الجمهورية الجزائرية الديمقراطية الشعبية
People's Democratic Republic of Algeria
وزارة التعليم العالي والبحث العلمي
Ministry of Higher Education and Scientific Research

University of Laghouat

Faculty of Technology

كلية التكنولوجيا

Department of Process Engineering

قسم هندسة الطرائق

Glass Technologies Course

(Lectures and Exercises with Solutions)

Designed by: Dr. BOUDAOUD Asma

Academic Year 2023/2024

Table of Contents

Table of Contents

Chapter I: Basic Concepts

Chapter II: Study of the Vitreous State According to Different Theories

Chapter III: Study of the Properties of Industrial Glasses

Chapter IV: Study of the Raw Materials for the Manufacture of Industrial Glasses

Chapter V: Elaboration of the Vitreous Melts and Glasses Fusion

Chapter VI: Forming Processes and Types of Glasses

Abbreviations

Abbreviations

Symbol	Designation
T	Temperature
P	Pressure
d	Bond length (bond distance)
μ	Dipole moment
R_C	Ionic radii of cations
R_a	Ionic radii of anions
χ	Electronegativity
$F_{A\text{-}O}$	Bond strength (Force of Attraction Oxygen)
Ed	Dissociation energy
Tf	Melting temperature
R	Rawson parameter
VS	Specific volume
H	Enthalpy
Cp	Specific heat capacity
Tg	Glass transition temperature
Tc	Crystallization temperature
DSC	Differential Scanning Calorimetry
DMA	Dynamic Mechanical Analysis
TGA	Thermogravimetric Analysis
RMN	Nuclear Magnetic Resonance
η	Viscosity
α	Coefficient of thermal expansion
Sc	Configuration entropy
Se	Excess entropy
UV	Ultraviolet
IR	Infrared

Symbol	Designation
n	Refractive index
i	Angle of refraction
R_F	Reflection factor
σ	Stress

Introduction

Introduction

This set of lecture notes and corrected exercises on glass technology is primarily designed for second-year Master's students in materials process engineering.

The study of glass technology is of paramount importance to grasp the fundamental concepts, various theories, properties, and manufacturing processes of this versatile material.

This course explores various aspects, ranging from the basics of the chemical composition of glass to the processes of development and forming, encompassing the different properties of glass.

The different chapters successively address the following themes:

Chapter I: Basic Concepts
Chapter II: Study of the vitreous state according to different theories
Chapter III: Study of the properties of industrial glasses
Chapter IV: Study of raw materials for the manufacturing of industrial glasses
Chapter V: Elaboration of vitreous melts and glass fusion
Chapter VI: Forming processes and types of glasses

These courses allow students to gain a deep understanding of glass, its composition, manufacturing processes, and shaping, as well as its role in various fields such as construction, packaging industry, medicine, and many others.

Chapter I: Basic Concepts

Chapter I: Basic Concepts

I. Fundamental Concepts in Chemistry

I.1. Atoms and Elements

Atoms are the fundamental units of matter. They consist of a central nucleus composed of protons (positively charged) and neutrons (neutral), surrounded by electrons (negatively charged) orbiting around the nucleus [1].

Chemical elements are substances composed of only one type of atom. There are more than 100 different elements, each having a unique atomic number [1].

Chemical elements are classified into large families or groups based on their chemical properties and arrangement in the periodic table of elements. The main families or groups of chemical elements include [1, 2]:

- Alkali Metals (Group 1): Example (1): Sodium (Na) and Potassium (K).

Chemical properties: They are highly reactive and easily form positive ions (cations). They react vigorously with water.

- Alkaline Earth Metals (Group 2): Example (2): Calcium (Ca) and Magnesium (Mg).

Chemical properties: Less reactive than alkali metals, but they also form cations.

- Transition Metals: Example (3): Iron (Fe), Titanium (Ti), and Chromium (Cr).

Chemical properties: They form a wide variety of compounds and exhibit great chemical stability.

- Heavy Metals: Example (4): Lead (Pb) and Barium (Ba).

Chemical properties: They have high atomic masses and can form toxic compounds.

- Non-metals: Example (5): Carbon (C), Silicon (Si), and Nitrogen (N).

Chemical properties: They tend to form covalent compounds rather than cations.

- Noble Gases (Group 18): Example (6): Argon (Ar) and Helium (He).

Chemical properties: They are highly stable and generally do not form chemical compounds.

- Halogens (Group 17): Example (7): Fluorine (F) and Chlorine (Cl).

Chemical properties: They are highly reactive and typically form negative ions (anions).

- Lanthanides and Actinides: Example (8): Cerium (Ce) and Uranium (U).

Chemical properties: They are often used in specific applications due to their magnetic and radioactive properties.

I.2. Molecules or Compounds

Molecules are particles composed of two or more atoms chemically bonded. Molecules can be formed from atoms of the same element (diatomic molecules, such as O_2 for oxygen) or atoms of different elements (polyatomic molecules, such as H_2O for water) [2].

I.3. Ions (Cations and Anions)

Ions are electrically charged particles. Ions can be formed from atoms or molecules [3].

- Cations are positively charged ions that form when atoms lose electrons.
- Anions are negatively charged ions that form when atoms gain electrons.

I.4. Chemical Bonds

Chemical bonds are interactions between atoms that allow the formation of molecules, crystals, and other structures. They are essential for maintaining the stability of substances and determining their properties [2, 3].

The main types of chemical bonds are [2, 3]:

I.4.1. Interatomic Bonds

Interatomic bonds are forces that hold atoms together to form molecules or chemical compounds.

a. Covalent Bond

Electron sharing between two atoms

Typically occurs between two non-metallic atoms

Covalent bonds are strong and contribute to the formation of stable molecules

b. Ionic Bond

Electron transfer from one atom to another to form positively charged ions (cations) and negatively charged ions (anions). Typically occurs between a metal and a non-metal (M-X)

Electrostatic forces then attract ions of opposite charges to each other

c. Metallic Bond

Valence electrons (outer electrons) are free to move throughout the material. This creates a "sea of electrons" that holds metallic cations together.

I.4.2. Intermolecular Bonds

Intermolecular bonds are forces that act between individual molecules within a substance.

a. Hydrogen Bond

Weak interaction between a hydrogen atom and an electronegative atom.

Although weak, hydrogen bonding can play a significant role in the structure and properties of molecules.

b. Van der Waals Forces

Van der Waals interactions are attractive forces between molecules. They result from temporary fluctuations in the electric charge of molecules.

There are three types:

- London Dispersion Forces are due to random fluctuations in the distribution of electrons within a molecule.
- Dipole-Dipole Forces arise from the interaction between the permanent electric dipoles of two molecules.
- Induced Dipole Forces result from the interaction between a permanent electric dipole and an induced electric dipole in another molecule.

I.5. Chemical and Nuclear Reactions

I.5.1. Chemical Reactions

Chemical reactions involve changes in the electrons in the outer shells of atoms [4].

They occur between common chemical elements and do not require the presence of radioactive elements.

Chemical reactions conserve chemical elements, meaning atoms are not transformed into atoms of another element.

Example (9): Reaction between hydrochloric acid and sodium hydroxide to form sodium chloride and water: $HCl + NaOH \rightarrow NaCl + H_2O$

1.5.2. Nuclear Reactions

Nuclear reactions involve a modification of the nucleus of an atom, producing nuclei with different mass and/or charge [4, 5].

They can occur between atomic nuclei or particles, or even spontaneously without collision.

Nuclear reactions are responsible for the formation of almost all heavy atoms in the universe and the production of solar energy in the hot and high-pressure interior of the Sun.

Example (10): Nuclear fission reaction of uranium-235 (U-235) in a nuclear power plant, where a uranium nucleus splits into smaller nuclei, releasing energy:

$$^{235}_{92}U + n \rightarrow {}^{141}_{56}Ba + {}^{92}_{36}Kr + 3n + énergie$$

Where: The nucleus of uranium-235 absorbs the neutron (n), forming an unstable compound nucleus ^{236}U.

The unstable compound nucleus splits into two smaller nuclei, typically barium nuclei (^{141}Ba) and krypton nuclei (^{92}Kr), along with the release of 3 neutrons.

II. Matter

Matter is anything that has mass and occupies space. It is composed of atoms, molecules, or ions [6].

II.1. States of Matter

The state of matter refers to the physical phase in which a substance exists at a given temperature and pressure.

The main states of matter are [5, 6]:

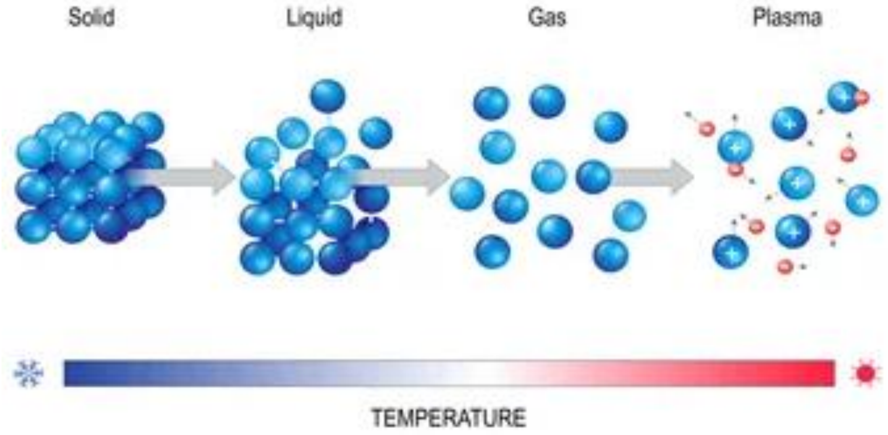


Figure I.1: The main states of matter

II.1.1. Solid

Particles are strongly bonded to each other in a regular crystalline structure. They cannot move freely. Solids have a definite shape and volume.

There are two different forms of solids (Figure I.2):

- Crystalline solids: Atoms in order, Example (11): Quartz: Silica SiO_2, and metals.
- Amorphous solids: Atoms in disorder, Example (12): Glasses: Silica SiO_2.

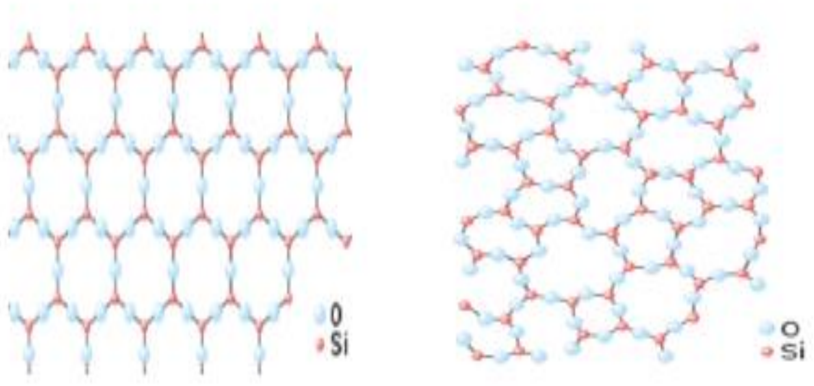


Figure I.2: Silica SiO_2: Quartz, Glasses

II.1.2. Liquid

Particles are bonded, but less tightly than in a solid. Atoms or molecules can move freely but remain close to each other. Liquids have a definite volume but take the shape of their container.

II.1.3. Gas

Particles are very far apart. Atoms or molecules move freely and have neither a definite shape nor volume. They completely fill their container.

II.1.4. Plasma

A very hot state of matter where atoms are ionized, creating a mixture of electrically charged particles. In plasma, electrons separate from atomic nuclei, forming a mixture of free ions and electrons. Plasma is generally disordered.

II.2. Changes of State

Changes in the state of matter from one state to another occur by modifying temperature and pressure conditions (Figure I.3) [6]:

- Melting: Transition from the solid state to the liquid state.
- Solidification/Freezing: Transition from the liquid state to the solid state.
- Evaporation: Transition from the liquid state to the gaseous state.
- Condensation: Transition from the gaseous state to the liquid state.
- Sublimation: Transition from the solid state to the gaseous state.
- Deposition: Transition from the gaseous state to the solid state.
- Deionization: Transition from the plasma state to the gaseous state.
- Ionization: Transition from the gaseous state to the plasma state.

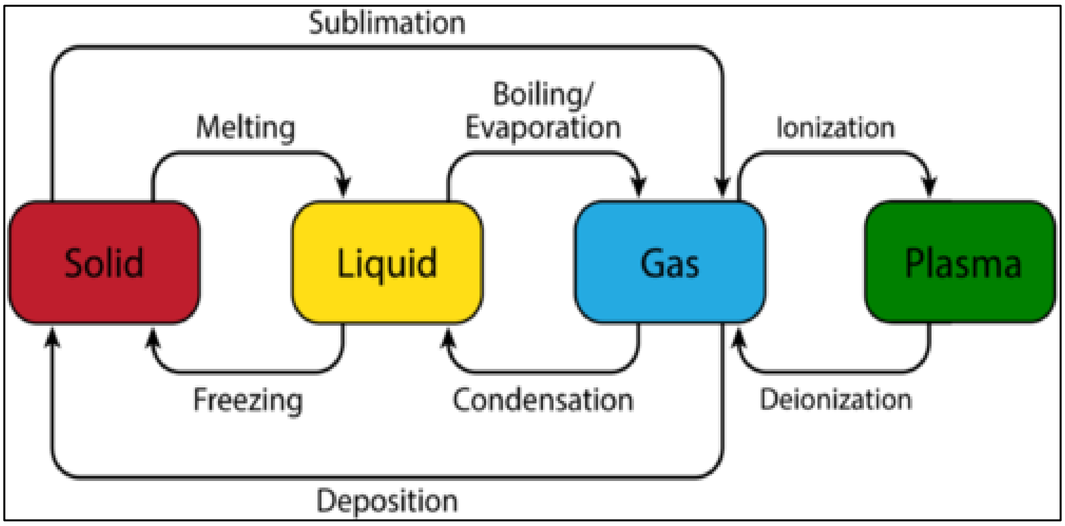


Figure I.3: Changes of State in Matter

II.3. Phase Diagram

The phase diagram is a graph that shows the different phases of a substance as a function of temperature and pressure.

The horizontal axis represents temperature, and the vertical axis represents pressure.

Phase boundaries outline the areas where a substance exists in a specific phase.

Triple points are specific points where all three phases (solid, liquid, and gas) coexist.

The critical point is a point where the liquid and gas phases can no longer be distinguished.

Sublimation and fusion curves represent transitions between the solid and gas phases and solid and liquid phases, respectively.

Vaporization and solidification curves represent transitions between the liquid and gas phases and liquid and solid phases, respectively [2, 6].

Example (13): The phase diagram of water (Figure I.4).

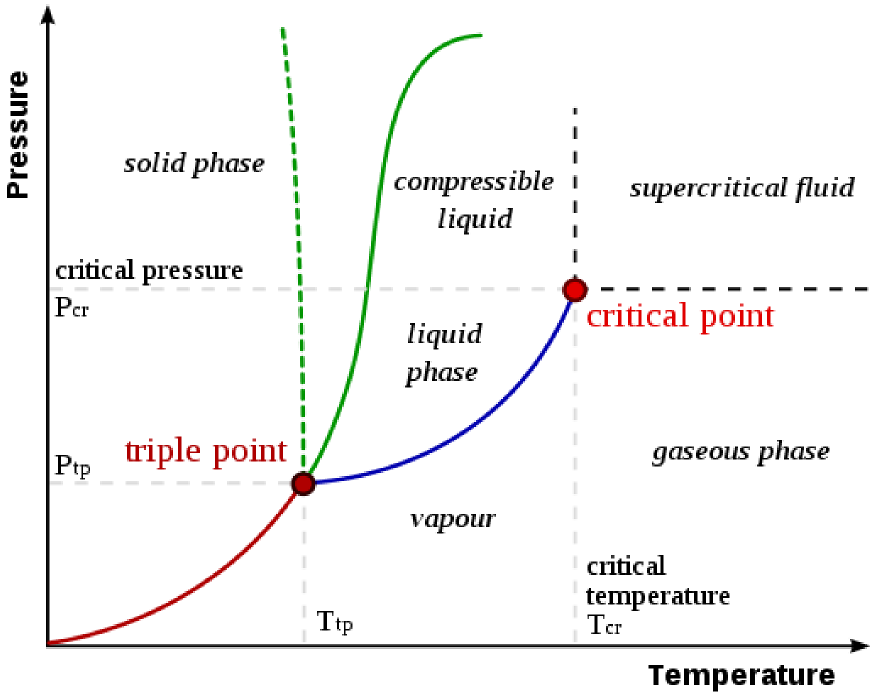


Figure I.4: Phase Diagram of Water.

Exercise Series No. 1

Exercise I.1

Consider the following chemical compounds: CuO, CO_2, HNO_3, NaOH, NaF, KClO, $NaHSO_4$

1. Identify the families of elements present in these compounds.
2. What are the chemical categories of these compounds?

Exercise I.2

1. Provide the IUPAC nomenclature for the following inorganic compounds:

ZnO, NO_2, BrO_3, HBr, HNO_2, HNO_3, $Mg(OH)_2$, FeS, Na_2SO_3, $NaHCO_3$

2. Provide the molecular formula for the following compounds:

Magnesium oxide; Phosphorus pentoxide; Barium hydroxide; Sulfur trioxide; Hydrogen fluoride; Hydrogen sulfide; Hydrogen nitrate; Silver sulfide; Sodium hydrogen sulfate.

Exercise I.3

Silicon dioxide, SiO_2, reacts with dissolved oxygen to form silicon tetraoxide, SiO_4^{4-}.

1. Write the balanced chemical equation for this reaction.
2. Propose the Lewis structures of SiO_2 and SiO_4^{4-}.
3. Predict the molecular geometry of SiO_2 and SiO_4^{4-} using the VSEPR theory.
4. Explain why the SiO_4^{4-} ion may exhibit a non-linear molecular geometry despite the octet rule.

Exercise I.4

Consider the following molecules: Ag, N_2, KCl, SF_6, P_2O_5

1. What are the types of chemical bonds?
2. Determine the number of intratomic bonds.
3. Calculate the ionic and covalent percentages of KCl if the bond length is d = 2.67 Å and the experimental dipole moment is $\mu_{exp} = 10.10$ Debye.

Exercise I.5

Identify the types of the following reactions and explain why:

1. Reaction between silicon dioxide (SiO_2) and water (H_2O) to form silicic acid (H_2SiO_4) and sodium hydroxide (NaOH).
2. Reaction between uranium (U) and a neutron (n) to form thorium (Th) and helium (He).
3. Reaction between silver nitrate ($AgNO_3$) and sodium chloride (NaCl) to form silver chloride (AgCl) and sodium nitrate ($NaNO_3$).
4. Reaction between deuterium (D) and tritium (T) to form helium (He) and a neutron (n).

Exercise I.6

Using the phase diagram of SiO_2 below:

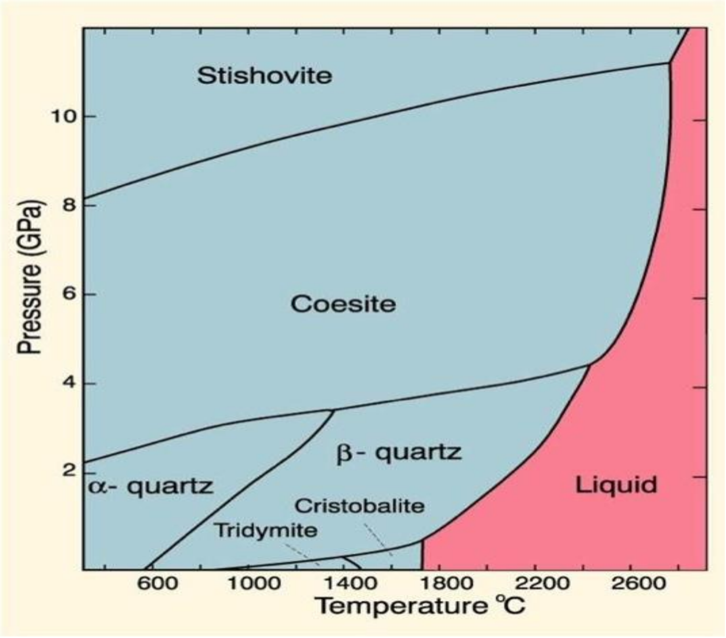


Figure I.5: Phase Diagram of SiO_2.

1. Identify the physical states of quartz, coesite, stishovite, tridymite, cristobalite, and silica.
1. Determine the critical and triple points on the diagram.
2. How can the SiO_2 phase diagram be used to explain the formation of quartz in the Earth?

Exercise Series No. 1: Solutions

Exercise I.1

1. Chemical Families of Elements:

Compounds	Chemical Families of Elements
CuO	Copper (metal) and oxygen (non-metal)
CO_2	Carbon (non-metal)
HNO_3	Hydrogen (non-metal), nitrogen (non-metal)
NaOH	Sodium (metal)
NaF	Fluorine (non-metal) (halogen)
KClO	Potassium (metal), chlorine (non-metal)
$NaHSO_4$	Sulfur (non-metal)

2. The chemical categories:

Compounds	The category of pure substance	Major categories
CuO,	Metallic oxide (MO)	Oxides
CO_2 ,	Non-metallic oxide (XO)	Oxides
HI	Hydride (HX)	Acids
HNO_3	Oxide acid (HXO)	Acids
NaOH	Hydroxides (MOH)	Bases
NaF	Binary salts (MX)	Salts
KClO	Ternary salts (MXO)	Salts
NaHSO4	Quaternary salts (MHXO)	Salts

Exercise I.2

1. IUPAC Nomenclature:

- ZnO: Zinc oxide
- NO_2: Nitrogen dioxide
- BrO_3: Bromine trioxide
- HBr: Hydrogen bromide
- HNO_2: Hydrogen nitrite
- HNO_3: Nitric acid
- $Mg(OH)_2$: Magnesium hydroxide

- FeS: Iron(II) sulfide
- Na_2SO_3: Sodium sulfite
- $NaHCO_3$: Sodium hydrogen carbonate

2. Chemical Formulas:

- Magnesium oxide: MgO
- Phosphorus pentoxide: P_2O_5
- Barium hydroxide: $Ba(OH)_2$
- Sulfur trioxide: SO_3
- Hydrogen sulfide: H_2S
- Silver sulfide: Ag_2S
- Nitric acid or hydrogen nitrate: HNO_3
- Sodium hydrogen sulfate: $NaHSO_4$

Exercise I.3

1. The chemical reaction equation for the formation of silicon tetraoxide, SiO_4:

$SiO_2 + O_2 \rightarrow SiO_4^{4-}$

2. Lewis structures:

Silicon dioxide, SiO_2, is as follows: O = Si = O

Silicon tetraoxide or Orthosilicate, SiO_4^{4-}, is as follows:

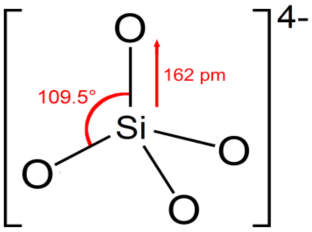


Figure I.6: Lewis structure of SiO_4^{4-}.

3. Molecular geometry:

- For silicon dioxide (SiO_2): Using the Valence Shell Electron Pair Repulsion (VSEPR) theory, silicon (Si) is surrounded by two double bonds with oxygen (O) atoms, resulting in an AX_2 type, which gives a linear geometry.
- For silicon tetraoxide (SiO_4^{4-}): Also using the VSEPR theory, one can predict a tetrahedral molecular geometry. Silicon (Si) is surrounded by four single bonds with oxygen (O) atoms, resulting in an AX_4 type, which gives a tetrahedral geometry.

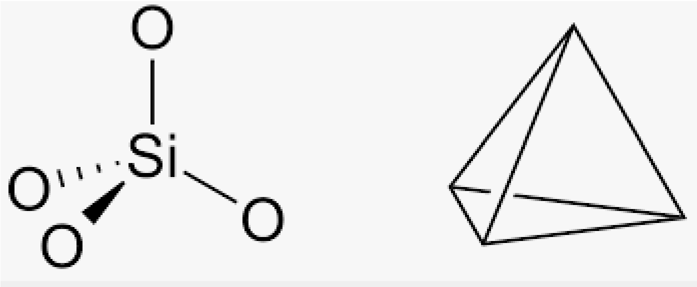


Figure I.7: The geometry of SiO_4^{4-}.

4. Explanation for why the $SiO4^{4-}$ ion can exhibit a non-linear molecular geometry despite the octet rule:

The SiO_4^{4-} ion can display a non-linear molecular geometry despite the octet rule due to the presence of non-bonding electron pairs.

Molecular geometry is determined by the Valence Shell Electron Pair Repulsion (VSEPR) theory, which considers repulsive interactions between electron pairs.

Exercise I.4

1. The types of chemical bonds in each molecule are as follows:

- Ag: Metallic bond
- N_2: Covalent bond
- KCl: Ionic bond
- SF_6: Covalent bond
- P_2O_5: Covalent bond

2. The number of intratomic bonds in each molecule is as follows:

- Ag: 1 metallic bond
- N_2: 3 intratomic bonds
- KCl: 1 intratomic bond
- SF_6: 6 intratomic bonds
- P_2O_5: 10 intratomic bonds

3. The ionic and covalent percentage of KCl:

To calculate the ionic percentage of KCl, we can use the following formula:

Ionic Percentage = (Experimental Dipole Moment / Theoretical Dipole Moment) x 100

If the bond is polar, two charges δ^+ and δ^- are placed on the atoms of the molecule (KCl) at a distance d with a dipole moment equal to: $\mu = q.d = \delta.e.d$ (in electron. Å)

With 1 electron, Å = 4.8 Debye, we have: $\mu = \delta.\ e.\ d.\ 4.8$ (in Debye); assuming $\delta=1$, we suppose that the bond is purely ionic (K^+, Cl^-).

The theoretical dipole moment is: Theoretical μ = 1.e. d .4.8 (in Debye) = 1x1x 2.67x4.8 = 12.82

In reality, the bond is partially ionic. That's why we have δ between 0 and 1.

The ionic percentage = (Experimental μ / Theoretical μ).100%

Ionic percentage = 10.10x100 / 12.82 = 78.8%

4. For the covalent percentage = 100 - 78.8 = 21.2%

Exercise I.5

1. Reaction: $SiO_2 + 4H_2O \rightarrow H_2SiO_4 + 2H_3O$

- Type of reaction: Hydrolysis (Chemical reaction)
- Explanation: Silicon dioxide (SiO_2) reacts with water (H_2O) to form silicic acid (H_2SiO_4) and sodium hydroxide (NaOH). Hydrolysis involves the breaking of chemical bonds by water.

2. Reaction: U → Th + He

- Type of reaction: Radioactive decay (Nuclear reaction)
- Explanation: Uranium (U) undergoes spontaneous nuclear transformation upon neutron impact to form thorium (Th) and helium (He). This type of reaction is characteristic of radioactive elements.

3. Reaction: $AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$

- Type of reaction: Double displacement reaction, Precipitation reaction (Chemical reaction)
- Explanation: Silver ions (Ag^+) from silver nitrate ($AgNO_3$) react with chloride ions (Cl^-) from sodium chloride (NaCl) to form silver chloride (AgCl) and sodium nitrate ($NaNO_3$). In double displacement reactions, cations exchange their anions.

4. Reaction: D + T → He + n

- Type of reaction: Nuclear fusion (Nuclear reaction)
- Explanation: Deuterium (D) and tritium (T) heavy nuclei fuse to form helium (He) and a neutron (n). Nuclear fusion reactions occur at extremely high temperatures and pressures, such as those present in the core of stars.

