ΔΙΕΡΓΑΣΙΕΣ ΔΙΑΧΩΡΙΣΜΟΥ

Μάθημα 1ο

Ακαδημαϊκό έτος 2017-2018

Separation Processes

- Since Antiquity (Βώλος ο Μενδησιος ή ψευδοδημόκριτος-distillation)
  - Metals, fragrances, paints, potash
  - Evaporation of seawater for salt production
  - Asphalt
  - Liquids distillation
- Separations in our body
  - Kidney (membrane for the selective separation of water from the metabolic by-products).

Separations by Crystallization

- Crystallization must surely rank as the oldest unit operation, in the chemical
- engineering sense.
- Sodium chloride, for example, has been manufactured by this process since the dawn of civilization.
- Today there are few sections of the
- chemical industry that do not, at some stage, utilize crystallization as a method of production, purification or recovery of solid material.

Separations by Crystallization

- Apart from being one of the best and cheapest methods available for the production of pure solids from impure solutions, crystallization has the additional advantage of giving an end product that has many desirable properties.
- Uniform crystals have good flow, handling and packaging characteristics: they also have an attractive appearance, and this latter property alone can be a very important sales factor.

Crystallization through the ages

- Crystallization belongs to the oldest unit operations known to mankind.
- Namely,the crystallization of salts can be found through the ages. Early civilizations in coastalareas used large open ponds, salines, to crystallize out the salt, which could then beeasily handled, stored, transported, traded, and finally used.
- Salines around the seaport of Ostia are said to have facilitated the development of Roma and the Roman Empire.

- Today, crystalline products can be found in every aspect of life.
- Relevant product properties are determined by crystal properties and thus tailored via crystallization.

Sugar,
table salt,
and chocolate

Crystallization…

- **Sugar** extracted from plants and crystallized to meet a certain particle size distribution, (PSD 700–800 mm, free of fines⇒ which allows a free-flowing product
- that does not agglomerate. Finally, the process arrives at purities of >99.5% in an essentially single-step process of a seeded batch crystallization.
- **Table salt** also is required to be free flowing and not to agglomerate even in the high relative humidity environment of a kitchen. Here, additives can be employed during the crystallization, which is usually continuously operated evaporation crystallization.

Crystallization

- Finally, one of the main components of chocolate, **cocoa fat** has to be crystallized in a certain crystal modification or polymorph to achieve the special mouth taste of chocolate.
- This modification is unstable at room temperature and achieved via melt crystallization, where the crystals of the desired modification are generated and grown via a temperature program. In addition, additives can be used to stabilize the required modification. The unstable modification of the fatty acid ester can recrystallize to a more stable one, resulting in undesired changes in the
- appearance of the product.

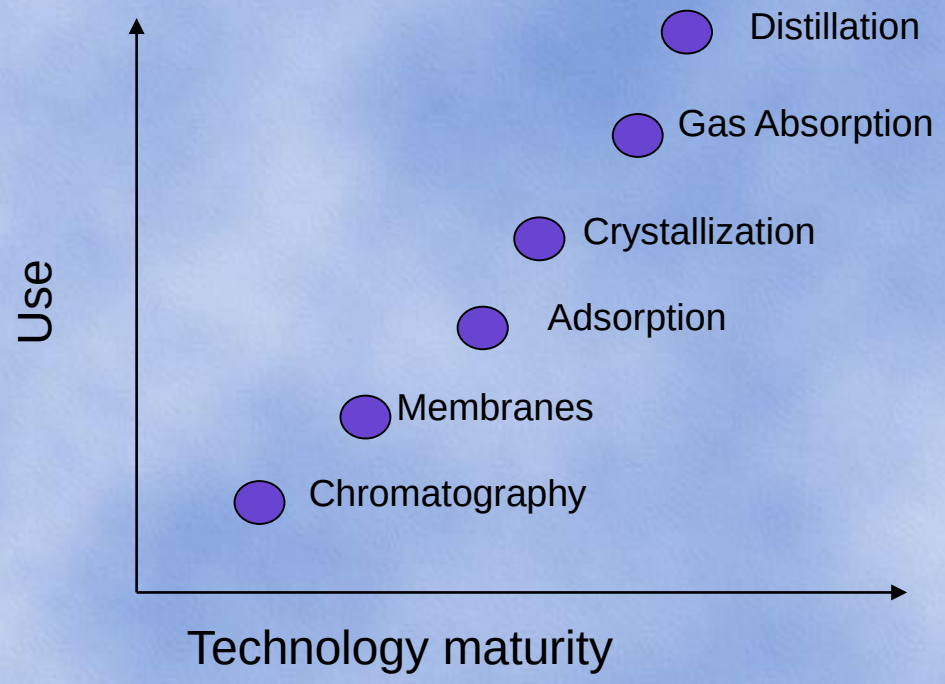
The Alchemists…
(Painting, 17th century)

