



# **UNIVERSITY OF ROME "LA SAPIENZA"**

## **NANOTECHNOLOGIES ENGINEERING**

### **PRODUCTION TECHNOLOGIES OF MICRO- AND NANOPARTICLES**

### **LABORATORY OF PRODUCTION TECHNOLOGIES OF MICRO- AND NANOPARTICLES**

PROF. MARCO STOLLER

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# **OUTLOOK**

## **EQUIPMENT, PRODUCTION AND CHARACTERIZATION OF MICROPARTICLES :**

- Fundamentals on the phenomena of nucleation, crystal growth;
- Material, energy and crystal population balances;
- Characterization of crystal shape;
- Measurement methods of crystal size distribution;
- Design and control of industrial crystallizers.

# **OUTLOOK**

## **EQUIPMENT, PRODUCTION AND CHARACTERIZATION OF NANOPARTICLES:**

- The technique of reaction-precipitation for the production of micro/nano particles and sol-gel material.
- Macro, meso and micro mixing;
- The traditional and advanced precipitation apparatuses;
- The spinning disc reactor and the technique for the dispersion of agglomerates;
- Measurement methods of nanoparticles size distributions and suspensions stability;
- Solid, liquid and gas phase methods for the production of nanoparticles.

# **OUTLOOK**

## **MEMBRANES AND APPLICATION IN NANOTECHNOLOGY:**

- Introduction to membrane technologies, in particular nanofiltration;
- membrane equations; membrane types; membrane fouling;
- the production of nanomaterial by membranes;
- functionalization of membranes by nanoparticles.

# **OUTLOOK**

## **SELECTED APPLICATIONS OF NANOPARTICLES PRODUCTS:**

- Micro- and nano particles for wastewater stream treatment, medical use and cosmetic industry.
- Quantum dots

# FINAL EXAM

Generally questions on **3 main topics** discussed during this course, held entirely in **English** and trying to cover all aspects.

*This course is intended to be joined to the exam of:*

*“Laboratory of production technologies of micro- and nanoparticles”, Prof. Marco Stoller.*

*The separated mark from the main course is given by deep discussion of one topic.*

*Concerning the lab work, the given mark participates at 50% to the final mark, given by Prof. A. Tamburrano after the exam of his course of competence.*

# **QUICK OVERVIEW ON LAB WORK**

- **EXPERIMENTS PERFORMED DURING THE COURSE OF “LABORATORY OF PRODUCTION TECHNOLOGIES OF MICRO- AND NANOPARTICLES”**

<b>SESSION ID</b>	<b>TOPIC</b>
1	Crystallization and dissolution of salts
2	Production of ferromagnetic nanoparticles
3	Coating of nanoparticles by nanotitania
4	Photocatalysis of organic dye by UV
5	Production of titania sol-gel

Lab work is organized by groups of 3-4 students each.



# **UNIVERSITY OF ROME “LA SAPIENZA” NANOTECHNOLOGIES ENGINEERING**

## **INTRODUCTION TO PRODUCTION TECHNOLOGIES OF MICRO- AND NANOPARTICLES**

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# DEFINITION OF NANOPARTICLES

- Nanoparticles are defined as solids having at least one dimension around  $10^{-9}$  m. Generally speaking, nanoparticles should have at least one main dimension less than 100 nm.
- For sake of comparison, the atomic dimension of Pb is around 0,35 nm. Therefore, spherical particles of 2 nm contain 10 -1000 atoms.
- Smaller particles have greater values of volume to surface ratio, as reported in the table below where interatomic space was supposed to be 0,2 nm.

Solid particle size and the fraction of atoms located at the particle surface.