Exercise I.6 :

1. Physical states:

- Quartz: Quartz is the stable phase of SiO_2 at ambient pressure and temperature. It is a crystalline solid with a trigonal lattice structure.
- Coesite: Coesite is a metastable phase of SiO_2 that forms at high pressures. It is a crystalline solid with a cubic lattice structure.
- Stishovite: Stishovite is the dense phase of SiO_2. It is a crystalline solid with a cubic lattice structure.
- Tridymite: Tridymite is a metastable phase of SiO_2 that forms at high temperatures. It is a crystalline solid with a hexagonal lattice structure.
- Cristobalite: Cristobalite is a metastable phase of SiO_2 that forms at high temperatures. It is a crystalline solid with a cubic lattice structure.
- Silica: Silica is a phase of SiO_2 present in the gaseous state.

2. Critical and triple points:

- The critical point is not determined in the SiO_2 phase diagram. The critical points of a substance are determined by the intersection of the solid-gas and liquid-gas lines in the substance's phase diagram.
- The triple point of a substance is the temperature and pressure at which the three phases of the substance (solid, liquid, and gas) coexist. It is not determined in the SiO_2 phase diagram.

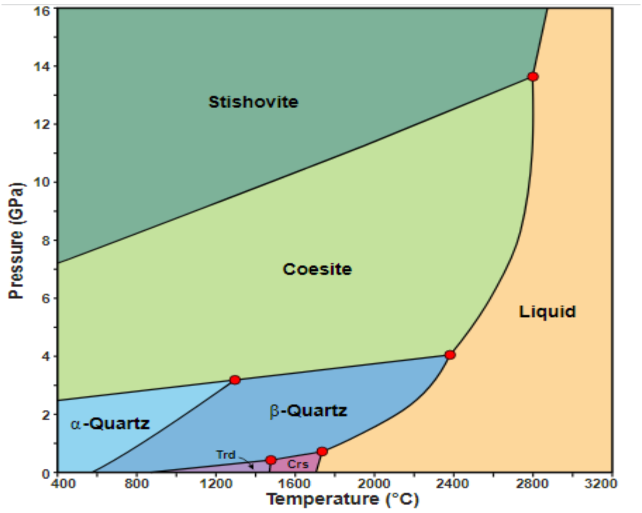


Figure I.5: Phase Diagram of SiO_2.

3. Formation of quartz in the Earth:

The SiO_2 phase diagram can be used to explain the formation of quartz in the Earth. Quartz generally forms at relatively low temperatures and pressures, under the conditions of the

Earth's crust. When silica (SiO_2) is subjected to appropriate temperatures and pressures, it can transform into quartz. However, in regions of the Earth's mantle where temperatures and pressures are higher, other phases of SiO_2, such as coesite or stishovite, may be stable. Thus, the formation of quartz in the Earth's mantle depends on the specific thermodynamic conditions of each region.

Chapter II: Study of the Vitreous State According to Different Theories

Chapter II: Study of the Vitreous State According to Different Theories

I. Introduction

I.1. Historical Overview

The discovery and manufacturing of glass have undergone the following stages throughout history [7, 8]:

- Natural glass formed over 100,000 years ago through the rapid solidification of molten rock, with humanity using obsidian to create arrowheads and knives (Figure II.1).

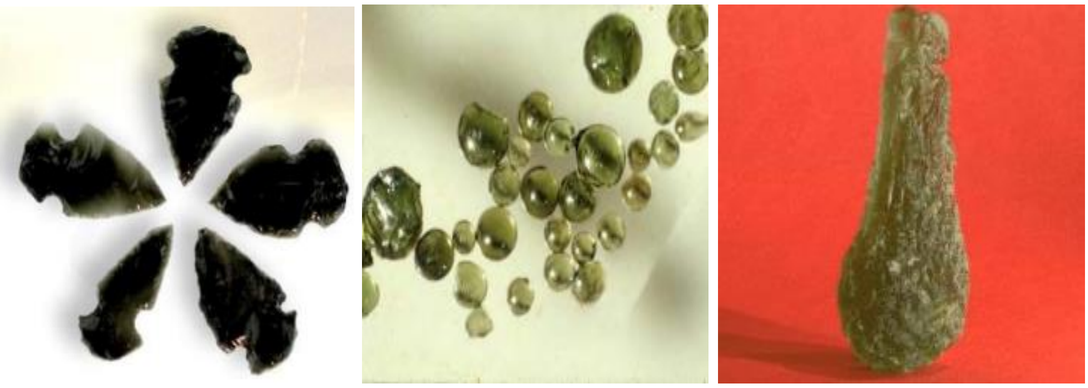


Figure II.1: Obsidian arrowheads; lunar volcanic glasses (3.5 million years); and Impact glasses (meteorite).

- Artificial glass accidentally created around 5000 years ago by a Phoenician merchant using sand and sodium nitrate.
- The Egyptians invented the casting technique to produce glass containers around 3000 years ago.
- The blowing technique was invented in Venice around 50 BCE.
- Venice dominated the art of glassmaking from the 10th to the 17th century.
- The glass industry developed in France during the time of Louis XIV.
- Nowadays, glass is widely used in various sectors due to the automation of manufacturing processes (Figure II.2).

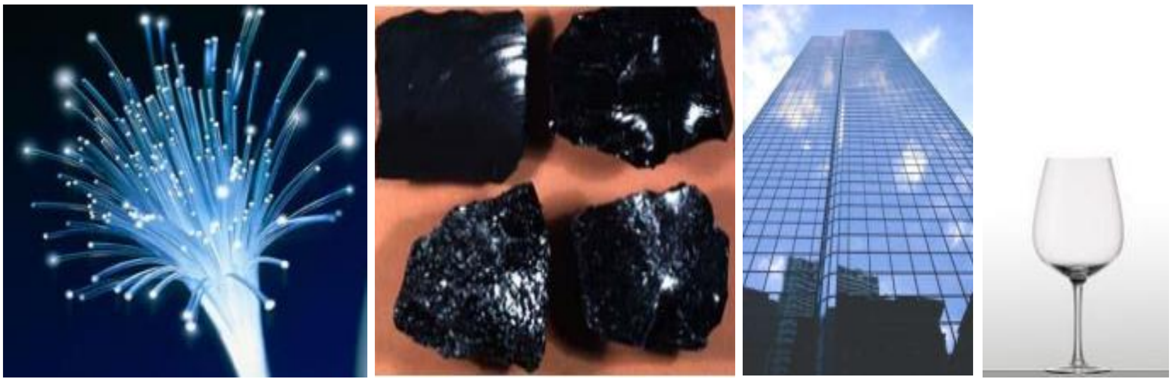


Figure II.2: Optical fibers, Storage glasses (nuclear waste), and Everyday objects.

I.2. Importance

The study of glass structure touches upon various fields [8]:

- Materials Science: Understanding the structure and properties of glasses to develop new materials and improve existing glasses.
- Physicochemistry: Understanding how chemical composition affects the properties of glasses and comprehending the fundamental properties (atomic and molecular structure) of glasses.
- Biology: Bioactive glasses used in medicine and dentistry require an understanding of their structure to optimize their biological properties.
- Geology: Vitreous minerals and amorphous volcanic rocks (such as obsidian) are examples of natural glasses. Natural glasses are studied in geology to understand their formation and origin.
- Archaeology and Anthropology: Ancient glasses provide information about ancient manufacturing techniques and trade.
- Environmental Science: Scientists study glass decomposition to develop more durable glass materials. Glasses can break down into small particles that may pollute the environment.

II. Definition of Glasses

The word "glass" can have various meanings. In everyday language, it refers to a fragile and transparent material. In scientific language, the term "glass" has a broad scope, and it is challenging to define [8].

Two ways to define glass are:

A classic definition by R. Haas states, "Glass is defined as a supercooled liquid that is frozen." Considering this definition, it ignores a whole class of glasses that have never been obtained from a liquid.

ASTM (American Society for Testing Materials) defines glass as a "non-organic product that has been cooled after melting under severe conditions, while avoiding crystallization." This essentially expresses the same thing as the previous definition, excluding polymer glasses. It is clear that a general definition of glass cannot be achieved through production methods.

Finally, with J. Zarzycki in 1982, we juxtapose two definitions: "Glass is a non-crystalline solid exhibiting a glass transition."

Glass families:

There are three main families of glass: metallic, organic, and inorganic.

- Metallic glasses are metal alloys rapidly cooled to prevent crystallization.
- Organic glasses are made from polymers.
- Inorganic glasses are the most common. Inorganic glasses are subdivided into subcategories based on the constitutive anion: (oxygen-based), halides (fluorine or chlorine-based), or chalcogenides (sulfur, selenium, or tellurium-based).

Industrial glasses are mainly silicate glasses, composed of silicon dioxide (SiO_2) and other mineral oxides like aluminum, calcium, sodium, and potassium.

Examples of industrial glasses: Silica glass (ordinary glass), Borosilicate glass (Pyrex glass), Lead glass (crystal glass), Quartz glass (optical glass), Bioactive glass (used in medicine and dentistry).

III. Vitreous State

The vitreous state is a state of matter that exhibits an ordered structure at short and medium distances but disorder at long distances. This means that the atoms or molecules composing glass are arranged regularly on a scale of a few angstroms ($1\ \text{Å} = 10^{-10}$ m) but randomly on a larger scale [9].

The vitreous state is a metastable state, intermediate between the crystal and the liquid. Its structure is often considered to be close to that of the liquid at a given moment; it's a "snapshot" of the liquid's structure. Unlike liquids, there is no atomic movement in glasses.

Glass atoms are disordered, but they vibrate around their equilibrium position. This vibration is characteristic of solids.

Compared to solids, glasses lack a distinct melting point. Instead, they exhibit a glass transition, which is a gradual phase transition between the liquid state and the vitreous state. This transition occurs when the cooling rate of the liquid is faster than the crystallization rate: Vr > Vc.

In summary, the vitreous state is a state of matter with the following properties [8, 9]:
Ordered structure at short and medium distances; Disordered structure at long distances.
No distinct melting point; Produced by rapid cooling; the vitrification method is quenching.

Theories of the Vitreous State:

The study of the vitreous state relies on different complementary theories, enhancing the understanding of the properties and behavior of vitreous materials in various contexts.

- Liquid Surfactant Theory: Glass is a liquid that has been rapidly cooled, preventing crystallization. It is a metastable state of the liquid, sharing some properties with liquids, including some molecular-level mobility.
- Structural Theory: Glass is a non-crystalline solid where atoms are arranged in a disordered manner. This approach aims to understand how atoms organize (or rather, do not organize) in glasses.
- Kinetic Theory: Cooling and heating rates, as well as transition speeds between states, are essential to explain glass properties. This approach focuses on these factors to explain glass properties.
- Glass Transition Theory: Glass undergoes a glass transition during cooling, where the material shifts from a supercooled liquid state to a vitreous state. This theory concentrates on the behavioral changes occurring during this transition.
- Thermodynamic Theory: Glass is a non-equilibrium material, characterized by a higher internal energy compared to its crystallized counterparts. This means that glass cannot spontaneously transform into a stable crystalline state, even over extended periods of time.

IV. Structure and Vitrification

Glass is an amorphous material, meaning it lacks a crystalline structure. Oxide glasses are composed of mineral oxides, which are chemical compounds containing oxygen and another chemical element, typically a metal: A_xO_y. There are two approaches to explain the formation of oxide glasses: structural and kinetic [10].

IV.1. Structural Theories

The structural approaches to the formation of oxide glasses are based on considerations related to crystallography and the nature of chemical bonds [11-16].

IV.1.1. Goldschmidt's Criterion (1926)

This criterion is a rule that explains how certain materials, especially inorganic oxides, can become glasses [11].

Goldschmidt developed his theory on vitrification for a simple oxide of the type A_xO_y (A being the cation).

A glass forms when the ratio of the ionic radii of cations to anions must be between 0.2 and 0.4: $0.2 < Rc/Ra < 0.4$.

This criterion in crystal chemistry is based on the idea that tetrahedral atomic arrangements with 4 anions at the corners are necessary for glass formation.

Goldschmidt's criterion is not always applicable.

Examples: Silica glass (SiO_2) satisfies Goldschmidt's criterion because $Rc/Ra = 0.22$. Beryllium oxide (BeO) does not satisfy Goldschmidt's criterion because $Rc/Ra = 0.17$. However, beryllium oxide can be vitrified in the presence of certain additives.

IV.1.2. Zachariasen's Criterion (1930)

This criterion determines whether a given configuration can form a glass or not.

Zachariasen proposed a model of disordered structure for oxide glasses [12].

For a simple oxide AxOy to form a glass, it must meet four conditions (Figure II.3):

1. Each cation atom is surrounded by a small number of oxygen atoms (3 or 4).
2. Oxygen polyhedra are connected to each other by their vertices (not by an edge or face).
3. At least three vertices of each polyhedron are connected to neighboring polyhedra.
4. An oxygen atom forms a maximum of two bonds with a cation atom.

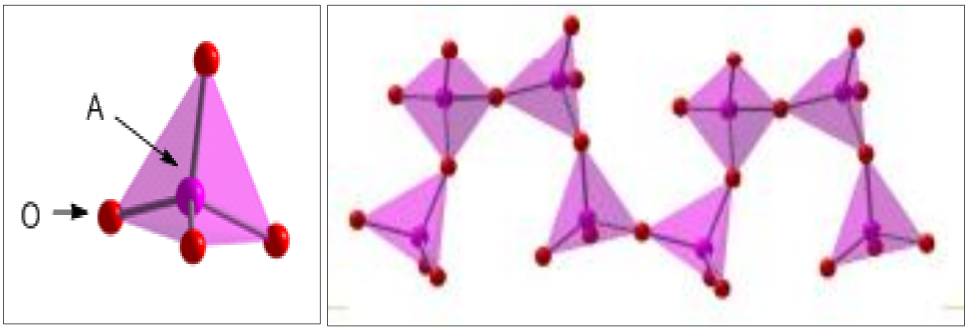


Figure II.3: Chemical structure of glass according to the Zachariasen criterion.

Oxides A_2O or AO cannot form glasses because they do not satisfy Zachariasen's rules.

Oxides A_2O_3, AO_2, and A_2O_5 can form glasses because the oxygen atoms arrange themselves into triangles, tetrahedra, and octahedra, respectively.

Zachariasen defined three classes of oxides:

- Network-forming oxides: These oxides, when cooled, lead to glass formation, such as SiO_2, GeO_2, B_2O_3, As_2O_3, and P_2O_5 (under pressure).
- Network-modifying oxides: These oxides disrupt the glass structure by introducing oxygen atoms not bonded to two cations, depolymerizing the network, such as alkali oxides (Na_2O) and alkaline-earth oxides (BaO).
- Intermediate oxides: Depending on the glass composition, other oxides behave either as network formers or modifiers, examples include Al_2O_3, Fe_2O_3, PbO, TiO_2, and ZnO.

Example (1): Breaking the Si-O-Si bond of the network-forming oxide SiO_2 in the presence of Na^+ forms the network-modifying oxide Na_2O.

IV.1.3. Smekal's Criterion

Other approaches have been proposed to explain glass formation, based on the nature of atomic bonds [13]:

Covalent and ionic bonds must be balanced to promote glass formation. (Covalent bonds are strong and rigid, preventing atoms from moving freely; ionic bonds are strong but exhibit high polarization, leading to defects in the network.)

The presence of Van der Waals bonds can also contribute to glass formation. (Van der Waals bonds are weak but allow some flexibility in the network.)

IV.1.4. Stanworth's Criterion

Stanworth's criterion is based on the idea that oxides with strong covalent bonds are more likely to form glasses (Covalent bonds are more difficult to rearrange than ionic bonds) [14].

The degrees of covalency in the cation-oxygen bonds, Stanworth obtained the same classification based on electronegativity (χ).

Network-forming cations had higher electronegativity (1.8-2) than network-modifying cations (1.5-1.7) and intermediates (0.7-1.2) (Table II.1).

Table II.1: Electronegativity of Various Glass Cations [4]

Network-forming cations	Network-modifying cations	Intermediates cations
Si: $\chi = 1.8$	Al: $\chi = 1.5$	Cs: $\chi = 0.7$
Ge: $\chi = 1.8$	Be: $\chi = 1.5$	K: $\chi = 0.8$
Sb: $\chi = 1.8$	Zr: $\chi = 1.6$	Rb: $\chi = 0.8$
B: $\chi = 2$	Ti: $\chi = 1.6$	Na: $\chi = 0.9$
P: $\chi = 2$	Sn: $\chi = 1.7$	Ba: $\chi = 0.9$
As: $\chi = 2$		Ca: $\chi = 1.0$
		Li: $\chi = 1.0$
		Sr: $\chi = 1.0$
		Mg: $\chi = 1.2$

IV.1.5. Sun's Criterion

Based on the theory of solid structure, it suggests that atoms must already be arranged in polymerized entities in the liquid for glass to form [15].

Sun's quantitative approach is based on the ratio of the dissociation energy of the oxide to the number of exchanged bonds.

The bond strength A-O (F_{A-O}) corresponds to the dissociation energy (E_d) divided by the number of oxygens surrounding the cation, i.e., the coordination number Z:

$$F_{A-O} = E_d/Z \quad \text{(II.1)}$$

Network-forming oxides have bond strengths exceeding 90 kcal/mol, while modifiers have bond strengths below 60 kcal/mol, and intermediate oxides have bond strengths between 60 and 73 kcal/mol.

IV.1.6. Rawson's Criterion

Rawson considered both bond strength ($F_{A\text{-}O}$) and the melting temperature (T_f) to assess vitrification ease, considering that the probability of vitrification of an oxide is higher when the thermal energy to be removed by quenching is low, limiting the possibilities of rearrangement by diffusion [16].

The Rawson parameter is given by [16]:

$$R = F_{A\text{-}O} / T_f \quad \text{(II.2)}$$

Example (2): $R_{SiO_2} = 0.053 < R_{GeO_2} = 0.078$ kcal/K mol

IV.2. Kinetic Theories

The kinetic approach helps understand why some materials form glasses while others do not. It also shows that the quenching rate plays a crucial role in glass formation [8 ,9].

The kinetics of vitrification is influenced by the rates of nucleation (N) and growth of nuclei (C), which are maximal at certain temperatures (Figure II.4).

If the nucleation and growth curves overlap over a wide temperature range, nuclei instantly develop into crystals (b).

If these curves are distinct, the supercooled liquid passes through a region where germ growth would be possible but where nuclei have not yet formed. At lower temperatures, nuclei appear, but their growth is inhibited because the growth rate is zero. This leads to the absence of crystal formation (a).

The quenching rate, i.e., the speed at which the material passes through the nucleation and growth phases, also influences glass formation.

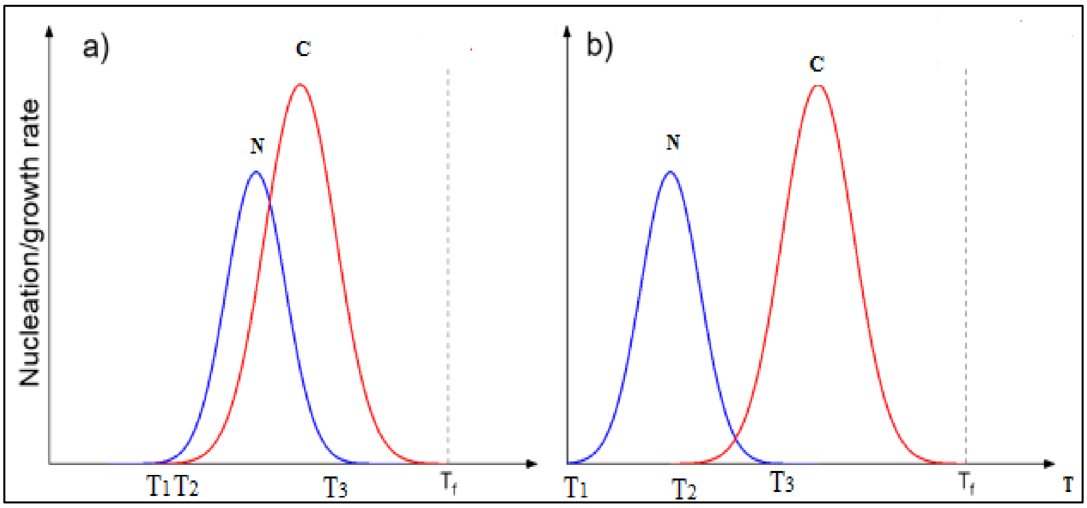


Figure II.4: Nucleation Rate and Growth Rate as a Function of Temperature

V. Glass Transition

Glasses are obtained by quenching (i.e. rapid cooling) the molten material (i.e. at the liquid state) to avoid possible crystallization. The thermal behavior of glass can be described by thermodynamic variables such as specific volume (V_S), enthalpy (H), and heat capacity (Cp) as a function of temperature [8, 9].

When comparing the curves of differential thermal analysis or the enthalpy of glass and crystal (Figure II.5), two additional phenomena are observed on the glass curve:

- Endothermic reaction: glass transition
- Exothermic reaction: crystallization

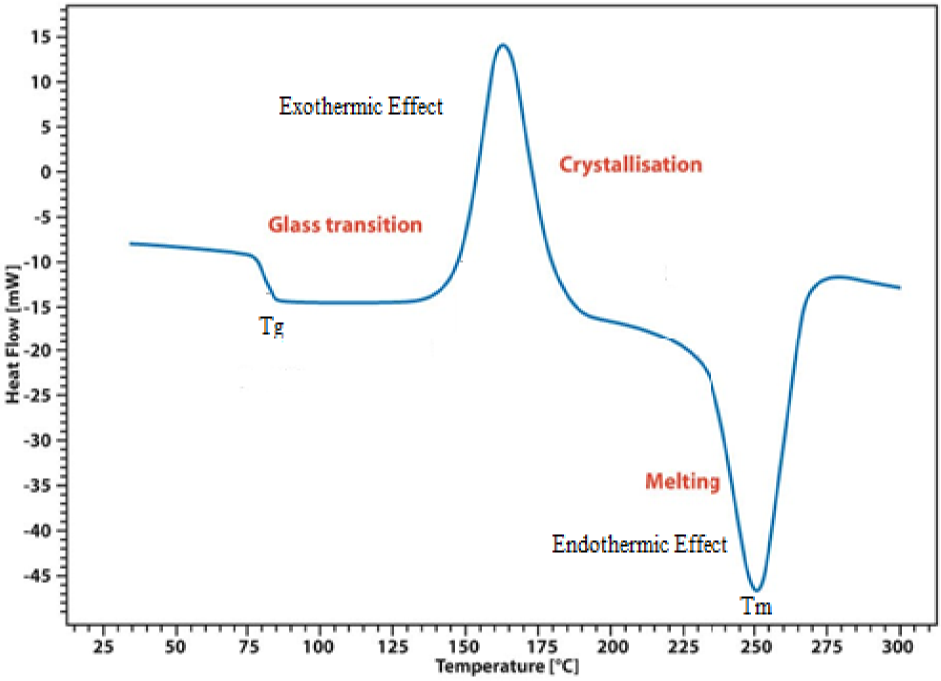


Figure II.5: The thermal analysis curve of glass (T_g: Glass transition temperature; T_c: Crystallization temperature; T_m: Melting temperature)

During cooling, a liquid can remain in a metastable supercooled state at a temperature below its melting temperature (T_m).

The transition from the supercooled liquid to glass is called the glass transition, defined by the glass transition temperature (T_g) (Figure II.6).

The cooling rate affects T_g, with higher rates leading to a transition at higher temperatures.

Glass has a higher molar volume than the corresponding crystal at room temperature due to its open structure, promoting the diffusion of small chemical species.

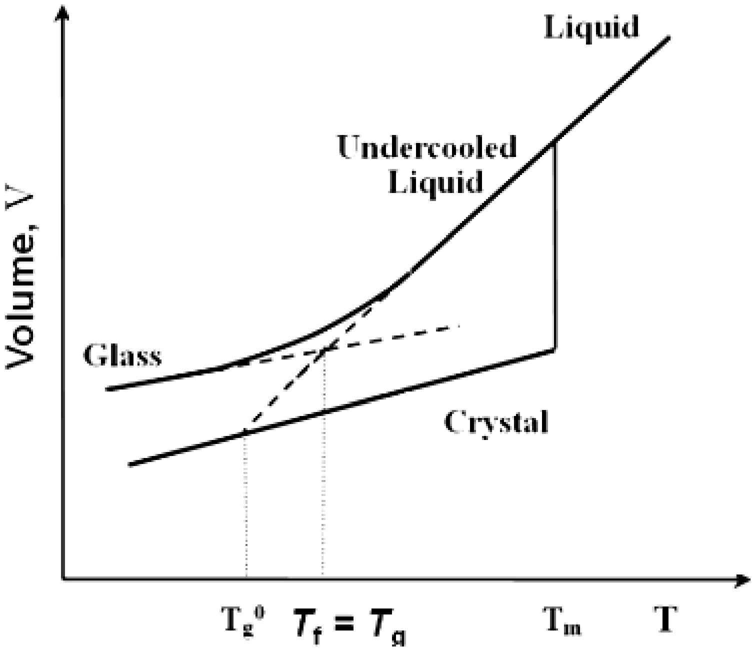


Figure II.6: The phenomenon of glass transition

V.1. Measurement Methods for Transition

Various experimental techniques can be used to determine the glass transition temperature of a compound. The most appropriate technique depends on the material under study [17]:

Differential Scanning Calorimetry (DSC): Measures changes in specific heat during the Tg transition.

Dynamic Mechanical Analysis (DMA): Measures mechanical properties in response to oscillating stress.

Thermogravimetric Analysis (TGA): Measures weight loss as a function of temperature.

Viscosity Measurement: Measures the material's viscosity at different temperatures.

Fluorescence or Phase-Contrast Microscopy: Observes structural and morphological changes.

Dilatometer: Measures volume variations as a function of temperature.

Nuclear Magnetic Resonance (NMR): NMR is a powerful technique to study molecular mobility, but it is less commonly used for the glass transition temperature of glassy materials.

X-Ray Reflectivity Measurement: This technique is often used for studying surface structure, and its application for Tg characterization is less frequent.

V.2. Factors Affecting Tg

The glass transition temperature of a material is influenced by various factors, including [9, 17]:

V.2.1. Molecular Structure

Molecular weight and its distribution play a role. For example, linear chain polymers generally have a lower Tg than cross-linked ones.

V.2.2. Heating/Cooling and Deformation Rates

Rates of heating, cooling, and deformation can modify the glass transition temperature. An increase in heating or deformation speed can lead to an increase in the glass transition temperature.

V.2.3. Mechanical Properties

The glass transition temperature is related to mechanical properties, such as tensile strength. Polymers with a higher Tg generally exhibit better mechanical, chemical, and thermal resistance.

V.2.4. Chemical Composition

Chemical composition, including additives, can alter the glass transition temperature. For instance, the addition of additives may modify the glass transition temperature of a material.

V.2.5. Thickness of Crystalline Lamellae

Polymers with thicker lamellae tend to have a higher glass transition temperature.

V.2.6. Measurement Conditions

The glass transition temperature may vary under different measurement conditions, such as pressure. An increase in pressure, for example, can lead to an increase in the glass transition temperature.

V.3. Main Theories of Transition

Despite scientific advancements, glass transition remains mysterious. The theories vary regarding its order, as it does not correspond to a first or second-order transition. Some theories consider it a kinetic phenomenon due to its impact on the cooling rate.

The main theories include (**Appendix 1**) [18, 19]:

- Free Volume Theory
- Gibbs-DiMarzio Theory
- Adam-Gibbs Theory
- Coupling Theories
- Mode-Coupling Theory

V.3.1 Free Volume Theory

The free volume theory is a structural theory of glass transition. It postulates that glass transition occurs due to a decrease in the free volume of molecules as the material is cooled. The free volume is defined as the difference between the total volume of the material and the volume occupied by the molecules [18].

The free volume is denoted as V_L:

$$V_L = V_{total} - V_{occupied} \qquad \text{(II.3)}$$

Where: V_{total} and $V_{occupied}$ correspond to the total volume and the occupied volume, respectively, which is the sum of volumes occupied by the atoms.

The theory relies on an equation relating viscosity (η) to temperature (T) and specific free volume (V_f), represented by the inverse of density (ρ), and B is a constant.