The efficiency of a separation depends on:

- Molecular properties
  - MW, volume, van der Waals surface, Molecular shape, Polarizability, dielectric constant, electric charge, dipole moment, gyroscopic ratio
- Thermodynamic and transport properties
  - Vapor pressure, solubility, adsorption, diffusivity

Chemical separation processes

- play a central role in chemical engineering

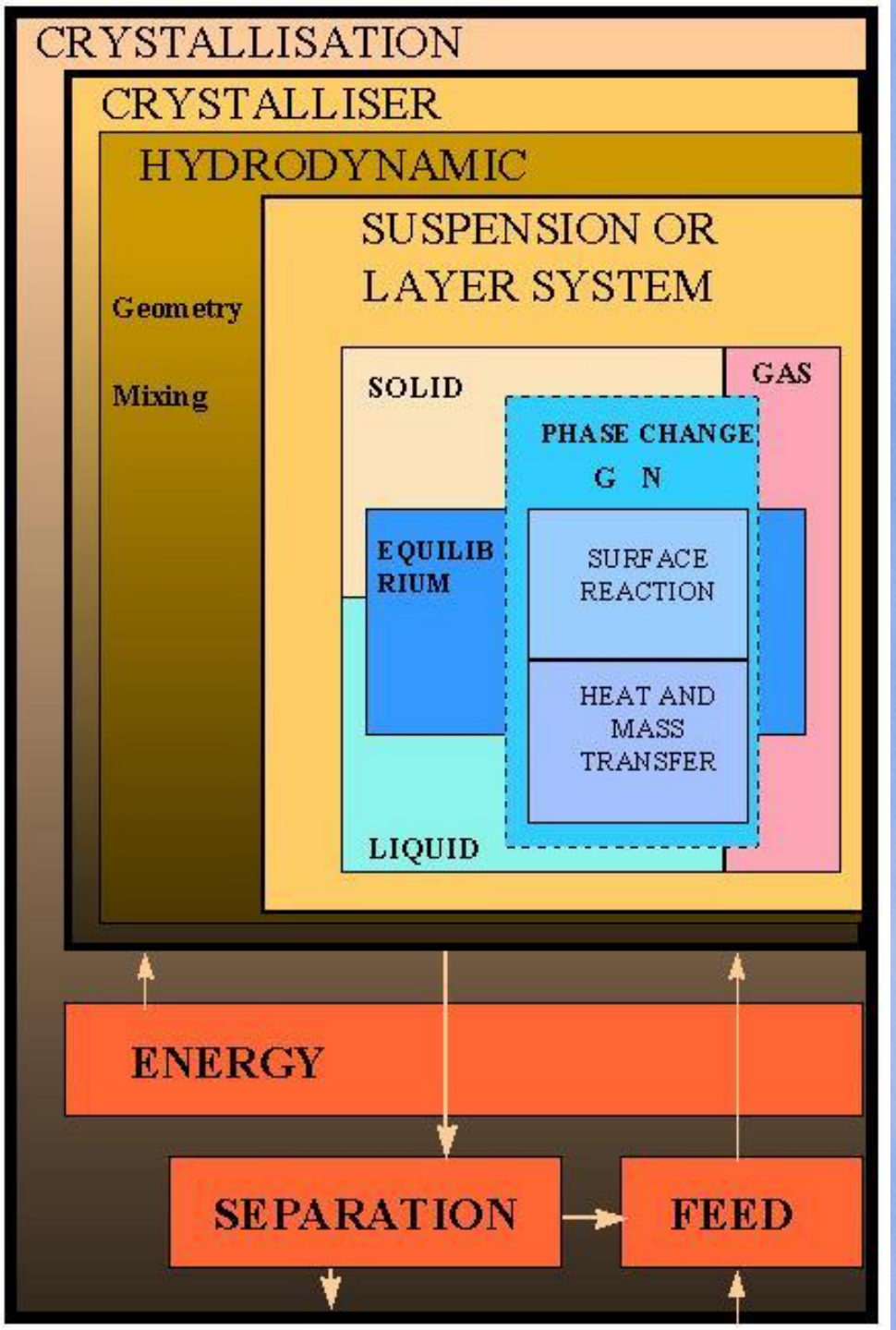


Purpose of this course

- Become familiar with separation technologies and the respective scientific fundamentals
- ***Crystallization***: Separation of solids from the liquid phase
  - Purification of products and of raw materials
  - Preparation of solids (misc. products, catalysts)

