IC 221 Industrial Inorganic Chemistry

Introduction to Inorganic Industries and Raw Materials

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Contents (3 hours)

1. Introduction to inorganic industries

- Industrial chemistry and chemical engineering
- Inorganic industries

2. Introduction to industrial inorganic Chemistry

- Application of Inorganic chemistry principle to the industries e.g. examples of metal and ceramic industries.

3. Inorganic Raw Materials

- Examples of raw materials in inorganic industries

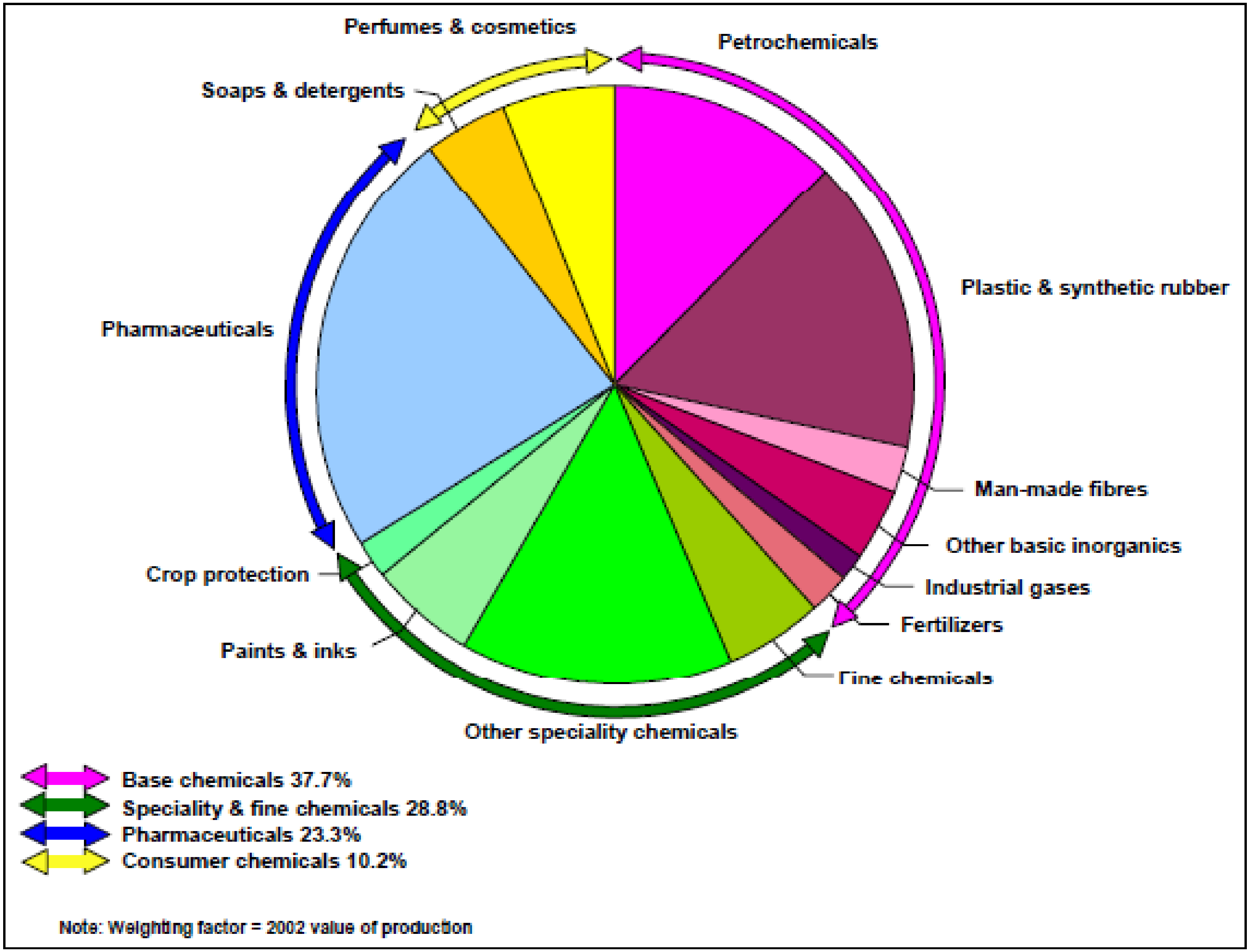
1.1 Industrial Chemistry / Chemical Engineering / Chemical Engineer

Chemical engineering is an intriguing, challenging, and flexible profession. Chemical engineering graduates work in a wide variety of industries, as indicated in Table A.

TABLE A **Initial Job Placement of Chemical Engineering Graduates in 2000–2001 in Percent (*Source:* AIChE, NY, NY).**

Industry	BS	MS	PhD
Chemical	23.3	1.8	21.3
Fuels	15.7	7.6	10.6
Electronics	15.9	27.4	29.5
Food/Consumer Products	10.6	6.6	4.3
Materials	3.1	2.5	3.4
Biotechnology & Related Industries (Pharmaceuticals)	9.3	14.7	15.9
Pulp & Paper	2.1	1.5	1.5
Engineering Services			
Design & Construction	5.6	6.6	1.9
Research & Testing	1.8	4.1	3.4
Environmental Engineering	2.4	2.5	1.5
Business Services	5.8	2.0	2.9
Other Industries	3.9	2.5	3.9

Chemical Industries



The field of industrial chemistry is broadly subdivided into inorganic and organic chemistry. Inorganic chemistry deals with all elements of the periodic table; organic chemistry is restricted to the element carbon in its association with a limited number of other elements.

It should be noted, that despite the limited number of elements involved in organic chemistry, there were about 16 million known organic compounds as opposed to only 1 – 2 million inorganic compounds at the end of 1996.

The natural sources for the industrial manufacture of inorganic products are numerous, ranging from air and water via sulphur, phosphates, mineral salts, metal oxides, and various inorganic ores. As opposed to the diversified inorganic raw materials base, the manufacturing of inorganic chemicals usually requires a few steps of operations, whereas productions of organic chemicals are often multi-step operations [71, CITEPA, 1997], [13, EIPPCB, 2000].