Number of atoms in a side	Number of atoms at the surface	Total number of atoms	Number ratio of surface atoms to the total (%)	Examples of particle size and powder
2	8	8	100	
3	26	27	97	
4	56	64	87.5	
5	98	125	78.5	
10	488	1,000	48.8	2 nm
100	58,800	$1 \times 10^6$	5.9	20 nm (colloidal silica)
1,000	$6 \times 10^6$	$1 \times 10^9$	0.6	200 nm (titanium dioxide)
10,000	$6 \times 10^8$	$1 \times 10^{12}$	0.06	2 $\mu$ m (light calcium carbonate)
100,000	$6 \times 10^{10}$	$1 \times 10^{15}$	0.006	20 $\mu$ m (green tea powder, chalk)

1 m =  $1 \times 10^6$   $\mu$ m =  $1 \times 10^9$  nm

## DEFINITION OF MICROPARTICLES

- Microparticles are defined as solids having at least one dimension around  $10^{-6}$  m, but may be classified as such even in the mm range.
- Particles with main dimension between 100nm and 1000nm are classified as sub-micronic. They represent the transition between micro- and nanoworld.
- Very often, micro and sub-micronic particles are grown up solids starting from nanoparticles.

For instance, nanoparticles are grown up solids starting from very small solid structures, such as crystallites.

As a consequence, size is determined by the more or less growth of the solids.