Crystallization

- Core of the materials science
- "Who dominates materials dominates technology." (Dr.Sekimoto, Japanese businessman and eminent scientist,specialist in communications. Chairman, NEC)
- Crystal Growth is a universal phenomenon in the field of materials.
- It has a long history but a significant impetus, which accelerated its evolution from "a substance potting art" to a science in its own right, was the invention of the transistor in 1948, and the subsequent need for high purity semiconductor single crystals.
- ***As a result crystal growth has developed into a core discipline in materials science***


CRYSTALLISATION
CRYSTALLISER
HYDRODYNAMIC
Geometry
Mixing
SUSPENSION OR
LAYER SYSTEM
SOLID
GAS
PHASE CHANGE
G N
EQUILIB
RIUM
SURFACE
REACTION
HEAT AND
MASS
TRANSFER
LIQUID
ENERGY
SEPARATION
FEED

Bibliography

- **Crystallization Technology Handbook**
  Alfons Mersmann (Editor) / Hardcover / Published 2001

- **Handbook of Industrial Crystallization**
  Allan S. Myerson / Hardcover / Published 2000

- **Precision Crystallization:** Theory and Practice of Controlling Crystal Size, I.H.Leubner, CRC Press 2010
- **Bioseparation Process Science**
  Antonio A. Garcia (Editor) / Paperback / Published 1999

- **Crystalization Processes**
  H. Ohtaki (Editor) / Paperback / Published 1997

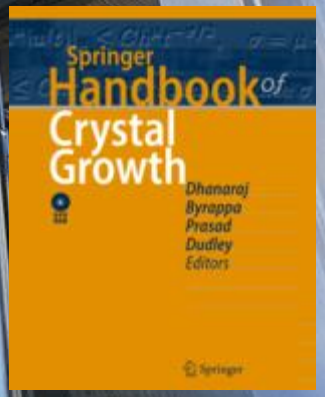
- **Encyclopedia of Separation Technology**
  Douglas M. Ruthven (Editor) / Hardcover / Published 1997

- **Fundamentals of Supercritical Fluids (Oxford Science Publications)**
  Anthony Clifford, Tony Clifford / Hardcover / Published 1999

- **Gas Separation by Adsorption Processes (Series on Chemical Engineering, Vol. 1)**
  R. T. Yang / Paperback / Published 1997
- **Membrane Technology and Applications**
  Richard W. Baker / Hardcover / Published 1999
- **Separation and Purification by Crystallization (ACS Symposium Series, No 667)**
  Gregory D. Botsaris (Editor), et al / Hardcover / Published 1997
- **Separation Process Principles**
  J. D. Seader, Ernest J. Henley / Hardcover / Published 1997
- **Separation Process Technology**
  Jimmy L. Humphrey, et al / Hardcover / Published 1997
- **Advances in Crystallization from Solutions (AIChe Symposium Series, Vol 80, No 240)**
  Gordon R. Youngquist (Editor) / Paperback / Published 1985
- **Advances in Industrial Crystallization**
  J. Garside, Elsevier, 1991
- **Chemical Engineering : Particle Technology and Separation Processes**
  J. M. Coulson / Paperback / Published 1991
- **Crystallization, Mullin, 4th ed.Butterworth, 2006**

