Mines Branch Information Circular IC-312

THEORY AND PRACTICE OF PRECIPITATION AND COPRECIPITATION, WITH PARTICULAR REFERENCE TO HYDROMETALLURGICAL PROCESSING

- Abstract -

Many factors are known to affect the extent of coprecipitation, and the correlation of these factors in practice is a difficult problem. An attempt is made in this paper to show the interconnection of the many phenomena that comprise coprecipitation, as well as the factors that affect it. Coprecipitation is of great importance in metallurgical processing, both from the point of view of minimizing it to ensure a pure product, and maximizing it to remove, or to collect and concentrate trace impurities. A comprehensive discussion of the effect of precipitation conditions on these two aspects is presented and a scheme for classifying coprecipitation mechanisms is introduced, along with diagnostic tests to establish which of these mechanisms is operative in a particular practical situation. The various major groups of slightly soluble salts capable of acting as collectors are listed and classified according to the nature of the chemical bonding involved and the modes of action which are the result. Finally, a recommended approach to precipitation and coprecipitation investigations to obtain the most useful data for process optimization is also given.

TABLE OF CONTENTS

INTRODUCTION

Coprecipitation is receiving wide interest. It is important in hydrometallurgy wherever there is a separation of phases. In analytical chemistry, errors due to coprecipitation occur both in gravimetry, in separation processes where either the element sought or the interferences to be eliminated are precipitated, and in volumetric methods in which a precipitate is the product of the chemical reaction. It is recognized that coprecipitation plays an important role in physiological processes, for example, there may be interchange between calcium and radioactive strontium in calcified tissue. Geological deposits nearly always contain foreign ions coprecipitated with the host phase. A recent impetus to coprecipitation study is its utilization as a means of concentration(1), which, for trace quantities of ions in solution, rivals solvent extraction in sensitivity.

The coprecipitation technique is being used to remove undesirable trace components from industrial solutions(2) and to concentrate trace elements from sea water(3). The action of synthetic inorganic ion-exchangers, developed to selectively remove certain metal ions from solution(4), and particularly to remove radioactive elements from solution(5), encompasses the same principles involved in coprecipitation phenomena.

Although chapters on coprecipitation are included in many textbooks on analytical chemistry(8,10,11,12,13), the fundamentals of coprecipitation are still imperfectly understood because the phenomenon involves not only the physical and chemical properties of substances, but also depends on the mechanism and rate of precipitate formation(14). Thus nucleation, crystal growth and precipitate aging are very important subjects in the study of coprecipitation. Except for two sources(6,15), authors seem to consistently shy away from presenting all these subjects in a single review. As a result, a summary of diagnostic tests to clarify coprecipitation mechanisms is noticeably lacking. In fact, the subject of coprecipitation is still in a state where even a description of the phenomenon is difficult, let alone an explanation for what is observed.

The purpose of this work is to review the theory of coprecipitation, with particular reference to process application. It has been necessary first to determine what are its theoretical fundamentals. Subsequently, charts and tables to aid in the application of these fundamentals (presented in Chapter 7) have been constructed. In the final chapter, a classification of water-insoluble salts which behave similarly with respect to coprecipitation has been provided. Cited examples have been drawn from research papers and industrial processes, to emphasize particular coprecipitation techniques.

1. COPRECIPITATION MECHANISMS

A precipitate formed by the combination of suitable reagents in solution is invariably contaminated by foreign ions present in the solution. The entire process by which an ordinarily soluble substance becomes incorporated into a precipitate is called coprecipitation. This incorporation occurs chiefly by three mechanisms: adsorption, solid solution formation and occlusion.

Adsorption

Adsorption at the solid interface occurs because the surface molecules or atoms are reactive. There exists an interphase tension, caused by a dissymmetry of forces acting on the molecules or atoms at or near the interface. Thus these surface molecules or atoms possess residual chemical forces. Due to a sorption of ions the precipitate surface becomes electrically charged. The charged surface then attracts from solution ions of opposite charge called counter ions. Counter ions are held in the solution phase close to the surface of the solid chiefly by an electrostatic force and can be displaced by other ions of higher charge. Although some counter ions are located close to the surface in a compact layer, some are contained in a three-dimensional region, the diffuse layer, which extends into the bulk of the solution. The origin of the diffuse character is thermal agitation, which provides a disordering force opposed to the ordering coulombic forces of attraction and repulsion. The charge on the solid surface due to adsorbed ions and the charge of opposite sign in the solution phase form the so-called electrical double layer.

Adsorption is strictly a surface phenomenon and implies that the adsorbed ions or molecules do not penetrate the solid phase by diffusion; in other words, the adsorbed phase and the precipitate phase need not be miscible.

Kolthoff(6) distinguished thus between adsorption and "real coprecipitation". Adsorbed substances are those that can be removed or replaced by washing the host precipitate with a suitable electrolyte solution. In "real coprecipitation" the impurities are present in the interior of the crystal and cannot be removed by the washing procedure.

Solid solution

If, due to similarity in size and structure, the adsorbed phase is miscible with and diffuses into the host phase, then a solid solution is formed. If the adsorbed phase and the precipitate phase are miscible in all proportions, then the solid solution is said to be composed of mixed crystals. If the solubility of the adsorbed phase in the precipitate is limited, then the solid solution is composed of anomalous mixed crystals. Coprecipitation by solid solution formation occurs mainly during the growth of the host crystal and it is, therefore, the chief coprecipitation mechanism when a precipitate is formed slowly from homogeneous solution(7) by a process in which the precipitant is generated at a controlled rate by a homogeneous chemical reaction within the solution. Coprecipitation by solid solution formation is a highly selective process, the selectivity and efficiency depending on the nature of the precipitate and the method of interaction of the coprecipitated species with the crystal matrix of the precipitate.

Occlusion

Authors differ in their definition of occlusion. According to Laitinen(8), Erday, Polos and Chalmers(9), occlusion is the carrying-down of impurities in the interior of primary particles by any mechanism. However, Salutsky(10) states: "occlusion of an impurity within a precipitate results when the precipitation is carried out in such a manner that the impurity is mechanically trapped by subsequent crystal layers". According to Kolthoff(6), in occlusion the impurities are absorbed during growth of the crystals and give rise to "imperfections" in the crystal. The foreign ions keep more or less of their water of hydration and are, therefore, not incorporated by the lattice. Skoog and West(11) define occlusion as the entrapment of counter ions by the rapidly growing solid. The definition by Skoog and West appears to best summarize the fundamentals of occlusion.

Simultaneous precipitation and post-precipitation

Coprecipitation is distinguished from simultaneous precipitation and post-precipitation. Simultaneous precipitation occurs when, for each of the substance precipitated, the ion product has exceeded the solubility product constant. Post-precipitation occurs from a supersaturated solution of the impurity; the precipitate and impurity come down in a consecutive manner, with a varying time interval between formation of the two phases. The term "gathering" is employed to describe the case where a trace impurity is brought down quantitatively, with a large quantity of precipitate under such conditions that both are insoluble. In practice, it is sometimes difficult to distinguish diagnostically between "gathering" and true co-precipitation.

2. ADSORPTION PROCESSES

Compounds most strongly adsorbed on precipitates are usually the products of chemical bonding with ions common to the precipitate lattice. If new chemical bonds are formed, the process is called chemisorption. In the absence of new chemical bond formation, the adsorbate is held by relatively weak, non-directional forces (e.g., electrical forces and/or van der Waals's forces(16)) and, in this case, the adsorption process is called physical adsorption.

Three main factors control the amount of adsorption of a foreign ion by a precipitate: surface area, surface charge, and the complexing ability of the foreign ion with the precipitate lattice ion of opposite charge. The surface area is controlled by the particle size of the adsorbent. In the absence of chemisorption, the sign of the surface charge depends on which precipitate lattice ion is in excess in solution, and the magnitude of the charge depends on the concentration of this ion. The complexing ability of the foreign ion depends on its adsorption energy, which must be greater than its solvation energy. That is, the adsorption product is sparingly soluble.

Surface adsorption is influenced by all experimental conditions, but it is particularly affected by the composition of the solution, the concentration of the components in it, and by temperature. For a given constant temperature, **adsorption** isotherms give the relationship between the quantity of solute adsorbed and the equilibrium concentration of the solute in the solution.

For ionic precipitation, Kolthoff(6) classified adsorption processes as follows:

a) adsorption of a salt having an ion in common with the lattice; adsorption of potential-determining ions;
b) exchange adsorption between lattice ions on the surface and foreign ions from the solution;
c) exchange between adsorbed counter ions and foreign ions in the solution;
d) molecular adsorption of non-electrolytes and true adsorption of salts; and
e) activated adsorption.

The chief characteristics of each class are considered below.

2.1 Adsorption of potential-determining ions (pdi)

In general, all ions that can transfer between phases, or build a new phase with one of the lattice* ions, are potential-determining ions. However, the precipitate lattice ions themselves are the most strongly adsorbed and the excess adsorption

---

* See glossary.

of one of the lattice ions over the stoichiometric ratio determines the sign and size of the surface charge. That is, an excess of lattice anions in solution gives to the precipitate surface a negative charge, while a positively charged surface is obtained in a solution with an excess of lattice cations. The activity of the lattice ions at which the net charge of the precipitate is zero, is called the point of zero charge, pzc(17,18). The potential difference, $\Delta\psi$, between the crystal and the solution, owing to which an electrical double layer is built up, depends on the equilibrium concentration of lattice ions (or foreign pdi) in accordance with the equation:

$$\Delta\psi = \frac{RT}{F} \ln \frac{C_i}{C_i^o} \qquad \{2\text{-}1\}$$

where C_i = concentration of lattice ions

C_i^o = concentration of lattice ions at pzc;

F,R,T = Faraday constant, molar gas constant and absolute temperature, respectively.

We find also that the adsorption of lattice ions per unit of precipitate is proportional to the logarithm of lattice ion concentration(8). The corresponding adsorption isotherm is:

$$\frac{x}{m} = k \ln \frac{C_i}{C_i^o}$$

where x = amount adsorbed (mg, g or moles);

m = weight of precipitate;

C_i = concentration of lattice ions;

C_i^o = iso-electric concentration, corresponding to $x = o$ when $C_i = C_i^o$;

or

$$\frac{x}{m} = k_1 + k_2 \log C_i \qquad \{2\text{-}2\}$$

Walton(14) points out that, although most work shows a logarithmic relationship between the concentration of an isotope in solution and the amount adsorbed on a carrier, some radioactive tracer studies show a linear relationship in certain concentration ranges.

2.2 Adsorption of pdi by ion exchange

Ion exchange is a surface reaction only and does not depend on isomorphism. The exchange between surface lattice ions and foreign potential-determining ions takes place in spite of the fact that the solubility product of the adsorbed compound is not exceeded.

It seems, therefore, as if the "solubility" of the compound in the adsorbed state upon a lattice already present is lower than its solubility as a separate phase.

Under ideal conditions, the extent of ion exchange is determined by the ratio of solubility products of the host precipitate and the new phase in accordance with the Paneth-

Fajans-Hahn **adsorption** rule$^{(11)}$, which states that those ions will be strongly adsorbed that form difficulty soluble or weakly dissociated compounds with the oppositely charged ions of the solid lattice. The extent of the ion exchange depends also on the **ratio of** concentrations of the competing ions. In the reaction:

$$\text{P surface} + \text{I solution} \rightleftarrows \text{I surface} + \text{P sulution}$$

where P stands for precipitate (lattice) ions and I for impurity or micro-component ions, the equilibrium is expressed by the equation:

$$K = \frac{(C_I)\text{ surface} \cdot (C_P)\text{ solution}}{(C_P)\text{ surface} \cdot (C_I)\text{ solution}} \qquad \{2\text{-}3\}$$

where C stands for concentration and K is the distribution coefficient.

If (C)solution and (C_P)surface have nearly constant values, then:

$$K^1 = \frac{(C_I)\text{ surface}}{(C_I)\text{ solution}} \qquad \{2\text{-}4\}$$

that is, the amount of microcomponent* adsorbed is proportional to its concentration in solution. Or, assuming a constant ratio for $\frac{(C_I)\text{surface}}{(C_P)\text{surface}}$, the equilibrium concentrations of microcomponent and macrocomponent* in solution are proportional to the solubility products of the corresponding compounds having a common component:

---

* See glossary.

$$K" = \frac{(C_I)\ \text{solution}}{(C_P)\ \text{solution}} = \frac{K\ \text{s.p.}\ (I)}{K\ \text{s.p.}\ (P)} \qquad \{2\text{-}5\}$$

where K" is the proportionality constant.

2.3 Exchange of counter ions

An electrically-charged surface attracts ions of opposite charge called counter ions. If thermal motion were absent or small compared with the electrical forces, an equivalent amount of counter ions would be attracted by the surface and would cover it, exactly neutralizing its charge. The surface and these neutralizing counter ions would form an electrical double layer. The rest of the solution would not be affected, since the counter ions screen the surface completely. The electrical potential would drop to zero within the double layer.

If thermal agitation is present, it will generally prevent the formation of such a compact double layer. The counter ions will tend only to concentrate near the surface and those nearer the surface will screen those farther away from its full effect; instead of being constant, the field will decrease with distance - rapidly near the surface and more slowly farther away.

Thus, the effect of thermal agitation is to create a "diffuse" double layer, often called Gouy or Gouy-Chapman double layer. The thickness of the diffuse layer increases as the ionic strength of the solution decreases.

Ordinarily, counter ions cannot cause a reversal of surface charge because, once the charge sinks to zero, there is none left to attract more counter ions. Thus, there is a natural maximum of counter ion exchange, equal to the amount of available counter ions in the double layer. For example, a negatively charged precipitate of silver iodide with adsorbed iodide ions will have a maximum of hydrogen counter ions equal to the number of adsorbed iodide ions, i.e.:

$$\mathrm{mAgI.nI^-} \mid \mathrm{nH^+}$$

where m,n are arbitrary numbers. If a potassium salt is added, then some potassium ions will exchange with the hydrogen ions and we find:

$$\mathrm{mAgI.nI^-} \mid \mathrm{nH^+} + \mathrm{yK^+} \rightarrow \mathrm{mAgI.nI^-} \mid \mathrm{(n-y)H^+.yK^+} + \mathrm{yH^+}$$

It is assumed that both ions (H^+,K^+) stay, independent of each other, in the double layer. Only their average "residence time" will vary. The exchange equilibrium is given by the equation (6,125):

$$\frac{yK^+}{(n-y)H^+} = k\frac{\{K^+\}}{\{H^+\}}$$

or

$$\left(\frac{K^+}{H^+}\right)_{\mathrm{surface}} = k\left(\frac{K^+}{H^+}\right)_{\mathrm{solution}} \qquad \{2\text{-}6\}$$

i.e., the ratio of both ions in the double layer is directly proportional to the ratio in solution.

It is characteristic of the phenomenon that the ratio of the concentrations determines the exchange, both ions occurring in the formula being equivalent. If equilibrium is reached, dilution of the system does not cause a shift in the ratio. The exchange is independent of the dilution. We see also that the total concentrations of electrolyte in the double layer and in the solution are not altered; only an exchange of counter ions has taken place.

Adsorption equations for counter ions are also based on the Stern model of the electrical double layer$^{(20,21)}$. In this model, the closest approach of counter ions to the surface is one (hydrated) ionic radius away, usually indicated by the distance δ. The potential at the distance δ from the surface, ψ_δ, is called the Stern potential. Direct measurement of ψ_δ for most systems is not possible. It is often assumed$^{(20)}$ that ψ_δ is equal to the zeta potential, which can be measured by one of several available electrokinetic techniques. Zeta potential is defined as the potential at the plane of shear (slipping plane) between the fixed layer of liquid adjacent to the particle and the liquid constituting the bulk solution.

The adsorption density, Γ_δ (amount absorbed per unit area), of adsorbed counter ions at the distance δ is given by the relationship:

$$\Gamma_\delta = 2rc \exp \frac{-zF\psi_\delta}{RT} \qquad \{2\text{-}7\}$$

where r = effective radius of the adsorbed counter ion;

c = bulk concentration of adsorbed counter ion;

z = valence;

Ψ_δ = potential at distance δ from the surface;

F,R,T = Faraday constant, molar gas constant and absolute temperature, respectively.

Counter ions that are held only by electrostatic forces are called indifferent electrolytes. Some counter ions exhibit surface activity, i.e., adsorption can proceed with a non-exact correspondence with change in the surface charge. For example, in the adsorption of barium ions on quartz, the barium ions are held partly by the energy of polarization. In adsorption of alkylamine ions on quartz, the alkylamine ions are held partly by van der Waals' energy associated with the alkyl group. Here adsorption differs from chemisorption by a lower attachment strength of the sorbed ions. The adsorption density of the surface-active counter ions is given by the equation:

$$\Gamma_\delta = 2rc \exp \frac{-zF\Psi_\delta - \Delta G_{spec.}}{RT} \qquad \{2\text{-}8\}$$

where $\Delta G_{spec.}$ is the free energy of specific adsorption, the remaining terms having the same meaning as in equation {2-6}.

2.4 Molecular adsorption

Adsorption of non-electrolytes involving van der Waals' forces, and the adsorption of ion pairs, for example, the adsorption of KI on AgI or $KBrO_3$ on $BaSO_4$ (which appears to involve the simultaneous occupation of adjacent sites by a foreign cation and anion), are usually expressed by the empirical adsorption isotherms of Freundlich(8,22) or Langmuir(8).

The Freundlich isotherm is expressed by the equation:

$$\frac{x}{m} = kc^{\frac{1}{n}} \qquad \{2\text{-}9\}$$

where k and n are constants and c is the equilibrium adsorbate concentration in the solution phase; x and m were defined in equation {2-2}. The Freundlich isotherm is usually adhered to in the adsorption (not ion exchange) of micro-amounts of ions and molecules. At low concentrations, the isotherm remains concave to the concentration axis. A plot of log $\frac{x}{m}$ vs log c gives a slope of $\frac{1}{n}$, which is a measure of the intensity of adsorption; the intercept k gives a measure of the adsorbent capacity(23).

For intermediate adsorption density and where data show that, for a sufficiently high concentration of adsorbate, the adsorption becomes independent of concentration, the behaviour is better described by the Langmuir isotherm:

$$\frac{x}{m} = \frac{qkc}{1 + kc} \qquad \{2\text{-}10\}$$

where q and k are two new constants. At high concentration, when 1 becomes negligible compared with kc, the equation gives $\frac{x}{m} = q$, a limit to the amount adsorbed; at low concentration, when kc is negligible compared with 1, then $\frac{x}{m} = qkc$, i.e., the amount adsorbed is directly proportional to concentration in solution.