Industrial chemistry : ***inorganic*** (all elements) and ***organic chemistry*** (carbon + a few others)

Inorganic products, e.g. sulphur, phosphates, mineral salts, metal oxides and inorganic ores.

1.2 Inorganic Industries

1.2.1 Types or inorganic chemical industries:

1) **Large Volume Inorganic Chemicals – Solids and Others (LVIC-S)**
2) Chlor-alkali (CAK),
3) Large Volume Inorganic Chemicals – Ammonia, Acids and Fertilisers (LVIC-AAF)
4) Specialty Inorganic Chemicals (SIC) industries

1.2.2 Other inorganic industries e.g. Metallic industries, Metal coating or plating, Ceramics and Glasses, Cement, Enamel, Electronics, etc.

Large Volume Inorganic Chemicals – Solids and Others (LVIC-S) involves

- Basic inorganic chemical e.g. ***salts*** (ammonium chloride, potassium chlorate, potassium carbonate, sodium carbonate, perborate, silver nitrate) or ***non-metals, metal oxides*** or other ***inorganic compounds*** (calcium carbide, silicon, silicon carbide).
- food and feed phosphates, e.g. inorganic phosphates, detergent phosphates
- iron oxide and chorosulphate
- sodium hydrogen sulphite and sodium thiosulphate
- potassium chlorate
- sodium sulphide
- And a lot more …..

1.3 Examples of processes used in inorganic chemical industries

- Soda ash and Sodium bicarbonate

The production of sodium carbonate in the EU-25 is based on the Solvay soda ash ammonia process [33, CEFIC-ESAPA, 2004] in which limestone, salt brine, ammonia and coke are the main raw materials (refer also to Figure 1.15).

Refined sodium bicarbonate is manufactured on the basis of a solution of sodium carbonate (or calcined soda) from the soda ash plant. The refined sodium bicarbonate plant is fully integrated with the soda ash plant operating by the Solvay process [33, CEFIC-ESAPA, 2004].

- Titanium Oxide

Two processes, the older sulphate process (extraction with sulphuric acid), or the newer chloride process (extraction with chlorine), manufacture TiO_2 [13, EIPPCB, 2000]. The starting materials for TiO_2 production on a worldwide basis are ilmenite and titaniferous slag in the case of the sulphate process, and leucoxene, rutile, synthetic rutile, ilmenite, or titaniferous slag for the chloride process [13, EIPPCB, 2000].

-Synthetic amorphous silica

The basic raw material for the production of synthetic silicas is waterglass or silanes. There are two main routes to these products: thermal and wet. The thermal route leads to pyrogenic silica and the wet route to precipitated silica and silica gel [13, EIPPCB, 2000].

1.4 Examples of Unit operation used

Unit process	LVIC-S industry product (or associated activity)
Combustion	Coke burning – thermal decomposition of limestone in the soda ash Solvay process (fuel burning, steam and power generation – refer also to the BREF on LCP)
Oxidation	Titanium dioxide – chloride route, zinc oxide, lead oxide, sodium perborate/percarbonate, synthetic amorphous silica (thermal route). For phosphoric acid production from elemental phosphorus – refer to the BREF on LVIC-AAF.
Neutralisation	Sodium salts, sodium tripolyphosphate (waste water treatment in LVIC-S industry complexes)
Silicate formation	Sodium silicate, precipitated silica
Electrolysis	Sodium chlorate. For caustic Soda – refer to the BREF on Chlor-Alkali
Double decomposition	Soda ash; sodium, potassium and magnesium salts (water softening in LVIC-S industry complexes)
Calcination	Soda ash, titanium dioxide (sulphate process route), sodium tripolyphosphate
Reduction	Calcium carbide, silicon carbide, sodium salts, titanium dioxide – sulphate route, zinc oxide
Halogenation	Titanium dioxide – chloride route, aluminium chloride
Hydration and Hydrolysis	Magnesium oxide, slaked lime, titanium dioxide – sulphate route
Pyrolysis or Cracking	Carbon black

1.4 Examples of Unit operation used (cont.)

Fluid flow	Heat transfer	Evaporation	Gas absorption
Adsorption	Distillation	Drying	Mixing
Classification	Sedimentation	Filtration	Screening
Crystallisation	Centrifugation	Size reduction	Materials handling.

These four units are commonly used in inorganic chemical industries.

1.4.1 Sedimentation

Many inorganic chemical products are obtained as precipitates, and these have to be settled-out before further treatment. It would be uneconomic to try to filter the whole reaction mass because of the very large volume of liquid that would have to pass through the filter, and so the mixture is concentrated with respect to its solid content. This is done by allowing the solid particles to fall to the bottom of a holding tank by gravity. The operation is known as sedimentation. The size of the tank is determined by the size and concentration of the solid particles in suspension, which in turn fix the length of time required for them to settle in a given depth. The particles, which settle to the bottom, form a sludge or slurry containing perhaps 20 to 50 % of solids. This is easily pumped out of the bottom of the tank and goes to a filter system as concentrated slurry. Sedimentation is applied, for instance, in the manufacturing of calcium chloride, precipitated calcium carbonate, sodium bicarbonate, and sodium perborate.

1.4.2 Filtration

In filtration the wet material, usually containing more than 50 % water is fed to a membrane in which the holes or pores are small enough for the water to pass through but too small for the solid particles to pass.

Filters vary enormously in type, and range from simple mesh belts moving in a continuous ribbon over rollers onto which the slurry is fed at one end and the drained material is scraped off the top of the belt at the other, two highly sophisticated automated machines operating at fairly high pressures and sequencing a series of complex operations to simulate continuous production (e.g. sophisticated filters in TiO_2 production).

Once a layer of material starts to build up at the core, any liquid that is being removed has to pass through this layer. To do this, a driving force must be applied. The driving force can simply be gravity but in general, a pressure has to be applied by a pump. Usually this pressure is applied through the slurry, but an important class of filters uses vacuum on the clear liquor side (e.g. sodium bicarbonate filters in the soda ash process).

