

SECTION -D

MDU (ROHTAK)

B.TECH 1ST YEAR

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(I) POLYMERS AND POLYMERIZATION

&

**(II) INSTRUMENTAL METHODS OF
ANALYSIS**

SECTION :-D

POLYMERS AND POLYMERISATION

Introduction

In polymer chemistry, **polymerization** is a process of reacting monomer molecules together in a chemical reaction to form polymer chains or three-dimensional networks. There are many forms of polymerization.

In chemical compounds, polymerization occurs via a variety of reaction mechanisms that vary in complexity due to functional groups present in reacting compounds and their inherent steric effects. In more straightforward polymerization, alkenes, which

are relatively stable due to σ bonding between carbon atoms, form polymers through relatively simple radical reactions; in contrast, more complex reactions such as those that involve substitution at the carbonyl group require more complex synthesis due to the way in which reacting molecules polymerize

As alkenes can be formed in somewhat straightforward reaction mechanisms, they form useful compounds such as polyethylene and polyvinyl chloride (PVC) when undergoing radical reactions which are produced in high tonnages each year^[4] due to their usefulness in manufacturing processes of commercial products, such as piping, insulation and packaging. In general, polymers such as PVC are referred to as "**homopolymers**," as they consist of repeated long chains or structures of the same monomer unit, whereas polymers that consist of more than one molecule are referred to as copolymers (or co-polymers).

Other monomer units, such as formaldehyde hydrates or simple aldehydes, are able to polymerize themselves at quite low temperatures ($>-80\text{ }^{\circ}\text{C}$) to form trimers; molecules consisting of 3 monomer units, which can cyclize to form ring cyclic structures, or undergo further reactions to form tetramers,¹ or 4 monomer-unit compounds. Further compounds either being referred to as oligomers in smaller molecules. Generally, because formaldehyde is an exceptionally reactive electrophile it allows nucleophilic addition of hemiacetal

Homopolymers



Copolymers



intermediates, which are in general short-lived and relatively unstable "mid-stage" compounds that react with other molecules present to form more stable polymeric compounds.

Polymerization that is not sufficiently moderated and proceeds at a fast rate can be very hazardous. This phenomenon is known as hazardous polymerization and can cause fires and explosions.

Step-growth

Step-growth polymers are defined as polymers formed by the stepwise reaction between functional groups of monomers, usually containing heteroatoms such as nitrogen or oxygen. Most step-growth polymers are also classified as condensation polymers, but not all step-growth polymers (like polyurethanes formed from isocyanate and alcohol bifunctional monomers) release condensate; in this case, we talk about addition polymers. Step-growth polymers increase in molecular weight at a very slow rate at lower conversions and reach moderately high molecular weights only at very high conversion (i.e., >95%).

To alleviate inconsistencies in these naming methods, adjusted definitions for condensation and addition polymers have been developed. A condensation polymer is defined as a polymer that involves loss of small molecules during its synthesis, or contains heteroatoms as part of its backbone chain, or its repeat unit does not contain all the atoms present in the hypothetical monomer to which it can be degraded.

Chain-growth

Chain-growth polymerization (or addition polymerization) involves the linking together of molecules incorporating double or triple carbon-carbon bonds. These unsaturated *monomers* (the identical molecules that make up the polymers) have extra internal bonds that are able to break and link up with other monomers to form a repeating chain whose backbone typically contains only carbon atoms. Chain-growth polymerization is involved in the manufacture of polymers such as polyethylene, polypropylene, and polyvinyl chloride (PVC). A special case of chain-growth polymerization leads to living polymerization.

In the radical polymerization of ethylene, its bond is broken, and the two electrons rearrange to create a new propagating center like the one that attacked it. The form this propagating center takes depends on the specific type of addition mechanism. There are several mechanisms through which this can be initiated.

The free radical mechanism is one of the first methods to be used. Free radicals are very reactive atoms or

molecules that have unpaired electrons. Taking the polymerization of ethylene as an example, the free radical mechanism can be divided into three stages: chain initiation, chain propagation, and chain termination.



Free radical addition polymerization of ethylene must take place at high temperatures and pressures, approximately 300 °C and 2000 atm. While most other free radical polymerizations do not require such extreme temperatures and pressures, they do tend to lack control. One effect of this lack of control is a high degree of branching. Also, as termination occurs randomly, when two chains collide, it is impossible to control the length of individual chains. A newer method of polymerization similar to free radical, but allowing more control involves the Ziegler-Natta catalyst, especially with respect to polymer branching.

Other forms of chain growth polymerization include cationic addition polymerization and anionic addition polymerization. While not used to a large extent in industry yet due to stringent reaction conditions such as lack of water and oxygen, these methods provide ways to polymerize some monomers that cannot be polymerized by free radical methods such as polypropylene. Cationic and anionic mechanisms are also more ideally suited for living polymerizations, although free radical living polymerizations have also been developed.

Esters of acrylic acid contain a carbon-carbon double bond which is conjugated to an ester group. This allows the possibility of both types of polymerization mechanism. An acrylic ester by itself can undergo chain-growth polymerization to form a homopolymer with a carbon-carbon backbone, such as poly(methyl methacrylate). Also, however, certain acrylic esters can react with diamine monomers by nucleophilic conjugate addition of amine groups to acrylic C=C bonds. In this case the polymerization proceeds by step-growth and the products are poly(beta-amino ester) copolymers, with backbones containing nitrogen (as amine) and oxygen (as ester) as well as carbon.

The Mechanism of Addition Polymerization

The formation of a polymer by addition polymerization is an example of a chain reaction. Once a chain reaction gets started, it is able to keep itself going. The three steps of this reaction to focus on are

- ⇒ how the reaction gets started (INITIATION)
- ⇒ how the reaction keeps going (PROPAGATION)
- ⇒ how the reaction stops (TERMINATION)

A Note About This Example:

There are various methods used to carry out addition polymerization chain reactions. The details vary according to the method used.

We will focus on a commonly used mechanism involving a free radical. Our example polymerization will combine ethylene (ethene) monomers ($\text{CH}_2=\text{CH}_2$), so our product will be

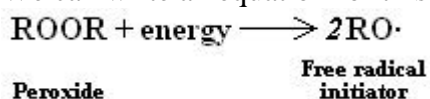
polyethylene. (Polyethylene is used to make food wrap, milk jugs, garbage bags, and many other plastic products.)

I. INITIATION

--- How the reaction gets started ---

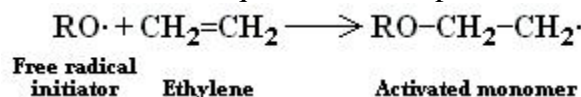
If you looked at Part 3 of this tutorial, you have already seen the first part of the initiation step of addition polymerization chain reaction. A peroxide molecule breaks up into two reactive free radicals. Light or heat can provide the energy needed for this process.

We can write an equation for this process:



The second part of initiation occurs when the free radical initiator attacks and attaches to a monomer molecule. This forms a new free radical, which is called the activated monomer.

We can write an equation for this process, too:

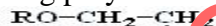


II. PROPAGATION

--- How the reaction keeps going ---

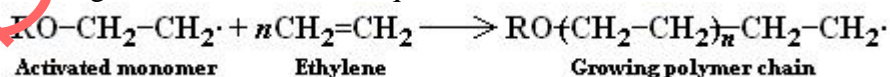
Top of Form

During a chain reaction, most of the time is spent in the propagation phase as the polymer chain grows. In the propagation phase, the newly-formed activated monomer attacks and attaches to the double bond of another monomer molecule. This addition occurs again and again to make the long polymer chain.



Bottom of Form

Once again, we can write an equation for this reaction:



The "n" stands for any number of monomer molecules, typically in the thousands.

III. TERMINATION

--- How the reaction stops ---

This chain reaction cannot go on forever. The reaction must terminate, but how? A growing polymer chain joins with another free radical. We watched a peroxide break up to form two radicals. It makes sense that two free radicals could join to make a stable bond.

The equation representing this step of the chain reaction can be written simply as:

$$R\cdot + R'\cdot \longrightarrow R-R'$$

Remember: The R and R' groups here can be the original free radicals, the growing polymer chains, or even one of each. Termination reactions can, however, be more complicated looking.

An Important Note:

Chemists can control the way a polymer does each of these steps by varying the reactants, the reaction times, and the reaction conditions.

The physical properties of a polymer chain depend on the polymer's average length, the amount of branching, and the constituent monomers.

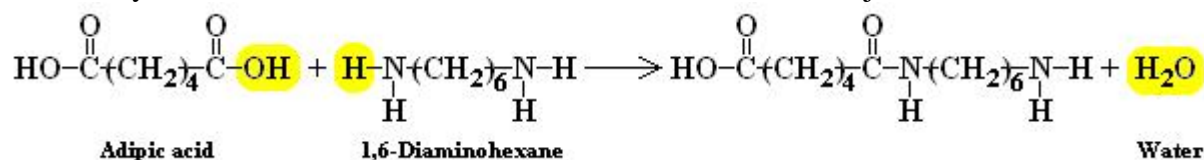
The Mechanism of Condensation Polymerization

You know that monomers that are joined by condensation polymerization have two functional groups. You also know (from Part 6) that a carboxylic acid and an amine can form an amide linkage, and a carboxylic acid and an alcohol can form an ester linkage. Since each monomer has two reactive sites, they can form long-chain polymers by making many amide or ester links. Let's look at two examples of common polymers made from the monomers we have studied.

Example

1:

A carboxylic acid monomer and an amine monomer can join in an amide linkage.



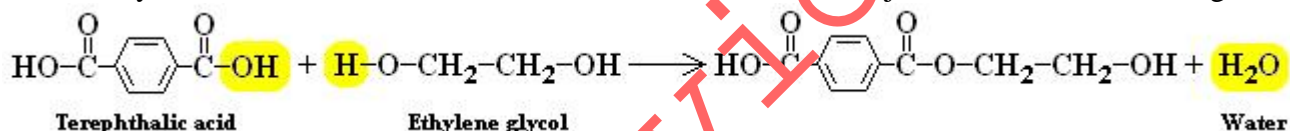
As before, a water molecule is removed, and an amide linkage is formed. Notice that an acid group remains on one end of the chain, which can react with another amine monomer. Similarly an amine group remains on the other end of the chain, which can react with another acid monomer.

Thus, monomers can continue to join by amide linkages to form a long chain. Because of the type of bond that links the monomers, this polymer is called a polyamide. The polymer made from these two six-carbon monomers is known as nylon-6,6. (Nylon products include hosiery, parachutes, and ropes.)

Example

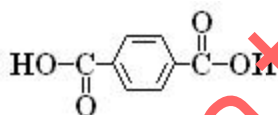
2:

A carboxylic acid monomer and an alcohol monomer can join in an ester linkage.



Top of Form

A water molecule is removed as the ester linkage is formed. Notice the acid and the alcohol groups that are still available for bonding.



Bottom of Form

Because the monomers above are all joined by ester linkages, the polymer chain is a polyester. This one is called PET, which stands for poly(ethylene terephthalate). (PET is used to make soft-drink bottles, magnetic tape, and many other plastic products.)

Let's summarize:

As difunctional monomers join with amide and ester linkages, polyamides and polyesters are formed, respectively. We have seen the formation of the polyamide nylon-6,6 and the polyester PET. There are numerous other examples.

Remember: The above process is called condensation polymerization because a molecule is removed during the joining of the monomers. This molecule is frequently water.

Thermoplastic

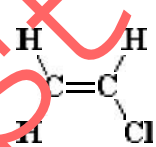
A **Thermoplastic**, also known as a **thermosoftening plastic**, is a polymer that becomes pliable or moldable above a specific temperature, and returns to a solid state upon cooling. Most thermoplastics have a high molecular weight, whose chains associate through intermolecular forces; this property allows thermoplastics to be remolded because the intermolecular interactions spontaneously reform upon cooling. In this way, thermoplastics differ from thermosetting polymers, which form irreversible chemical bonds during the curing process; thermoset bonds break down upon melting and do not reform upon cooling.

PVC : Poly(vinyl chloride)

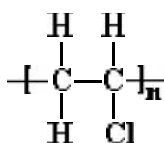
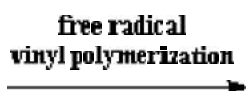
Poly(vinyl chloride) is the plastic known at the hardware store as PVC. This is the PVC from which pipes are made, and PVC pipe is everywhere. The plumbing in your house is probably PVC pipe, unless it's an older house. PVC pipe is what rural high schools with small budgets use to make goal posts for their football fields. But there's more to PVC than just pipe. The "vinyl" siding used on houses is made of poly(vinyl chloride). Inside the house, PVC is used to make linoleum for the floor. In the seventies, PVC was often used to make vinyl car tops.

PVC is useful because it resists two things that hate each other: fire and water. Because of its water resistance it's used to make raincoats and shower curtains, and of course, water pipes. It has flame resistance, too, because it contains chlorine. When you try to burn PVC, chlorine atoms are released, and chlorine atoms inhibit combustion.

Structurally, PVC is a vinyl polymer. (well, duh!) It's similar to polyethylene, but on every other carbon in the backbone chain, one of the hydrogen atoms is replaced with a chlorine atom. It's produced by the free radical polymerization of vinyl chloride.



vinyl chloride

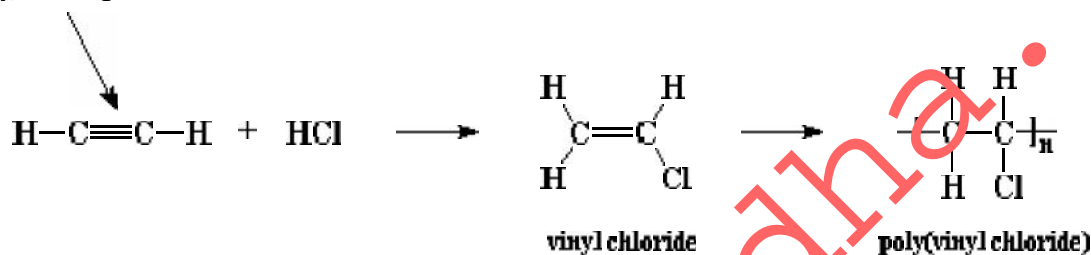


poly(vinyl chloride)

And here, my friends, is that monomer, vinyl chloride:

PVC was one of those odd discoveries that actually had to be made twice. It seems around a hundred years ago, a few German entrepreneurs decided they were going to make loads of cash lighting people's homes with lamps fueled by acetylene gas. Wouldn't you know it, right about the time they had produced tons of acetylene to sell to everyone who was going to buy their lamps, new efficient electric generators were developed which made the price of electric lighting drop so low that the acetylene lamp business was finished. That left a lot of acetylene laying around.

leftover acetylene from the
acetylene lamp fiasco

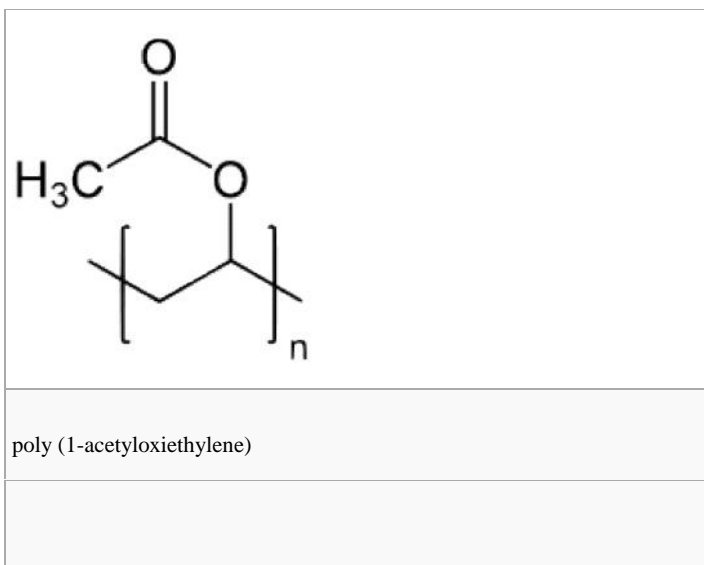


So in 1912 one German chemist, Fritz Klatte decided to try to do something with it, and reacted some acetylene with hydrochloric acid (HCl). Now, this reaction will produce vinyl chloride, but at that time no one knew what to do with it, so he put it on the shelf, where it polymerized over time. Not knowing what to do with the PVC he had just invented, he told his bosses at his company, Greisheim Electron, who had the material patented in Germany. They never figured out a use for PVC, and in 1925 their patent expired.

Wouldn't you know it, in 1926 the very next year, an American chemist, Waldo Semon was working at B.F. Goodrich when he independently invented PVC. But unlike the earlier chemists, it dawned on him that this new material would make a perfect shower curtain. He and his bosses at B.F. Goodrich patented PVC in the United States (Klatte's bosses apparently never filed for a patent outside Germany). Tons of new uses for this wonderful waterproof material followed, and PVC was a smash hit the second time around.

Polyvinyl acetat

Polyvinyl acetate



Polyvinyl acetate, PVA, PVAc, poly(ethenyl ethanoate), is a rubbery synthetic polymer with the formula $(C_4H_6O_2)_n$. It belongs to the polyvinyl esters family with the general formula $-[RCOOCHCH_2]-$. It is a type of thermoplastic.

It should not be confused with the related polymer polyvinyl alcohol, which is also called PVA.

Polyvinyl acetate is a component of a widely-used type of glue, referred to variously as wood glue, white glue, carpenter's glue, school glue, Elmers glue (especially in the US) or PVA glue.

