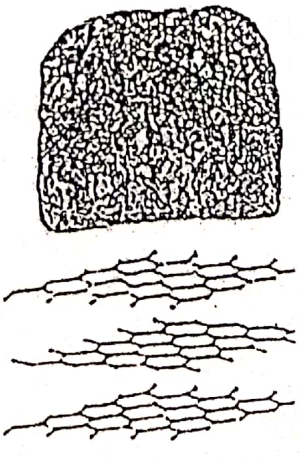
As a catalyst and catalyst support: - Alumina catalyses a variety of reactions that are useful industrially. In its largest scale application, alumina is the catalyst in the Claus process for converting hydrogen sulfide waste gases into elemental sulfur in refineries. It is also useful for dehydration of alcohols to alkenes. Alumina serves as a catalyst support for many industrial catalysts, such as those used in hydrodesulfurization and some Ziegler-Natta polymerizations. Zeolites are produced from alumina.

Gas purification and related absorption applications: -Alumina is widely used to remove water from gas streams. Other major applications are below.

As an abrasive: - Aluminium oxide is used for its hardness and strength. It is widely used as a coarse or fine abrasive, including as a much less expensive substitute for industrial diamond. Many types of sandpaper use aluminium oxide crystals. In addition, its low heat retention and low specific heat make it widely used in grinding operations, particularly cutoff tools. As the powdery abrasive mineral aloxite, it is a major component, along with silica, of the cue tip "chalk" used in billiards. Aluminium oxide powder is used in some CD/DVD polishing and scratch-repair kits. Its polishing qualities are also behind its use in toothpaste. Alumina can be grown as a coating on aluminium by anodising or by plasma electrolytic oxidation (see the "Properties" section, above). Both its strength and abrasive characteristics are due to aluminium oxide's great hardness (position 9 on the Mohs scale of mineral hardness). Most pre-finished wood flooring now uses aluminium oxide as a hard protective coating.

Niche applications and research themes: -In lighting, transparent alumina is used in some sodium vapor lamps. Aluminium oxide is also used in preparation of coating suspensions in compact fluorescent lamps. In chemistry laboratories, alumina is a medium for chromatography, available in basic (pH 9.5), acidic (pH 4.5 when in water) and neutral formulations. Health and medical applications include it as a material in hip replacements. As well, it is used as a dosimeter for radiation protection and therapy applications for its optically stimulated luminescence properties. Aluminium oxide is widely used in the fabrication of superconducting devices, particularly single electron transistors and superconducting quantum interference devices (SQUID), where it is used to form highly resistive quantum tunneling barriers.

Carbon

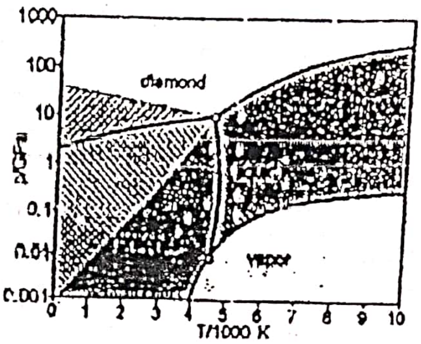
Appearance:	
Clear (diamond).	black (graphite)
	

General properties: -	
Name, symbol, number	carbon, C, 6
Element category	nonmetal
Group, period, block	14, 2, p
Standard atomic weight	12.0107(8)□g·mol^{-1}
Electron configuration	$1s^2\ 2s^2\ 2p^2$ or [He] $2s^2\ 2p^2$
Electrons per shell	2,4 (Image)
Physical properties: -	
Phase	Solid
Sublimation point	3915 K, 3642 ° C, 6588 ° F
Triple point	4600 K (4327°C), 10800[2][3] kPa
Heat of fusion	117 (graphite) kJ·mol^{-1}
Specific heat capacity	(25 °C) 8.517(graphite), 6.155(diamond) J·mol^{-1}·K^{-1}

- Carbon is the chemical element with symbol C and atomic number 6.
- As a member of group 14 on the periodic table, it is nonmetallic and tetravalent—making four electrons available to form covalent chemical bonds.
- There are three naturally occurring isotopes, with ^{12}C and ^{13}C being stable, while ^{14}C is radioactive, decaying with a half-life of about 5730 years.
- Carbon is one of the few elements known since antiquity. The name "carbon" comes from Latin language *carbo*, coal.
- There are several allotropes of carbon of which the best known are graphite, diamond, and amorphous carbon.
- The physical properties of carbon vary widely with the allotropic form. For example, diamond is highly transparent, while graphite is opaque and black. Diamond is among the hardest materials known, while graphite is soft enough to form a streak on paper (hence its name, from the Greek word "to write"). Diamond has a very low electrical conductivity, while graphite is a very good conductor. Under normal conditions, diamond has the highest thermal conductivity of all known materials. All the allotropic forms are solids under normal conditions but graphite is the most thermodynamically stable.
- All forms of carbon are highly stable, requiring high temperature to react even with oxygen. The most common oxidation state of carbon in inorganic compounds is +4, while +2 is found in carbon monoxide and other transition metal carbonyl complexes. The largest sources of inorganic carbon are limestones, dolomites and carbon dioxide, but significant quantities occur in organic deposits of coal, peat, oil and methane clathrates. Carbon forms more compounds than any other element, with almost ten million pure organic compounds described to date, which in turn are a tiny fraction of such compounds that are theoretically possible under standard conditions.
- Carbon is the 15th most abundant element in the Earth's crust, and the fourth most abundant element in the universe by mass after hydrogen, helium, and oxygen. It is present in all known lifeforms, and in the human body carbon is the second most

abundant element by mass (about 18.5%) after oxygen. This abundance, together with the unique diversity of organic compounds and their unusual polymer-forming ability at the temperatures commonly encountered on Earth, make this element the chemical basis of all known life.

Characteristics



Theoretically predicted phase diagram of carbon

The different forms or *allotropes* of carbon include the hardest naturally occurring substance, diamond, and also one of the softest known substances, graphite. Moreover, it has an affinity for bonding with other small atoms, including other carbon atoms, and is capable of forming multiple stable covalent bonds with such atoms. As a result, carbon is known to form almost ten million different compounds; the large majority of all chemical compounds. Carbon also has the highest melting and sublimation point of all elements. At atmospheric pressure it has no melting point as its triple point is at 10.8 ± 0.2 MPa and 4600 ± 300 K, so it sublimates at about 3900 K.

Carbon sublimes in a carbon arc which has a temperature of about 5800 K. Thus, irrespective of its allotropic form, carbon remains solid at higher temperatures than the highest melting point metals such as tungsten or rhenium. Although thermodynamically prone to oxidation, carbon resists oxidation more effectively than elements such as iron and copper that are weaker reducing agents at room temperature.

Carbon compounds form the basis of all known life on Earth, and the carbon-nitrogen cycle provides some of the energy produced by the Sun and other stars. Although it forms an extraordinary variety of compounds, most forms of carbon are comparatively unreactive under normal conditions. At standard temperature and pressure, it resists all but the strongest oxidizers. It does not react with sulfuric acid, hydrochloric acid, chlorine or any alkalis. At elevated temperatures carbon reacts with oxygen to form carbon oxides, and will reduce such metal oxides as iron oxide to the metal. This exothermic reaction is used in the iron and steel industry to control the carbon content of steel:

$$Fe_3O_4 + 4\ C_{(s)} \rightarrow 3\ Fe_{(s)} + 4\ CO_{(g)}$$

with sulfur to form carbon disulfide and with steam in the coal-gas reaction:

$$C_{(s)} + H_2O_{(g)} \rightarrow CO_{(g)} + H_{2(g)}.$$

Carbon combines with some metals at high temperatures to form metallic carbides, such as the iron carbide cementite in steel, and tungsten carbide, widely used as an abrasive and for making hard tips for cutting tools.

As of 2009, graphene appears to be the strongest material ever tested. However, the process of separating it from graphite will require some technological development before it is economical enough to be used in industrial processes.

The system of carbon allotropes spans a range of extremes:

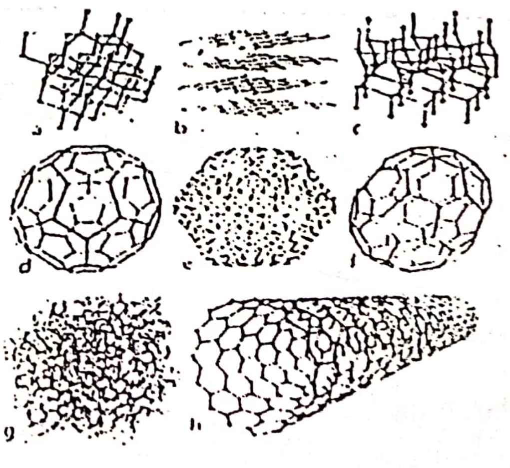
Synthetic nanocrystalline diamond is the hardest material known.	Graphite is one of the softest materials known.
Diamond is the ultimate abrasive.	Graphite is a very good lubricant.
Diamond is an excellent electrical insulator.	Graphite is a conductor of electricity.
Diamond is the best known naturally occurring thermal conductor	Some forms of graphite are used for thermal insulation (i.e. firebreaks and heat shields)
Diamond is highly transparent.	Graphite is opaque.
Diamond crystallizes in the cubic system.	Graphite crystallizes in the hexagonal system.
Amorphous carbon is completely isotropic.	Carbon nanotubes are among the most anisotropic materials ever produced.

Allotropes

Main article: Allotropes of carbon

Atomic carbon is a very short-lived species and, therefore, carbon is stabilized in various multi-atomic structures with different molecular configurations called allotropes. The three relatively well-known allotropes of carbon are amorphous carbon, graphite, and diamond. Once considered exotic, fullerenes are nowadays commonly synthesized and used in research; they include buckyballs, carbon nanotubes, carbon nanobuds and nanofibers. Several other exotic allotropes have also been discovered, such as lonsdaleite, glassy carbon, carbon nanofoam and linear acetylenic carbon.

- The amorphous form is an assortment of carbon atoms in a non-crystalline, irregular, glassy state, which is essentially graphite but not held in a crystalline macrostructure. It is present as a powder, and is the main constituent of substances such as charcoal, lampblack (soot) and activated carbon.
- At normal pressures carbon takes the form of graphite, in which each atom is bonded trigonally to three others in a plane composed of fused hexagonal rings, just like those in aromatic hydrocarbons. The resulting network is 2-dimensional, and the resulting flat sheets are stacked and loosely bonded through weak van der Waals forces. This gives graphite its softness and its cleaving properties (the sheets slip easily past one another). Because of the delocalization of one of the outer electrons of each atom to form a π-cloud, graphite conducts electricity, but only in the plane of each covalently bonded sheet. This results in a lower bulk electrical conductivity for carbon than for most metals. The delocalization also accounts for the energetic stability of graphite over diamond at room temperature.



Some allotropes of carbon: a) diamond; b) graphite; c) lonsdaleite; d–f) fullerenes (C_{60}, C_{540}, C_{70}); g) amorphous carbon; h) carbon nanotube.

- At very high pressures carbon forms the more compact allotrope diamond, having nearly twice the density of graphite. Here, each atom is bonded tetrahedrally to four others, thus making a 3-dimensional network of puckered six-membered rings of atoms. Diamond has the same cubic structure as silicon and germanium and because of the strength of the carbon-carbon bonds, it is the hardest naturally occurring substance in terms of resistance to scratching. Contrary to the popular belief that *"diamonds are forever"*, they are in fact thermodynamically unstable under normal conditions and transform into graphite. But due to a high activation energy barrier, the transition into graphite is so extremely slow at room temperature as to be unnoticeable.
- Under some conditions, carbon crystallizes as lonsdaleite. This form has a hexagonal crystal lattice where all atoms are covalently bonded. Therefore, all properties of lonsdaleite are close to those of diamond.
- Fullerenes have a graphite-like structure, but instead of purely hexagonal packing, they also contain pentagons (or even heptagons) of carbon atoms, which bend the sheet into spheres, ellipses or cylinders.

Occurrence

Graphite ore. Raw diamond crystal.

Isotopes:

Isotopes of carbon are atomic nuclei that contain six protons plus a number of neutrons (varying from 2 to 16). Carbon has two stable, naturally occurring isotopes. The isotope carbon-12 (^{12}C) forms 98.93% of the carbon on Earth, while carbon-13 (^{13}C) forms the remaining 1.07%. The concentration of ^{12}C is further increased in biological materials because biochemical reactions discriminate against ^{13}C. In 1961 the International Union of Pure and Applied Chemistry (IUPAC) adopted the isotope carbon-12 as the basis for atomic weights. Identification of carbon in NMR experiments is done with the isotope ^{13}C.

Carbon-14 (^{14}C) is a naturally occurring radioisotope which occurs in trace amounts on Earth of up to 1 part per trillion (0.0000000001%), mostly confined to the atmosphere and superficial deposits, particularly of peat and other organic materials. This isotope decays by 0.158 MeV β^- emission. Because of its relatively short half-life of 5730 years, ^{14}C is virtually absent in ancient rocks, but is created in the upper atmosphere (lower stratosphere and upper troposphere) by interaction of nitrogen with cosmic rays. The abundance of ^{14}C in the atmosphere and in living organisms is almost constant, but decreases predictably in their bodies after death. This principle is used in radiocarbon dating, invented in 1949, which has been used extensively to determine the age of carbonaceous materials with ages up to about 40,000 years.