The main factors are the viscosity of the fluid, the depth of filter cake, and its porosity. It is ideal to keep the depth or thickness small, the porosity high and the viscosity low. In practice there is a need to compromise between a small depth, which means frequent breaks in operation to remove the cake and a greater depth with greater resistance and hence a longer filtration time. The porosity is largely a function of the particle sizes of the solid. A solid with many small particles is going to have a much poorer porosity than a coarse granular material. The conditions of precipitation ought to be controlled carefully to try to obtain the best particle size for filtration. Finally, the viscosity is a factor that can be reduced by taking advantage of the fact that liquid viscosities are greatly reduced as the temperature is increased.

Filtration is applied across the LVIC-S industry, for instance in the manufacturing of aluminium sulphate, soda ash, zinc sulphate, zinc chloride, and silica gel.

1.4.3 Drying

This is an important operation; especially in the inorganic chemical industry where many of the products are solids, which have to be dried before they can be stored, packed, or distributed.

Drying is generally understood to mean the removal of unwanted water from a solid. Many LVIC-S processes involve precipitation and subsequent filtration of a solid product. This will leave it with a water content of perhaps 10 to 30 % most of which will be necessary to remove. This is accomplished by heating the wet material in a relatively dry gas stream (usually air).

Drying is usually thought of as a two-stage process. In the first, the solid is assumed to be thoroughly wet on the surface and the drying is simply evaporation of water into a stream of gas. As the drying proceeds, the surface of the solid develops dry areas since the water held in the interstices of the solid cannot diffuse to the surface at as fast a rate as it is being removed by the stream of warm dry gas. During the first stage, the drying takes place at a constant rate, which depends upon the temperature and gas velocity. When the second stage is reached, the drying rate decreases steadily with time. Eventually a stage is reached where no further drying occurs (an 'equilibrium moisture content' is reached).

Many different types of industrial dryers are applied in the LVIC-S industry, such as spray dryers, or horizontal rotating drum dryers. Continuous dryers are usually large tubular rotating drums set at a slight angle to the horizontal. The wet material enters at the top and the hot gases at the bottom, thus achieving countercurrent flow. The slow rotation of the drum causes the material to shower down through the hot gases during its passage through the machine, thus exposing a large surface area to the drying action.

Drying is applied for instance in the manufacturing of aluminium fluoride, sodium bicarbonate, sodium tripolyphosphate, sodium perborate, and several other LVIC-S industry products.

1.4.4 size reduction

Most reactions, whether chemical or physical, occur on surfaces and rates are nearly always expressed in relation to surface areas. Thus, when solids are processed, the first step is usually to disintegrate, crush or grind them to a powder so that the surface area per unit volume is very much increased. This then accelerates the rate at which the desired reaction will take place, be it a chemical reaction such as oxidation or a physical operation such as dissolution. To make a powder from a solid by mechanical means requires rather large amounts of energy and this energy is proportional to the amount of new surface that is produced.

Crushing is generally used to signify the reduction of material from very large pieces, such as those originating from large scale mining or quarrying operations, to fairly coarse material perhaps 5 to 10 cm in size (e.g. lumps of limestone used in the soda ash process). Grinding generally implies taking a feed of an already crushed material and producing a powder, which may vary from particles as small as a few microns to ones as large as 50 mm. The machines for crushing tend to be very large pieces of heavy engineering equipment, whilst those used for fine grinding often are pieces of precision engineering equipment. Dry powders are characterised by their particle size, or more properly by the particle size distribution since no powder is made up of particles of one uniform size. Size reduction is applied for instance in the soda ash industry (limestone crushing), the titanium dioxide industry (ilmenite grinding, titanium dioxide pigment micronising), as well as in crushing sodium tripolyphosphate and sodium silicate products.

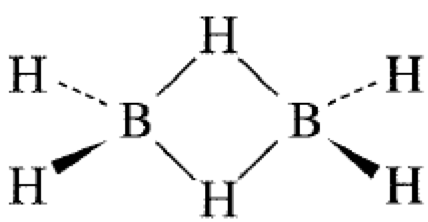
2.1 What's inorganic chemistry?

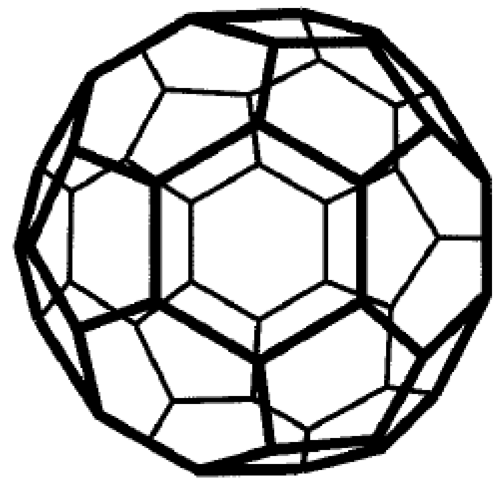
→If organic chemistry is a chemistry of "hydrocarbon"

→"Inorganic Chemistry" is then a chemistry of everything else.

→ Including organometallic chemistry, catalysis in organic reaction, bioinorganic, etc.

→Almost limitless field.