Literature

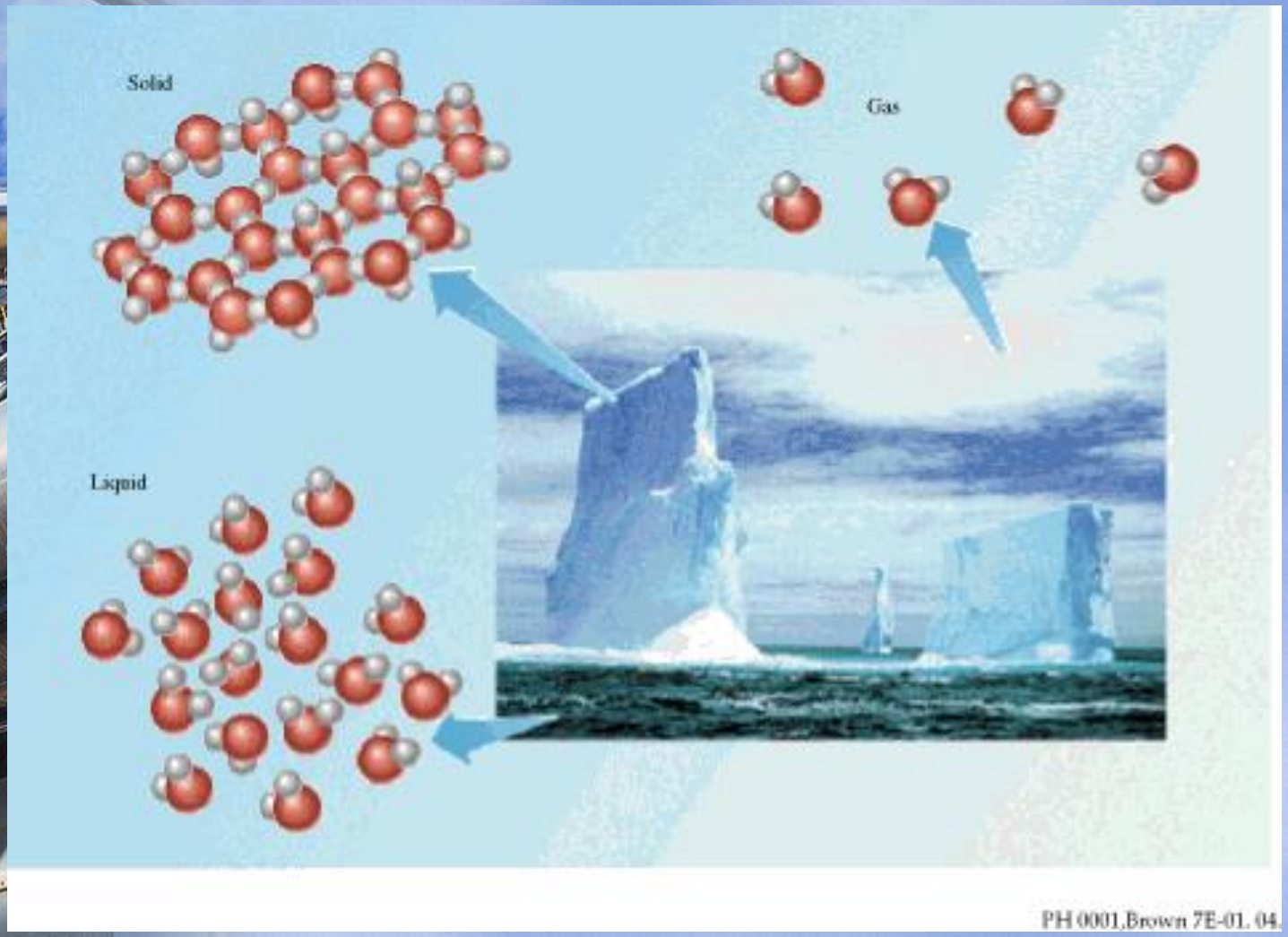
- Keshra Sangwal: Additives and Crystallization Processes, from Fundamentals to Applications, J.Wiley, 2007
- **Crystallization of Organic Compounds: An Industrial Perspective [Hardcover]** Hsien-Hsin Tung , Edward L. Paul Michael Midler James A. McCauley, J.Wiley, 2009
- Springer Handbook of Crystal Growth, Dhanaraj, G.; Byrappa, K.; Prasad, V.; Dudley, M. (Eds.), 2010, 1818pp, DVD



Crystallization

- Separation method of a substance in a more or less pure state from a mixture of substances
- The separation of substances from mixtures is possible provided that special thermodynamic conditions may be established
- For *mixtures* in the liquid state, under these specific conditions, the component molecules tend towards the crystalline state to lower the energy of the system
- The *ordered rearrangement of molecules in the crystalline lattice* involves the release of a latent heat as phase change takes place

Planet Earth is composed of many mixtures



Mixtures

Heterogeneous mixtures : has one or more visible boundaries between the components.