There are 15 known isotopes of carbon and the shortest-lived of these is ^{8}C which decays through proton emission and alpha decay and has a half-life of 1.98739×10^{-21} s.[41] The exotic

^{19}C exhibits a nuclear halo, which means its radius is appreciably larger than would be expected if the nucleus were a sphere of constant density.

Inorganic compounds: - Commonly carbon-containing compounds which are associated with minerals or which do not contain hydrogen or fluorine, are treated separately from classical organic compounds; however the definition is not rigid. Among these are the simple oxides of carbon. The most prominent oxide is carbon dioxide (CO_2). This was once the principal constituent of the paleoatmosphere, but is a minor component of the Earth's atmosphere today. Dissolved in water, it forms carbonic acid (H_2CO_3), but as most compounds with multiple single-bonded oxygens on a single carbon it is unstable. Through this intermediate, though, resonance-stabilized carbonate ions are produced. Some important minerals are carbonates, notably calcite. Carbon disulfide (CS_2) is similar.

The other common oxide is carbon monoxide (CO). It is formed by incomplete combustion, and is a colorless, odorless gas. The molecules each contain a triple bond and are fairly polar, resulting in a tendency to bind permanently to hemoglobin molecules, displacing oxygen, which has a lower binding affinity. Cyanide (CN^-), has a similar structure, but behaves much like a halide ion (pseudohalogen). For example it can form the nitride cyanogen molecule ($(CN)_2$), similar to diatomic halides. Other uncommon oxides are carbon suboxide (C_3O_2), the unstable dicarbon monoxide (C_2O), carbon trioxide (CO_3), cyclopentanepentone (C_5O_5), cyclohexanehexone (C_6O_6), and mellitic anhydride ($C_{12}O_9$).

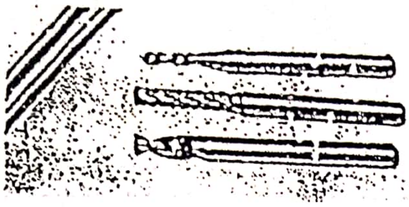
Production

Graphite: - Commercially viable natural deposits of graphite occur in many parts of the world, but the most important sources economically are in China, India, Brazil, and North Korea.[65] Graphite deposits are of metamorphic origin, found in association with quartz, mica and feldspars in schists, gneisses and metamorphosed sandstones and limestone as lenses or veins, sometimes of a meter or more in thickness. Deposits of graphite in Borrowdale, Cumberland, England were at first of sufficient size and purity that, until the 1800s, pencils were made simply by sawing blocks of natural graphite into strips before encasing the strips in wood. Today, smaller deposits of graphite are obtained by crushing the parent rock and floating the lighter graphite out on water.

Diamond: - Only a very small fraction of the diamond ore consists of actual diamonds. The ore is crushed, during which care has to be taken in order to prevent larger diamonds from being destroyed in this process and subsequently the particles are sorted by density. Today, diamonds are located in the diamond-rich density fraction with the help of X-ray fluorescence, after which the final sorting steps are done by hand. Before the use of X-rays became commonplace, the separation was done with grease belts; diamonds have a stronger tendency to stick to grease than the other minerals in the ore.

Applications

1. Pencil leads for mechanical pencils are made of graphite (often mixed with a clay or synthetic binder).
2. Sticks of vine and compressed charcoal.
3. A cloth of woven carbon filaments
4. Silicon carbide single crystal
5. The C_{60} fullerene in crystalline form



6. Tungsten carbide milling bits

Carbon is essential to all known living systems, and without it life as we know it could not exist alternative biochemistry. The major economic use of carbon other than food and wood is in the form of hydrocarbons, most notably the fossil fuel methane gas and crude oil (petroleum). Crude oil is used by the petrochemical industry to produce, amongst others, gasoline and kerosene, through a distillation process, in refineries. Cellulose is a natural, carbon-containing polymer produced by plants in the form of cotton, linen, and hemp. Cellulose is mainly used for maintaining structure in plants. Commercially valuable carbon polymers of animal origin include wool, cashmere and silk. Plastics are made from synthetic carbon polymers, often with oxygen and nitrogen atoms included at regular intervals in the main polymer chain. The raw materials for many of these synthetic substances come from crude oil.

The uses of carbon and its compounds are extremely varied. It can form alloys with iron, of which the most common is carbon steel. Graphite is combined with clays to form the 'lead' used in pencils used for writing and drawing. It is also used as a lubricant and a pigment, as a molding material in glass manufacture, in electrodes for dry batteries and in electroplating and electroforming, in brushes for electric motors and as a neutron moderator in nuclear reactors.

Charcoal is used as a drawing material in artwork, for grilling, and in many other uses including iron smelting. Wood, coal and oil are used as fuel for production of energy and space heating. Gem quality diamond is used in jewelry, and Industrial diamonds are used in drilling, cutting and polishing tools for machining metals and stone. Plastics are made from fossil hydrocarbons, and carbon fiber, made by pyrolysis of synthetic polyester fibers is used to reinforce plastics to form advanced, lightweight composite materials.

Carbon black is used as the black pigment in printing ink, artist's oil paint and water colours, carbon paper, automotive finishes, India ink and laser printer toner. Carbon black is also used as a filler in rubber products such as tyres and in plastic compounds. Activated charcoal is used as an absorbent and adsorbent in filter material in applications as diverse as gas masks, water purification and kitchen extractor hoods and in medicine to absorb toxins, poisons, or gases from the digestive system. Carbon is used in chemical reduction at high temperatures. Coke is used to reduce iron ore into iron. Case hardening of steel is achieved by heating finished steel components in carbon powder. Carbides of silicon, tungsten, boron and titanium, are among the hardest known materials, and are used as abrasives in cutting and grinding tools. Carbon compounds make up most of the materials used in clothing, such as natural and synthetic textiles and leather, and almost all of the interior surfaces in the built environment other than glass, stone and metal.

- :Clay: -

Clay is a naturally occurring material composed primarily of fine-grained minerals. Clay deposits are mostly composed of clay minerals, a subtype of phyllosilicate minerals, which impart plasticity and harden when fired or dried; they also may contain variable amounts of water trapped in the mineral structure by polar attraction. Organic materials which do not impart plasticity may also be a part of clay deposits.

Formation Clay minerals are typically formed over long periods of time by the gradual chemical weathering of rocks, usually silicate-bearing, by low concentrations of carbonic acid and other diluted solvents. These solvents, usually acidic, migrate through the weathering rock after leaching through upper weathered layers. In addition to the weathering process, some clay minerals are formed by hydrothermal activity. Clay deposits may be formed in place as residual deposits in soil, but thick deposits usually are formed as the result of a secondary sedimentary deposition process after they have been eroded and transported from their original location of formation. Clay deposits are typically associated with very low energy depositional environments such as large lakes and marine deposits. Primary clays, also known as kaolins, are located at the site of formation. Secondary clay deposits have been moved by erosion and water from their primary location.

Definition Clays are distinguished from other fine-grained soils by differences in size and mineralogy. Silts, which are fine-grained soils that do not include clay minerals, tend to have larger particle sizes than clays, but there is some overlap in both particle size and other physical properties, and there are many naturally occurring deposits which include both silts and clays. The distinction between silt and clay varies by discipline. Geologists and soil scientists usually consider the separation to occur at a particle size of 2 µm (clays being finer than silts), sedimentologists often use 4-5 µm, and colloid chemists use 1 µm. Geotechnical engineers distinguish between silts and clays based on the plasticity properties of the soil, as measured by the soils' Atterberg Limits. ISO 14688 grades clay particles as being smaller than 2 µm and silts larger.

Grouping There are three or four main groups of clays: kaolinite, montmorillonite-smectite, illite and chlorite. Chlorites are not always considered a clay, sometimes being classified as a separate group within the phyllosilicates. There are approximately 30 different types of "pure" clays in these categories, but most "natural" clays are mixtures of these different types, along with other weathered minerals. Varve (or *varved clay*) is clay with visible annual layers, formed by seasonal differences in erosion and organic content. This type of deposit is common in former glacial lakes. When glacial lakes are formed there is very little movement of the water that makes the lake, and these eroded soils settle on the lake bed. This allows such an even distribution on the different layers of clay. Quick clay is a unique type of marine clay indigenous to the glaciated terrains of Norway, Canada, Northern Ireland and Sweden. It is a highly sensitive clay, prone to liquefaction, which has been involved in several deadly landslides.

Historical and modern uses: - Dry clay is normally much more stable than sand with regard to excavations.

Clays exhibit plasticity when mixed with water in certain proportions. When dry, clay becomes firm and when fired in a kiln, permanent physical and chemical reactions occur. These reactions, among other changes, cause the clay to be converted into a ceramic material. Because of these properties, clay is used for making pottery items, both utilitarian and decorative. Different types of clay, when used with different minerals and firing conditions, are used to produce earthenware, stoneware and porcelain. Prehistoric humans discovered the useful properties of clay, and one of the earliest artifacts ever uncovered is a drinking vessel made of sun-dried clay. Depending on the content of the soil, clay can appear in various colors, from a dull gray to a deep orange-red.

Clay tablets were used as the first known writing medium, inscribed with cuneiform script through the use of a blunt reed called a stylus.

Clays sintered in fire were the first form of ceramic. Bricks, cooking pots, art objects, dishware and even musical instruments such as the ocarina can all be shaped from clay before being fired.

Clay is also used in many industrial processes, such as paper making, cement production and chemical filtering. Clay is also often used in the manufacture of pipes for smoking tobacco. Until the late 20th century bentonite clay was widely used as a mold binder in the manufacture of sand castings.

Clay, being relatively impermeable to water, is also used where natural seals are needed, such as in the cores of dams, or as a barrier in landfills against toxic seepage ('lining' the landfill, preferably in combination with geotextiles).

Recent studies have investigated clay's absorption capacities in various applications, such as the removal of heavy metals from waste water and air purification.

Medical and agricultural uses

A traditional use of clay as medicine goes back to prehistoric times. An example is Armenian bole, which is used to soothe an upset stomach, similar to the way parrots (and later, humans) in South America originally used it.

A more recent, and more limited, use is as a specially formulated spray applied to fruits, vegetables and other vegetation to repel or deter codling moth damage, and at least for apples, to prevent sun scald.

A recent article in *The Journal of Antimicrobial Chemotherapy* found that certain iron-rich clay was effective in killing bacteria.

- :Mica: -

The mica group of sheet silicate (phyllosilicate) minerals includes several closely related materials having highly perfect basal cleavage. All are monoclinic with a tendency towards pseudo-hexagonal crystals and are similar in chemical composition. The highly perfect cleavage, which is the most prominent characteristic of mica, is explained by the hexagonal sheet-like arrangement of its atoms. The word "mica" is thought to be derived from the Latin word *micare*, meaning "to glitter", in reference to the brilliant appearance of this mineral (especially when in small scales).

Mica classification: -

Chemically, micas can be given the general formula

$X_2Y_{4-6}Z_8O_{20}(OH,F)_4$

in which X is K, Na, or Ca or less commonly Ba, Rb, or Cs;

Y is Al, Mg, or Fe or less commonly Mn, Cr, Ti, Li, etc.;

Z is chiefly Si or Al but also may include Fe^{3+} or Ti.

Structurally, micas can be classed as *dioctahedral* ($Y = 4$) and *trioctahedral* ($Y = 6$). If the X ion is K or Na the mica is a *common* mica whereas if the X ion is Ca the mica is classed as a *brittle mica*.

Trioctahedral micas

Common micas: Phlogopite, Biotite, Zinnwaldite, Lepidolite, Muscovite

Brittle micas: Clintonite

Interlayer deficient micas

Very fine-grained micas with typically more variation in ion and water content are informally termed *clay micas*. They include

- Hydro-muscovite with H_3O^+ along with K in the *X* site;
- Illite with a K deficiency in the *X* site and correspondingly more Si in the *Z* site;
- Phengite with Mg or Fe^{2+} substituting for Al in the *Y* site and a corresponding increase in Si in the *Z* site.

Occurrence: - Mica is widely distributed and occurs in igneous, metamorphic and sedimentary regimes. Large crystals of mica used for various applications are typically mined from granitic pegmatites.

Until the 19th century, large crystals of mica were quite rare and expensive as a result of the limited supply in Europe. However, their price dramatically dropped when large reserves were found and mined in Africa and South America during the early 1800s. The largest documented single crystal of mica (phlogopite) was found in Lacey mine, Ontario, Canada; it measured 10×4.3×4.3 m and weighed about 330 metric tons. Similar-sized crystals were also found in Karelia, Russia.

The British Geological Survey reports that as of 2005, Kodarma district in Jharkhand state in India had the largest deposits of mica in the world. China was the top producer of mica with almost a third of the global share, closely followed by the USA, South Korea and Canada. Large deposits of sheet Mica were mined in New England from the 19th Century to the 1960s. Large mines existed in Connecticut, New Hampshire, and Maine.

Scrap and flake mica is produced all over the world. Flake mica comes from several sources: the metamorphic rock called schist as a by-product of processing feldspar and kaolin resources, from placer deposits, and from pegmatites. Sheet mica is considerably less abundant than flake and scrap mica. Sheet mica is occasionally recovered from mining scrap and flake mica. The most important sources of sheet mica are pegmatite deposits.

Properties and uses.

Electronics

A number of mica insulator slices for TO-3 and TO-264 packages.