2.2 What are in the general inorganic chem.

e.g. 1) Atomic Structure

2) Bond Theory

3) Symmetry and Group Theory

4) Crystalline Solid State

5) Acid Base

6) Oxidation Reduction

7) Coordination Chemistry

8) Organometallic

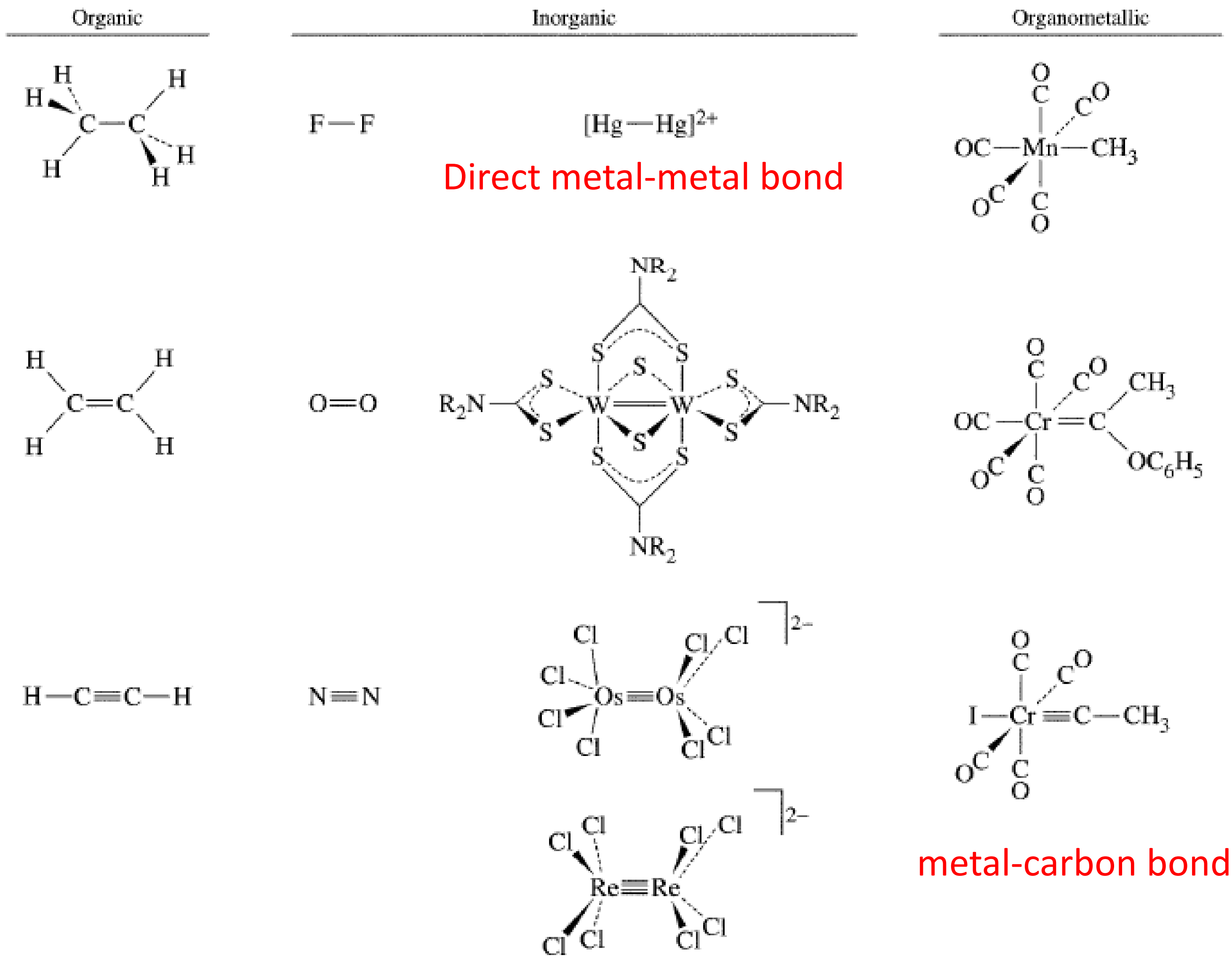
9) etc.

How this relates to the industrial?

2.3 Contrast / Comparison → for example

-Bonding

→ single double and triple covalent bonds are found in both

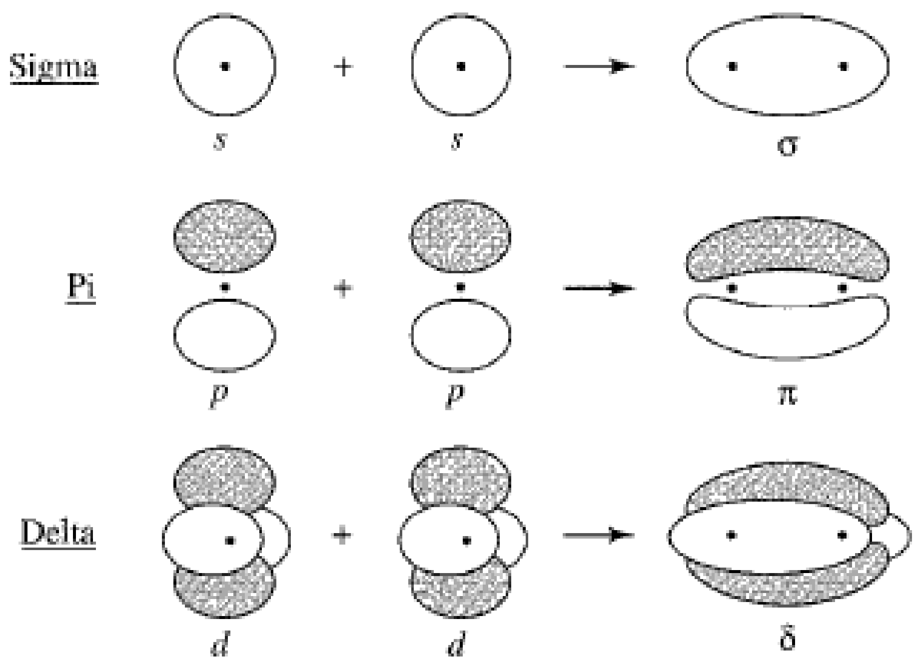


→ Carbon : C has 6 electrons → [He] $2s^2 \cdot 2p^2$

Thus when bonding only s- and p-orbitals are involved.

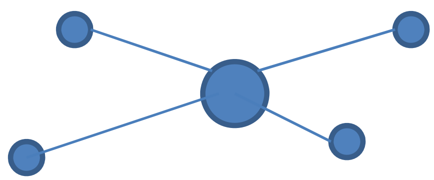
This occurs in only hydrocarbon compounds, but in inorganic or organometallic compounds the delta bond are formed instead due to the involvement of d-orbital.