The basic equation is: $\eta (T) = \eta_0 \exp [BV_0 / V_f (T)]$ (II.4)

The basic transfer is assumed to occur at a temperature T_0, where $T_g > T_0$, so the William–Landel–Ferry equation is:

$$\eta (T) = \eta_0 \exp [BT_0 / (T-T_0)] \qquad \text{(II.5)}$$

It is possible to relate the coefficient of expansion to free volume using the following equation:

$$(\partial V_{(L)})/\partial T = V(\alpha_L - \alpha_g) \qquad \text{(II.6)}$$

Where: α_L and α_g represent the coefficients of expansion for the supercooled liquid and glass, respectively;

And the difference in coefficients of expansion is inversely proportional to Tg as follows:

$$(\alpha_L - \alpha_g)\, T_g = cst = 0.113 \qquad (II.7)$$

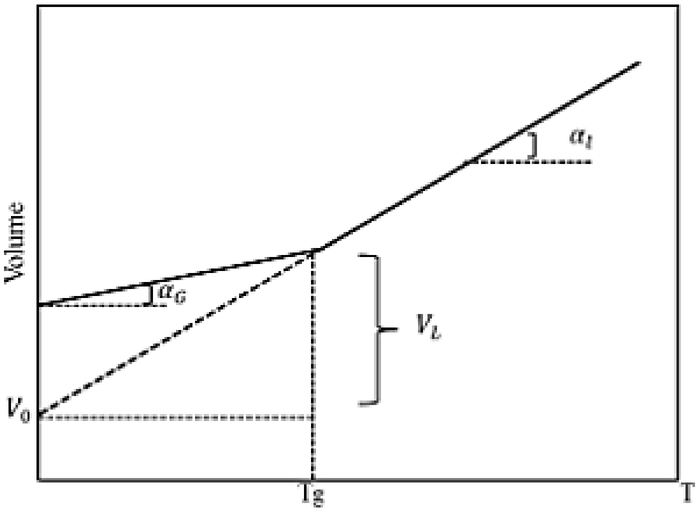


Figure II.7: Coefficients of Expansion Curve of Glass

The free volume theory works well for temperatures above T_g; however, its application at lower temperatures leads to some misunderstandings.

V.3.2. Gibbs-DiMarzio Theory

Introduced by Josiah Willard Gibbs and Edward DiMarzio in 1958

The glass transition is attributed to an increase in the configurational entropy (Sc) of molecules as they transition from the liquid state to the amorphous solid state, i.e., the glass transition is due to the relaxation of molecular movements.

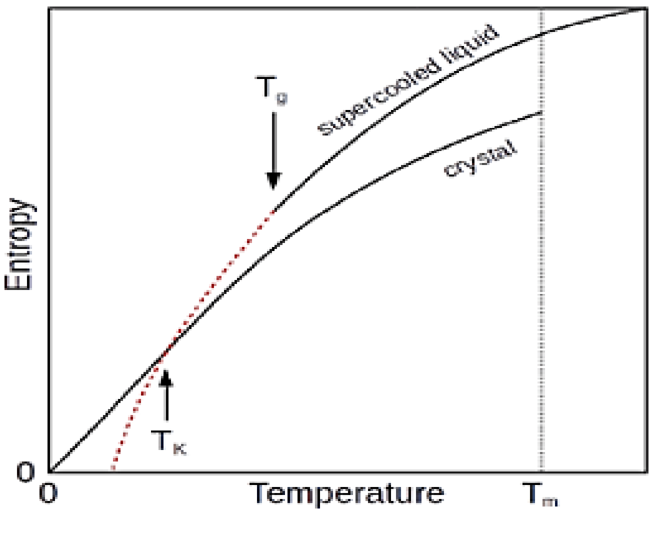


Figure II.8: Relaxation Curve of Glass

At the temperature, denoted as T, between T_K and the conventionally obtained T_g, the system will undergo a transition. Experimentally, T is defined as approximately equal to Tg – 50K. Additionally, T can be viewed as the glass transition temperature for a system that has undergone infinitely slow cooling. At this temperature, S_C is assumed to be zero (degrees of freedom related to vibration are not considered). In other words, this would be within the framework of an ideal or perfect glass.

V.3.3. Adam-Gibbs Theory 1965

The glass transition occurs when molecules become unable to move cooperatively. According to Adam and Gibbs, the relaxation time of supercooled liquids, i.e., liquids capable of forming glasses, is related to SC, which depends on the number of molecules involved in a cooperative arrangement.

It is described by the following relationship:

$$\tau = \tau_0 \, exp(C_{AG}/T \, S_c) \qquad \text{(II.8)}$$

Where: τ_0 and C_{AG} are constants independent of T and P; C_{AG} is proportional to the activation free energy via the difference in chemical potential (Δμ) for local arrangements.

This theory has been a subject of discussion in the scientific community because it is challenging to determine the configurational entropy. They propose, supported by the work of other researchers, that SC is equal to the excess entropy (S_e), which is defined as the entropy difference between the liquid and the crystal, given by the equation:

$$S_e = \int_T^0 \left(C_{p,l} - C_{p,c}\right) \, d\ln(T) \qquad \text{(II.9)}$$

Where: $C_{p,l}$ and $C_{p,c}$ correspond to the constant-pressure heat capacities of the liquid and the crystal, respectively.

Exercise Series No. 2

Exercise II.1

Classify the following glasses based on their family (metallic, organic, or inorganic):

Borosilicate Glass; Poly(methyl methacrylate) (PMMA); Lead Glass; Quartz Glass;

Zr-Ti-Cu-Ni-Be Alloy; Copper Glass; Polycarbonate; Vitreloy 4

Exercise II.2

Check if the following compounds satisfy the Goldschmidt and Zachariasen criteria for the formation of oxide glasses using the provided data. Explain.

B_2O_3, BeO, BeF_2, GeO_2, P_2O_5, As_2O_3, As_2O_7

Data:

Table II.2: Atomic numbers and Ionic radii of various atoms

Atoms	O	B	Be	F	Ge	P	As
Atomic numbers (Z)	8	5	4	9	32	15	33
Ionic radii (R) pm	140	23	27	133	53	44	58

Exercise II.3

Consider the following chemical compounds: Na_2O, SiO_2, PbO.

1. Verify if these compounds satisfy the conditions of the Zachariasen criterion for glass formation.
2. Identify the role of each of these compounds in the glass structure according to the Sun criterion. Explain.

Data:

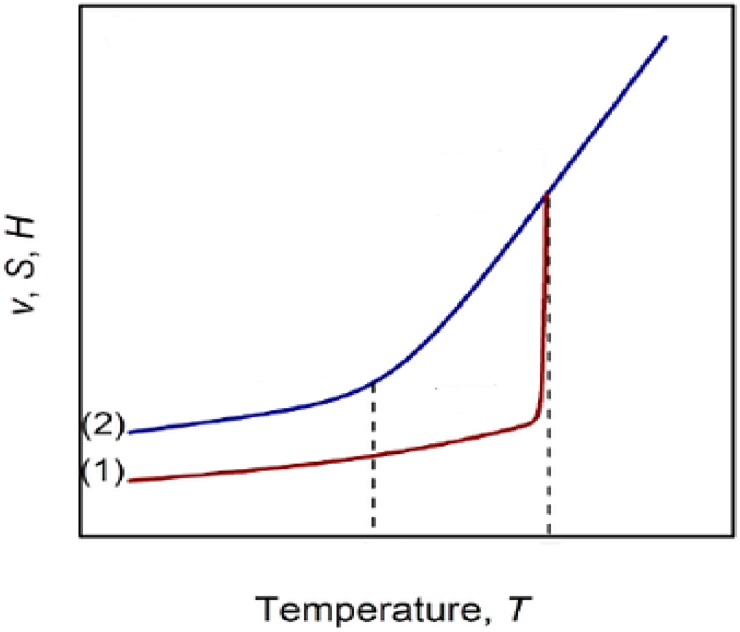
Table II.3: Atomic numbers and Dissociation energy of various atoms

Atoms	Si	Na	Pb
Atomic numbers (Z)	14	11	15
Dissociation Energy (E_d) Kcal/mol	424	120	145

Exercice II.4

1. Identify the curves representing the transitions between crystal and glass in the figure below.

2. Complete the data of the curves and determine the glass transition temperature as well as the melting temperature.
3. What analysis techniques are frequently used to precisely evaluate the glass transition temperature?



Exercise II.5

Assuming we have two different polymers: Poly(methyl methacrylate) PMMA cooled at a rate of 100°C per minute and Polystyrene cooled at a rate of 1°C per minute.

Determine which of these polymers will have a higher glass transition temperature (T_g) and explain why.

Exercise II.6

The glass transition is a thermal transition corresponding to the transformation from a supercooled liquid to a glassy state during cooling. This transition depends on the cooling rate.

During a slow cooling at 0.2°C/min, a glass transition temperature T_g of 50°C is measured for a given glassy material.

What will be the approximate value of T_g if the same material is cooled at a rate of 75°C/min?

Exercise Series No. 2: Solutions

Exercise II.1

The classification of different types of glasses mentioned in the exercise:

- Borosilicate Glass: Inorganic glass, Chemical composition: Silica-SiO_2 (80%) + Boric anhydride-B_2O_3 (13%) + Sodium-Na_2O (4%) + Alumina-Al_2O_3 (3%).
- Poly(methyl methacrylate) (PMMA): Organic glass, Chemical formula: -[CH3OCOC(CH3)-CH2]n-, methyl ester of poly(methacrylic acid).
- Lead Glass: Inorganic glass, Composition is generally SiO2-PbO, K2O.
- Quartz Glass: Inorganic glass, Chemical formula: SiO_2.
- Zr-Ti-Cu-Ni-Be Alloy: Metallic glass, composed of several metals and metalloids. Composition: Zr47Ti8Cu7.5Ni10Be27.5.
- Copper Glass: Inorganic glass, Composition is generally SiO_2-CuO.
- Polycarbonate: Organic glass, Chemical formula: -[CO-O-pPh-C$(CH_3)_2$-pPh-O]n.
- Vitreloy 4: Metallic glass composed of several metals and metalloids. Composition: Zr41.2Ti13.8Cu12.5Ni10Be22.5.

Exercise II.2

1. Goldschmidt Criterion:

- B_2O_3: Rc/Ra = 23/140 ≈ 0,164, which does not satisfy the condition $0,2 < Rc/Ra < 0,4$.
- Therefore, B_2O_3 so BeO does not meet the Goldschmidt criterion.
- BeO: $Rc/Ra = 0,19 < 0,2$; so, BeO does not meet the Goldschmidt criterion.
- BeF_2: $Rc/Ra = 0,08 < 0,2$; so, BeF_2 does not meet the Goldschmidt criterion and non-oxide.
- GeO_2: $Rc/Ra = 0,27 < 0,4$; so, GeO_2 meet the Goldschmidt criterion.
- P_2O_5: $Rc/Ra = 0,09 < 0,2$; so, P_2O_5 does not meet the Goldschmidt criterion.
- As_2O_3: $Rc/Ra = 0,16 < 0,2$; so, As_2O_3 does not meet the Goldschmidt criterion.
- As_2O_7: $Rc/Ra = 0,11 < 0,2$; so, As_2O_7 does not meet the Goldschmidt criterion.

2. Zachariasen Criterion:

- B_2O_3: B_2O_3 satisfies all four conditions of the Zachariasen criterion.

Explanation: The oxide B_2O_3 is of the type A_2O_3, and each boron atom is surrounded by 3 oxygen atoms. The oxygen polyhedra are connected by their vertices, at least three vertices of each polyhedron are connected to neighboring polyhedra, and an oxygen atom exchanges a maximum of two bonds with a boron atom.

- BeO: BeO does not satisfy the conditions of the Zachariasen criterion.

Explanation: Beryllium atoms are surrounded by only one oxygen atom, which does not comply with condition 1.

- BeF_2: BeF_2 does not satisfy the conditions of the Zachariasen criterion.

  Explanation: Beryllium atoms are surrounded by six fluorine atoms and not oxygen, which does not comply with condition 1.

- GeO_2: GeO_2 satisfies all four conditions of the Zachariasen criterion.

Explanation: The oxide GeO_2 is of the type AO_2, and each germanium atom is surrounded by four oxygen atoms. The oxygen polyhedra are connected by their vertices, at least three vertices of each polyhedron are connected to neighboring polyhedra, and an oxygen atom exchanges a maximum of two bonds with a germanium atom, and the oxygens form tetrahedra.

- P_2O_5: P_2O_5 satisfies the conditions of the Zachariasen criterion.

Explanation: The oxide P_2O_5 is of the type A_2O_5, and each phosphorus atom is surrounded by 3 oxygen atoms. The oxygen polyhedra are connected by their vertices, at least three vertices of each polyhedron are connected to neighboring polyhedra, and an oxygen atom exchanges a maximum of two bonds with a phosphorus atom.

- As_2O_3: As_2O_3 satisfies the Zachariasen criterion.

Explanation: The oxide As_2O_3 is of the type A_2O_3.

- As_2O_7: As_2O_7 satisfies the Zachariasen criterion.

Explanation: The oxide As_2O_7 is of the type A_2O_7.

Exercise II.3

1. Zachariasen Criterion:

- Na_2O does not satisfy the Zachariasen rules because it is an oxide of type A_2O.
- SiO_2 satisfies the Zachariasen rules because it is an oxide of type AO_2, and the oxygens form tetrahedra.
- PbO does not satisfy the Zachariasen rules because it is an oxide of type AO.

2. The role of each compound according to the Sun criterion:

We calculated the bonding forces.

$F_{Na-O} = E_d/Z = 140/6 = 23.33$ Kcal/mol;

$F_{Si-O} = E_d/Z = 424/4 = 106$;

$F_{Pb-O} = E_d/Z = 145/2 = 72.5$ Kcal/mol

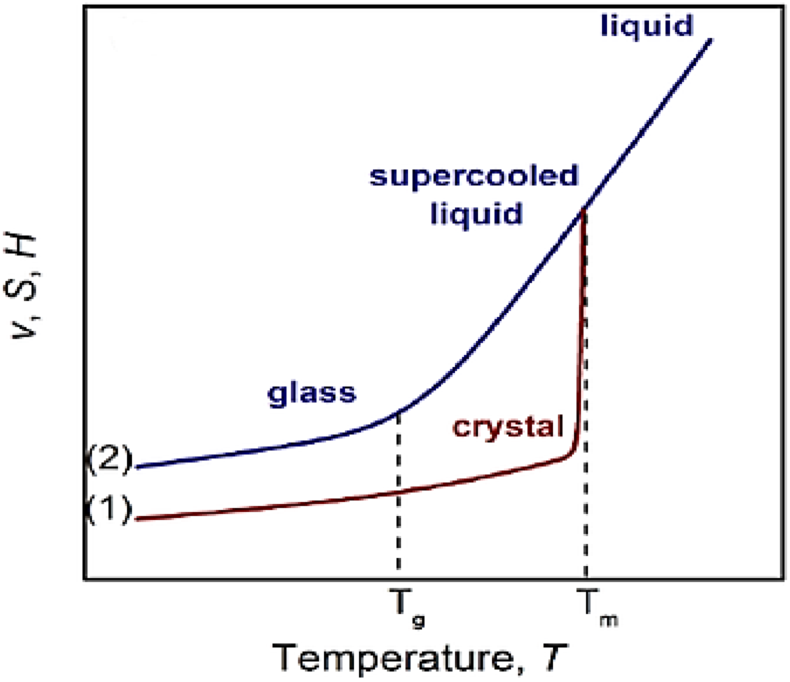
Na_2O is a modifier because the Na-O bonding strength (F_{Na-O}) is less than 60 Kcal/mol.

SiO_2 is a former because the Si-O bonding strength (F_{Si-O}) is greater than 90 Kcal/mol.

PbO is an intermediate because the Pb-O bonding strength (F_{Pb-O}) is between 60 and 73 Kcal/mol.

Exercice II.4

1. The curves representing the transitions between crystal and glass are: Curve (1) - Crystal and Curve (2) - Glass.
2. The data from the curves and the glass transition temperature, as well as the melting temperature, are indicated in the following figure:



3. The analysis techniques frequently used to precisely evaluate the glass transition temperature are:
   - DSC (Differential Scanning Calorimetry)
   - DMA (Dynamic Mechanical Analysis)
   - TGA (Thermogravimetric Analysis).

Exercise II.5

The poly(methyl methacrylate) (PMMA) will have a higher glass transition temperature (Tg) than polystyrene.

In summary, PMMA will have a higher Tg than polystyrene because it is cooled more rapidly.

Exercise II.6

The glass transition temperature (Tg) at 0.2 °C/min

Tg at 0.2°C/min, which is 50°C: 0.2°C/min → 50°C.

75°C/min → Tg (°C)

Therefore: Tg = 50 x 75 / 0.2 = 18,750°C.

Chapter III: Study of the Properties of Industrial Glasses

Chapter III: Study of the Properties of Industrial Glasses

I. Introduction

Industrial glass possesses numerous properties that give it its unique characteristics. These properties can be classified into several categories, including thermal, chemical, optical, mechanical, and acoustic (**Appendix 2**) [17, 20].

II. Optical Properties

The optical properties of glasses are based on the interaction of light or electromagnetic wave energy with the medium (absorption, reflection, and diffraction of light).

Glasses are interesting for optics because they are isotropic, homogeneous, and have variable properties depending on the composition (lack of stoichiometry).

They can be manufactured in large dimensions, unlike crystals [20].

II.1. Transparency

Transparency is a property of matter that allows light to pass through without being absorbed. The absorption of radiation is a resonance phenomenon: electrically charged particles in matter can absorb light energy when the frequency of light is close to their natural frequency.

Metals are opaque because they contain free electrons that can oscillate at any frequency. These free electrons absorb all radiations, regardless of their frequency.

Oxide glasses do not contain free electrons. Therefore, they absorb less radiation than metals.

However, oxide glasses still absorb some radiations [20, 21]:

- Electronic transitions absorb ultraviolet (UV) radiations, which have high frequencies.
- Molecular vibrations absorb infrared (IR) radiations, which have lower frequencies.

Glass is not completely transparent to radiation energy.

The transparency of glass is an important property that allows its use in many applications, such as windows, lenses, and prisms.

II.2. Absorption

The absorption of radiation by glass leads to the production of heat. This heat can be problematic for optical systems and windows, as it can cause overheating.

Glass is a material that absorbs a portion of the radiation that strikes it. Solar radiation consists of visible light, ultraviolet, and infrared. Glass is transparent to visible light but absorbs ultraviolet and infrared radiations.

Glass is transparent to visible light, allowing light to pass through without absorption. Visible light has a wavelength, between 0.4 and 0.7 microns (Figure III.1).

Glass transmits 43% of visible light, 3% of ultraviolet, and 54% of infrared. The amount of radiation transmitted through glass depends on the wavelength of the radiation. Glass is more transparent to visible light than to ultraviolet and infrared radiations [22].

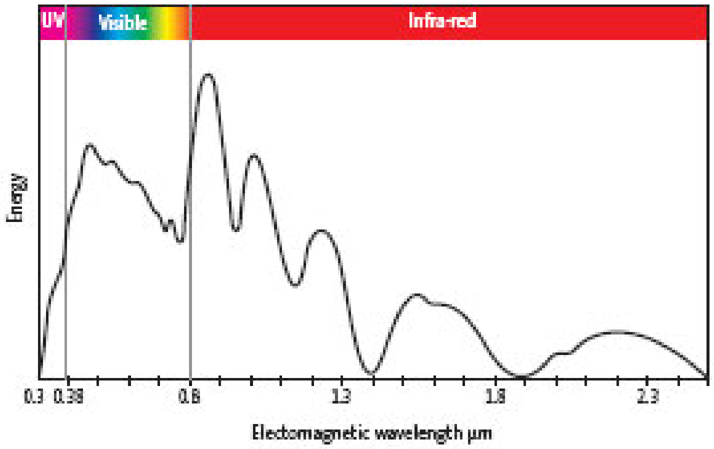


Figure III.1: Spectrum of global solar radiation according to EN 410

II.3. Refraction

Refraction is the change in direction of a light ray as it passes from one medium to another. The change in the direction of the light ray is due to the change in the speed of light propagation in the two media.

Descartes' law relates the refractive index (n) of the two media to the angle of incidence and the angle of refraction (i).

Descartes' law, which can be expressed as follows:

$$n_1 \sin(i_1) = n_2 \sin(i_2) \qquad \text{(III.1)}$$

- The refractive index (n) is a dimensionless number that characterizes the propagation of light in a medium. It is defined as the ratio of the speed of light in a vacuum (V_0) to its speed in the considered medium (V_m):

$$n = V_0 / V_m \qquad \text{(III.2)}$$

The angle of refraction is the angle formed by the refracted light ray with the normal to the surface separating the two media.

The refractive index of glass is related to its composition.

Glasses rich in former oxides, such as silica, have a lower refractive index than glasses rich in alkali and alkaline-earth oxides. This is because former oxides have stronger covalent bonds than alkali and alkaline-earth oxides. Stronger covalent bonds make it more challenging to align the electric charges of glass atoms and molecules, resulting in a lower refractive index.

According to electromagnetic theory, the refractive index increases with the number of dipoles and their polarizability. Glasses rich in former oxides, with poorly polarizable bridging oxygens, are expected to have a low refractive index.

For silica n_D = 1,459, and for soda-lime glass, n_D = 1,520.

The refraction of light when it enters glass is the basis of the development of the optical industry (Figure III.2).

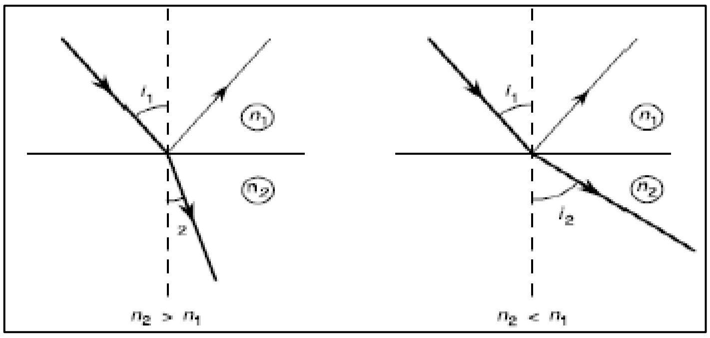


Figure III.2: Refraction and reflection of a light ray at the interface of two transparent media

Fresnel Reflection Factor: $R_F = [(n_2 - n_1)/(n_2+n_1)]^2$ (III.3)

Optical transmission: Ratio of transmitted flux to incident flux (Figure III.3)

$$T = I/I_0 \qquad \text{(III.4)}$$

$$I_1 = I_0 - R_F I_0 \qquad \text{(III.5)}$$

$$I = I_2 - R_F I_2 \qquad \text{(III.6)}$$

$$I_2 = I_1 \, e^{-kl} \qquad \text{(III.7)}$$

Where: k is the absorption coefficient (depends on the type of glass); l is thickness.

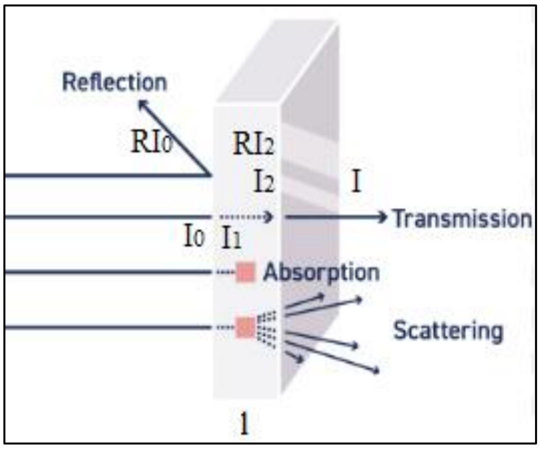


Figure III.3: Optical transmission of glass

II.4. Optical Filters

Glass optical filters can be used to block or transmit a range of wavelengths of light. For example:

- Glasses rich in nickel and cobalt oxides only transmit ultraviolet light.
- Glasses containing CeO_2 absorb in the ultraviolet.
- Iron-rich phosphate glasses absorb near-infrared light.
- Black glasses with chrome and manganese oxides only transmit near-infrared light.
- Glass optical filters are available in a variety of types and compositions, allowing them to be tailored to a wide range of applications, such as sunglasses, heat-resistant filters, and optical instruments.

III. Mechanical Properties

Glasses exhibit several mechanical properties that distinguish them from other materials, such as: Mechanical strength, Viscosity and density, Dilatability, Hardness, Elasticity [20, 21].

III.1. Mechanical Strength

The mechanical strength of glass is a crucial factor to consider in the design and manufacturing of glass objects. Understanding the mechanical properties of glass allows for the design of objects that are more resistant to damage [21].

III.1.1. Brittle Fracture

Glass is a brittle material, meaning it breaks easily when subjected to tension. The mechanical strength of glass depends on the presence of microcracks-small fissures that form on the glass surface.

These microcracks can result from impacts, scratches, or manufacturing defects. The presence of microcracks weakens the glass, making it more prone to breakage. Glass fracture is abrupt and occurs perpendicular to the maximum tensile stress, meaning it happens suddenly without any warning signs.

A solid glass behaves like a perfectly elastic solid: the (reversible) deformation ε is proportional to the stress σ:

$$\sigma = \gamma\, \varepsilon \quad \text{(III.8)}$$

With: γ being the modulus of elasticity.

III.1.2. Static Fatigue

The glass's resistance to fatigue depends on the duration of the applied load and the presence of ambient humidity. Fatigue is a phenomenon that can lead to failure at a subcritical stress. It is exacerbated in the presence of ambient humidity, as moisture can accelerate glass corrosion.

- Thermal tempering and chemical tempering are techniques that can enhance the mechanical strength of glass.
- Thermal tempering involves rapidly cooling the glass, creating a compressive state on the surface.
- Chemical tempering involves ion exchange on the glass surface, also creating a compressive state.

III.2. Viscosity and Density

III.2.1. Viscosity

Glass is an amorphous material exhibiting viscoelastic behavior within a range of the transition temperature. In this range, glass cannot be characterized by a single quantity, such as Young's modulus or viscosity. To understand glass behavior in industrial applications, like thermal tempering, it's necessary to conduct elementary stress experiments (creep and relaxation). These experiments determine values for viscoelastic parameters, such as the relaxation modulus and viscosity coefficient. Understanding the relaxation functions of these stress types is crucial for comprehending glass behavior in complex-shaped pieces.

Examples of industrial applications where understanding the viscoelastic behavior of glass is important:

- Thermal tempering, a process involving heating glass to its transition temperature and rapidly cooling it, creating an internally stressed state that enhances shock resistance.
- The manufacturing of complex-shaped parts can generate three-dimensional stresses in the glass. Understanding the viscoelastic behavior of glass is essential for designing parts that will withstand these stresses [20, 21].

III.2.2. Density

The density of glass is significant for several reasons. Firstly, it is easy to measure, making it useful for production checks. Secondly, it can be used to understand the glass structure. For instance, a higher density may indicate a glass containing more pure silica.

The density of glass typically ranges between 2.5 and 2.6 g/cm^3, slightly lower than that of pure silica at 2.65 g/cm^3. This difference is attributed to other components in glass, such as sodium and calcium oxides, which take up slightly more space.

The molar volume, defined as the volume occupied by one mole of a substance, is usually expressed in cubic centimeters per mole (cm^3/mol). The molar volume of glass can be calculated from the density using the following formula:

$$V_M = \rho / (\Sigma\ Xi\ Mi) \qquad \text{(III.9)}$$

Where: V_M is the molar volume, ρ is the density, Xi is the mole fraction of component i, and Mi is the molecular weight of component i.

III.3. Dilatability

Glasses, like all solid bodies, exhibit thermal dilatability. Thermal dilatability is the property of a material to expand or contract based on temperature.