# THE MICRO- AND NANO WORLD

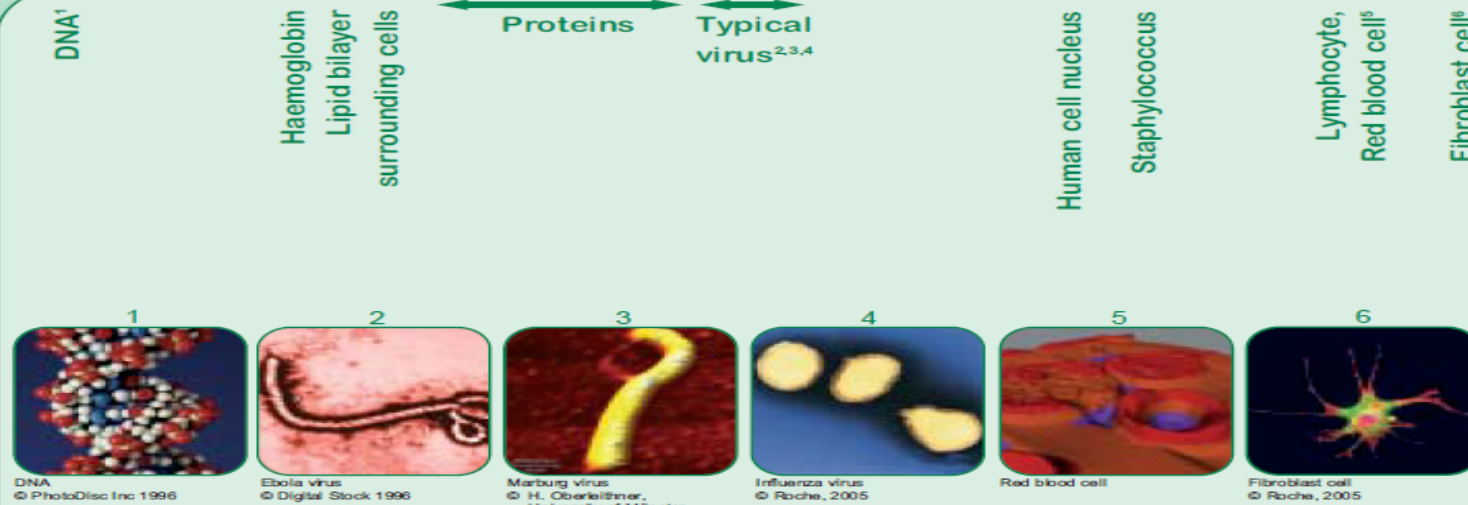
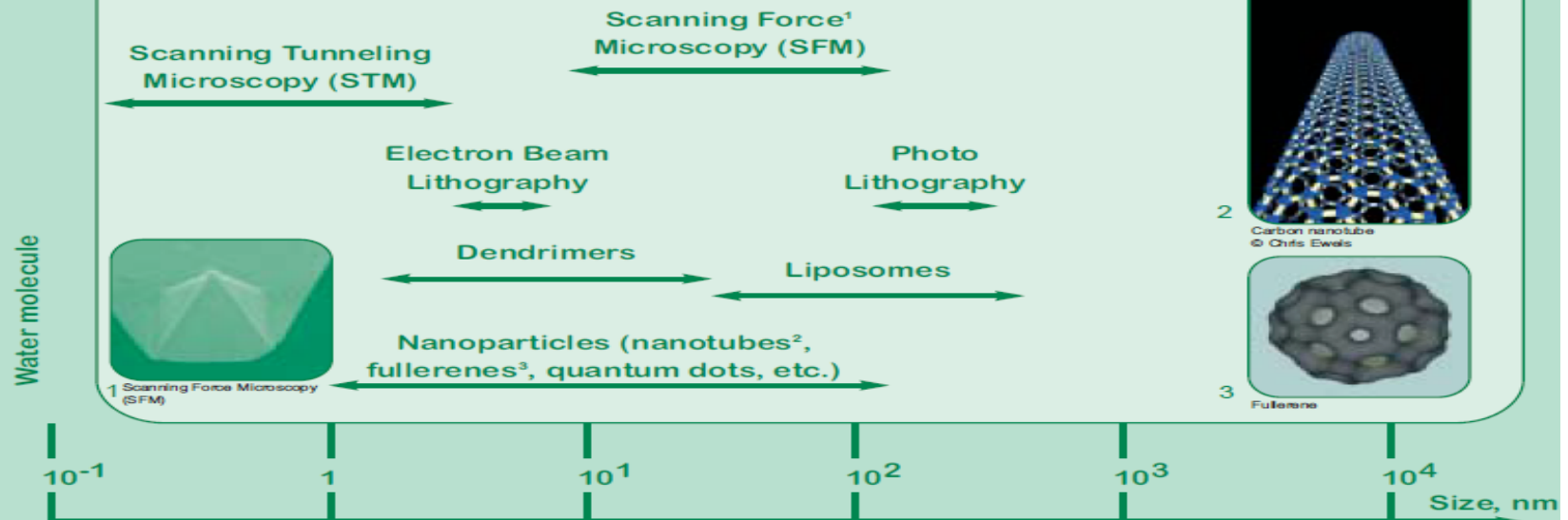
	0.01nm	0.1nm (1Å)	1 nm	10nm	100nm	1μm	10 μm
Wave length			X-ray	Ultraviolet	Visible light	Infrared	
Pore		Micropore	Mesopore		Macropore		
Atomic radius	Hydrogen	Lead					
Metal			Gold, silver colloid		Ferrite	Atomized iron powder	
Inorganic				Magnetic bacteria Colloidal silica TiO <sub>2</sub> (catalyst)	TiO <sub>2</sub> (pigment) FCM nanocomposite oxide particles Colloidal CaCO <sub>3</sub>	Blue powder Fine ground CaCO <sub>3</sub>	
Organic		Fullerene	Nanodiamond	Carbon black Carbon nanotube (diameter)		Graphite	
Bio, pharmaceutical			DNA dia Virus	PMMA nanoparticles PLGA nanospheres Liposome		Toner Starch Red blood cell Biologic cell	
Aerosol					Mitochondria Dry Powder Inhalation Cigarette smoke		

FCM : Flash Creation Method

PLGA : Poly-lactic-glycolic acid (Spherical crystallization method)