Preparation

PVAc is a vinyl polymer. Polyvinyl acetate is prepared by polymerization of vinyl acetate monomer (free radical vinyl polymerization of the monomervinyl acetate).

Discovery

The monomer, vinyl acetate, was on an industrial scale first produced by addition of acetic acid to acetylene with a mercury(I) salt^[3] but it is now primarily made by palladium catalyzed oxidative addition of acetic acid to ethylene.

Properties

The degree of polymerization of polyvinyl acetate typically is 100 to 5000. The ester groups of the polyvinyl acetate are sensitive for alkali and will slowly convert PVAc into polyvinyl alcohol and acetic acid.

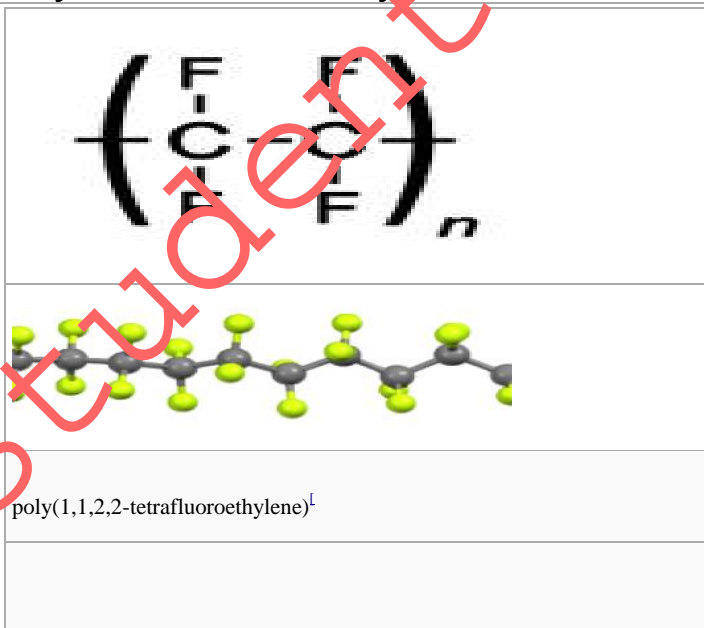
Under alkaline conditions, boron compounds such as boric acid or borax cause the polymer to cross-link, forming tackifying precipitates or slime.

Applications and uses

As an emulsion in water, PVAc emulsions are used as adhesives for porous materials, particularly for wood, paper, and cloth, and as a consolidant for porous building stone, in particular sandstone.^[4] Uses:

- as wood glue PVAc is known as "white glue" and the yellow "carpenter's glue" or PVA glue.
- as paper adhesive during paper packaging converting
- in bookbinding and book arts, due to its flexible strong bond and non-acidic nature (unlike many other polymers). The use of PVAc on the Archimede Palimpsest during the 20th century greatly hindered the task of disbinding the book and preserving and imaging the pages in the early 21st century, in part because the glue was stronger than the parchment it held together.
- for handcrafted works.

Polytetrafluoroethylene



Polytetrafluoroethylene (PTFE) is a synthetic fluoropolymer of tetrafluoroethylene that finds numerous applications. The most well known brand name of PTFE is **Teflon** by DuPont Co.

PTFE is a fluorocarbon solid, as it is a high-molecular-weight compound consisting wholly of carbon and fluorine. PTFE is hydrophobic: neither water nor water-containing substances wet PTFE, as fluorocarbons demonstrate mitigated London dispersion forces due to the high electronegativity of fluorine. PTFE has one of the lowest coefficients of friction against any solid.

PTFE is used as a non-stick coating for pans and other cookware. It is very non-reactive, partly because of the strength of carbon-fluorine bonds, and so it is often used in containers and pipework for reactive and corrosive chemicals. Where used as a lubricant, PTFE reduces friction, wear, and energy consumption of machinery.

It is commonly believed that Teflon, like velcro, is a spin-off product from the NASA space projects. However, that is not so, even though both products have been used by NASA

History

PTFE was accidentally discovered in 1938 by Roy Plunkett, in New Jersey while he was working for Kinetic Chemicals. As Plunkett was attempting to make a new Chlorofluorocarbon refrigerant, the tetrafluoroethylene gas in its pressure bottle stopped flowing before the bottle's weight had dropped to the point signaling "empty." Since Plunkett was measuring the amount of gas used by weighing the bottle, he became curious as to the source of the weight, and finally resorted to sawing the bottle apart. Inside, he found it coated with a waxy white material which was oddly slippery. Analysis of the material showed that it was polymerized perfluoroethylene, with the iron from the inside of the container having acted as a catalyst at high pressure. Kinetic Chemicals patented the new fluorinated plastic (analogous to known polyethylene) in 1941,^[3] and registered the Teflon trademark in 1945.

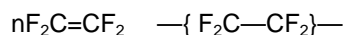
DuPont, which founded Kinetic Chemicals in partnership with General Motors, was producing over two million pounds (900 tons) of Teflon brand PTFE per year in Parkersburg, West Virginia, by 1948.^[6] An early advanced use was in the Manhattan Project as a material to coat valves and seals in the pipes holding highly reactive uranium hexafluoride at the vast K-25 uranium enrichment plant at Oak Ridge, Tennessee.^[7]

In 1954, French engineer Marc Grégoire created the first pan coated with Teflon non-stick resin under the brand name of Tefal after his wife urged him to try the material he had been using on fishing tackle on her cooking pans.^[8] In the United States, Kansas City, Missouri resident Marion

A. Trozzolo, who had been using the substance on scientific utensils, marketed the first US-made Teflon coated frying pan, "The Happy Pan", in 1961.^[9]

Formation

It is formed by the polymerization of tetrafluoroethylene:



Properties



PTFE is often used to coat non-stick frying pans as it is hydrophobic and possesses fairly high heat resistance.

PTFE is a thermoplastic polymer, which is a white solid at room temperature, with a density of about 2.2 g/cm^3 . According to DuPont, its melting point is 327°C (621°F), but its mechanical properties degrade above 260°C (500°F).^[10] PTFE gains its properties from the aggregate effect of carbon-fluorine bonds, as do all fluorocarbons.

| Property | Value |
|----------------------------|--|
| Density | 2200 kg/m^3 |
| <u>Melting point</u> | 327°C |
| <u>Thermal expansion</u> | $135 \cdot 10^{-6} \text{ K}^{-1}$ ^[11] |
| <u>Thermal diffusivity</u> | $0.124 \text{ mm}^2/\text{s}$ ^[12] |

| | |
|------------------------------------|---|
| <u>Young's modulus</u> | 0.5 GPa |
| <u>Yield strength</u> | 23 MPa |
| Bulk resistivity | $10^{18} \cdot \text{cm}$ ^[13] |
| Coefficient of friction | 0.05–0.10 |
| <u>Dielectric constant</u> | $\epsilon = 2.1, \tan(\delta) < 5(-4)$ |
| Dielectric constant (60 Hz) | $\epsilon = 2.1, \tan(\delta) < 2(-4)$ |
| <u>Dielectric strength</u> (1 MHz) | 60 MV/m |

The coefficient of friction of plastics is usually measured against polished steel. PTFE's coefficient of friction is 0.05 to 0.10,^[10] which is the third-lowest of any known solid material (BAM being the first, with a coefficient of friction of 0.02; diamond-like carbon being second-lowest at 0.05). PTFE's resistance to van der Waals forces means that it is the only known surface to which gecko cannot stick.^[11]

PTFE has excellent dielectric properties. This is especially true at high radio frequencies, making it suitable for use as an insulator in cables and connector assemblies and as a material for printed circuit boards used at microwave frequencies. Combined with its high melting temperature, this makes it the material of choice as a high-performance substitute for the weaker and lower melting point polyethylene that is commonly used in low-cost applications.

Because of its chemical inertness, PTFE cannot be cross-linked like an elastomer. Therefore, it has no "memory" and is subject to creep. This is advantageous when used as a seal, because the material creeps a small amount to conform to the mating surface. However, to keep the seal from creeping too much, fillers are used, which can also improve wear resistance and reduce friction. Sometimes, metal springs apply continuous force to PTFE seals to give good contact, while permitting a beneficially low percentage of creep.

Thermosetting polymer

A thermosetting plastic, also known as a thermoset, is polymer material that irreversibly cures. The cure may be done through heat (generally above 200 °C (392 °F)), through a chemical reaction (two-part epoxy, for example), or irradiation such as electron beam processing.

Thermoset materials are usually liquid or malleable prior to curing and designed to be molded into their final form, or used as adhesives. Others are solids like that of the molding compound used in semiconductors and integrated circuits (IC). Once hardened a thermoset resin cannot be reheated and melted back to a liquid form.

According to IUPAC recommendation: A thermosetting polymer is a prepolymer in a soft solid or viscous state that changes irreversibly into an infusible, insoluble polymer network by curing. Curing can be induced by the action of heat or suitable radiation, or both. A cured thermosetting polymer is called a thermoset.

Process

The curing process transforms the resin into a plastic or rubber by a cross-linking process. Energy and/or catalysts are added that cause the molecular chains to react at chemically active sites (unsaturated or epoxy sites, for example), linking into a rigid, 3-D structure. The cross-linking process forms a molecule with a larger molecular weight, resulting in a material with a higher meltingpoint. During the reaction, the molecular weight has increased to a point so that the melting point is higher than the surrounding ambient temperature, the material forms into a solid material.

Uncontrolled reheating of the material results in reaching the decomposition temperature before the melting point is obtained. Therefore, a thermoset material cannot be melted and re-shaped after it is cured. This implies that thermosets cannot be recycled, except as filler material

Properties

Thermoset materials are generally stronger than thermoplastic materials due to this three dimensional network of bonds (cross-linking), and are also better suited to high-temperature applications up to the decomposition temperature. However, they are more brittle. Many thermosetting polymers are difficult to recycle.

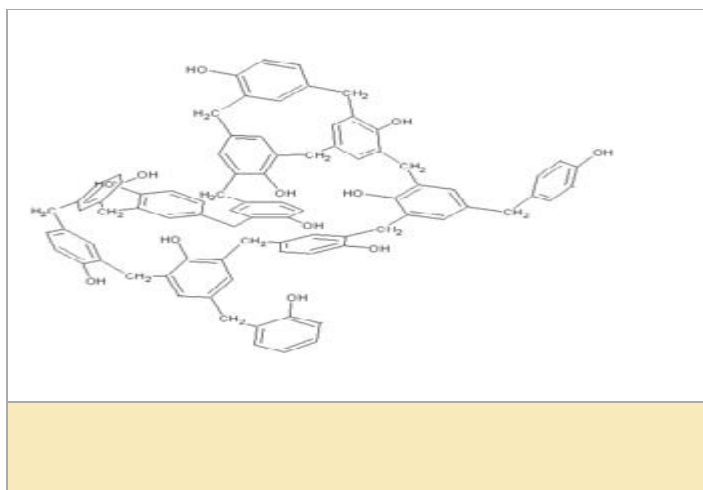
Examples

- Polyester fibreglass systems: sheet molding compounds and bulk molding compounds)

- Vulcanized rubber
- Bakelite, a phenol-formaldehyde resin used in electrical insulators and plasticware
- Duroplast, light but strong material, similar to bakelite used for making car parts
- Urea-formaldehyde foam used in plywood, particleboard and medium-density fiberboard
- Melamine resin used on worktop surfaces^[3]
- Epoxy resin used as the matrix component in many fiber reinforced plastics such as glass reinforced plastic and graphite-reinforced plastic)
- Polyimides used in printed circuit boards and in body parts of modern airplanes
- Cyanate esters or polycyanurates for electronics applications with high demands on dielectric properties and high glass temperature requirements in composites
- Mold or mold runners (the black plastic part in integrated circuits or semiconductors)

Phenol formaldehyde resin

Phenol formaldehyde resin



Phenol formaldehyde resins (PF) are synthetic polymers obtained by the reaction of phenol or substituted phenol with formaldehyde. Phenolic resins are mainly used in the production of circuit boards. They are better known however for the production of molded products including pool balls, laboratory countertops, and as coatings and adhesives. In the form of Bakelite, they are the earliest commercial synthetic resin.

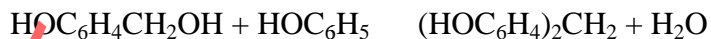
Formation and structure

Phenol-formaldehyde resins, as a group, are formed by a step-growth polymerization reaction that can be either acid- or base-catalysed. Since formaldehyde exists predominantly in solution as a dynamic equilibrium of methylene glycol oligomers, the concentration of the *reactive* form of formaldehyde depends on temperature and pH.

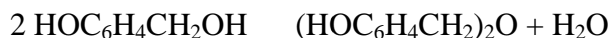
Phenol is reactive towards formaldehyde at the ortho and para sites (sites 2, 4 and 6) allowing up to 3 units of formaldehyde to attach to the ring. The initial reaction in all cases involves the formation of a hydroxymethyl phenol:



The hydroxymethyl group is capable of reacting with either another free ortho or para site, or with another hydroxymethyl group. The first reaction gives a methylene bridge, and the second forms an ether bridge:



The diphenol $(\text{HOC}_6\text{H}_4)_2\text{CH}_2$ (sometimes called a "dimer") is called bisphenol F, which is itself an important monomer in the production of epoxy resins. Bisphenol-F can further link generating tri- and tetra- and higher phenol oligomers.



Novolac

Novolacs (originally Novolak, the name given by Leo Baekeland) are phenol-formaldehyde resins made where the molar ratio of formaldehyde to phenol is less than one. The polymerization is brought to completion using acid-catalysis such as oxalic acid, hydrochloric acid or sulfonate acids. The phenol units are mainly linked by methylene and/or ether groups. Novolacs are commonly used as photoresists. The molecular weights are in the low thousands, corresponding to about 10-20 phenol units.

Hexamethylenetetramine or "hexamine" is a hardener that is added to crosslink novolac. At a temperature $>90^{\circ}\text{C}$, the hexamine forms crosslinks to form methylene and dimethylene amino bridges.

Resols

Base-catalysed phenol-formaldehyde resins are made with a formaldehyde to phenol ratio of greater than one (usually around 1.5). These resins are called resols. Phenol, formaldehyde, water and catalyst are mixed in the desired amount, depending on the resin to be formed, and are then heated. The first part of the reaction, at around 70°C , forms a thick reddish-brown tacky material, which is rich in hydroxymethyl and benzylic ether groups.

The rate of the base-catalysed reaction initially increases with pH, and reaches a maximum at about $\text{pH} = 10$. The reactive species is the phenoxide anion ($\text{C}_6\text{H}_5\text{O}^-$) formed by deprotonation of phenol. The negative charge is delocalised over the aromatic ring, activating sites 2, 4 and 6, which then react with the formaldehyde.

Being thermosets, hydroxymethyl phenols will crosslink on heating to around 120°C to form methylene and methyl ether bridges through eliminating water molecules. At this point the resin is a 3-dimensional network, which is typical of polymerised phenolic resins. The high crosslinking gives this type of phenolic resin its hardness, good thermal stability, and chemical imperviousness. Resols are referred to as "one step" resins as they cure without a cross linker unlike novolacs, a "two step" resin.

Resoles are major polymeric resin materials widely used for gluing and bonding building materials. Exterior plywood, oriented strand boards (OSB), engineered laminated composite lumber (LCL) are some of typical applications.

Crosslinking and the phenol/formaldehyde ratio

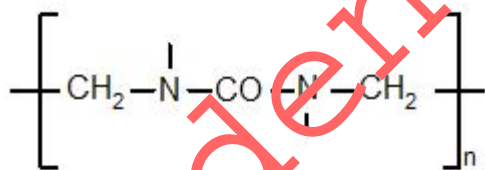
When the molar ratio of formaldehyde:phenol reaches one, in theory every phenol is linked together via methylene bridges, generating one single molecule, and the system is entirely crosslinked. This is why novolacs (F:P <1) don't harden without the addition of a crosslinking agent, and why resoles with the formula F:P >1 will.

Applications

Phenolic resins are found in myriad industrial products. Phenolic laminates are made by impregnating one or more layers of a base material such as paper, fiberglass or cotton with phenolic resin and laminating the resin-saturated base material under heat and pressure. The resin fully polymerizes (cures) during this process. The base material choice depends on the intended application of the finished product. Paper phenolics are used in manufacturing electrical components such as punch-through boards and household laminates. Glass phenolics are particularly well suited for use in the high speed bearing market. Phenolic micro-balloons are used for density control. Snooker balls as well as balls from many table-based ball games are also made from phenol formaldehyde resin. The binding agent in normal (organic) brake pads, brake shoes and clutch disks are phenolic resin.

The Dutch forger Han van Meegeren mixed phenol formaldehyde with his oil paints before baking the finished canvas in order to fake the drying out of the paint over the centuries.

Urea-formaldehyde



Urea-formaldehyde, also known as **urea-methanal**, named so for its common synthesis pathway and overall structure,^[1] is a non-transparent thermosetting resin or plastic, made from urea and formaldehyde heated in the presence of a mild base such as ammonia or pyridine. These resins are used in adhesives, finishes, MDF, and molded objects.

Properties

Urea-formaldehyde resin's attributes include high tensile strength, flexural modulus, and heat distortion temperature, low water absorption, mould shrinkage, high surface hardness, elongation at break, and volume resistance.

Chemical structure

The chemical structure of UF resins can be described as that of polymethylene. This description leaves the details of the structure undetermined, which can vary linearly and branched. These are grouped by their average molar mass and the content of different functional groups. Changing synthesis conditions of the resins give good designing possibilities for the structure and resin properties.