Mica has a high dielectric strength and excellent chemical stability, making it a favoured material for manufacturing capacitors for radio frequency applications. It has also been used as an insulator in high voltage electrical equipment, and between the bars of commutators in direct current motors and generators. Mica is used because it can be split into very thin slices, and this keeps its thermal resistance low while retaining sufficient dielectric strength to prevent current from flowing across it at moderate voltages. The insulation is usually necessary when the heat sink is earthed (grounded) while the electronic component's metal surfaces will be connected to a power supply or signal line. If they were in direct contact this could form a short circuit. Heat sink insulation can also be necessary to prevent the heat sink from acting like an antenna if the component is connected to a rapidly varying signal.

Isinglass.

Thin transparent sheets of mica called "isinglass" were used for peepholes in boilers and lanterns because they were less likely to shatter compared to glass when exposed to extreme temperature gradients. Such peepholes were also used in "isinglass curtains" in horse-drawn carriages and early 20th century cars. A book about a journey in a Model T Ford car describes isinglass curtains as follows: "Oiled canvas side curtains were put-up over the windows for wind, rain, and cold (there were no heaters) and were held in place with rods that fit into the doors and twisting button snaps around the perimeter... 'Isinglass' peepholes in the curtains allowed limited visibility. Isinglass was made of thin sheets of cracked mica."

Other

Resin-bonded mica or micanite or built up micanite from splittings or agglomerated micanite made from pulped mica powder are called micanites. All these products have additives, like resins, and the resultant products, while having inferior insulation properties to natural "mica insulators" are called micanites or micafoliums.

Mica is also birefringent and is commonly used to make quarter and half wave plates.

Illites or *clay micas* have a low cation exchange capacity for 2:1 clays. K+ ions between layers of mica prevent swelling by blocking water molecules.

Because mica can be pressed into a thin film, it is often used on Geiger-Müller tubes to detect low penetrating alpha particles.

Some brands of toothpaste include powdered white mica. This acts as a mild abrasive to aid polishing of the tooth surface, and also adds a cosmetically-pleasing glittery shimmer to the paste. The shimmer from mica is also used in makeup, as it gives a translucent "glow" to the skin or helps to mask imperfections.

Mica is used in the production of pearlescent pigments. Many metallic looking pigments are composed of a substrate of mica coated with another mineral, usually titanium dioxide (TiO_2). The resultant pigment produces a reflective color depending on the thickness of the coating. These products are used to produce automobile paint, shimmery plastic containers, high quality inks used in advertising and security applications.

Mica sheets are used to provide structure for heating wire (such as in Kanthal or Nichrome) in heating elements and can withstand up to 900 °C (1,650 °F). Because mica is resistant to heat, it is used instead of glass in windows for stoves and kerosene heaters..

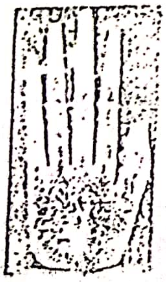
Another use of mica is in the production of ultraflat thin film surfaces (e.g. gold surfaces) using mica as substrate. Although the deposited film surface is still rough due to deposition kinetics, the back side of the film at mica-film interface provides ultraflatness, when the film is removed from the substrate.

It is also used as an insulator in concrete block, home attics, and can be poured into walls (usually in retrofitting uninsulated open top walls).

May also be used as a soil conditioner, especially in potting soil mixes and in gardening plots.

Muscovite mica is the most common substrate for sample preparation for the atomic force microscope. Freshly-cleaved mica surfaces have been used as clean imaging substrates in atomic force microscopy, enabling for example the imaging of bismuth films, plasma glycoproteins, membrane bilayers, and DNA molecules.

Greases used for axles are composed of a compound of fatty oils to which mica, tar or graphite is added to increase the durability of the grease and give it a better surface.



Hand carved from mica from the Hopewell tradition

Mica in ancient times

Human use of mica dates back to pre-historic times. Mica was known to ancient Egyptian, Greek and Roman civilizations, Chinese civilization, as well as the Aztec civilization of the New World.

The earliest use of mica has been found in cave paintings created during the Upper Paleolithic period (40,000 BC to 10,000 BC). The first hues were red (iron oxide, hematite, or red ochre) and black (manganese dioxide, pyrolusite), though black from juniper or pine carbons has also been discovered. White from kaolin or mica was used occasionally.

A few kilometers northeast of Mexico City stands the ancient site of Teotihuacan. The most striking visual and striking structure of Teotihuacan is the towering Pyramid of the Sun. The pyramid contained considerable amounts of mica in layers up to 30 cm (12 in) thick.

Throughout the ages, fine powders of mica have been used for various purposes, including decorative purposes. The colored Gulal and Abeer used by Hindus of north India during holi festival contain fine small crystals of mica. The majestic Padmanabhapuram palace, 65 km (40 mi) from Trivandrum in India, has colored mica windows.

- :Silicate: -

A silicate is a compound containing a silicon bearing anion. The great majority of silicates are oxides, but hexafluorosilicate ($[SiF_6]^{2-}$) and other anions are also included. This article focuses mainly on the Si-O anions. Silicates comprise the majority of the earth's crust, as well as most planets and moons. Sand, Portland cement, and thousands of minerals are examples of silicates. Silicate compounds, including the minerals, consist of silicate anions whose charge is balanced by various cations. Myriad silicate anions can exist, and each can form compounds with many different cations. Hence this class of compounds is very large. Both minerals and synthetic materials fit in this class.

Structural principles In the vast majority of silicates, including silicate minerals, the Si occupies a tetrahedral environment, being surrounded by 4 oxygen centres. In these structures, the chemical bonds to silicon conform to the octet rule. These tetrahedra sometimes occur as isolated SiO_4^{4-} centres, but most commonly, the tetrahedra are joined together in various ways, such as pairs ($Si_2O_7^{6-}$) and rings ($Si_6O_{18}^{12-}$). Commonly the silicate anions are chains, double chains, sheets, and three-dimensional frameworks. All such species have negligible solubility in water at normal conditions.

Occurrence in solution: - Silicates are well characterized as solids, but are less commonly observed in solution. The anion SiO_4^{4-} is the conjugate base of silicic acid, $Si(OH)_4$, and both are elusive as are all of the intermediate species. Instead, solutions of silicates usually observed as mixtures of condensed and partially protonated silicate clusters. The nature of soluble silicates is relevant to understanding biomineralization and the synthesis of aluminosilicates, such as the industrially important catalysts called zeolites.

Silicates with non-tetrahedral silicon: - Although the tetrahedron is the common coordination geometry for silicon compounds, silicon is well known to also adopt higher coordination numbers. A well known example of such a high coordination number is hexafluorosilicate (SiF_6^{2-}). Octahedral coordination by 6 oxygen centres is observed. At very high pressure, even SiO_2 adopts this geometry in the mineral stishovite, a dense polymorph of silica found in the lower mantle of the Earth. This structure is also formed by shock during meteoritic impacts. Octahedral Si in the form of hexahydroxysilicate ($[Si(OH)_6]^{2-}$) is observed in thaumasite[citation needed] a mineral occurring rarely in nature but sometimes observed amongst other calcium silicate hydrate artificially formed in cement and concrete submitted to a severe sulfate attack.

Silicate rock and minerals : -Diatomaceous earth, as viewed under a microscope, is a soft, siliceous, sedimentary rock made up of the cell walls/shells of single cell diatoms. Diatom cell walls are made up of biogenic silica; silica synthesised in the diatom cell by the polymerisation of silicic acid. This image of diatomaceous earth particles in water is at a scale of 6.236 pixels/μm, the entire image covers a region of approximately 1.13 by 0.69 mm.

In geology and astronomy, the term silicate is used to denote types of rock that consist predominantly of silicate minerals. On Earth, a wide variety of silicate minerals occur in an even wider range of combinations as a result of the processes that form and re-work the crust. These processes include partial melting, crystallization, fractionation, metamorphism, weathering and diagenesis. Living things also contribute to the silicate cycle near the Earth's surface. A type of plankton known as diatoms construct their exoskeletons, known as tests, from silica. The tests of dead diatoms are a major constituent of deep ocean sediment.

Silica, or silicon dioxide, SiO_2, is sometimes considered a silicate, although it is the special case with no negative charge and no need for counter-ions. Silica is found in nature as the mineral quartz, and its polymorphs.

Mineralogy: -Mineralogically, silicate minerals are divided according to structure of their silicate anion into the following groups:

- Nesosilicates (lone tetrahedron) - $[SiO_4]^{4-}$, eg olivine.
- Sorosilicates (double tetrahedra) - $[Si_2O_7]^{6-}$, eg epidote, melilite group.
- Cyclosilicates (rings).- $[Si_nO_{3n}]^{2n-}$, eg tourmaline group.
- Inosilicates (single chain) - $[Si_nO_{3n}]^{2n-}$, eg pyroxene group.
- Inosilicates(double chain) - $[Si_{4n}O_{11n}]^{6n-}$, eg amphibole group.
- Phyllosilicates (sheets) - $[Si_{2n}O_{5n}]^{2n-}$, eg micas and clays.
- Tectosilicates (3D framework) - $[Al_xSi_yO_{2(x+y)}]^{x-}$, eg quartz, feldspars, zeolites.

  Note that tectosilicates can only have additional cations if some of the silicon is replaced by a lower-charge cation such as aluminium. Al for Si substitution is common.

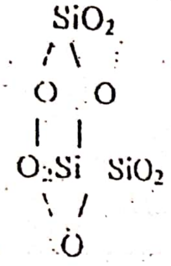
Silicates

The silicates are the largest, the most interesting and the most complicated class of minerals than any other minerals. Approximately 30% of all minerals are silicates and some geologists estimate that 90% of the Earth's crust is made up of silicates, SiO_4^{4-} based material. Thus, oxygen and silicon are the two most abundant elements in the earth's crust.

Silicates is based on the basic chemical unit SiO_4^{4-}, tetrahedron shaped anionic group. The central silicon ion has a charge of positive four while each oxygen has a charge of negative two (-2) and thus each silicon-oxygen bond is equal to one half (½) the total bond energy of oxygen. This condition leaves the oxygens with the option of bonding to another silicon ion and therefore linking one SiO_4^{4-} tetrahedron to another.

In the extreme case, the tetrahedra are arranged in a regular, orderly fashion forming a three-dimensional network. Quartz is such a structure, and its formula is SiO_2. If silica in the molten state is cooled very slowly it crystallizes at the freezing point. But if molten silica is cooled more rapidly, the resulting solid is a disorderly arrangement which is called glass, often also called *quartz*.

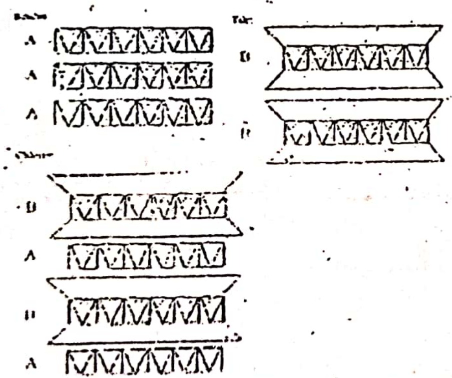
Benitoite $BaTi(SiO_3)_3$ contain three silica rings, but these are relaxed 6-atom rings



The precious stone beryl $Be_3Al_2(SiO_3)_6$ contain six-silica rings.

Single chain silica are called pyroxenes.. Some synthetic metasilicates $Na_2(SiO_3)$ have been shown to contain the simple chain silicates $(SiO_3)_n$, in which the Si-O bonds of the type Si-O-Si are 168 nm, with the Si-O-Si angles of 137°. The Si=O bonds are shorter, 1.57 nm. The natural pyroxenes include enstatite, $MgSiO_3$, diopside, $CaMg(SiO_3)_2$, and jadeite, $NaAl(SiO_3)_2$. The true asbestoses such as crocidolite or blue asbestos consist of double chain silicates. Asbestoses have been identified as carcinogens, and its application has since been limited due to a ban to limit its exposure to the public. Federal Health Canada has given some strict guidelines for the applications of crocidolite. Most comercial asbestoses are chrysotile, which contain layers of silicate sheet as we shall below.

The diagram below shows the arrangement of sheets in brucite, $Mg(OH)_2$, in which the sheets consist of corner sharing octahedrons of $Mg(OH)_6$. In chlorite, there are two types of sheets. Half of the sheets are the same as those of brucite, but half of the brucite-sheets are sandwiched between sheets of silicates. The talc consists of only the sandwiched sheets.



The diagram came from a polysome series which discusses sheet silicates. Serpentine, $Mg_3(OH)_4Si_2O_5$, has curved sheets. The comercial asbestos chrysotile is a sheet silicate, but the sheets are rolled up like a tube. These tubes appear as fibers, and they are usually known as asbestos.

What are asbestoses?

Asbestos is the name applied to six naturally occurring minerals that are mined from the earth. The different types of asbestos are: Amosite, Chrysotile, Tremolite, Actinolite, Anthephyllite, Crocidolite.

Of these six, three are used more commonly. Chrysotile (white) is the most common, but it is not unusual to encounter Amosite (brown / off-white), or Crocidolite (blue) as well. Asbestos are noncombustable fiberous material, and they have been used for termal insulation material, brake linings, construction material, and filters. When mixed with cement, it reinforce the mechanical strength of concret. It decomposes due to loss of water, and forms forsterite and silica at high temperature.