Two quantities are used to characterize thermal dilatability:

- The linear expansion coefficient: $\alpha = \Delta l / l\ \Delta T$ (III.10)
- The volumetric expansion coefficient: $\beta = \Delta V / V\ \Delta T$ (III.11)

Where: l is the length; V is the volume of glass; and T is the temperature.

Thermal dilatability is crucial in practical terms. Materials with a low coefficient of thermal expansion are less likely to deform or break when subjected to temperature changes.

For example, alkali borosilicates, which have a low coefficient of thermal expansion, are used to manufacture shock-resistant containers.

Examples of industrial applications where thermal dilatability is important:

- Glass manufacturing: The thermal dilatability of glasses must be considered to avoid cracks and deformations during the manufacturing process and to ensure structural stability.
- Use of glass in high-temperature applications: Glasses with a low coefficient of thermal expansion are used in high-temperature applications, such as in furnaces.

III.4. Hardness

The hardness of glass refers to its resistance to penetration. Material hardness is measured using the Mohs scale; for example, the hardness of soda-lime glass is approximately 6.

Glass hardness can be studied in more detail through indentation techniques, with the Vickers technique being the most common. During indentation, four phenomena occur:

- Elastic deformation, which is reversible and diminishes over time.
- Densification, an increase in the local density of the glass.
- Plastic flow, an irreversible deformation of the glass.
- Formation of a network of microcracks. Examples of industrial applications where glass hardness is important:
- Glass manufacturing: Glass hardness must be considered to prevent scratches and damage during the manufacturing process and to ensure structural strength.
- Use of glass in safety applications: Hard glasses are used to protect individuals against injuries.

III.5. Elasticity

Glass, below its glass transition temperature, behaves as an elastic and brittle solid. When a glass specimen is subjected to a tensile or flexural test, its deformation is perfectly reversible until fracture, and unexpectedly, the fracture plane is always perpendicular to the maximum tensile stress at that point. After fracture, the fragments of the specimen can be assembled to regain its initial shape and dimensions.

Young's modulus: The ratio of Young's modulus to the density can affect the quality of glass in several ways (Table III.1):

- Rigidity and strength: Glass with a high Young's modulus and low density is rigid and strong, suitable for applications demanding high strength, such as containers resistant to thermal shocks.
- Elasticity and flexibility: Glass with a low Young's modulus and high density is more elastic and flexible, which may be desirable for certain applications, but it can also make it brittle, such as optical fibers that require great flexibility for light transmission.
- Transparency and optical index: Maintaining a proper balance between these properties is essential to preserve the transparency and optical index of the glass.

However, other factors like chemical composition and structure also influence the quality of the glass.

Table III.1: Young's Modulus E and Density ρ of Some Industrial Glasses.

Glasses	E (GPa)	ρ (g/cm^3)	E/ρ
Soda-lime	66	2.5	26.4
Borosillicate	68	2.4	28.3
SiO_2	70	2.2	31.8
B_2O_3	17	1.82	9.3
GeO_2	43	3.64	11.8

IV. Thermal Properties

The thermal properties of glass are crucial in various applications. These properties include specific heat (measuring the energy needed to change temperature), the coefficient of thermal expansion (influencing thermal deformation), and thermal conductivity (determining the speed of temperature change). Concrete examples of how the thermal properties of glass are utilized in practical applications include [20, 22]:

The specific heat of glass is used to calculate the amount of energy needed to heat or cool a glass object.

The coefficient of thermal expansion of glass is used to calculate the thermal stresses that can occur in a glass object when subjected to temperature changes.

Glass with a low coefficient of thermal expansion is less likely to crack or break due to temperature changes.

The thermal conductivity of glass is used to calculate the speed at which heat propagates through a glass object.

Glass with low thermal conductivity is more resistant to thermal shocks.

Thermal properties of glass are also crucial for the safety of glass products.

IV.1. Specific Heat

Specific heat is a measure of the amount of thermal energy needed to increase the temperature of a substance by 1 degree Celsius. In the case of glass, specific heat increases with temperature. This is because glass atoms have more thermal energy at higher temperatures.

For silica-based glasses, the Dulong and Petit law states that the specific heat of solids is equal to 3R per gram-atom, where R is the gas constant. The specific heat of the molten glass is much higher and almost independent of temperature. This is because the atoms in the molten glass are free to move, allowing for greater absorption of thermal energy.

The sharp discontinuity from glass to molten glass allows for an easy determination of the glass transition temperature using calorimetric techniques (ATD and DSC). Calorimetric techniques measure the amount of energy absorbed or released by a substance as a function of temperature.

IV.2. Thermal Conductivity

Thermal conductivity is a measure of the amount of heat that passes through a material's surface per unit of time and unit temperature difference (**Appendix 2**).

In the case of glass, thermal conductivity is due to two mechanisms:

- Phononic conduction is the conduction of heat through the vibrations of glass atoms. Vibrations are transmitted from one atom to another, allowing heat to propagate.
- Photonic conduction is the conduction of heat through infrared radiation. Glass atoms absorb infrared radiation, warming them. The heated atoms then emit infrared radiation, allowing heat to spread.
- Phononic conduction is weak in glass because glass atoms are rigidly bound. Photonic conduction is more significant in glass as glass is transparent to infrared radiation. The thermal conductivity of glass increases with temperature as photonic conduction becomes more important.

The Deissler expression calculates thermal conductivity (Kr) based on the photonic conductivity (βe) of a homogeneous medium, with thickness e and bounded by two surfaces with emissivities ε_1 and ε_2. Emissivity is a measure of a material's ability to emit infrared radiation..

$$K_r = \frac{4n^2\sigma T^3 e}{\frac{1}{\varepsilon_1} + \frac{1}{\varepsilon_2} - 1 + \frac{3\beta_e}{4}} \quad (\text{III}.12)$$

Where: σ Boltzmann constant (W/m^2K^4); n Refractive index; and T Temperature (K)

IV.3. Thermal Expansion

Thermal expansion is a property of materials that measures the increase in volume of a material per unit temperature.

In the case of glass, thermal expansion is due to the anharmonicity of atomic vibrations, meaning they are not perfectly sinusoidal.

Due to anharmonicity, the amplitude of atomic vibrations increases with temperature, leading to an expansion of the glass volume.

The coefficient of thermal expansion of glass measures the increase in volume per unit temperature and is expressed in ppm/°C.

Hard glasses have a low coefficient of thermal expansion, while soft glasses have a high coefficient of thermal expansion. Silica has a very low coefficient of thermal expansion, approximately 0.5 ppm/°C.

Thermal expansion is an important thermal property of glass as it affects the mechanical properties and stability of glass. In particular, thermal expansion influences the possibilities of glass welding.

Glass welding is a process that involves joining two glass pieces by fusing their edges. For successful welding, it is crucial that both glass pieces have a similar coefficient of thermal expansion. If the coefficient of thermal expansion of the two glass pieces is too different, the weld may crack or break.

V. Electrical Properties

Among the electrical properties of glasses, conductivity and dielectric properties are predominant [23, 24].

V.1. Electrical Conductivity

Electrical conductivity is a property that measures the amount of electric current that can pass through a material. In the case of glass, electrical conductivity is very low at room temperature due to the rigid binding of glass atoms, hindering ion movement.

The mobility of alkali ions is the main cause of electrical conductivity in glass at room temperature. Alkali ions are positive ions that can move more easily than negative ions. It is possible to achieve higher electrical conductivity in glasses, but it is more challenging. This can be done by adding elements to the glass composition that increase ion mobility.

Examples of applications:

Applications of electrically conductive glasses include pH electrodes, fuel cells, and batteries.

- pH electrodes are used to measure the pH of a solution. They consist of a thin glass in contact with the solution. Alkali ions from the glass move into the solution, creating an electric potential.
- Fuel cells and batteries use electrically conductive glasses to transport ions between electrodes.
- Superionic-conductive glasses are a type of glass with very high electrical conductivity. They are studied for potential applications in fuel cells and batteries.

V.2. Dielectric Properties

Glass is generally a dielectric, meaning it does not conduct electricity. However, glasses exhibit dielectric loss, meaning they dissipate some of the electrical energy as heat. This dielectric loss is due to the presence of defects in the glass structure.

Electrically conductive glasses are called ionic glasses, consisting of a network of ions that can move freely.

VI. Acoustic Properties

Sound waves transmitted through the air cause the walls to vibrate. The greater the mass of a wall, the more impervious it is to vibrations. Therefore, the thickness of glass is an important factor in acoustic insulation.

For example: A 10 mm thick glass is thicker than a 4 mm glass and is therefore more effective in terms of acoustic insulation. Similarly, an insulated glazing composed of two 4 mm glasses has a total thickness of 8 mm but is less effective than a 6 mm glass.

To improve the acoustic performance of insulated glazing, it is possible to combine two glasses of different thicknesses or use products specifically designed for acoustic insulation. These products typically consist of a flexible interlayer that absorbs vibrations.

VII. Chemical Properties

The chemical inertness of glass is one of its most important properties. It allows glass to resist a wide range of chemicals and temperatures [23, 24].

Glass is highly chemically inert, meaning it is resistant to most chemicals and is chemically stable.

The chemical inertness of glass is due to its amorphous structure. The atoms of glass are bonded in a disordered manner, making it difficult to react with other substances.

Hydrofluoric acid is a highly corrosive acid that can dissolve glass. Alkaline products such as soda and potash can also attack glass.

Concrete runoff waters are rich in lime and cement, which are alkaline substances. These substances can react with glass to form corrosive products.

Action of fire on glass:

- Glass is a non-combustible material.
- It does not decompose in the presence of fire.
- It does not oxidize in the presence of fire.

Exercise Series No. 3

Exercise III.1

1. What is the range of wavelengths of electromagnetic radiation responsible for the sensation of light?
2. How does the efficiency of different wavelengths of radiation on the eye contribute to the phenomenon of physiological vision?
3. How to convert the energy flux emitted by a radiation source into luminous flux, taking into account the different efficiencies of various wavelengths of radiation?

Exercise III.2

To design two types of medical glasses, one for correcting vision problems and the other for protection against sunlight:

1. What are the required optical properties for each type of glass used?
2. What type of radiation should be absorbed and reflected by each type of glass, and what is the corresponding wavelength range?
3. How can the energy intervals of light be calculated for these two types of glass?

Exercise III.3

1. Calculate the depth of microcracks (L) in microns for a sodocalcic glass cylinder with a rupture stress of 30 MPa.
2. Calculate the expected rupture stress (σ) in MPa for another glass piece with a measured microcrack depth of approximately 200 nm.
3. Determine which piece of glass has the greater mechanical strength?

Exercise III.4

As part of choosing the most suitable glass for making windows, the following values are given for two types of industrial glass (Glass E and Glass S), as follows:
Where: E: Young's Modulus and ρ: density

Table III.2: Young's Modulus E and Density ρ of Glass E and Glass S.

Glass	**E (GPa)**	**ρ (g/cm^3)**
Glass E	73	2.5
Glass S	87	2.6

1. Calculate the Young's Modulus to density ratio.
2. What type of glass is suitable for manufacturing oven windows?

Exercise III.5

A cylindrical glass has an initial length of 50 cm and an initial diameter of 1 cm. At a temperature of 300 K, it is subjected to a temperature of 330 K.

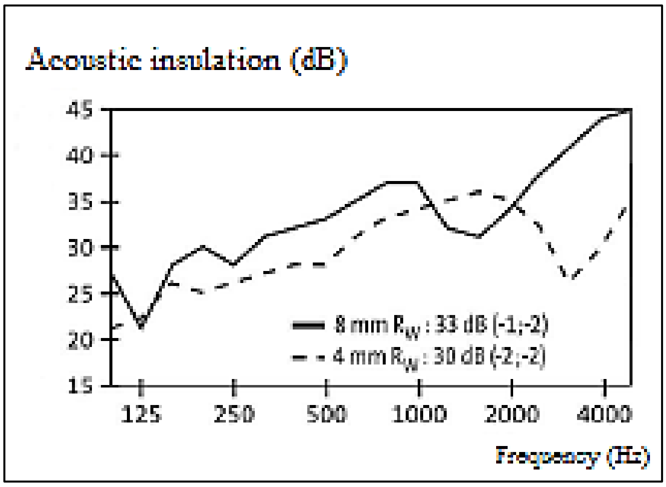
1. Calculate the length of the glass at 330 K.
2. Calculate the change in volume of the glass.

Data:

Linear expansion coefficient of the glass: $\alpha = 1.2 \times 10^{-5}$ °C^{-1}

Exercise III.6

To study the influence of glass thickness on its effectiveness in terms of sound insulation, the following results have been collected and are illustrated in the following figure:



- For a thickness of 8 mm, Rw (C; Ctr) = 33 dB (-1;-2).
- For a thickness of 4 mm, Rw (C; Ctr) = 30 dB (-2;-2).

1. Why is it crucial to compare the one-third octave values of the sound reduction index R and the noise spectrum?
2. What distinction can be made between Rw and RA?
3. How do the coefficients C and Ctr influence the level of sound insulation?
4. Can you determine the sound insulation level of the two types of glass based on these results?

Exercise Series No. 3: Solutions

Exercise III.1

1. The visual sensation we experience is due to the action of electromagnetic radiation with wavelengths between 0.38 µm and 0.78 µm.
2. Radiations that, with varying efficiency depending on their wavelength, enable the physiological phenomenon of vision.
3. The luminous efficiency of different radiations allows the transformation of the energy flux emitted by a radiation source into luminous flux.

The spectral luminous efficiency is based on the spectral sensitivity of the human eye, which varies with wavelength. To obtain luminous flux, you can use the following formula:

Luminous Flux (lumen) = Energy Flux (watt) x Spectral Luminous Efficiency (lumen/watt)

Exercise III.2

1. Optical properties required for each type of glass used:

Vision correction glasses:

Appropriate refractive ability to correct vision problems (myopia, hypermetropia, astigmatism)

High transmittance to allow clear and sharp vision

Sunglasses:

High absorption of UV rays to protect the eyes from damage

Reflection of visible light to reduce glare

2. Types of radiation to be absorbed and reflected by each type of glass, and the corresponding wavelength range:

- For vision correction glasses: the glass should be transparent to visible light (400 to 700 nm) and adjusted to compensate for specific vision problems, so no filtration is necessary.
- For sunglasses: the glass should absorb UV-A (315-400 nm) and UV-B (280-315 nm) rays while allowing the transmission of visible light and reflecting a portion of visible light (380-780 nm) to reduce glare.

3. Energy intervals for these two types of glass:

The energy carried by a photon of light can be calculated using the following relation: E = h f where E represents energy in joules, h is the Planck constant (6.626 x 10^{-34} Js), c is the speed of light (3 x 10^{8} m/s), and f is the frequency of the photon, given by the formula: f = c / λ, where λ is the wavelength of the photon in meters.

- To absorb UV-A (315-400 nm):

Minimum energy (E_{min}) : E = h c / λ_{max}= 6,3 10^{-19} J; λ_{min} = 315 nm = 3,15 10^{-7} m

Maximum energy (E_{max}) : E = h c / λ_{min}= 4,96 10^{-19} J; λ_{max} = 400 nm = 4 10^{-7} m

- To absorb UV-B (280-315 nm):

Minimum energy (E_{min}): E = h c / λ_{max}= 7,09 10^{-19} J ; λ_{min} = 280 nm = 2,8 10^{-7} m

Maximum energy (E_{max}): E = h c / λ_{min}= 6,3 10^{-19} J; λ_{min} = 315 nm = 3,15 10^{-7} m

- To reflect a portion of visible light (380-780 nm):

Minimum energy (E_{min}): E = h c / λ_{max} = 5,22 10^{-19} J ; λ_{min} = 380 nm = 3,8 10^{-7} m

Maximum energy (E_{max}): E = h c / λ_{min}= 2,54 10^{-19} J ; λ_{max} = 780 nm = 7,8 10^{-7} m

Exercise III.3

1. The depth of microfissures:

Let's use the formula $\sigma = 400\ L^{1/2}$ to calculate the depth of microfissures (L) when σ = 30 MPa, so: L = $(30/400)^{2}$

L ≈ 0.005625 mm, which is approximately 5.63 µm

2. Resistance verification:

Now, using the measured depth of microfissures of 200 = 0.2 µm in the formula to calculate the expected rupture stress (σ):

$\sigma = 400\ L^{1/2} = 400 \times (0.2)^{0.5} \approx 5.65$ MPa.

3. The first piece of glass (question 1) has a rupture stress of 30 MPa, while the second piece (question 2) has an expected rupture stress of 5.65 MPa.

Therefore, the first piece of glass exhibits greater resistance.

Exercise III.4

The Young's Modulus to density ratio:

- For glass E: E/ $\boldsymbol{\rho}$ = 73/2.5 = 29.2 GPa g/cm³
- For glass S: E/ $\boldsymbol{\rho}$ = 87/2.6 = 33.46 GPa g/cm³

The E/ $\boldsymbol{\rho}$ ratio for glass S (33.46) is higher than that of glass E (29.2), indicating that glass S provides a better combination of stiffness and strength for this application.

Exercise III.5

1. The length of the glass at 330 K:

Using the linear expansivity formula for glass:

$\alpha = \Delta l / l\ \Delta T \Rightarrow \alpha = (l - l_0) / l\ \Delta T$

$\Rightarrow l = l_0 / (1 - \alpha\ \Delta T) \Rightarrow l = 50 / (1 - 1{,}2\ 10^{-5} \times 30) = 50{,}18$ cm

2. The change in volume of the glass:

The change in volume is given by the formula: $\Delta V = V - V_0$

$V = \pi r^2 l \Rightarrow V = 39{,}391\ cm^3$

$V_0 = \pi r^2 l_0 \Rightarrow V_0 = 39{,}25\ cm^3$

So: $\Delta V = 0{,}14\ cm^3$

Exercise III.6

1. The importance of comparing third-octave values of the Sound Reduction Index (R):

It is crucial to compare third-octave values of the Sound Reduction Index (R) and the noise spectrum because the noise spectrum represents the noise level as a function of frequency. The Sound Reduction Index (R) is a measure of sound insulation for a given frequency. By comparing third-octave values of the Sound Reduction Index (R) and the noise spectrum, it is possible to determine if a construction is effective in reducing all types of noise.

2. The distinction between Rw and RA:

- Rw and RA are two indices of sound reduction.
- Rw is the weighted sound reduction index, while RA is the weighted sound reduction index for a specific application.
- Rw is an overall measure of sound insulation, while RA is a more specific measure of sound insulation for a particular application.

3. The influence of coefficients C and Ctr on the level of sound insulation:

- The coefficient C is a correction coefficient used to account for noise attenuation by the lateral walls of the sound field.
- The coefficient Ctr is a correction coefficient used to account for the frequency of the noise.
- A higher C coefficient means that sound insulation is reduced due to noise attenuation by the lateral walls of the sound field.
- A higher Ctr coefficient means that sound insulation is reduced for frequencies above 500 Hz.

4. The possibility of determining the sound insulation levels of the two types of glass: Yes, it is possible to determine the sound insulation level of the two types of glass based on these results. Based on the provided results, the sound insulation level of an 8 mm thick glass is higher than that of a 4 mm thick glass for all frequencies, except for frequencies between 1000 Hz and 2000 Hz. Therefore, the 8 mm thick glass offers better sound insulation than the 4 mm thick glass.

Chapter IV: Study of the Raw Materials for the Manufacture of Industrial Glasses

Chapter IV: Study of Raw Materials for the Manufacture of Industrial Glasses

I. Introduction

The manufacturing of glass begins with the weighing and mixing of various raw materials or batch preparation to create a charge for the melting furnace. The different chemical compositions influence the properties of the final glass product.

The properties of glass vary according to its basic components, and these components can be classified based on their role in the glass composition as follows [8, 23]:

- Network formers;
- Network modifiers;
- Intermediates

II. Glass Compositions

Formers, modifiers, and intermediates are key components in glass compositions, playing specific roles in the structure and properties of the material. Here is an explanation of the roles of each component:

II.1 Network Formers

Network formers are elements that constitute the structure of the glass. They are typically oxides, such as silicon (in the form of SiO_2), boron (in the form of B_2O_3), phosphorus (in the form of P_2O_5), germanium (in the form of GeO_2), and arsenic (in the form of As_2O_3).

Network formers create a three-dimensional network of covalent or ionic bonds. This network is responsible for the rigidity and strength of the glass.

Example: SiO_2 forms chains such as -O-Si-O-Si-O-Si-O-

II.2 Network Modifiers

Network modifiers are elements that modify the properties of the glass, such as its melting temperature, impact resistance, or transparency. They are typically alkali or alkaline earth metal oxides, such as soda (Na_2O), potash (K_2O), or lime (CaO).

Network modifiers lower the glass's melting temperature by breaking some of the covalent or ionic bonds in the network. They can also modify the glass's impact resistance or transparency.

The discovery of glass involved the simultaneous heating of sand and natural alkali carbonate, resulting in the following reaction: $SiO_2 + Na_2CO_3 \rightarrow Na_2SiO_3 + CO_2$

The introduction of sodium oxide (Na_2O) into the silica network has two major roles (Figure IV.1):

- It breaks the O-Si-O-Si-O chains, creating -Si-O-Na^+ groups that reduce viscosity.
- It significantly lowers the liquidus temperature.

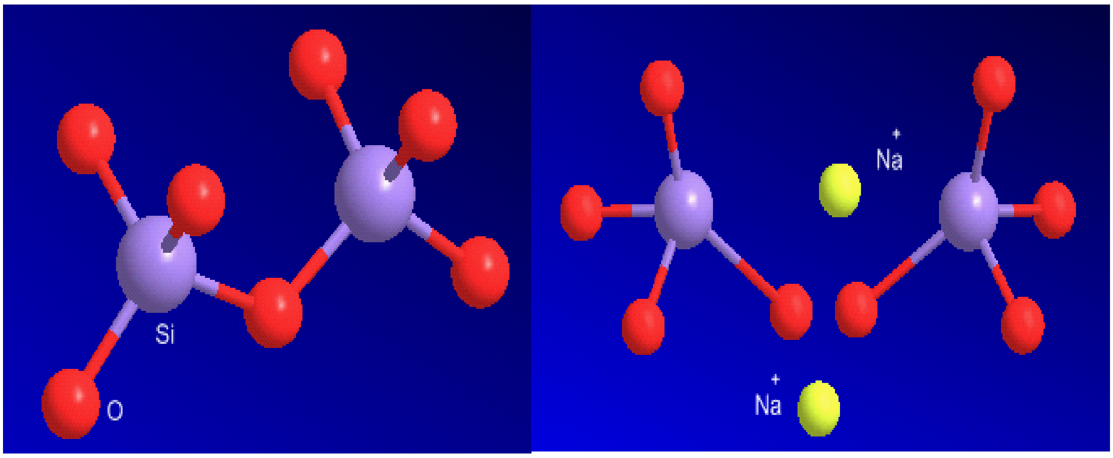


Figure IV.1: Chemical Structure of Glass

Comparison of phase diagrams between SiO_2-Na_2O and SiO_2-CaO highlights the importance of alkalis in glass formation (**Appendixe 3**). In summary, glass formation is attributed to the introduction of alkali oxides into the silica network.

II.3. Intermediates

Intermediates are elements that occupy an intermediate position between network formers and network modifiers.

They may have properties similar to both types of elements. Intermediates are typically metallic oxides, such as zinc (ZnO) or titanium (TiO_2). It is important to note that in certain types of glass, such as non-oxide glasses (chalcohalides, metallic glasses, etc.), one cannot speak in terms of network formers and modifiers because these glasses have different structures and do not follow the same composition principles.

III. Raw Materials

The raw materials used in glass manufacturing are both natural and industrial [25, 26].

III.1. Natural Raw Materials

The primary natural raw materials include:

- Silicon oxide (SiO_2): Generally obtained from sand or quartz, it is the main component of glass, representing approximately 70% of its composition.
- Sodium oxide (Na_2O): Also known as soda, it is typically obtained from sodium salts, used as a glass-forming agent, and represents about 15% of the glass composition.
- Calcium oxide (CaO): Also known as lime, it is usually obtained from limestone or dolomite, used to stabilize the glass, and represents about 10% of its composition.
- Potassium oxide (K_2O): Potash is used to reduce the viscosity of molten glass and facilitate its flow. It is typically obtained from potassium salts.

III.2. Industrial Raw Materials

Industrial raw materials include:

- Soda ash: Produced by the combustion of certain plants, rich in sodium carbonate, used as an alternative to natural soda.
- Potash ash: Produced by the combustion of certain plants, rich in potassium carbonate, and can be used as an alternative to soda.
- Limestone: Used as a source of calcium oxide, it can be extracted from quarries or produced by the calcination of natural limestone.
- Dolomite: Used as a source of magnesium oxide (MgO), it can be extracted from quarries or produced by the calcination of natural dolomite.
- Feldspar: Used as a source of aluminum oxides (Al_2O_3) and silicon, it can be extracted from quarries or produced by grinding feldspathic rocks.
- Fly ash: Produced by coal combustion, it can be used as a source of silicon and aluminum oxides.
- Glass cullet: Produced during glass recycling, it can be used as a source of silicon, sodium, and calcium oxides.

- Manganese ash: Produced during manganese steel production, it can be used as a source of manganese oxide for glass coloring.

III.3. Roles of Raw Materials

III.3.1. Glass-Forming

Glass is an amorphous material, meaning it has no crystalline structure. It is formed by the melting of several components,

- Natural Raw Materials: Sand (provides silica SiO_2).
- Industrial Raw Materials: Boron (secondary glass-forming agent), lead oxides, aluminum, zinc, etc.

III.3.2. Fluxing

The glass melting temperature is high, around 1,500 °C. Fluxes are substances that lower the glass melting temperature, facilitating the manufacturing process.

- Natural Raw Materials: Sodium carbonate (Na_2CO_3).
- Industrial Raw Materials: Soda (as carbonate or nitrate), Potash (potassium carbonate - K_2CO_3). Lithium, strontium oxides, etc.

III.3.3. Stabilizing

Glass is a fragile material. Stabilizers are substances that strengthen the glass structure, providing better resistance to shocks and temperature variations.

- Natural Raw Materials: Limestone, Dolomite, Phonolite (providing calcium, magnesium, and aluminum oxides).
- Industrial Raw Materials: No specific category.

III.3.4. Refining

Refining substances eliminate air bubbles from glass, giving it a smooth and shiny surface.

- Natural Raw Materials: No specific category, as refining agents may vary according to needs.
- Industrial Raw Materials: Arsenic oxides (As_2O_5) and antimony (Sb_2O_3), nitrates.

III.3.5. Decolorizing

Natural glass is often slightly colored yellow or green due to the presence of metallic oxides, such as iron oxide. Decolorizers remove colorations from glass.

- Natural Raw Materials: No specific category, as decolorizers may vary according to needs.
- Industrial Raw Materials: Manganese dioxide (MnO_2), titanium oxide, or antimony selenium oxide, cobalt, rare earth elements.

III.3.6. Coloring

Glass can be colored by adding colorants to the composition. Colorants are substances that absorb or reflect certain wavelengths of light, giving glass its color.

- Natural Raw Materials: No specific category, as colorants vary according to desired colors.
- Industrial Raw Materials: Coal, coke, iron chromite, cobalt oxide, manganese oxide, copper oxide, nickel oxide, silver, gold, lithium, cerium, lead, and other elements depending on the desired color (Table IV.1).

Table IV.1: Examples of Glass Colorants [17]

The Component	Color
Cobalt oxide and manganese.	Blue.
Chrome and silver.	Yellow.
Copper oxide.	Red.
Manganese oxide.	Violet.
Gold.	Pink and Ruby Red.
Selenium.	Orange-yellow to red.

III.3.7. Additives and Cullet Utilization

Various additives are introduced for specific color effects.

Cullet, recycled glass, can constitute 10 to 80% of the batch, reducing costs and energy consumption.

Internally generated cullet is preferred for quality control.

III.4. Properties of Raw Materials

The raw materials used in the manufacturing of industrial glasses have specific properties that influence the characteristics of the final glass product (Table VI.2).