Summarizing, for the process of true adsorption of indifferent electrolytes, the characteristic relationship is

$$\Delta\ (\log \frac{x}{m}) = k.\ \Delta\ (\log c)$$

For the adsorption of potential-determining electrolytes the characteristic relationship is

$$\Delta\ (\frac{x}{m}) = k.\ \Delta\ (\log c)$$

while, for adsorption by ion exchange, a linear relationship is characteristic

$$\Delta\ (\frac{x}{m}) = k\Delta c$$

2.5 Activated adsorption

Of the many particles reaching, and attached to the surface by van der Waals' forces, a few may acquire enough energy to become chemisorbed. The rate of reaching equilibrium with respect to chemisorption may be slow and will be greatly affected by temperature. This is called activated adsorption. Hence, activated adsorption on an accessible surface is always chemisorption, but chemisorption may be either simple or activated.

An example is the adsorption of water on calcium fluoride. At low temperatures, the water is adsorbed in the molecular form, but at 400°C, an activated adsorption occurs with the evolution of an equivalent of hydrogen fluoride.

If the adsorption energy is great enough to overcome the dissociation energy of a weak acid, the weak acid will be adsorbed in the ionized form. For example, the pH indicator, thymolphthalein in solution at pH9, is present in the molecular, colourless form. A saturated solution of lanthanum hydroxide has a pH of about 9, and when a suspension of this base is shaken with the indicator, the colour of the suspension becomes blue. After settling, the supernatant liquid is colourless; but the precipitate on which the indicator is adsorbed in the ionized form turns dark blue.

Thus, two effects are evident due to positive adsorption of the weak acid. Its concentration at the interface becomes greater than in the bulk of the solution; also, in the adsorbed state, it exhibits a greater tendency to ionize. Due to these effects, there is also a "promotion" of adsorption of selected cations which otherwise would not be adsorbed. Thus, the adsorbed weak acid can then act as a bridge for the adsorption of cations.

The greater tendency to ionize exhibited by adsorbed H_2S over that exhibited by H_2S in the bulk solution, is cited(25) as an explanation for the increased reactivity of Zn^{2+} at the surface of HgS. Hydrous oximes such as Fe_2O_3 and Al_2O_3, that come down in amorphous or finely crystalline form, have a great tendency to adsorb water and OH^- ions, which then attract heavy metal cations to the surface.

However, if too high a concentration of the weak acid or chelating agent is used, soluble metal complexes may form, which may then not be adsorbed.

3. SOLID SOLUTION FORMATION

The extent of solid solution formation depends on how readily the adsorbed ions or ion pairs are incorporated by the precipitate. Chemical and structural properties of both the adsorbed substance and the host precipitate are involved. Often it is difficult to determine what properties dominate the incorporation process.

3.1 Isomorphism

In general, an adsorbate is efficiently collected if it is isomorphous with the host precipitate and a solid solution is formed. Two compounds are said to be isomorphous if their internal crystal structure is similar. However, solid solutions will be formed by isomorphous crystals only if the interatomic bonds in the two crystals are also similar.

According to Skoog and West(6), two compounds are isomorphous if they have:

1) the same type chemical formulas;
2) components whose sizes relative to one another are about the same;
3) component atoms are joined together by the same type of bonding.

If the solubility of one compound in the other is continuous from 0 to 100%, then true mixed crystals are said to be formed(10). In this case, some of the sites normally occupied by the atoms or ions of the host compound are filled with atoms or ions of the isomorphous compound. Usually, in such an isostructural replacement, the lattice constants of the components do not differ by more than ± 5% from each other.

Many examples of coprecipitation involving non-isostructural replacement are known, in which case the miscibility of the compounds is limited and the solids are referred to as anomalous mixed crystals.

Solid solutions are formed chiefly by incorporation of the adsorbate during crystal growth; however, diffusion of the micro-component into the host lattice does occur also, especially during aging at an elevated temperature.

Isomorphous replacement is of very common occurrence in minerals and much valuable data on this phenomenon exist in geochemical literature(26). For interchangeability of ions, V. M. Goldschmidt formulated specific rules:

1) For two ions to be able to replace each other in a crystal structure, their ionic radii should not differ by more than 15%.

2) When two ions, having the same charge but different radii, compete for a lattice site, the ion with the smaller radius is

preferentially incorporated in the lattice.

3) When two ions, having similar radii but different charges, compete for a lattice site, the ion with the higher charge is preferentially incorporated in the lattice.

Ahrens(27) finds that these rules apply to those elements which form essentially ionic bonds, but are inadequate for covalent compounds and most sulphide minerals.

Knowledge of the type of bonding between elements in minerals is, therefore, required.

3.2 Size of atoms and ions

According to a simple hard-sphere model, the atom is spherically symmetrical(53). The electron density is greatest at the nucleus and decreases exponentially as r, the distance from the nucleus, increases. It remains finite, however, for all finite values of r, so that the atom extends to infinity; the greatest part of the atom, however, is near the nucleus - within 1 or 2 Å. Thus it is impossible to isolate an individual atom and determine for it a size or radius which will correctly describe that atom when it is associated with others of the same or different kind in a bulk of material. Any determination of atomic radius must be based upon the atom in its natural environment, as it exists in a mass of pure element or covalently bonded material. It appears that the size of atoms, when they are bonded to each other to form a molecule of an element, and those obtained in purely covalent compounds in which chemical bonds are between atoms of different elements, are identical. As a consequence, the terms atomic radius and covalent radius may be used synonymously.

The atomic radius, therefore, can be measured only as a part of the distance between two atoms that appear to be in contact. If the atoms are of the same element, then the radius is taken as half the internuclear distance. However, for atoms of the same element, there can be two internuclear distances, because the distance between atoms within a molecule is not the same as the distance between atoms of separate molecules. For bonded atoms within a molecule, one-half the bond length is the "covalent radius". Molecules are held by weak "van der Waals' forces"* and the interatomic distance is about 40%, or more, longer than that of the covalent bond.

Metallic radius is half the internuclear distance between nearest neighbours in a metallic crystal. Pauling has shown that metallic and covalent radii are so closely related that they may be used interchangeably. Accordingly, one set of values is sufficient for radii of atoms as they exist in metals or in covalent crystals of the element.

Interionic distances in ionic crystals may be correlated with each other and reduced to more useful terms, by assuming

---

* See glossary.

that each ion involved has a definite radius and that the sum of such radii gives the measured interionic distance. The magnitude of individual ionic radii is thereby dependent upon the method used to apportion interionic distances between the ions in question. The apportionment of interionic distances has been approached theoretically by Pauling(29,30), who emphasized that useful values for ionic radii are those which, when added together with such suitable corrections as are necessary, give the equilibrium interionic distances in crystals. Because the equilibrium interionic distance for two ions is determined not only by the nature of the electron distributions for the ions, but also by the structure of the crystal and the ratio of cation and anion, it was necessary that Pauling base his treatment upon certain so-called standard crystals. For this purpose, Pauling chose alkali halides. His calculated radii are, therefore, relative to those of alkali metal and halide ions and are not absolute in the sense that their sums will always give observed interionic distances. For multivalent ions, such radii are actually those which these ions would possess if they were to keep their individual electronic distributions, but behave in coulombic attraction as if they were univalent. Such radii are termed univalent radii. Pauling has shown that crystal radii, which express correct interionic distances when added, can be calculated from univalent radii by multiplication with an appropriate correction factor in terms of the equation:

$$R_x = R_1 z^{\frac{-2}{n-1}} \qquad \{3\text{-}1\}$$

where R_x and R_1 are, respectively, crystal and univalent radii, z is the ionic charge, and n is a repulsion exponent related to repulsive forces arising from interpenetration of the two ions.

Robertson(31) has shown how Pauling's univalent ionic and single-bond covalent radii are correlated with the ionic heat of hydration.

Ionic radii, listed by Goldschmidt(35), are based on measured distances in crystals which are structurally ionic. A large proportion of these compounds were oxides and cation radii were obtained by subtracting an O^{2-} radius of 1.32 Å. Goldschmidt radii are for six-fold coordination.

According to Pauling, radii of isoelectronic ions (i.e., in the same inert gas sequence, e.g., Ne, O^{2-}, F^-, Na^+, Mg^{2+} etc.) can be obtained from the inverse relationship:

$$r = \frac{1}{Z_{eff}} \qquad \{3\text{-}2\}$$

where Z_{eff} is the effective nuclear charge. The effective nuclear charge is equal to the actual nuclear charge minus the amount of electronic screening, and for a given isoelectronic sequence:

$$r = \frac{K}{Z - S} \qquad \{3\text{-}3\}$$

where S is the screening constant for each ion and K is a constant.

Ahrens(32) found that, within an isoelectronic sequence, ionic radius varies regularly with ionization potential and with charge. He observed that for ions of constant charge within a sequence:

$$r = \frac{1}{I^2}$$

where I is the ionization potential.

Ahrens introduced various empirical adjustments to bring Pauling's radii more into line with observed interionic distances. He also derived additional ionic radii by interpolation methods involving comparisons with ionization potentials.

Schomaker and Stevenson(119) considered that the additivity of covalent radii for bond lengths is not generally valid; the covalent radii must be used with a correction for the effect of the ionic character of the bond. In a recent compilation of ionic radii for use in geochemistry, given by Whittacker and Muntus(33), coordination number and valency are taken into account. A comprehensive table of ionic radii is also given by Smith(34). The handbook by Samsonov(35) gives a comparative table of ionic radii from Goldschmidt, Pauling, Ahrens etc., as well as covalent and metallic radii of elements.

3.3 Bonding in crystals

Metallic bonding in crystal structure occurs where atoms are crowded closely together and some of the outer electrons of each atom are common to all neighbouring atoms. The crystals are soft and have a moderately low melting point. Elements of B-groups of metals and semi-metals generally form metallic compounds with each other.

In covalent bonding, the centers of the constituent atoms are farther apart than in the case of metallic bonding, and the outer electrons, instead of being shared with any and all neighbours, are shared in pairs with one atom only. The bonding electrons are nearly fixed in position in the structure. The crystals are brittle and hard and have a high melting point. Elements of A-groups of metals and non-metals generally form ionic compounds. The greater the ratio of the size of cation to anion, the greater is the tendency toward ionic bonding. Many chemical and physical properties, such as coordination number, interionic distance, molecular volume, density, hardness etc., are interpreted from the ratio of cation to anion radius(36).

In van der Waals' bonding, the units of structure are molecules instead of atoms or ions, and the intermolecular bonding force is of much smaller magnitude than the metallic, covalent and ionic bonding forces. The crystals are soft, weak and plastic and the melting point is very low.

Intermediate bond types occur and there is every gradation possible between the purely metallic bond and the purely covalent bond and between the purely covalent bond and the purely ionic bond. The chemical bonding with characteristics intermediate between ideally covalent and ideally ionic is due to resonance between the two ideal kinds of bonding.

The partially covalent bond is stronger than the simple ionic bond and the lattice energy is larger (more negative). Low solubility has also been mentioned as a frequent, but not invariable, consequence of high lattice energy and partially covalent bonds.

3.4 Guides to the nature of the bond

Refractive index, heat of formation, melting point and polarizability of constituent cations and anions are considered as guides to the nature of the bond in isomorphous minerals and inorganic compounds. Anions are usually polarized to a greater degree than cations and light interaction with the anion usually makes the principal contribution to the total refractive index. Covalent bonds are characterized by a high refractive index; ionic bonds by a low refractive index.

In general, a relatively high heat of formation is indicative of a relatively high degree of ionic character, whereas a relatively low heat of formation indicates a relatively high degree of covalency.

Melting points are useful, but not absolute criteria for indicating bond character; melting points are greatly influenced by crystal structure(37). The melting point of crystals with pure covalent bonds is higher than that of ionic crystals; however, a degree of covalency is reached, such that the melting point is influenced by molecular forces rather than by bond structure. For example, the melting point of MgF_2 (ionic bonds) is 1400°C, that of SiF_4 (covalent bonds) is -77°C. Transition from ionic to covalent bonding is usually accompanied by a reduction in the melting point.

The greater the degree of polarization (deformation) of the constituent cations and anions, the greater is the covalent character of the bond. Covalency is favoured by a number of factors, summarized in a series of generalizations known as Fajans' rules(38). Thus, increased covalency is favoured by:

1) large charge upon either cation or anion;

2) small cation size;

3) large anion size;

4) cation with a non-inert gas atom structure.

Electronegativity is often used as a guide to the nature of the chemical bond. Pauling(29) defined electronegativity as "the power of an atom in a molecule to attract electrons to itself". Quantitatively, electronegativity is expressed in terms of bond dissociation energy, in kilocalories per mole or in electron volts.

The difference in electronegativity between the atoms is regarded as a measure of the degree of electron transfer from one atom to the other on forming the chemical bond between them. The bigger the electronegativity difference between two bond-forming atoms, the greater the degree of ionic character, and *vice versa*. A Sargent-Welch table (catalog number S-18806) of periodic properties of the elements, reproduced in Figure 3.1, conveniently lists Pauling's electronegativities. This table includes a chart showing how the ionic character of a bond varies with the difference in electronegativity.

Sanderson$^{(39)}$ defined an average electronic density as $\frac{3Z}{4\pi r^3}$, where Z is the atomic number and $\frac{4}{3}\pi r^3$ is the volume of the electronic sphere, defined by the non-polar covalent radius r. The average number of electrons per cubic angstrom thus calculated was found to correspond in a general way to the accepted electronegativity values of the elements.

Sanderson considers that the non-polar covalent radius, the homonuclear bond energy and the electronegativity are the most fundamentally useful atomic properties. He uses these parameters to calculate the average bond energy and the partial charge remaining on bonded atoms$^{(39)}$.

Increased covalency is associated also with a large ionic potential, ϕ, which is defined by the ratio of charge to ion radius, $\phi = \frac{z}{r}$(40). The smaller the difference in polarizing power, the easier it is for bonds of a minor constituent to be accepted into the covalent structure of the host.

Difference in electronegativity	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9	2.0	2.1	2.2	2.3	2.4	2.5	2.6	2.7	2.8	2.9	3.0	3.1	3.2
Percent ionic character %	0.5	1	2	4	6	9	12	15	19	22	26	30	34	39	43	47	51	55	59	63	67	70	74	76	79	82	84	86	88	89	91	92

Group 1A	2A	3B	4B	5B	6B	7B	8			1B	2B	3A	4A	5A	6A	7A	8A
H 2.1 1 1.008																	He -- 2 4.003
Li 1.0 3 6.939	Be 1.5 4 9.012											B 2.0 5 10.811	C 2.5 6 12.011	N 3.0 7 14.007	O 3.5 8 16.000	F 4.0 9 18.998	Ne -- 10 20.183
Na 0.9 11 22.990	Mg 1.2 12 24.312											Al 1.5 13 26.982	Si 1.8 14 28.086	P 2.1 15 30.974	S 2.5 16 32.064	Cl 3.0 17 35.453	Ar -- 18 39.948
K 0.8 19 39.102	Ca 1.0 20 40.08	Sc 1.3 21 44.956	Ti 1.5 22 47.90	V 1.6 23 50.942	Cr 1.6 24 51.996	Mn 1.5 25 54.938	Fe 1.8 26 55.847	Co 1.8 27 58.933	Ni 1.8 28 58.71	Cu 1.9 29 63.546	Zn 1.6 30 65.37	Ga 1.6 31 69.72	Ge 1.8 32 72.59	As 2.0 33 74.922	Se 2.4 34 78.96	Br 2.8 35 79.904	Kr -- 36 83.80
Rb 0.8 37 85.47	Sr 1.0 38 87.62	Y 1.3 39 88.905	Zr 1.4 40 91.22	Nb 1.6 41 92.906	Mo 1.8 42 95.94	Tc 1.9 43 (97)	Ru 2.2 44 101.07	Rh 2.2 45 102.905	Pd 2.2 46 106.4	Ag 1.9 47 107.868	Cd 1.7 48 112.40	In 1.7 49 114.82	Sn 1.8 50 118.69	Sb 1.9 51 121.75	Te 2.1 52 127.60	I 2.5 53 126.904	Xe -- 54 131.30
Cs 0.7 55 132.905	Ba 0.9 56 137.34	La *1.1 57 138.91	Hf 1.3 72 178.49	Ta 1.5 73 180.95	W 1.7 74 183.85	Re 1.9 75 186.2	Os 2.2 76 190.2	Ir 2.2 77 192.2	Pt 2.2 78 195.09	Au 2.4 79 196.967	Hg 1.9 80 200.59	Tl 1.8 81 204.37	Pb 1.8 82 207.19	Bi 1.9 83 208.98	Po 2.0 84 (210)	At 2.2 85 (209)	Rn -- 86 (222)
Fr 0.7 87 (223)	Ra 0.9 88 (226)	Ac **1.1 89 (227)															

*	Ce 1.1 58 140.12	Pr 1.1 59 140.91	Nd 1.2 60 144.24	Pm -- 61 (145)	Sm 1.2 62 150.35	Eu -- 63 151.96	Gd 1.1 64 157.25	Tb 1.2 65 158.92	Dy -- 66 162.50	Ho 1.2 67 164.93	Er 1.2 68 167.26	Tm 1.2 69 168.93	Yb 1.1 70 173.04	Lu 1.2 71 174.97
**	Th 1.3 90 232.038	Pa 1.5 91 (231)	U 1.7 92 238.03	Np 1.3 93 (237)	Pu 1.3 94 (242)	Am 1.3 95 (243)	Cm 96 (247)	Bk 97 (247)	Cf 98 (251)	Es 99 (254)	Fm 100 (257)	Md 101 (256)	No 102 (254)	Lw 103 (257)

KEY

Symbol -	Zn 1.6	- Electronegativity (Pauling's)
Atomic Number -	30	
	65.37	- Atomic Weight

Fig. 3.1 Periodic table of the elements and their electronegativity.

4. DISTRIBUTION LAWS

The incorporation of a microcomponent into a solid phase can be treated as an ion-exchange process, i.e., the exchange of a macrocomponent ion by a microcomponent ion. The replacement of ions within the solid may be regarded as a two-step process involving surface adsorption, followed by incorporation into the host lattice with ~~free~~ diffusion. For example:

$$P^+(\text{ads}) + I^+(\text{soln}) \rightleftarrows I^+(\text{ads}) + P^+(\text{soln})$$

$$I^+(\text{ads}) + AP(\text{solid}) \rightleftarrows AI(\text{solid}) + P^+(\text{ads})$$

The overall equilibrium is given by the equation

$$AP(\text{solid}) + I^+(\text{soln}) \rightleftarrows AI(\text{solid}) + P^+(\text{soln}) \qquad \{4\text{-}1\}$$

For the reaction {4-1} the thermodynamic equilibrium constant, K_a, is defined in the relation

$$\Delta G^\circ = -RT \ln K_a$$

where K_a is the ratio of the product of activities of products and reactants, ΔG° is the standard free-energy change for the ion-exchange process and R and T are the molar gas constant and absolute temperature, respectively.

In practice, the equilibrium is usually expressed by a distribution coefficient which mathematically is the slope of the ion-exchange isotherm (plot of the amount of microcomponent incorporated vs. amount of microcomponent in solution) at one specific point. The use of the distribution coefficient is particularly advantageous if the microcomponent is present only in trace quantities. In such cases, the exchange extends only over a short section of the isotherm near the origin. Usually this short section is practically linear so that, in the range under consideration, the distribution coefficient is independent of concentration.