Silicon dioxide

Preferred IUPAC name: - Silicon dioxide
Systematic name: -Silanedione
Other names: -Quartz, Silica

Properties: -

Molecular formula	SiO_2
Molar mass	60.0843 g/mol
Appearance	white powder
Density	2.634 g/cm^3
Melting point	1650(±75) °C
Boiling point	2230 °C
Solubility in water	0.012 g/100 mL

The chemical compound silicon dioxide, also known as silica (from the Latin *silex*), is an oxide of silicon with a chemical formula of SiO_2 and has been known for its hardness since antiquity. Silica is most commonly found in nature as sand or quartz, as well as in the cell walls of diatoms. Silica is the most abundant mineral in the Earth's crust.

Silica is manufactured in several forms including fused quartz, crystal, fumed silica (or pyrogenic silica, trademarked Aerosil or Cab-O-Sil), colloidal silica, silica gel, and aerogel. In addition, silica nanosprings are produced by the vapor-liquid-solid method at temperatures as low as room temperature.

Silica is used primarily in the production of window glass, drinking glasses, and beverage bottles. The majority of optical fibers for telecommunications are also made from silica. It is a primary raw material for many whiteware ceramics such as earthenware, stoneware, porcelain, as well as industrial Portland cement.

Silica is common additive in the production of foods, where it is used primarily as a flow agent in powdered foods, or to absorb water in hygroscopic applications. It is the primary component of diatomaceous earth which has many uses ranging from filtration to insect control. It is also the primary component of rice husk ash which is used, for example, in filtration and cement manufacturing.

Thin films of silica grown on silicon wafers via thermal oxidation methods can be quite beneficial in microelectronics, where they act as electric insulators with high chemical stability. In electrical applications, it can protect the silicon, store charge, block current, and even act as a controlled pathway to limit current flow.

A silica-based aerogel was used in the Stardust spacecraft to collect extraterrestrial particles. Silica is also used in the extraction of DNA and RNA due to its ability to bind to the nucleic acids under the presence of chaotropes. As hydrophobic silica it is used as a defoamer component. In hydrated form, it is used in toothpaste as a hard abrasive to remove tooth plaque.

In its capacity as a refractory, it is useful in fiber form as a high-temperature thermal protection fabric. In cosmetics, it is useful for its light-diffusing properties and natural absorbency.

Colloidal silica is used as a wine and juice fining agent. In pharmaceutical products, silica aids powder flow when tablets are formed.

Crystal structure

Tetrahedral structural unit of silica (SiO_2), the basic building block of the most ideal glass former. In the vast majority of silicates, the Si atom shows tetrahedral coordination, with 4 oxygen atoms surrounding a central Si atom. The most common example is seen in the quartz crystalline form of silica SiO_2. In each of the most thermodynamically stable crystalline forms of silica, on average, all 4 of the vertices (or oxygen atoms) of the SiO_4 tetrahedra are shared with others, yielding the net chemical formula: SiO_2. (this can be understood as each oxygen, which is bonded to 2 Si atoms contributes 1/2 to the stoichiometry).

The amorphous structure of glassy silica (SiO_2) in two-dimensions. No long-range order is present, however there is local ordering with respect to the tetrahedral arrangement of oxygen (O) atoms around the silicon (Si) atoms. Note that a fourth oxygen atom is bonded to each silicon atom, either behind the plane of the screen or in front of it; these atoms are omitted for clarity. SiO_2 has a number of distinct crystalline forms (polymorphs) in addition to amorphous forms. With the exception of stishovite and fibrous silica, all of the crystalline forms involve tetrahedral SiO_4 units linked together by shared vertices in different arrangements. Silicon-oxygen bond lengths vary between the different crystal forms, for example in α-quartz the bond length is 161 pm, whereas in α-tridymite it is in the range 154–171 pm. The Si-O-Si angle also varies between a low value of 140° in α-tridymite, up to 180° in β-tridymite. In α-quartz the Si-O-Si angle is 144°.

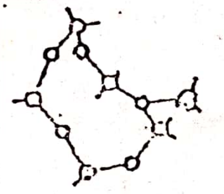
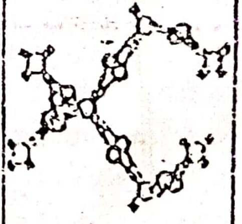
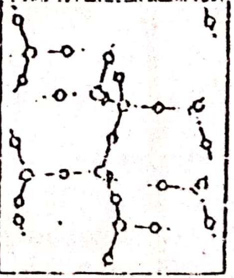
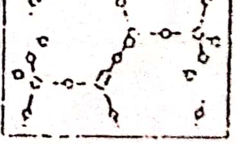
Fibrous silica has a structure similar to that of SiS_2 with chains of edge-sharing SiO_4 tetrahedra. Stishovite, the higher pressure form, in contrast has a rutile like structure where silicon is [illegible] coordinate. The density of stishovite is 4.287 g/cm³, which compares to α-quartz, the densest of the low pressure forms, which has a density of 2.648 g/cm³. The difference in density can be ascribed to the increase in coordination as the six shortest Si-O bond lengths in stishovite (four Si-O bond lengths of 176 pm and two others of 181 pm) are greater than the Si-O bond length (161 pm) in α-quartz. The change in the coordination increases the ionicity of the Si-O bond. But more important is the observation that any deviations from these standard parameters constitute microstructural differences or variations which represent an approach to an amorphous, vitreous or glassy solid.

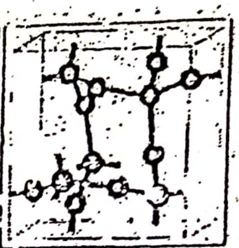
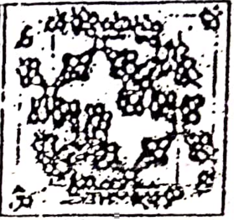
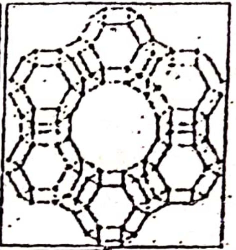
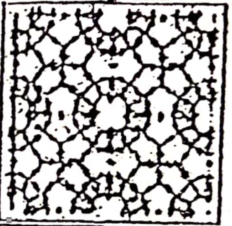
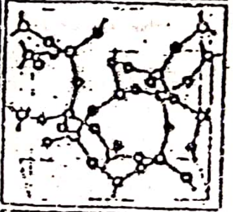
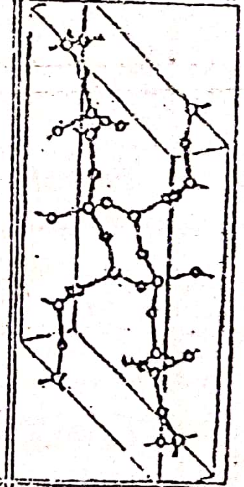
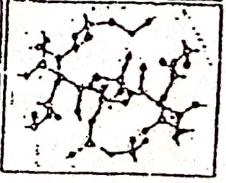
The high pressure minerals, seifertite, stishovite, and coesite, on the other hand, have a higher density and index of refraction when compared to quartz. This is probably due to the intense compression of the atoms that must occur during their formation, resulting in a more condensed structure.

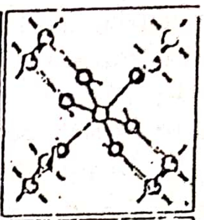
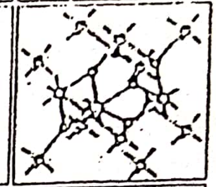
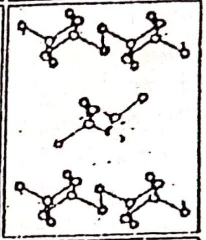
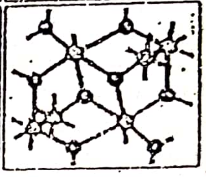
Faujasite silica is another form of crystalline silica. It is obtained by dealumination of a low-sodium, ultra-stable Y zeolite with a combined acid and thermal treatment. The resulting product contains over 99% silica, has high crystallinity and high surface area (over 800 m^2/g). Faujasite-silica has very high thermal and acid stability. For example, it maintains a high degree of long-range molecular order (or crystallinity) even after boiling in concentrated hydrochloric acid.

Molten silica exhibits several peculiar physical characteristics that are similar to the ones observed in liquid water: negative temperature expansion, density maximum, and a heat capacity minimum. When molecular silicon monoxide, SiO, is condensed in an argon matrix cooled with helium along with oxygen atoms generated by microwave discharge, molecular SiO_2 is produced which has a linear structure. Dimeric silicon dioxide, $(SiO_2)_2$ has been prepared by reacting O_2 with matrix isolated dimeric silicon monoxide, (Si_2O_2). In dimeric silicon dioxide there are two oxygen atoms bridging between the silicon atoms with an Si-O-Si angle of 94° and bond length of 164.6 pm and the terminal Si-O bond length is 150.2 pm. The Si-O bond length is 148.3 pm which compares with the length of 161 pm in α-quartz. The bond energy is estimated at 621.7 kJ/mol.

Crystalline forms of SiO_2

Form	Crystal symmetry Pearson symbol, group No.	Notes	Structure
α-quartz	rhombohedral (trigonal) hP9, $P3_121$ No.152	Helical chains making individual single crystals optically active; α-quartz converts to β-quartz at 846 K	
β-quartz	hexagonal hP18, $P6_222$, No.180	closely related to α-quartz (with an Si-O-Si angle of 155°) and optically active; β-quartz converts to β-tridymite at 1140 K	
α-tridymite	orthorhombic oS24, $C222_1$, No.20	metastable form under normal pressure	
β-tridymite	hexagonal hP12, $P6_3/mmc$, No. 194	closely related to α-tridymite; β-tridymite converts to β-cristobalite at 2010 K	

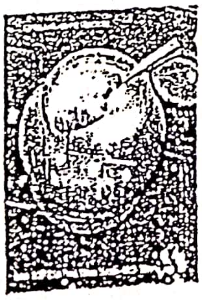
α-cristobalite	tetragonal tP12, $P4_12_12$, No. 92	metastable form under normal pressure	
β-cristobalite	cubic cF104, Fd3m, No.227	closely related to α-cristobalite; melts at 1978 K	
faujasite	cubic cF576, Fd3m, No.227	sodalite cages connected by hexagonal prisms; 12-membered ring pore opening; faujasite structure.	
melanophlogite	cubic (cP*, $P4_232$, No.208) or tetragonal ($P4_2$/nbc)	Si_5O_{10}, Si_6O_{12} rings; mineral always found with hydrocarbons in interstitial spaces-a clathrasil	
keatite	tetragonal tP36, $P4_12_12$, No. 92	Si_5O_{10}, Si_4O_{14}, Si_8O_{16} rings; synthesised from glassy silica and alkali at 600–900K and 40–400 MPa.	
moganite	monoclinic mS46, C2/c, No.15	Si_4O_8 and Si_6O_{12} rings	
coesite	monoclinic mS48, C2/c, No.15	Si_4O_8 and Si_8O_{16} rings; 900 K and 3–3.5 GPa	

stishovite	Tetragonal tP6, $P4_2/mnm$, No.136	One of the densest (together with seifertite) polymorphs of silica; rutile-like with 6-fold coordinated Si; 7.5–8.5 GPa	
poststishovite	orthorhombic oP12, Pnc2, No.30		
fibrous	orthorhombic oI12, Ibam, No.72	like SiS_2 consisting of edge sharing chains	
seifertite	orthorhombic oP, Pbcn	One of the densest (together with stishovite) polymorphs of silica; is produced at pressures above 40 GPa.	

Application

Quartz glass When silicon dioxide SiO_2 is cooled rapidly enough, it does not crystallize but solidifies as a glass. The glass transition temperature of pure SiO_2 is about 1600 K. Like most c the crystalline polymorphs the local atomic structure in pure silica glass is regular tetrahedra of oxygen atoms around silicon atoms. The difference between the glass and the crystals arises in the connectivity of these tetrahedral units. SiO_2 glass consists of a non-repeating network of tetrahedra, where all the oxygen corners connect two neighbouring tetrahedra. Although there is no long range periodicity in the glassy network there remains significant ordering at length scales well beyond the SiO bond length. One example of this ordering is found in the preference of the network to form rings of 6-tetrahedra.

Chemistry



Manufactured silica fume at maximum surface area of 380 m^2/g. Silicon dioxide is formed when silicon is exposed to oxygen (or air). A very shallow layer (approximately 1 nm or 10 Å) of so-called native oxide is formed on the surface when silicon is exposed to air under ambient conditions. Higher temperatures and alternative environments are used to grow well-controlled layers of silicon dioxide on silicon, for example at temperatures between 600 and 1200 °C, using so-called dry or wet oxidation with O_2 or H_2O, respectively. The depth of the layer of silicon replaced by the dioxide is 44% of the depth of the silicon dioxide layer produced.

Alternative methods used to deposit a layer of SiO_2 include

- Low temperature oxidation (400–450 °C) of silane
  $SiH_4 + 2\,O_2 \rightarrow SiO_2 + 2\,H_2O$.
- Decomposition of tetraethyl orthosilicate (TEOS) at 680–730 °C
  $Si(OC_2H_5)_4 \rightarrow SiO_2 + 2\,H_2O + 4\,C_2H_4$.
- Plasma enhanced chemical vapor deposition using TEOS at about 400 °C
  $Si(OC_2H_5)_4 + 12\,O_2 \rightarrow SiO_2 + 10\,H_2O + 8\,CO_2$.
- Polymerization of tetraethyl orthosilicate (TEOS) at below 100 °C using amino acid as catalyst.