Production

There is approximately 1 million metric tons of urea-formaldehyde produced every year. Over 70% of this production is then put into use by the forest industry products. It produces a great resin for bonding particleboard (61%), medium density fiberboard (27%), hardwood plywood (5%), and laminating adhesive (7%).

General uses



A range of objects made from urea-formaldehyde

Urea-Formaldehyde is everywhere and used in many manufacturing processes due to its useful properties. Examples include decorative laminates, textiles, paper, foundry sand molds, wrinkle resistant fabrics, cotton blends, rayon, corduroy, etc. It is also used to glue wood together. Urea formaldehyde was commonly used when producing electrical appliances casing (e.g. desk lamps).

The product is widely chosen as an adhesive resin due to its high reactivity, good performance, and low price. Urea-formaldehyde resin is a chemical combination of urea and formaldehyde. Amino resins are considered a class of thermosetting resins of which urea-formaldehyde resins make up 80% produced globally. Examples of amino resins include automobile tires in order to improve the bonding of rubber to tire cord, paper for improving tear strength, molding electrical devices, molding jar caps, etc.

Agricultural use

Urea formaldehyde is also used in agriculture as a controlled release source of nitrogen fertilizer. Urea formaldehyde's rate of decomposition into CO_2 and NH_3 is determined by the action of microbes found naturally in most soils. The activity of these microbes, and, therefore, the rate of nitrogen release, is temperature dependent. The optimum temperature for microbe activity is approximately 70-90 °F (approx 20-30°C).

Urea-formaldehyde foam insulation

Urea-formaldehyde foam insulation (UFFI) can make a great synthetic insulation. It is basically foam like shaving cream and easily injected into walls with a hose. It is made by using a pump set and hose with a mixing gun to mix the foaming agent and resin. The liquid foam is sprayed into areas in need of insulation. It hardens within minutes but cures within a week. UFFI is generally spotted in homes built before the seventies; one should look in basements, crawl spaces, attics, and unfinished attics. Visually it looks like oozing liquid that has been hardened. Over time, it tends to vary in shades of butterscotch but new UFFI is a light yellow color. Early forms of UFFI tended to shrink significantly though updated catalysts and foaming technology have reduced shrinkage to minimal levels (between 2-4%). The foam dries with a dull matte color with no shine. It will be a dry and crumbly texture.

Elastomer

An **elastomer** is a polymer with viscoelasticity (colloquially "elasticity"), generally having low Young's modulus and high yield strain compared with other materials. The term, which is derived from *elastic polymer*, is often used interchangeably with the term rubber, although the latter is preferred when referring to vulcanisates. Each of the monomers which link to form the polymer is usually made of carbon, hydrogen, oxygen and/or silicon. Elastomers are amorphous polymers existing above their glass transition temperature, so that considerable segmental motion is possible. At ambient temperatures, rubbers are thus relatively soft ($E \sim 3\text{MPa}$) and deformable. Their primary uses are for seals, adhesives and molded flexible parts.

Examples of elastomers

Unsaturated rubbers that can be cured by sulfur vulcanization:

- Natural polyisoprene: cis-1,4-polyisoprene natural rubber (NR) and trans-1,4-polyisoprene gutta-percha
- Synthetic polyisoprene (IR for Isoprene Rubber)
- Polybutadiene (BR for Butadiene Rubber)
- Chloroprene rubber (CR), polychloroprene, Neoprene, Baypren etc.

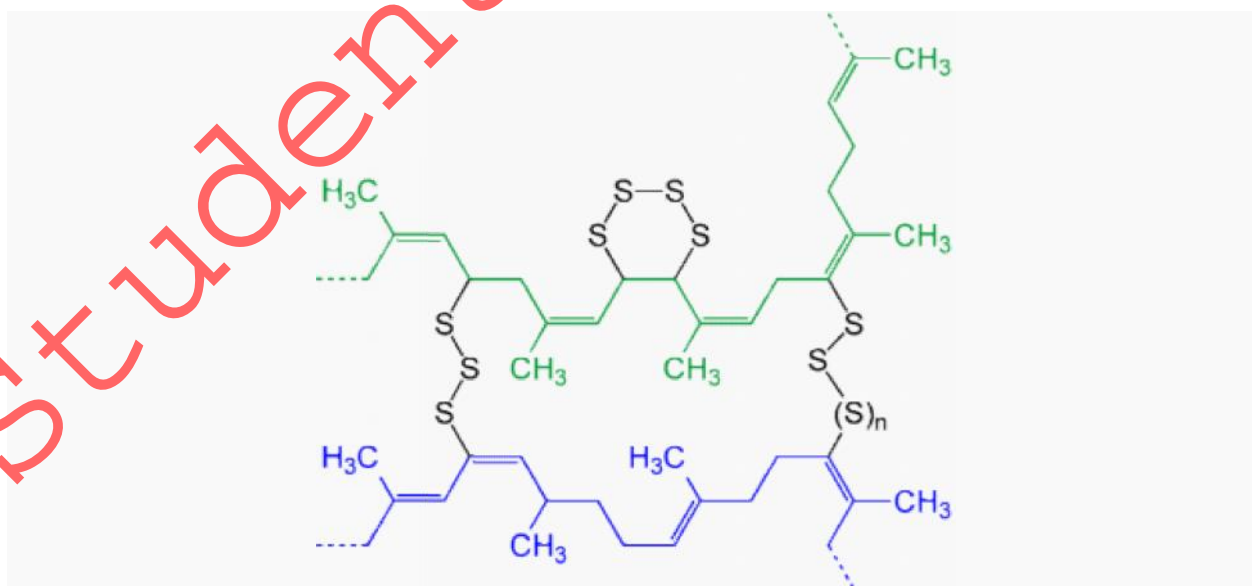
- Styrene-butadiene Rubber (copolymer of styrene and butadiene, SBR)
- Nitrile rubber (copolymer of butadiene and acrylonitrile, NBR), also called Buna N rubbers.

Vulcanization of Rubber

Vulcanization or **vulcanisation** is a chemical process for converting rubber or related polymers into more durable materials via the addition of sulfur or other equivalent "curatives." These additives modify the polymer by forming crosslinks (bridges) between individual polymer chains.^[1] Vulcanized materials are less sticky and have superior mechanical properties. A vast array of products are made with vulcanized rubber including tires, shoe soles, hoses, and hockey pucks. The process is named after Vulcan, Roman god of fire. Hard vulcanized rubber is sometimes sold under the brand names ebonite or vulcanite, and is used to make hard articles such as bowling balls and saxophone mouth pieces.

Natural vs vulcanized rubber

Uncured natural rubber is sticky, deforms easily when warm, and is brittle when cold. In this state, it is a poor material when a high level of elasticity is required. The reason for inelastic deformation of un-vulcanized rubber can be found in its chemical structure: rubber is composed of long polymer chains. These chains can move independently relative to each other, which lets the material change shape. Crosslinking introduced by vulcanization prevents the polymer chains from moving independently. As a result, when stress is applied the vulcanized rubber deforms, but upon release of the stress, the article reverts to its original shape.



Schematic presentation of two strains (**blue** and **green**) of natural rubber after vulcanization with elemental sulfur.

Process

Vulcanization is generally irreversible, similar to other thermosets and in contrast to thermoplastic processes (the melt-freeze process) that characterize the behavior of most modern polymers. The cross-linking is usually done with sulfur, but other technologies are known, including peroxide-based systems.

The main polymers subjected to vulcanization are polyisoprene (natural rubber) and styrene-butadiene rubber (SBR), which are used for most passenger tires. The "cure package" is adjusted specifically for the substrate and the application. The reactive sites—"cure sites"—are allylic hydrogen atoms. These C-H bonds are adjacent to carbon-carbon double bonds. During vulcanization, some of these C-H bonds are replaced by chains of sulfur atoms that link with a cure site of another polymer chain. These bridges contain between one and eight atoms. The number of sulfur atoms in the crosslink strongly influences the physical properties of the final rubber article. Short crosslinks give the rubber better heat resistance. Crosslinks with higher number of sulfur atoms give the rubber good dynamic properties but with lesser heat resistance. Dynamic properties are important for flexing movements of the rubber article, e.g., the movement of a side-wall of a running tire. Without good flexing properties these movements rapidly form cracks and, ultimately, make the rubber article fail.



"Vulcanization curve" showing the increase in viscosity of the polymeric material during crosslinking. The steepness of the curve is strongly affected by the nature of the accelerators and other additives.

Vulcanization methods

A variety of methods exist for vulcanization. The economically most important method (vulcanization of tires) uses high pressure and temperature. A typical vulcanization temperature for a passenger tire is 10 minutes at 170 °C. This type of vulcanization is called compression molding. The rubber article is intended to adopt the shape of the mold. Other methods, for instance to make door profiles for cars, use hot air vulcanization or microwave heated vulcanization (both continuous processes).

Synthetic rubber

Synthetic rubber is any type of artificial elastomer, invariably a polymer. An elastomer is a material with the mechanical (or material) property that it can undergo much more elastic deformation under stress than most materials and still return to its previous size without permanent deformation. About 15 billion kilograms of rubbers are produced annually, and of that amount two thirds is synthetic.

Styrene-butadiene

Styrene-butadiene or **styrene-butadiene rubber** (SBR) describe families of synthetic rubbers derived from styrene and butadiene. These materials have good abrasion resistance and good aging stability when protected by additives. About 50% of car tires are made from various types of SBR. The styrene/butadiene ratio influences the properties of the polymer: with high styrene content, the rubbers are harder and less rubbery.^[1] SBR is not to be confused with a thermoplastic elastomer made from the same monomers, styrene-butadiene block copolymer.

Types of SBR

SBR is derived from two monomers, styrene and butadiene. The mixture of these two monomers are polymerised by two basically different processes: from solution (S-SBR) or as an emulsion (E-SBR).^[2]

Emulsion polymerisation

E-SBR produced by emulsion polymerisation is initiated by free radicals. Reaction vessels are typically charged with the two monomers, a free radical generator, and a chain transfer agent such as an alkyl mercaptan. Radical initiators include potassium persulfate and hydroperoxides in combination with ferrous salts. Emulsifying agents include various soaps. By "capping" the growing organic radicals, mercaptans (e.g. dodecylthiol), control the molecular weight, and hence the viscosity, of the product. E-SBR is more widely used. Typically, polymerizations are allowed to proceed only to ca. 70%, a method called "short stopping". In this way, various additives can be removed from the polymer.^[1]

Solution polymerisation

Solution-SBR is produced by an anionic polymerization process. Polymerisation is initiated by alkyl lithium compounds. Water is strictly excluded. The process is homogeneous (all components are dissolved), which provides greater control over the process, allowing tailoring of the polymer. The organolithium compound adds to one of the monomers, generating a carbanion that then adds to another monomer, and so on. Relative to E-SBR, S-SBR is increasingly favored because it offers improved wet grip and rolling resistance, which translate to greater safety and better fuel economy, respectively..^[3]

Buna S

The material was initially marketed with the brand name **Buna S**. Its name derives Bu for butadiene and Na for sodium (natrium in several languages including Latin, German and Dutch), and **S** for styrene.

Properties

| Property | S-SBR | E-SBR |
|-----------------------------------|-------|-------|
| Tensile strength (MPa) | 18 | 19 |
| Elongation at tear (%) | 565 | 635 |
| Mooney viscosity (100 °C) | 48.0 | 51.5 |
| Glass transition temperature (°C) | -65 | -50 |
| Polydispersity | 2.1 | 4.5 |

Applications

The elastomer is used widely in pneumatic tires, shoe heels and soles, gaskets and even chewing gum. It is a commodity material which competes with natural rubber. Latex (emulsion) SBR is extensively used in coated papers, being one of the most cost-effective resins to bind pigmented coatings. It is also used in building applications, as a sealing and binding agent behind renders as an alternative to PVA, but is more expensive. In the latter application, it offers better durability, reduced shrinkage and increased flexibility, as well as being resistant to emulsification in damp conditions. SBR can be used to 'tank' damp rooms or surfaces, a process in which the rubber is painted onto the entire surface (sometimes both the walls, floor and ceiling) forming a continuous, seamless damp proof liner; a typical example would be a basement.

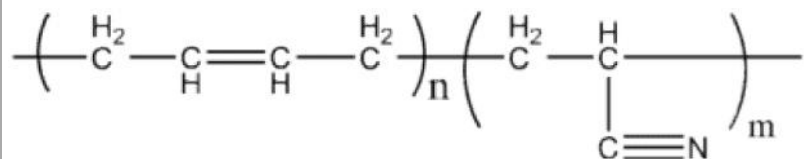
Additionally, it is used in some rubber cutting boards.

History

SBR is a replacement for natural rubber. It was originally developed prior to World War II in Germany. Industrial manufacture began during World War 2, where it was used extensively to replace the Far-East natural rubber supplies captured by the Japanese.

Nitrile rubber(NBR or Buna –N or GR –N)

Nitrile rubber



Nitrile rubber, also known as **Buna-N**, **Perbunan**, or **NBR**, is a synthetic rubber copolymer of acrylonitrile (ACN) and butadiene. Trade names include **Nipol**, **Krynac** and **Europrene**.

Nitrile butadiene rubber (NBR) is a family of unsaturated copolymers of 2-propenenitrile and various butadiene monomers (1,2-butadiene and 1,3-butadiene). Although its physical and chemical properties vary depending on the polymer's composition of nitrile, this form of synthetic rubber is generally resistant to oil, fuel, and other chemicals (the more nitrile within the polymer, the higher the resistance to oils but the lower the flexibility of the material).

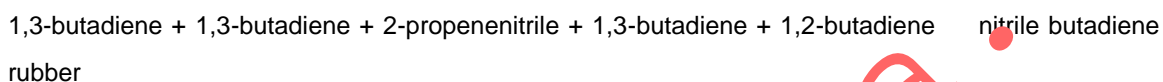
It is used in the automotive and aeronautical industry to make fuel and oil handling hoses, seals, and grommets. It is used in the nuclear industry to make protective gloves. NBR's ability to withstand a range of temperatures from -40 °C to +108 °C makes it an ideal material for aeronautical applications. Nitrile butadiene is also used to create moulded goods, footwear, adhesives, sealants, sponges, expanded foams, and floor mats.

Its resilience makes NBR a useful material for disposable lab, cleaning, and examination gloves. Nitrile rubber is more resistant than natural rubber to oils and acids, but has inferior strength and flexibility. Nitrile gloves are nonetheless three times more puncture-resistant than natural rubber gloves.^[1]

Nitrile rubber is generally resistant to aliphatic hydrocarbons. Nitrile, like natural rubber, can be attacked by ozone, aromatic hydrocarbons, ketones, esters and aldehydes.

Production

Emulsifier (soap), 2-propenenitrile, various butadiene monomers (including 1,3-butadiene, 1,2-butadiene), radical generating activators, and a catalyst are added to polymerization vessels in the production of hot NBR. Water serves as the reaction medium within the vessel. The tanks are heated to 30–40 °C to facilitate the polymerization reaction and to promote branch formation in the polymer. Because several monomers capable of propagating the reaction are involved in the production of nitrile rubber the composition of each polymer can vary (depending on the concentrations of each monomer added to the polymerization tank and the conditions within the tank). One repeating unit found throughout the entire polymer may not exist. For this reason there is also no IUPAC name for the general polymer. The reaction for one possible portion of the polymer is shown below:



Monomers are usually permitted to react for 5 to 12 hours. Polymerization is allowed to proceed to ~70% conversion before a “shortstop” agent (such as dimethyldithiocarbamate and diethyl hydroxylamine) is added to react with the remaining free radicals. Once the resultant latex has “shortstopped”, the unreacted monomers are removed through a steam in a slurry stripper. Recovery of unreacted monomers is close to 100%. After monomer recovery, latex is sent through a series of filters to remove unwanted solids and then sent to the blending tanks where it is stabilized with an antioxidant. The yielded polymer latex is coagulated using calcium nitrate, aluminium sulfate, and other coagulating agents in an aluminium tank. The coagulated substance is then washed and dried to crumb rubber.

The process for the production of cold NBR is very similar to that of hot NBR. Polymerization tanks are heated to 5–15 °C instead of 30–40 °C. Under lower temperature conditions, less branching will form on polymers (the amount of branching distinguishes cold NBR from hot NBR).

Applications



A disposable nitrile rubber glove. Nitrile gloves are available in different colours, the most common being blue and purple

The uses of nitrile rubber include non-latex gloves for the healthcare industry, automotive transmission belts, hoses, O rings, gaskets, oil seals, V belts, synthetic leather, printer's roller, and as cable jacketing; NBR latex can also be used in the preparation of adhesives and as a pigment binder.

Unlike polymers meant for ingestion, where small inconsistencies in chemical composition/structure can have a pronounced effect on the body, the general properties of NBR are not altered by minor structural/compositional differences. The production process itself is not overly complex, the polymerization, monomer recovery, and coagulation processes require some additives and equipment, but they are typical of the production of most rubbers. The necessary apparatus is simple and easy to obtain. For these reasons, the substance is widely produced in poorer countries where labor is relatively cheap. Among the highest producers of NBR are mainland China and Taiwan.