4.1 Berthelot-Nernst distribution law

The fundamental law that controls the distribution (i.e., partition) of a trace component between coexisting phases was first published by Berthelot (1872) and later given a theoretical foundation by Nernst (1891). It is usually referred to as the Berthelot-Nernst distribution law. According to this law, at equilibrium, the ratio of the concentration of the microcomponent in the solid, C_s, to its concentration in the liquid, C_l, is a constant, i.e.,

$$\frac{C_s \text{ (g. microcomponent/cc solid)}}{C_l \text{ (g. microcomponent/cc soln.)}} = k \qquad \{4\text{-}2\}$$

The constant k is called the distribution or partition coefficient$^{(41)}$.

The Berthelot-Nernst distribution law is adhered to if the partition takes place from a dilute solution in which both phases are at equilibrium and the microcomponent has the same molecular state in both phases. A major change in the composition of the liquid or the solid affects the value of k.

4.2 Homogeneous distribution law

A more convenient form of the distribution law was introduced by Henderson and Kracek$^{(42)}$. Here the term distribution not only means partition between phases, but also, when the law is obeyed, signifies a continuous distribution of the microcomponent throughout the solid phase. Thus, in the absence of concentration gradients of the microcomponent in the crystal, the partition of the microcomponent between the precipitate and aqueous solution is expressed by the equation

$$\left(\frac{I}{P}\right)_{\text{solid}} = D\left(\frac{I^+}{P^+}\right)_{\text{solution}} \qquad \{4\text{-}3\}$$

Here the ratio of the amount of microcomponent to the amount of macrocomponent $\left(\frac{I}{P}\right)$ in the crystal depends on the ratio of the amounts of the two components in solution. Thus, D is defined by ratios instead of concentration units. Equation {4-3} is based on a model in which the entire solid phase is in equilibrium with the entire liquid phase and thus characterizes the homogeneous distribution law. D is called the <u>homogeneous distribution coefficient</u> and is related to k as follows$^{(41)}$:

$$D = k\left(\frac{\text{grams macrocomponent/cc of saturated solution}}{\text{gram macrocomponent/cc of solid}}\right) \qquad \{4\text{-}4\}$$

In the absence of concentration gradients in the coexisting phases, D represents a state of thermodynamic equilibrium and is then a function of temperature only. Under these conditions, $D = k = K_0$, where K_0(14) is the ratio of solubilities of the salts AP and AI having a common anion. For non-ideal conditions:

$$D = K_0 \left(\frac{\gamma_{AP}}{\gamma_{AI}}\right)^2 \exp\left[\frac{-\Delta G_I}{RT}\right] \qquad \{4\text{-}6\}$$

where γ_{AP} and γ_{AI} are the activity coefficients of the macro-component and microcomponent salts having a common anion, A^-, and ΔG_I is the excess partial molar free energy of solid solution. The excess free energy of solid solution formation is the partial molar free energy change involved in transferring one mole of microcomponent, as cation, from a large quantity of ideal solid solution to the real solid solution of the same mole fraction(123). Thus, the direct connection between D and K_0 is masked by the non-ideal behaviour of the solution expressed by the activity coefficients and by the non-ideal behaviour of the solid, expressed by the excess function.

For values of D greater than unity, the precipitate is enriched in the microcomponent; for values of D less than unity, the aqueous solution is enriched in the microcomponent.

4.3 Logarithmic distribution law

The logarithmic distribution law, derived by Doerner and Hoskins(43), is based on a model in which only the surface of the solid phase is in equilibrium with the aqueous phase and the rate of mixing in the solid is small compared to the rate of precipitation. This law is adhered to where crystal growth takes place from a supersaturated solution. Such conditions prevail when a precipitate is formed slowly, using the technique of precipitation from homogeneous solution(2) or by slow evaporation of supersaturated solution. Each crystal layer, as it forms, is in equilibrium with the particular concentration of solution existing at that time and the number of crystals is, in the main, the same during the entire process of crystallization (heterogeneous nucleation). As a result, the concentration of the microcomponent within the crystal varies continuously from the centre to the periphery.

Putting equation {4-3} in a differential form, the following equation is obtained:

$$\frac{d(I_0^+ - I^+)}{d(P_0^+ - P^+)} = \lambda \frac{I^+}{P^+}$$

where P^+ and I^+ are the total quantities of microcomponent and macrocomponent, respectively, in solution at any time, P_0^+ and I_0^+ are the corresponding quantities of macrocomponent and microcomponent initially present in solution. The distribution coefficient, λ, is characteristic of the precipitating system. If this equation is integrated over the conditions of precipitation, the logarithmic distribution law of Doerner and Hoskins is obtained:

$$\log \left(\frac{I_0}{I_f}\right)_{\text{solution}} = \lambda \log \left(\frac{P_0}{P_f}\right)_{\text{solution}} \qquad \{4\text{-}7\}$$

in which I_0 and I_f represent the initial amount and the final amount (i.e., before and after precipitate formation) of the microcomponent in aqueous solution, and P_0 and P_f have a corresponding representation for the macrocomponent.

For small amounts of I coprecipitated, the most probable error in λ is minimized by using an alternate form of equation {4-7}(80):

$$\log\left(1+\frac{\text{total moles I in final precipitate}}{\text{total moles I in final solution}}\right) = \lambda \log\left(1+\frac{\text{total moles P in final precipitate}}{\text{total moles P in final solution}}\right) \tag{4-8}$$

For values of λ greater than unity, the precipitate is enriched in the microcomponent which is concentrated near the centers of the crystals. For values of λ less than unity, the microcomponent is found near the surface or the crystals and it is the solution that is enriched in microcomponent.

4.4 Experimental techniques

To determine the nature of the distribution, λ and D are plotted against the fraction of macrocomponent precipitated (see figures 4.1, 4.2 and 4.3). When λ is constant over the entire precipitation range, the logrithmic law is adhered to; when D is constant over the entire precipitation range, the homogeneous distribution law is obeyed.

The coefficients λ and D are calculated using the results of analyses of the solution before and after precipitate formation, or from the results of analyses of the precipitate and the filtrate. If the precipitate is formed by the technique of precipitation from homogeneous solution, fractional yields of precipitate are obtained by allowing the reaction to proceed for different time intervals,at the end of which the precipitate is filtered. If the precipitate is formed by the direct addition of precipitant, fractional yields of precipitate are obtained by adding different substoichiometric amounts of the precipitant.

Solid solution formation is an <u>enrichment system</u> if λ and D have high positive values in the initial fractions of the precipitate and D is increasing in the late fractions (figure 4.1). In such a system, λ usually decreases slightly as the fraction of precipitate becomes larger because increased contact time favours homogeneous distribution. In <u>derichment systems</u>, λ and D are less than unity and D decreases in the late fractions of the precipitate because longer contact time permits recrystallization which favours enrichment in solution (fig. 4.2).

Anomalous mixed crystal formation is indicated if λ begins near zero in the initial precipitate fractions, remains near zero during the precipitation process, but rapidly approaces unity in the very last stage of precipitation. This is because macrocomponent ions compete successfully with microcomponent

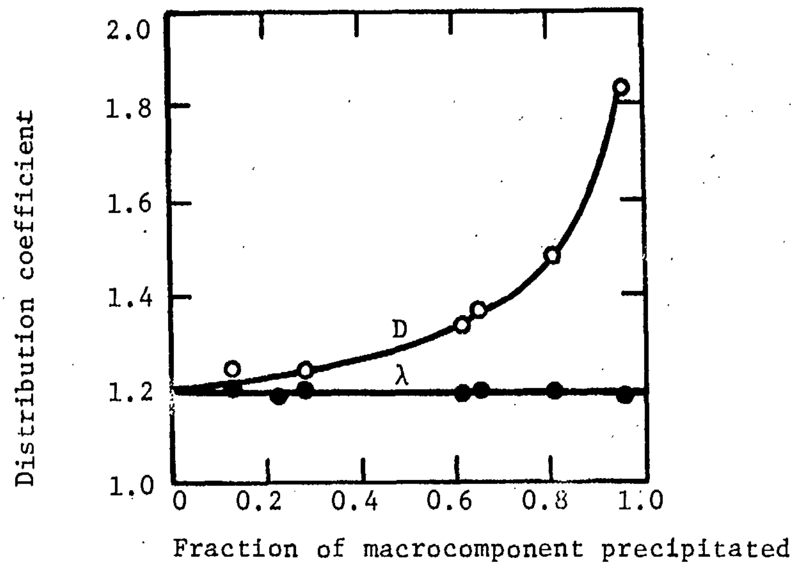


Figure 4.1 Variation of D and λ with fractional yield of precipitate in an enrichment system.

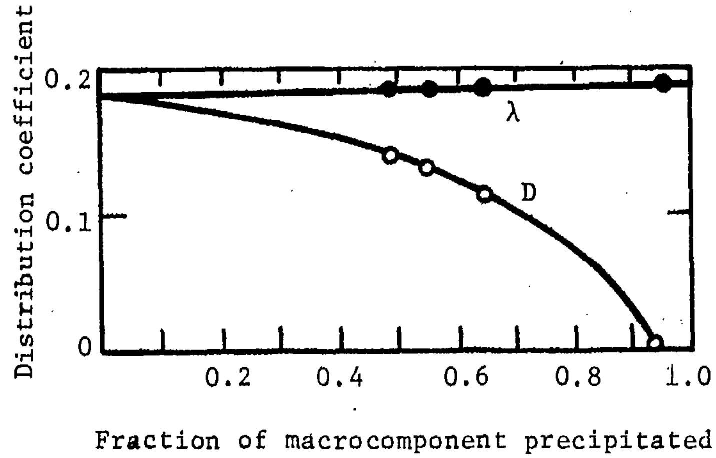


Figure 4.2 Variation of D and λ with fractional yield of precipitate in a derichment system.

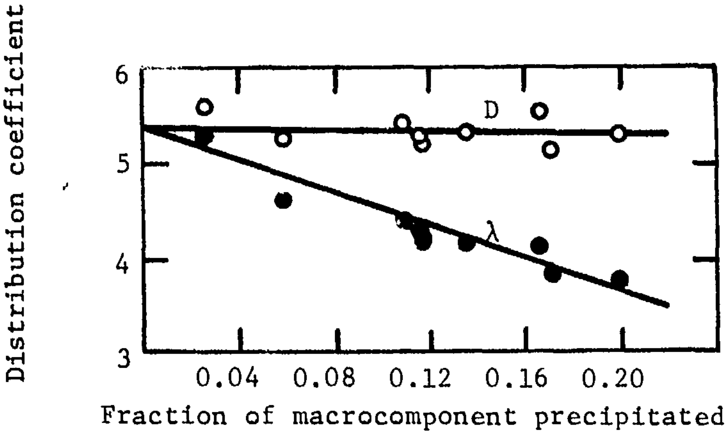


Figure 4.3 Distribution of microcomponent in an enrichment system upon slow crystallization (with vigorous agitation) from a supersaturated solution. A homogeneous precipitate results due to prolonged digestion through recrystallization and diffusion processes.

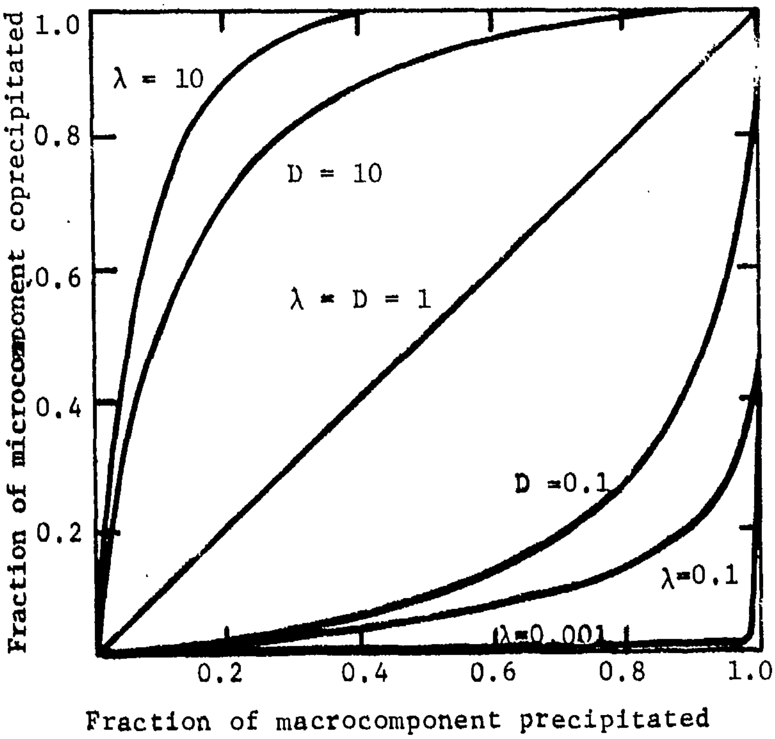


Figure 4.4 Efficiency with which the microcomponent is carried for various values of the distribution coefficients, D and λ

ions during the precipitation process, but there is strong adsorption of microcomponent ions at the end of the precipitation process. For such a system, it is possible to precipitate all but a small fraction of the macrocomponent without the characteristic sharp rise in coprecipitation. As a result, coprecipitation can be minimized by using a two-stage precipitation technique(2).

The values of D and λ are not affected by the rate of stirring, but a marked variation in the values occurs if the solution is not stirred at all. Both D and λ are affected by the rate of precipitate formation. The λ value approaches its maximum value of D ($\lambda_{max} = D$) as the supersaturation approaches zero, i.e., when the rate of formation of the precipitate is extrapolated to zero.

The distribution laws are of value for comparing various separation methods. The greater the deviation of the values of D and λ from unity, the greater the separation.

The efficiency of the separation under given conditions is seen in a plot of the fraction of microcomponent coprecipitated vs. fraction of macrocomponent precipitated. For the same value of D and λ ($D = \lambda$), it is seen in figure 4.4 that coprecipitation is favoured in a system that obeys the logarithmic law. Therefore, if the purpose is to enrich the solid in microcomponent, then precipitation conditions are chosen which favour the logarithmic distribution, for example, slow precipitation from a supersaturated solution followed immediately by filtration. If the purpose is to maintain coprecipitation at a minimum, then conditions are chosen which favour homogeneous distribution, for example, rapid relief of supersaturation followed by prolonged digestion.

5. OCCLUSION

The occlusion mechanism plays a very important role in the technique of concentration by coprecipitation. Kolthoff(11) defined occlusion as the process which occurs when foreign ions are adsorbed at the surfaces of a growing precipitate and are then covered over by the subsequent formation of new layers. He maintained that, in the absence of mixed crystal formation, coprecipitation due to occlusion is "real coprecipitation". Essentially, occlusion is the entrapment of counter ions during the growth, recrystallization or agglomeration of the precipitate.

The amount of coprecipitation by occlusion depends chiefly on four factors:

1) the sign and amount of charge on the precipitate surface;
2) the strength of adsorption forces between the microcomponent and precipitate surface;
3) the concentration of the microcomponent; and
4) the rate of entrapment of the adsorbed microcomponent, i.e., on the rate of precipitate formation.

The entrapment mechanism and some chemical and physical characteristics of precipitates containing occluded impurities will be discussed. The mechanics and kinetics of precipitate formation will be considered in the next chapter.

5.1 Entrapment mechanism

If, in the early stages of precipitation, the solution contains an excess of lattice cations, e.g., to a concentrated solution of $BaCl_2$ is added a dilute solution of Na_2SO_4, the barium cations are preferentially adsorbed and give to the precipitate surface a positive charge. This charge is balanced by the negative charge of the counter anions (Cl^-) in the diffuse part of the electrical double layer. With further addition of Na_2SO_4, the precipitant anions (SO_4^{2-}) displace the chloride counter anions and combine with the adsorbed barium ions. If the precipitation takes place rapidly, some of the chloride counter anions are not displaced in time and become completely surrounded by the growing solid. In this case, there is entrapment of surface-adsorbed lattice cations (Ba^{2+}) and chloride anions. If the order of mixing of reagents is reversed so that to a strong solution of Na_2SO_4 is added a dilute solution of $BaCl_2$, the sulphate anion will give a negative charge to the precipitate surface and sodium ions will be entrapped.

From a complex solution, evidence suggests those ions are preferably entrapped that form strong bonds with the surface-adsorbed ions; otherwise, they are pushed away from newly-formed crystal layers and, consequently, are not trapped by them. The adsorption energy of counter ions must be greater than their hydration energy. That is, the less soluble the adsorption product, the greater its adsorbability(45). Nevertheless, the bond between surface-adsorbed ions (those that determine the surface charge) and counter ions is chiefly electrical in nature and all ions with electrical sign opposite to that on the surface compete for adsorption sites in the electrical double layer. Thus, indifferent ions that adsorb weakly are also trapped and hinder entrapment of substances that adsorb strongly.

Adsorbed substances on certain sites prevent three-dimensional growth of crystals. From a supersaturated solution in the presence of some impurities, fine-grained, ill-formed or dendritic crystallites (branch-like crystalline structures) may be produced. Dendritic growth provides a means of entrapping adsorbed compounds and solvent in re-entrant angle traps(14). That is, if the ions diffuse to the crystal surface more rapidly than the solvating molecules can diffuse away, the growth of normally fast-growing surfaces is blocked; however, the corners continue to grow and, subsequently, to join over entrapped ions and possibly over entrapped pools of solution.

Entrapment can occur also by recrystallization, after primary precipitate particles have formed(59). Rapid recrystallization of a fresh precipitate extracts, temporarily, a relatively large quantity of adsorbate, because the surface originally exposed becomes buried. The aggregation of particles is faster than the release of adsorbate into solution.

Eventually, the abnormally rich solid approaches equilibrium by continued recrystallization and entrapped compounds are released.

Entrapped radioelements can be distinguished in radioautographs(15); a non-uniform distribution of the entrapped radioactive material is seen, often concentrated along certain internal surfaces or areas of the crystal. Different elements concentrate at different surfaces, but the behaviour of a given element seems to be consistent(11).

Gordon, Teicher and Burtt(44) studied Mn(II) coprecipitation on basic stannic sulphate which was precipitated from homogeneous solution by the hydrolysis of urea. The rate of formation of the precipitate was controlled by changing the temperature of the hydrolysis reaction. At 76°C, the rate of precipitate formation was slow and coprecipitation of Mn(II) occurred only in the very last fraction of the tin precipitated. This is characteristic of a system in which anomalous mixed crystals are formed. At 97°C, precipitation was rapid and most of the manganese was coprecipitated in the early stages of the precipitation process, where less than 25% of the tin was precipitated. The authors attribute this coprecipitation in the early stages of precipitate formation to occlusion caused by the initial supersaturation effect. Coprecipitation by occlusion during the formation of the major portion of the precipitate was not a significant factor. Thus, during the intermediate stages of precipitation, the precipitate was much more selective in its choice of cations. In the final stages of precipitation, the precipitate behaved as an adsorbent for manganous ions.