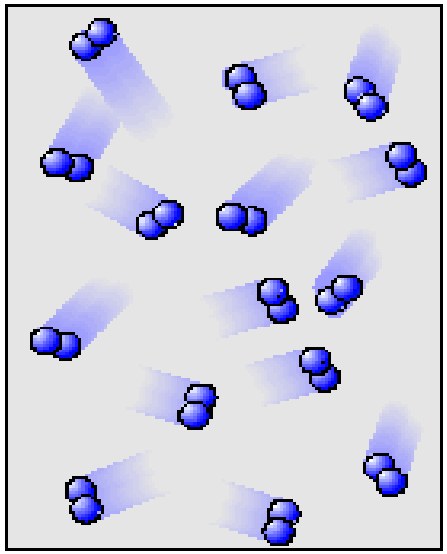
Homogeneous mixtures : have no visible boundaries because the components are mixed as individual atoms, ions, and molecules.

Solutions : **A** solution is also a homogeneous mixture

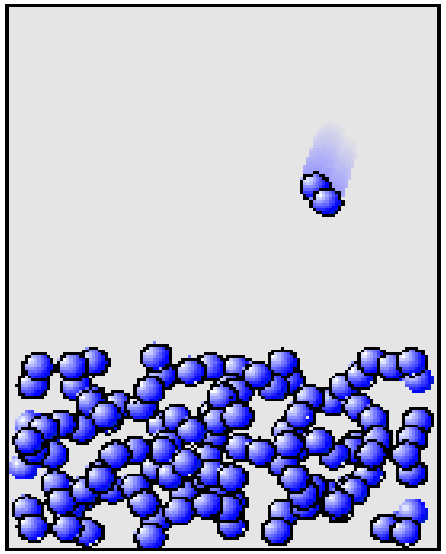
Solutions in water are called ***aqueous solutions***, and are very important in chemistry.

Although solutions are normally considered as liquids, they can exist in all three physical states.

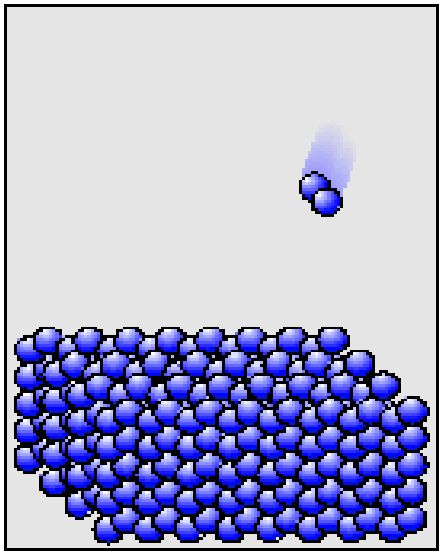
States of Matter



gas
disorder



liquid
short range order



solid
long range order

Conversions between states are called "phase transitions" or "changes of state"

Separating Mixtures

- The components in a mixture retain their identities
- We use properties that distinguish the components to separate mixtures
- the more similar the properties are, the more difficult it is to separate them

Separating Mixtures

Basic strategies for separation

- **phase conversion**: convert components of the mixture into other forms that are easy to isolate
- **phase transfer**: add a new phase that collects some components from the mixture

Separation Methods 1

TECHNIQUE	BASIS FOR SEPARATION
adsorption / desorption	**phase transfer to a solid surface**
chromatography	**phase transfer from a mobile mixture to a stationary phase**
condensation (Συμπύκνωση)	**phase separation by condensing gases in the mixture to liquids**
dialysis (διαπίδυση)	**phase transfer through a porous membrane that allows some molecules to pass through, but not others**
effusion (Διάχυση)	**gases with faster molecules flow through tiny pinholes faster than gases with slow molecules**

Separation Methods 2

TECHNIQUE	BASIS FOR SEPARATION
dissolution (washing, solvent extraction)	**soluble components can be washed away, leaving behind insoluble components (phase transfer to a washing solvent)**
electrorefining (ηλεκτροδιΰλιση)	**separate a metal from impurities by dissolving it and then plating it onto an electrode**
filtration	**collect solid particles on a filter**
floatation (Επίπλευση)	**dense components sink, and lighter ones float**
ion exchange	**ions in the mixture bind to surfaces with oppositely charged sites (phase transfer to an ion exchange resin)**

Separation Methods 3

TECHNIQUE	BASIS FOR SEPARATION
precipitation	convert solutes to an easily separated solid form
scrubbing	bubble mixture through a solution that selectively absorbs a component (phase transfer from gas to solution)
stripping	a gas bubbled through the mixture carries off the most volatile components (phase transfer from solution to gas)
volatilization (drying, distillation, sublimation)	components with widely differing volatility can be driven out of the mixture by heating (phase change from solid or liquid to gas)

Separating Mixtures

Filtration : Separates components of a mixture based upon *differences in particle size.* Normally separating a precipitate from a solution, or particles from an air stream.