A hydrogenated version of nitrile rubber, HNBR, also known as HSN (highly saturated nitrile) is commonly used to manufacture o-rings for automotive air-conditioning systems.^[2]

In January 2008 the European Commission imposed fines totaling €34,230,000 on the Bayer and Zeon groups for fixing prices for nitrile butadiene rubber, in violation of the EU ban on cartels and restrictive business practices (Article 81 of the EC Treaty and Article 3 of the EEA Agreement).^[3]

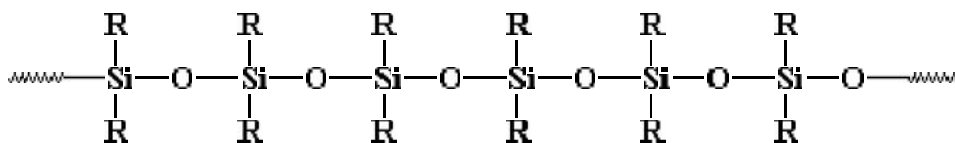
Criminals have also been known to wear these gloves during the commission of their crimes. These gloves are often chosen because of their tight, thin fit that allows the hands to remain dexterous. Ironically, because of the thinness of these gloves, fingerprints may actually pass through the material as glove prints, thus transferring the wearer's prints onto whatever surface is touched or handled.^{[4][5]}

Dangers

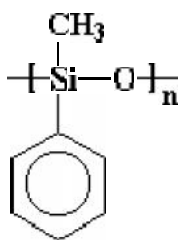
Do not use these gloves when working with red fuming nitric acid, as sudden combustion of these two chemicals could cause serious chemical burns. Caution must be taken when working with the acid and the gloves at the same time.

Silicone

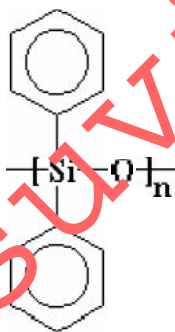
Silicones are used for a lot of things. They can be elastomers and lubricating oils. The caulking in your bathroom is probably made of a silicone. Silicones are also used to make the heat resistant tiles on the bottom of the space shuttle. Take a look at the picture on the right and you'll see how good silicones can be at deflecting heat. Back on earth, silicones are used to make hair conditioners that don't cause buildup.



Silicones are inorganic polymers, that is, there are no carbon atoms in the backbone chain. The backbone is a chain of alternating silicon and oxygen atoms. Each silicon has two groups attached to it, and these can be any organic groups. The picture at the top of this page shows methyl groups attached to the silicon atoms. This polymer is called polydimethylsiloxane. It is the most common silicone. Want to see some others? Polymethylphenylsiloxane and polydiphenylsiloxane are also popular with the kids these days.

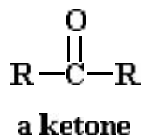
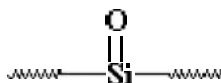


polymethylphenylsiloxane



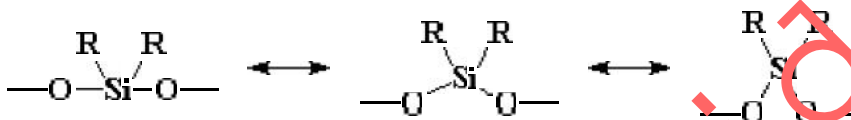
polydiphenylsiloxane

"Polysiloxane" is the proper name for silicones. But when they were discovered it was thought that they had "silicone" groups in the backbone chain. When the real structure was discovered, it was too late, and the name stuck.



Scientists once thought this was the structure of polysiloxanes, so they named them "silicones", by comparison carbon-containing ketones, shown on the right. Of course, this is not the structure.

Silicones make good elastomers because the backbone chain is very flexible. The bonds between a silicon atom and the two oxygen atoms attached to it are very flexible. The angle formed by these bonds can open and close like a scissors without much trouble. This makes the whole backbone chain flexible.



If you want to know how to make silicones, [click here](#)

Polydimethylsiloxane does something really strange when you mix it with boric acid, or $\text{B}(\text{OH})_3$. The mixture is soft and pliable, you can mold it into any shape easily with your fingers. But it is also very bouncy. What's more, push it gently and it gives way, but hit it hard with a hammer and it cracks! Strangely, if you spread it over newspaper, and pull it away, it gets printed with a mirror image of the newspaper text. No industrial use was ever found for this wonder material, but tons of it have been sold as toy called Silly Putty.

Silicones are inert, synthetic compounds with a variety of forms and uses. Typically heat-resistant and rubber-like, they are used in sealants, adhesives, lubricants, medical applications (e.g., breast implants), cookware, and insulation.

Silicones are polymers that include silicon together with carbon, hydrogen, oxygen, and sometimes other chemical elements. Some common forms include silicone oil, silicone grease, silicone rubber, and silicone resin.

Properties

Some of the most useful properties of silicones include:

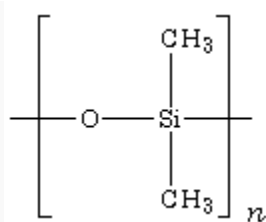
- Low thermal conductivity
- Low chemical reactivity
- Low toxicity
- Thermal stability (constancy of properties over a wide temperature range of –100 to 250 °C).
- The ability to repel water and form watertight seals, although silicones are not hydrophobes.
- Does not stick to many substrates, but adheres very well to others, e.g. glass.
- Does not support microbiological growth.

Silicones have excellent resistance to oxygen, ozone, and ultraviolet (UV) light. This property has led to widespread use of silicones in the construction industry (e.g. coatings, fire protection, glazing seals) and the automotive industry (external gaskets, external trim).

- Good electrical insulation. Because silicone can be formulated to be electrically insulative or conductive, it is suitable for a wide range of electrical applications.

They have high gas permeability: at room temperature (25 °C), the permeability of silicone rubber for such gases as oxygen is approximately 400 times ^[citation needed] that of butyl rubber, making silicone useful for medical applications in which increased aeration is desired. Consequently, silicone rubbers cannot be used where gas-tight seals are necessary.

Chemistry



Chemical structure of the silicone polydimethylsiloxane (PDMS).

More precisely, called polymerized siloxanes or polysiloxanes, silicones are mixed inorganic-organic polymers with the chemical formula $[R_2SiO]_n$, where R is an organic group such as methyl, ethyl, or phenyl. These materials consist of an inorganic silicon-oxygen backbone ($\cdots Si-O-Si-O-Si-O\cdots$) with organic side groups attached to the silicon atoms, which are four-coordinate.

In some cases, organic side groups can be used to link two or more of these -Si-O- backbones together. By varying the -Si-O- chain lengths, side groups, and crosslinking, silicones can be

synthesized with a wide variety of properties and compositions. They can vary in consistency from liquid to gel to rubber to hard plastic. The most common siloxane is linear polydimethylsiloxane (PDMS), a silicone oil. The second largest group of silicone materials is based on silicone resins, which are formed by branched and cage-like oligosiloxanes.

Synthesis

Silica (silicon dioxide), common in sandstone, beach sand, and similar natural materials, is the initial material from which silicones are produced; silica is also widely used in producing glass. Silicones are synthesized from chlorosilanes, tetraethoxysilane, and related compounds.

In producing the silicone PDMS, the starting material is dimethyldichlorosilane, which reacts with water as follows:



During polymerization, this reaction evolves hazardous hydrogen chloride gas.

For consumer and medical uses, a process was developed in which the chlorine atoms in the silane precursor were replaced with acetate groups, which produce the less dangerous acetic acid (the acid found in vinegar) as the reaction product of a much slower curing process. This chemistry is used in many consumer applications, such as silicone caulk and adhesives.

Branches or cross-links in the polymer chain can be introduced by using silane precursors with more acid-forming groups and fewer methyl groups, such as methyltrichlorosilane. Ideally, each molecule of such a compound becomes a branch point. This process can be used to produce hard silicone resins. Similarly, precursors with three methyl groups can be used to limit molecular weight, since each such molecule has only one reactive site and so forms the end of a siloxane chain. Modern silicone resins are generally made using tetraethoxysilane, which reacts in a more mild and controllable manner than chlorosilanes.

Combustion

When silicone is burned in air or oxygen, it forms solid silica (silicon dioxide) as a white powder, char, and various gases. The readily dispersed powder is sometimes called silica fume.

Uses

Silicones are used in many familiar products, and included as components in diverse others.

Aquarium joints

In making aquariums, manufacturers now commonly use 100% silicone sealant to join glass plates. Glass joints made with silicone sealant can withstand great pressure, making obsolete the original aquarium construction method of angle-iron and putty. This same silicone is used to make hinges in aquarium lids or for minor repairs. However, not all commercial silicones are safe for aquarium manufacture, nor is silicone used for the manufacture of acrylic aquariums as silicones do not have long-term adhesion to plastics.^[8]

Automotive

In the automotive field, silicone grease is typically used as a lubricant for brake components since it is stable at high temperatures, is not water-soluble, and is far less likely than other lubricants to foul. Automotive spark plug wires are insulated by multiple layers of silicone to prevent sparks from jumping to adjacent wires, causing misfires. Silicone tubing is sometimes used in automotive intake systems (especially for engines with forced induction). Sheet silicone is used to manufacture gaskets used in automotive engines, transmissions, and other applications. Automotive body manufacturing plants and paint shops avoid silicones, as they may cause "fish eyes", small, circular craters in the finish. Additionally, silicone compounds such as silicone rubber are used as coatings and sealants for airbags; the high strength of silicone rubber makes it an optimal adhesive/sealant for high impact airbags.

Coatings

Silicone films can be applied to such silica-based substrates as glass to form a covalently bonded hydrophobic coating.

Many fabrics can be coated or impregnated with silicone to form a strong, waterproof composite such as silnylon.

Cookware



Soup ladle and pasta ladle made of silicone.

- As a low-taint, non-toxic material, silicone can be used where contact with food is required. Silicone is becoming an important product in the cookware industry, particularly bakeware and kitchen utensils.
- Silicone is used as an insulator in heat resistant potholders and similar items, however it is more conductive of heat than similar less dense fiber-based products. Silicone oven mitts are able to withstand temperatures up to 260 °C (500 °F), allowing reaching into boiling water.
- Molds for chocolate, ice, cookies, muffins and various other foods.
- Non-stick reusable mats used on baking sheets.
- Other products such as steamers, egg boilers or poachers, cookware lids, pot holders, trivets, and kitchen mats.

Defoaming

Silicones are used as active compound in defoamers due to their low water solubility and good spreading properties.

Dry cleaning

Liquid silicone can be used as a dry cleaning solvent, providing an "environmentally friendly" alternative to the traditional chlorine-containing perchloroethylene (perc) solvent. Also, liquid silicone is chemically inert, not reacting with fabrics or dyes during the cleaning process, thus reducing the amount of fading and shrinking experienced by many garments

dry-cleaned with the more reactive perc. Use of silicones in dry cleaning reduces the environmental impact of a typically high-polluting industry. A siloxane-based decamethylpentacyclosiloxane (DS) process has been patented by the company GreenEarth Cleaning.

Electronics

Electronic components are sometimes encased in silicone to increase stability against mechanical and electrical shock, radiation and vibration, a process called "potting".

Silicones are used where durability and high performance are demanded of components under hard conditions, such as in space (satellite technology). They are selected over polyurethane or epoxy encapsulation when a wide operating temperature range is required (−65 to 315 °C). Silicones also have the advantage of little exothermic heat rise during cure, low toxicity, good electrical properties and high purity.

The use of silicones in electronics is not without problems, however. Silicones are relatively expensive and can be attacked by solvents.^[9] Silicone easily migrates as either a liquid or vapor onto other components.

Silicone contamination of electrical switch contacts can lead to failures by causing an increase in contact resistance, often late in the life of the contact, well after any testing is completed.^{[10][11]} Use of silicone-based spray products in electronic devices during maintenance or repairs can cause later failures.

Firestops

Silicone foam has been used in North American buildings in an attempt to firestop openings within fire-resistance-rated wall and floor assemblies to prevent the spread of flames and smoke from one room to another. When properly installed, silicone-foam firestops can be fabricated for building code compliance. Advantages include flexibility and high dielectric strength. Disadvantages include combustibility (hard to extinguish) and significant smoke development.

However, silicone-foam firestops have been the subject of controversy and press attention due to smoke development from pyrolysis of combustible components within the foam, hydrogen gas escape, shrinkage, and cracking. These problems have been exposed by whistleblower Gerald W. Brown, and have led to reportable events among licensees (operators of nuclear power plants) of the Nuclear Regulatory Commission (NRC).

Lubricants

Silicone greases are used for many purposes, such as bicycle chains, airsoft gun parts, and a wide range of other mechanisms. Typically, a dry-set lubricant is delivered with a solvent carrier to penetrate the mechanism. The solvent then evaporates, leaving a clear film that lubricates but does not attract dirt and grit as much as an oil-based or other traditional "wet" lubricant.

Silicone personal lubricants are also available for use in medical procedures or sexual activity. See below.

Medicine

Silicone is used in microfluidics, seals, gaskets, shrouds, and other applications requiring high biocompatibility. Additionally the gel form, is used in bandages and dressings, energy bracelets, breast implants, testicle implants, pectoral implants, contact lenses, and a variety of other medical uses.

Scar treatment sheets (see silicone scar sheets) are often made of medical grade silicone due to its durability and biocompatibility. Polydimethylsiloxane is often used for this purpose, since its specific crosslinking results in a flexible and soft silicone with high durability and tack.

Polydimethylsiloxane (PDMS) has been used as the hydrophobic block of amphiphilic synthetic block copolymers used to form the vesicle membrane of polymersomes.

Moldmaking

Two-part silicone systems are used to create rubber molds used to cast resins, foams, rubber, and low-temperature alloys. A silicone mold generally requires little or no mold-release or surface preparation, as most materials do not adhere to silicone. For experimental uses, ordinary one-part silicone can be used to make molds or to mold into shapes. If needed, common vegetable cooking oils or petroleum jelly can be used on mating surfaces as a mold-release agent.

Toys

Silicone balls have become a juggler's favorite due to the high bounce back, and are used as a response system in low-response yo-yos. Silly Putty (a Crayola product) and similar materials include the silicones dimethyl siloxane, polydimethylsiloxane, and decamethyl cyclopentasiloxane, with other ingredients. This substance is noted for its unusual characteristics: It bounces, but breaks when given a sharp blow; it can also flow like a liquid, and will form a puddle given enough time.

The global demand on silicones approached US\$ 12.5 billion in 2008, approximately 4% up from the previous year. It continues similar growth in the following years to reach US\$13.5 billion by 2010. The annual growth is expected to rebound to 7% when the economy revives, boosted by broader applications, introduction of novel products and increasing awareness of using more environmentally friendly materials. The leading global manufacturers of silicone base materials belong to three regional organizations: the European Silicone Center (CES) in Brussels, Belgium; the Environment Health and Safety Council (SEHSC) in Herndon, Virginia, USA; and the Silicone Industry Association of Japan (SIAJ) in Tokyo, Japan.

Introduction to Polymeric composite

Any of the combinations or compositions that comprise two or more materials as separate phases, at least one of which is a polymer. By combining a polymer with another material, such as glass, carbon, or another polymer, it is often possible to obtain unique combinations or levels of properties. Typical examples of synthetic polymeric composites include glass-, carbon-, or polymer-fiber-reinforced thermoplastic or thermosetting resins, carbon-reinforced rubber, polymer blends, silica- or mica-reinforced resins, and polymer bonded or -impregnated concrete or wood. It is also often useful to consider as composites such materials as coatings (pigment-binder combinations) and crystalline polymers (crystallites in a polymer matrix). Typical naturally occurring composites include wood (cellulosic fibers bonded with lignin) and bone (minerals bonded with collagen). On the other hand, polymeric compositions compounded with a plasticizer or very low proportions of pigments or processing aids are not ordinarily considered as composites.

Typically, the goal is to improve strength, stiffness, or toughness, or dimensional stability by embedding particles or fibers in a matrix or binding phase. A second goal is to use inexpensive, readily available fillers to extend a more expensive or scarce resin; this goal is increasingly important as petroleum supplies become costlier and less reliable. Still other applications include the use of some fillers such as glass spheres to improve processability, the incorporation of dry-lubricant particles such as molybdenum sulfide to make a self-lubricating bearing, and the use of fillers to reduce permeability.

The most common fiber-reinforced polymer composites are based on glass fibers, cloth, mat, or roving embedded in a matrix of an epoxy or polyester resin. Reinforced thermosetting resins containing boron, polyaramids, and especially carbon fibers confer especially high levels of strength and stiffness. Carbon-fiber composites have a relative stiffness five times that of steel. Because of these excellent properties, many applications are uniquely suited for epoxy and polyester composites, such as components in new jet aircraft, parts for automobiles, boat hulls, rocket motor cases, and chemical reaction vessels.

Although the most dramatic properties are found with reinforced thermosetting resins such as epoxy and polyester resins, significant improvements can be obtained with many reinforced thermoplastic resins as well. Polycarbonates, polyethylene, and polyesters are among the resins available as glass-reinforced composition. The combination of inexpensive, one-step fabrication by injection molding, with improved properties has made it possible for reinforced

thermoplastics to replace metals in many applications in appliances, instruments, automobiles, and tools.

In the development of other composite systems, various matrices are possible; for example, polyimide resins are excellent matrices for glass fibers, and give a high-performance composite. Different fibers are of potential interest, including polymers [such as poly(vinyl alcohol)], single-crystal ceramic whiskers (such as sapphire), and various metallic fibers.