Table IV.2: Properties of Some Raw Materials Used in the Manufacturing of Industrial Glasses [9, 20]

Raw Material - Natural Source	**Component**	**Role**	**Properties**
Silica Sand	SiO_2	Primary Glass-Forming Agent	− Constitutes the basic structure of glass. − Exhibits good resistance to chemical agents (very stable molecular structure and strong covalent bonds). − Silica has a low coefficient of thermal expansion (strong bonds hinder atom movement, reducing expansion).
Borax Powder	B_2O_3	Secondary Glass-Forming Agent	– Lowers the melting point, enhances chemical and mechanical resistance, and corrosion resistance.
Natural Phosphate Calcium Phosphate Phosphoric Acid	P_2O_5	Secondary Glass-Forming Agent	– Improves transparency. – Reduces glass resistance to chemical agents.
Bauxite, Clay	Al_2O_3	Stabilizer	– Hardens the glass: Improves mechanical, thermal, and chemical resistance.
Potash Potassium Carbonate	K_2O	Fluxing Agent	− Enhances glass fluidity. − Lowers the melting temperature and facilitates workability
Litharge, Galena	PbO	Fluxing Agent, Densifies Glass	– Facilitates fusion. – Increases glass density and improves brilliance. – Enhances the refractive index
Soda, Sodium	Na_2O	Fluxing	− Improves glass fluidity.

Carbonate		Agent	− Lowers the melting temperature.
Limestone (Calcium Carbonate) Shells	CaO	Stabilizer	− Hardens the glass and improves chemical resistance. − Lowers the melting temperature and enhances thermal resistance.
Dolomite, Serpentine	MgO	Stabilizer	− Hardens the glass: Improves mechanical and thermal resistance
Soda, Sodium Carbonate	Na_2CO_3	Mild Alkaline Fluxing Agent	− Lowers the melting temperature. − Enhances fluidity.

III.5. Preliminary Preparation of Raw Materials

Preliminary treatments of raw materials are essential for glass manufacturing. They prepare the raw materials by making them compatible with the melting process (Figure IV.2) [25, 26].

III.5.1. Key Treatments

The most common treatments include:

- Extraction/Harvesting: Raw materials are collected from their natural environment.
- Grinding: Raw materials are ground into a very fine powder.
- Leaching/Lixiviation: Impurities are removed by washing with water or chemical solutions.
- Drying: Raw materials are dried to eliminate absorbed water.
- Sorting/Screening: Raw materials are separated by size.
- Wet Grinding: Grinding is refined in the presence of a liquid binder.

III.5.2. Supplementary Treatments

Other treatments can be applied based on specific needs. For example:

- Calcination is used to decompose certain compounds, such as carbonates. Dehydration is used to remove water from hydrated salts.

- Chemical treatments are employed to selectively add or remove elements.
- Concentration/Refining is used to separate pure elements from by-products.
- Composition/Purity control is conducted through chemical analyses to ensure that raw materials meet the required specifications.

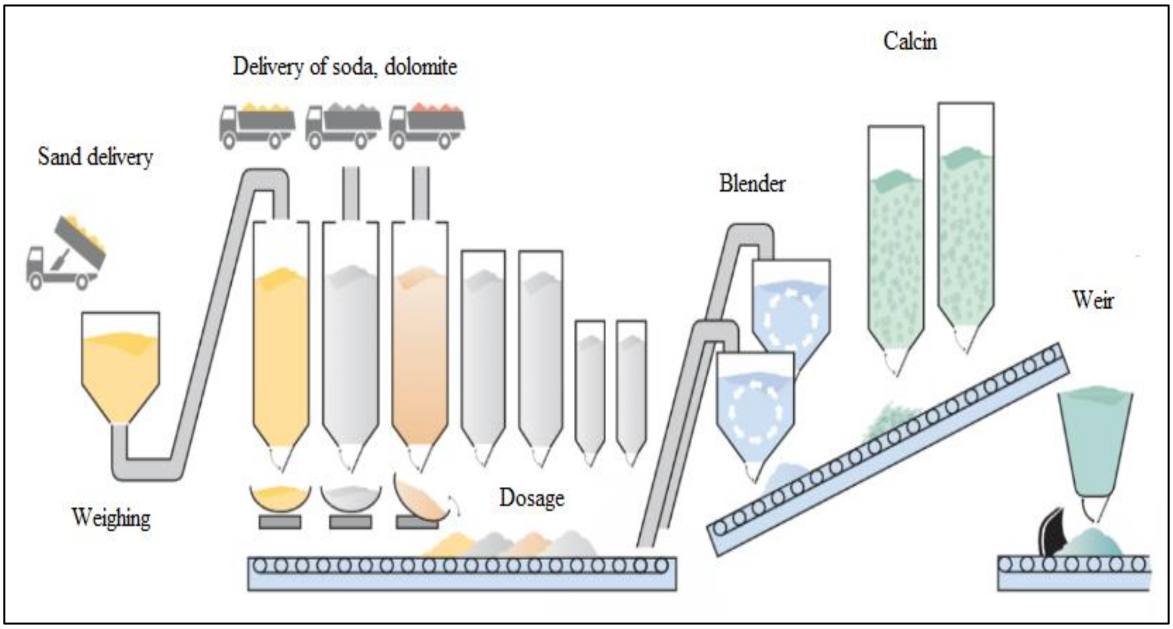


Figure IV.2: Stages of Preliminary Preparation of Raw Materials

III.6. Preparation of the Initial Mixtures

The quantity of each component in the initial mix determines the properties of the final glass [26,27]:

III.6.1. Silica Glasses

Composition: At least 96% silica (96-99.9%) + 0.1% to 3% Aluminum oxide (Al_2O_3) + 0.1% to 2% Sodium oxide (Na_2O) + .1% to 1% Calcium oxide (CaO) + Less than 1% other trace oxides (e.g., Fe_2O_3)

Properties: High purity (optical transparency), resistance to high temperatures, corrosion, and thermal shocks. Silica glass has high transmission levels up to a wavelength of about 190 nm, making it suitable for UV sterilization.

Applications: Glassware, optical fibers, flat screens, mirrors, and electronic components (halogen lamp tubes) (Figure IV.3) [20, 27].

Figure IV.3: Object made of Silica Glass (Halogene Lamp)

III.6.2. Quartz Glasses

Quartz glasses are a type of silica glass, but they are less pure than silica glasses.

Composition: Silica (99.9%) + Less than 0.1 Other trace oxides (e.g., Al_2O_3, Na_2O, Fe_2O_3)

Properties: High purity (optical transparency), resistance to high temperatures, corrosion, and thermal shocks.

Applications: Manufacturing tubes, rods, plates, and laboratory vessels (Figure IV.4) [20, 27].

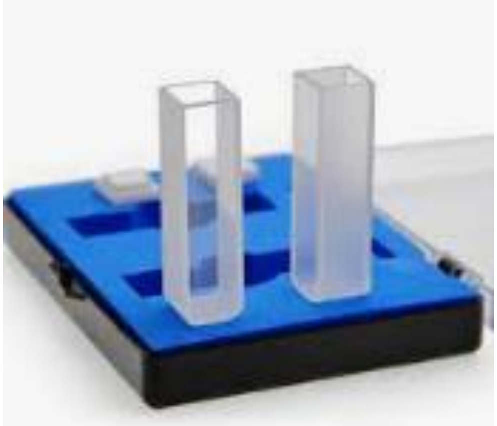


Figure IV.4: Object made of Quartz Glass (Spectrophotometer Cell)

III.6.3. Soda-Lime Glasses

Soda-lime glasses are the most common.

Composition: Silica-SiO2 (72-85%) + Soda-Na_2O (10-13%) + Lime-CaO (5%)

Properties: Good chemical stability but sensitive to thermal shocks. Softening temperature for 70% silica = 700°C. High coefficient of expansion: 86×10^{-7} (from 0 to 300°C).

Can be used up to approximately 80 - 90 °C; Good electrical insulator; Good transmission of the visible light spectrum.

Applications: Manufacturing flat and hollow glass, electric bulbs, and in bottling (Figure IV.5) [20, 27].

Figure IV.5: Object made of Soda-Lime Glass (Bottles)

III.6.4. Borosilicate Glasses (Pyrex - 1915)

Composition: Silica-SiO_2 (80%) + Boric Anhydride-B_2O_3 (13%) + Soda-Na_2O (4%) + Alumina-Al_2O_3 (3%)

Properties: Good resistance to thermal shocks. Softening temperature for 80% silica = 820°C. Very low coefficient of expansion: 32×10^{-7} (from 0 to 300°C).

Applications: Laboratory and kitchenware, insulation (glass fibers), storage of radioactive waste (Figure IV.6).

Figure IV.6: Object made of Borosilicate Glass (Kitchen Utensils)

III.6.5. Aluminosilicate Glasses

Composition: Silica-SiO_2 (60-80%) + Alumina-Al_2O_3 (10-25%) + Alkali Oxides-CaO (5-15%)

Properties: Heat, corrosion, and thermal shock resistance, low coefficient of expansion.

Applications: Glasses for ovens, glasses for the production of optical fibers (Figure IV.7) [20, 27].

Figure IV.7: Object made of Aluminosilicate Glass (Oven Glasses)

III.6.6. Lead Glasses

Composition: Contain lead: Silica-SiO_2 (62%) + Lead Oxide-PbO (21%) + Potash-K_2O (7%)

Properties: Brilliance, very high coefficient of expansion: 90×10^{-7} (from 0 to 300°C).

Applications: Glassware, stained glass (Figure IV.8) [20, 27].

Figure IV.8: Object made of Lead Glass (Crystalware)

III.6.7. Glass Ceramics

Composition: Glass and ceramic mix: Silica-SiO_2 (75%) + Alumina-Al_2O_3 (15%) + Titanium Salt (5%) + Lithium Oxide-Li_2O (3%)

Properties: Resistance to thermal shocks, scratches, and corrosion.

Applications: Cooktops, ovens, flat screens, and mirrors for giant telescopes (Figure IV.9) [20, 27].

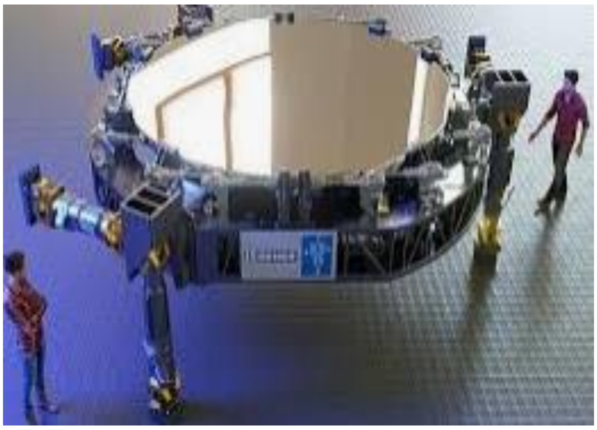


Figure IV.9: Object made of Glass Ceramics (Giant Telescope)

III.6.8. Bioactive Glass

Composition: SiO_2: silicon dioxide, or silica (45%) + Na_2O: sodium oxide, or soda (24.5%) + CaO: calcium oxide, or lime (24.5%) + P_2O_5: phosphorus pentoxide, or phosphorus pentoxide (6%)

Properties: Bioactivity: ability to generate a layer of hydroxyapatite at the interface of surrounding tissues; Biocompatibility: ability to be tolerated by the organism; Mechanical resistance: ability to withstand mechanical forces; Permeability: ability to allow the passage of ions and molecules; Resorbability: ability to be replaced by bone tissue.

Applications: Bioactive glasses are used in various medical applications, including Dentistry: dental restorations, dental implants, etc.; Orthopedic surgery: bone implants, fixations, etc.; Restorative surgery: wound healing, etc. (Figure IV.10) [20, 27].

Figure IV.10: Object made of Bioactive Glass (Bone Substitute)

IV. Industrial method of Glass manufacturing

The glass manufacturing process, from handling raw materials to loading the furnace, involves several steps as follows (Figure IV.11) [25]:

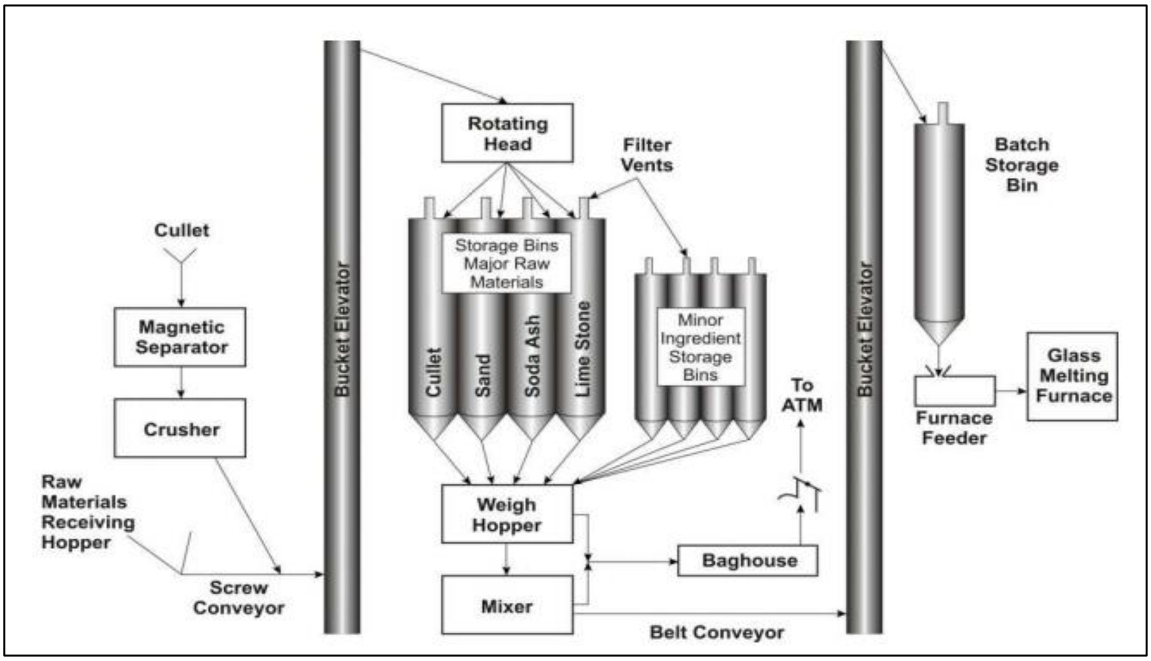


Figure IV.11: Glass Manufacturing Process: From Handling Raw Materials to Loading the Furnace

IV.1. Handling Raw Materials

Raw materials (train, truck, barrels) are unloaded through different systems and then transported to storage by belts, screws, and bucket elevators. The materials are crushed, ground, and sieved before being stored in elevated bins [26].

IV.2. Batch Preparation

Dry ingredients pass through a gravity feeding system to a doser and mixer. Crushed cullet is added, and the final mixture goes into a hopper before being fed into the furnace. The crushing and handling equipment is separated from the furnace in the batch preparation plant [25, 26].

IV.3. Effective Mixing

Correct mixing of dry ingredients is crucial for glass quality. In homogeneities can increase melting time and affect product quality. Extreme care is taken to ensure that materials have the right particle size, are accurately weighed, and thoroughly mixed. Large plants use highly automated batch preparation with computer-controlled weighing [25, 26].

IV.4. Mixing Techniques

Different techniques are used depending on the type of glass. Mixers are used for glasses like high silica, soda-lime, borosilicate, or aluminosilicate. Wet mixing involves adding a small amount of liquid, and water (2-4% by weight) prevents charge segregation during transport, reduces dust, and ensures homogeneity. Charge agglomeration, using Muller-type mixers, is employed for glasses with high lead oxide content [25, 26].

IV.5. Furnace Loading

The final batch is transported directly to the furnace or via a refractory-lined extension (doghouse). Upon entry, the batch spreads like a blanket over the molten glass surface, the pattern depending on specific furnace operating conditions [25, 26].

IV.6. Electrical Energy

The specific energy consumption for batch preparation depends on the type of glass produced, typically ranging from about 0.24 to 1.2 million Btu per ton of glass, encompassing industry-wide usage for this stage. It's worth noting that energy can also be consumed during the crushing, grinding, and sieving of raw materials before shipment to the glass plant [25].

IV.7. Pollution Management

Particle emissions during glass batch preparation are a major concern. Effective control measures can achieve 99-100% reduction. Waste is also generated during the receiving and transferring of raw materials, but residues from bag filters can be recycled [26].

Exercise Series No.4

Exercise IV.1

A type of industrial glass has the following chemical composition:

Silica (SiO_2): 68 to 74%
Alumina (Al_2O_3): 0.3 to 3%
Soda (Na_2O): 12 to 16%
Potash (K_2O): 0 to 1%
Lime (CaO): 7 to 14%

1. Determine the role of each of these components.
2. What are the expected properties of this type of glass?

Exercise IV.2

What are the application domains of these types of glass?

Soda-lime glasses
Alumino-silicate glasses
Borosilicate glasses

Exercise IV.3

Provide the compositions and type of glasses with the following characteristics:

1. Bioactivity; Permeability; Resorbability
2. Brilliance; Very high coefficient of expansion

Exercise IV.4

A glass sample has a composition comprising 30 kg of aluminum, 10 kg of lime, and 160 kg of silica.

1. Calculate the relative proportion of each component.
2. Deduce the type of this glass.

Data: Molar masses (g/mol): O=16, Si=28, Ca=20, Al=13

Exercise IV.5

A borosilicate glass contains 13 mol% Boric Anhydride-B_2O_3, 4 mol% Soda-Na_2O, and 3 mol% Alumina-Al_2O_3.

1. Calculate the molar ratio O/Si.
2. Calculate the mass composition of this glass.
3. What mass of calcium oxide (CaO) must be added to 2 kg of silica (SiO_2) to achieve a molar ratio O/Si equal to 2.7.

Data: Molar masses (g/mol): O=16, Si=28, Ca=20, Al=13, Na=23, B=10.81

Exercise IV.6

Consider the glass manufacturing compounds: Na_2CO_3, $CaCO_3$, SiO_2

1. Write the chemical decomposition reactions of these compounds.
2. We want to mix these compounds to obtain a glass with the following mass proportions: 75% SiO_2, 15% Na_2O, and 10% CaO.
3. Determine the required quantity of Na_2CO_3 and $CaCO_3$ to mix with a preparation of 200 kg of this glass.

Data: Molar masses (g/mol): O=16, Si=28, Ca=20, Na=23

Exercise Series No. 4: Solutions

Exercise IV.1

1. Role of each component:

- Silica (SiO_2): Silica is the main vitrifying agent and the essential component that gives glass its structure.
- Alumina (Al_2O_3): Alumina is a stabilizer that strengthens the glass and improves its heat resistance.
- Soda (Na_2O): Soda is a fluxing agent that lowers the fusion temperature of the mixture.
- Potash (K_2O): Potash is also a fluxing agent and can be added in small quantities to modify certain glass properties.
- Lime (CaO): Lime acts as a stabilizer.

2. Expected properties of the glass:

- Silica (SiO2): Silica is responsible for the strength and transparency of the glass.
- Alumina (Al2O3): Alumina is suitable for applications requiring high strength.
- Soda (Na2O): Soda facilitates the glass formation during the manufacturing process.
- Potash (K2O): Potash does not play a major role in its composition.
- Lime (CaO): Lime enhances the durability and strength of the glass.

Therefore, the expected properties of this type of glass are:

- High mechanical strength.
- Heat resistance.
- High transparency.
- Good durability.
- Chemical resistance.

3. Application areas: This type of industrial glass is commonly used in the following areas:

- Manufacturing glass containers such as bottles, jars, and glasses.
- Arts and decoration industry, for stained glass production.
- Construction sector, for windows, mirrors, and durable glazing.
- Automotive sector, for windshields and side windows.

- Chemical and laboratory applications, due to its chemical resistance.
- Packaging industry, for glass containers in food and pharmaceuticals.

Exercise IV.2

The application areas of these types of glass are as follows:

1. Soda-lime glasses
- Flat and hollow glass manufacturing
- Electric bulbs
- Glass bottles
2. Alumino-silicate glasses
- Glass for furnaces
- Glass for the production of optical fibers
3. Boro-silicate glasses
- Laboratory and kitchen utensils
- Insulation (glass fibers)
- Storage of radioactive waste

Exercise IV.3

1. Type: Bioactive glass

Composition: SiO_2 (silicon dioxide, or silica) 45% + Na_2O (sodium oxide, or soda) 24.5% + CaO (calcium oxide, or lime) 24.5% + P_2O_5 (phosphorus pentoxide) 6%

2. Type: Lead glass

Composition: Contains lead - Silica-SiO_2 62% + Lead oxide-PbO 21% + Potash-K_2O 7%

Exercise IV.4

1. The relative proportion of each component:
- The mass proportions:

$Y_{\%}(SiO_2) = m_{SiO2} \times 100 / m_T \Rightarrow Y_{\%} = 160 \times 100/200 = 80\%$

$Y_{\%} = m_{AlO3} \times 100 / m_T \Rightarrow Y_{\%} = 30 \times 100/200 = 15\%$

$Y_{\%} = m_{CaO} \times 100 / m_T \Rightarrow Y_{\%} = 10 \times 100/200 = 5\%$

- The molar proportions :

$n_{SiO2} = m/M = 160\ 10^3 /60 = 2666{,}66$ mol

$n_{AlO3} = m_{AlO3}/M_{AlO3} = 30\ 10^3/61 = 491{,}8$ mol

$n_{CaO} = m_{CaO}/M_{CaO} = 10\ 10^3/36 = 277{,}77$ mol

$n_T = 2666{,}66 + 491{,}8 + 277{,}77 = 3436{,}23$ mol

$X\%\ (SiO_2) = n_{SiO2} \times 100 / n_T \Rightarrow X\%\ (SiO_2) = 2666{,}6 \times 100/ 3436{,}23 = 77{,}60\%$

$X\% = n_{AlO3} \times 100 / n_T \Rightarrow X\%\ (SiO_2) = 491{,}8 \times 100/ 3436{,}23 = 14{,}31\%$

$X\% = n_{CaO} \times 100 / n_T \Rightarrow X\%\ (SiO_2) = 277{,}77 \times 100/ 3436{,}23 = 8{,}08\%$

2. The type of this glass is Alumino-silicates because its composition is:

Silica-SiO_2 (60-80%) + Alumina-Al_2O_3 (10-25%) + Alkali oxides-CaO (5-15%)

<u>Exercise IV.5</u>

1. The molar ratio O/Si:

Molar ratio O/Si = Number of moles of silicon (Si) / Number of moles of oxygen (O)

Number of moles of SiO_2: n = 100 – (13+4+3) = 80 mol

$SiO_2 \rightarrow Si + 2O$ => Number of moles of O: $n_O = 80 \times 2 = 160$ mol

$B_2O_3 \rightarrow 2B + 3O$ => Number of moles of O: $n_O = 13 \times 3 = 39$ mol

$Na_2O \rightarrow 2Na + O$ => Number of moles of O: $n_O = 4$ mol

$Al_2O_3 \rightarrow 2Al + 3O$ => Number of moles of O: $n_O = 3 \times 3 = 9$ mol

So: Total number of moles of O : $n_{TO} = 212$ mol

Molar ratio O/Si= 212/ 80= 2.65

2. The mass composition of this glass :

SiO_2: m = n x M = 80 x 60 = 4800 g

B_2O_3: m = n x M = 13 x 69.6 = 904.8 g

Na_2O: m = n x M = 4 x 62 = 248 g

Al_2O_3: m = n x M = 3 x 74 = 222 g

$m_T = 6174.8$ g

$P_{SiO2} = m_{SiO2} \times 100 / m_T = 77.74\ \%$

$P_{B2O3} = m_{B2O3} \times 100 / m_T = 14.65\ \%$

$P_{Na2O} = m_{Na2O} \times 100 / m_T = 4.02\ \%$

$P_{Al2O3} = m_{Al2O3} \times 100 / m_T = 3.59\ \%$

3. The mass of calcium oxide (CaO):

Number of moles of silicon (Si): n_{SiO2} = m /M = 2000/60 = 33.33 mol

$SiO_2 \rightarrow Si + 2O$ => Number of moles: n_{Si} = 33.33 mol

=> Total Number of moles of O: n_{TO} = 2.7 x 33.33 = 90 mol

Number of moles of O in CaO: n_O = 90 – (2 x 33.33) = 23.34 mol = n_{CaO} ,

Because: $CaO \rightarrow Ca + O$

So: $m_{CaO} = n_{CaO} \times M_{CaO}$ => m_{CaO} = 23.34 x 36 = 840.24 g

<u>Exercise IV.6</u>

1. Chemical decomposition reactions of these compounds:
    - Decomposition of Na_2CO_3 : $Na_2CO_3 \rightarrow Na_2O + CO_2$ (1)
    - Decomposition of $CaCO_3$: $CaCO_3 \rightarrow CaO + CO_2$ (2)
    - No decomposition needed for SiO_2
2. The required quantity of Na_2CO_3 and of $CaCO_3$:
    - Masses of Na_2O, CaO :

$X_{Na2O} = m_{Na2O} \times 100 / m_T$ => $m_{Na2O} = X_{Na2O} \times m_T / 100$ => m_{Na2O} = 15 x 200/100 = 30 Kg

$X_{CaO} = m_{CaO} \times 100 / m_T$ => $m_{CaO} = X_{CaO} \times m_T / 100$ => m_{CaO} = 10 x 200/100 = 20 Kg

- Masses of Na_2CO_3 et de $CaCO_3$:

After the chemical reaction (1): $n_{Na2CO3} = n_{Na2O}$, avec n = m/M

So: $m_{Na2CO3} / M_{Na2CO3} = m_{Na2O} / M_{Na2O}$ => $m_{Na2CO3} = m_{Na2O} \times M_{Na2CO3} / M_{Na2O}$

=> m_{Na2CO3}= 30 x 106 / 62 = 51,29 Kg

After the chemical reaction (2): $n_{CaCO3} = n_{CaO}$, avec n = m/M

So: $m_{CaCO3} / M_{CaCO3} = m_{CaO} / M_{CaO}$ => $m_{CaCO3} = m_{CaO} \times M_{CaCO3} / M_{CaO}$

=> m_{Na2CO3}= 20 x 80 / 56= 28,57 Kg

Chapter V: Elaboration of the Vitreous Melts and Glasses Fusion

Chapter V: Elaboration of the glass melts and glass fusion

I. Introduction

The stages of glass manufacturing encompass several distinct phases [21, 25, 28]:

- Preparation of raw materials.
- Fusion of the mixture.
- Shaping to give the glass the desired form.
- Treatment, primarily the cooling of the glass.

Within the scope of industrial activities, quality is ensured through rigorous controls, followed by shipment (Figure V.1).

In this chapter, the part related to the fusion of the mixture will be addressed, including the concepts, the vitrifiable starting mix, fusion furnaces, and the involved chemical reactions.