PMMA : Polymethylmethacrylate

## Mastering Artificial Nanostructures



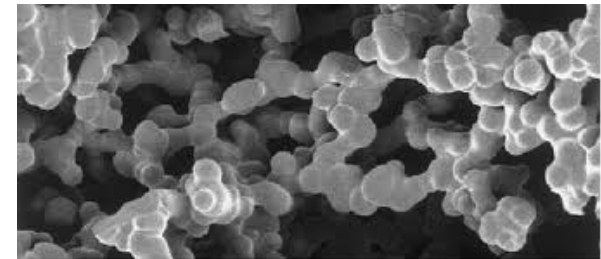
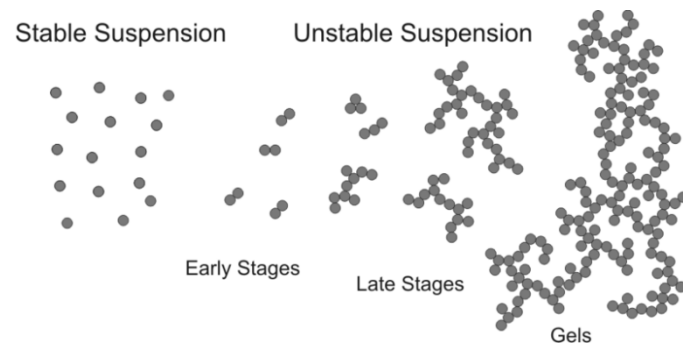
## Biological Nanostructures

# DEFINITION OF AGGREGATION AND AGGLOMERATION

- Smaller particles suffers aggregation and/or agglomeration, which is different than the growth of solids in size. The first one is more stable than the second one:

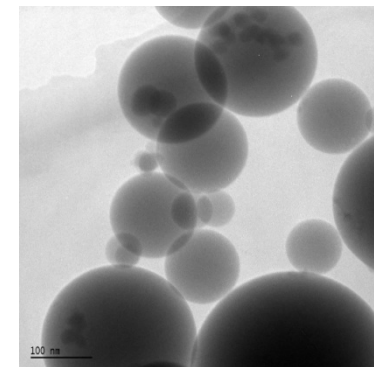
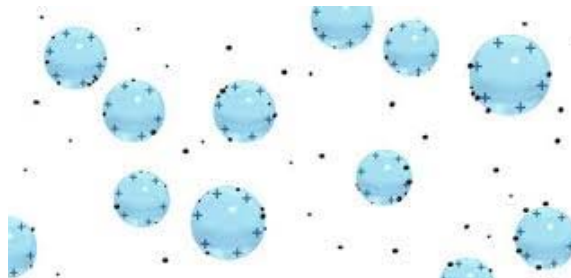
- **AGGREGATION**

Given by physical  
Interconnection  
among particles  
trough bridges.



- **AGGLOMERATION**

Given by electrostatic  
interaction among particles  
in clusters



## DEFINITION OF MATERIALS

- Three main material classes can be identified:
- **Metals**

**This type of materials has characteristics like, high electrical and thermal conductivity, the ability to be deformed or cut into new shapes without breaking, and high mechanical strength. Since metals must be reduced from chemical compounds, they tend to be somewhat more costly than non-metallic materials, and they are often vulnerable to corrosion damage as the metals react with their environment to re-form those compounds. They tend to be shiny and malleable. Metals have these characteristics because they have nonlocalized electrons.**

# DEFINITION OF MATERIALS

- **Ceramics**

Ceramics are generally compounds between metallic and nonmetallic elements and include such compounds as oxides, nitrides, and carbides. Typically they are insulating (not electrical or thermally conductive) and resistant to high temperatures and harsh environments (corrosion resistant). They usually have lower electrical and thermal conductivity, higher stiffness, good resistance to corrosive environments, and lower fracture toughness than metals. With the exception of glasses, ceramics usually cannot be reshaped easily. To shape a ceramic, a mixture of ceramic powders, water, and binder materials is molded into the desired dimensions to form a temporary shape. These temporary shapes called "green bodies" are then dried to remove water and heated to allow the binder materials to oxidize, leaving the ceramic powder particles to bond to each other during the high temperature baking.