Pyrogenic silica (sometimes called fumed silica or silica fume), which is a very fine particulate form of silicon dioxide, is prepared by burning $SiCl_4$ in an oxygen rich hydrocarbon flame to produce a "smoke" of SiO_2:

$$SiCl_4 + 2\,H_2 + O_2 \rightarrow SiO_2 + 4\,HCl.$$

Amorphous silica, silica gel, is produced by the acidification of solutions of sodium silicate to produce a gelatinous precipitate that is then washed and then dehydrated to produce colorless microporous silica.

Quartz exhibits a maximum solubility in water at temperatures about 340 °C This property is used to grow single crystals of quartz in a hydrothermal process where natural quartz is dissolved in superheated water in a pressure vessel which is cooler at the top. Crystals of 0.5–1 kg can be grown over a period of 1–2 months. These crystals are a source of very pure quartz for use in electronic applications.

Fluorine reacts with silicon dioxide to form SiF_4 and O_2 whereas the other halogen gases (Cl_2, Br_2, I_2) react much less readily.

Silicon dioxide is attacked by hydrofluoric acid (HF) to produce hexafluorosilicic acid:

$$SiO_2 + 6\,HF \rightarrow H_2SiF_6 + 2\,H_2O.$$

HF is used to remove or pattern silicon dioxide in the semiconductor industry.

Silicon dioxide dissolves in hot concentrated alkali or fused hydroxide:

$$SiO_2 + 2\,NaOH \rightarrow Na_2SiO_3 + H_2O.$$

Silicon dioxide reacts with basic metal oxides (e.g. sodium oxide, potassium oxide, lead(II) oxide, zinc oxide, or mixtures of oxides forming silicates and glasses as the Si-O-Si bonds in silica are broken successively). As an example the reaction of sodium oxide and SiO_2 can produce sodium orthosilicate, sodium silicate, and glasses, dependent on the proportions of reactants:

$$2\,Na_2O + SiO_2 \rightarrow Na_4SiO_4;$$
$$Na_2O + SiO_2 \rightarrow Na_2SiO_3;$$
$$(0.25–0.8)Na_2O + SiO_2 \rightarrow \text{glass}.$$

Examples of such glasses have commercial significance e.g. soda lime glass, borosilicate glass, lead glass. In these glasses, silica is termed the network former or lattice former.

Bundle of optical fibers composed of high purity silica.

With silicon at high temperatures gaseous SiO is produced:

$$SiO_2 + Si \rightarrow 2\ SiO\ (gas).$$

Sol-gel: -

The sol-gel process is a wet chemical technique used for the fabrication of both glassy and ceramic materials. In this process, the sol (or solution) evolves gradually towards the formation of a gel-like network containing both a liquid phase and a solid phase. The basic structure or morphology of the solid phase can range anywhere from discrete colloidal particles to continuous chain-like polymer networks.[34][35]

The term "colloid" is specific to the size of the individual particles, which are greater than atoms but small enough not to settle to the bottom of a container immediately. Their dynamic behavior is governed by forces of gravity and sedimentation, but may remain suspended in a liquid medium indefinitely. This critical size range (or particle width) typically ranges from tens of angstroms to a few microns.

1. In basic solutions ($pH > 7$), the particles may grow to sufficient size to become colloids. Particles like these may become highly ordered in a manner similar to those seen in precious opal.
2. Under acidic conditions ($pH < 7$), a more open continuous network of chain-like polymers is formed. Polymers like this can be useful due to their viscosity, which allows them to be drawn or spun from solution into fibers, or drawn as thin films into surface coatings. Such glass fiber is useful for guided lightwave transmission, with ceramic fiber providing excellent thermal insulation.

In either case, the sol evolves towards the formation of a 2-phase gel. In the case of the colloid, the number of particles in an extremely dilute suspension may be so low that a significant amount of solvent may need to be removed initially for the gel-like properties to be recognized. This can be accomplished in any number of ways. The simplest method is to allow time for sedimentation to occur, and then pour off the remaining liquor. A variable speed centrifuge can also be used to accelerate the process of liquid removal.

Removal of the remanent solvent phase requires a drying process, which is typically accompanied by a significant amount of shrinkage and densification. Since the water will most likely reside within microstructural pores, the rate at which the solvent can be removed is ultimately determined by the distribution of pore room in the gel. Subsequent thermal treatment (or low temperature sintering at 500–600 °C) may be performed in order to obtain a higher density product. With regard to methods of application:

1. The sol can be deposited on a substrate to form a film using dip-coating or spin-coating;
2. It can be cast into a suitable container with the desired shape;
3. It can be used to synthesize fine high-purity powders.[36][37]

The sol-gel approach is a cheap and low-temperature technique that maintains a high degree of chemical purity. Thus it allows for total control of the product's chemical composition. It can be used in ceramics manufacturing processes, as an investment casting material, or as a means of producing thin films or coatings.[38]

Sol-gel derived components have diverse applications in optics, electronics, energy, space, physical and chemical sensors, biosensors, controlled drug release in medicine, and chemical separation on a cellular level. Ceramic powders of a wide range of chemical composition can be

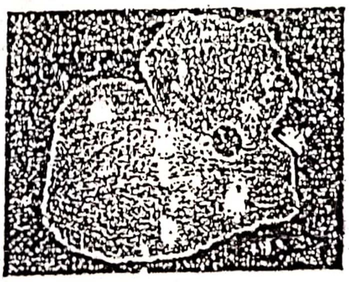
formed by such techniques. The generation of particles uniform in size and shape was investigated extensively by Egon Matijevic and his co-workers. In the case of chromium, aluminum, and titanium salts, spherical particles were formed whereas particles of crystallographic symmetry resulted from solutions of copper and iron salts.[36][37][39][40][41][42][43][44]
In 1956, Kolbe described the formation of spherical silica particles in basic solution. The mechanisms of precipitation—and the chemical conditions that skew the structure toward linear or branched structures—are the most critical issues faced in the chemistry laboratory by sol-gel scientists. Again, these are the factors which will ultimately determine the form of the microstructure over a range of length scales in the green or unfired body. Factors, such as chemical acidity which lead to the formation of linear polymers (as opposed to particles), are ideal for the formation of spinnable solutions such as those used for the formation of thin films and coatings as well as optical quality fiber.

Biomaterials

Silicification is quite common in the biological world and occurs in bacteria, single-celled organisms, plants, and animals (invertebrates and vertebrates). Crystalline minerals formed in this environment often show exceptional physical properties (e.g. strength, hardness, fracture toughness) and tend to form hierarchical structures that exhibit microstructural order over a range of scales. The minerals are crystallized from an environment that is undersaturated with respect to silicon, and under conditions of neutral pH and low temperature (0–40 °C). Formation of the mineral may occur either within or outside of the cell wall of an organism, and specific biochemical reactions for mineral deposition exist that include lipids, proteins, and carbohydrates. Silica is a material strengthener of bone and can be fetched in the trace silicon compounds in beer.

20

- :Zeolite: -



Zeolites are microporous. aluminosilicate minerals commonly used as commercial adsorbents. The term zeolite was originally coined in 1756 by Swedish mineralogist Axel Fredrik Cronstedt, who observed that upon rapidly heating the material stilbite, it produced large amounts of steam from water that had been adsorbed by the material. Based on this, he called the material *zeolite*, from the Greek ζέω (zeō), meaning "boil" and λίθος (*lithos*), meaning "stone".
As of January 2008, 175 unique zeolite frameworks have been identified, and over 40 naturally occurring zeolite frameworks are known.

Zeolites are widely used in industry for water purification, as catalysts, and in nuclear reprocessing. Their biggest use is in the production of laundry detergents. They are also used in medicine and in agriculture.

Properties: - Zeolites have a porous structure that can accommodate a wide variety of cations, such as Na^+, K^+, Ca^{2+}, Mg^{2+} and others. These positive ions are rather loosely held and can readily be exchanged for others in a contact solution. Some of the more common mineral zeolites are analcime, chabazite, clinoptilolite, heulandite, natrolite, phillipsite, and stilbite. An example mineral formula is: $Na_2Al_2Si_3O_{10}\cdot 2H_2O$, the formula for natrolite.

Natural zeolites form where volcanic rocks and ash layers react with alkaline groundwater. Zeolites also crystallize in post-depositional environments over periods ranging from thousands to millions of years in shallow marine basins. Naturally occurring zeolites are rarely pure and are contaminated to varying degrees by other minerals, metals, quartz, or other zeolites. For this reason, naturally occurring zeolites are excluded from many important commercial applications where uniformity and purity are essential.

Zeolites are the aluminosilicate members of the family of microporous solids known as "molecular sieves." The term molecular sieve refers to a particular property of these materials, i.e., the ability to selectively sort molecules based primarily on a size exclusion process. This is due to a very regular pore structure of molecular dimensions. The maximum size of the molecular or ionic species that can enter the pores of a zeolite is controlled by the dimensions of the channels. These are conventionally defined by the ring size of the aperture, where, for example, the term "8-ring" refers to a closed loop that is built from 8 tetrahedrally coordinated silicon (or aluminum) atoms and 8 oxygen atoms. These rings are not always perfectly symmetrical due to a variety of effects, including strain induced by the bonding between units that are needed to produce the overall structure, or coordination of some of the oxygen atoms of the rings to cations within the structure. Therefore, the pores in many zeolites are not cylindrical.

Sources: -

Conventional open pit mining techniques in Arkansas, Idaho and New Mexico are used to mine natural zeolites. The overburden is removed to allow access to the ore. The ore may be blasted or stripped for processing by using tractors equipped with ripper blades and front-end loaders. In processing, the ore is crushed, dried, and milled. The milled ore may be air-classified as to particle size and shipped in bags or bulk. The crushed product may be screened to remove fine material when a granular product is required, and some pelletized products are produced from fine material.

Currently, the world's annual production of natural zeolite is about 4 million tons. Of this quantity, 2.6 million tons are shipped to Chinese markets to be used in the concrete industry. Eastern Europe, Western Europe, Australia, and Asia are world leaders in supplying the world's demand for natural zeolite. By comparison, only 57,400 metric tons of zeolite (only 1% of the world's current production) is produced in North America; only recently has North America realized the potential for current and future markets.

There are several types of synthetic zeolites that form by a process of slow crystallization of a silica-alumina gel in the presence of alkalis and organic templates. One of the important processes used to carry out zeolite synthesis is sol-gel processing. The product properties depend on reaction mixture composition, pH of the system, operating temperature, pre-reaction 'seeding' time, reaction time as well as the templates used. In sol-gel process, other elements (metals, metal oxides) can be easily incorporated. The silicalite sol formed by the hydrothermal method is very stable. Also the ease of scaling up this process makes it a favorite route for zeolite synthesis.

Synthetic zeolites hold some key advantages over their natural analogs. The synthetics can, of course, be manufactured in a uniform, phase-pure state. It is also possible to manufacture desirable zeolite structures, which do not appear in nature. Zeolite A is a well-known example. Since the principal raw materials used to manufacture zeolites are silica and alumina, which are among the most abundant mineral components on earth, the potential to supply zeolites is virtually unlimited. Finally, zeolite manufacturing processes engineered by man require significantly less time than the 50 to 50,000 years prescribed by nature. Disadvantages include the inability to create crystals with dimensions of a comparable size to their natural counterparts.

Uses

Commercial and domestic

Zeolites are widely used as ion-exchange beds in domestic and commercial water purification, softening, and other applications. In chemistry, zeolites are used to separate molecules (only molecules of certain sizes and shapes can pass through), as traps for molecules so they can be analyzed. Zeolites have the potential of providing precise and specific separation of gases including the removal of H_2O, CO_2 and SO_2 from low-grade natural gas streams. Other separations include noble gases, N_2, O_2, freon and formaldehyde. However, at present, the true potential to improve the handling of such gases in this manner remains unknown.

Petrochemical industry

Synthetic zeolites are widely used as catalysts in the petrochemical industry, for instance in fluid catalytic cracking and hydro-cracking. Zeolites confine molecules in small spaces, which causes changes in their structure and reactivity. The hydrogen form of zeolites (prepared by ion-exchange) are powerful solid-state acids, and can facilitate a host of acid-catalyzed reactions, such as isomerisation, alkylation, and cracking. The specific activation modality of most zeolitic catalysts used in petrochemical applications involves quantum-chemical Lewis acid site reactions. Catalytic cracking uses a furnace and reactor. First, crude oil distillation fractions are heated in the furnace and passed to the reactor. In the reactor, the crude meets with a catalyst such as zeolite. It goes through this step three times, each time getting cooler. Finally, it reaches a step known as separator. The separator collects recycled hydrogen. Then it goes through a fractionator and becomes the final item.

Nuclear industry

Zeolites have uses in advanced reprocessing methods, where their micro-porous ability to capture some ions while allowing others to pass freely allow many fission products to be efficiently removed from nuclear waste and permanently trapped. Equally important are the mineral properties of zeolites. Their alumino-silicate construction is extremely durable and resistant to radiation even in porous form. Additionally, once they are loaded with trapped fission products, the zeolite-waste combination can be hot pressed into an extremely durable ceramic form, closing the pores and trapping the waste in a solid stone block. This is a waste form factor that greatly reduces its hazard compared to conventional reprocessing systems.

Heating and refrigeration

Zeolites can be used as solar thermal collectors and for adsorption refrigeration. In these applications, their high heat of adsorption and ability to hydrate and dehydrate while maintaining structural stability is exploited. This hygroscopic property coupled with an inherent exothermic (heat-producing) reaction when transitioning from a dehydrated to a hydrated form make natural zeolites useful in harvesting waste heat and solar heat energy.