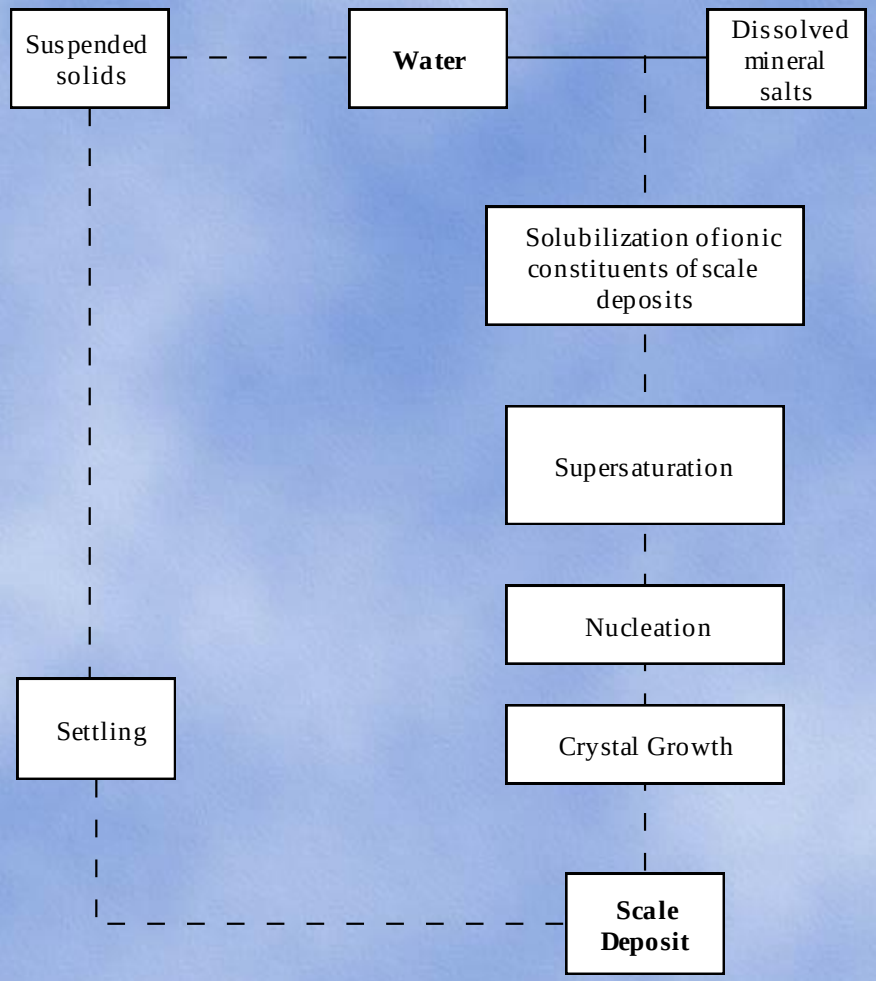
Crystallization : Separation is based upon *differences in solubility* of components in a mixture.

Distillation : separation is based upon *differences in volatility*.

Extraction : Separation is based upon *differences in solubility* in different solvents (major material).

Chromatography : Separation is based upon *differences in solubility* in a solvent versus a stationary phase.

Scale Deposits (καθαλατώσεις) Formation in water systems: A special case of separation where crystallization is instrumental



Crystallization

- Crystallization from solutions is an important process for separation and for the purification for a broad spectrum of industries :
  - Sugar
  - NaCl
  - Fertilizers
  - Pharmaceutical
  - Catalysts
  - Chemical specialties, substances of high added value

Table 1.1 Examples for the annual production of crystalline products in various fields.