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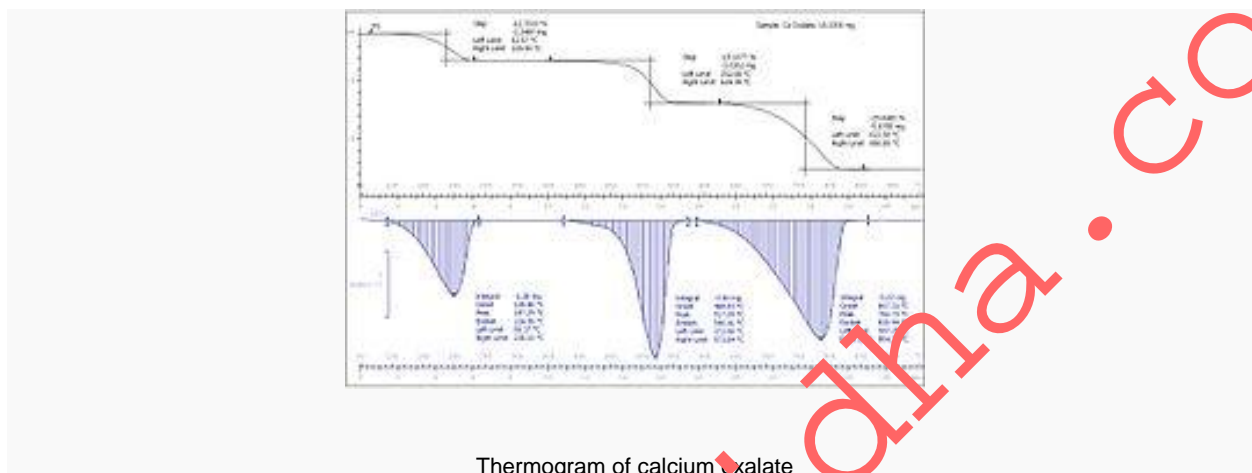
ANALYTICAL METHODS OF ANALYSIS

Thermogravimetric analysis

Thermogravimetric analysis or **thermal gravimetric analysis** is a type of testing performed on samples that determines changes in weight in relation to a temperature program in a controlled atmosphere. Such analysis relies on a high degree of precision in three measurements: weight, temperature, and temperature change. As many weight loss curves look similar, the weight loss curve may require transformation before results may be interpreted. A derivative weight loss curve can identify the point where weight loss is most apparent. Again, interpretation is limited without further modifications and deconvolution of the overlapping peaks may be required. To determine composition and purity one must take the mass of the substance in the mixture by using thermal gravimetric analysis. Thermal gravimetric analysis is the act of heating a mixture to a high enough temperature so that one of the components decomposes into a gas, which dissociates into the air. It is a process that utilizes heat and stoichiometry ratios to determine the percent by mass ratio of a solute. If the compounds in the mixture that remain are known, then the percentage by mass can be determined by taking the weight of what is left in the mixture and dividing it by the initial mass. Knowing the mass of the original mixture and the total mass of impurities liberating upon heating, the stoichiometric ratio can be used to calculate the percent mass of the substance in a sample. TGA is commonly employed in research and testing to determine characteristics of materials such as polymers, to determine degradation temperatures, absorbed moisture content of materials, the level of inorganic and organic components in materials, decomposition points of explosives, and solvent residues. It is also often used to estimate the corrosion kinetics in high temperature oxidation.

Simultaneous TGA-DTA/DSC measures both heat flow and weight changes (TGA) in a material as a function of temperature or time in a controlled atmosphere. Simultaneous measurement of these two material properties not only improves productivity but also simplifies interpretation of the results. The complementary information obtained allows differentiation between endothermic and exothermic events with no associated weight loss (e.g. melting and crystallization) and those that involve a weight loss (e.g. degradation).

Equipment



The analyzer usually consists of a high-precision balance with a pan (generally platinum) loaded with the sample. That pan resides in a furnace and is heated or cooled during the experiment. A different process using a quartz crystal microbalance has been devised for measuring smaller samples on the order of a microgram (versus milligram with conventional TGA).^[1] The sample is placed in a small electrically heated oven with a thermocouple to accurately measure the temperature. The atmosphere may be purged with an inert gas to prevent oxidation or other undesired reactions. A computer is used to control the instrument.

Methodology

TGA is a process that utilizes heat and stoichiometry ratios to determine the percent by mass of a solute. Analysis is carried out by raising the temperature of the sample gradually and plotting weight (percentage) against temperature. The temperature in many testing methods routinely reaches 1000°C or greater. After the data are obtained, curve smoothing and other operations may be done to find the exact points of inflection.

A method known as hi-resolution TGA is often employed to obtain greater accuracy in areas where the derivative curve peaks. In this method, temperature increase slows as weight loss increases. This is to more accurately identify the exact temperature where a peak occurs. Several modern TGA devices can vent burnoff to an infrared spectrophotometer to analyze composition.

APPLICATION OF TGA:-

Thermal Analysis of Pharma Materials

DSC, TG/DTA and TG/DTA-IR are often used for characterisation of pharma materials. DSC, alone or in combination with hot-stage microscopy, is able to differentiate between different polymorphic structures and, by using different heating rates, can investigate the transformations which occur during the polymorphic transformation. By using appropriate heating rates, polymorphic purity can be determined, and can involve heating rates up to 750°C/min. TGA is often used to measure residual solvents and moisture, but can also be used to determine solubility of pharma materials in solvents. Analysis of pharma materials is probably the largest area of application for thermal analysis.

Thermal Analysis of Polymers

Polymers represent another large area in which thermal analysis finds strong applications. Thermoplastic polymers are commonly found in everyday packaging and household items, but in the analysis of the raw materials, effects of the many additives used (including stabilisers and colours) and fine-tuning of the moulding or extrusion processing used can be achieved by using DSC. An example is oxidation induction time (OIT) by DSC which can determine the amount of oxidation stabiliser present in a thermoplastic (usually a polyolefin) polymer material. Compositional analysis is often made using TGA, which can separate fillers, polymer resin and other additives. TGA can also give an indication of thermal stability and the effects of additives such as flame retardants.

Thermal Analysis of Metals

Production of many metals (cast iron, grey iron, ductile iron, compacted graphite iron, 3000 series aluminium alloys, copper alloys, silver, and complex steels) are aided by a production technique also referred to as thermal analysis. A sample of liquid metal is removed from the furnace or ladle and poured into a sample cup with a thermocouple embedded in it. The temperature is then monitored, and the phase diagram arrests (liquidus, eutectic, and solidus) are noted. From this information chemical composition based on the phase diagram can be calculated, or the crystalline structure of the cast sample can be estimated. Strictly speaking, these measurements are *cooling curves* and a form of sample controlled thermal analysis whereby the cooling rate of the sample is dependent on the cup material (usually bonded sand) and sample volume which is normally a constant due to the use of standard sized sample cups.

Thermal Analysis of Foods

Most foods are subjected to variations in their temperature during production, transport, storage, preparation and consumption, e.g., pasteurization, sterilization, evaporation, cooking, freezing, chilling, etc. Temperature changes cause alterations in the physical and chemical properties of food components which influence the overall properties of the final product, e.g., taste, appearance, texture and stability. Chemical reactions such as hydrolysis, oxidation or reduction may be promoted, or physical changes, such as evaporation, melting, crystallization, aggregation or gelation may occur. A better understanding of the influence of temperature on the properties of foods enables food manufacturers to optimize

processing conditions and improve product quality. It is therefore important for food scientists to have analytical techniques to monitor the changes that occur in foods when their temperature varies. These

Thermal Analysis of Printed Circuit Boards (PCB)

Power dissipation is an important issue in present-day PCB design. Power dissipation will result in temperature difference and pose a thermal problem to a chip. In addition to the issue of reliability, excess heat will also negatively affect electrical performance and safety. The working temperature of an IC should therefore be kept below the maximum allowable limit of the worst case. In general, the temperatures of junction and ambient are 125 °C and 55 °C, respectively.

Differential scanning calorimetry

Differential scanning calorimetry or **DSC** is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned.

The technique was developed by E.S. Watson and M.J. O'Neill in 1962, and introduced commercially at the 1963 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy. The first adiabatic differential scanning calorimeter that could be used in biochemistry was developed by P.L. Privalov and D.R. Monaselidze in 1964. The term DSC was coined to describe this instrument which measures energy directly and allows precise measurements of heat capacity.

Detection of phase transitions

The basic principle underlying this technique is that when the sample undergoes a physical transformation such as phase transitions, more or less heat will need to flow to it than the reference to maintain both at the same temperature. Whether less or more heat must flow to the sample depends on whether the process is exothermic or endothermic. For example, as a solid sample melts to a liquid it will require more heat flowing to the sample to increase its temperature at the same rate as the reference. This is due to the absorption of heat by the sample as it undergoes the endothermic phase transition from solid to liquid. Likewise, as the sample undergoes exothermic processes (such as crystallization) less heat is required to raise the sample temperature. By observing the difference in heat flow between the sample and reference, differential scanning calorimeters are able to measure the amount of heat absorbed or released during such transitions. DSC may also be used to observe more subtle physical changes, such as glass transitions. It is widely used in industrial settings as a quality control instrument due to its applicability in evaluating sample purity and for studying polymer curing.

DTA

An alternative technique, which shares much in common with DSC, is differential thermal analysis (DTA). In this technique it is the heat flow to the sample and reference that remains the same rather than the

temperature. When the sample and reference are heated identically phase changes and other thermal processes cause a difference in temperature between the sample and reference. Both DSC and DTA provide similar information. DSC measures the energy required to keep both the reference and the sample at the same temperature whereas DTA measures the difference in temperature between the sample and the reference when they are both put under the same heat.

DSC curves

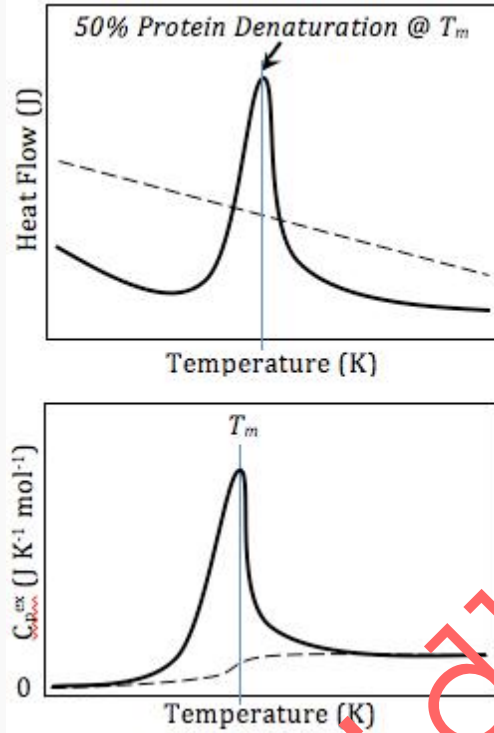
The result of a DSC experiment is a curve of heat flux versus temperature or versus time. There are two different conventions: exothermic reactions in the sample shown with a positive or negative peak depending on the kind of technology used in the experiment. This curve can be used to calculate enthalpies of transitions. This is done by integrating the peak corresponding to a given transition. It can be shown that the enthalpy of transition can be expressed using the following equation:

$$\Delta H = KA$$

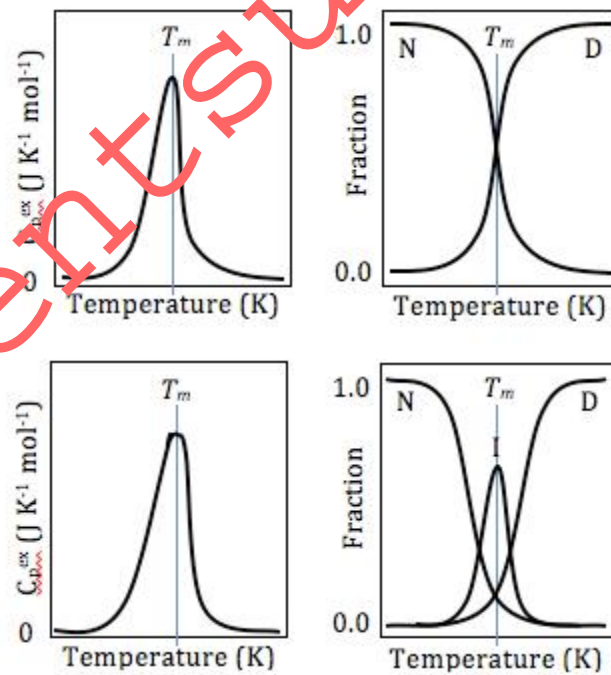
where ΔH is the enthalpy of transition, K is the calorimetric constant, and A is the area under the curve. The calorimetric constant will vary from instrument to instrument and can be determined by analyzing a well-characterized sample with known enthalpies of transition.

Applications

Differential scanning calorimetry can be used to measure a number of characteristic properties of a sample. Using this technique it is possible to observe fusion and crystallization events as well as glass transition temperatures T_g . DSC can also be used to study oxidation, as well as other chemical reactions. Glass transitions may occur as the temperature of an amorphous solid is increased. These transitions appear as a step in the baseline of the recorded DSC signal. This is due to the sample undergoing a change in heat capacity; no formal phase change occurs. As the temperature increases, an amorphous solid will become less viscous. At some point the molecules may obtain enough freedom of motion to spontaneously arrange themselves into a crystalline form. This is known as the crystallization temperature (T_c). This transition from amorphous solid to crystalline solid is an exothermic process, and results in a peak in the DSC signal. As the temperature increases the sample eventually reaches its melting temperature (T_m). The melting process results in an endothermic peak in the DSC curve. The ability to determine transition temperatures and enthalpies makes DSC a valuable tool in producing phase diagrams for various chemical systems.



Top: A schematic DSC curve of amount of energy input (y) required to maintain each temperature (x), scanned across a range of temperatures. Bottom: Normalized curves setting the initial heat capacity as the reference. Buffer-buffer baseline (dashed) and protein-buffer variance (solid).



Normalized DSC curves using the baseline as the reference (left), and fractions of each conformational state (y) existing at each temperature (right), for two-state (top), and three-state (bottom) proteins. Note the minuscule broadening in the peak of the three-state protein's DSC curve, which may or may not appear statistically significant to the naked eye.

Examples

The technique is widely used across a range of applications, both as a routine quality test and as a research tool. The equipment is easy to calibrate, using low melting indium at 156.5985 °C for example, and is a rapid and reliable method of thermal analysis.

Polymers

DSC is used widely for examining polymers to check their composition. Melting points and glass transition temperatures for most polymers are available from standard compilations, and the method can show possible polymer degradation by the lowering of the expected melting point, T_m , for example. T_m depends on the molecular weight of the polymer, so lower grades will have lower melting points than expected. The percentage crystallinity of a polymer can be found from the crystallization peak of the DSC graph since the heat of fusion can be calculated from the area under an absorption peak. DSC can also be used to study thermal degradation of polymers. Impurities in polymers can be determined by examining thermograms for anomalous peaks, and plasticisers can be detected at their characteristic boiling points.

Liquid crystals

DSC is used in the study of liquid crystals. As some forms of matter go from solid to liquid they go through a third state, which displays properties of both phases. This anisotropic liquid is known as a liquid crystalline or mesomorphous state. Using DSC, it is possible to observe the small energy changes that occur as matter transitions from a solid to a liquid crystal and from a liquid crystal to an isotropic liquid.^[5]

Oxidative stability

Using differential scanning calorimetry to study the stability to oxidation of samples generally requires an airtight sample chamber. Usually, such tests are done isothermally (at constant temperature) by changing the atmosphere of the sample. First, the sample is brought to the desired test temperature under an inert atmosphere, usually nitrogen. Then, oxygen is added to the system. Any oxidation that occurs is observed as a deviation in the baseline. Such analysis can be used to determine the stability and optimum storage conditions for a material or compound.^[4]

Safety Screening

DSC makes a reasonable initial safety screening tool. In this mode the sample will be housed in a non-reactive crucible (often gold, or gold plated steel), and which will be able to withstand pressure (typically up to 100 bar). The presence of an exothermic event can then be used to assess the stability of a substance to heat. However, due to a combination of relatively poor sensitivity, slower than normal scan rates (typically 2-3 °/min - due to much heavier crucible) and unknown activation energy, it is necessary to deduct about 75-100 °C from the initial start of the observed exotherm to **suggest** a maximum temperature for the material. A much more accurate data set can be obtained from an adiabatic calorimeter, but such a test may take 2-3 days from ambient at a rate of a 3 °C increment per half hour.

Drug analysis

DSC is widely used in the pharmaceutical and polymer industries. For the polymer chemist, DSC is a handy tool for studying curing processes, which allows the fine tuning of polymer properties. The cross-linking of polymer molecules that occurs in the curing process is exothermic, resulting in a positive peak in the DSC curve that usually appears soon after the glass transition. In the pharmaceutical industry it is necessary to have well-characterized drug compounds in order to define processing parameters. For instance, if it is necessary to deliver a drug in the amorphous form, it is desirable to process the drug at temperatures below those at which crystallization can occur.

General chemical analysis

Freezing-point depression can be used as a **purity analysis** tool when analysed by Differential scanning calorimetry. This is possible because the temperature range over which a mixture of compounds melts is dependent on their relative amounts. Consequently, less pure compounds will exhibit a broadened melting peak that begins at lower temperature than a pure compound.

Basic concept of Spectroscopy



Analysis of white light by dispersing it with a prism is an example of spectroscopy.

Spectroscopy is the study of the interaction between matter and radiated energy.^{[1][2]} Historically, spectroscopy originated through the study of visible light dispersed according to its wavelength, e.g., by a prism. Later the concept was expanded greatly to comprise any interaction with radiative energy as a function of its wavelength or frequency. Spectroscopic data is often represented by a spectrum, a plot of the response of interest as a function of wavelength or frequency.