Detergents

The largest single use for zeolite is the global laundry detergent market. This amounted to 1.44 million metric tons per year of anhydrous zeolite A in 1992.

Construction

Synthetic zeolite is also being used as an additive in the production process of warm mix asphalt concrete. The development of this application started in Germany in the 1990s. It helps by decreasing the temperature level during manufacture and laying of asphalt concrete, resulting in lower consumption of fossil fuels, thus releasing less carbon dioxide, aerosols, and vapours. Other than that, the use of synthetic zeolite in hot mixed asphalt leads to easier compaction and, to a certain degree, allows cold weather paving and longer hauls.

When added to Portland cement as a pozzolan, it can reduce chloride permeability and improve workability. It reduces weight and helps moderate water content while allowing for slower drying which improves break strength.

Gemstones

Thomsonites, one of the rarer zeolite minerals, have been collected as gemstones from a series of lava flows along Lake Superior in Minnesota and to a lesser degree in Michigan, U.S.A. Thomsonite nodules from these areas have eroded from basalt lava flows and are collected on beaches and by scuba divers in Lake Superior.

These thomsonite nodules have concentric rings in combinations of colors: black, white, orange, pink, red, and many shades of green. Some nodules have copper inclusions and rarely will be found with copper "eyes." When polished by a lapidary the thomsonites sometimes display chatoyancy.

Space hardware testing: - Zeolites can be used as a molecular sieve in cryosorption pumps for rough pumping of vacuum chambers that can be used to simulate space-like conditions to test hardware bound for space.

Medical: - Zeolite-based oxygen concentrator systems are widely used to produce medical-grade oxygen. The zeolite is used as a molecular sieve to create purified oxygen from air using its ability to trap impurities, in a process involving the adsorption of nitrogen, leaving highly purified oxygen and up to 5% argon.

QuikClot brand hemostatic agent, which is used to stop severe bleeding, contains a calcium-loaded form of zeolite.

Biomedical applications of zeolites include their use as detoxicants and decontaminants, as vaccine adjuvants, and as antibacterial agents They are also used for delayed release drug delivery, as antitumor adjuvants, as antidiarrheal agents, in hemodialysis, to improve bone formation, and in the treatment of diabetes mellitus.

Zeolites are used in the treatment of Lyme disease, as a detoxifier.

Use as nutritional supplements: -Zeolites are used as nutritional supplements. Some clinoptilolite-based dietary supplements have demonstrated antioxidant activity in humans.

Agriculture

In agriculture, clinoptilolite (a naturally occurring zeolite) is used as a soil treatment. It provides a source of slowly released potassium. If previously loaded with ammonium, the zeolite can serve a similar function in the slow release of nitrogen. Zeolites can also act as water moderators, in which they will adsorb up to 55% of their weight in water and slowly release it under plant demand. This property can prevent root rot and moderate drought cycles.

Animal husbandry

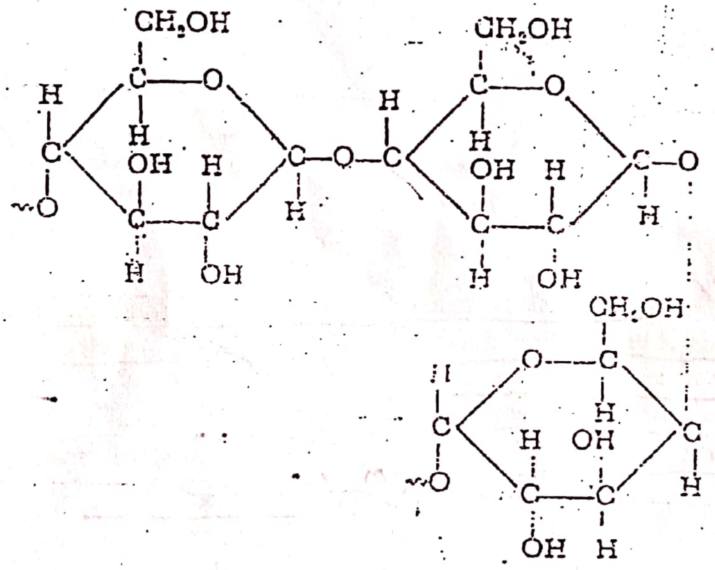
"Both natural and synthetic zeolites have been used in animal nutrition mainly to improve performance traits and, based on their fundamental physicochemical properties, they were also tested and found to be efficacious in the prevention of ammonia and heavy metal toxicities, poisonings as well as radioactive elements uptake and metabolic skeletal defects."
In concentrated animal growing facilities, the addition of as little as 1% of a very low sodium clinoptilolite was shown to improve feed conversion, reduce airborne ammonia up to 80%, act as a mycotoxin binder, and improve bone density.[14] It can be used in general odor elimination for all animal odors.

Unit III

Cellulose, $(C_6H_5O_{10})_n$ **:** Cellulose forms the chief constituent of the cell wall of all plants. The purest natural form of cellulose is cotton (about 90% cellulose). Flax, hemp, jute, etc. are other vegetable fibres and contain a higher percentage of cellulose.

In order to get pure cellulose from cotton-wool, it is treated in succession with dilute alkali, dilute acid, water, alcohol and ether. This treatment removes impurities and incrustations and cellulose which is very stable towards dilute acids and alkalies is obtained as a white amorphous mass.

Cellulose is a white solid insoluble in water and usual organic solvents. It, however, dissolves in ammoniacal copper hydroxide solution. On careful hydrolysis cellulose gives cellobiose which on further hydrolysis gives D (+) glucose which exists in the β–form. Cellulose is, therefore, composed of D (+) glucose units (β–form), and its structure can be represented as follows :



A mixture of concentrated sulphuric acid and acetic anhydride converts cellulose into the octacetate of cellobiose. The octacetate on hydrolysis gives cellobiose. This reaction has an important bearing upon the elucidation of the structure of cellulose.

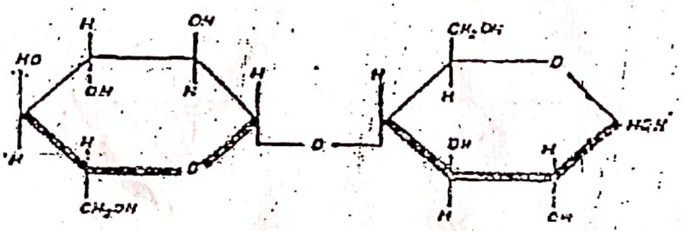
Nitro-cellulose (cellulose nitrates) : When treated with a nitrating mixture ($HNO_3+H_2SO_4$) cellulose gives a trinitrate. Each glucose unit in cellulose has only three free hydroxyl groups and hence the highest nitrate ester is a trinitrate.

Cellulose trinitrate $[C_6H_7O_2(ONO_2)_3]_n$ is employed under the name of gun-cotton in propellant explosives and for blasting. Gun cotton burns with extreme rapidity but explodes when detonated. A development of great importance is the use of gun-cotton and pyroxylin in the production of smokeless powder.

If a dilute mixture of nitric acid and sulphuric acid is used, the mono and di-nitrate of cellulose are formed. These are grouped together under the name pyroxylin and dissolve readily in a mixture of alcohol and ether, such a solution being known as collodion.

Cellobiose : It can be prepared from cellulose by acetylating pure cellulose (e. g. good filter paper) with acetic anhydride in the presence of concentrated sulphuric acid and hydrolysing the octa-acetate of cellobiose thus formed with potassium hydroxide.

Cellobiose is a white crystalline solid (M. P. 225°), soluble in water and is dextro-rotatory. On hydrolysis with dilute acids or by the enzyme *emulsin*, it gives two molecules of D(+) glucose. It reduces ammoniacal silver nitrate and Fehling's solutions. It forms an oxime and an osazone and undergoes mutarotation. Its structure is represented as shown below.



Cellobiose

Q **Celluloid** is made by mixing pyroxylin and camphor in a suitable solvent such as alcohol. It is used as a plastic being readily moulded at 80°. It has, however, the disadvantage of being dangerously inflammable. Pyroxylin is also used in the manufacture of lacquers, particularly for motor cars.

Artificial Silk : Q (1) **Acetate Silk :** When cellulose is treated with acetic anhydride and acetic acid in the presence of sulphuric acid or zinc chloride, cellulose is converted into cellulose triacetate. The triacetate is then hydrolysed to the diacetate. The diacetate is then washed, dried and dissolved in a mixture of solvents, the main constituent of which is, generally, acetone. The syrupy solution is then forced through a spinneret into a warm chamber, whereupon the solvent evaporates leaving behind fine threads of cellulose acetate. Cellulose acetate (silk) possesses a good lustre and great tenacity and is insensitive to moisture. This silk burns with difficulty. However, it is less readily dyed than rayon (see below). It is also costly.

(2) **Cuprammonium process (cupra silk) :** In this process cellulose is dissolved in ammoniacal copper hydroxide solution. The solution of cellulose thus obtained is then forced through a spinneret into a sulphuric acid bath when cellulose is precipitated as fine threads. Cuprammonium silk is comparatively very cheap.

(3) **Viscose Silk (rayon) :** When cellulose is treated with a concentrated solution of sodium hydroxide and carbon dioxide passed into it, sodium cellulose xanthate soluble in sodium hydroxide is formed.

$(C_6H_{10}O_5)_n + nCS_2 + nNaOH \rightarrow [C_6H_9O_4.OC(=S)SNa]_n + nH_2O$

This alkaline solution of cellulose xanthate has a high viscosity (hence the name of the process as viscose process). This alkaline solution is then forced through a spinneret into a sulphuric acid bath, whereupon cellulose is precipitated as fine threads.

Cellophane : When viscose solution is passed through a narrow slit into an acid bath, cellulose is precipitated as very thin sheets. When these sheets are coated with nitrocellulose lacquer, they become moisture-proof.

Cellulose ethers are obtained by the interaction of alkyl halides or sulphates with cellulose in the presence of alkali. Some of these cellulose ethers are of great industrial importance due to the instability and resistance to chemical attack. The most important ones are ethyl-cellulose and benzylcellulose.

Paper : Paper was formerly made from linen waste. Now most of the paper is made from wood-pulp. There are two main processes in use : (1) the caustic soda process and (2) the sulphite process.

(1) In the caustic soda process wood chips are boiled in iron vessels with dilute caustic soda for several hours under a pressure of 6–8–atmospheres and at a temperature of 160°. By this treatment compounds collectively known as lignin are removed. The pulp is then washed with water and worked up for making paper.

(2) In the sulphite process wood chips are digested at 130°–150° with an aqueous solution of calcium and magnesium bisulphite. These reagents also dissolve lignin without doing any harm to the cellulose fibre.

Starch : It occurs abundantly as a reserve food carbohydrate in the tubers, seeds and fruits of many plants. The rich source of starch is potatoes, maize, wheat, etc.

Manufacture of starch : The process ~~of manufacture of~~ starch is mainly a mechanical separation of starch from other associated materials in the source and differs in individual cases. In America the main source of starch is maize while in other countries potato, rice or wheat is used.

[The steps in the isolation of starch from corn are described below.]

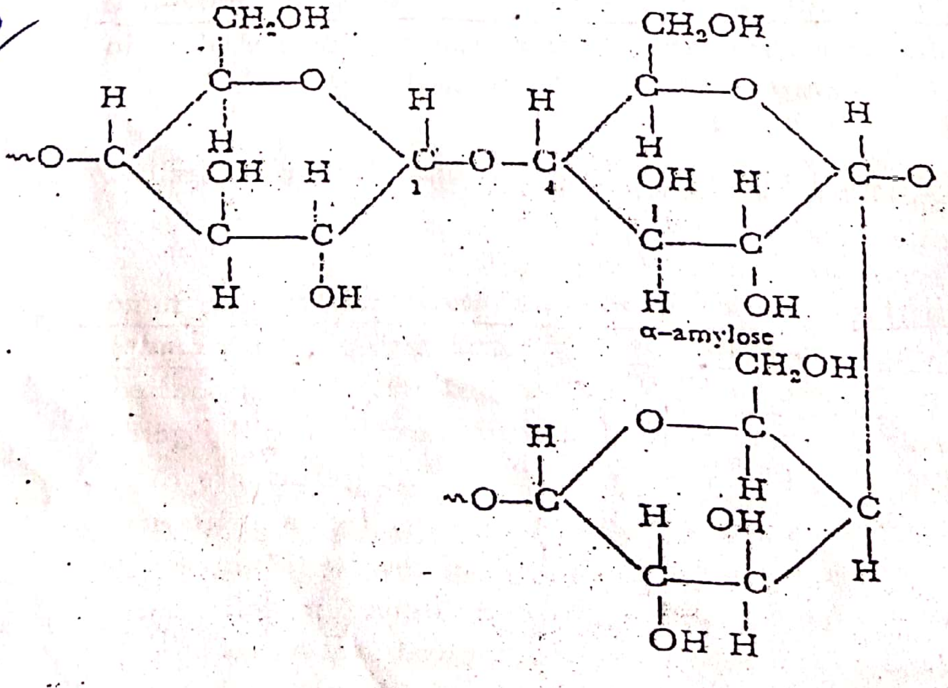
[Corn is first steeped into warm water containing some sulphur dioxide which prevents the fermentation. This causes the hull to swell and soften. The steeped corn is then passed through a mill that ruptures the hull without crushing the germ (germs contain a high percentage of oil). The germs are then separated from the starch and hull fragments by a floatation process. After this the product is filtered through fine sieves, when starch granules pass through and other materials are retained behind. The starch is then allowed to settle. It is then collected and dried with hot air. Similar methods can be employed for preparing starch from wheat, rice, etc.