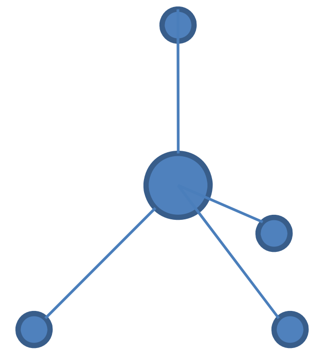
Delta bond is a quadruply bond containing 1 sigma and 2 pi.



-Coordination Number and Geometry

Consider :





-What are coordination number and geometry?

→organic – usually coordination number = 4 (e.g. for C in CH_4).

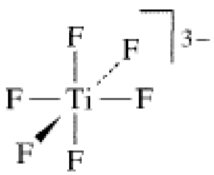
→Inorganic – higher coordination number is frequently found

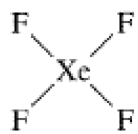
– e.g. $[TiF_6]^{3-}$ where the coordination number = 6.

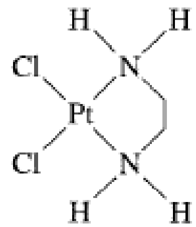
For geometry of compounds,

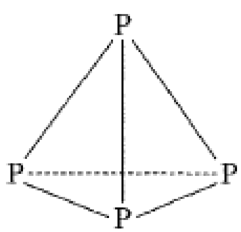
In case of CN=4 → only square planar and tetrahedral are found in organic.

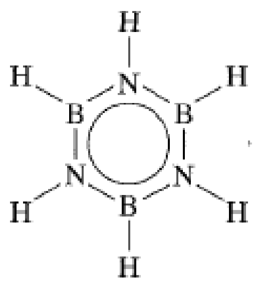
→ other geometries are also found, e.g. octadral (CN=6).

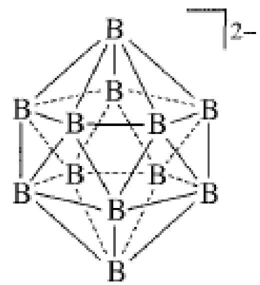






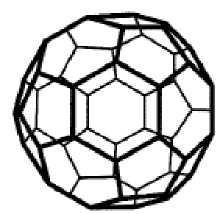




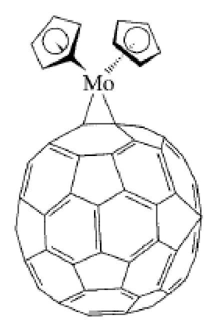


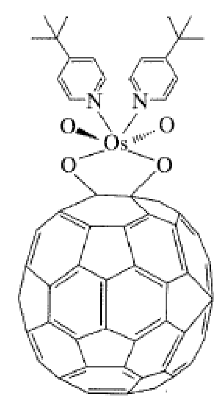
$B_{12}H_{12}^{2-}$ (not shown: one hydrogen on each boron)

→ Carbon is not only involved in organic maerials, it is also found in organometallic compounds. Even molecules that contains only C, e.g. diamond, graphite and C60, are “inorganic”.