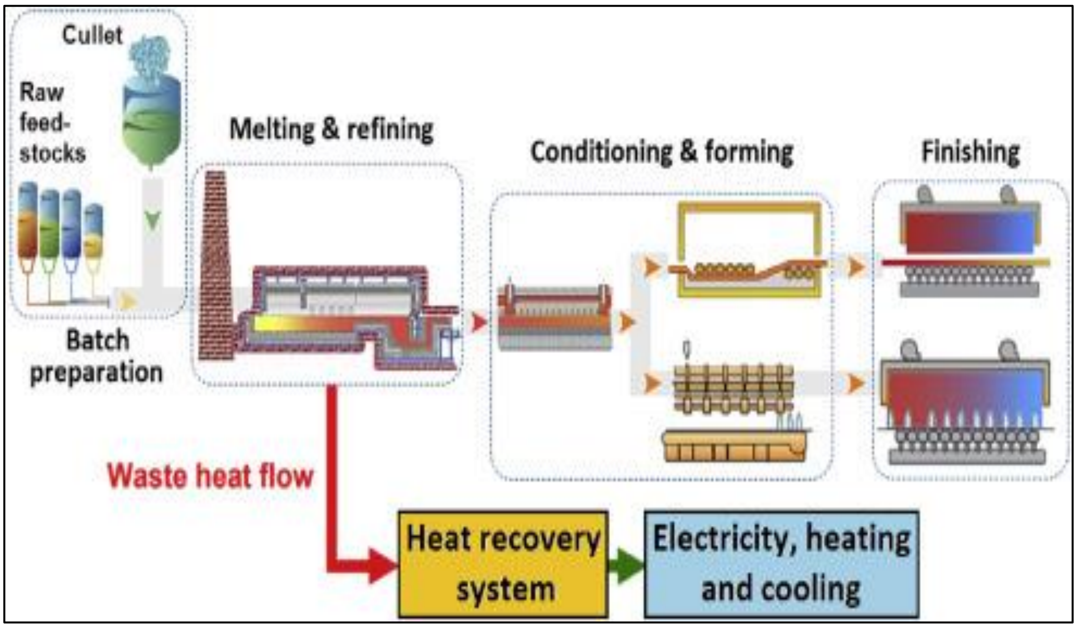


Figure V.1: General Glass Manufacturing Process

II. Composition and Selection of Raw Materials

II.1. Composition of Glasses

Glass is primarily composed of silica dioxide (SiO_2) in large quantities, along with other compounds such as sodium oxide (Na_2O), calcium oxide (CaO), aluminum oxide (Al_2O_3), etc.

These compounds are chosen based on the desired properties of the final glass.

The selection of raw materials, whether natural or recycled, is one of the crucial steps in glass manufacturing.

The choice between natural raw materials and cullet depends on various factors, including the specifications of the final product, local availability, costs, environmental considerations, and government regulations [25, 26].

II.2. Selection of Raw Materials

The choice between natural raw materials and cullet is one of the crucial steps in glass manufacturing.

The selection depends on several factors, including the specifications of the final product, local availability, costs, environmental considerations, and government regulations [26, 28].

II.2.1. Natural Raw Materials

The main natural raw materials are [21, 25]:

- Quarry Sand: Primary source of silica dioxide (SiO_2).
- Sodium Carbonate: Obtained by a chemical reaction between sodium chloride and calcium carbonate, providing sodium oxide (Na_2O).
- Limestone and Dolomite: Supplying calcium oxide (CaO) and magnesium oxide (MgO), respectively.
- Minerals such as Feldspar, Nepheline, and Phonolite: Sources of aluminum oxide (Al_2O_3).
- Sodium Sulfate: Source of sulfur trioxide (SO_3), acting as an oxidizing agent.
- Slag: Iron and calcium silicates produced by blast furnaces, contributing to the reducing character of the glass.
- Coal: Preferred for high-quality glasses as a reducing agent.
- Chromite: Natural oxide of chromium and iron used as a coloring agent for green glasses.

These natural raw materials are often chosen for their purity and local availability, with the following material characterizations:

- Particle Size Distribution: Must be suitable, neither too fine to avoid dust formation nor too coarse to avoid slowing down the melting rate.
- Absence of Non-Fusible Heavy Minerals: Raw materials must not contain non-melted components.

- Limited Moisture Content: For moisture-sensitive products to prevent agglomeration.

II.2.2. Recovery (Cullet) Required Raw Materials

Cullet is recycled glass. It offers several advantages, including reduced energy consumption and promoting sustainability.

Cullet is commonly used in the production of colored or packaging glass to reduce costs and environmental impact.

Specifications for the Use of Recovered Glass:

- Infusible Rate: Must be less than 50 g/ton to avoid the presence of contaminants such as gravel and porcelain.
- Free Reducer Rate: Must be less than 500 g/ton to exclude elements like papers and plastics.
- Free Metal Rate: Must be less than 5 g/ton to minimize the presence of undesirable metals.

III. Glass Fusion

III.1. Definition and Principle of Fusion

The fusion of the glass mixture is the process of transforming a mixture of raw materials into a homogeneous and transparent glass. This occurs at high temperatures when the materials melt and combine to form a vitreous substance.

The fusion of the glass mixture involves heating a mixture of raw materials to a high temperature until it becomes liquid. This allows for a chemical and physical transformation of the material [22, 26].

III.2. Factors Influencing Fusion

III.2.1. Temperature

The fusion temperature varies depending on the raw materials used as follows:

Artisanal glasses have a fusion temperature between 1200 and 1400 °C.

Borosilicate glass, used in laboratories, has a fusion temperature of 800-1300°C.

Quartz glass has a very high melting point, around 1600-2100°C [22, 29].

III.2.2. Fusion Time

The duration for which the material is exposed to the fusion temperature can influence its final properties.

III.2.3. Driving Gases

The use of gases can facilitate fusion by reducing the required temperature.

III.3. Fusion Process

The fusion reaction of sand (silica) for glassmaking involves mixing silica with sodium carbonate, which acts as a flux by lowering the fusion temperature of the mixture [22, 29].

In the absence of sodium carbonate, silica would melt at around 1730 °C, but with sodium carbonate, the fusion temperature is lowered, allowing the mixture to fuse at lower temperatures.

Calcium carbonate provides chemical protection to the glass, protecting it, especially from interactions between silica and carbonates, playing a crucial role in the glass fusion process.

Silica (silicon dioxide) is chemically stable and represents over 60% of the Earth's crust mass. It is reduced by carbothermic reaction in arc furnaces at over 2000 °C, according to the reaction: $SiO_2 + 2\ C \rightarrow Si + 2\ CO$.

Thus, the presence of fluxes such as sodium carbonate helps reduce the fusion temperature of the mixture, facilitating the glassmaking process at more economical temperatures: $SiO_2(s) \rightarrow SiO_2(l)$

III.3.1. Decomposition of the Vitrifiable Mixture

Once melted, the mixture is homogenized to ensure a uniform distribution of components [23, 26].

During glass manufacturing, some raw materials may undergo thermal decomposition reactions during melting due to temperature, playing a crucial role in the raw materials fusion process for glass manufacturing.

For example, soda (Na_2CO_3) can decompose into sodium oxide (Na_2O) and carbon dioxide (CO_2) according to the reaction:

$$2Na_2CO_3(s) \rightarrow 2Na_2O\ (l) + 2CO_2\ (g)$$

At specific temperatures, other decomposition reactions can also occur. For example, around 800°C, the following reaction may take place:

$$Na_2CO_3(s) + CaCO_3(s) \rightarrow Na_2Ca(CO_3)_2(s)$$

$$Na_2Ca(CO_3)_2(s) + 2SiO_2(s) \rightarrow Na_2SiO_3(s) + CaSiO_3(s) + 2CO_2(g)$$

And around 1000°C, the decomposition reaction of soda into sodium silicate and carbon dioxide occurs:

$$Na_2CO_3(s) + SiO_2(s) \rightarrow Na_2SiO_3(s) + CO_2(g)$$

$$CaCO_3(s) + SiO_2\ (s) \rightarrow CaSiO_3(s) + CO_2(g)$$

III.3.2. Glass Fusion Furnaces

The glass fusion process takes place in furnaces of various shapes and dimensions depending on the nature and quality of the glass being produced [29, 30].

These furnaces can be powered by electrical energy, radiant energy from air-gas flames, or radiant energy from oxy-fuel-gas flames.

The refractories, highly resistant to mechanical and chemical corrosion by the molten glass at 1550°C, are generally composed of mixtures of oxides (silica, zirconia, and alumina) obtained through electrofusion or high-pressure sintering.

Heating can be provided by:

- Electrical energy through submerged electrodes, an efficient solution in terms of thermal efficiency, clean but expensive, therefore reserved for special glasses.
- Radiant energy from air-gas flames, on the surface of the glass bath, a technology that is quite polluting in terms of dust (sulfates), CO_2, SO_2, NO_x.
- Radiant energy from oxy-gas flames, replacing the combustion air with oxygen, a solution designed to reduce NO_x emissions.

Glass fusion is an energy-intensive operation, and significant progress is still expected in furnace operation and design to reduce their energy consumption.

After these steps, the glass can be shaped into various products such as bottles, windows, glasses, etc.

The glass manufacturing process may vary depending on the specifications of the final product and the technologies used, but the basic steps generally remain the same.

Types of Furnaces

Glass fusion occurs in furnaces made of refractory materials capable of withstanding very high temperatures, exceeding 1,800°C.

The two main processes used are the batch process, for the production of small quantities of glass, and the continuous process, for the mass production of industrial glass.

a. Batch Process Furnaces

The batch process is used to produce glass in small quantities and includes two types of furnaces (Figure V.2):

- Pot furnaces, allowing the production of small quantities of glass in refractory pots heated by gas or oil.
- Platinum crucible furnaces, used for special glasses

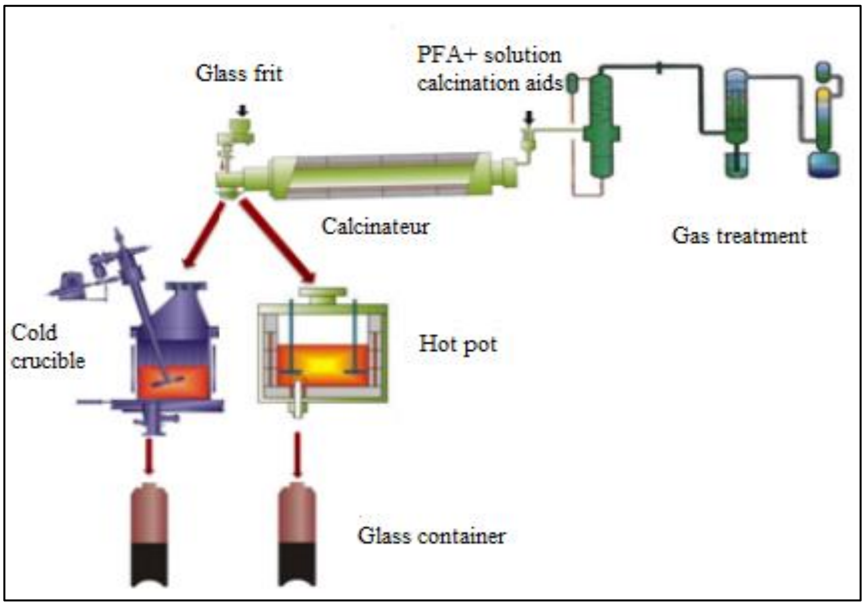


Figure V.2: The Continuous and Batch Processes: Crucible Furnace and Pot Furnace.

b. Continuous Process Furnaces

The continuous process is used for the mass production of industrial glass. It occurs exclusively in continuous furnaces, also known as tank furnaces, which are continuously fed with raw materials.

The amount of molten glass is nearly constant in the furnace.

There are two types of tank furnaces: those for flat glass and those for container glass. The lifespan of these furnaces is estimated to be around 10 years.

Tank furnaces are made of refractory materials and consist of a long rectangular corridor that can measure up to 50 meters in length and 10 meters in width.

They allow for campaigns of 3 to 5 years, producing up to 600 tons of formed glass per day.

The operational lifespan of tank furnaces has significantly improved since the 2000s, reaching up to 12 years for float glass furnaces.

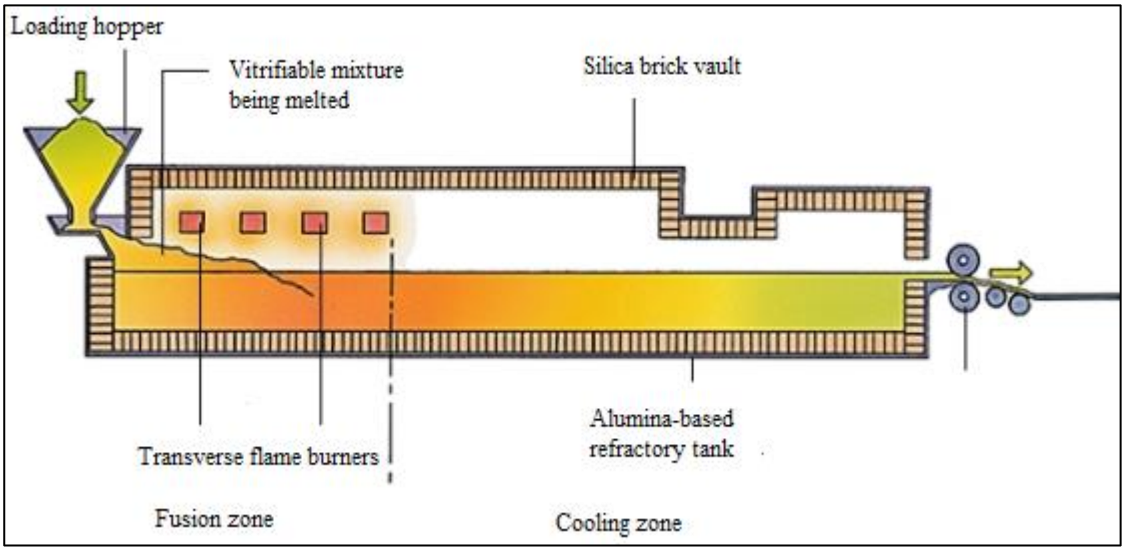


Figure V.3: The Continuous Process: The Tank Furnace

IV. Glass Refinement

Glass refinement is a crucial step in the glass manufacturing process.

Molten glass undergoes a refining process to eliminate impurities and unwanted air or gas bubbles referred to as "boils," "bubbles," or "chips."

This is achieved by maintaining the glass at high temperatures and gently stirring to promote the removal of impurities.

Gaseous inclusions are undesirable as they can adversely affect the quality of the glass, including its transparency, mechanical strength, or appearance.

In some applications, such as for LCD screen glasses, refining requirements are very strict.

Gaseous inclusions can have various origins:

- Trapped air in raw materials: Raw materials used in glass manufacturing are often powdery, facilitating the entrapment of air.
- Degassing of raw materials: Some raw materials, like carbonated materials, release gases during melting, such as the decomposition of sodium carbonate (Na_2CO_3) and sodium sulfate (Na_2SO_4) at high temperatures.
- Chemical reactions between glass and furnace materials: Chemical reactions between glass and furnace materials, such as refractories or metals, can also generate gaseous inclusions.

There are several refining methods, including [30, 31]:

IV.1. Mechanical Refinement

This method involves stirring the molten glass to promote the rise of gaseous inclusions.

IV.2. Mechanical Bubbling

Mechanical bubbling can be used to accelerate the refining process.

Tubes called bubblers, supplied with air, are placed at the bottom of the furnaces to facilitate the elimination of gas bubbles.

IV.3. Chemical Refinement

This method involves adding a refining agent to the molten glass.

The refining agent decomposes at high temperatures, releasing a gas that promotes the rise of gaseous inclusions.

IV.4. Formation of CO_2 and SO_2 Bubbles

Significant amounts of CO_2 and SO_2 occur during the decomposition reaction of sodium carbonate and sodium sulfate. CO_2 and SO_2 bubbles form within the glass bath, leading to upward movements.

As the following decomposition reaction of sodium sulfate occurs

1400°C : $Na_2SO_4 \rightarrow Na_2O + SO_2 + \frac{1}{2} O_2$

IV.5. Delayed Reaction of Sodium or Calcium Sulfate

To accelerate the refining phase, a delayed reaction of sodium or calcium sulfate occurs around 1400°C. For example, the following reaction may take place:

$2Na_2SO_4 + C \rightarrow 2Na_2O + 2SO_2 + CO_2$

IV.6. Redox Reactions

Redox reactions are of great importance in the glass manufacturing process as they influence the color and properties of the glass.

The raw materials used in glass manufacturing can be classified based on their redox potential and their ability to generate active oxygen or consume oxygen.

In the glass manufacturing process, redox equilibrium is typically achieved during the refining process, with intense bubbling being essential for obtaining homogeneous glass.

The redox state of the glass depends on the gas mixture generated during the refining process, rather than the atmosphere under which it was developed.

Among the raw materials used in glass manufacturing are sodium sulfate (Na_2SO_4) and sodium carbonate (Na_2CO_3). Sodium sulfate is a source of SO_3, an oxidizing agent, while sodium carbonate is a reducing agent. Other raw materials, such as iron and calcium silicates produced by blast furnaces, also contribute to a reducing character.

At the end of the elaboration, the glass will have an overall redox potential measurable by an electrochemical probe or by calculating the Fe^{2+}/Fe^{3+} ratio. This redox parameter plays a significant role in the color of the glass:

White glass is generally oxidized (redox number = +5): residual sulfur is then in the sulfate form $(SO_4)^{2-}$ with an Fe^{2+}/total Fe ratio of approximately 10%.

Amber glass is always highly reduced (redox number = -23): residual sulfur is then in the sulfide form (S^{2-}) with an Fe^{2+}/Fe^{3+} ratio of approximately 80%.

Redox reactions can occur in the molten glass depending on the composition.

For example, iron (Fe) present in certain raw materials can react to reduce ferrous ions (Fe^{2+}) to ferric ions (Fe^{3+}): $2Fe_2O_3 + 3C \rightarrow 4Fe + 3CO_2$

In summary, redox reactions are essential in glass manufacturing as they determine the color and properties of the glass. The raw materials used, such as sodium sulfate and sodium carbonate, play a crucial role in the redox balance of the glass, and the redox state of the glass depends on the gas mixture generated during the refining process.

V. Glass Homogenization

The homogenization of glass is a crucial step in the glass manufacturing process. To achieve high-quality glass, it is necessary to have a phase of mechanical stirring of the glass bath, where the molten glass is continuously agitated to ensure that all components are uniformly distributed. This guarantees the transparency and quality of the glass.

This operation can only be achieved through natural convection currents generated by the existence of thermal gradients within the furnace, especially the temperature differences between the colder bottom of the furnace and the warmer surface.

This stirring operation is essential to homogenize the glass during its formation and complete the dissolution of any remaining raw materials [29, 30].

VI. Quenching

Quenching is a critical stage in the glass manufacturing process that involves the rapid cooling of the molten glass to achieve the desired viscosity for subsequent shaping or casting operations. the quenching process typically takes place at temperatures ranging from 1530°C to 1550°C. At these high temperatures, the glass is in a highly fluid state, with a viscosity low enough to allow for efficient forming and shaping [8].

The quenching process is essential for several reasons [8, 32]:

- It reduces the temperature of the molten glass to a suitable viscosity level, allowing for easier handling and shaping.
- It helps to prevent the formation of defects or internal stresses in the glass structure by controlling the cooling rate.
- It prepares the glass for further processing, such as annealing, pressing, or blowing, depending on the desired final product.
- Proper control of the quenching stage is crucial in ensuring the quality and consistency of the final glass products, as it directly affects the physical and mechanical properties of the glass.

Exercise Series No. 5

Exercise V.1

Write the chemical reactions of the thermal decomposition of the raw materials used to form glass at different temperatures (800, 1000, and 1400 °C).

Exercise V.2

The decomposition of borax ($Na_2B_4O_7.10H_2O$) can occur in several successive stages depending on the temperature and reaction conditions, forming boron oxide (B_2O_3) and sodium oxide (Na_2O), which are raw materials used in glass manufacturing.

Provide the reactions corresponding to each of the following steps:

1. Dehydration at a temperature above 50°C
2. Low-temperature thermal decomposition, around 320°C
3. Thermal decomposition starting from 800°C

Exercise V.3

Cullet is recycled glass, usually derived from collected glass waste, processed, and transformed into new raw materials for glass manufacturing.
It is obtained by melting this glass waste at high temperatures.

1. What are the advantages of cullet in the production of recycled glass?
2. Why is cullet commonly used in the production of colored or packaging glass?
3. What are the specifications for the use of recovered glass?

Exercise V.4

The inappropriate composition of raw materials can influence the fusion temperature of glass, leading to defects.

1. Explain the relationship between glass compositions and fusion temperatures.
2. Indicate the optimal fusion temperature for each type of glass:

- Artisanal glass
- Borosilicate glass
- Quartz glass

Exercise V.5

Glass furnaces are essential equipment in glass manufacturing. They are used to heat the raw materials to a sufficiently high temperature for them to melt.

1. What are the main types of glass furnaces?
2. What is the operating principle of each type of furnace?
3. When to use each type of furnace?

Exercise V.6

The raw materials used in glass manufacturing can be classified based on their redox potential and their ability to generate active oxygen or consume oxygen.

1. What are the two categories of raw materials based on their redox potential?
2. What factors influence the redox balance of glass during refining?
3. Explain how the color of glass is affected by its redox potential.

Exercise Series No. 5: Solutions

Exercise V.1

The chemical reactions of the raw materials used to form glass at different temperatures are as follows:

- Chemical reactions at 800 °C:

Decomposition of sodium carbonate (Na_2CO_3) into sodium oxide (Na_2O) and carbon dioxide (CO_2):

$2Na_2CO_3 \rightarrow 2\,Na_2O + 2\,CO_2$

- Chemical reactions at 1000 °C:

Reaction between sodium carbonate (Na_2CO_3) and silica (SiO_2) to form sodium silicate (Na_2SiO_3)

$Na_2CO_3 + SiO_2 \rightarrow Na_2SiO_3 + CO_2$

Reaction between calcium carbonate ($CaCO_3$) and silica (SiO_2) to form calcium silicate ($CaSiO_3$)

$CaCO_3 + SiO_2 \rightarrow CaSiO_3 + CO_2$

- Chemical reactions at 1400 °C:

Decomposition of sodium sulfate (Na_2SO_4) into sodium oxide (Na_2O), sulfur dioxide (SO_2), and half a molecule of oxygen (½ O_2)

$Na_2SO_4 \rightarrow Na_2O + SO_2 + \frac{1}{2} O_2$

Reaction between sodium sulfate (Na_2SO_4) and carbon (C) to form sodium oxide (Na_2O), sulfur dioxide (SO_2), and carbon dioxide (CO_2)

$2Na_2SO_4 + C \rightarrow 2Na_2O + 2\,SO_2 + CO_2$

Decomposition of calcium sulfate ($CaSO_3$) into calcium oxide (CaO) and sulfur dioxide (SO_2)

$CaSO_3 \rightarrow CaO + SO_2$

Exercise V.2

The reactions corresponding to each step are as follows:

1. Dehydration at a temperature above 50°C:

Borax gradually loses its crystallization water.

$Na_2B_4O_7.10H_2O \rightarrow Na_2B_4O_7 + 10H_2O$

2. Low-temperature thermal decomposition, around 320°C:

Anhydrous borax begins to decompose into sodium metaborate ($Na_2B_2O_4$) and boron oxide (B_2O_3):

$Na_2B_4O_7 \rightarrow Na_2B_2O_4 + B_2O_3$

3. Thermal decomposition starting from 800°C:

At temperatures above 800°C, sodium metaborate further decomposes into boron oxide and sodium oxide:

$Na_2B_2O_4 \rightarrow B_2O_3 + Na_2O$

Exercise V.3

1. The advantages of cullet in the production of recycled glass include the reduction of energy consumption and the promotion of sustainability. By using cullet, one contributes to minimizing the environmental impact associated with glass manufacturing while optimizing resources.
2. Cullet is commonly employed in the production of colored or packaging glass to decrease costs and environmental impact. This is explained by the ability to integrate cullet into the glass manufacturing process, thus saving on raw materials and promoting a more environmentally friendly approach.
3. Specifications for the use of recovered glass include:

- Infusible Rate: Must be less than 50 g/ton to avoid the presence of contaminants such as gravel and porcelain.
- Free Reducer Rate: Must be less than 500 g/ton to exclude elements like paper and plastics.
- Free Metal Rate: Must be less than 5 g/ton to minimize the presence of undesirable metals.

This verification ensures that the recovered glass used in the production process meets specific standards, thereby ensuring the quality of the final product and reducing risks associated with the presence of contaminants.

Exercise V.4

1. The Relationship Between Glass Compositions and Melting Temperatures:

The composition of glass is a crucial factor influencing its melting temperature (T_m). Generally, the glasses melting temperature decreases as the content of fluxing agent increases

Fluxing agents are substances with lower melting points than silica (T_m = 1730°C), the primary component of glass. Common fluxing agents include sodium oxide (Na_2O) (T_m = 330°C), potassium oxide (K_2O) (T_m = 310°C), and calcium oxide (CaO) (T_m = 1200°C).

The relationship between glass composition and its melting temperature can be explained by the theory of chemical bonding. Silica is a tetrahedral material, meaning each silicon atom is bonded to four oxygen atoms. These bonds are strong and robust, making silica highly heat-resistant. Fluxing agents, on the other hand, have weaker bonds. When fluxing agents are added to silica, they weaken the bonds between oxygen atoms, making the glass more fluid and less heat-resistant.

2. Optimal Melting Temperatures:

- Artisanal Glasses: Artisanal glasses are typically made from a composition containing around 70% silica, 20% fluxing agents, and 10% other substances. This composition allows for a glass with a melting temperature low enough to be easily worked by glass artisans. The optimal melting temperature for artisanal glasses generally ranges between 1200 and 1400 °C.
- Borosilicate Glass: Borosilicate glass is a type of glass that contains a significant amount of boron. Boron has a very low melting point (294°C). As a result, borosilicate glass has a much lower melting temperature than ordinary glass. The optimal melting temperature for borosilicate glass typically ranges from 800 to 1300°C.
- Quartz Glass: Quartz glass is a type of glass composed mainly of silica, with a silica content exceeding 90%. Silica has a very high melting point of 1730°C. Consequently, quartz glass has a very high melting temperature. The optimal melting temperature for quartz glass generally ranges between 1600 and 2100°C.

Exercise V.5

1. The main types of glass furnaces are:

- Pot furnaces
- Tank furnaces
- Platinum crucible furnaces

2. The operating principle of each type of furnace:

- Pot furnaces operate on a discontinuous process. They are used for manual manufacturing processes such as blowing and casting. Production is done on a unit basis, and the operational duration of a pot furnace is limited to a few weeks, after which the pots are replaced. Pots remain in operation for only a few weeks. The lifespan of the pots is limited to a few months of use.
- Platinum crucible furnaces also operate on a discontinuous process. They are used for subsequent glass shaping operations. These furnaces are employed for processes like thermoforming or fusing, allowing for slow cooling of blown glass pieces. The operational duration of a platinum crucible furnace is limited to a few months of use.
- On the other hand, tank furnaces operate on a continuous process. They are used to create the glass material from the mixture of vitrifiable materials. The operational duration of a tank furnace can extend up to 12 years. Tank furnaces are powered by gas or fuel.

3. Use of each type of furnace:

Different types of glass furnaces are utilized for various applications, depending on production requirements.

- Pot furnaces are generally used for the production of small quantities of glass, such as artisanal glass. They are also employed for the production of special glasses, including laboratory glass and optical glass.
- Platinum crucible furnaces are typically used for the production of special glasses like borosilicate glass and high-lead-content glass. They are also utilized for the production of high-quality glasses, such as optical glass and laboratory glass.
- Tank furnaces are generally used for the mass production of glass, including flat glass, hollow glass, and packaging glass. They are also employed for the production of common glasses like household glass and automotive glass.

Exercise V.6

1. The two categories of raw materials based on their redox power are:

Oxidizing raw materials and reducing raw materials. An example of an oxidizing raw material is sodium sulfate (Na_2SO_4). An example of a reducing raw material is sodium carbonate (Na_2CO_3).

2. Factors influencing the redox balance of glass during refining are:

- The composition of raw materials,
- Temperature,
- Pressure, and gas flow.

3. Explanation of how the color of glass is affected by its redox power:

The color of glass is influenced by its redox power because metallic ions present in the glass can change their valence depending on the redox state of the glass.

For example, iron (Fe) can exist in the ferrous (Fe^{2+}) or ferric (Fe^{3+}) forms.

White glass is generally oxidized, meaning ferrous ions are present in the ferrous form. Amber glass is always highly reduced, indicating that ferrous ions are present in the ferric form.

.