Salutsky(10) concludes that manganese occlusion in the initial stages of precipitation occurs during the nucleation period. When the precipitation rate is reduced by lowering the hydrolysis temperature, fewer nuclei are formed and the initial coprecipitation by occlusion is eliminated.

5.2 Characteristics of occlusion

From their work with radioactive elements, Bonner and Kahn(15) found that occlusion is characterized by:

1) variations in the values of the distribution coefficient obtained under similar conditions;

2) suppression of carrying (incorporation) by the presence of an excess of the lattice ion whose charge is of the same sign as the traces (microcomponent) or by the presence of other, highly-charged ions of the same sign;

3) ordered discontinuities in the distribution of the tracer in the crystal as shown by radioautographs.

Hermann(124) found that the coprecipitation of americium with lanthanum oxalate (an enrichment system) decreased as the rate of precipitation increased. At a constant rate of precipitation, the "observed" logarithmic distribution coefficient was substantially constant, independent of the quantity of lanthanum precipitated. His experimental data indicated that the logarithmic distribution coefficient, λ, varies directly with the rate of precipitation in derichment systems ($\lambda < 1$), but inversely with the rate of precipitation in enrichment systems ($\lambda > 1$).

Hermann and Suttle(123,124) separate that part of incorporation due to solid solution from that part due to occlusion, by identifying these phenomena with the following differential equation:

$$\frac{dy\,(\text{macrocomponent})}{dx\,(\text{microcomponent})} = \left(\frac{1}{2}\right)\left(\frac{y^{o}}{x}\right) + \frac{(Y-y^{o})}{x} \qquad \{5\text{-}1\}$$

where y and x are the total quantities of macrocomponent and microcomponent ions, respectively, in solution at any time, y^{o} is the total quantity of macrocomponent ion in a saturated solution and λ is the logarithmic distribution coefficient. The first part of the right-hand side of equation {5-1} is identified with incorporation under equilibrium conditions (solid solution formation) and the second part contributes to incorporation by occlusion.

Hermann and Suttle define <u>fractional supersaturation</u> S as follows:

$$S = \frac{(y - y^{o})}{y} \qquad \{5\text{-}2\}$$

where y and y^{o} have the same notation as in equation {5-1} and S lies within the interval from 0 to 1. They then find the following relation between S, λ and the "observed" logarithmic distribution coefficient λ^1:

$$\lambda^1 = \frac{\lambda}{\{1 + (\lambda - 1)S\}} \qquad \{5\text{-}3\}$$

These equations show how occlusion depends on the degree of supersaturation and, therefore, on the rate of precipitate formation.

Schneider and Rieman$^{(45)}$ show that digestion is more effective in removing occluded barium salts, such as barium iodide or nitrate, from a barium sulphate precipitate, than in removing barium nitrite, which is thought to be incorporated as a solid solution.

Occlusion is more prevalent with colloidal precipitation than with large crystalline precipitates. Freshly precipitated hydroxides and sulphides generally contain a moderate quantity of occluded impurities, most of which are released upon aging of the precipitate in the mother liquor.

6. PRECIPITATE FORMATION

The rate of precipitate formation determines the surface area of the precipitate particles, the degree of order in the crystals and the extent of entrapment of adsorbed material. The rate at which the precipitate is produced is dependent on two factors: the rate of nuclei formation and the rate of growth of nuclei to crystal size. The supersaturation phenomenon is the driving force that produces these changes.

Haber(46) described precipitation in terms of aggregation velocity and orientation velocity. In supersaturated solutions, molecules or aggregates of molecules accumulate to give larger aggregates. The speed of this process is the aggregation velocity. The aggregates formed from highly supersaturated solutions are mixed in an arbitrary manner (there is no orderly growth) and the separated particles are amorphous, that is, they do not show an X-ray pattern. The disordered aggregates tend to reach a state of order and the speed with which this process takes place is called the orientation velocity.

Von Weimarn(47) recognized two stages in the process of precipitate formation: the first, in which the molecules in solution condense to ultramicroscopic nuclei, and the second which is concerned with diffusion-controlled growth of nuclei. The velocity, W, of nuclei formation was given by:

$$W = K\frac{\text{precipitation pressure}}{\text{precipitation resistance}} = K\,\frac{Q - L}{L} \qquad \{6\text{-}1\}$$

where Q is the total concentration of substance which forms the precipitate, L the solubility of coarse crystals and K is a constant. The value of Q - L is called the absolute supersaturation and $\frac{Q - L}{L}$ is the relative supersaturation.

The rate of growth, V, of nuclei to crystal size is a function of the absolute supersaturation and is given by the simplified Noyes-Nernst expression(13):

$$V = k(Q - L) \qquad \{6\text{-}2\}$$

in which k is a proportionality constant.

Thus a supersaturated solution contains a greater quantity of dissolved salt, Q, than is predicted by the solubility product L; and, according to Von Weimarn, the relative supersaturation is the driving force for nuclei formation, while the absolute supersaturation is the driving force for crystal growth.

6.1 Supersaturation

Ostwald(48) considered that a supersaturated solution is metastable and can remain indefinitely in a metastable state until suitably inoculated for crystal formation. Beyond the metastable limit, the solution was regarded as labile, i.e., it was subject to spontaneous crystallization. By plotting solubility vs temperature (supersolubility curves), early workers found that some substances possessed a large metastable region and others a small metastable region.

Supersaturation depends on the difference between the total hydration energy of precipitating ions and the lattice plus surface energies of the precipitate particles. The Ostwald-Freundlich equation$^{(8)}$, derived for non-ionic solids, relates the solubility of the solid to its state of subdivision:

$$\frac{RT}{M} \ln \frac{S_2}{S_1} = \frac{2\gamma}{\rho}\left(\frac{1}{r_2} - \frac{1}{r_1}\right) \qquad \{6\text{-}3\}$$

in which S_2 and S_1 are the solubilities of spherical particles of radii r_2 and r_1 respectively, M is the molecular weight, γ the surface tension at the solid-liquid interface and ρ is the density of the solid. The quantity RT has its usual significance. If r_1 is very large then $\frac{1}{r_1}$ is negligible and S_1 may be replaced by S, the solubility of large crystals. Therefore:

$$RT \ln \frac{S_r}{S} = \frac{2\gamma V}{r} \qquad \{6\text{-}4\}$$

where V is the molar volume and S_r is the solubility of particles of radius r.

For ionic solids, the solubility can be expressed by the solubility product, therefore:

$$RT \ln \frac{(K_{s.p.})_r}{K_{s.p.}} = \frac{2\gamma V}{r} \qquad \{6\text{-}5\}$$

These equations show that crystals possessing a high surface tension and a large molecular volume have a greater tendency to form supersaturated solutions. A rough correlation of calculated surface tension has been observed both with hardness(3) and with melting point(47).

6.2 Nucleation

By nucleation is meant the formation within a supersaturated solution of the first particles of precipitate capable of spontaneous growth. Klein and Gordon(49) consider that it is during the nucleation period that the number of precipitate particles and their final size are fixed. Walton(14) states that nucleation controls the number, size and structure of the precipitate particles.

Nucleation is regarded as a series of stepwise reactions proceeding as follows:

$$A + A = A_2$$

$$A_2 + A = A_3$$

$$A_{x-1} + A = A_x \text{ (critical cluster or nucleus)}$$

$$A_x + A \xrightarrow{\text{nucleation}} A_{x+1}$$

$$A_{x+1} + A \longrightarrow \text{crystal growth}$$

All polymers smaller than the nucleus are called clusters. Polymers exceeding the nucleus size are termed crystallites or particles. They are in a separate phase and their solubilities decrease with increasing size in a manner indicated by equation {6-3}. Recently, Kampmann(50) dropped the restriction that nucleation occurs by aggregation of monomers only and assumes that particles may grow by aggregation of clusters, while they dissolve by dissociation of monomers only.

The interaction between ions and molecules which leads to cluster formation and to nuclei may be likened to a chemical reaction. In a chemical reaction the activation energy is a barrier which must be surmounted before products may be formed; similarly, the energy barrier to nucleation must be overcome before crystallization can occur. This energy barrier to nucleation is overcome by the creation of a supersaturated solution.

Two theoretical approaches to nucleation have been proposed. The classical theory as given by Volmer-Becker-Doering-Frenkel(14) uses the work of formation of the nucleus as the activation energy for the nucleation rate. The more empirical approach, developed by Christiansen and Nielson(51), concerns itself with the nature of the induction period, which is the interval between the time of mixing two solutions to form a supersaturated solution and the time when precipitation is first observed. The difference between the two nucleation theories hinges upon the variability of the nucleus size with electrolyte concentration(52). The Volmer theory relates the size of the critical cluster, or nucleus, to the degree of supersaturation, whereas the Christiansen theory postulates a true critical size for the nucleus, and the size is invariant with the supersaturation. The two nucleation theories lead to different concepts of supersaturation.

a) Volmer-Becker-Doering-Frenkel theory of nucleation

The rate of nucleation, $\frac{dN}{dt}$, is derived from the law of mass action and is expressed by the equation:

$$\frac{dN}{dt} = j = A \exp \left(\frac{- \Delta G^{o}}{kT}\right) \qquad \{6\text{-}6\}$$

where ΔG^{o} is the standard free-energy change required to create the surface of the new phase, A is a constant, k and T have their usual significance. For a spherical nucleus of diameter i created from stationary ions, where the change in energy of the system is related to the bonds formed, ΔG^{o} is given by:

$$\Delta G^{o} = \frac{\pi i^{3}}{6} (\Delta Gv) + \pi i^{2} \gamma \qquad \{6\text{-}7\}$$

where ΔGv is the volume free-energy change (negative sign) and γ is the interfacial energy per unit area of surface. For large nuclei, the volume term predominates, for small nuclei, the surface term predominates. In terms of supersaturation, ΔGv is given by:

$$\Delta Gv = \frac{mkT}{v} \ln S = \frac{4\gamma}{i} \qquad \{6\text{-}8\}$$

where m is the number of ions in the neutral molecule, S (i.e., $\frac{Q}{L}$) is the supersaturation(53) and v is the volume per molecule. The maximum free-energy change, i.e., the activation energy barrier to nucleation, is given by:

$$\Delta G^* = \frac{16\pi\gamma^3 v^2}{3(mkT \ln S^*)^2} \qquad \{6\text{-}9\}$$

where S* is the critical supersaturation.

The theory predicts, therefore, a critical supersaturation, S*, from which γ can be calculated. It predicts that both the size of the nucleus and the rate of nucleation vary with supersaturation.

It is postulated(54) that a supersaturated solution is not really supersaturated with respect to molecular dissolution (monomers) of the crystal phase. Rather, excess solute over the saturation limit exists as a separate "phase" in the form of groups or clusters. Thus a supersaturated solution is composed of clusters dispersed in an essentially homogeneous phase of the saturated molecular solution. These clusters are the building blocks during crystal growth.

It is not ruled out that the clusters, together with the media in which they occur, constitute a colloidal system. Small amounts of ionic material suffice to create the double layers essential to long-time stability. Hirano(55) electrolyzed a saturated solution of sodium nitrate between two platinum electrodes; solute crystals appeared first only on the cathode and in its neighbourhood, the initial crystallization was never found in the anodal region. He assumes the phenomenon is due to the movement of the charged nuclei toward the cathode. He points out that a glass surface, being negatively charged with respect to the electrolytic solution, behaves like a cathode and causes cataphoresis and crystal formation. This is the well known creeping phenomenon.

b) Christiansen-Nielsen theory of nucleation

The Christiansen-Nielson theory$^{(51)}$ is based on the interpretation of the length of the induction period, which is presumed to be closely related to the order of the nucleation reaction. The induction period is the time interval between the time of mixing two solutions to form a supersaturated solution and the time when precipitation is first observed. As in the Becker-Doering theory, ion clusters are considered to be formed by bimolecular steps leading to a critical nucleus, which then grows spontaneously. Christiansen and Nielson proposed that the precipitation rate, R, could be expressed in terms of the ion concentration, c, by:

$$R = k_1 c^p \qquad \{6\text{-}11\}$$

where p is the number of ions in the critical cluster. They argued that, provided the precipitate particles become visible when $c \sim c_o$, then the induction time, t_I, is related to concentration by:

$$\frac{1}{t_I} = k_2 c_o^{p-1} \qquad \{6\text{-}12\}$$

where c_0 is the initial concentration just after mixing.

The Christiansen-Nielson theory predicts a small critical nucleus size independent of the amount of supersaturation. The theory assumes that the supersaturated solution initially contains no clusters and that some finite time interval is required to form the nuclei, with precipitation again occurring when there is an appreciable concentration of clusters. It is considered that nucleation and growth occur during the induction period; at the end of the induction period, growth alone occurs.

In summary, both nucleation theories consider a slow growth process to exist during the induction period, the end of which is marked by the disappearance of an appreciable fraction of free ions from solution. Becker and Doering assume that the critical nuclei grow rapidly to form droplets and a steady-state concentration of solute ions exists which is much lower than the concentration that would correspond to supersaturation. Nucleation is therefore a high-order process (proportional, say, to c^{100}). Christiansen and Nielson consider, since the induction period is a relatively low-order function (3rd to 9th power) of concentration, then the critical nucleus contains a relatively small number of ions. They assume, therefore, the existence of a small critical nucleus, of size independent of the supersaturation ratio. The growth process is considered to proceed only by the disappearance of free ions from solution.

c) Homogeneous nucleation

Both nucleation theories predict a critical supersaturation for the onset of homogeneous nucleation (i.e., the nuclei are the same compound as the precipitate). At the critical supersaturation concentration, crystal formation proceeds spontaneously, thus the attainment of critical supersaturation is characterized by the sudden appearance of a large number of precipitate nuclei.

As a practical matter, homogeneous nucleation is difficult to attain. Trace amounts of insoluble matter which act as nucleation sites, are always present in reagent and solvents. In nucleation studies, reagent solutions are usually purified of such insoluble matter by the precipitation of a small portion of the reagent and subsequent filtration.

d) Heterogeneous nucleation

The nucleation which occurs on foreign surfaces such as those of impurities, vessel walls or gas bubbles, is called heterogeneous nucleation. The presence of a preformed interface lowers the energy barrier to nucleation and hence catalyzes the nucleation process.

Not all impurity particles are equally efficient in serving as nucleation sites. Favourable nucleation sites in the substrate will be those where strong adsorption occurs, particularly if bonding with the substrate is possible. The degree of effectiveness is determined also by the lattice match between the precipitate crystal and the impurity substrate.

In coherent nucleation(14), the position of depositing ions onto an ionic substrate is determined entirely by the substrate lattice configuration. In incoherent nucleation, clustering is determined by the lattice of the deposit rather than the substrate. The critical supersaturation, necessary for heterogeneous nucleation, increases with mismatch between nucleus and substrate.

It is a common occurrence in cases where orientation of the nuclei is determined by the orientation of the substrate lattice, that nucleation occurs in a random fashion at various sites on a substrate surface. This case of oriented overgrowth is called epitaxy. Much interest has been shown in trying to explain why one type of heterogeneous nucleation occurs in a random fashion, while another leads to ordered nucleation and growth.

At a higher supersaturation, if the growing crystal cannot dissipate heat fast enough, it can adjust its surface area to optimize heat dissipation by taking on a dendritic form. There is evidence to suggest that adsorbed soluble impurities can prevent three-dimensional growth and also cause dendritic growth. The side branches of dendrites may fall off and act as nuclei for further crystallization. When such primary nuclei give birth to large numbers of fresh nuclei, the process is termed secondary nucleation(56). The rate of secondary nucleation is dependent on the degree of agitation of the solution, the degree of supersaturation and the type of crystal which is being formed. This kind of nucleation has just begun to receive interest, because it is now relatively clear that the nucleations that occur in the suspensions of crystals encountered in industrial crystallizers are predominantly secondary nuclei.

6.3 Particle number

Only heterogeneous nucleation occurs below the critical supersaturation that is required for homogeneous nucleation. The number of solid-phase impurity particles present in solution is fixed ($\sim 10^6 - 10^8$ heteronuclei per ml); hence the number of precipitate particles formed is fixed. However, if the impurity particles are of varying nucleation efficiency, the particle number will vary with supersaturation. It was pointed out that at a certain degree of supersaturation secondary nucleation can occur and therefore a greater number of particles than expected will be produced.

When the critical supersaturation required for homogeneous nucleation is reached, there is a large irruption of nuclei, the number depending on the solution concentration. Unless agglomeration takes place, each nucleus can grow to form a new particle.

6.4 Particle size

Particle size is dependent on the relative rates of nuclei formation and particle growth. If the impurity particles are all equally efficient in catalyzing heterogeneous nucleation, the particle size will increase uniformly with increasing supersaturation. If the impurity particles are of varying nucleation efficiency, particle size will vary with supersaturation. A maximum particle size is usually found at or about the concentration corresponding to that causing homogeneous nucleation, because maximum solute is then delivered for the growth of each crystal.

At the critical supersaturation, homogeneous nucleation competes with crystal growth, and the particle size decreases with a further increase in concentration.

6.5 Amorphous precipitates

At critical supersaturation, the critical nucleus is typically the size of a few unit cells. At a much higher concentration of reagents the critical nucleus is much smaller and loses its identity with the crystal phase. If the critical nucleus is less than one unit cell, the crystallite must start growing without "knowing" what configuration it is finally to assume. Under these conditions, amorphous or partially crystalline material is produced.

The chief parameters which lead to an amorphous phase are high supersaturation and a large unit cell. Agglomeration of the small crystallites also favours an amorphous precipitate.

6.6 Colloidal precipitates

When the nuclei grow to microscopic size, 0.001 to 1μ in diameter, their surface-to-weight ratio (specific surface) is very high and adsorption is of primary importance in determining their properties and behaviour. The particles show a high absorptive capacity for their own (lattice) ions. The electric charge of the adsorbed ions is balanced by the charge of the counter ions. This arrangement of charge around the particle (electrical double layer)* causes one particle to repel another.

Since water is a highly polar solvent, the particles also have a high attraction for water molecules. Particles which show little attraction for water form hydrophobic colloids. Particles which show a strong affinity for water form hydrophilic colloids or gels. When the particles making up the colloidal system are caused to come together and adhere to one another, the result is a mass of material that settles out rapidly from solution. The resulting mass is called a colloidal precipitate and the process by which it is formed is termed flocculation or coagulation. Flocculation of colloidal

---

* See glossary.

dispersions by high polymers(57) is of great importance in industrial practice.

Colloidal precipitates have no regularity in structure and appear as large amorphous masses, sometimes described as curdy, gel-like or slimy. Because of their great adsorption capacity, colloidal precipitates are excellent scavengers (collectors) of trace substances from solution.

