9.5 PRECIPITATION

The terms defined in this sub-chapter are connected mainly with contamination phenomena which occur during the formation of precipitates and during separation processes in analytical chemistry, i.e., with the phenomenon of coprecipitation and postprecipitation. Only aqueous solutions in the temperature range 0 °C to 100 °C are considered.

Solution

A homogeneous liquid phase comprising at least two different substances.

Solvent

A liquid (usually the major component of a solution) which is used to dissolve a solute or solutes.

Solute

The minor component of a solution which is regarded as having been dissolved by the solvent.

Dissolution

A mixing of two phases with the formation of one homogeneous phase (i.e., the solution).

Saturated solution

A solution which has the same concentration of a solute as one that is in equilibrium with undissolved solute at specified values of the temperature and pressure.

Saturation (noun)

The state of a saturated solution.

Solubility product

The product of the ion activities raised to appropriate powers of an ionic solute in its saturated solution expressed with due reference to the dissociation equilibria involved and the ions present.

Solubility

The analytical composition of a saturated solution, expressed in terms of the proportion of a designated solute in a designated solvent, is the solubility of that solute. The

solubility may be expressed as a concentration, molality, mole fraction, mass fraction, mole ratio, etc.

Supersaturated solution

A labile or metastable solution which contains a higher concentration of solute than a saturated solution at the same temperature and pressure.

Supersaturation (noun)

The state of supersaturated solution.

Nucleus

The smallest solid phase aggregate of atoms, molecules, or ions which is formed during a precipitation and which is capable of spontaneous growth.

Nucleation

The process by which nuclei are formed in a solution. The condensation of a single chemical compound is called homogeneous nucleation. The simultaneous condensation of more than one compound is called simultaneous nucleation. The consideration of a compound on a foreign substance is called heterogeneous nucleation.

Rate of nucleation

The number of nuclei formed in unit time per unit volume of the liquid phase.

Precipitate

(noun) A solid phase formed within a liquid phase.
(verb) To produce a precipitate.

Precipitation

The formation of a precipitate.

Precipitation from homogeneous solution (PFHS)

The formation of a precipitate which is generated homogeneously, and generally slowly, by a precipitating agent within a solution.

Collection

The planned removal from solution of a micro- or macro-component by the intentional formation of a contaminated host precipitate, or by the adsorption or entrapment of the component by an added solid.

Collector (scavenger)

A solid substance added to or formed within a solution to collect a micro- or macro-component.

Coagulation (flocculation)

The formation and growth of aggregates ultimately leading to phase separation on a macroscopic scale.

Agglomeration

The formation and growth of aggregates ultimately leading to phase separation by the formation of precipitates of larger than colloidal size.

Adsorption

An increase in the concentration of a dissolved substance at the interface of a condensed and a liquid phase due to the operation of surface forces. Adsorption can also occur at the interface of a condensed and a gaseous phase.

Adsorbent

A condensed phase at the surface of which adsorption may occur.

Adsorbate

The material accumulated on the surface of an adsorbent by the process of adsorption.

Occlusion (molecular)

The process of incorporation of foreign substances as molecular species within the precipitates as they are formed.

Mechanical entrapment

(a) The process of random incorporation of comparatively small quantities of other phases (e.g., water, dust, particles, etc.) in the bulk of a precipitate during its formation.

(b) The deliberate capture of small quantities of such phases by the deliberate addition of solids to a liquid phase. (The term *inclusion* is not recommended.)

Mixed Crystal or Solid Solution

A crystal which contains a second constituent which fits into and is distributed in the lattice of the host crystal. (The use of *solid solution* for amorphous materials is not recommended.)

Distribution Laws

During the formation of a mixed crystal from a solution containing two components 'A' and 'B', the latter may, as an ideal limiting case, be distributed according to the equation

$$K_{A,B} = b(a_0 - a)/a(b_o - b)$$

In this homogeneous distribution, a_0 and b_o are the respective concentrations in the solution before crystallization, and a and b are the respective concentrations in the solution after crystallization. $K_{A,B}$ is usually called the *separation factor*. The term *homogeneous distribution coefficient* is not recommended. As another ideal limiting case, the distribution of the microcomponent may follow the equation of Doerner and Hoskins

$$\ln(a_o/a) = \lambda \ln(b_o/b)$$

(logarithmic distribution) where λ is usually called the *Logarithmic distribution coefficient*, the meaning of the other symbols remaining the same as above. Exactly homogeneous or logarithmic distributions are extreme cases and are very seldom encountered.

Coprecipitation

The simultaneous precipitation of a normally soluble component with a macrocomponent from the same solution by the formation of mixed crystals, by adsorption, occlusion or mechanical entrapment.

Postprecipitation

The subsequent precipitation of a chemically different species upon the surface of an initial precipitate usually, but not necessarily, including a common ion.

Reprecipitation

The planned repetition of a precipitation in order to remove chemically different species from a previous precipitate or to improve its stoichiometry.

Aging

The time-dependent change of the properties of a precipitate, e.g., loss of water, growth of crystals, recrystallization, decrease of the specific surface, loss of coprecipitated substances, which generally improve the filtering properties. The process of aging is very often promoted by maintaining the precipitate and precipitation medium together at elevated temperatures for a period of time. The terms *chemical, physical* and *thermal aging* may be used in cases in which some of the (usually combined) effects named above are to be emphasized specifically.

Ostwald Ripening

The growth of larger crystals from those of smaller size which have a higher solubility than the larger ones.