Chapter VI: Forming Processes and Types of Glasses

Chapter VI: Forming Processes and Types of Glass

I. Introduction

Glass Manufacturing involves blending natural raw materials (sand, limestone) and industrial chemicals (sodium carbonate) in defined proportions. This mixture is then melted in a furnace to form a homogeneous liquid known as molten glass. The molten glass is subsequently shaped and cooled to create the final object.

The general stages of the glass manufacturing process are as follows [10, 23]:

- Batch Preparation or Composition Preparation: Glass raw materials, such as sand (silica), soda, and limestone, are mixed and heated in a furnace known as a batch house.
- Glass Melting: The batch is heated to a high temperature to transform it into a liquid state that can be shaped.
- Forming or Shaping: The molten glass is shaped using various techniques such as blowing, rolling, or drawing.
- Annealing: The glass is slowly cooled at a lower temperature to solidify and strengthen the material.
- Quality Controls: Finished products undergo inspection to ensure compliance with company standards and requirements.

II. Glass Categories

Various shaping processes allow the classification of glass products into several major categories [25,26, 32]:

- Flat Glass (window glass, mirrors...)
- Hollow Glass (bottles, jars, vials, decorative objects...)
- Textile and Non-textile Glass Fibers
- Other Glasses (cellular glass, optical glass, television tubes, tubes and bulbs,...)

III. Flat Glasses

III.1. Definition of Flat Glasses

Flat glasses are glass products manufactured in the form of sheets, primarily used for the production of windows and mirrors (Figure VI.1) [26].

They are predominantly produced by the glass industry and widely utilized in the construction sector for glazing.

The industrial production of flat glass has a positive impact on the environment, as flat glass is a recyclable material.

Figure VI.1: Flat Glasses

III.2. Manufacturing and Forming

III.2.1. Manufacturing Processes

a. Float Process

The most widely used method for manufacturing flat glass is the float process, also known as the float glass process. Nowadays, over 80% of the flat glass produced globally is float glass created through floating. This continuous process is employed for the production of high-quality flat glass, including windows, mirrors, and solar panels. The process involves several stages as follows (Figure VI.2) [26]:

- Melting: The glass is melted at approximately 1350-1550 °C.
    - Gas bubbles are eliminated through centrifugation.
    - Glass homogenization is achieved through stirring.
- Floating or Sealing: The molten glass is poured onto a bath of molten tin at around 550-600 °C.
    - As glass is less dense than tin, it floats on top.
    - The ribbon's thickness is controlled by the glass pouring speed and the tin bath's depth.

- Slow Cooling or Drawing: The glass ribbon is slowly cooled to around 60 °C.
  - Slow cooling helps release internal stresses in the glass.
- Control and Cutting: Controlled using a laser to detect imperfections.
  - The glass ribbon is cut into sheets of the desired size.
- Storage and Shipping: The glass sheets are then stored and shipped.

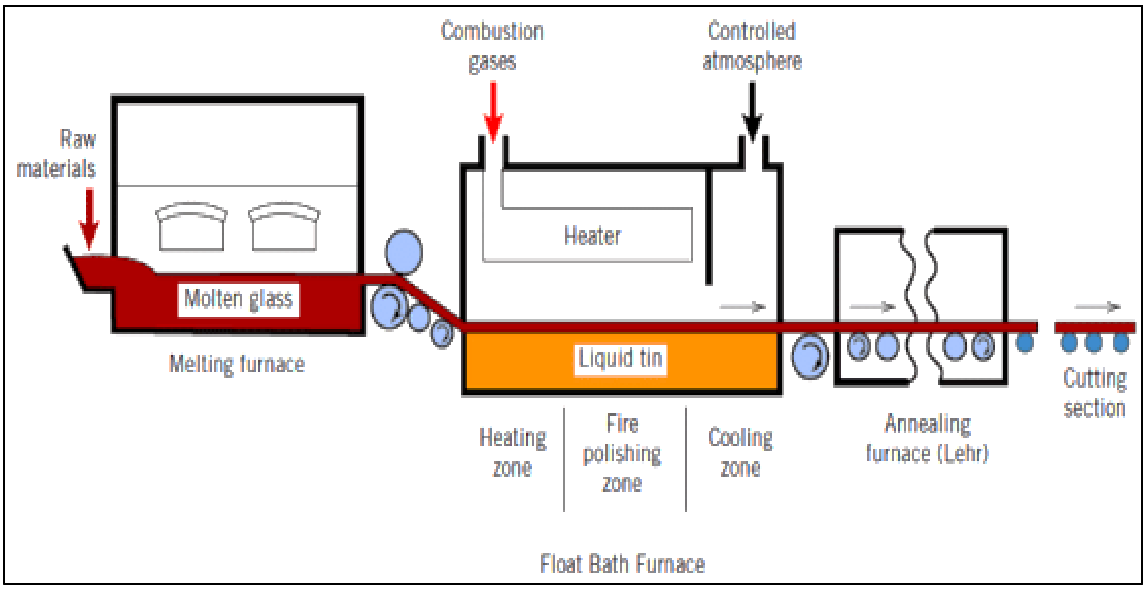


Figure VI.2: Float Glass Manufacturing Process

b. Other Processes

Various processes for manufacturing flat glass allow for the production of glasses with diverse properties, catering to the needs of numerous applications. There are other processes for manufacturing flat glass, such as [26, 31]:

- TWIN Process: The TWIN process involves pouring two streams of molten glass side by side in a high-temperature furnace. The two streams solidify, sticking together, forming a ribbon of glass with two parallel faces.
- Patterned Glass: Patterned glass is a type of cast glass that has been decorated on the surface. The decoration is applied to the glass before it solidifies.
- Wired Glass: Wired glass is a type of glass reinforced with glass or metal wires. The wires are incorporated into the molten glass before it solidifies.
- Profiled Glass: Profiled glass is a type of glass shaped into a specific form. The glass can be profiled before or after it solidifies.

- Fourcault Process and Pittsburgh Process: The Fourcault and Pittsburgh processes are methods for manufacturing sheet glass that use mechanical blowing to shape the glass.
- Libbey Owens (Colburn) Process: The Libbey Owens process is a method for manufacturing sheet glass that uses suction blowing to shape the glass.
- Glass Ceramic: Glass ceramic is a material that combines the properties of glass and ceramics. Glass ceramic is made from glass that is then annealed at high temperatures. Annealing causes the glass to crystallize, providing improved mechanical and thermal properties.

III.2.2. Forming of Flat Glass

a. Glass Pressing

Glass pressing is a glass shaping technique involving pressing pre-formed glass into a mold.

There are two main glass pressing methods:

- Pinch Pressing: A manual process used to make simple objects like reflectors.
- Mechanical Pressing: An industrial process used to make complex objects such as optical lenses or glazing.

The mechanical pressing occurs in two steps:

Glass reheating: The glass is heated to its softening temperature, approximately 700 °C.

Glass pressing: The glass is pressed into a mold using an automatic piston. Glass pressing offers several advantages:

It enables mass production at low cost.

It allows for the creation of complex-shaped objects.

It provides control over glass properties such as strength and transparency. Glass pressing is used for various glass products, including culinary glasses, electrical insulators, optical lenses, and glazing.

b. Glass Bending

Glass bending is a shaping technique involving curving a flat glass sheet. There are three main glass bending processes:

Sand Bending: A manual process used to create large objects like glass tables or glazing.

Bending on Metallic or Refractory Molds: An industrial process used for small objects like optical mirrors.

Skeletal Bending: An industrial process for creating large objects such as windshields or automotive glasses. Glass bending offers several advantages:

It allows for the creation of complex-shaped objects.

It provides control over glass properties such as strength and transparency. Glass bending is used for a wide variety of glass objects, including glass tables, glazing, optical mirrors, windshields, and automotive glasses.

c. Glass Fusing

Glass fusing is a glass shaping technique involving the fusion of pre-cut glass pieces of different colors. The glass fusing process consists of three steps:

- Preparation of Glass Pieces: Glass pieces are cut to the desired size and shape.
- Placement of Glass Pieces: Glass pieces are arranged on a supporting glass plate, adjusting or juxtaposing them.
- Fusion of Glass Pieces: The glass pieces are heated in a furnace to a temperature of 830 °C, allowing them to fuse and weld together.

Glass fusing allows for the creation of large objects such as paintings, sculptures, or light fixtures.

d. Glass Thermoforming

Glass thermoforming is a glass shaping technique involving heating a glass sheet to 650 °C and pressing it onto a refractory mold.

There are two main types of molds used for glass thermoforming:

- Dies: Custom-made molds crafted from a refractory base. They allow for the creation of complex and unique shapes.
- Biscuits: Standard molds, less expensive than dies. They allow for the creation of simpler and repetitive shapes.

Glass thermoforming can be combined with other glass shaping techniques, such as fusing, to create even more complex and decorative objects.

Glass thermoforming is a technique used to create a wide variety of objects, including paintings, sculptures, light fixtures, wall coverings, and glazing.

e. Glass Lamination

Glass lamination is an industrial process involving pressing molten glass between two rollers.

Lamination enables the production of large, high-quality glass sheets.

The glass lamination process consists of three steps:

- Molten glass is poured at the exit of the melting furnace.
- Molten glass is pressed between two rotating rollers. The rollers are spaced a few millimeters apart, allowing the glass to spread into a ribbon.
- The glass ribbon is transported into an annealing furnace to cool and solidify it.

Glass lamination is used for the production of various glass products, including glazing, mirrors, printed glass panels, and decorative products.

III.3. Annealing of Flat Glasses

Annealing is a thermal process involving heating flat glass to a high temperature and then slowly cooling it. Its purpose is to eliminate internal stresses in the glass, enhancing its mechanical and optical properties.

Internal stresses are forces within the glass that can make it fragile and prone to cracking. Annealing eliminates these stresses by allowing the glass to heat up and cool down uniformly.

Annealing also improves the optical quality of the glass by removing surface defects and promoting a smoother surface.

The annealing process is typically carried out in a tunnel furnace. The glass is heated to a temperature between 500 and 600 °C and then cooled at a controlled rate.

The duration of treatment varies depending on the glass thickness and desired properties. Without this step, most manufactured objects would crack or break [31].

III.4. Quality Controls for Flat Glasses

Quality controls for finished flat glass products are essential to ensure compliance with standards and customer specifications, ensuring the quality and safety of flat glass. Some quality controls for flat glass include [31]:

- Material Controls: Ensuring the quality of materials used, such as glass sand, quartz, feldspar, and calcium silicate, is crucial for the final quality of flat glass.

- Temperature Controls: Precise temperatures during annealing are essential to optimize the dimensional stability of glass and minimize defects.
- Annealing Duration Control: Annealing duration must be controlled to ensure even annealing and prevent overflow or cracking.
- Surface Control: The flat glass surface must be smooth and regular, without.

IV. Hollow Glasses

IV.1. Definition of Hollow Glasses

Hollow glasses encompass all glass articles that do not have a flat surface, such as glassware, laboratory tubes, containers, etc.

While, in some cases, they may be crafted from flat glass, as in the case of curved glass (Figure VI.3) [28]

Figure VI.3: Hollow Glasses

IV.2. Manufacturing and Forming

The manufacturing and shaping of hollow glass involve the use of different processes to produce hollow glass items such as bottles, flasks, jars, culinary and table glassware, and art elements. After the feeder stage, which involves supplying the glass machine with material, the shaping (forming) steps for hollow glass vary depending on the process used (see figure VI.4). The main manufacturing processes for hollow glass are blowing, pressing, blow-blow and press-blowing (Figure VI.4) [29, 30].

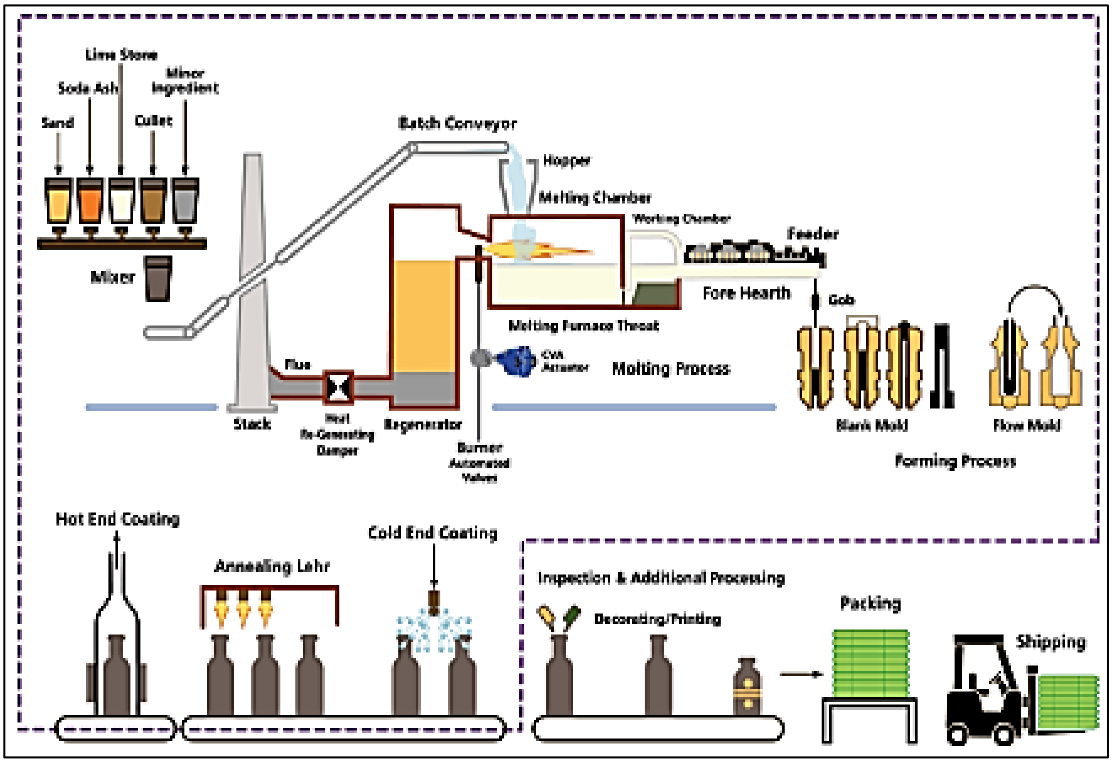


Figure VI.4: Hollow Glass Manufacturing Process

IV.2.1. Glass Blowing

Hollow glass blowing is a glass manufacturing technique that involves shaping a glass droplet, called a parison, directing it into a blank mold, and blowing it to achieve the desired shape.

This process is used in the production of bottles, flasks, jars, and other hollow glass products. It can be carried out in an artisanal or industrial manner, involving the use of a blowing pipe and molds to shape the glass.

Hollow glass blowing can also be a craft, where scientific glassblowers create or repair laboratory glassware, transforming glass tubes or bars using a torch and a glassblowing lathe.

IV.2.2. Glass Pressing

Hollow glass pressing is a glass manufacturing technique that involves molding molten glass in a mold using a plunger to form the final article.

This method is used to produce hollow glass items such as culinary and table glassware, jars, insulators, bricks, paving stones, mirrors, and headlamp lenses.

Unlike hollow glass blowing, where the shape is obtained by blowing, hollow glass pressing allows shaping the piece by pressing molten glass into the mold using a plunger.

IV.2.3. Combined Techniques

The Blow-Blow process is a hollow glass manufacturing technique invented in 1925 that is still used today (Figure IV.5).

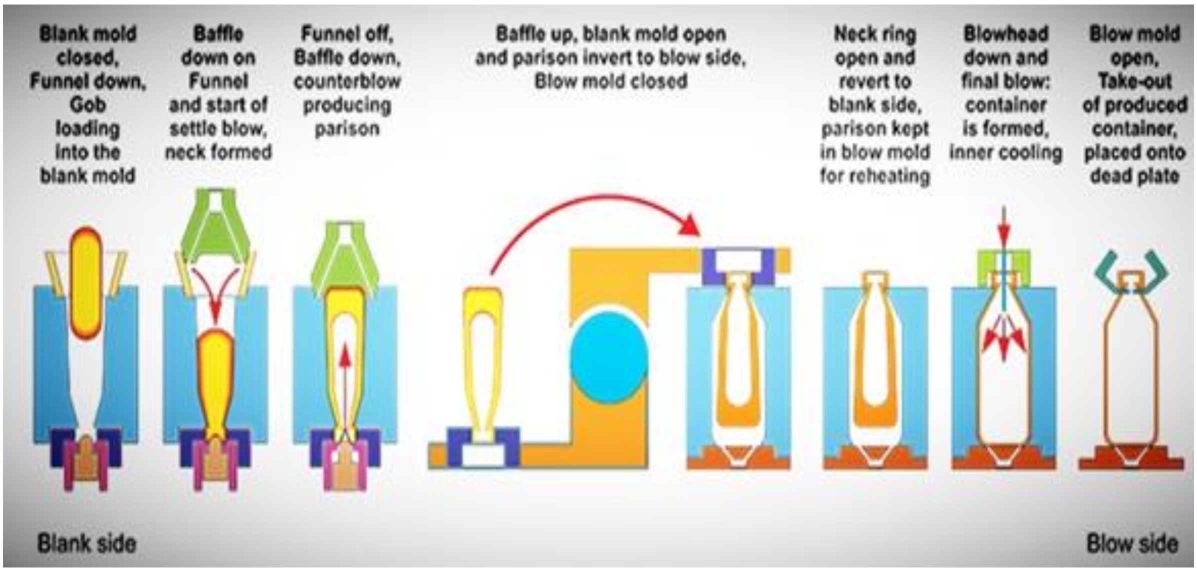


Figure IV.5: Blow - Blow Process.

This technique involves forming an oblong glass droplet from the molten mass, which is directed to the blank mold through a channel.

In the Blow-Blow process, the blank mold is equipped at its lower part with a plunger of 2 to 3 cm covered by the glass through energy.

This glass droplet, or parison, is directed towards the blank mold. In the Blow-Blow process, the latter is equipped at its lower part with a plunger of 2 to 3 cm covered by the glass through energy.

The blank mold is then sealed from the top with the blank bottom. The glass is then blown into the mold to give it the desired shape.

The Press-Blow process represents one of the most frequently used methods in the industrial production of hollow glass. In this process, the glass droplet enters the mold from the top, while the pressing matrix is introduced from the bottom.

Once the droplet has settled in the preforming mold, it is sealed from the top using the blank bottom.

The pressing matrix then moves upward, shaping both the body and the mouth of the glass object. As soon as the pressing matrix is removed from the body, it is transferred to the finishing mold.

Unlike the Blow-Blow process, the shaping of the mouth occurs last in the Press-Blow process.

IV.3. Annealing of Hollow Glass

Hollow glasses, such as bottles, flasks, jars, and culinary and table glassware, undergo a similar annealing process to flat glass.

This process involves heating the glass to a specific temperature, followed by controlled cooling.

During annealing, the glass is exposed to high temperatures to eliminate internal stresses resulting from the initial forming process.

This heat treatment optimizes the dimensional stability of the glass, reducing the risk of distortion or subsequent cracking.

Annealing also contributes to improving optical quality by eliminating surface defects and promoting a smoother surface.

The annealing process for hollow glass may vary depending on the specifications of the final product and the desired quality standards.

Precise control of temperatures, cooling rates, and treatment durations is essential to achieve uniform results and meet the specific requirements of each application.

IV.4. Quality Controls

Depending on the type of final product, various tests are implemented to ensure compliance with the requirements specified in the customer's specifications [30].

For packaging glass, an initial test is performed on the molten material by passing a glass sample through a device measuring the color or transparency of the material (spectrophotometer). If the result does not meet the standards, adjustments to the melting bed are proposed to bring it into compliance.

Then, several tests are performed on the shaped material to ensure the quality of the final product.

These tests include:

- Compression test: ensures the strength of the packaging.
- Flatness control of the ring: prevents any problems during capping or corking.
- Appearance control: identifies the presence of glazes, bubbles, unfused grains, etc., that could lead to long-term fragility of the packaging.

- Dimensional control: measures total length, inner and outer diameter, etc., using automatic vision throughout production.
- Body and bottom control of the bottle: identifies any defects and potential cracks in the packaging.

V. Glass Fibers

V.1. Definition of Glass Fibers

Glass fiber is a strand of glass used in various applications, particularly in the glass industry and in the production of composites. It was patented in 1930 and has recently revolutionized the glass industry due to its mechanical and optical qualities [29].

Glass fiber is used for insulation, reinforcement, and optics (Figure VI.5).

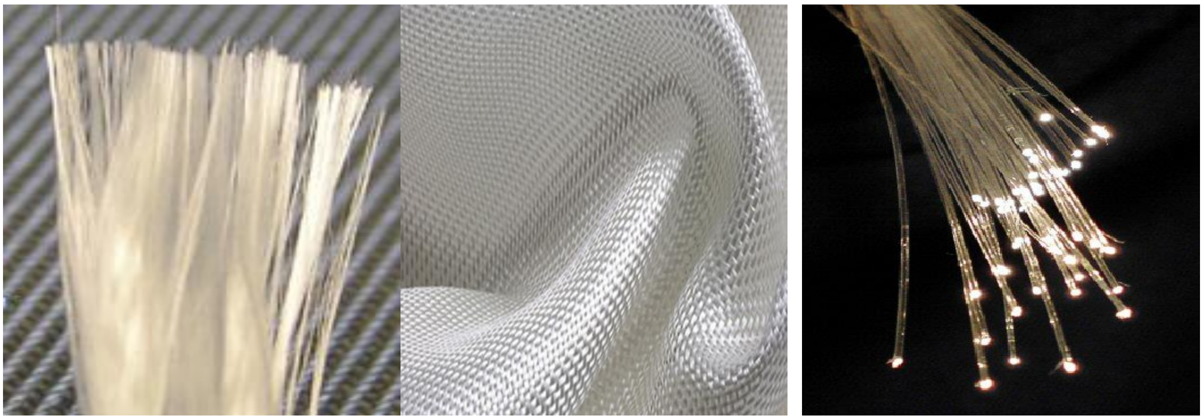


Figure VI.5: Glass Fibers

Insulation glass fibers are manufactured from specific glasses containing components such as alumina and calcium, which enhance their insulation properties. They are produced in the form of an entanglement of relatively short fibers, often referred to as "glass wool".

On the other hand, reinforcement glass fibers are primarily produced in the form of continuous or discontinuous textile fibers and are incorporated into organic polymers to form reinforced plastic.

Reinforcement glass fibers are made from different types of glass, such as Type A glass, Type C glass, and Type AR glass, etc., which have specific compositions in terms of percentages of silica, alumina, lime, magnesia, sodium carbonate, and boron trioxide (**Appendix 4**).

Optical fiber is mainly composed of silica and composite glasses. Plastic is used to manufacture the plastic sheath of the optical fiber.

V.2. Manufacturing and Forming

V.2.1. Simple Process

The glass fiber manufacturing process includes several key steps [29, 33]:

- Composition: Glass is obtained from a mixture of silica, alumina, magnesium carbonates, calcium, sodium, and potassium. These oxides are weighed and mixed in a mixer to form a homogeneous mixture called "batch". The batch is then heated to a temperature of 1,550°C in a furnace.
- Melting: Melting is an important step as it transforms the oxide mixture into a viscous liquid. The mixture is heated up to 1,550°C in furnaces to form molten glass. At this temperature, the oxides combine to form a viscous liquid.
- Fiberization: The molten glass is drawn through a die to obtain filaments or fibers with a diameter of 3 to 20 mm. The die is a precisely sized orifice that determines the fiber diameter. The fiber diameter is important as it determines the properties of the fibers. Larger diameter fibers are stronger, while smaller diameter fibers are more flexible. The molten glass is drawn through the die under the influence of gravity or centrifugal force.
- Drawing: The fibers are drawn to achieve the desired diameter. Drawing elongates and refines the fibers. It also improves the mechanical properties of the fibers. There are three drawing principles: mechanical drawing, centrifugal drawing, and fluid drawing. Some of these principles can be combined.
  - Mechanical Drawing: Mechanical drawing is the most common manufacturing process for glass fibers. It involves passing molten glass through a die, which is a perforated device that determines the fiber diameter. The glass is maintained at a temperature of 1250°C in the die. Upon exiting the die, the glass is drawn at a speed of up to 50 m/s. Drawing elongates and refines the fibers. The obtained diameters range from 5 to 25 µm. The fibers are then gathered to form a yarn. A yarn consists of 100 to 2000 filaments (Figure VI.6).

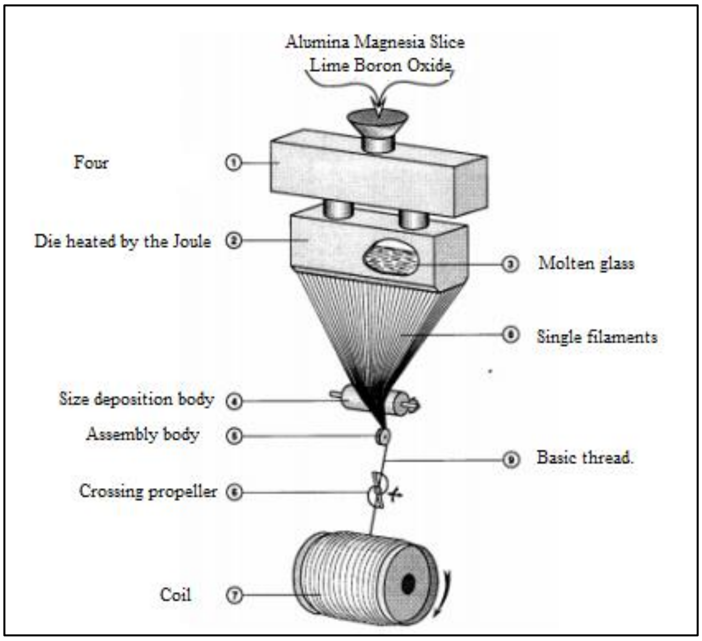


Figure VI.6: Mechanical Drawing

- Centrifugal Drawing: The centrifugal drawing process is a manufacturing method for glass fibers that uses centrifugal force to stretch molten glass (Figure VI.7).

Molten glass is poured onto a rapidly rotating refractory disc, typically spinning between 3000 and 4000 revolutions per minute. Centrifugal force causes the stretching of the glass into fibers with a diameter ranging from 10 to 25 µm. The fibers are then cooled and collected.

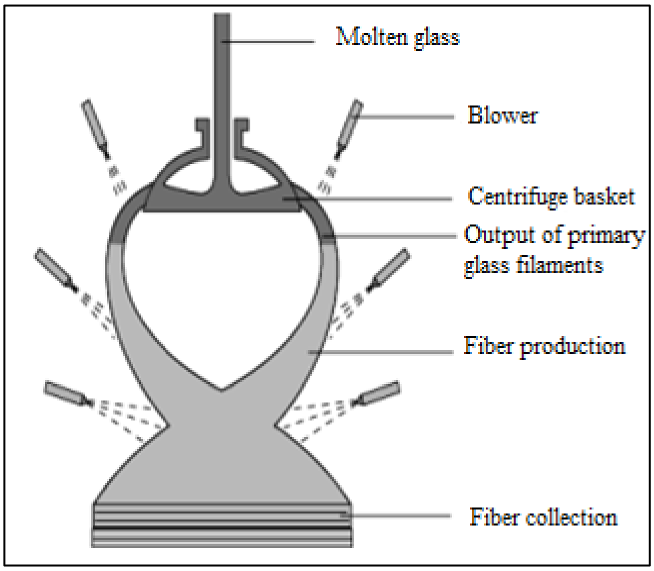


Figure VI.7: Centrifugal Drawing

- Fluid Drawing: The fluid drawing process is a manufacturing method for glass fibers that employs a stream of hot fluid to disperse molten glass into fibers (Figure VI.8).

Molten glass is poured onto a metal plate. A stream of hot fluid, usually air or oxygen, is then directed onto the molten glass. The fluid stream causes the glass to break into fibers with a diameter ranging from 0.05 to 10 µm.