# DEFINITION OF MATERIALS

- **Polymers**

Plastics (or polymers) are generally organic compounds based upon carbon and hydrogen. They are very large molecular structures. Usually they are low density and are not stable at high temperatures. They can be readily formed into complex shapes. Their strength, stiffness, and melting temperatures are generally much lower than those of metals and ceramics. Their light weight, low cost, and ease of forming make them the preferred material for many engineering applications.



## DEFINITION OF MATERIALS

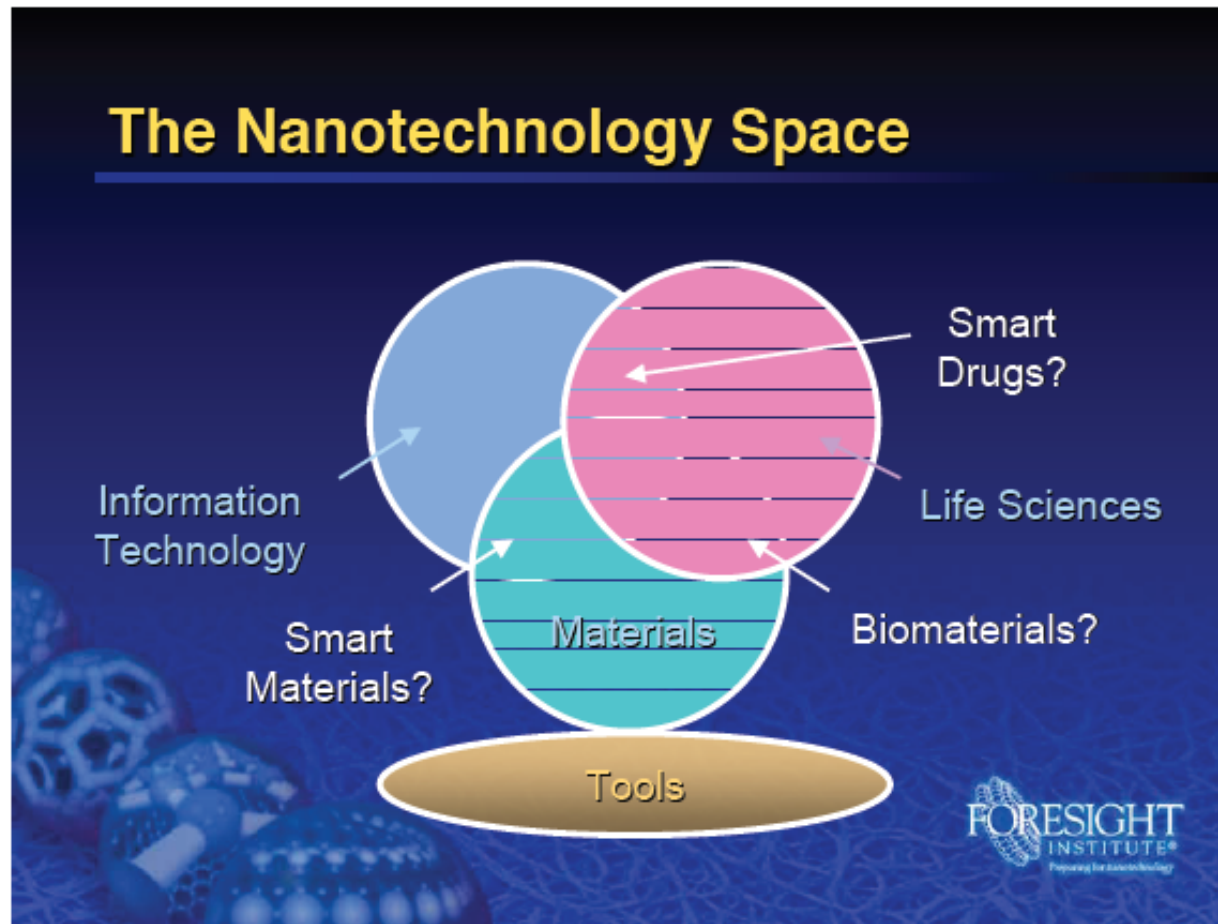
- **Composites**

A combination of two or more materials differing in form or composition. The different parts still have the same features they originally did, that is, they do not dissolve or merge completely into one another, however, their properties are enhanced by each other. Normally, the components can be physically identified and exhibit an interface (boundary) between one another. Fiberglass, a combination of glass and a polymer, is an example. Concrete and plywood are other familiar composites. Many new combinations include ceramic fibers in metal or polymer matrix.

# DEFINITION OF NANOSTRUCTURED MATERIALS

- A nanostructured material is defined as a material being structured by particles having a characteristic length of less than 100 nm.
- This term includes many nanotechnology products such as: nanoparticles, nanocrystalline materials, nanowires, nanotubes, nanofibrilles, nanomembranes (that is materials with nanopores) and so on.
- These materials exhibit different properties if compared to the macro scale.
- Nature uses nanotechnologies from its existence: as an example, fragile chalk that forms the shell of some marine creatures become very hard and transparent.