Spectrometry and **spectrography** are terms used to refer to the measurement of radiation intensity as a function of wavelength and are often used to describe experimental spectroscopic methods. Spectral measurement devices are referred to as spectrometers, spectrophotometers, spectrographs or spectral analyzers.

Daily observations of color can be related to spectroscopy. Neon lighting is a direct application of atomic spectroscopy. Neon and other noble gases have characteristic emission colors, and neon lamps use electricity to excite these emissions. Inks, dyes and paints include chemical compounds selected for their spectral characteristics in order to generate specific colors and hues. A commonly encountered molecular spectrum is that of nitrogen dioxide. Gaseous nitrogen dioxide has a characteristic red absorption feature,

and this gives air polluted with nitrogen dioxide a reddish brown color. Rayleigh scattering is a spectroscopic scattering phenomenon that accounts for the color of the sky.

Spectroscopic studies were central to the development of quantum mechanics and included Max Planck's explanation of blackbody radiation, Albert Einstein's explanation of the photoelectric effect and Niels Bohr's explanation of atomic structure and spectra. Spectroscopy is used in physical and analytical chemistry because atoms and molecules have unique spectra. These spectra can be interpreted to derive information about the atoms and molecules, and they can also be used to detect, identify and quantify chemicals. Spectroscopy is also used in astronomy and remote sensing. Most research telescopes have spectrographs. The measured spectra are used to determine the chemical composition and physical properties of astronomical objects (such as their temperature and velocity).

Theory

One of the central concepts in spectroscopy is a resonance and its corresponding resonant frequency. Resonances were first characterized in mechanical systems such as pendulums. Mechanical systems that vibrate or oscillate will experience large amplitude oscillations when they are driven at their resonant frequency. A plot of amplitude vs. excitation frequency will have a peak centered at the resonance frequency. This plot is one type of spectrum, with the peak often referred to as a spectral line, and most spectral lines have a similar appearance.

In quantum mechanical systems, the analogous resonance is a coupling of two quantum mechanical stationary states of one system such as an atom, via an oscillatory source of energy such as a photon. The coupling of the two states is strongest when the energy of the source matches the energy difference between the two states. The energy (E) of a photon is related to its frequency (ν) by $E = h\nu$ where h is Planck's constant, and so a spectrum of the system response vs. photon frequency will peak at the resonant frequency or energy. Particles such as electrons and neutrons have a comparable relationship, the de Broglie relations, between their kinetic energy and their wavelength and frequency and therefore can also excite resonant interactions.

Spectra of atoms and molecules often consist of a series of spectral lines, each one representing a resonance between two different quantum states. The explanation of these series, and the spectral patterns associated with them, were one of the experimental enigmas that drove the development and acceptance of quantum mechanics. The hydrogen spectral series in particular was first successfully explained by the Rutherford-Bohr quantum model of the hydrogen atom. In some cases spectral lines are well separated and distinguishable, but spectral lines can also overlap and appear to be a single transition if the density of energy states is high enough.

Beer–Lambert law

In optics, the **Beer–Lambert law**, also known as **Beer's law** or the **Lambert–Beer law** or the **Beer–Lambert–Bouguer law** (named after August Beer, Johann Heinrich Lambert, and Pierre Bouguer) relates the absorption of light to the properties of the material through which the light is travelling.



An example of Beer–Lambert law: green laser light in a solution of Rhodamine 6B. The beam intensity becomes weaker as it passes through solution

Equations

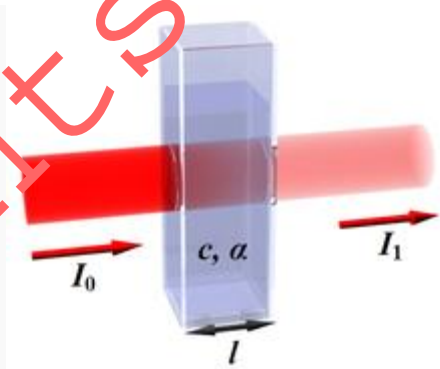


Diagram of Beer–Lambert absorption of a beam of light as it travels through a cuvette of width .

The law states that there is a logarithmic dependence between the transmission (or transmissivity), T , of light through a substance and the product of the absorption coefficient of the substance, α , and the distance the light travels through the material (i.e., the path length), l . The absorption coefficient can, in turn, be written as a product of either a molar absorptivity (extinction coefficient) of the absorber, ϵ , and the molar concentration c of absorbing species in the material, or an absorption cross section, σ , and the (number) density N' of absorbers.

For liquids, these relations are usually written as:

$$T = \frac{I}{I_0} = 10^{-\alpha \ell} = 10^{-\epsilon \ell c}$$

whereas for gases, and in particular among physicists and for spectroscopy and spectrophotometry, they are normally written

$$T = \frac{I}{I_0} = e^{-\alpha' \ell} = e^{-\sigma \ell N}$$

where I_0 and I are the intensity (or power) of the incident light and the transmitted light, respectively; σ is cross section of light absorption by a single particle and N is the density (number per unit volume) of absorbing particles.

The base 10 and base e conventions must not be confused because they give different values for the absorption coefficient: $\alpha \neq \alpha'$. However, it is easy to convert one to the other, using $\alpha' = \alpha \ln(10) \approx 2.303\alpha$.

The transmission (or transmissivity) is expressed in terms of an absorbance which, for liquids, is defined as

$$A = -\log_{10} \left(\frac{I}{I_0} \right)$$

whereas, for gases, it is usually defined as

$$A' = -\ln \left(\frac{I}{I_0} \right).$$

This implies that the absorbance becomes linear with the concentration (or number density) of absorbers, according to

$$A = \epsilon \ell c = \alpha \ell$$

and

$$A' = \sigma \ell N = \alpha' \ell$$

for the two cases, respectively.

Thus, if the path length and the molar absorptivity (or the absorption cross section) are known and the absorbance is measured, the concentration of the substance (or the number density of absorbers) can be deduced.

Although several of the expressions above often are used as Beer–Lambert law, the name should strictly speaking only be associated with the latter two. The reason is that historically, the Lambert law states that

absorption is proportional to the light path length, whereas the Beer law states that absorption is proportional to the concentration of absorbing species in the material.^[1]

If the concentration is expressed as a mole fraction i.e., a dimensionless fraction, the molar absorptivity (ϵ) takes the same dimension as the absorption coefficient, i.e., reciprocal length (e.g., m^{-1}). However, if the concentration is expressed in moles per unit volume, the molar absorptivity (ϵ) is used in $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$, or sometimes in converted SI units of $\text{m}^2\cdot\text{mol}^{-1}$.

The absorption coefficient α' is one of many ways to describe the absorption of electromagnetic waves. For the others, and their interrelationships, see the article: Mathematical descriptions of opacity. For example, α' can be expressed in terms of the imaginary part of the refractive index, n , and the wavelength of the light (in free space), λ_0 , according to

$$\alpha' = \frac{4\pi\kappa}{\lambda_0}.$$

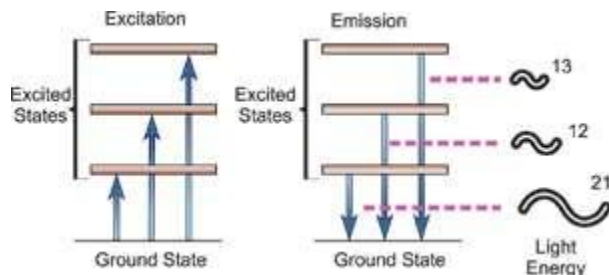
In molecular absorption spectrometry, the absorption cross section σ is expressed in terms of a linestrength, S , and an (area-normalized) lineshape function, f . The frequency scale in molecular spectroscopy is often in cm^{-1} , wherefore the lineshape function is expressed in units of $1/\text{cm}^{-1}$, which can look funny but is strictly correct. Since N is given as a number density in units of $1/\text{cm}^3$, the linestrength is often given in units of $\text{cm}^2\text{cm}^{-1}/\text{molecule}$. A typical linestrength in one of the vibrational overtone bands of smaller molecules, e.g., around $1.5\ \mu\text{m}$ in CO or CO_2 , is around $10^{-23}\ \text{cm}^2\text{cm}^{-1}$, although it can be larger for species with strong transitions, e.g., C_2H_2 . The linestrengths of various transitions can be found in large databases, e.g., HITRAN. The lineshape function often takes a value around a few $1/\text{cm}^{-1}$, up to around $10/\text{cm}^{-1}$ under low pressure conditions, when the transition is Doppler broadened, and below this under atmospheric pressure conditions, when the transition is collision broadened. It has also become commonplace to express the linestrength in units of $\text{cm}^{-2}/\text{atm}$ since then the concentration is given in terms of a pressure in units of atm. A typical linestrength is then often in the order of $10^{-3}\ \text{cm}^{-2}/\text{atm}$. Under these conditions, the detectability of a given technique is often quoted in terms of $\text{ppm}\cdot\text{m}$.

The fact that there are two commensurate definitions of absorbance (in base 10 or e) implies that the absorbance and the absorption coefficient for the cases with gases, A' and α' , are $\ln 10$ (approximately 2.3) times as large as the corresponding values for liquids, i.e., A and α , respectively. Therefore, care must be taken when interpreting data that the correct form of the law is used.

The law tends to break down at very high concentrations, especially if the material is highly scattering. If the light is especially intense, nonlinear optical processes can also cause variances.

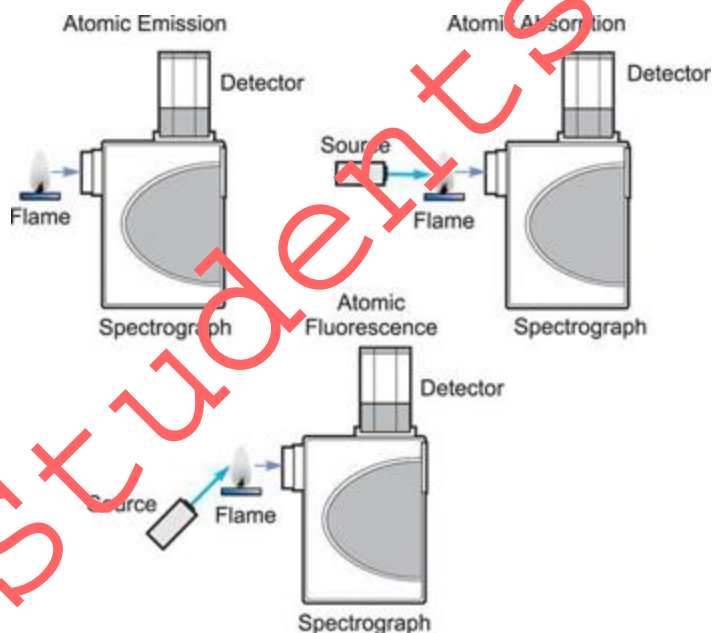
Absorption, Emission Spectroscopy

Atomic Absorption, Emission and Fluorescence Techniques



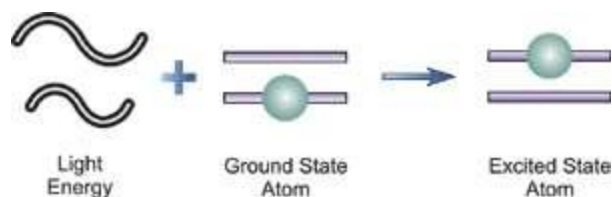
Energy Transitions

Atomic spectroscopy is the determination of elemental composition by its electromagnetic or mass spectrum. The study of the electromagnetic spectrum of elements is called Optical Atomic Spectroscopy. Electrons exist in energy levels within an atom. These levels have well defined energies and electrons moving between them must absorb or emit energy equal to the difference between them. In optical spectroscopy, the energy absorbed to move an electron to a more energetic level and/or the energy emitted as the electron moves to a less energetic energy level is in the form of a photon. The wavelength of the emitted radiant energy is directly related to the electronic transition which has occurred. Since every element has a unique electronic structure, the wavelength of light emitted is a unique property of each individual element. As the orbital configuration of a large atom may be complex, there are many electronic transitions which can occur, each transition resulting in the emission of a characteristic wavelength of light, as illustrated below.



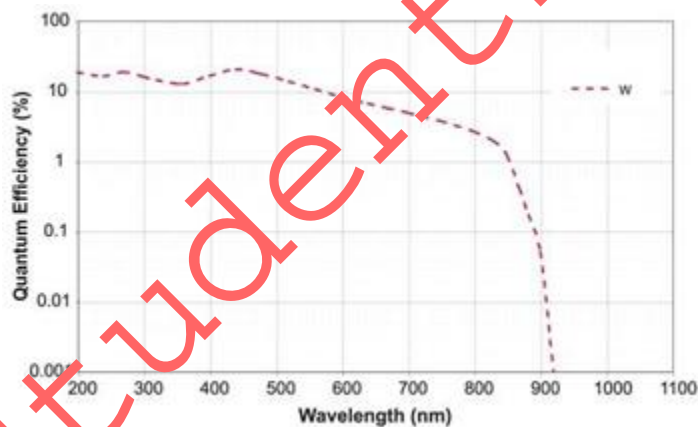
How the three techniques are implemented.

The science of atomic spectroscopy has yielded three techniques for analytical use: Atomic Absorption. Atomic Emission. Atomic Fluorescence. The process of excitation and decay to the ground state is involved in all three fields of atomic spectroscopy. Either the energy absorbed in the excitation process, or the energy emitted in the decay process is measured and used for analytical purposes.



The atomic absorption process

If light of just the right wavelength impinges on a free, ground state atom, the atom may absorb the light as it enters an excited state in a process known as atomic absorption. This process is illustrated on the right. Atomic absorption measures the amount of light at the resonant wavelength which is absorbed as it passes through a cloud of atoms. As the number of atoms in the light path increases, the amount of light absorbed increases in a predictable way. By measuring the amount of light absorbed, a quantitative determination of the amount of analyte element present can be made. The use of special light sources and careful selection of wavelength allow the specific quantitative determination of individual elements in the presence of others. The atom cloud required for atomic absorption measurements is produced by supplying enough thermal energy to the sample to dissociate the chemical compounds into free atoms. Aspirating a solution of the sample into a flame aligned in the light beam serves this purpose. Under the proper flame conditions, most of the atoms will remain in the ground state form and are capable of absorbing light at the analytical wavelength from a source lamp. The ease and speed at which precise and accurate determinations can be made with this technique have made atomic absorption one of the most popular methods for the determination of metals.



ICCD Quantum Efficiency relevant to Atomic spectroscopy

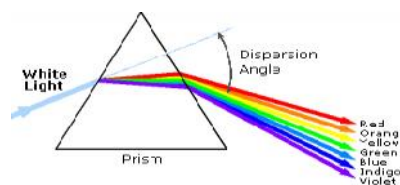
In atomic emission, a sample is subjected to a high energy, thermal environment in order to produce excited state atoms, capable of emitting light. The energy source can be an electrical arc, a flame, or more recently, a plasma. The emission spectrum of an element exposed to such an energy source consists of a

collection of the allowable emission wavelengths, commonly called emission lines, because of the discrete nature of the emitted wavelengths. This emission spectrum can be used as a unique characteristic for qualitative identification of the element. Atomic emission using electrical arcs has been widely used in qualitative analysis. Emission techniques can also be used to determine how much of an element is present in a sample. For a "quantitative" analysis, the intensity of light emitted at the wavelength of the element to be determined is measured. The emission intensity at this wavelength will be greater as the number of atoms of the analyte element increases. The technique of flame photometry is an application of atomic emission for quantitative analysis.

The third field of atomic spectroscopy is atomic fluorescence. This technique incorporates aspects of both atomic absorption and atomic emission. Like atomic absorption, ground state atoms created in a flame are excited by focusing a beam of light into the atomic vapor. Instead of looking at the amount of light absorbed in the process, however, the emission resulting from the decay of the atoms excited by the source light is measured. The intensity of this "fluorescence" increases with increasing atom concentration, providing the basis for quantitative determination. The source lamp for atomic fluorescence is mounted at an angle to the rest of the optical system, so that the light detector sees only the fluorescence in the flame and not the light from the lamp itself. It is advantageous to maximize lamp intensity since sensitivity is directly related to the number of excited atoms which in turn is a function of the intensity of the exciting radiation.

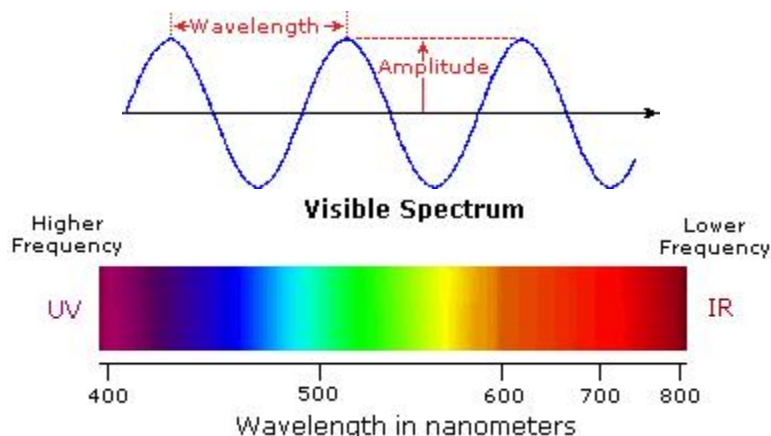
While atomic absorption is the most widely applied of the three techniques and usually offers several advantages over the other two, particular benefits may be gained with either emission or fluorescence in special analytical situations.