C_{60}

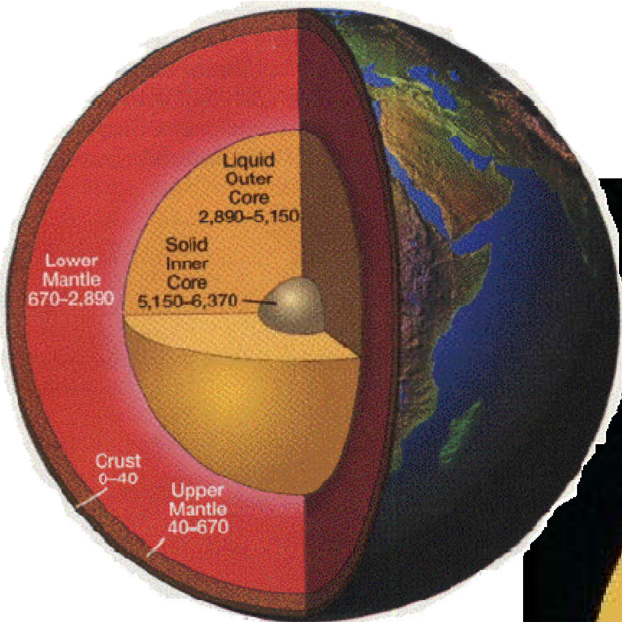


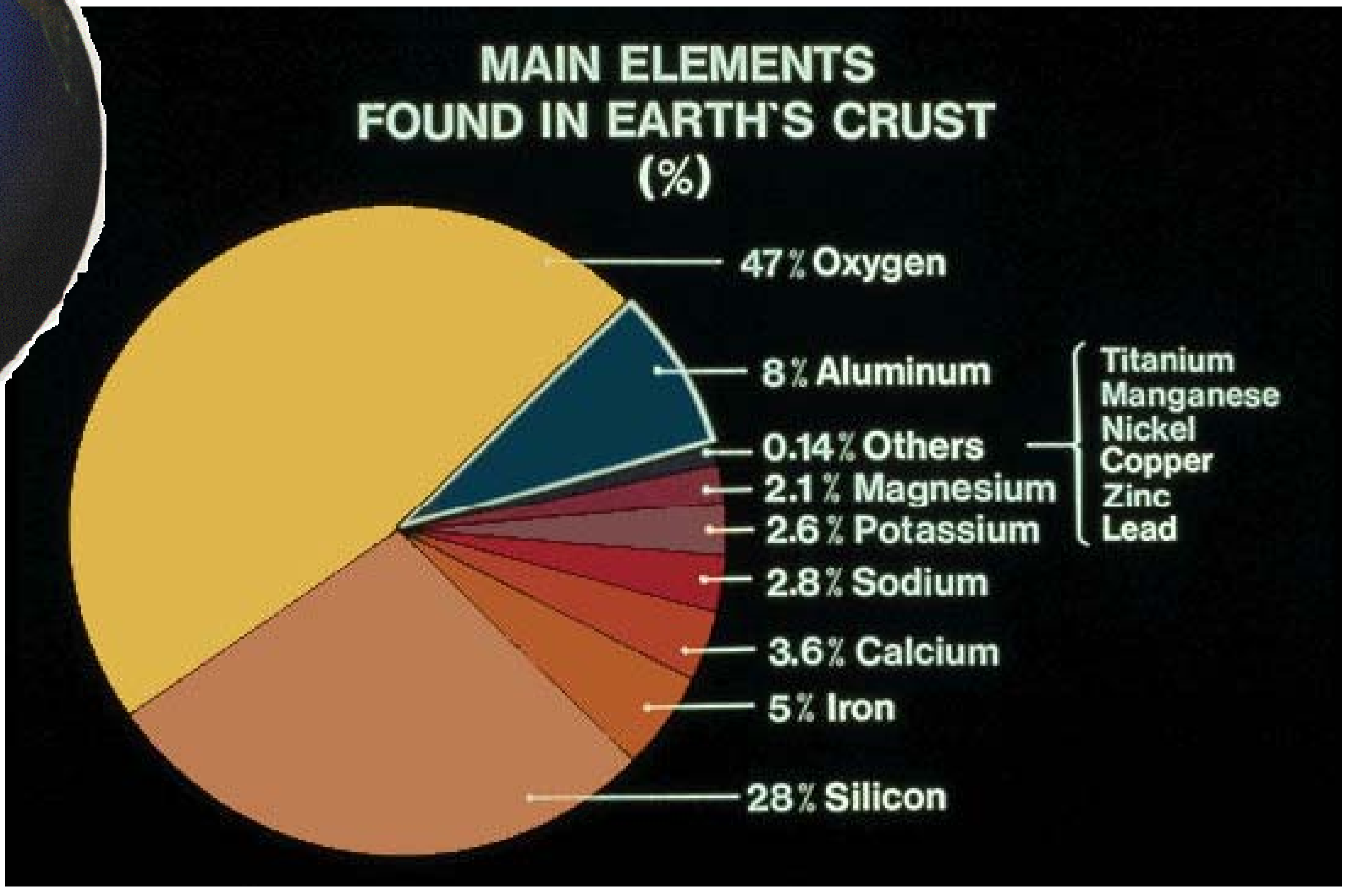


2.4 Distribution of elements on earth

$$4\,KAlSi_3O_8(s) + 4\,CO_2 + 22\,H_2O \longrightarrow 4\,K^+ + 4\,HCO_3^- + Al_4Si_4O_{10}(OH)_8(s) + 8\,H_4SiO_4(aq)$$

aluminosilicate — higher concentration of Al — silicate (leached away)





Sometimes the minerals have been classified by the solubility in 1) water and 2) magma.

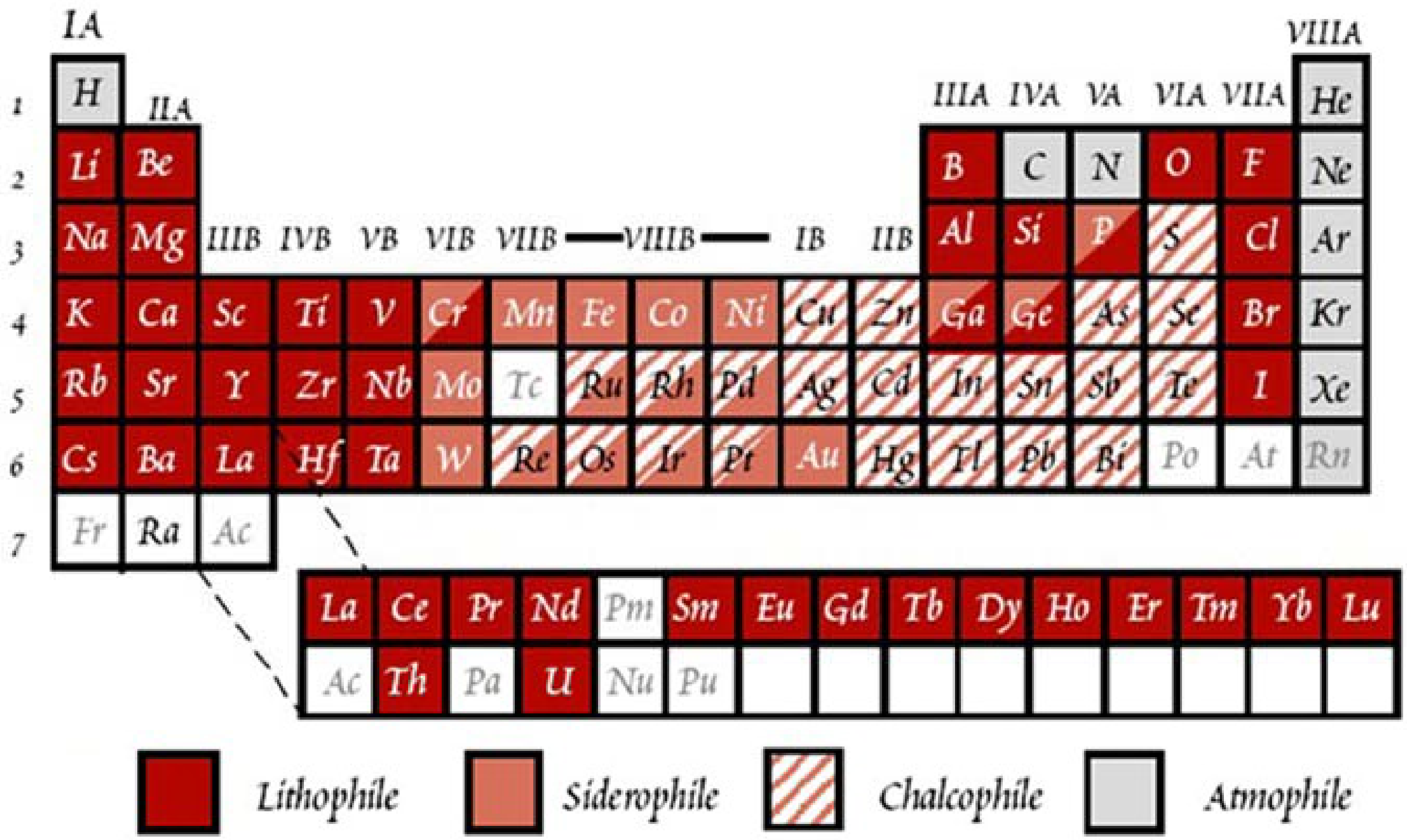
Goldschmidt classified the periodic table as