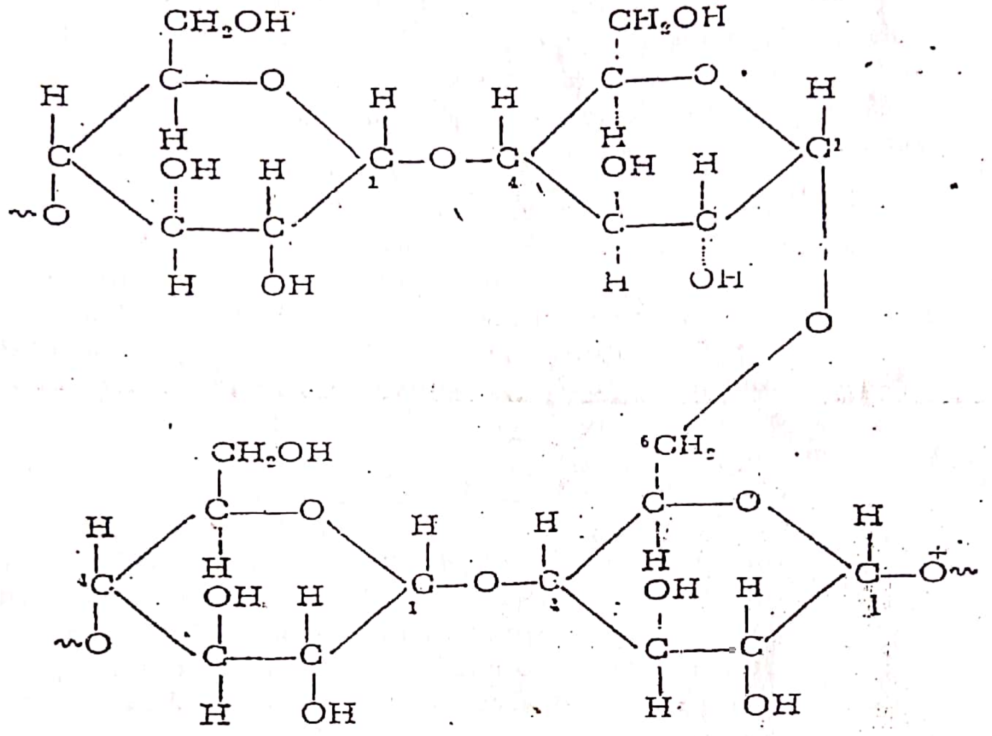
Properties : Starch is a white hygroscopic powder without any taste or smell. It is interesting to find that starch exists in the plants as microscopic granules. The size, shape and other characteristics of the granules depend upon the source of the starch. Potato starch granules, for example, are among the largest in size, whereas rice starch has a very tiny granules.

Starch is insoluble in water but when heated with water, the granules swell up and burst forming an opalescent solution. When starch is treated with dilute (5–10%) hydrochloric acid for several days, it is converted into a soluble variety and it dissolves easily in water to give a clear solution. Soluble starch can also be prepared by heating it with glycerol. Starch consists of two fractions (1) ∝-amylose or granulose and (2) β–amylose, starch cellulose or amylopectin. It is ∝-amylose which is soluble in water which gives a blue colour with iodine. The colour is due to the absorption of iodine on the surface of the starch and not to the formation of any definite compound. Amylopectin is insoluble in water and gives red colour with iodine. ∝–Amylose and β–amylose, both, can be hydrolysed to maltose by the enzyme diastase, and to D (+) glucose by dilute acids.

The structures of ∝–amylose and β–amylose are not known exactly; but it is believed that amylose consists of long chains of glucose units joined as ∝–glucosides. The most generally accepted structure for β–amylose is a branched chain structure made up of glucose units.

The structure of ∝–amylose and β–amylose can be represented as follows .





β–amylose

Uses of starch : Starch is a very valuable commercial commodity. Starch is used as a source of glucose that can be used for the preparation of vinegar or as a sweetening agent. Laundry starch is a very familiar material and it can be used as a sizing agent and in the manufacture of adhesives. It also forms one of the basic raw materials for the manufacture of ethyl alcohol by fermentation.

Dextrins : Dextrins are formed by the partial hydrolysis of starch by boiling with water under pressure at about 250°. They are also prepared by heating starch with water containing a little nitric acid at 110°. Dextrins contain amylodextrin, soluble starch, Achroo-dextrin, erythrodextrin etc. They are white powders and are used for making adhesives and confectionery, for sizing paper, etc.

Glycogen : Glycogen is a reserve carbohydrate of the animal organism, where it is found in the liver and the muscles. It is a white amorphous powder which dissolves fairly easily in hot water and does not form a paste like starch. The solution is dextrorotatory, the specific rotation being almost the same as starch ($[\alpha]_D = +198°$).

In its chemical behaviour glycogen shows a considerable resemblance to starch. Like starch it can be readily hydrolysed to glucose by dilute acids. The enzyme diastase converts it into maltose. Glycogen is, therefore, supposed to possess a structure similar to starch.

Inulin : It occurs in many plants e. g. in the roots of dandelion and in the tubers of dahlia. It is a white powder dissolving in hot water like starch. The solution is lævorotatory ($[\alpha]^{20} = 38°$). The solution does not give any colouration with iodine.

On hydrolysis by dilute acids inulin give D (—) fructose. Its molecular weight determinations give a value of about 5000. Therefore, its structure appears to correspond with about 30 fructose units [$(C_6H_{10}O_5)_{30}$].

Raw starch is sold according to the raw material from which it is made. Corn starch is sold as both pearl starch, a granular form, and as powdered. The latter is slightly more expensive. Potato starch is sold as domestic and imported. Rice starch is produced domestically. Wheat starch is offered as thick-boiling starch, which gives a heavier paste for a given starch content. Laundry starch is usually raw corn starch, often sold in lump form. It is first shaped into blocks by letting the starch liquor drain in boxes having perforated bottoms covered with filter cloths. The blocks are cut into sections and partly dried in a warm chamber. The brown crust which forms is scraped off, the blocks wrapped in paper and allowed to dry very slowly. The blocks break up of themselves into irregularly shaped forms termed "crystals" by the trade. Starches are also used for the manufacture of glucose, in paper sizings, in adhesives, in cosmetics, and as filers in varied food products.

Sago is a granulated or ground starch prepared from the crushed and washed pith of the sago palm, *Metroxylon laeve* or *Metroxylon rumphii,* and from the trunks of several other palms and cycads which grow in the East Indies and the Philippines. When finely powdered it is sago flour. The uses parallel those of other starches, as a textile sizing and in the manufacture or preparation of food products. A form of pudding from it is particularly well known.

Tapioca starch is the starch from the Brazilian arrowroot, usually *Manihot utilissima.* It is also called cassava starch, and the roots from which it is produced, cassava roots. In finely ground form it is known as tapioca flour, in larger granules, usually of uniform size, it is tapioca. The uses are similar to those of other starches, and include in the tropics, manufacture of cassava bread from the flour.

Iodized starch or starch iodide is a dark-colored starch powder containing 2 per cent of iodine. It is used in medicine as a disinfectant and internal and external antiseptic. The British pharmacopoeia increases the iodine content to 5 per cent.

Thin-boiling starch or soluble starch is a name for products obtained by a controlled hydrolysis of starch. They are produced by acid treatment at a definite pH with temperature control. Since the procedure represents a mild degree of hydrolysis the products may contain some dextrins.

Chlorinated starch or oxidized starch represents a further degree of hydrolysis and is usually obtained by treatment with sodium hypochlorite.

ALCOHOLS

Alcohols are organic compounds characterized by the presence of the hydroxyl group. The hydrogen of the hydroxyl group may react to form new compounds as in the formation of alcoholates or the hydroxyl group may react as a whole as in the formation of esters. The organic radical may be very simple as in methyl alcohol, or highly complex as in geraniol. It may be saturated or unsaturated, straight chain or cyclic. If cyclic, the hydroxyl group occurs in the side chain. Aromatic compounds which have a hydroxyl group attached to a ring carbon atom are phenols. These differ in properties from alcohols. An alcohol may contain more than one hydroxyl group, such as glycol with two, and glycerol with three. Scientific usage attaches the "ol" ending to indicate that a compound is chemically an hydroxyl derivative, although industrial usage frequently ignores this, as in using the term "glycerine" instead of "glycerol".

The most common alcohol, ethyl alcohol, is next in importance to water as a solvent and may be said to occupy the same position in organic chemistry as water does in inorganic chemistry. When only alcohol is specified ethyl alcohol is meant. The subject is complicated by the fact that the same compound may be an alcohol and an acid, or an ether and an alcohol, or may contain even more complex combinations. In classifying these mixed types of compounds, they have been placed according to the chemical property which appears most important in the major use of the material.

The carbinol type of nomenclature is based on representing alcohols as substituted methyl alcohols. Thus methyl alcohol is carbinol, CH_3OH, methyl carbinol is CH_3CH_2OH, one hydrogen being replaced by CH_3. Similarly, dimethyl carbinol is $(CH_3)_2CHOH$, trimethyl carbinol $(CH_3)_3COH$, and methyl propyl carbinol $(CH_3)(C_3H_7)CHOH$.

Methyl alcohol, methanol, wood alcohol or wood spirit, CH_3OH, is the simplest possible representative of the alcohol class, and is miscible with water, alcohol or ether. It is a colorless, limpid liquid. A characteristic odor usually associated with it is largely due to impurities, and modified but not eliminated when the alcohol is pure. The historic method of manufacture perpetuated in the name wood spirit, is by destructive distillation of wood. The distillate also contains acetic acid, acetone and methyl acetate. After neutralizing the organic acids with lime, the liquid is again distilled, dried by treatment with calcium chloride and fractionally redistilled to separate other volatile substances present. The major modern method of preparation is from carbon monoxide by reaction with hydrogen under pressure in the presence of a catalyst, said to be composed of zinc oxide and chromic acid. Higher alcohols and water are produced at the same time but methyl alcohol can be separated from these by fractional distillation.

Grades sold are natural crude; denaturing grade; pure, natural or synthetic; 97 per cent, natural or synthetic; and 95 per cent, natural or synthetic. The pure is normally guaranteed to be over 99.5 per cent. The balance in all cases is largely water. A definite trend to the use of the term methanol rather than methyl alcohol or wood alcohol is encouraged in the trade, to avoid confusion with alcohol, meaning ethyl alcohol. Because of its poisonous nature, methanol is a major denaturant for ethyl alcohol to render it nonpotable and therefore tax-free. Methyl alcohol is more expensive than tax-free ethyl alcohol but does not have the government restrictions that hamper the user of the latter. Therefore it is frequently substituted as a solvent where possible. It is a raw material for the manufacture of formaldehyde and many synthetic organic chemicals. A minor use is as a fuel. Another important application is as a radiator anti-freeze, where it replaces a greater weight of ethyl alcohol required for an equivalent lowering of the freezing point.

Ethyl alcohol, alcohol or ethanol, C_2H_5OH, is a clear colorless liquid of characteristic odor when pure, miscible with water and ether. Commercially it is produced in enormous quantities from molasses, a by-product of the sugar industry. This is fermented with yeast, and is classed as molasses alcohol, from its source. Alcohol is also produced by fermentation of starch from grain, and called grain alcohol. This term is sometimes incorrectly used as a synonym for ethyl alcohol, regardless of source. The fermentation yields as a by-product a spent mash which is high in proteins, containing nearly all of the protein of the original grain. In the process the starch is first hydrolyzed to sugars by the yeast, and these are acted on by another ferment of the yeast to form alcohol and carbon dioxide. Therefore the industry is a major source of supply of the by-product, carbon dioxide. Alcohol has been produced by hydrolysis of wood cellulose with acid to form sugars, which are then fermented. Synthetic ethyl alcohol has also been produced by the catalytic union of ethylene and water. In all cases it is purified by fractional distillation, sometimes also by treatment with activated carbon. Distillation through an efficient fractionating column yields a constant-boiling mixture with water, containing 95 per cent of alcohol and 5 per cent of water by volume. This may be refined to absolute alcohol by adding benzene and distilling, a ternary benzene-alcohol-water compound being separated in the distillation. Grading is on a basis of the proof gallon which contains 50 per cent of water and 50 per cent of alcohol by volume. Thus absolute alcohol or anhydrous alcohol is 200 proof, or 100 per cent pure ethyl alcohol.

Alcohol is quoted as 190 proof, and absolute, with the additional designation as from grain, from molasses or synthetic. This designation of the source is not because of distinguishable differences in the product, although salesmen for alcohol sometimes contend that such differences are detectable, but because of government restrictions. The U.S.P. grades for these concentrations correspond to not less than 94.9 per cent by volume at 15.5° C. for the ordinary grade, and not less than 99 per cent by weight for the absolute. Grain alcohol commands a premium and the law requires that it be used in manufacture of potable beverages. The use of alcohol is hedged about with many governmental restrictions as to permits. While inherently not a very expensive material, when not denatured, ethyl alcohol is subject to a tax which is often 90 per cent of the selling price, which makes it expensive.

Tax-paid alcohol is used in making flavoring extracts, which are usually alcoholic solutions of essential oils or other flavoring ingredients. It is used in perfumes and in many medicines.