Visible and Ultraviolet Spectroscopy



An obvious difference between certain compounds is their color. Thus, quinone is yellow; chlorophyll is green; the 2,4-dinitrophenylhydrazone derivatives of aldehydes and ketones range in color from bright yellow to deep red, depending on double bond conjugation; and aspirin is colorless. In this respect the human eye is functioning as a spectrometer analyzing the light reflected from the surface of a solid or passing through a liquid. Although we see sunlight (or white light) as uniform or homogeneous in color, it is actually composed of a broad range of radiation wavelengths in the ultraviolet (UV), visible and infrared (IR) portions of the spectrum. As shown on the right, the component colors of the visible portion can be separated by passing sunlight through a prism, which acts to bend the light in differing degrees according to wavelength. Electromagnetic radiation such as visible light is commonly treated as a wave phenomenon, characterized by a wavelength or frequency. **Wavelength** is defined on the left below, as the distance between adjacent peaks (or troughs), and may be designated in meters, centimeters or nanometers (10^{-9} meters). **Frequency** is the number of wave cycles that travel past a fixed point per unit of time, and is usually given in cycles per second, or hertz (Hz). Visible wavelengths cover a range from

approximately 400 to 800 nm. The longest visible wavelength is red and the shortest is violet. Other common colors of the spectrum, in order of decreasing wavelength, may be remembered by the mnemonic: **ROY G BIV**. The wavelengths of what we perceive as particular colors in the visible portion of the spectrum are displayed and listed below. In horizontal diagrams, such as the one on the bottom left, wavelength will increase on moving from left to right.

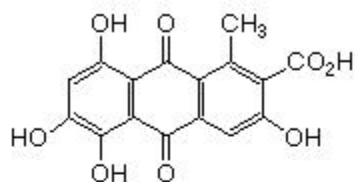


- **Violet:** 400 - 420 nm
- **Indigo:** 420 - 440 nm
- **Blue:** 440 - 490 nm
- **Green:** 490 - 570 nm
- **Yellow:** 570 - 585 nm
- **Orange:** 585 - 620 nm
- **Red:** 620 - 780 nm

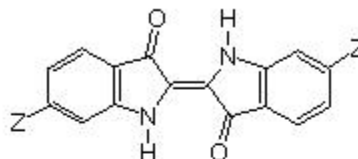
When white light passes through or is reflected by a colored substance, a characteristic portion of the mixed wavelengths is absorbed. The remaining light will then assume the complementary color to the wavelength(s) absorbed. This relationship is demonstrated by the color wheel shown on the right. Here, complementary colors are diametrically opposite each other. Thus, absorption of 420-430 nm light renders a substance yellow, and absorption of 500-520 nm light makes it red. Green is unique in that it can be created by absorption close to 400 nm as well as absorption near 800 nm.

Early humans valued colored pigments, and used them for decorative purposes. Many of these were inorganic minerals, but several important organic dyes were also known. These included the crimson pigment, kermesic acid, the blue dye, indigo, and the yellow saffron pigment, crocetin. A rare dibromo-indigo derivative, punicin, was used to color the robes of the royal and wealthy. The deep orange hydrocarbon carotene is widely distributed in plants, but is not sufficiently stable to be used as permanent pigment, other than for food coloring. A common feature of all these colored compounds, displayed below, is a system of **extensively conjugated pi-electrons**.

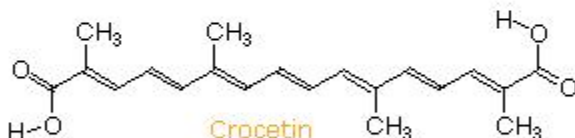
Some Natural Organic Pigments



**Kermesic Acid
(Carminic Acid)**
from the insect *Coccus cacti*

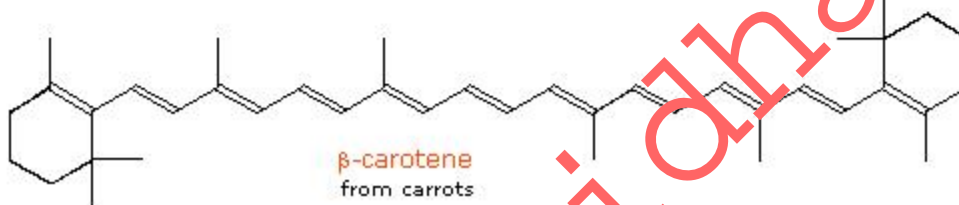


**Z=H
Indigo**
from *Isatis tinctoria* (woad)



Crocetin
from saffron

**Z=Br
Punicin or Tyrian Purple**
from mollusks of the genus *Murex*



β -carotene
from carrots

UV-Visible Absorption Spectra

To understand why some compounds are colored and others are not, and to determine the relationship of conjugation to color, we must make accurate measurements of light absorption at different wavelengths in and near the visible part of the spectrum. Commercial optical spectrometers enable such experiments to be conducted with ease, and usually survey both the near ultraviolet and visible portions of the spectrum.

The visible region of the spectrum comprises photon energies of 36 to 72 kcal/mole, and the near ultraviolet region, out to 200 nm, extends this energy range to 143 kcal/mole.

Ultraviolet radiation having wavelengths less than 200 nm is difficult to handle, and is seldom used as a routine tool for structural analysis.



The energies noted above are sufficient to promote or excite a molecular electron to a higher energy orbital. Consequently, absorption spectroscopy carried out in this region is sometimes called "electronic spectroscopy". A diagram showing the various kinds of electronic excitation that may occur in organic molecules is shown on the left. Of the six transitions outlined, only the two lowest energy ones (left-most, colored blue) are achieved by the energies available in the 200 to 800 nm spectrum. As a rule, energetically

avored electron promotion will be from the **highest occupied molecular orbital (HOMO)** to the **lowest unoccupied molecular orbital (LUMO)**, and the resulting species is called an **excited state**. For a review of molecular orbitals [click here](#).

When sample molecules are exposed to light having an energy that matches a possible electronic transition within the molecule, some of the light energy will be absorbed as the electron is promoted to a higher energy orbital. An optical spectrometer records the wavelengths at which absorption occurs, together with the degree of absorption at each wavelength. The resulting spectrum is presented as a graph of absorbance (A) versus wavelength, as in the isoprene spectrum shown below. Since isoprene is colorless, it does not absorb in the visible part of the spectrum and this region is not displayed on the graph. **Absorbance** usually ranges from 0 (no absorption) to 2 (99% absorption), and is precisely defined in context with spectrometer operation.

Because the absorbance of a sample will be proportional to the number of absorbing molecules in the spectrometer light beam (e.g. their molar concentration in the sample tube), it is necessary to correct the absorbance value for this and other operational factors if the spectra of different compounds are to be compared in a meaningful way. The corrected absorption value is called "molar absorptivity", and is particularly useful when comparing the spectra of different compounds and determining the relative strength of light absorbing functions (chromophores). **Molar absorptivity** (ϵ) is defined as:

Molar Absorptivity, $\epsilon = A / c l$ (where A= absorbance, c = sample concentration in moles/liter & l = length of light path through the sample in cm.)

If the isoprene spectrum on the right was obtained from a dilute hexane solution ($c = 4 \times 10^{-5}$ moles per liter) in a 1 cm sample cuvette, a simple calculation using the above formula indicates a molar absorptivity of 20,000 at the maximum absorption wavelength. Indeed the entire vertical absorbance scale may be changed to a molar absorptivity scale once this information about the sample is in hand. Clicking on the spectrum will display this change in units.

| Chromophore | Example | Excitation | λ_{max} , nm | | Solvent | |
|-------------|--------------|-------------------|----------------------|--------|---------|--------|
| C=C | Ethene | \rightarrow * | 171 | 15,000 | hexane | |
| C C | 1-Hexyne | \rightarrow * | 180 | 10,000 | hexane | |
| C=O | Ethanal | n \rightarrow * | 290 | 15 | hexane | |
| | | \rightarrow * | 180 | 10,000 | hexane | |
| N=O | Nitromethane | n \rightarrow * | 275 | 17 | ethanol | |
| | | \rightarrow * | 200 | 5,000 | ethanol | |
| C-X | X=Br | Methyl bromide | n \rightarrow * | 205 | 200 | hexane |
| | X=I | Methyl Iodide | n \rightarrow * | 255 | 360 | hexane |

From the chart above it should be clear that the only molecular moieties likely to absorb light in the 200 to 800 nm region are pi-electron functions and hetero atoms having non-bonding valence-shell electron pairs. Such light absorbing groups are referred to

as **chromophores**. A list of some simple chromophores and their light absorption characteristics is provided on the left above. The oxygen non-bonding electrons in alcohols and ethers do not give rise to absorption above 160 nm. Consequently, pure alcohol and ether solvents may be used for spectroscopic studies.

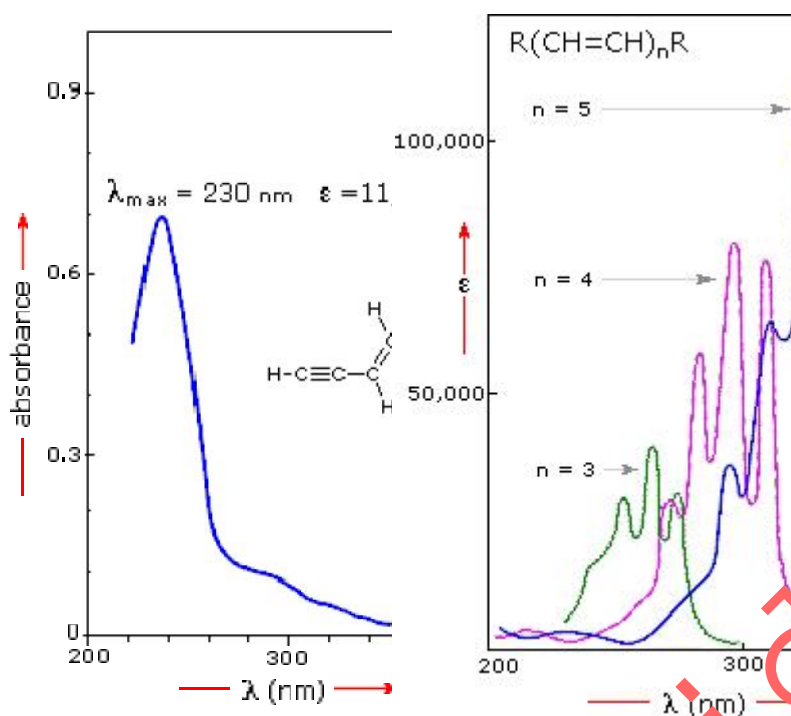
The presence of chromophores in a molecule is best documented by UV-Visible spectroscopy, but the failure of most instruments to provide absorption data for wavelengths below 200 nm makes the detection of isolated chromophores problematic. Fortunately, conjugation generally moves the absorption maxima to longer wavelengths, as in the case of isoprene, so conjugation becomes the major structural feature identified by this technique.

Molar absorptivities may be very large for strongly absorbing chromophores ($>10,000$) and very small if absorption is weak (10 to 100). The magnitude of ϵ reflects both the size of the chromophore and the probability that light of a given wavelength will be absorbed when it strikes the chromophore.

The Importance of Conjugation

A comparison of the absorption spectrum of 1-pentene, $\lambda_{\text{max}} = 178 \text{ nm}$, with that of isoprene (above) clearly demonstrates the importance of chromophore conjugation. Further evidence of this effect is shown below. The spectrum on the left illustrates that conjugation of double and triple bonds also shifts the absorption maximum to longer wavelengths. From the polyene spectra displayed in the center diagram, it is clear that each additional double bond in the conjugated pi-electron system shifts the absorption maximum about 30 nm in the same direction. Also, the molar absorptivity (ϵ) roughly doubles with each new conjugated double bond. Spectroscopists use the terms defined in the table on the right when describing shifts in absorption. Thus, extending conjugation generally results in bathochromic and hyperchromic shifts in absorption.

The appearance of several absorption peaks or shoulders for a given chromophore is common for highly conjugated systems, and is often solvent dependent. This fine structure reflects not only the different conformations such systems may assume, but also electronic transitions between the different vibrational energy levels possible for each electronic state. Vibrational fine structure of this kind is most pronounced in vapor phase spectra, and is increasingly broadened and obscured in solution as the solvent is changed from hexane to methanol.

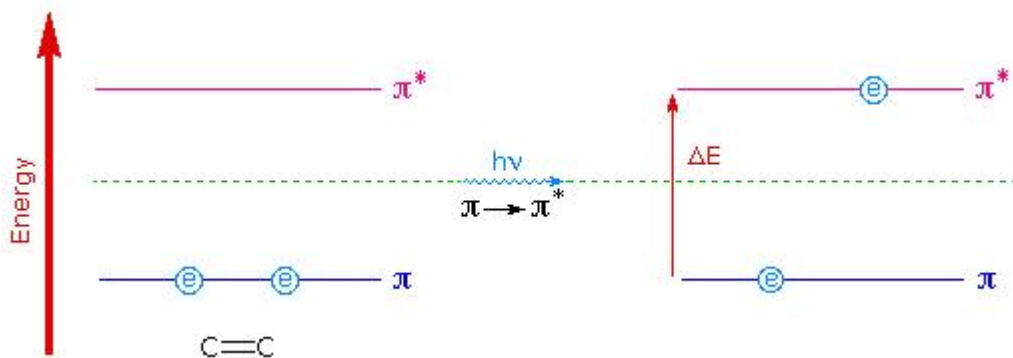


Terminology for Absorption Shifts

| Nature of Shift | Descriptive Term |
|-----------------------|------------------|
| To Longer Wavelength | Bathochromic |
| To Shorter Wavelength | Hypsochromic |
| To Greater Absorbance | Hyperchromic |
| To Lower Absorbance | Hypochromic |

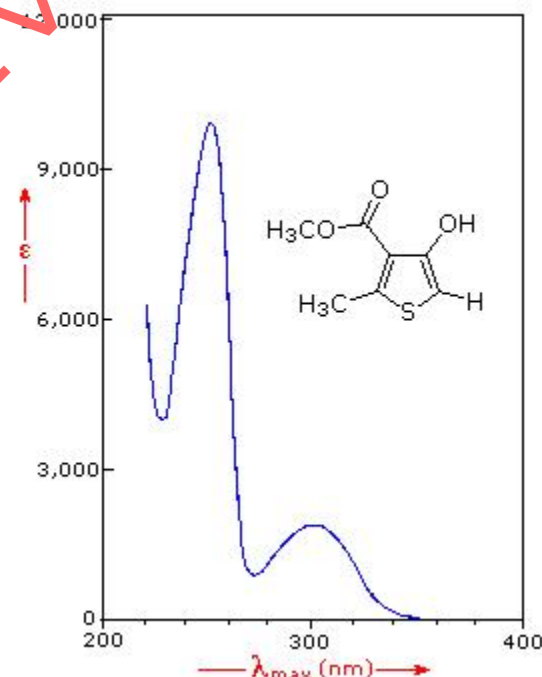
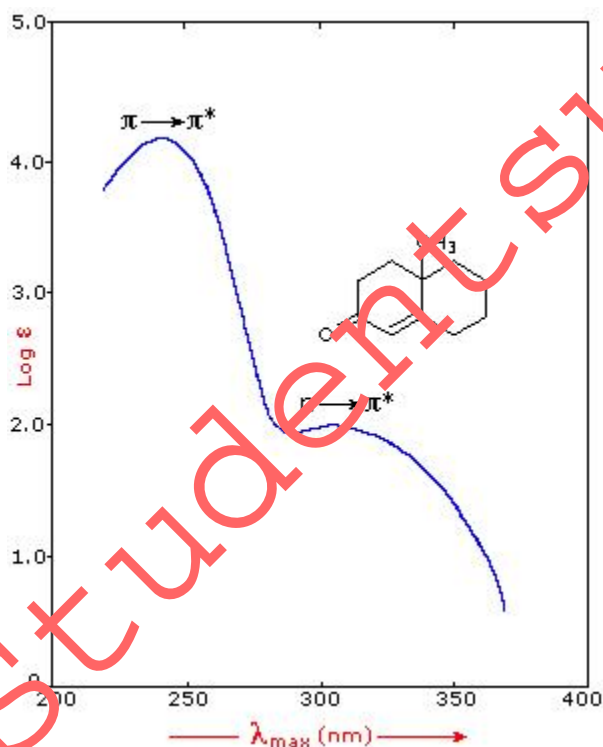
To understand why conjugation should cause bathochromic shifts in the absorption maxima of chromophores, we need to look at the relative energy levels of the pi-orbitals. When two double bonds are conjugated, the four p atomic orbitals combine to generate four pi-molecular orbitals (two are bonding and two are antibonding). This was described earlier in the section concerning diene chemistry. In a similar manner, the three double bonds of a conjugated triene create six pi-molecular orbitals, half bonding and half antibonding. The energetically most favorable $\pi \rightarrow \pi^*$ excitation occurs from the highest energy bonding pi-orbital (**HOMO**) to the lowest energy antibonding pi-orbital (**LUMO**).

The following diagram illustrates this excitation for an isolated double bond (only two pi-orbitals) and, on clicking the diagram, for a conjugated diene and triene. In each case the HOMO is colored blue and the LUMO is colored magenta. Increased conjugation brings the HOMO and LUMO orbitals closer together. The energy (E) required to effect the electron promotion is therefore less, and the wavelength that provides this energy is increased correspondingly (remember $\lambda = h \cdot c / E$).