# APPLICATIONS OF NAOTECHNOLOGIES



# NEAR TERM MARKET IMPACT OF NANOTECHNOLOGIES

## Market Impact - Near Term

- Tools
- Composite materials
- Coatings
- Catalysts



# NANOTECHNOLOGIES: AN INDUSTRIAL OPPOTUNITY

- Nanotechnologies exists since centuries and “secrets were wisely kept secret”:
  - Paintings: Incas vs Egyptians
  - Teflon: DuPont vs the world
- The study of nanotechnology fills the competitive gap by unveiling the secrets: it may reduce the quality gap of products in the market, thus giving the opportunity to weaker companies to grow up, and leading at the end to a benefit for the community.
- Quality, and not quantity, are required: TiO<sub>2</sub> nanoparticles have a market worldwide of only 50 t/y.

# MAIN NANOSTRUCTURED MATERIALS

- The materials are distinguished by their bulk appearance:
  - Powders
  - Dispersions (powder in liquid)
  - Coating (thin films covering surfaces)
- Nanocomposites are a growing technology. Macrosolids are strengthened by the presence of interconnecting and/or overlaying nanoparticles (called whiskers).

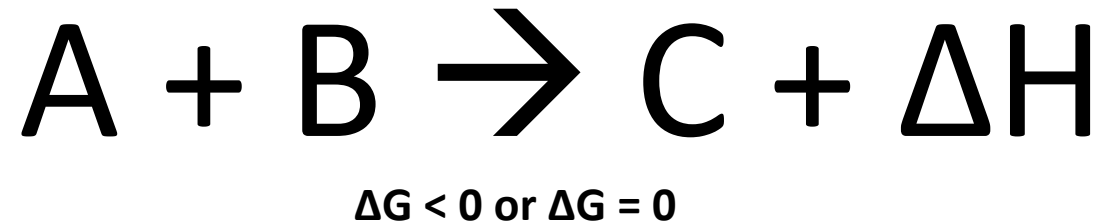
# IMPORTANCE OF THE NANOSCALE

- Nanostructures may interfere (negatively or positively) with many biological entities (cells, bacteria) since of same scale.
- Nanoparticles have a smaller dimension than visible light wavelength, that is 400-700 nm. They may exhibit optical characteristics that differs much from their macrostructure and/or bulk. E.g. turbidity may be absent in some nanoparticles suspensions.
- The ratio between nanoparticles and atoms is low, therefore nanoparticles exhibit stronger border effects with increased chemical potential values. This lead to increased physical and chemical surface activities.