The term tincture is used to differentiate an alcoholic extract for medical use from solutions in other solvents. Other important uses are in organic synthesis, for the manufacture of celluloid and other plastics, in antiseptics and disinfectants, as a solvent for gums, particularly shellac, and in general as the solvent for organic substances, much as water is a solvent for inorganic substances. Automobile-radiator antifreeze use consumes large volumes. Its use as a blend with gasoline as a motor fuel has made substantial progress in Europe and to a lesser extent in the United States. The anhydrous grade is necessary for this, and butyl alcohol must be added as a mutual solvent to prevent separation into layers in the presence of a small amount of water.

Nearly all alcoholic beverages are alcoholic solutions having characteristic tastes and aromas because the purification by distillation has intentionally not been complete. They are listed briefly because they are commercial forms of tax-paid alcohol. They are described without the detail of the legal definitions.

Whiskey is the alcohol at 85-100 proof, distilled from a fermented grain mash. Rye whiskey means that rye predominated in the mash, corn whiskey or bourbon whiskey that corn predominated. Scotch whiskey and Irish whiskey take their names from characteristic odors derived from peat smoke in preparation rather than from the raw materials. Rum is similarly produced from fermented molasses, at 85-100 proof. Wine is fermented grape juice, brandy the alcohol distilled from wine to a concentration of 90-100 proof. Wine will contain only 12-16 per cent of alcohol from fermentation, but sherry, port and tokay wines are fortified to 20-22 per cent, and occasionally even to 28 per cent with brandy or grain alcohol. Beer is a malt beverage containing 3.5-7 per cent of alcohol, to which the hops and processing give characteristic flavors. Liqueurs of varied names are flavored syrups fortified with alcohol. Gin is made from alcohol by distillation through a mixture of herbs and berries in which juniper, coriander, etc., predominate, adjusted to 85-100 proof. Gin and the liqueurs are the only beverages made directly from alcohol, the others being unrefined or only partially refined alcohol.

Completely denatured alcohol is that to which materials have been added to make it objectionable as to odor and taste and therefore nonpotable. As an incidental factor it is made poisonous because that is the nature of the denaturants used. It is tax-free and no permit for its use is required.

Completely denatured alcohol has been prepared in the past with gasoline, wood alcohol, pyridine, etc. Formulas are changed rather frequently. The following are typical: Formula CD11 contains 3 gallons of Pontol K, 1 gallon of aviation gasoline, 0.5 gallon of Agdite or 1 gallon of Hydronol and 3 gallons of a preparation designated as ST115, per 100 gallons of alcohol. The denaturants added to CD12 are similar with an increase of Pontol K to 4 gallons and replacement of ST115 by 2 gallons of methyl isobutyl ketone. Formula CD13 differs from CD11 in increase of ST115 to 4 gallons and replacement of Pontol K by 2 gallons of methyl isobutyl ketone. The composition of the named denaturants is not generally known. Completely denatured alcohol is widely used as a solvent, as anti-freeze for automobile radiators, as a cleaning agent for metals in industrial plants, as a fuel, in cements, paint- and varnish removers, in spirit varnishes and in other products where no physiological application is possible. Completely denatured alcohol should not be used as a rubbing alcohol. For that purpose special denatured formula 23G is used with additions made by the bottler.

Special solvent-alcohol is a completely denatured and therefore tax-free grade. No permit is required. It may not be used for anti-freeze purposes. It is anhydrous and a typical formula contains 5 gallons of Tecsol, 2.5 gallons of Pontol K, 2.5 gallons of isopropyl alcohol and 0.5 gallon of aviation gasoline per 100 gallons of absolute alcohol. As the name indicates, it is used largely as a solvent for lacquer, resins, etc.

Specially denatured alcohol is permitted for use where completely denatured alcohol will not serve the purpose and where it is not intended for food, medicinal or beverage purposes. The denaturant added therefore depends on the application or the industry in which the alcohol is used. To obtain such alcohol it is necessary to have a permit, and if a substantial amount is required, to file a bond. Specially denatured alcohol is tax-free. It is sold as 190 proof and anhydrous. The following are examples of denaturants added to suit industrial applications for which large volumes are quoted. Formula SD1 contains 5 gallons of approved wood alcohol in 100 gallons of ethyl alcohol. Formula SD23G contains 10 gallons of U.S.P. acetone and 4.25 ounces of sucrose octoacetate in 100 gallons of ethyl alcohol. Special denatured alcohol formulas are numbered to 47, with some having as many as seven subformulas indicated by letter designation. Where alcohol is required for chemical purposes, a special denatured formula is ordinarily used. Formula SD1 is authorized for over 200 different uses, such as the manufacture of acetaldehyde and ether, making textile soaps, etc.

Propyl alcohol, C_3H_7OH, is the next member of the family above ethyl alcohol. Normal propyl alcohol is a straight-chain compound and is not available in quantity. The usual commercial product is isopropyl alcohol or isopropanol, $(CH_3)_2CHOH$, a colorless liquid having less odor than ethyl alcohol and of slightly higher boiling point. It mixes with water, alcohol and ether. The major source is by synthesis from natural gas, or from cracking gases from the oil industry, propylene being first obtained, this dissolved in sulfuric acid and the resulting unstable propyl hydrogen sulfate hydrolyzed with water. Acetone can be reduced by hydrogen at 120° C. with a nickel catalyst to give isopropyl alcohol. Various grades are denaturing, refined 91 per cent, refined 98 per cent, technical 91 per cent and technical 98 per cent. The balance in each case is largely water, the 91 per cent grade being a constant boiling mixture with 9 per cent of water. Isopropyl alcohol is used as a substitute for ethyl alcohol in many solvent applications to avoid the restrictions of alcohol permits, but cannot be so used in food products. Isopropyl alcohol is also used to form esters and other organic derivatives. It is only slightly more expensive than completely denatured alcohol.

[illegible] acid. Various grades are sold, domestic C.P., domestic commercial, imported 85 per cent, and imported commercial. It is used in skin preparations, as a fixative in perfumes, for production of synthetic organic chemicals and for sulfation to give alkyl sulfates, used as detergents. The price varies with the grade, corresponding to the purpose for which the material is suitable.

Diacetone alcohol or 4-hydroxy-2-keto-4-dimethyl pentane, $CH_3COCH_2C(CH_3)_2OH$, is a colorless liquid miscible with water, alcohol or ether. It is both a ketone and an alcohol, prepared synthetically. Diacetone alcohol is sold as pure, and as a technical grade which contains some acetone. It is a solvent for lacquers, plastics and resins, available at a price permitting its use as a solvent.

Ethylene glycol, $(CH_2OH)_2$, is miscible with water or alcohol and is prepared by heating ethylene dichloride or ethylene chlorohydrin with a suitable alkaline solution under pressure. It is the simplest polyhydric alcohol. The colorless syrupy liquid is hygroscopic. It is used as an antifreeze solution in automobile radiators, as a coolant in airplane engines; in the manufacture of explosives and for a great variety of purposes to replace glycerine in nonfood uses. For example, some brands of cigarettes use it or its derivatives as the hygroscopic agent in place of glycerine; it is quite widely used in cosmetics. The manufacture from it of glycol dinitrate, $(CH_2NO_3)_2$, as a substitute for nitroglycerine, replaces the by-product glycerine as a raw material with a synthetic product available in any reasonable amount.

Propylene glycol, $CH_3(CH_2OH)_2$, is closely related to ethylene glycol in preparation, properties and uses.

Diethylene glycol, $CH_2OHCH_2OCH_2CH_2OH$, is a colorless, syrupy, liquid, miscible with water and alcohol, and very hygroscopic. It is structurally an ether as well as an alcohol. The production is probably as a by-product in the manufacture of ethylene glycol, although it can be synthesized as a primary product. It is used as a solvent for nitrocellulose and gums, as a moistening and softening agent for glue, parchment paper, etc., in the printing of textiles, and in the manufacture of explosives. In these uses it largely replaces glycerine.

Triethylene glycol, $CH_2OH(CH_2OCH_2)_2CH_2OH$, is a colorless, hygroscopic liquid which is both an ether and an alcohol. It is soluble in water but immiscible with organic hydrocarbons. Commercially it is probably from by-product sources, and is usually contaminated with homologues. Uses are as a solvent for nitrocellulose and gums and as a plasticizer in varied applications. Derivatives have similar uses.

Ethylene chlorohydrin, CH_2ClCH_2OH, is both an alcohol and a halogen derivative, the stage intermediate between ethylene dichloride and ethylene glycol. It is produced by the reaction of ethylene and hydrogen chloride gas. The colorless liquid is miscible with water and is sold as a 40 per cent chemistry:

Glycerol or glycerine, $C_3H_5(OH)_3$, is a trihydric alcohol present in fats and fatty oils, where it is esterified with the higher aliphatic acids. It is a viscous liquid colorless when pure, miscible with water or alcohol, and is very hygroscopic. Glycerine is obtained from fats and saponifiable oils by hydrolysis. Soap-lye contains a high proportion of water, the salt with which the soap was salted out, impurities separated from the raw materials used in soap manufacture, residual lye and 3-5 per cent of glycerine. A higher concentration of glycerine is obtained when fats are split to give fatty acids by means of the Twitchell reagent. Crude glycerine is obtained from these by precipitating soap and other impurities with lime and concentrating to about 80 per cent glycerine. Refined glycerine is obtained by distillation. A 95 per cent glycerine free from solids is prepared by distillation under reduced pressure with superheated steam. The colorless product is obtained by treatment with charcoal to remove yellow coloring matter.

Glycerine which contains no impurity but moisture, is prepared by redistillation and treatment with activated carbon to give a C.P. grade. The U.S.P. grade is colorless and contains not less than 95 per cent of glycerine. Other grades sold are dynamite; saponification, basis 88 per cent; soap-lye, basis 80 per cent; and yellow distilled. Various grades are used in printer's inks, plastic clays, polishes, as an antifreeze when the price permits, in making nitroglycerine which/absorbed in carrier is dynamite, as a textile softener and solvent for textile chemicals, as a lubricant, in plastics, paper, ink, leather, etc., as a softener, in cosmetics, as a solvent for drugs and essential oils, as a moistening and flavoring agent in tobacco, as a preservative for foodstuffs, and in many similar ways. Because of its derivation as a relatively minor by-product the price is subject to wide fluctuation and substitutes of more stable price tend to be preferred by manufacturers.

Mannitol or mannite, $C_6H_8(OH)_6$, is a hexahydroxy alcohol extracted from manna. The sweetness is comparable to that of sugar. It is expensive and use is limited to replacement of sugar in diets for diabetics and to requirements as a laboratory reagent.

Sorbitol or sorbit, $C_6H_8(OH)_6$, is an hexahydroxy alcohol, very soluble in water or alcohol and isomeric with mannitol and dulcitol. It was originally obtained from the fruit of a mountain ash but is now produced by the electrolytic reduction of glucose in solution. While a crystalline substance, the commercial form is as a solution containing about 15 per cent of water. Quotations are on the basis of the anhydrous sorbitol present. It is used as a plasticizer to replace glycerine where the larger molecular weight offers technical or practical advantages.

Borneol, bornyl alcohol or Borneo camphor, $C_{10}H_{17}OH$, is soluble in alcohol or ether and slightly soluble in water. It is found in solid masses in a tree native to Sumatra and Borneo and also occurs mixed with an essential oil in an Asiatic woody herb. These two forms are optically active, the first being

Oxalic acid, $(COOH)_2.2H_2O$, is sold in the form of colorless crystals which effloresce in dry air. It is the simplest dibasic organic acid. In the form of the acid potassium salt or the calcium salt it occurs in many plants. It is among the strongest of the organic acids, and is moderately soluble in cold water, extremely soluble in hot, and very soluble in alcohol or ether. Oxalic acid is produced from many organic oxygen-containing compounds by fusion with caustic alkali. Cellulose in the form of wood shavings or sawdust is the usual starting material. This is heated with a strong aqueous solution of potassium and sodium hydroxides at 240-250° C. Milk of lime is added to the solution of the salt formed, to precipitate calcium oxalate. The latter is treated with sulfuric acid, which precipitates calcium sulfate and liberates free oxalic acid. Calcium oxalate may be present as an impurity. It may also be produced by the oxidation of sugar with nitric acid. Oxalic acid is sold in large volume. It is used as a purifying agent in many processes such as in the manufacture of glycerine, as a precipitant for lime where its removal is desired, as a bleaching agent as in bleaching straw, or wood, to remove ink and rust spots because of its ability to form soluble iron compounds, as an ingredient of metal polish, largely as a salt, in printing and dyeing textiles, and for many analogous purposes. It is covered by the Caustic Poison Act, which is given in Appendix A.

Furfural or furfuraldehyde, C_4H_3OCHO, is a colorless to reddish brown liquid, very soluble in water, alcohol or ether. It darkens on exposure to the air and is obtained from the pentoses of corn cobs, oat hulls, straw, jute, corn stalks, etc., by digesting these or similar products with moderately concentrated sulfuric acid. The term furfurol, which implies an alcohol structure, is also used for this aldehyde. Both refined and technical grades are sold. It is used in the manufacture of synthetic resins and molding compounds, disinfectants, deodorants, as a preservative of glue, in light-sensitive printing plates, as a nitrocellulose solvent and for the production of numerous chemical derivatives. It is the inexpensive starting material for derivatives of furfurane, C_4H_4O.