6.7 Aging

Aging includes all irreversible chemical and structural changes that occur in a precipitate after it has been formed.

Initially, a very fine crystalline precipitate is formed with a disordered lattice. This is known as the active form of the precipitate. A metastable equilibrium is established between the active precipitate and the mother liquor. The active precipitate shows a maximum solubility, absorbability and peptization. With time, limiting values for these parameters are attained and the inactive form of the precipitate is said to form.

a) Active form of precipitate

For slightly soluble substances, the supersaturation limit is reached rapidly and usually the fresh precipitate is composed of amorphous or very fine crystals with a disordered lattice. The disorder in the lattice is enhanced by the presence of coprecipitated foreign ions.

A fresh precipitate is porous and spongy. The particles are separated by fine capillaries filled with mother liquor. These capillaries allow ions on the inside to communicate with the solution on the outside.

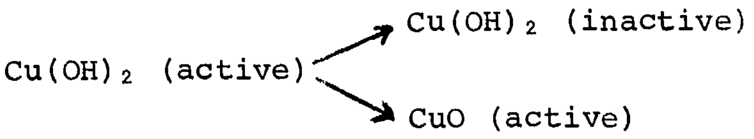
Recrystallization and perfection of crystals proceed while the precipitate is in this metastable form. The important parameters for recrystallization are the composition of the mother liquor, temperature and time. It takes time to transfer material across a phase boundary and equilibrium between a precipitate and solution is often not established for hours or even days.

In general the rate of recrystallization increases with the solubility of the particles in the particular medium; specifically, the rate of recrystallization depends upon the solubility of the lattice material in the liquid film around the particles. Lattice ions at highly active spots rapidly enter the adjacent liquid film, as a result of which their concentration exceeds that corresponding to saturation in contact with normal (inactive) surfaces. The liquid film becomes supersaturated and lattice material deposits between the particles. Thus, particles are cemented to form imperfect crystals with a mosaic structure. At a low temperature the rate of cementing of particles may exceed the rate of formation of fresh particles.

Hard, ionic crystals that tend to produce highly supersaturated solutions, age rapidly by recrystallization. Soft crystals age chiefly by thermal agitation in the interior of the crystals, resulting in a perfection of the latter without growth of the particles. This internal aging is tremendously accelerated by an increase in temperature.

Another form of aging occurs with voluminous precipitates by the spontaneous loss of gel water, resulting in the formation of a granular mass.

Active forms of unstable crystalline modifications may undergo two kinds of change. Either the active form of the unstable modification becomes inactive, or a more stable modification is formed. For example, dehydration occurs if a metal oxide is more stable than the primarily precipitated hydroxide:



b) Inactive form of precipitate

Aging proceeds towards the formation of the thermodynamically most stable product, i.e., the inactive form of the precipitate. In the inactive form the precipitate consists of coarser, perfected crystals of the stable modification of the compound; in this form the surface free energy is at a minimum.

A precipitate may have together amorphous as well as crystalline components. In such non-homogeneous solids the more active components are dissolved more rapidly and the solubility measured may depend on the nature of the remaining solid.

The measured solubility product refers to the most active component. Between the limiting values of the active and inactive form, all values of the solubility product are possible. The difference in solubility between the active and inactive forms of the same compound can be striking, e.g., for $Ni(OH)_2$ (active) $pK_{so} = 14.7$, for $Ni(OH)_2$ (inactive) $pK_{so} = 17.2$; for $Mg(OH)_2$ (active) $pK_{so} = 9.2$, for $Mg(OH)_2$ (inactive) $pK_{so} = 10.9$.

Aging in the mother liquor at an elevated temperature is called digestion. Elevation in temperature greatly speeds up the aging process and thereby the filterability of the precipitate is improved. A product precipitated at room temperature, at first amorphous, will usually show a sharp X-ray pattern after a few hours at the boiling point. Experimental evidence indicates that the digestion process consists chiefly of the cementing together of crystals. It seems that the growth process during aging plays but a minor role compared with the aggregation process.

The rate of aging is decreased by the presence of an adsorbed layer of impurity. It is also influenced greatly by the presence of excess lattice ions in solution. The rate of aging is increased in the presence of excess lattice anions, but is impeded by an excess of lattice cations.

The relationship between aging and coprecipitation has been studied extensively by Kolthoff and his co-workers(58,59,60, 61,62). Since equilibrium is reached slowly, long-term effects are important. However, the more dramatic changes in coprecipitation as the result of aging probably occur in the first 30 minutes(63):

7. COPRECIPITATION PRACTICE

7.1 Concentration by coprecipitation

Coprecipitation makes possible the concentration of substances which are present in solution at well below their normal solubility. Generally mixed crystal formation is advantageous where it can be applied because it promotes selectivity and gives a high partition ratio in an enrichment system. For a large partition ratio the host precipitate should be considerably more soluble than the trace precipitate, but it should be sufficiently insoluble to allow the ratio of metal ion precipitated/metal ion in solution, to be about 100(64).

To aid in the selection of a salt which can serve as a host precipitate, tables 7.2, 7.3 and 7.4 give a collection of pK values (negative logarithms) of solubility product constants of inorganic salts. The values were obtained chiefly from compilations by Sillen and Martell(65) and by Frieser and Fernando(22).

The fact that coprecipitation by mixed crystal formation and by occlusion occurs in the initial stage of precipitate formation is often used to remove traces of impurities from concentrated solutions of salts. Only a small fraction of the salt need be precipitated to carry down a predominant fraction of the impurity(66).

7.2 Preformed precipitate

Although most efficient coprecipitation is obtained if the microcomponent is present during precipitate formation (internally formed precipitate), a sizable fraction of the microcomponent can frequently be removed from solution by adding a preformed precipitate (externally formed precipitate). A preformed precipitate is usually made in a separate vessel and subsequently added to the solution. However it is just as satisfactory, and somewhat more convenient, to employ for this purpose a precipitate obtained by the interaction of two reactants at the interface of their solutions. Thus if a ferric salt is carefully added to an alkaline solution, ferric hydroxide forms at the interface between the two solutions, but on subsequent stirring appears to the bulk of the solution to be preformed(11).

In a study of ion exchange of radioactive lead between lead sulphate and solution, Kolthoff and von Fischer(59) showed that a fresh precipitate temporarily extracts a relatively large quantity of radioactive lead because the surface originally exposed to rich radioactive solution is buried by recrystallization, so that the precipitate in effect performs a multiple extraction. Thus duration of aging should be taken into account in tests with preformed precipitates.

Table 7.1

pK values of salts of monovalent cations and oxycations and of tetravalent cations

Atomic No.		OH^-	S^{2-}	CO_3^{2-}	SO_4^{2-}	CrO_4^{2-}	PO_4^{3-}	AsO_4^{3-}	SeO_3^{2-}	SeO_4^{2-}	$C_2O_4^{2-}$	Cl^-	Br^-	I^-	CN^-	SCN^-	MoO_4^{2-}	CH_3COO^-
29	Cu^+	14.7	48									6.5	8.3	12.0	11.0	10.8		
47	Ag^+	7.6	49.2	11.1	4.8	11.6	21.0	22.0	15	5	11	10.0	12.3	16.1	15.7	12.0	11.5	
79	Au^+	19												22.2				
80	Hg^+	22.8		16.1	6.2	8.7			14			17.9	21.9	28.4				9.4
81	Tl^+	-0.2	22.1			12.9	7.2			4		3.7	5.4	7.2				
83	BiO^+	9.4																
14	Si^{4+}	2.7																
22	Ti^{4+}	38																
33	Ge^{4+}	45																
40	Zr^{4+}	51																
44	Ru^{4+}	43.7																
50	Sn^{4+}	57																
58	Ce^{4+}	50.4																
73	Hf^{4+}	55																
82	Pb^{4+}	64																
84	Po^{4+}	37																
90	Th^{4+}	44.9					5.8		19.9									
92	U^{4+}	51.9																
41	Nb^{5+}	68																
42	Mo^{6+}	75																
91	Pa^{5+}	55																

Table 7.2

pK values of salts of divalent cations and oxycations

Atomic No.		OH$^-$	S^{2-}	CO$_3{}^{2-}$	SO$_4{}^{2-}$	CrO$_4{}^{2-}$	PO$_4{}^{3-}$	AsO$_4{}^{3-}$	Fe(CN)$_6{}^{4-}$	SeO$_3{}^{2-}$	SeO$_4{}^{2-}$	SiO$_3{}^{2-}$	C$_2$O$_4{}^{2-}$	F$^-$	Cl$^-$	Br$^-$	I$^-$	IO$_3{}^-$	BrO$_3{}^-$	SCN$^-$	SO$_3{}^-$	MoO$_4{}^{2-}$	WO$_4{}^2$
4	Be^{2+}	21.5																					
12	Mg^{2+}	11.0		5.0				19.7		4.9			4	8.18									
20	Ca^{2+}	5.3		8.3	4.6	3.1	28.7	18.2		5.5	3	11	8	6				6.1			5.0		8.0
22	TiO^{2+}	28.6																					
23	V^{2+}	15																					
23	VO^{2+}	23.5					24.1																
24	Cr^{2+}	18																					
25	Mn^{2+}	12.8	11.0	10.1				28.7	12.1	6.9		13											
26	Fe^{2+}	15.1	17.3	10.4								19	6.7										
27	Co^{2+}	15.7	22.1	12.1				28.1	16.0	6.8													
28	Ni^{2+}	14.7	20.7	8.18				25.5	14.0	5.0								7.8					
29	Cu^{2+}	19.7	35.1	9.6		5.4		35.1	15.7	7.7			9.4					7.0					
30	Zn^{2+}	17.2	21.5	10.7			32.0	27.0	15.3	6.6		21	8.6					7.7					
38	Sr^{2+}	3		9.2	6.1	5.3		18.1		6.0	4.6	5	7.3	8.54				6.5					
46	Pd^{2+}	31																					
48	Cd^{2+}	14	26.1	11.3				32.7	15.2	8.9													
50	Sn^{2+}	26.8	26.9																				
56	Ba^{2+}	2		8.3	10.0	9.9	38.2	50		7.5	10	5	7.8	10.3				9.1	5.3				
78	Pt^{2+}	35																					
80	Hg^{2+}	25.5	51.5												14.2	19.0	28.4	12.5					116.9
82	Pb^{2+}	14.4	27.1	12.8	7.8	15.7	42.1	35.4	14.5	11.5	6.8	17	11.1	7.6	4.8	5.3	8.2	12.6		7.5		15.0	
88	Ra^{2+}																						
92	UO$_2{}^{2+}$	21.6							13.1	10.4								7.0			8.6		

Table 7.3

pK values of salts of tervalent cations

Atomic No.		OH^-	S^{2-}	$PO_4{}^{3-}$	$AsO_4{}^{3-}$	$Fe(CN)_6{}^{4-}$	$SeO_3{}^{2-}$	$C_2O_4{}^{2}$
5	B^{3+}	30.4						
13	Al^{3+}	31.6	6.7	18.2	15.8			
21	Sc^{3+}	29.7						
22	Ti^{3+}	52.8						
23	V^{3+}	34						
24	Cr^{3+}	30.2			20.1			
25	Mn^{3+}	36						
26	Fe^{3+}	37.2	88	21.9	20.2	40.6	30.7	
27	Co^{3+}	43	126					
28	Ni^{3+}							
31	Ga^{3+}	36.3				33.8		
33	As^{3+}							
39	Y^{3+}	23.3						
44	Ru^{3+}	35						
49	In^{3+}	33.2	73.2			43.7	32.6	
51	Sb^{3+}	41.4	58.5					
57	La^{3+}	19.0	12.7					26.6
58	Ce^{3+}	21.2	10.2				24.4	28.6
59	Pr^{3+}	21.5						
60	Nd^{3+}	22						
61	Pm^{3+}	34						
62	Sm^{3+}	22.0						
63	Eu^{3+}	21.5						
64	Gd^{3+}	22.7						
70	Yb^{3+}	23.6						
70	Au^{3+}	45.2						
81	Tl^{3+}	43.6					38.7	
83	Bi^{3+}	31.0	60.1	22.9	9.4			

7.3 Effect of the rate of precipitate formation

The rate of precipitate formation is an extremely important parameter in coprecipitation. It determines the physical properties of the precipitate particles and strongly affects the mechanism, selectivity and the amount of coprecipitation.

The best way to control the rate of precipitate formation is by the technique of precipitation from homogeneous solution. By this technique the precipitant is generated at a controlled rate by a homogeneous chemical reaction within the solution (2). Usually nucleation occurs on solid impurities present in the solvent or in the reagents. Such conditions favour slow precipitation, and coprecipitation occurs chiefly by solid solution formation. Contamination by surface adsorption and by occlusion is at a minimum. Under such conditions the distribution coefficient, λ, is constant. However the value of λ is different for different rates of precipitate formation.

Mixing dilute solutions of reactants at an elevated temperature produces a microscopic crystalline precipitate. Growth is rapid under such conditions and coprecipitation by occlusion is favoured. Mixing somewhat stronger solutions of reactants gives an amorphous precipitate strongly contaminated by occluded matter. Concentrated solutions of reagents at a low temperature give colloidal precipitates which are contaminated chiefly by surface adsorbed matter. Critical supersaturation is exceeded under these conditions; the reacting molecules produce many new particles but contribute little to crystal growth.

7.4 Two-stage precipitation

In the technique of precipitation from homogeneous solution, coprecipitation by anomalous mixed crystal formation (non-isomorphous replacement) occurs in the final stage of precipitate formation. This sharp increase in coprecipitation in the final stage of precipitation can be avoided by using a two-stage precipitation technique(2). A precipitate containing most, but not all, of the substance is first formed and aged under conditions of greater solubility (higher acidity, complexing agent etc.) and is filtered under these same conditions. Next, precipitation of the balance of the substance is effected yielding a greatly reduced quantity of precipitate which is filtered separately and then combined with the first precipitate. The combined precipitates contain only a fraction of the impurity that would be carried down in a single-stage precipitation.

7.5 Digestion

Digestion of a precipitate in the mother liquor at an elevated temperature is often used to decrease contamination and to improve filterability. During digestion the precipitate surface is decreased with a concomitant decrease in adsorbed material. Also, since occluded ions keep more or less of their water of hydration, the force by which cations and anions in the solid attract each other is diminished and precipitates with much occluded matter age more rapidly. However if the precipitate is contaminated by very much absorbed matter, the aging processes in the mother liquid are then greatly retarded. Recrystallization and thermal aging may be very slow and consequently both adsorbed and occluded matter will re-enter the liquor phase very slowly, or perhaps not at all.

Kolthoff and Noponen(58) showed that an excess of either of the lattice ions repressed the speed of aging of barium sulphate. The speed of aging decreased in the following order:

$$Ba^{2+} = SO_4{}^{2-} > 0.005\ M\ SO_4{}^{2-} > 0.033\ M\ SO_4{}^{2-} > 0.005\ M\ Ba^{2+}$$

The speed of aging is greater in a solution containing excess anion rather than excess cation because cations are more strongly adsorbed than anions.

Recrystallization is more rapid under conditions that favour greater solubility of the lattice material in the liquid film around the precipitate particles. Thus the addition of ammonia increases the rate of aging of silver bromide(60). However silver bromide ages rapidly even in the absence of ammonia. The authors suggest that under conditions of minimum solubility the silver bromide molecules located on a large active surface are much richer in energy than those on a normal well-aged surface. A tremendously rapid aging occurred in an excess of bromide solution, due to complex formation ($AgBr_2^-$). The negatively charged complex produced a colloidal system. Aging in an excess of bromide solution was strongly promoted when the solution was coagulated with 0.2 M KNO_3.

7.6 Reprecipitation

Impurities that are incorporated in the solid phase (mixed crystal formation) cannot be removed by washing or by digestion in the mother liquor. Such impurities are removed by dissolution and reprecipitation of the filtered precipitate in a solution free of the contaminant. Upon reprecipitation, the contaminant concentration in the new solution is much smaller than in the original, therefore only a fraction of the amount of contaminant is carried down upon reprecipitation. Often the amount of impurity carried down in the second precipitation is so small that it may be neglected in an analytical procedure.

Purification may be effected also by aging the filtered precipitate in a new solution under conditions that favour rapid recrystallization.

7.7 Washing

The removal of adsorbed substances from a crystalline precipitate by washing with water is limited only by the extent to which re-dissolution can be tolerated. Solubility losses are decreased by washing with a solvent of lower dielectric constant, e.g., a solution of alcohol. Washing with a saturated solution of the salt is not recommended.

Colloidal precipitates must be washed with a suitable electrolyte to prevent removal of the coagulating agent. A straight water wash will bring the precipitate back into the colloidal state. For negatively-charged precipitates, the counter cations are usually replaced by a wash with a solution of hydrogen or ammonium ions, since the adsorbed acid or ammonium salt can usually be volatilized on heating. For a positively-charged precipitate, the replacement of one counter anion by another serves no useful purpose, since the adsorbed metal ion, although it forms a new salt, is not volatilized on heating.