→ Lithophile (Rock-loving elements)

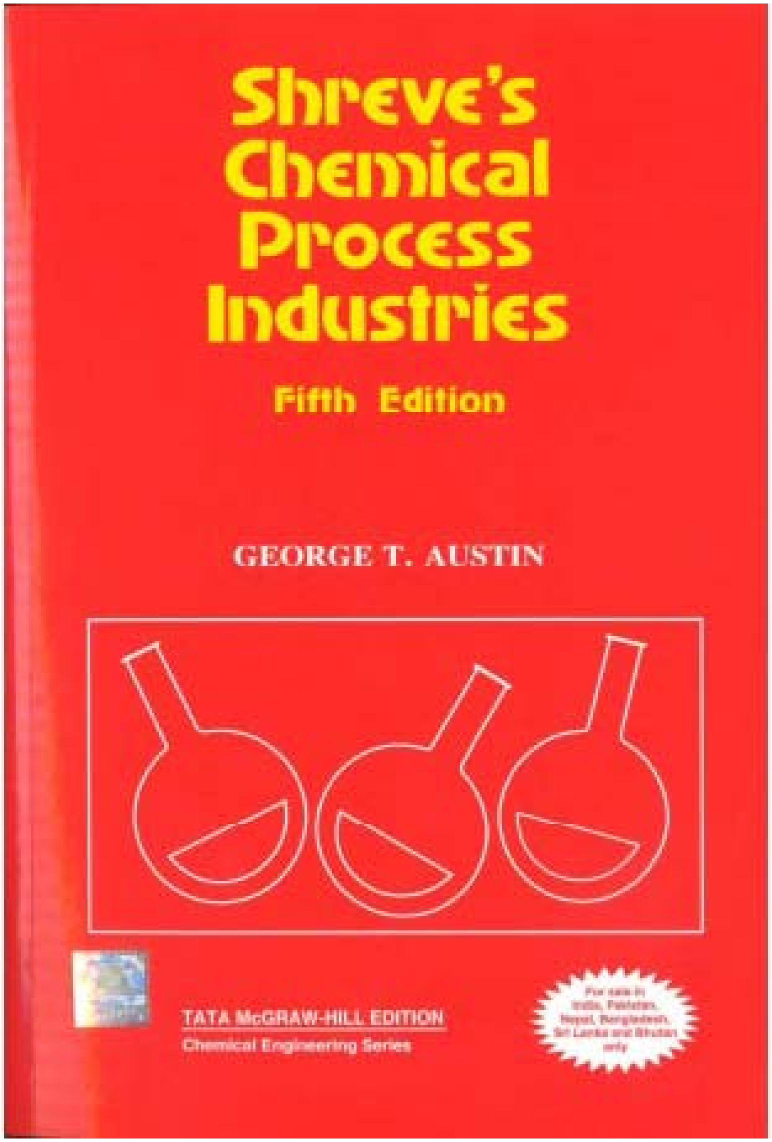
→ Sidrophile (Iron-loving elements)

→ Chalocophile (Sulfur-loving elements)

→ Atmosphile (Gas-loving elements)



2.5 Examples of Processes in an industry.



e.g.

1) Industrial Carbon : *Carbon black, Activated carbon, Graphite and diamonds.*

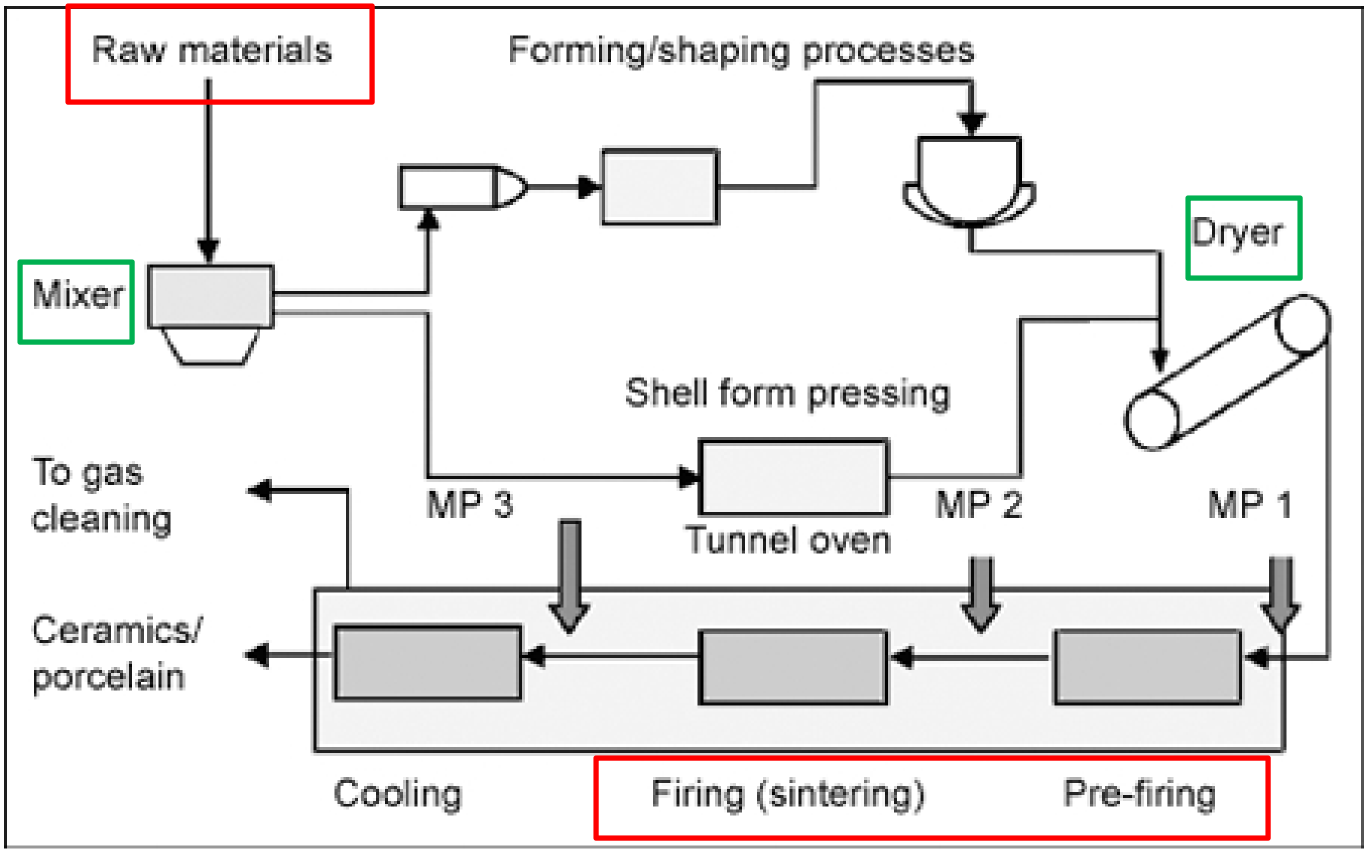
2) Ceramic, Cement and Glass Industry.