## DEFINITION OF CHEMICAL REACTION

A chemical reaction is a process that leads to the transformation of one set of chemical substances to another. Generally for **chemical synthesis** we have:

TIME (KINETICS: REACTION RATE)



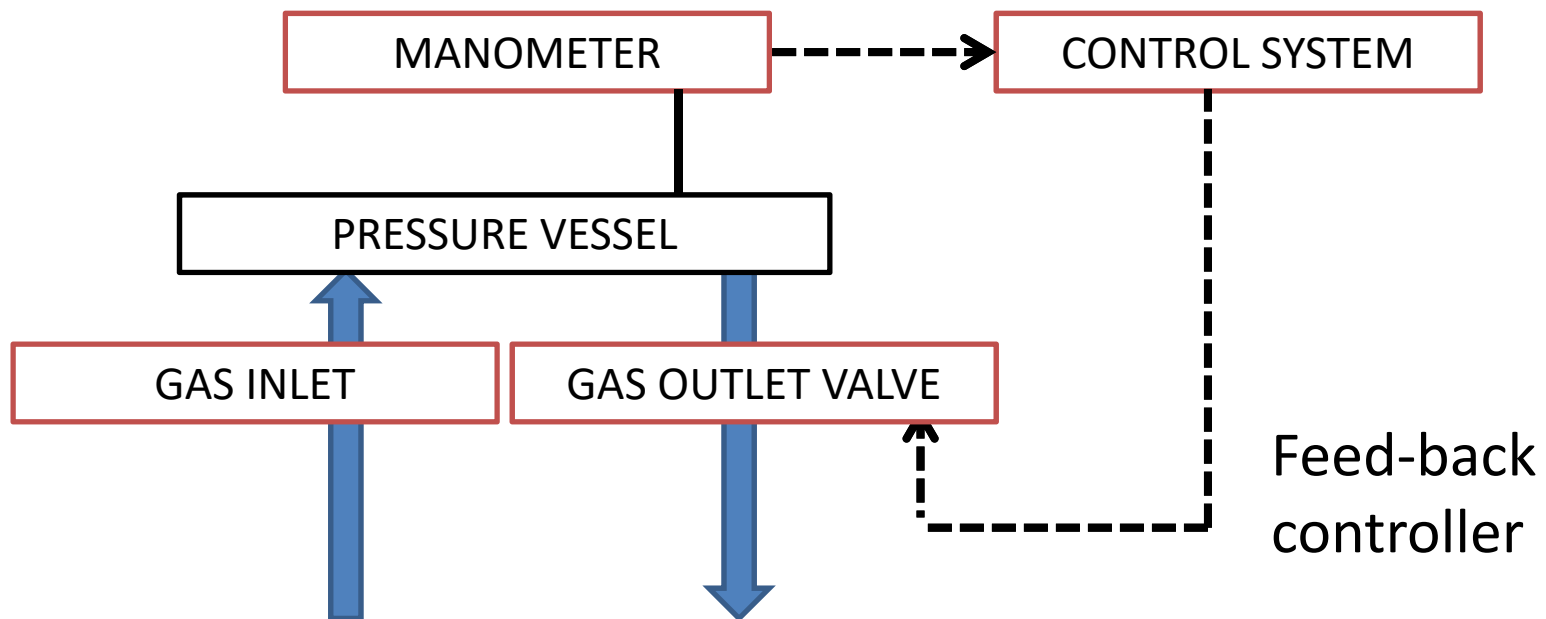
Other basic reactions are dissociation ( $AB \rightarrow A + B + \Delta H$ ) and metathesis ( $AH + B \rightarrow A + BH + \Delta H$ ).

Chemical reactions may not complete when reaching their chemical equilibrium ( $A + B \leftrightarrow C + \Delta H$ ).