7.8 Classification of coprecipitation

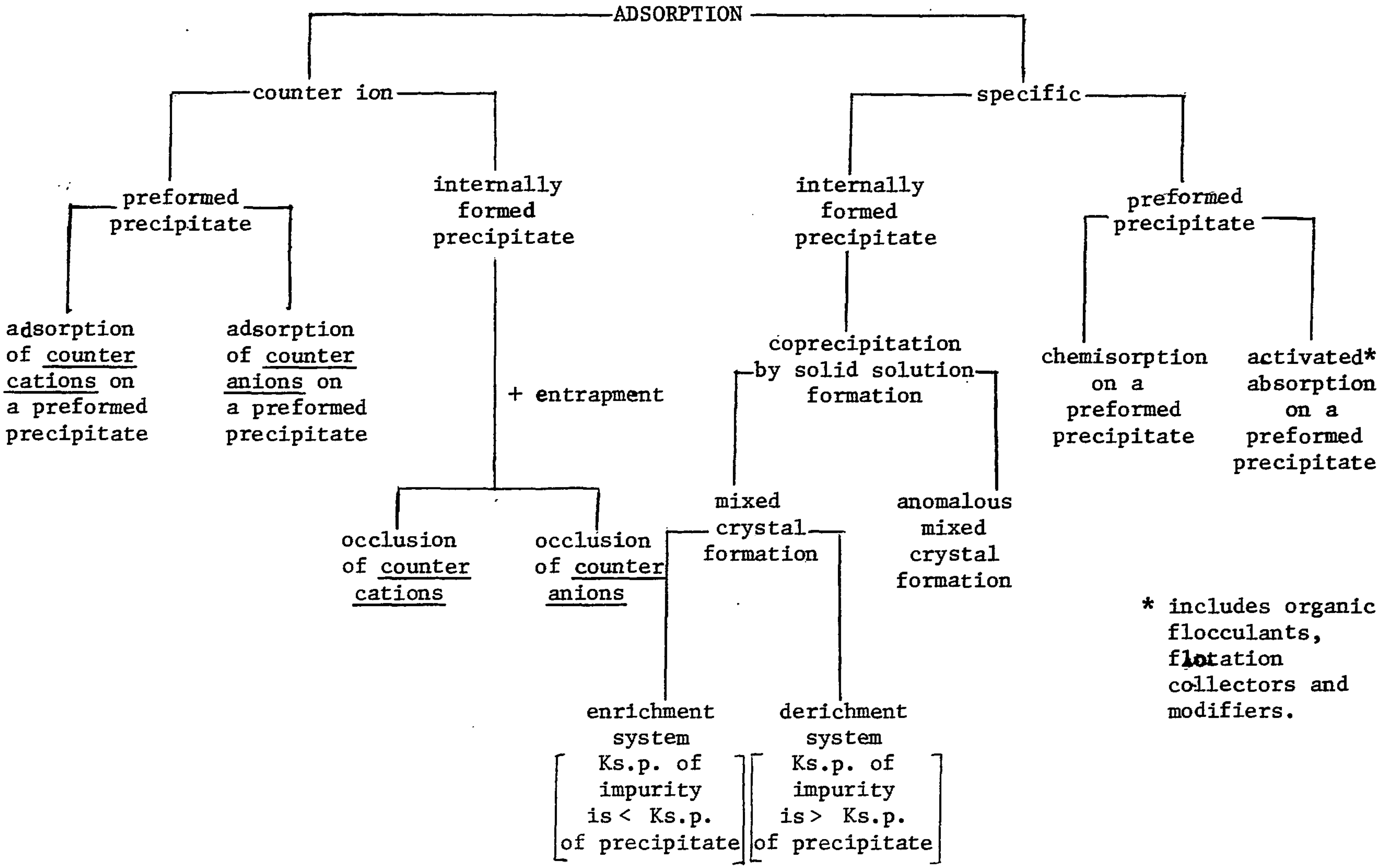
In this paper, coprecipitation is classified according to the nature of predominant coprecipitation mechanism and on whether coprecipitation takes place during precipitate formation or on a preformed precipitate. The three principal coprecipitation mechanisms are surface adsorption, occlusion and solid solution formation. These mechanisms may be distinguished since:

1) surface adsorbed substances can be removed from the solid by washing with a suitable electrolyte;

2) occluded matter re-enters the solution phase during digestion in the mother liquor (a small amount will desorb, due to decrease in surface area);

3) in contrast to adsorption and occlusion, solid solution formation is characterized by an increase in coprecipitation by digestion in the mother liquor.

Figure 7.1 is a chart of this classification scheme to assist in visualizing it. Figure 7.2 shows the usual methods of removing coprecipitated matter. Table 7.4 shows the principal characteristics of coprecipitation classes indicated in figure 7.1.



* includes organic flocculants, flotation collectors and modifiers.

Figure 7.1 Description of coprecipitation class based on the mechanism of adsorption and on whether there is ion entrapment.

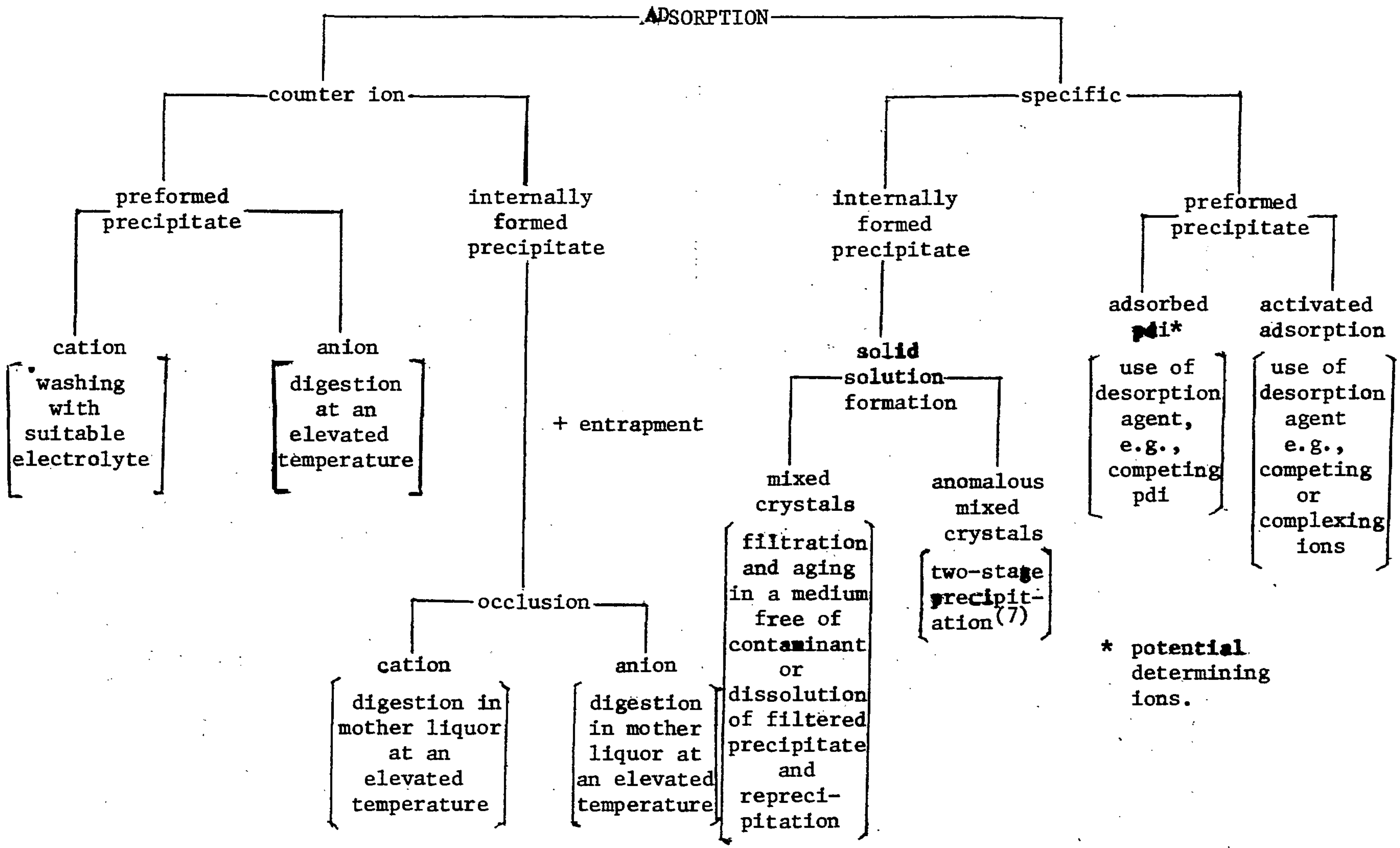


Figure 7.2 Usual methods of removing coprecipitated matter.

Table 7.4

Principal characteristics of coprecipitation classes

A. Coprecipitation with internally-formed precipitates

Coprecipitation class	Characteristics
Mixed crystal formation	
a) Enrichment system	D, λ are reproducible. $D > 1$, $\lambda > 1$. D, λ are not affected by initial molar ratio of microcomponent to macrocomponent. Coprecipitation occurs in the initial stage of precipitate formation. D, λ and separation efficiency decrease with an increase in temperature. D, λ and separation efficiency decrease with an increase in the rate of precipitate formation. Amount of coprecipitation increases with aging to an equilibrium value. Continuous distribution of trace radioelement is shown by radioautographs.

Coprecipitation class	Characteristics
b) Derichment system	D, λ are reproducible. $D < 1$, $\lambda < 1$. D, λ are not affected by initial molar ratio of microcomponent to macrocomponent. Maximum coprecipitation occurs in the final stage of precipitate formation. D, λ decrease, separation efficiency increases with an increase in temperature. D, λ and amount of coprecipitation increase with an increase in the rate of precipitate formation. Amount of coprecipitation decreases with aging to an equilibrium value.
Anomalous mixed crystal formation...	D, λ are reproducible. Solubility of macro-concentration of impurity in host precipitate is limited, a plot of log (moles microcomponent in solid) vs. log (moles microcomponent in solution) shows a maximum.

Coprecipitation class	Characteristics
	No suppression of coprecipitation by a lattice ion possessing charge of the same electrical sign. Continuous distribution of trace radioelement is shown by radioautographs.
Occlusion of counter ions ...	D, λ are not reproducible. Amount of coprecipitation due to occlusion is suppressed by excess lattice ion of the same electrical sign. Amount of coprecipitation due to occlusion is suppressed by the presence of other high charge ions of the same electrical sign. In enrichment systems, an increased rate of precipitation leads to decreased coprecipitation and hence to lower numerical values of λ. In derichment systems, an increased rate of precipitation leads to increased coprecipitation and hence to higher numerical values of λ.

Coprecipitation class	Characteristics
	Discontinuous distribution of trace radioelement is shown by radioautographs.
B. Coprecipitation with externally-formed (preformed) precipitates	
Adsorption of potential-determining ions (pdi)...	The surface charge of colloidal particles can be neutralized by very small quantities of adsorbed pdi of opposite charge and the coagulated colloid is not peptized by washing with water. Equilibrium is reached rapidly. Amount adsorbed is decreased by addition of competing pdi to the solution. Amount adsorbed decreases as age of preformed precipitate increases. If there is solid solution formation, then coprecipitation increases with prolonged digestion.
Activated adsorption...	Amount of absorption is greatly affected by temperature, by the adsorption energy and, in the case of a

	weak electrolyte, by its dissociation energy.
Adsorption of counter cations ...	Amount adsorbed depends on surface charge and on the concentration of competing ions. Colloids coagulated by neutralization of the surface charge are peptized by washing with water.
Adsorption of counter anions ...	Amount of adsorption depends on the surface charge and on the concentration of competing ions. Colloids which were coagulated by neutralization of the surface charge are peptized when washed with water.

8. CLASSIFICATION OF COLLECTORS

The preceding discussion has shown that coprecipitation efficiency depends on many factors. It depends on the physico-chemical properties of the microcomponent, the host precipitate and the solution phase, as well as on temperature, the order of mixing of reagents etc.

Since coprecipitation is greatly affected by the solubilities of substances, tables of solubility products have a heuristic value. The solubility product quantitatively establishes the effect on solubility of the charge and size of the constituent ions, as well as on the nature of the chemical bond between them. The less polar the chemical bond, the less effect a polar solvent, such as water, will have on solubility.

The nature of the chemical bond between crystal constituents is thus of fundamental importance in precipitate formation and allows a broad, although arbitrary classification of the large number of water-insoluble salts. In this paper the salts are therefore divided into four classes, according to the nature of the bond between the constituents: ionic, ionic-coordinate, ionic-covalent ($\gtrsim 50\%$ ionic) or covalent-ionic ($\gtrsim 50\%$ covalent) bonds.

Ionic salts possess certain common properties. They are relatively soluble in water. They tend to form highly supersaturated solutions. Coprecipitation is greatly affected by the ratio of microcomponent cation radius to the anion radius of the host precipitate. A freshly formed precipitate ages relatively rapidly by recrystallization. Filterability is improved by aging in the mother liquor.

In contrast, covalent salts are very insoluble in water and possess little tendency to form supersaturated solutions. Critical supersaturation values are easily exceeded, the fresh precipitate is amorphous or colloidal and surface adsorption is high. Due to the directional properties of the covalent bonds, polymorphism is a common occurrence. Aging occurs by adjustment of bonds and is usually a slow process. Similarity in crystal structure may be of greater importance in coprecipitation than the radius ratio or solubility considerations. Defects in crystal structure and incorporation of foreign ions are quite common. In particular, the insoluble salts of transition elements tend to form mixed crystals, because they have similar charge, size and bond structure.

However, pure ionic or pure covalent chemical bonds are not common in nature. Bonds are predominantly intermediate in character or mixed, possessing some ionic and some covalent character. Heavy metal oxides and sulphides are examples of salts having intermediate bond character. The M-O bond has about 30% covalent character, the M-S bond is about 70% covalent. Alkali metal-hydroxide bonds are chiefly ionic, but as we proceed across the periodic table to heavier elements, there is an increasing tendency for metals to form bonds with more covalent character. Starting with the first transition s series and with increasing charge, the oxides become more stable than the hydroxides.

Many anions, such as S^{2-}, O^{2-}, SO_4^{2-}, CO_3^{2-} etc., form coordination bonds by sharing their non-bonded pairs of electrons. Such bonds have some directional character and are therefore partly covalent. Many coordinated complexes are formed only in relatively concentrated solutions of their ions and under conditions such that basic salts are more stable than pure salts. Insoluble ferrocyanides and jarosites are examples of coordination compounds reviewed in this paper. These salts form precipitates of variable composition which depends on the properties of the mother solution.

8.1 Ionic crystals

The solubility of ionic salts is greatly affected by the charge and size of the constituent ions. Insoluble compounds, such as $BaSO_4$, $SrCO_3$, CaC_2O_4, contain two highly charged, large ions. The lattice energy of such compounds is large and negative. Highly supersaturated solutions of these salts can be prepared so that heterogeneous nucleation and crystal growth proceed rapidly.

An ionic precipitate is expected to adsorb and occlude highly charged ions from solution and to incorporate ions of appropriate size and charge. Adsorption by ion exchange is common and the two reviews by Pekarek and Vesely(67,68) on synthetic inorganic ion-exchangers give many examples of ion-exchange properties of ionic salts.

a) Sulphates

Sill(69) found that "probably all positive ions having a charge greater than two and an ionic radius larger than about 1.1Å can be carried on $BaSO_4$ precipitate to better than 99%.. ..." He found that uranium and transuranic elements would coprecipitate on $BaSO_4$, provided that they were in the tervalent or quadrivalent state and that the coprecipitation was carried out in the presence of potassium ions. He found also that uranium and transuranium elements can be prevented from precipitating if they are oxidized to the hexavalent state, in which the oxygenated cation is too large to fit into the $BaSO_4$ lattice. These findings have been applied in the determination of plutonium-241 in effluents(70).

Berak, Moravec and Sara(71) have reported the formation of a metastable product obtained with $CaSO_4$ fixed in a $BaSO_4$ lattice. When the product is placed in water, the $CaSO_4$ component is eluted with consequent rapid recrystallization of the whole mass. During this process cations, the sulphates of which are isomorphous with $BaSO_4$, are rapidly incorporated and thus removed from solution.

Sill and Willis(72) coprecipitated submicrogram quantities of thorium on $BaSO_4$ from sulphuric acid solutions. They determined radioisotopes of Ce, Ba, La and Np after their coprecipitation by $BaSO_4$(73).

The fact that aging of $BaSO_4$ proceeds more rapidly in sulphate solutions than in solutions in which barium ions are in excess, is explained by Kolthoff and Noponen(58) by assuming that barium ions are more strongly attracted to the $BaSO_4$ lattice than are sulphate ions and the concentration of Ba^{2+} ions in the liquid film around the precipitate particles is much greater than that of SO_4^{2-} ions, although both are present in the same concentration in the bulk of the solution.

The aging of lead sulphate precipitates has been studied by Kolthoff and co-authors(74,75,76).

b) Carbonates

Saylor(77) discussed the reasons why aragonite is formed instead of calcite under conditions such that calcite is the more stable modification of calcium carbonate. He shows that preferential adsorption takes place upon crystal faces. Due to this adsorption the growth of faces perpendicular to themselves is obstructed. It is thought that anions, carbonate or bicarbonate - or even a high-temperature form of water - are adsorbed on the calcite nuclei and this adsorption prevents further growth. Aragonite crystallizes because it can grow more quickly under these conditions than calcite can form crystal nuclei.

Saylor suggests that in general, supersaturation results if absorbed material dirties the surface of any crystal nucleus as soon as it appears.

Papers in references 78, 79, 80, 81 deal with coprecipitation by calcium carbonate. Kinsman and Holland(81) show that the value of the distribution coefficient depends on the kinetics and mechanism of crystal growth, and that this must be true for all distribution coefficients determined under conditions such that the rate of crystal growth is greater than the rate of diffusion within the growing crystals.

c) Phosphates

Chuiko, Kovaleva and Kravtsova(82) studied the coprecipitation of trace quantities of an element by a partially precipitated host compound. They found that by this technique aluminum phosphate can be used as a collector for chromium and iron.

According to the same authors(83), the solubility of metal phosphates decreases sharply in the order M^{+} -- M^{4+} and when a metal present as a microcomponent forms a much less soluble compound that the host, it is possible in many cases to concentrate the microcomponent by precipitating only a fraction of the macrocomponent, even when no isomorphism exists. A procedure is given for concentrating micro amounts of iron in solutions of Ni, Co, Zn and Cu salts by the partial precipitation of these salts as phosphates. The iron is then separated from the phosphates of these metals (Ni, Co, Cu) by coprecipitation with aluminum hydroxide from ammoniacal solutions.

The sorption of orthophosphate on crystalline metal oxides was investigated(84). The amount of orthophosphate sorbed per unit area of surface appears to be independent of the sintering temperature of the oxide. Monolayer coverages are predicted from geometric considerations of the orthophosphate molecule and the metal-oxide surfaces presumed to be present.

d) Oxalates

Distribution coefficients of rare earth oxalates have been investigated by a number of authors. Feibush, Rowley and Gordon(85) found no correlation between the distribution coefficient λ and the solubility product ratio. They infer that the value of λ is determined by the kinetics of the precipitation process rather than the solubilities of the substances.

Munakata, Toyomasu and Shigematsu(86) found that the distribution coefficient in the Ca - Sr oxalate system was determined by the ratio of the solubility products rather than the rate constants. Neither the solubility product nor precipitation rate, however, was correlated to the distribution coefficient for coprecipitation in rare earth-rare earth oxalate systems.

Block and Gordon(87) found the distribution coefficient to be functionally related to the experimentally determined first-order precipitation rate constants when a trace quantity of Ce(III) is coprecipitated with carrier U(IV) oxalate. The Ce(III) - U(IV) oxalate system obeys a distribution law modified to include ion charge rather than the unmodified Doerner-Hoskins logarithmic distribution law.

8.2 Coordination complexes

Very little work has been done to determine the collecting properties of this class of compounds. Because these compounds form precipitates slowly, the chief coprecipitation mechanism is likely to be solid solution formation or ion-exchange adsorption. Radius ratios must greatly affect coprecipitation efficiency. Charge neutrality must determine the stoichiometry of the precipitate. Undoubtedly such compounds often serve as "gathering" agents for cocrystallizing substances.

a) Ferrocyanides

The hexacyanoferrate ion yields complex salts with many cations. More than one cation species can participate in the reaction and the possibility of substituting one metal ion for another depends on the dimensions of the two cations, their ionization potentials and on their concentrations. Insoluble metal ferrocyanides are stable in a broad spectrum of pH values and therefore can often serve as collectors or as gathering agents for trace quantities of other salts. Recently, more has become known of the chemistry and structure of insoluble ferrocyanides, and this knowledge can be used as a guide in the study of other coordination compounds, i.e., on how solution composition and temperature affects the composition of such compounds.