3) Salt and sodium compounds : *Sodium Chloride, sodium sulfate, sodium peroxide, etc.*

4) Soda Ash, Caustic Soda, etc.

5) Others

Ceramics Industrials

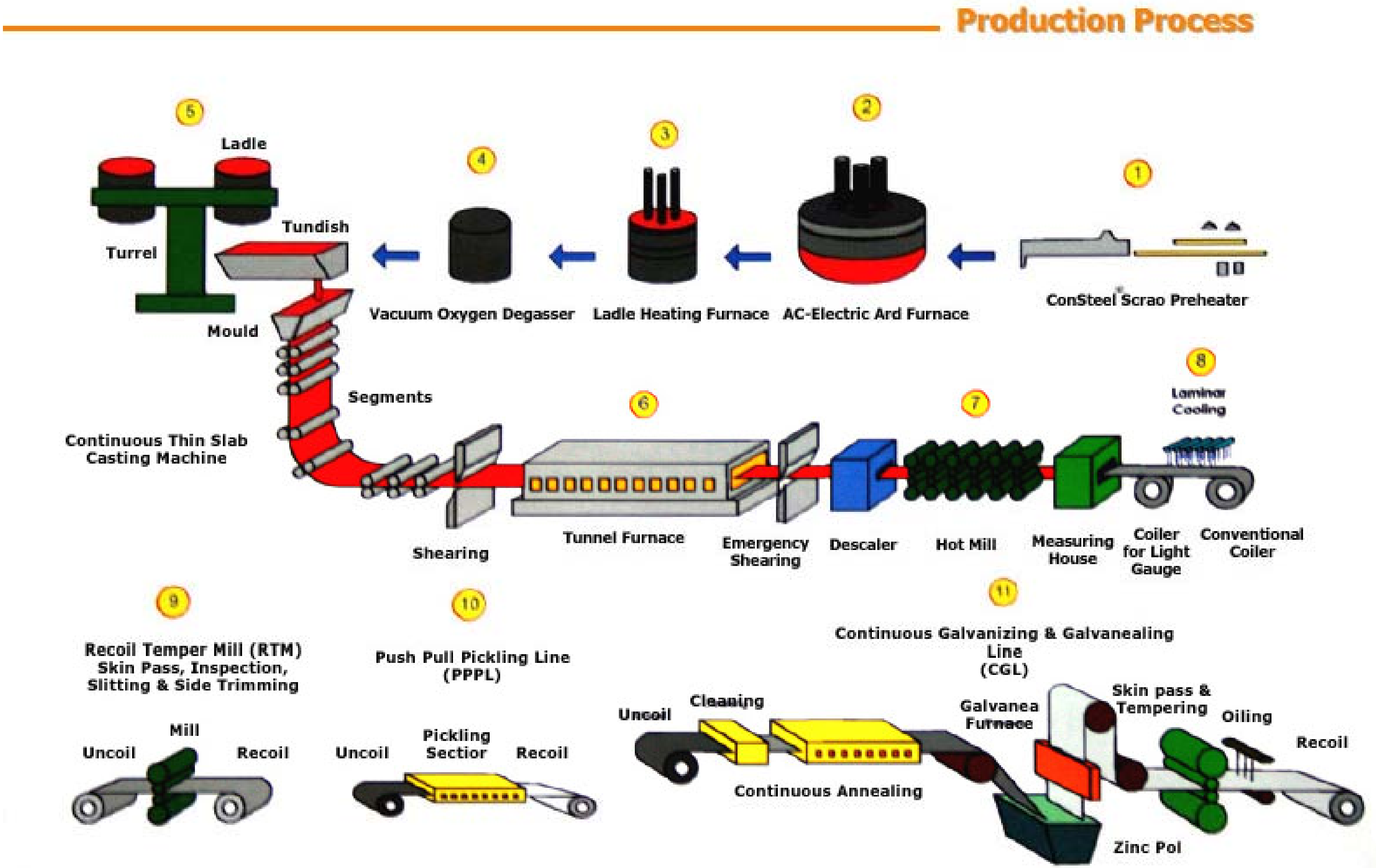


Raw Materials
-e.g. Clay, feldspar and sand → structure of raw materials

Firing Process
- Solid-state reaction, solid-liquid interaction, crystallisation, etc.

Glaze, Pigment, Stain, colour-glass

Iron smelting process



<u>Group Essay</u> (2-3 people) → 3%

Describe the ways "*Inorganic Chemistry*" involved in an "*Industry*".

- explain the process of the selected factory.

- explain how the inorganic chemistry takes part in each unit in the selected factory.

*** about 10 pages ± 2*

*** give the references you used at the end of the essay.*