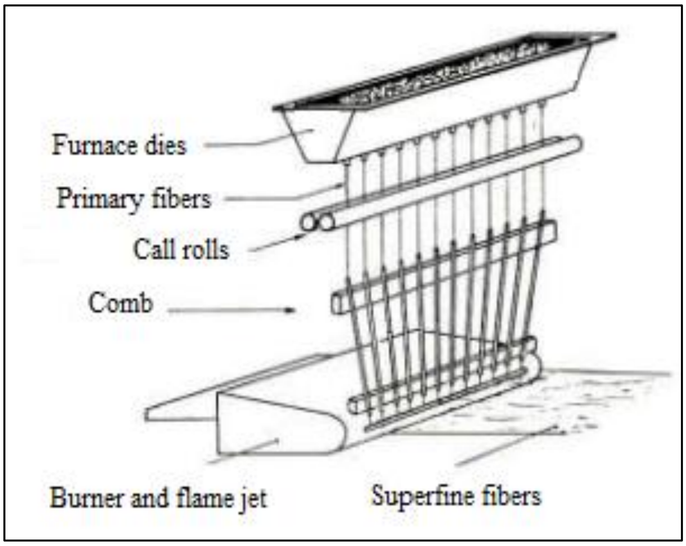


Figure VI.8: Fluid Drawing

V.2.1. Mixed Process

The mixed process for manufacturing glass fiber combines the centrifugal process with fluid drawing. This process has been developed worldwide since 1954 [33, 34].

In this method, a bowl perforated with several thousand holes is placed in the centrifuge, rotating at a speed of 3000 rpm. The molten glass is introduced into the spinning plate, heated to around 1000° to 1100°C, and rotated at a very high speed.

The central part of the plate is a peripheral crown with thousands of holes through which the glass exits the plate.

The glass fibers are then stretched by fast currents of hot gas and undergo a fluid treatment to obtain so-called "superfine" glass fibers.

This highly flexible process allows for the production of bulk fibers with diameters ranging from 1 to 6 µm.

- Sizing: The fibers are coated with a substance to make them more flexible and improve their adhesion to the resin. The commonly used substance is a liquid resin, applied to the fibers through spraying or immersion.
- Winding: The fibers are wound onto coils to facilitate their handling and storage.

- Weaving: The fibers can be woven to form glass fiber fabrics. Weaving allows for the creation of strong and resistant structures.

V.3. Optical Fibers

The manufacturing of optical fiber involves several key steps. First, a cylindrical preform is made from a silicon compound called silica. Subsequently, this preform undergoes a drawing process, followed by polishing. These steps are essential to obtain a high-quality optical fiber with optimal transmission characteristics and lifespan.

The manufacturing of optical fibers is divided into two main processes: the fabrication of optical fiber preforms and the drawing process (Figure VI.9).

The production of optical fiber preforms mainly involves processes such as MCVD (Modified Chemical Vapor Deposition), OVD (Outer Vapor Phase Deposition), and VAD (Vapor Phase Axial Deposition) [23].

Finally, the optical fiber preform is placed in a drawing tower, where it is stretched to form a thin optical fiber.

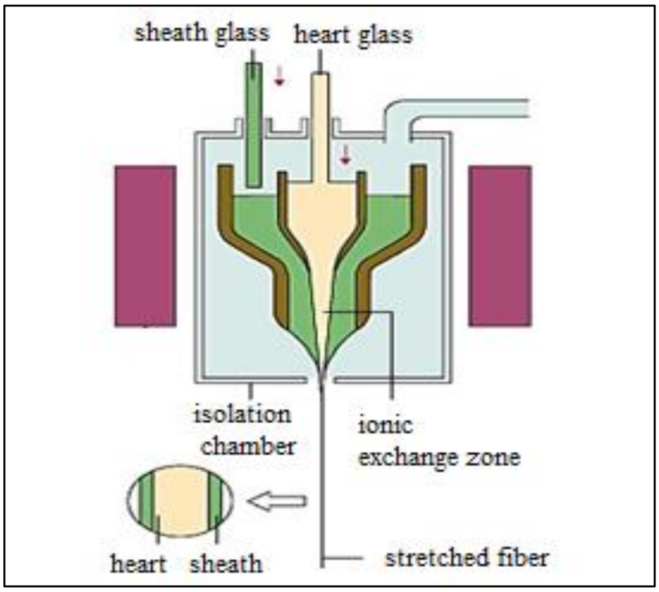


Figure VI.9: Manufacturing of Optical Fibers

V.4. Quality Control

Quality control for fiberglass is important to ensure that fiberglass products meet specified requirements.

Quality control is performed at all stages of production, from fiber manufacturing to the treatment of finished products. Raw Material Control: Raw materials used for fiberglass manufacturing are inspected to ensure they meet the required specifications. These raw materials include glass sand, quartz, feldspar, and calcium silicate. Manufacturing Control: Manufacturing control is conducted to ensure that the production process complies with standards. This control includes the measurement of temperatures, pressures, and flow rates. Finished Product Control: Finished fiberglass products are inspected to ensure they meet specified requirements [31].

This control includes measurements of dimensions, strength, durability, and impact resistance.

Common quality control tests for fiberglass include [33]:

- Tensile Strength: This test measures the force required to break a fiberglass strand.
- Flexural Strength: This test measures the force required to twist a fiberglass strand.
- Compression Strength: This test measures the force required to crush a fiberglass strand.
- Impact Resistance: This test measures a fiberglass strand's ability to resist an impact.
- Light Transmission: This test measures a fiberglass strand's ability to transmit light.

VI. Optical Glasses

VI.1. Definition of Optical Glasses

An optical glass is a high-quality glass suitable for creating optical systems such as optical lenses, prisms, or mirrors. Optical glass contains additives designed to modify certain optical properties such as refractive index, dispersion, transmittance, thermal expansion, and other parameters [26, 29].

Optical glasses are used for various applications, including nonlinear optics, acoustics, and electronics.

Figure VI.10: Optical Glasses

VI.2. Manufacturing and Forming

Shaping optical glasses is a complex process that requires precision and meticulous craftsmanship. Optical glasses are made from various materials, including mineral glass, organic glass, and plastic.

Shaping optical glasses is a complex process that demands a deep understanding of glass properties.

The general steps in this process are as follows, but they may vary depending on the type of glass and the desired application [31].

- Roughing: This step involves cutting the glass to the desired size. It is typically done using a saw or carbide wheel.
- Surfacing: The most crucial step in shaping optical glasses is surfacing, where the shape and optical properties of the glass are determined. Surfacing is usually done using a milling machine. The milling machine is equipped with cutters of different shapes and sizes to sculpt the glass as needed.
- Polishing: After surfacing, the glass is polished to achieve a smooth and shiny surface. Polishing is generally done using a machine called a polisher. The polisher is equipped with polishing discs that render the glass surface perfectly smooth.
- Treatments: Optical glasses can undergo treatments to enhance their optical or mechanical properties. Common treatments include anti-reflective, anti-scratch, and anti-static treatments.

VI.3. Quality Control

Rigorous quality control is essential to ensure the quality and safety of final optical products.

Common steps in the quality control of final optical glass products include [29,31]:

- Visual Inspection: Visual inspection is the first step of quality control, involving a naked-eye examination of the glass to detect visible defects such as scratches, cracks, inclusions, or bubbles.
- Dimensional Measurements: Glasses are then measured to verify that they have the correct dimensions. These measurements are typically done using calipers or a micrometer.
- Optical Tests: Glasses are tested to check their optical properties, including light transmission, dispersion, and refraction. These tests are usually conducted using a spectrometer or refractometer.
- Mechanical Tests: Glasses can also be tested for their mechanical properties, such as bending strength, tensile strength, and impact resistance. These tests are generally performed using a tensile testing machine or an impact testing machine.
- Depending on the application, specific tests such as biocompatibility for medical instruments or debris resistance for military applications may be conducted.
- Defects detectable during quality control include scratches that may affect clarity, cracks that could lead to breakage, inclusions causing optical distortions, bubbles influencing light transmission, size defects impacting proper functioning, optical defects affecting image quality, and mechanical defects compromising durability.

Exercise Series No. 6

Exercise VI.1

The glass manufacturing process is a complex series of steps aimed at transforming raw materials into a final product.

- List the general steps involved in the glass manufacturing process.

Exercise VI.2

Shaping glass to achieve the desired form is one of the crucial steps in glass production and varies depending on the final product.

1. What is the significance of this step in the glass production process?
2. Identify the different categories of glass based on their shaping process.

Exercise VI.3

The processes used in the production of flat glass vary in terms of technique and product. Among these processes, we find:

- TWIN Process
- Fourcault and Pittsburg Process
- Float Process
- Libbey Owens (Colburn) Process

1. What is the most commonly adopted process for manufacturing flat glass?
2. Which flat glass production process involves pouring two streams of molten glass side by side in a high-temperature furnace?
3. What is the glass manufacturing process for window glass that uses blow-and-draw technique to shape the glass?

Exercise VI.4

Identify the type of quality control corresponding to the following descriptions for the final glass packaging product:

a. Measures total length, inner and outer diameters using automatic vision.
b. Identifies the presence of glazes, bubbles, unfused grains, etc.

c. Detects possible defects and cracks in the packaging.
d. Ensures the strength of the packaging.
e. Prevents any issues during capping or corking.

Exercise VI.5

There are three distinct techniques for shaping hollow glass.

1. List these three techniques.
2. Compare these three techniques.

Exercise VI.6

Fiberglass is among the most advanced forms of glass.

- Explain the importance of fiberglass by mentioning its application areas.

Exercise Series No. 6: Solutions

Exercice VI.1

The general steps involved in the glass manufacturing process are:

- Preparation of the melting bed or composition: Raw materials for glass, such as sand (silica), soda, and limestone, are mixed and heated in a furnace called a melting arch.
- Glass elaboration: The melting bed is heated to a high temperature to become liquid and can be shaped.
- Forming or Shaping: The molten glass is shaped using various techniques such as blowing, rolling, or drawing.
- Annealing: The glass is annealed at a lower temperature to solidify and harden the material.
- Quality controls: Finished products are inspected to ensure compliance with company standards and requirements.

Exercise VI.2

1. The significance of glass shaping in the glass production process: Glass shaping is a crucial step in the glass production process as it allows obtaining the desired shapes and qualities for the final product. Different categories of glass are manufactured using specific shaping processes tailored to their respective applications.

2. The different categories of glass based on their shaping process are:

- Flat glass (window glass, mirrors, etc.).
- Hollow glass (bottles, jars, vials, decorative items, etc.).
- Textile and non-textile fiberglass.
- Other glasses (cellular glass, optical glass, TV tubes, tubes, and bulbs, etc.).

Exercise VI.3

1. The most commonly adopted process for manufacturing flat glass: the float process, nowadays, more than 80% of the flat glass produced worldwide is float glass.

2. The flat glass production process that involves pouring two streams of molten glass side by side in a high-temperature furnace: the "TWIN" process. This process

produces a ribbon of glass with two parallel faces, which is useful for certain applications such as mirrors.

3. The glass manufacturing process for window glass that uses blow-and-draw technique to shape the glass: the Fourcault and Pittsburgh processes are glass manufacturing processes that use mechanical blowing to shape window glass.

Exercise VI.4

The type of quality control corresponding to the descriptions in the following table:

Description	**Quality Control**
Measures total length, inner and outer diameters using automatic vision.	Dimensional Control
Identifies the presence of glazes, bubbles, unfused grains, etc.	Appearance Control
Spots potential defects and cracks in the packaging.	Body and Bottom of the Bottle Control
Ensures the strength of the packaging.	Compression Test
Prevents any issues during capping or corking.	Flange Flatness Control

Exercise VI.5

1. The three techniques for shaping hollow glass are as follows:

- Glass blowing
- Glass pressing
- Press-and-blow

2. Comparison of the three techniques: Each of the three techniques has its advantages and disadvantages.

- Glass blowing enables the production of intricately shaped, large-sized, and thin-walled articles. However, it is a lengthy and intricate process that requires skilled labor.

- Glass pressing is a faster and simpler process compared to glass blowing. It does not require skilled labor, but it limits the complexity of possible shapes and the size of articles.
- Press-and-blow is a combination of the two preceding techniques. It allows for the production of large-sized and intricately shaped articles while being faster and simpler than glass blowing.

<u>Exercise VI.6</u>

Importance of Fiberglass:

- Fiberglass is a form of glass composed of fine glass fibers. These fibers are produced by melting glass and forcing it through small holes. The fibers are then bonded together to form a fabric or thread.
- Fiberglass is a highly resilient and durable form of glass. It is also lightweight and easy to work with. These properties make fiberglass an ideal material for a variety of applications.
- Fiberglass is an important material applied in a wide range of fields. Its properties of strength, durability, lightweight nature, and ease of working make it an ideal material for many applications.

Applications of Fiberglass: Fiberglass is used in a diverse range of applications, including:

- **Engineering:** Fiberglass is used in construction, aerospace, marine, and automotive industries. It is employed to reinforce structures, manufacture composites, and produce lightweight and durable components.
- **Construction:** Fiberglass is used to manufacture construction materials such as fiberglass panels, fiberglass pipes, and fiberglass membranes. These materials are fire-resistant, corrosion-resistant, and weather-resistant.
- **Insulation:** Fiberglass is used for thermal and acoustic insulation. It is effective in blocking heat and noise while being lightweight and easy to install.
- **Electronics:** Fiberglass is used in electronic components such as optical fibers, printed circuits, and filters. It is valued for its light transmission properties and impact resistance.

- **Art and Design:** Fiberglass is used in the fabrication of sculptures, furniture, and other decorative objects. It is utilized for its properties of strength and lightweight construction.

Bibliographical References

Bibliographical References

1. Pauling, L. (1988). "General Chemistry". Dover Publications.

2. Bardez, E. (2009). "Exercices et problèmes de chimie générale: avec rappels de cours et méthodes". Dunod.

3. Weller, M., Overton, T., Rourke, J., & Armstrong, F. (2014). "Inorganic Chemistry" (6th Edition). OUP Oxford.

4. Housecroft, C. E., & Constable, E. C. (2010). "Chimie inorganique". De Boeck Supérieur.

5. Germain, G., Chareton, A., Trémillon, B., & Damon, M. (2001). "Chimie générale". Masson.

6. Tro, N. J. (2013). "Chemistry: A Molecular Approach" (1st Edition). Pearson.

7. Histoire du verre – Association Française des Souffleurs de Verre Scientifiques." Les Souffleurs de la Science, https://les-souffleurs-de-la-science.fr/histoire-du-verre/.

8. Shelby, J.E. (2005). "Introduction to Glass Science and Technology" Royaume-Uni: Royal Society of Chemistry, 291

9. Henrivaux, J., Riche, M.A. (1897). "Le Verre et le Cristal" France: P. VicqDunod et cie, 782

10. Fanderlik, I., (2013). "Silica Glass and Its Application". Pays-Bas: Elsevier Science, 305

11. Goldschmidt, V.M., (1926). "Die Gesetze der Krystallochemie" Naturwissenschaften, 14(21), 477-485.

12. Zachariasen, W.H., (1932). "The Atomic Arrangement in Glass" Journal of the American Chemical Society. 1932, 54(10), 3841-3851.

13. Smekal, A., (1929). "Zur Theorie der Glasbildung" Zeitschrift für Anorganische und Allgemeine Chemie, 178(1), 309-318.

14. Stanworth, J.E., (1950)."Physical Properties of Glass" Oxford: Clarendon Press, 1950.

15. Sun, K.H., (1947). "Fundamental Condition of Glass Formation" Journal of the American Ceramic Society, 30(9), 277-281.

16. Rawson, H., (1967). "Inorganic Glass-Forming Systems" . London: Academic Press.

17. Wolfram, H., Beall, G.H., (2019). "Glass-Ceramic Technology" . Royaume-Uni: Wiley, 448

18. Ediger, M.D., Angell, C.A., Nagel, S.R. (1996). "Supercooled Liquids and Glasses". The Journal of Physical Chemistry, 100(31), 13200-13212.

19. Götze, W. (1999). "Recent Tests of the Mode-Coupling Theory of the Glass Transition".

Journal of Physics: Condensed Matter, 11(10A), A1-A45.

20. Techniques de l'Ingénieur, (2023). "Verres - Propriétés et applications": Dossier complet":https://www.techniques-ingenieur.fr/base-documentaire/electronique photonique - th13/materiaux-pour-l-optique-et-les-lasers-42450210/verres-af3601/

21. Le Bourhis, E., (2014). "Glass Mechanics and Technology". (2nd Edition). Wiley, 2014. ISBN: 978-3-527-33705-7.416

22. Long, B., (1933). "Les propriétés physiques et la fusion du verre". France: Dunod,.489

23. Scholze, Horst. , (1980). "Le Verre: nature, structure et propriétés". Allemagne: Institut du verre, 364

24. PRIMEVerre, (2023), "Propriétés du verre": http://www.primeverre.com/tout-sur-le-verre/proprietes/

25. Peligot, E., (1877). "Le verre: son histoire, sa fabrication". France: J. Claye et Ce., 495

26. Paprec, (2023). "La fabrication du verre" :https://www.paprec.com/fr/solutions/les-matieres-que-nous-valorisons/verre/la-fabrication-du-verre/

27. Paprec, (2023). "La classification des différents types de verre" : https://www.paprec.com/fr/solutions/les-matieres-que-nous-valorisons/verre/la-classification-des-differents-types-de-verre/ (25/01/2024)

28. Barton, J. and Guillemet, C., (2005). "Les étapes de l'élaboration du verre". Le verre: Science et technologie, Les Ulis: EDP Sciences, 194-197.

29. Infovitrail, "Le verre - infovitrail.com." : https://infovitrail.com/contenu.php/fr/u/le-verre--.(20/01/2024)

30. Pajean, G., (2007). Fabrication du verre creux. Une petite encyclopédie du verre. Verre, vol. 13, n°6, pp. 8-13.

31. Techniques de l'Ingénieur, (2023). "Élaboration du verre": https://www.techniques-ingenieur.fr/base-documentaire/construction-et-travaux-publics- th3 /techniques-du-batiment-les-fenetres-et-les-portes-43818210/verre-le-materiau-tba1960/elaboration-du-verre-tba1960 niv10002.html

32. Varshneya, A.K. (2006). "Fundamentals of Inorganic Glasses". Society of Glass Technology.

33. Frederick, T., Wallenberger, P., Bingham, A., (2010). "Fiberglass and Glass Technology: Energy-Friendly Compositions and Applications" Allemagne: Springer US, 474

34. Kiron, M.I., (2022). "Glass Fiber: Types, Properties, Manufacturing Process and Uses": https://textilelearner.net/glass-fiber-types-properties/

Appendixes

Appendixes

Appendixe 1: Strengths and Weaknesses of Each Theory

Theory	Strengths	Weaknesses
Volume Free Theory	- Simple and intuitive. - Successfully used to explain a wide range of phenomena related to glass transition. - Works well for temperatures above Tg.	- Attempts to use models to determine the free volume lead to values incompatible with estimates from actual measurements of the VFT. - The volume at the glass transition is not constant for a given substance.
Gibbs-DiMarzio Theory	- This theoretical approach has generated a wide range of quantitative predictions regarding glass formation.	- The theory relies on T_0 to extrapolate the vanishings of SC, while dynamic changes depend on Tg.
Adam-Gibbs Theory	- Plausibility of the assumptions in this theory.	- This model fails in real glass -forming liquids at temperatures Tg > 20-30 K.

(Note: The translation assumes "VL" refers to "Volume Libre" and "T.V.P" refers to "Transition Vitreuse Point").

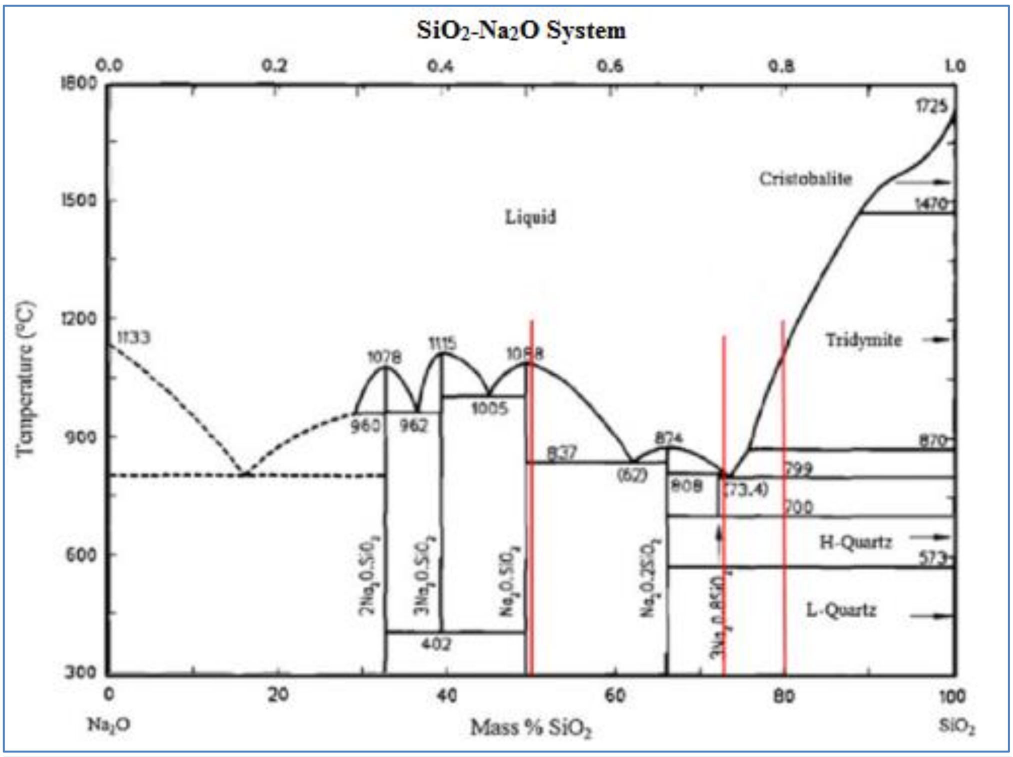
Appendixe 2: Various Properties of Some Industrial Glasses

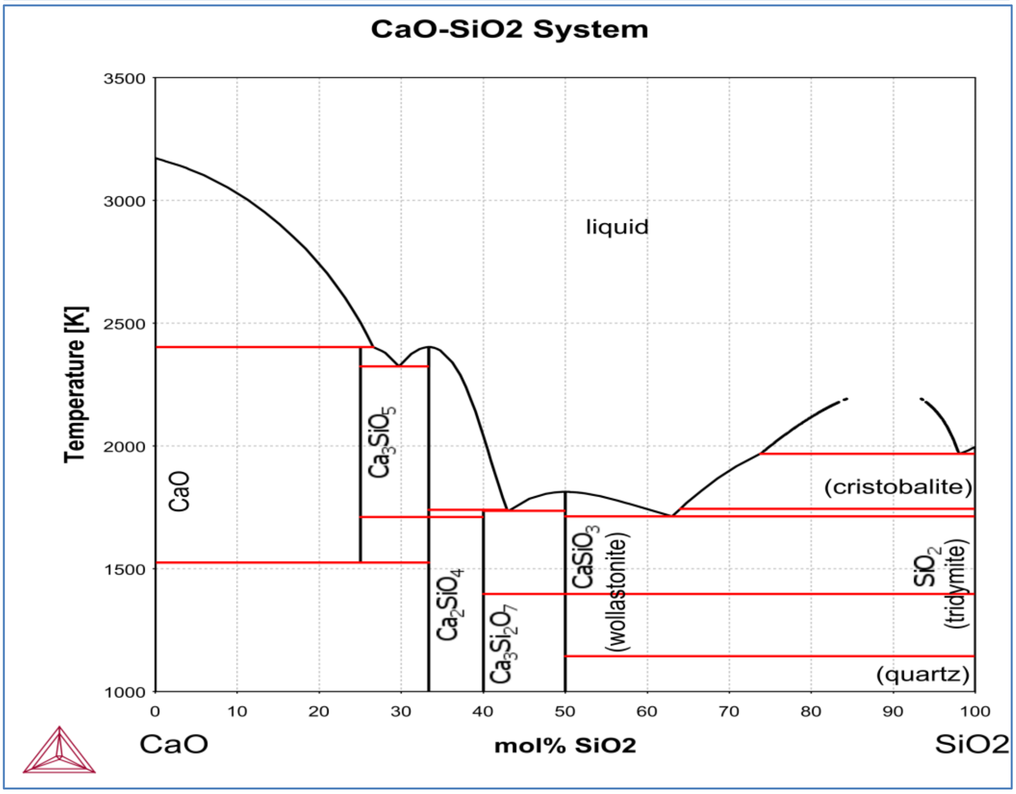
Properties	**Soda-Lime Glass**	**Silica Glass SiO_2**	**Borosilicate Glass B_2O_3**	**Germanate Glass GeO_2**
Optical Properties	Refractive Index: ~1.5	Refractive Index: ~1.5	Refractive Index: ~1.5-1.6	Refractive Index: ~1.7
	Transparency in the visible			
Mechanical Properties	Tensile Strength: ~30-70 MPa	Tensile Strength: ~50-100 MPa	Tensile Strength: ~60-120 MPa	Tensile Strength: ~60-150 MPa
	Young's Modulus: ~70-90 GPa	Young's Modulus: ~70-90 GPa	Young's Modulus: ~70-100 GPa	Young's Modulus: ~80-120 GPa
Thermal Properties	Thermal Conductivity: ~0.7-1.5 W/m•K	Thermal Conductivity: ~1.2-1.4 W/m•K	Thermal Conductivity: ~1-1.2 W/m•K	Thermal Conductivity: ~1-2 W/m•K
	Thermal Expansion Coefficient: ~8-9 x 10^{-6}/°C	Thermal Expansion Coefficient: ~4-5 x 10^-6/°C	Thermal Expansion Coefficient: ~3-5 x 10^{-6}/°C	Thermal Expansion Coefficient: ~6-9 x 10^{-6}/°C
Electrical Properties	Dielectric Constant: ~7-10	Dielectric Constant: ~3-4.5	Dielectric Constant: ~3-6	Dielectric Constant: ~8-12
Phonetic Properties	Low Acoustic Insulation	Medium Acoustic Insulation	Low Acoustic Insulation	Low Acoustic Insulation
Chemical Properties Properties	High Chemical Resistance			
	Soda-Lime Glass			

(Note:

- It should be noted that actual values may vary depending on the exact composition and manufacturing process of each type of industrial glass.
- "W/m•K" stands for watts per meter-kelvin, "MPa" stands for megapascals, "GPa" stands for gigapascals, and "°C" stands for degrees Celsius.)

Appendixe 3: Binary phase diagrams of SiO_2-Na_2O and CaO-SiO_2





Appendixe 4: Composition of Fiber glass

Type of Fiber glass		**Composition (%)**
Insulation Fibers	Glass Wool	SiO_2 : 50-60%, Al_2O_3 : 10-20%, CaO : 10-20%
Reinforcement Fibers	A-Type Glass	SiO_2 : 70 -72%, Al_2O_3 : 0,5- 2,5%, CaO : 5-10%, MgO : 1- 4%, Na_2O : 12- 15%, B_2O_3 : 0- 0,5%
	C-Type Glass	SiO_2 : 60-65%, Al_2O_3 : 10-15%, CaO : 10-15%, MgO : 5-10%, Na_2O : 3-5%, B_2O_3 : 2-5%
	E-Type Glass	SiO_2 : 53-55%, Al_2O_3 : 15-25%, CaO : 10-20%, MgO : 5-10%, Na_2O : 3-5%, B_2O_3 : 2-5%
	R-Type Glass	SiO_2 : 58 - 60%, Al_2O_3 : 23,5 -25,5%, CaO et MgO : 14- 17%.
	S-Type Glass	SiO_2 : 64- 65%, Al_2O_3 : 24-25%, MgO : 10- 11%, Na_2O et K_2O: 0- 1%
	AR-Type Glass	SiO_2 : 61%, Al_2O_3 : 10%, CaO : 10%, MgO : 5%, Na_2O : 3%, B_2O_3 : 2%