Precipitates of various compositions are formed when a solution of a transition metal salt is mixed with a solution of $H_4Fe(CN)_6$, $Na_4Fe(CN)_6$ or $K_4Fe(CN)_6$. The composition depends upon the initial ratio of reacting components, acidity and the order of mixing the reagents. The possible reactions between potassium ferrocyanide and a bivalent cation$^{(82)}$ are generalized as follows:

$$2M^{2+} + \{Fe(CN)_6\}^{4-} = M_2\{Fe(CN)_6\} \qquad \{8\text{-}1\}$$

$$nK^+ + mM^{2+} + q\{Fe(CN)_6\}^{4-} \rightleftarrows K_nM_m\{Fe(CN)_6\}_q \qquad \{8\text{-}2\}$$

For the reaction {8-2}, n,m and q may have various values corresponding to complexes having variable $\frac{K^+}{M^{2+}}$ ratios. It appears that in compounds such as ferric ferricyanide (Berlin green), potassium ferric ferrocyanide (Prussian blue) and insoluble potassium ferrous ferrocyanide ($K_2FeFe(CN)_6$), there is the same arrangement of Fe atoms on a cubic face-centered lattice$^{(88)}$. Potassium ions are inserted in alternate unit cells to preserve the charge balance. Lithium and cesium with very small and very large ions respectively, do not form compounds with this structure. Possibly these salts could be used to coprecipitate traces of K^+ and Na^+ from solutions of salts of lithium and cesium. Because of the partly covalent nature of the M - $Fe(CN)_6$ bonds, the possibility of substituting an alkali metal ion for M depends on the dimensions of the two cations and on their ionization potentials(89).

The formation of Ni, Co, Mn and Cd ferrocyanides(90) and the formation of ferrocyanides of Fe(III), La(III) and Ce(III)(92,91) and of ferricyanides of Ag(I), Cu(II) and Cd(II)(93) have been studied.

By using complexing agents with ferrocyanide, Cheng(94) developed a qualitative test for zinc and manganese, and a quantitative volumetric method for the determination of manganese.

Tananaev and Glushkova(95) used ferrocyanide to isolate small amounts (~ 0.01 g/l) of thallium from solutions containing non-ferrous metals such as Cu, Ni, Co, Cd and Zn.

b) Jarosites

Jarosites are included here because they are important in present day zinc technology and because they are a good example of precipitates that form only in the more concentrated solutions of their constituent ions. Jarosites are a group of insoluble, crystalline, basic iron compounds of the general formula $MFe_3(SO_4)_2(OH)_6$, where M can be

Na, K, Rb, NH_4, Ag, Pb/2 or H_3O (96). These compounds are usually deficient in K, Na or NH_4 and it is suggested that such precipitates are solid solutions of the particular jarosite and hydroxonium jarosite(97).

It is noted(96) that, although some As, Sb, Ge and other elements toxic to zinc electrolysis are removed by jarosite, freshly precipitated ferric hydroxide is a more effective scavenger for these elements.

The jarosite process is also discussed by White(98) and by Steintveit(99); flowsheets for the jarosite process are found in reference 100.

8.3 Ionic-covalent compounds

Hydroxides

The hydroxide precipitates represent a large group of collectors characterized by the unique property of having hydroxide and hydrogen ions as potential-determining ions. Thus, the pH of the solution has a strong effect on the solubility, structure and sorptive properties of the hydroxide precipitates.

Many hydroxide crystals have structures intermediate in character between molecular and ionic. The hydroxides of some divalent metals, e.g., $Ca(OH)_2$, $Mg(OH)_2$, $Cd(OH)_2$, $Fe(OH)_2$ and $Ni(OH)_2$ have layered lattices or lattices containing molecules bound by hydrogen bonds into sheets, chains or space-filling frameworks. A review of structural differences between the different metal hydroxides is given by Wells(101).

It is important that for heavy polyvalent cations the oxide is the thermodynamically stable form rather than the hydroxide(102). The crystalline lattice of the metal oxide merely provides a large surface area for adsorption of water molecules by ion-dipole attraction.

Since hydrous oxides are very insoluble substances, only colloidal precipitates are usually obtained, more or less contaminated by surface-adsorbed impurities. Adsorption appears to proceed by ion exchange, and many oxides such as silica, alumina, ferric oxide etc., have found use as inorganic ion-exchangers(67).

The oxides are amphoteric and their dissociation in solution is represented as follows:

$$\text{M - OH} \xrightarrow[\text{conditions}]{\text{acid}} \text{M}^+ + \text{OH}^- \qquad \{9\text{-}3\}$$

$$\text{M - OH} \xrightarrow[\text{conditions}]{\text{basic}} \text{M - O}^- + \text{H}^+ \qquad \{9\text{-}4\}$$

In acid solutions, the oxides act as anion exchangers, and in basic solutions, as cation exchangers. Near the zero point of charge (zpc), dissociation can take place according to both schemes and the oxide can serve both as anion and cation exchanger.

If the charge on the solid is established only by hydrogen and by hydroxyl ions, the zpc is given the special name "isoelectric point" (IEPS). It appears that the isoelectric point of a simple oxide is related to the appropriate cationic charge and radius, as follows(103):

$$\text{pH(IEPS)} = A - B\{\frac{Z}{R} + 0.0029\ C + a\}$$

where Z = cationic charge

$R = r_+ + 2r_0$;

r_+ = cationic radius in Å;

r_0 = oxygen ion radius, 1.4Å;

A,B = constants for all materials;

C = correction for crystal field stabilization of M-OH bonds;

a = combined corrections for coordination number and state of hydration.

It is found also that the zpc of an unaltered mixed oxide, silicate or phosphate, in a system devoid of specific electrolytes other than potential-determining ions, is approximately the average of the IEPS values of its component oxides weighted on an atomic basis(104). Probable IEPS ranges characteristic of the cation oxidation state are given by Parks(103):

M_2O	IEPS > pH 11.5
MO	$8.5 < \text{IEPS} < 12.5$
M_2O_3	$6.5 < \text{IEPS} < 10.4$
MO_2	$0 < \text{IEPS} < 7.5$
M_2O_5, MO_3	< IEPS 0.5

The adsorbability of a cation on an oxide surface is dependent to a large extent on the solubility product of its hydroxide. Adsorption increases with decreasing solubility of the adsorbed compound. For example, Donaldson and Fuller(105) found that for hydrous SnO_2 there is a selectivity series of divalent, transition metal ions:

$$Cu > Zn > Co > Fe > Ni > Mn$$

which is exactly the same as that found for these ions on activated alumina. In the same paper(105) for hydrous SnO_2, there is a table of distribution coefficients for Cu, Zn, Co, Fe, Ni and Mn at several concentrations of each ion. This selectivity series also closely parallels the order of the solubility of the equilibrium constants for the active form of the corresponding hydroxides. For example, the same series is observed when the pH of incipient precipitation is found in the titration of 0.1N - metal sulphate solutions with 0.1N - NaOH (106). However, the position of a member in such a series depends greatly on the experimental conditions.

It is shown(107) that exchange of alkali metal ions in colloidal aluminum silicates follows the series of hydrodynamic radii. Selective adsorption of alkali metals on permutit (artificial clay) takes place in the order:

$$Cs > Rb > K > Na > Li$$

This series is the same as the lyotropic series which shows the relative replacing power of cations on negatively-charged surfaces. Thus, the degree of hydration of cation plays an important role in their adsorbability on colloidal hydrous oxides.

It was noted previously that divalent hydroxides age rapidly by recrystallization, trivalent hydroxides age slowly by thermal agitation and quadrivalent oxides age very little. The tendency to form amorphous hydroxide or oxide precipitate increases with the valency of the ion. For a group of oxides of metals of the same oxidation state, the one with the greatest solubility ages the most rapidly. Chalyi and Rhozhenko(108) discuss experimental methods used to study the aging mechanism of metal hydroxides.

Metal oxides are a very important group of collectors and their adsorption properties are studied continually. Adsorption behaviour of sixty-one radioactive ions on manganese dioxide was reported(120). Sorption studies on ferric hydroxide continue(122).

8.4 Covalent ionic compounds

a) Sulphides

The sulphide ion tends to form covalent bonds with heavy polarizable cations. The metal-sulphur bond is about 70% covalent and the criterion for isomorphism is the formation of a similar number of bonds. Thus we find such atoms as Cu, Fe, Mo, Sn, Ag and Hg replacing Zn in zinc blends.

Hydrogen sulphide precipitates a large list of heavy metals from aqueous solution(116,117). Ions of the following metals are precipitated in acid solution (0.1 to 0.3M HCℓ): Cu, Pb, Bi, Cd, Hg, Ru, Rh, Pd, Os; and As, Sb, Sn, Ge, Re, Au, Pt, Ir, Se, Te, Mo. The smaller, more hydrated ions: Ni^{2+}, Co^{2+}, Fe^{2+}, Mn^{2+} and Zn^{2+} are precipitated in basic solutions.

Elements that acquire a state of high oxidation, for example, As(V), Sb(V) and Sn(IV), do not exist as positive ions in solution; instead, they attain inert gas structure by sharing electrons with sulphide, oxide, hydroxide or halide ions and so exist in solution as anions of hydrogen acid or as undissociated weak acids. It is assumed that the complex ion H_3S^+ is formed at high hydrogen concentration, which then combines with anions to form precipitates such as As_2S_5, GeS_2 and Re_2S_7 (109).

The sulphides CuS, PbS and Bi_2S_3 do not precipitate completely in strong acid solution. In a number of systems sulphides exhibit opposite acid-base properties and come down as complex precipitates, e.g., $Ag_2S \cdot In_2S_3$, $Tl_2S \cdot As_2S_3$ (110). Metal sulphides such as PbS, HgS, and Ag_2S form unionized complexes with H_2S of the type $MS \cdot zH_2S$ (111), hence the concentration of these metal sulphides in solution may be greater than is indicated by the solubility product constant.

Precipitates of ZnS, CuS and NiS are not known to form complexes with H_2S. There is evidence, however, which indicates strong adsorption of H_2S on ZnS colloidal particles. This strong adsorption prevents rapid crystal growth and thus contributes to tendency of supersaturation and poor filtration of the ZnS precipitate.

The crystal patterns of FeS, CoS and NiS are made by the sulphide ions, and such structures are peculiar in that some metal ions can be missing. In such compounds the metal ion is very small compared with the non-metal and charge neutrality is maintained by some of the metal ions being in a higher oxidation state.

Compounds deviate from normal stoichiometric proportions when atoms of one of the constituent occupy interstitial positions(112). Where anions and cations differ in size, the smaller cation is more likely to become the interstitial intruder. A characteristic of such compounds is that partial replacement of one kind of atom by another is extremely common, e.g., ZnS may contain up to 20% Fe.

According to Weyl(113), the surface energy of a homogeneous solid is decreased by advancing the most polarizable ions into the extreme outer layer and retracting the least polarizable ones. This distortion has a depth action and produces an electrical double layer.

Because the M-S bond is to a considerable degree directional, simple sulphides exhibit a greater variety of different structures, often of great complexity. The metallic

s

properties of many sulphides show that all the bonding electrons are probably not behaving as in simple covalent crystals. The less stable form of crystal structure is formed initially and transformation to the stable form occurs during aging. Considerable change in both physical and chemical properties of sulphides occur during aging(109).

The aging of metal sulphides and the effect of solution conditions on the sulphide structure are discussed by Kolthoff and Moltzau(25). They report that a freshly precipitated HgS,which is rapidly formed, is of a more crystalline nature than a correspondingly fresh precipitate of ZnS, which is formed relatively slowly from acid solution. It is thought that the crystallization velocity of ZnS is relatively very small. They found that freshly precipitated CuS or HgS "promoted" the precipitation of ZnS. This promotion is attributed to the presence of an adsorbed layer of H_2S on the CuS and HgS respectively. The adsorbed H_2S has a much stronger tendency to ionize than that which is present in the bulk of the solution. Thus, the concentration of HS^- or S^{2-} on the surface is much greater than in the bulk of the solution; consequently, the speed of precipitation of ZnS is much greater at the interface than in the bulk of the solution.

Rudney(109) stresses the importance of solution conditions on the formation of sulphide precipitates. Since the sulphides are extremely insoluble, the rate or formation of their nuclei is large, consequently the nuclei do not grow but produce a sol which then coagulates. Because the sol adsorbs S^{2-} or HS^- ions, the colloidal particles become negatively charged. On coagulation, counter ions are trapped by the precipitate. Rudnev notes that a sulphide precipitate often acts as a "gathering" agent for micro-quantities of insoluble substances.

Lehrman, Been amd Mandel studied the coprecipitation of barium ions by sulphides of the ammonium sulphide group(114). Their results show that no sulphate ion is formed in the precipitation of Ni, Co, Zn, Fe and Mn sulphides. In every case, less barium is coprecipitated if it is added to a preformed precipitate of the sulphides than if barium is present in the original solution. After precipitation of Ni, Co and Mn sulphides, there is a large loss of barium ions due to post precipitation. In contrast, there is only a small loss with ZnS due to post precipitation and none with FeS precipitates.

The possibility of using hydrogen sulphide gas (H_2S) as a reagent for large-scale hydrometallurgical processing both for bulk precipitation of metal sulphides and for selective precipitation of one metal in the presence of others, has been examined by Simons(111). Simons discusses the process adopted by Moa Bay Mining Company for the recovery of nickel and cobalt from lateritic iron ores. He shows that metals not usually regarded as precipitable by H_2S from acid media (e.g., Ni, Co) can, in fact, be concentrated in this way if operating conditions are selected to give adequately rapid reaction rates.

b) Silver iodide

From electronegativity values, the Ag-I bond has about 91% covalent character. The adsorption of thorium ions on silver iodide sols was studied by Matijevic et al(115). Differences in adsorption at various pH revealed the strong influence of the hydrolysis of thorium ions upon adsorption. The hydrolysed ionic species adsorbed more strongly on the surface of AgI than the single hydrated ion, even though the latter carries a higher charge.

9. CONCLUSION

Much of the literature on coprecipitation published up to now simply consists of collections of empirical data and, as such, is of only limited application and interest. It is strongly urged that future investigations in this field should be based on the physiochemical properties of the constituents. Appropriate variables associated with these properties should be measured and controlled.

The following physiochemical properties of constituents and their compounds are relevant in coprecipitation:

- electron configuration,
- ionization potential,
- electronegativity value,
- covalent radius,
- ionic charge,
- ionic radius,
- ionic radius ratio,
- crystal morphology,
- crystal coordination number,
- lattice parameters,
- defects in crystal structure,
- character of chemical bonds,
- solubility product constant.

The liquid phase properties such as temperature, concentration of components, pH and ionic strength should be given.

There should be information on the precipitation process, for example:

a) Precipitation method - Precipitation from homogeneous solution or by direct mixing, in which case the reagent ratio is important.

b) Supersaturation.

c) Nucleation - Homogeneous or heterogeneous and the nature of the substrate.

d) Host precipitate - Internally-formed (IFP) or externally-formed (EFP) precipitate, particle size and whether the precipitate is crystalline, amorphous or colloidal and its point of zero charge.

e) Aging - Liquid phase properties, lattice constituent in excess, temperature and time.

Diagnostic tests should be made to determine the coprecipitation mechanism; adsorption, occlusion and/or solid solution formation. For adsorption, the adsorption isotherm is determined; for an ion-exchange process the distribution cofficient is found. If coprecipitation is by solid solution formation, then the distribution coefficients D and λ are obtained under conditions of near-equilibrium. It is important to obtain the distribution coefficients at both high and low concentrations of the microcomponent.

ACKNOWLEDGEMENT

The author is indebted to J. C. Ingles, Head of the Chemical Analysis Section, and to A. W. Ashbrook and D. J. Francis, for reading the paper and offering many helpful suggestions.

REFERENCES

1. West, T.S.; Analysis for Industry, *The Industrial Chemist*, (4) 191-193 and (5) 251-243, (1961).
2. Signalov, I. N., Dushina, A. P. and Aleskovskii, V. B.; Applying Silicate - Calcium Materials to Purify Waste Water from Nickel Ions, *Tsvetnye Metally*, (6) 27-30, (1972), (Russian).
3. Kim, Y. S. and Zeitlin, H.; The Role of Iron (III), Hydroxide as a Collector of Molybdenum from Sea Water, *Anal. Chim. Acta*, *46*, 1-8 (1969).
4. Qureshi, Mohsin; Kumar, Rajendra and Rathore, H. S.; Separation of Cadmium (II) from Zn(II) and other Metal Ions on a Cadmium Selective Exchanger: Titanium Selenite, *Anal. Chem.*, *44*, 6 1081-1084, (1972).
5. Cook, G. B. and Duncan J. F.; *Modern Radiochemical Practice*, London: Oxford University Press (1952).
6. Kolthoff, I. M.; Theory of Coprecipitation - The Formation and Properties of Crystalline Precipitates, *J. Phys. Chem.*, *36*, 860-881, (1932).
7. Gordon, L.; Salutsky, M. L. and Willard, H. H.; *Precipitation from Homogeneous Solution*, New York: John Wiley & Sons (1959).

8. Laitinen, H. A.: *Chemical Analysis*, Toronto: McGraw-Hill Book Co. (1960).

9. Erdey, L.; Polos, L. and Chalmers, R. A.: Development and Publication of New Gravimetric Methods of Analysis, *Talanta, 17*, 1143-1155 (1970).

10. Kolthoff, Elving and Sandell: *Treatise on Analytical Chemistry* (Ch. 18, Salutsky, M. L., Precipitates: Their Formation, Properties and Purity), New York: The Interscience Encyclopedia (1959).

11. Skoog, D. A. and West, D. M.: *Fundamentals of Analytical Chemistry*, Toronto: Holt, Rinehart and Winston (1966).

12. King, E. J.: *Qualitative Analysis and Electrolytic Solutions*, New York: Harcourt, Brace and Company (1959).

13. Kolthoff, I. M. and Sandell, E. B.: *Textbook of Quantitative Inorganic Analysis*, New York: The MacMillan Company (1947).

14. Walton, A. G.: *The Formation and Properties of Precipitates* , New York: Interscience Publishers (1967).

15. Wahl, A. C. and Bonner, N. A. (Editors): *Radioactivity Applied to Chemistry*, New York: John Wiley & Sons (1951).

16. Wiberg, K. B.: *Physical Organic Chemistry*, New York: John Wiley & Sons (1964).

17. Honig, E. P. and Hengst, J. H. Th.: Points of Zero Charge of Inorganic Precipitates, *J. Colloid and Interface Science*, *29*, (3) 510-520 (1969).

18. Parks, G. A.: The Isoelectric Points of Solid Oxides, Solid Hydroxides, and Aqueous Hydroxo Complex Systems, *Chem. Rev.*, *65*, 177-198 (1965).