Product	Produced in	Production (t/a)
Sodium chloride	2001 in the EU	38 350 000
Sugar	2001 in the EU	15 000 000
Caprolactam	2002 worldwide	3 500 000
Ascorbic acid	2009 worldwide	110 000
Acetylsalicylic acid	2008 worldwide	35 000

What is sought using crystallization as a technique?

- Production of pure products
- Synthesis of products with specific characteristics
  - Crystallites size distribution
  - density
  - Filterability
  - Viscosity of suspensions(in the liquid phase or in air)
  - Particles rheology

The main task in the field of crystallization is the development of theories and techniques to control the purity, size distribution and shape of the produced crystallites

Last 40 years…

- Important steps in understanding fundamentals of crystallization which helped in the design of the respective reactors (crystallizers)
- Fundamental problem is the prediction of size (size distribution) in the practice of crystallization
- Development and treatment of the methodology of population balance of the crystals
- A.D.Randolph, M.A.Larson : Theory of Particulate Processes, 2nd Edition, Academic Press, San Diego CA 1988

Other important landmarks...

- Realization of the importance of secondary nucleation (δευτερογενής πυρηνογένεση) due mainly to the contact between crystals, and with the impeller of the reactor
- Secondary nucleation, plays important role in several cases, in determining the operation of the crystallizers

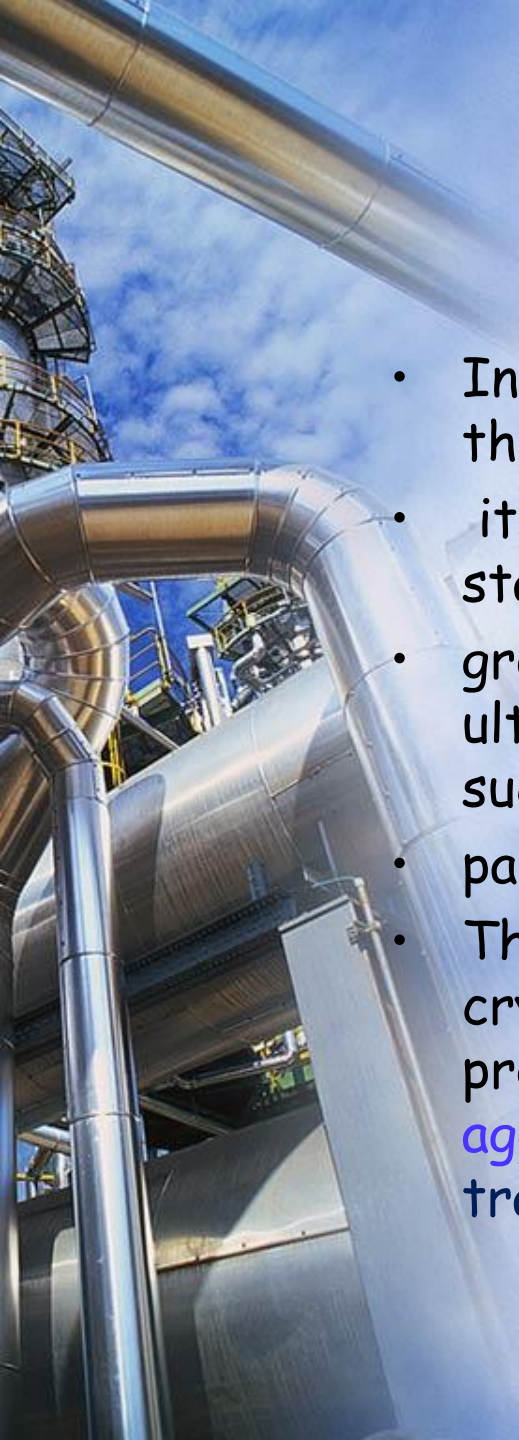
Review Articles

- J. Garside, *Chem. Eng. Science*, **40** (1985) 3
- J.W.Mullin, in Kirk Othmer Encyclopedia of Chemical Technology, **vol.7**, p.243, Wiley New York, 1979
- M.A.Larson, *AIChE Symp. Ser.* **240** (1984)39
- J.Garside, *AIChE, Symp.Ser.* **240** (1984) 23