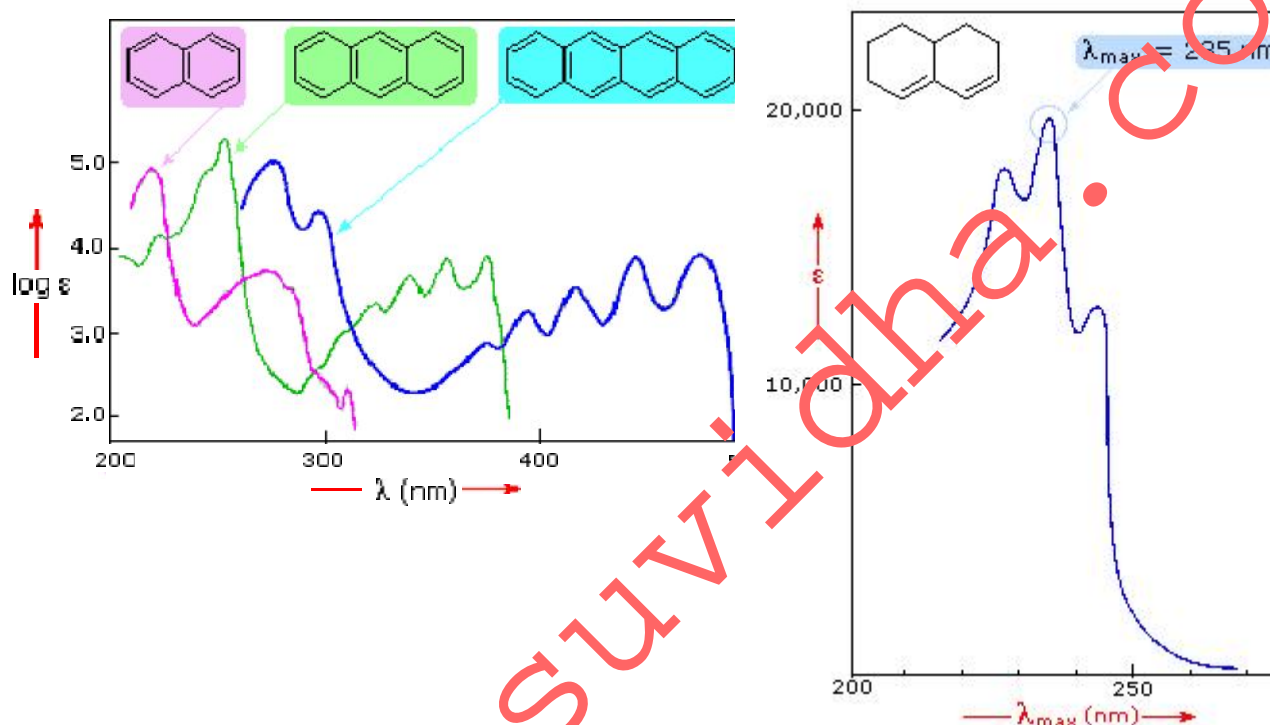
Examples of $\pi \rightarrow \pi^*$ Excitation
 Click on the Diagram to Advance

Many other kinds of conjugated pi-electron systems act as chromophores and absorb light in the 200 to 800 nm region. These include unsaturated aldehydes and ketones and aromatic ring compounds. A few examples are displayed below. The spectrum of the unsaturated ketone (on the left) illustrates the advantage of a logarithmic display of molar absorptivity. The $\pi \rightarrow \pi^*$ absorption located at 242 nm is very strong, with an $\epsilon = 18,000$. The weak $n \rightarrow \pi^*$ absorption near 300 nm has an $\epsilon = 100$.



Benzene exhibits very strong light absorption near 180 nm ($\epsilon > 65,000$), weaker absorption at 200 nm ($\epsilon = 8,000$) and a group of much weaker bands at 254 nm ($\epsilon = 240$). Only the last

group of absorptions are completely displayed because of the 200 nm cut-off characteristic of most spectrophotometers. The added conjugation in naphthalene, anthracene and tetracene causes bathochromic shifts of these absorption bands, as displayed in the chart on the left below. All the absorptions do not shift by the same amount, so for anthracene (green shaded box) and tetracene (blue shaded box) the weak absorption is obscured by stronger bands that have experienced a greater red shift. As might be expected from their spectra, naphthalene and anthracene are colorless, but tetracene is orange.



The spectrum of the bicyclic diene (above right) shows some vibrational fine structure, but in general is similar in appearance to that of isoprene, [shown above](#). Closer inspection discloses that the absorption maximum of the more highly substituted diene has moved to a longer wavelength by about 15 nm. This "substituent effect" is general for dienes and trienes, and is even more pronounced for enone.

Infrared spectroscopy

Infrared spectroscopy (IR spectroscopy) is the spectroscopy that deals with the infrared region of the electromagnetic spectrum, that is light with a longer wavelength and lower frequency than visible light. It covers a range of techniques, mostly based on absorption spectroscopy. As with all spectroscopic techniques, it can be used to identify and study chemicals. A common laboratory instrument that uses this technique is a Fourier transform infrared (FTIR) spectrometer.

The infrared portion of the electromagnetic spectrum is usually divided into three regions; the near-, mid- and far- infrared, named for their relation to the visible spectrum. The higher-energy near-IR, approximately $14000\text{--}4000\text{ cm}^{-1}$ ($0.8\text{--}2.5\text{ }\mu\text{m}$ wavelength) can excite overtone or harmonic vibrations. The mid-infrared, approximately $4000\text{--}400\text{ cm}^{-1}$ ($2.5\text{--}25\text{ }\mu\text{m}$) may be used to study the fundamental vibrations and associated rotational-vibrational structure. The far-infrared, approximately $400\text{--}10\text{ cm}^{-1}$ ($25\text{--}1000\text{ }\mu\text{m}$), lying adjacent to the microwave region, has low energy and may be used for rotational spectroscopy. The names and classifications of these subregions are conventions, and are only loosely based on the relative molecular or electromagnetic properties.

Theory

Infrared spectroscopy exploits the fact that molecules absorb specific frequencies that are characteristic of their structure. These absorptions are resonant frequencies, i.e. the frequency of the absorbed radiation matches the frequency of the bond or group that vibrates. The energies are determined by the shape of the molecular potential energy surfaces, the masses of the atoms, and the associated vibronic coupling.

In particular, in the Born–Oppenheimer and harmonic approximations, i.e. when the molecular Hamiltonian corresponding to the electronic ground state can be approximated by a harmonic oscillator in the neighborhood of the equilibrium molecular geometry, the resonant frequencies are determined by the normal modes corresponding to the molecular electronic ground state potential energy surface. Nevertheless, the resonant frequencies can be in a first approach related to the strength of the bond, and the mass of the atoms at either end of it. Thus, the frequency of the vibrations can be associated with a particular bond type.

Number of vibrational modes

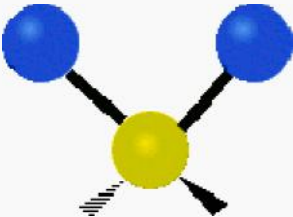
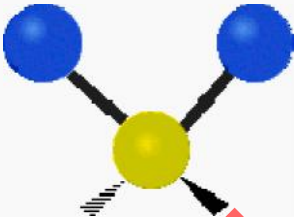
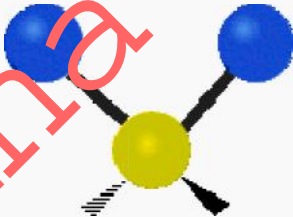
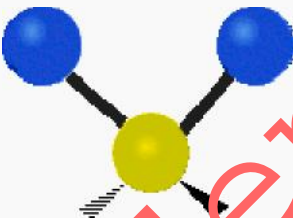
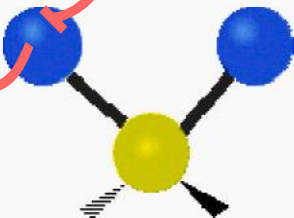
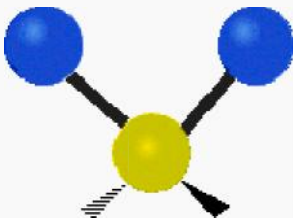
In order for a vibrational mode in a molecule to be "IR active," it must be associated with changes in the dipole. A permanent dipole is not necessary, as the rule requires only a change in dipole moment.^[1]

A molecule can vibrate in many ways, and each way is called a *vibrational mode*. For molecules with N atoms in them, linear molecules have $3N - 5$ degrees of vibrational modes, whereas nonlinear molecules have $3N - 6$ degrees of vibrational modes (also called vibrational degrees of freedom). As an example H_2O , a non-linear molecule, will have $3 \times 3 - 6 = 3$ degrees of vibrational freedom, or modes.

Simple diatomic molecules have only one bond and only one vibrational band. If the molecule is symmetrical, e.g. N_2 , the band is not observed in the IR spectrum, but only in the Raman spectrum. Asymmetrical diatomic molecules, e.g. CO , absorb in the IR spectrum. More complex molecules have many bonds, and their vibrational spectra are correspondingly more complex, i.e. big molecules have many peaks in their IR spectra.

The atoms in a CH₂ group, commonly found in organic compounds, can vibrate in six different ways:

symmetric and antisymmetric stretching, scissoring, rocking, wagging and twisting, as shown below. Some are IR active, the remaining are Raman active.

| Symmetrical stretching (IR Inactive) | Antisymmetrical stretching (IR Active) | Scissoring (IR Inactive) |
|---|---|---|
|  |  |  |
| Rocking (IR Active) | Wagging (IR Active) | Twisting (IR Inactive) |
|  |  |  |

(These figures do not represent the "recoil" of the C atoms, which, though necessarily present to balance the overall movements of the molecule, are much smaller than the movements of the lighter H atoms).

Special effects

The simplest and most important IR bands arise from the "normal modes," the simplest distortions of the molecule. In some cases, "overtone bands" are observed. These bands arise from the absorption of a photon that leads to a doubly excited vibrational state. Such bands appear at approximately twice the energy of the normal mode. Some vibrations, so-called 'combination modes,' involve more than one normal mode. The phenomenon of Fermi resonance can

arise when two modes are similar in energy; Fermi resonance results in an unexpected shift in energy and intensity of the bands etc.

Uses and applications

Infrared spectroscopy is a simple and reliable technique widely used in both organic and inorganic chemistry, in research and industry. It is used in quality control, dynamic measurement, and monitoring applications such as the long-term unattended measurement of CO₂ concentrations in greenhouses and growth chambers by infrared gas analyzers.

It is also used in both criminal and civil cases, for example in identifying polymer degradation. It can be used in detecting how much alcohol is in the blood of a suspected drunk driver measured as 1/10,000 g/mL = 100 µg/mL.^[4] A useful way of analysing solid samples without the need for cutting samples uses ATR or attenuated total reflectance spectroscopy. Using this approach, samples are pressed against the face of a single crystal. The infrared radiation passes through the crystal and only interacts with the sample at the interface between the two materials.

With increasing technology in computer filtering and manipulation of the results, samples in solution can now be measured accurately (water produces a broad absorbance across the range of interest, and thus renders the spectra unreadable without this computer treatment).

Some instruments will also automatically tell you what substance is being measured from a store of thousands of reference spectra held in storage.

Infrared spectroscopy is also useful in measuring the degree of polymerization in polymer manufacture. Changes in the character or quantity of a particular bond are assessed by measuring at a specific frequency over time. Modern research instruments can take infrared measurements across the range of interest as frequently as 32 times a second. This can be done whilst simultaneous measurements are made using other techniques. This makes the observations of chemical reactions and processes quicker and more accurate.

Infrared spectroscopy has also been successfully utilized in the field of semiconductor microelectronics.^[4] for example, infrared spectroscopy can be applied to semiconductors like silicon, gallium arsenide, gallium nitride, zinc selenide, amorphous silicon, silicon nitride, etc.

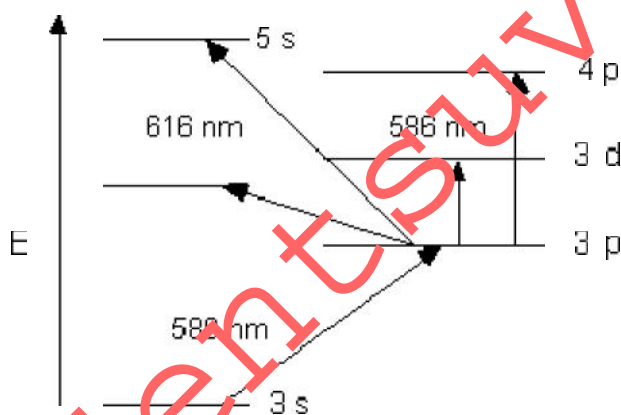
The instruments are now small, and can be transported, even for use in field trials.

FLAME PHOTOMETRY

In previous sections, examples of molecular absorption spectroscopy were introduced. These give broad band spectral peaks due to presence of vibrational and rotational levels associated with each electronic level. On the contrary, atomic spectra are composed of separate lines due to transitions between different electronic levels. Atoms do not contain vibrational and rotational levels associated with electronic levels, thus leading to line spectra.

Atomic spectroscopy is divided into three types which are absorption, emission, and luminescence spectroscopy, All yielding line spectra.

Flame photometry is an atomic emission technique which may be regarded as the simplest of atomic spectroscopic methods and is very similar to the flame test which is applied for detection of alkali metals. Flame photometry is good only for elements that are easily excited and do not require very high temperatures (Na, K, Li, Ca are the most widely determined atoms by this technique).

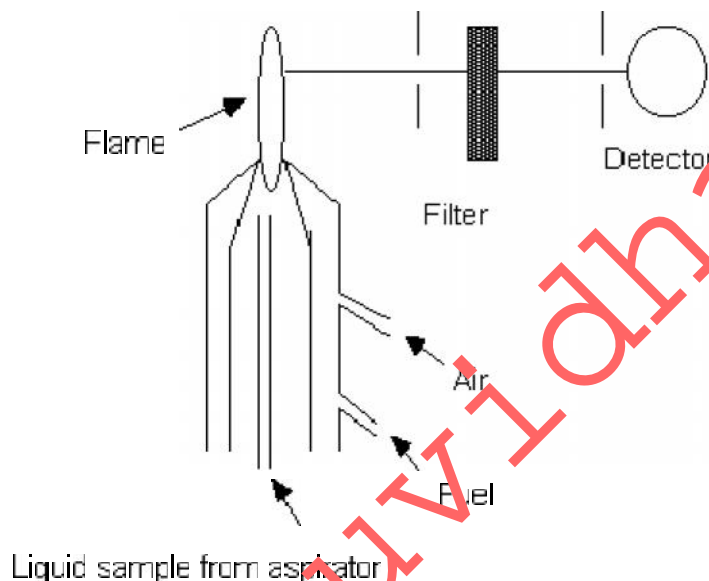


Energy level diagram for atomic sodium

Instrumentation

A flame photometer instrument is extremely simple where the sample in solution is aspirated through an aspirator or nebulizer into the flame which is usually a propane / air fuel or, even, a purified natural gas/air mixture. The sample matrix evaporates followed by atomization of the sample. Atoms present in the high temperature zone of the flame are excited to higher energy

levels by absorbing energy from the flame. As excited atoms return to the ground state they emit radiation in definite wavelength depending on the energy level from which each atom drops. This gives rise to a line spectrum. However, in flame photometry a pre-selected filter (depending on the atom in question) is used and it is the intensity of the emission line that is practically measured and is related to the original concentration of the sample in solution. The detector is usually a phototube or a photomultiplier tube depending on the quality of the instrument. A schematic diagram of a simple flame photometer is shown in Figure 2.



A schematic of a simple flame photometer instrument.

Filters can be changed or selected to suit the determination of the element in question.

Qualitative Versus Quantitative

Atomic emission based on flame photometry is used for quantitative determinations only. This is because quantitative analysis using atomic emission requires advanced equipments and measurement of exact location of each emission line followed by comparison with standard line sheets. However, it is possible to use the machine for the qualitative and quantitative determination of the elements of the first and second groups of the periodic table, since these elements exhibit good emission and very intense and few emission lines, using regular flames usually utilized in flame photometry.

Applications

Flame Photometric Determination of sodium, Potassium, and Lithium

Analytical methods for the determination of sodium, potassium, and lithium are limited except those techniques based on atomic spectroscopy. The simplest versions of atomic spectroscopic methods are emission methods based on flames, using filters for wavelength selection. This is termed flame photometry and is widely used for routine analysis of samples containing species like Na, K, Li, and Ca. Emission signal at a specific wavelength is proportional to the concentration of analyte which emits at that wavelength.

Chemicals and Reagents

a. Provided

1. Standard Na, K, and Li solutions (1000 ppm each).
2. Sample of unknown concentrations of Na, K, and Li.

b. Need Preparation

1. Prepare standard Na, K, and Li solutions that are 1, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 ppm of each metal ion.

Apparatus

1. Flame photometer equipped with Na, K, and Li filters.

Procedure

1. Follow instructions for the correct operation of the flame photometer available.
2. Adjust the signal, using the Na filter, to zero using distilled or ionized water.
3. Read the signal for the Na set of standards and then that of the unknown sample.
4. If the signal obtained for the sample is out of range, dilute a portion of the sample properly till a signal within the range is obtained.
5. Construct a calibration curve for Na in the sample and report your results in ppm.
6. Repeat steps 2-5 for K and finally for Li and find the concentration of each species in the sample. Results should also be reported in ppm analyte.