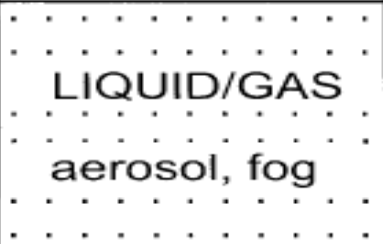

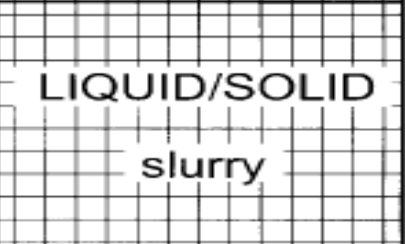
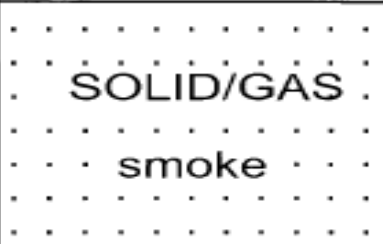

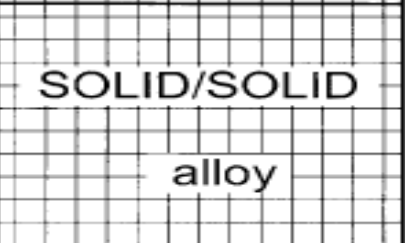
# DEFINITION OF CHEMICAL PROCESS AND CONTROL

A chemical process is the design of subsequent and/or connected equipment capable to fulfill the requirements for product production. Chemical processes need to be controlled on main parameters, measured by a measuring sensor. This gives rise to an error if compared to the set-point value. As a function of the error value, a specific control strategy is applied on the manipulated variables in order to minimize the error.



# DEFINITION OF PHASES

Starting from GAS, LIQUID and SOLID we may have:

disperse phase	gaseous	 GAS	 GAS/LIQUID foam	 GAS/SOLID solid foam
	liquid	 LIQUID/GAS aerosol, fog	 LIQUID/LIQUID emulsion	 LIQUID/SOLID slurry
	solid	 SOLID/GAS smoke	 SOLID/LIQUID suspension	 SOLID/SOLID alloy
		gaseous	liquid	solid
		continuous phase		

# DEFINITION OF PHASES

Phase transition requires energy!



disperse phase	gaseous	GAS · · · · ·	GAS/LIQUID foam	GAS/SOLID solid foam
	liquid	LIQUID/GAS aerosol, fog	LIQUID/LIQUID emulsion	LIQUID/SOLID slurry
	solid	SOLID/GAS smoke	SOLID/LIQUID suspension	SOLID/SOLID alloy
		continuous phase		
		gaseous	liquid	solid



## DEFINITION OF PHASES

Examples	Class	Disperse phase	Continuous phase
<i>Disperse systems</i>			
fog, spray, vapor, tobacco smoke, aerosol sprays, flue gases	liquid or solid aerosols	liquid or solid	gas
milk, butter, mayonnaise, asphalt, cosmetic creams	emulsions	liquid	liquid
inorganic colloids (gold, silver iodide, sulfur, metallic hydroxides)	sols or colloidal suspensions	solid	liquid
clay, mud, toothpaste	slurry	solid	liquid
opal, pearls, colored glass, pigmented plastics	solid dispersions	solid	solid
foam	liquid foams	gas	liquid
meerschaum mineral, foamed plastics	solid foams	gas	solid
<i>Macromolecular colloids</i>			
jelly, glue	gel	macromolecules	solvent

## 4<sup>th</sup> STATE OF MATERIA: PLASMA

- Heating a gas may ionize its molecules or atoms (reducing or increasing the number of electrons in them), thus turning it into a plasma, which contains charged particles: positive ions and negative electrons or ions. The presence of a non-negligible number of charge carriers makes the plasma electrically conductive so that it responds strongly to electromagnetic fields. Plasma, therefore, has properties quite unlike those of solids, liquids, or gases and is considered a distinct state of matter. Like gas, plasma does not have a definite shape or a definite volume unless enclosed in a container; unlike gas, under the influence of a magnetic field, it may form structures such as filaments, beams and double layers.