Crystallization

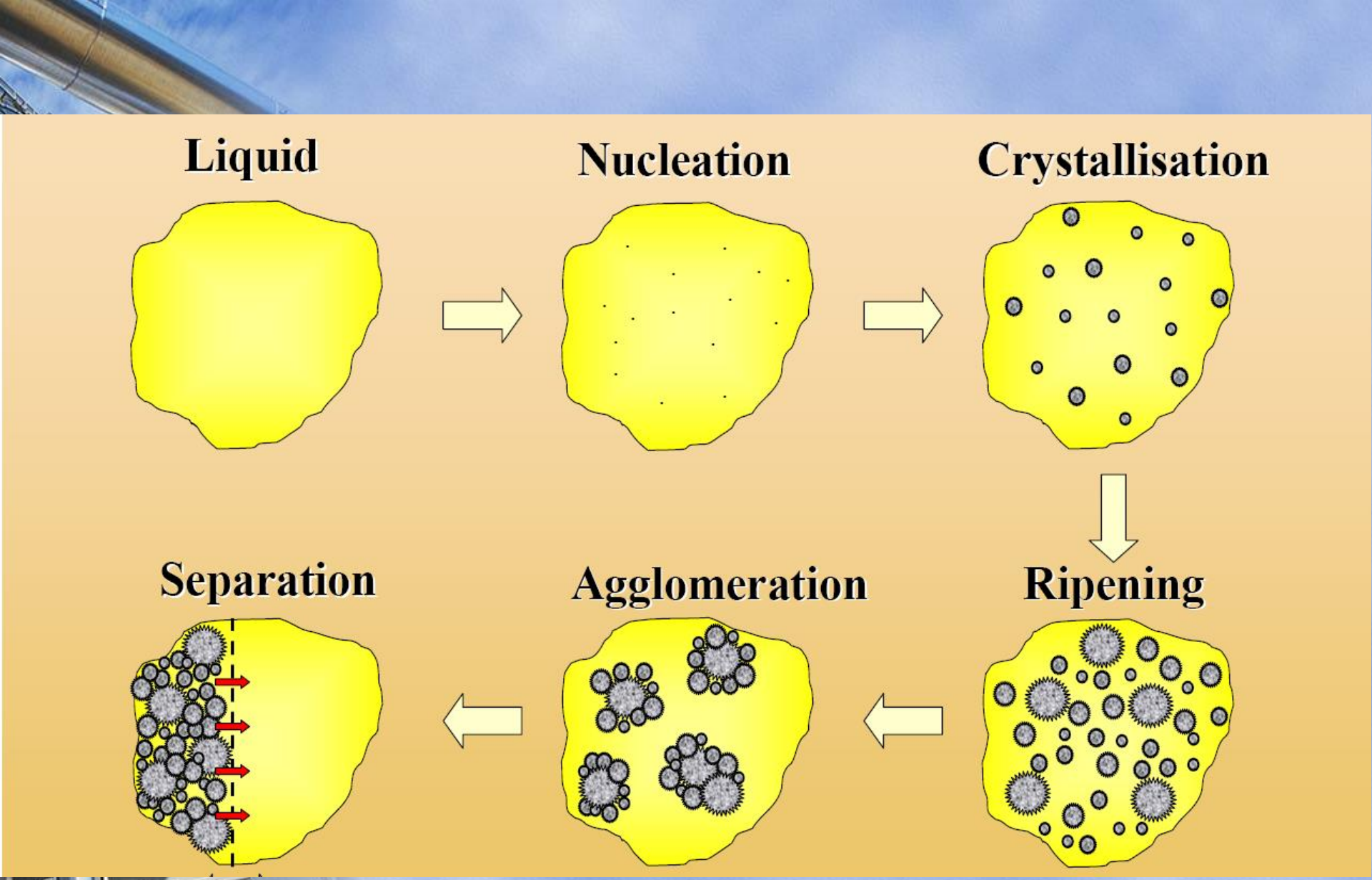
Crystallization from solution is a separation technique where a solid phase is separated from a mother liquor.

The dispersed phase of a mixture consisting of numerous "solid particles" also forms the final product, that has to meet the required product specifications.



Crystalline products

- In different industries, the important requirements that a crystallized solid-state product has to fulfill are:
- its phase or polymorph, thermodynamic and kinetic stability during its storage life
- growth morphology and size distribution, which ultimately determine the product solid-state properties such as separation, flow, compaction, dissolution, and
- packing.
- The above requirements are met by controlling crystallization conditions which determine various processes such as nucleation, crystal growth, aggregation, Ostwald ripening, and phase transformation.


Liquid
Nucleation
Crystallisation
Ripening
Agglomeration
Separation