19. Helfferich, F.: *Ion Exchange*, Toronto: McGraw-Hill Book Company (1962).

20. MacKenzie, J. M. W.: Zeta-Potential Studies in Mineral Processing: Measurement, Techniques and Applications, *Minerals, Science and Eng.*, *3*, (3) 25-43, July 1971.

21. Fuerstenau, D. W.: Interfacial Processes in Mineral/Water Systems, *Pure and Applied Chemistry*, *24*, (1) 135-164 (1970).

22. Freiser, H. and Fernando, Q,: *Ionic Equilibria in Analytical Chemistry*, New York: John Wiley & Sons (1963).

23. Adamson, A. W.: *Physical Chemistry of Surfaces*, New York: Interscience (1967).

24. Kolthoff, I. M.: Adsorption on Ionic Lattices, *J. Phys. Chem.*, *40*, 1027-1040 (1936).

25. Kolthoff, I. M. and Moltzau, D. R.: Induced Precipitation and Properties of Metal Sulfides, *Chem. Revs.*, *17*, (3) 293-325, (1935).

26. Ahrens, L. H. et. al. (editors), (L. V. Tavson, Factors Controlling the Diadochic Distribution of the Trace Elements during the Crystallizations of Magmas, p. 219), *Physics and Chemistry of the Earth, 6,* New York: The MacMillan Company (1965).

27. Ahrens, L. H.: The Use of Ionization Potentials, Part. 2, Anion Affinity and Geochemistry, *Geochimica et Cosmochimica Acta, 3,* 1-29, (1953).

28. Sanderson, R. T.: *Chemical Periodicity,* New York: Reinhold (1960).

29. Pauling, *The Nature of the Chemical Bond,* New York: Cornell University Press (1948).

30. Pauling, L.: The Sizes of Ions and the Structure of Ionic Crystals, *J. Am. Chem. Soc., 49,* (3) 765-790, (1927).

31. Robertson, W. D.: Correlation of Ionic and Atomic Radii with the Heat of Hydration, *J. Chem. Physics, 18,* (10) 1365-1366, (1950).

32. Ahrens, L. H.: The Use of Ionization Potentials, Part I - Ionic Radii of the Elements, *Geochimica et Cosmochimica Acta, 2,* 155-169, (1952).

33. Whittacker, E. J. W. and Muntus, R.: Ionic Radii for Use in Geochemistry, *Geochimica et Cosmochimica Acta, 34,* 945-956, (1970).

34. Smith, F. G.: *Physical Geochemistry*, Reading, Massachusetts: Addison-Wesley Publishing Company (1963).

35. Samsonov, G. V. (editor), *Handbook of the Physicochemical Properties of the Elements*, New York: IFI/Plenum Data Corporation (1968).

36. Pauling, L.: The Influence of Relative Ionic Sizes on the Properties of Ionic Compounds, *J. Am. Chem. Soc.*, *50*, 1936-1045, (1928).

37. Wells, A. F., *Structural Inorganic Chemistry*, London: Oxford University Press (1950).

38. Moeller, T.: *Inorganic Chemistry*, New York: John Wiley & Sons (1952).

39. Sanderson, R. T.: *Chemical Bonds and Bond Energy*, New York: Academic Press (1971).

40. Cartledge, G. H., Studies on the Periodic System .1, The Ionic Potential as a Periodic Function, *J. Am. Chem. Soc.*, *50*, (11) 2855-2872, (1928).

41. McIntire, W. L.: Trace Element Partition Coefficients - A Review of Theory and Applications to Geology, *Geochimica et Cosmochimica Acta*, *27*, 1209-1264, (1963).

42. Henderson, L. M. and Kracek, F. C.: The Fractional Precipitation of Barium and Radium Chromates, *J. Am. Chem. Soc.*, *49*, (3) 738-749, (1927).

43. Doerner, H. A. and Hoskins, W. M.: Coprecipitation of Radium and Barium Sulphates, *J. Am. Chem. Soc.*, *47*, (3) 662-675, (1925).

44. Gordon, L.; Teicher, H. and Burtt, B. P.: Coprecipitation from Homogeneous Solution - Manganese(II) on Basic Stannic Sulphate, *Anal. Chem.*, *26*, (6) 992-996, (1954).

45. Schneider F. and Rieman, W.: The Mechanism of Coprecipitation of Anions by Barium Sulphate, *J. Am. Chem. Soc.*, *59*, 354-357, (1937).

46. Haber, F.: *Ber. 55*, 1717 (1922); ref. 14, p. 101.

47. Von Weimarn, P. P., The Precipitation Laws, *Chem. Revs.*, 217-242, (1925).

48. Ostwald, W., *Z. Physik. Chem. Leipzig*, *22*, 289, (1897); see ref. 4, p. 127.

49. Klein, D. H. and Gordon, L.: Nucleation in Analytical Chemistry, *Talanta*, *1*, 334-343, (1958).

50. Kampmann, L.: On the Theory of Precipitation III, *Ber. Bunsenges, Physik. Chem.*, *77*, 304-310, (1973).

51. Christiansen, J. A. and Nielsen, A. E.: On the Kinetics of Formation of Precipitates of Sparingly Soluble Salts, *Acta Chem. Scand.*, *5*, 673-675, (1951).

52. Walton, A. G.: Nucleation and the Interfacial Tension of Sparingly Soluble Salts, *Microchim. Acta, 3,* 422-430, (1963).

53. Walton, A. G.: ref. 14, p. 5.

54. Gilman, J. J. (editor): (R. O. Grisdale, Growth from Molecular Complexes), *The Art and Science of Growing Crystals,* New York: John Wiley & Sons (1963).

55. Hirano, Koichi: Cataphoresis of Crystal Nuclei, *Nature, 174,* (8) 268-269, (1954).

56. Melia, T. P. and Moffitt, W. P.: Secondary Nucleation from Aqueous Solution, *I & E C Fundamentals, 3,* (4) 313-317, (1964).

57. Faust, D. and Hunter, J. V. (editors): (V. K. LaMer, Coagulation Versus the Flocculation of Colloidal Dispersions by Polyelectrolytes), *Principles and Applications of Water Chemistry,* New York: John Wiley & Sons (1966).

58. Kolthoff, I. M. and Noponen, G. E.: Studies on Aging of Fresh Precipitates .XIX, Aging of Freshly Precipitated Barium Sulphate in Dilute Barium and Sulphate Solutions, *J. Am. Chem. Soc., 60,* (3) 499-511, (1938).

59. Kolthoff, I. M. and von Fischer, W.: Studies on Aging of Precipitates .XXIV, The Apparent Effect of Filtration upon the Aging of Fresh Lead Sulphate - Aging of Lead Sulphate in

Excess of Lead and of Sulphate, *J. Am. Chem. Soc.*, *61*, (1) 191-197, (1939).

60. Kolthoff, I. M. and O'Brien, A.S.: Studies on Aging and Formation of Precipitates. XXXI - The Aging of Silver Bromide, *J. Am. Chem. Soc.*, *61*, (12) 3414-3419, (1939).

61. Kolthoff, I. M. and Halversen, R. A.: Studies on Aging and Coprecipitation, XXVII - The Coprecipitation of Nitrate with Lead Sulphate and the Decomposition of Coprecipitated Nitrate on Heating, *J. Phys. Chem.*, *43*, 605-611, (1939).

62. Kolthoff, I. M. and Noponen, G. E.: Studies on Aging of Fresh Precipitates, XVIII - The Mixed-Crystal Formation between Barium Sulphate and Potassium Permanganate, *J. Phys. Chem.*, *42*, 237-243, (1938).

63. Laitinen, H. A., ref. 4, p. 156.

64. West, T. S.: Separation of Traces of Inorganic Ions from Aqueous Solutions by Gas-, Liquid- and Solid-Phase Distribution Procedures, *Anal. Chim. Acta*, *25*, 405-421, (1961).

65. Sillen and Martell, *Stability Constants of Metal-Ion Complexes*, Special Publication No. 17, London: The Chemical Society (1964).

66. Chuiko, V. T.: Concentration Methods in the Determination of Traces of Nickel, *Zhurnal Analiticheskoi Khimii* (J. Anal. Chem. USSR), *2*, (6) 328-333, (1947), (Russian).

67. Vesely, V. and Pekarek, V.: Synthetic Inorganic Ion-Exchangers --1. Hydrous Oxides and Acidic Salts of Multivalent Metals, *Talanta*, *19*, 219-262, (1972).

68. Pekarek, V and Vesely, V.: Synthetic Inorganic Ion-Exchangers --2. Salts of Heteropolyacids, Insoluble Ferrocyanides, Synthetic Aluminosilicates and Miscellaneous Exchangers, *Talanta*, *19*, 1245-1283, (1972).

69. Sill, C. W.: Separation and Radiochemical Determination of Uranium and the Transuranium Elements using Barium Sulphate, *Health Physics*, *17*, 89-107, (1969).

70. Darrall, K. G.; Hammond, G. C. M. and Tyler, J. F. C.: The Determination of Plutonium-241 in Effluents, *Analyst*, *98*, (5) 358-363, (1973).

71. Berak, L.; Moravec, J. and Sara, V.: A Contribution to the Study of Selective Strontium Sorbents Obtained by Incorporating Calcium Sulphate into Barium Sulphate by the Heat Treatment of their Mixtures, *J. Inorg. Nucl. Chem.*, *29*, 2637-2647, (1967).

72. Sill, C. W. and Willis, C.P.: Precipitation of Submicrogram Quantities of Thorium by Barium Sulphate and Application to Fluorometric Determination of Thorium in Mineralogical and Biological Samples, *Anal. Chem.*, *36*, (3) 622-630, (1964).

73. Sill, C. W. and Willis, C.P.: Determination of Radioisotopes of Ce, Ba, La and Np after Separation by Barium Sulphate, *Anal. Chem.*, *38*, (1) 97-102, (1966).

74. Kolthoff, I. M. and Rosenblum, C.: Structural Changes Taking Place during the Aging of Freshly Formed Precipitates - I - Aging of Lead Sulphate Precipitated at Room Temperature, *J. Am. Chem. Soc., 56,* (6) 1264-1269, (1934).

75. Kolthoff, I. M. and Rosenblum, C.: Structural Changes Taking Place upon Aging of Freshly Prepared Crystalline Precipitates - 5 - The Thermal Aging of Freshly Prepared Lead Sulphate, *J. Am. Chem. Soc., 57,* (12) 2573-2577, (1935).

76. Kolthoff, I. M. and van't Riet, B.: Studies on Formation and Aging of Precipitates - 66 - Precipitation of Lead Sulphate at Room Temperature, *J. Phys. Chem., 63,* (6) 817-823, (1959).

77. Saylor, C. H.: Calcite and Aragonite, *J. Phys. Chem., 32,* 1441-1460, (1928).

78. Holland, H. D.; Borosik, M.; Munoz, J. and Oxburgh, U. M.: The Coprecipitation of Sr^{2+} with Aragonite and of Ca^{2+} with Strontianite between 90° and 100°C, *Geochim. et Cosmochim. Acta, 27,* 957-977, (1963).

79. Holland, H. D.; Holland, H. J. and Munoz, J. L.: The Coprecipitation of Cations with $CaCO_3$ --2. The Coprecipitation of Sr^{2+} with Calcite between 90° and 100°C, *Geochim. et Cosmochim, Acta, 28,* 1287-1301, (1964).

80. Tsusue, A. and Holland H. D.: The Coprecipitation of Cations with $CaCO_3$ --3. The Coprecipitation of Zn^{2+} with Calcite

between 50 and 250°C, *Geochim. et Cosmochim. Acta, 30,* (439-453, (1966).

81. Kinsman, D. J. J. and Holland, H. D.: The Coprecipitation of Cations with $CaCO_3$ --4. The Coprecipitation of Sr^{2+} with Aragonite between 16 and 96°C, *Geochim. et Cosmochim. Acta, 33,* 1-17, (1969).

82. Chuiko, V. T.; Kovaleva, N. V. and Kravtsova, A. A.: Metal Phosphates as Collectors (Coprecipitants) Communication 1. Coprecipitation of Chromium and Iron with Aluminum (Zinc) Phosphate during Partial Precipitation of the Macrocomponent, *J. Anal. Chem. USSR,* (10) 614-618, (1972), (English).

83. Chuiko, V. T.; Kravtsova, A. A. and Kovaleva, N. V.: Metal Phosphates as Collectors (Coprecipitants) Communication 2. Determination of Micro-amounts of Iron in Nickel, Cobalt, Zinc and Copper Salts, *J. Anal. Chem. USSR,* (10) 712-713, (1972), (English).

84. Vissers, D. R.: The Sorption of Orthophophate on Crystalline Metal Oxides, *J. Phys. Chem., 72,* (9) 3236-3244, (1968).

85. Feibush, A. M.; Rowley, K. and Gordon, L.: Coprecipitation in some Binary Systems of Rare Earth Oxalates, *Anal. Chem., 30,* (10) 1605-1609, (1958).

86. Munakata, Megumu; Toyomasu, Shigiki and Shigematsu, Twunenobu: Quantitative Treatment of the Distribution Coefficient for Coprecipitation of Metal Oxalates, *Anal. Chem., 44,* (12) 2057-2060, (1972).

87. Block, J. and Gordon, L.: Coprecipitation with Uranium Oxalate, *Talanta, 10,* 351-365, (1963).

88. Wells, A. F.: ref. 37, p. 543.

89. Bellomo, A.: Formation of Copper(II), Zinc(II), Silver(I) and Lead(II) Ferrocyanides, *Talanta, 17,* 1109-1114, (1970).

90. Bellomo, A.: De Marco, D. and Casale, A.: Formation of Nickel, Cobalt, Manganese and Cadmium Ferrocyanides, *Talanta, 19,* 1236-1240, (1972).

91. Cosgrove, J. G.; Collins, R. L. and Murty, D. S.: Preparation of Ferrous Ferricyanide (not Turnbull's Blue), *J. Am. Chem. Soc., 95:4,* 1083-1086, (1973).

92. Bellomo, A.; De Marco, D. and Casale, A.: Formation of Ferrocyanides --3. Fe(III), La(III) and Ce(III), *Talanta, 20,* 355-358, (1973).

93. Bellomo, A.; Casale, A and De Marco, D.: Formation of Ferrocyanides --1. Silver(K), Copper(II) and Cadmium(II), *Talanta, 20,* 335-338, (1973).

94. Cheng, K. L.: Precipitation of Metals with Potassium Ferrocyanide in Presence of Complexing Agents, *Anal. Chem., 27,* (10) 1594-1596, (1955).

95. Tananaev, I. V. and Glushkova, M. A.: Ferrocyanide Method of Extracting Small Amounts of Thallium from Solutions of Non-Ferrous Metals, *J. Applied Chem. USSR, 32,* 1947-1951, (1959), (English).

96. Wood, J. and Haigh, C.: Jarosite Process Boosts Zinc Recovery in Electrolytic Plants, *World Mining (Intern. ed.), 25,* (9) 34-38, (1972).

97. Haigh, C. J.; The Hydrolysis of Iron in Acid Solutions, *Proc. Aust. Inst. Min. Met.,* (9) 49-56, (1967).

98. White, L.: Electrolytic Zinc Plant is Latest Addition to Growing TG Complex, *Eng. and Mining J., 173,* (7) 66-76, (1972).

99. Steintveit, G.: Treatment of Zinc Leach Plant Residues by the Jarosite Process, *Advances in Extraction Metallurgy and Refining, Proceedings of International Symposium* (1971), pp. 521-528.

100. *Lead & Zinc (AIME World Symposium), 2,* pp. 229-244, New York: The Am. Inst. of Min. Metall. and Petroleum Eng. (1970).

101. Wells, A. F.: ref. 37, p. 420.

102. Weiser, H. B. and Milligan, W. O.: The Constitution of Colloidal Systems of the Hydrous Oxides, *Chem. Revs., 25,* 1-30, (1939).

103. Parks, G. A.: The Isoelectric Points of Solid Oxides, Solid Hydroxides and Aqueous Hydroxo Complex Systems, *Chem. Revs., 65,* 177-198, (1965).

104. Stumm, W. (Symp. Chairman): *(Equilibrium Concepts in Natural Water Systems,* G. A. Parks, Aqueous Surface Chemistry of Oxides and Complex Oxide Minerals), Advances

in Chemistry, Series 67; Washington: Am. Chem. Society (1967).

105. Donaldson, J. D. and Fuller, M. J.: Ion Exchange Properties of Tin(IV) Materials --1. Hydrous Tin(IV) Oxide and its Cation Exchange Properties, *J. Inorg. Nucl. Chem.*, *30*, 1083-1092, (1968).

106. Arden, T. V. and Harbutt, J.: The Separation of Uranium from other Metals in Sulphate Solution by Fractional Hydrolysis - 1 - Hydrolysis in Sulphate Solution, *J. Appl. Chem.*, *8*, (3) 141-159, (1958).

107. Jenny, H.: Studies on the Mechanism of Ionic Exchange in Colloidal Aluminum Silicates, *J. Phys. Chem.*, *36*, 2217-2258, (1932).

108. Chalyi, V. P. and Rozhenko, S. P.: A Study of the Kinetics and Ageing Mechanism of Metal Hydroxides --1. Investigation of Indium Hydroxide by X-Ray Photography, *J. Inorg. Chem. USSR*, *2*, (9) 37-47, (1957).

109. Rudnev. N. A.: Investigation of the Coprecipitation of Sulphides by Means of Radioactive Indicators, *J. Anal. Chem. USSR*, *8*, 1-10, (1953).

110. Rudnev, N. A. and Dzhumaev, R. M.: Coprecipitation in the Hg^{2+}, Cd^{2+}, $H^{+} \parallel S^{2-}$ System, *Russian Journal of Inorganic Chemistry*, *11*, (5) 584-587, (1966).

111. *Unit Processes in Hydrometallurgy*, *Metallurgical Society Conferences*, *vol. 24*, (C. S. Simons, Hydrogen Sulphide as a

Hydrometallurgical Reagent), New York: Gordon and Breach Science Publishers (1964).

112. Girifalco, L. A.: *Atomic Migration in Crystals*, New York: Blaisdell Publishing Company (1964).

113. Gomer, R. and Smith, C. S. (editors), *Structure and Properties of Solid Surfaces*, (W. A. Weyl, Wetting of Solids as Influenced by the Polarizability of Surface Ions), Chicago: The University of Chicago Press (1953).

114. Lehrmen, L.; Been, J. and Mandel, I.: The Coprecipitation of Barium Ion with the Sulphides of the Ammonium Sulphide Group in the Presence of Ammonium Ion, *J. Am. Chem. Soc.*, *63*, (5) 1348-1350, (1941).

115. Matijevic, E.; Abramson, M. B.; Ottewill, R. H., Schulz, K. F. and Kerker, M.: Adsorption of Thorium Ions on Silver Iodide Sols, *J. Phys. Chem.*, *65*, (10) 1724-1729, (1961).

116. Hillebrand, W. F.; Lundell, G. E. F.; Bright, H. A. and Hoffman, J. I., *Applied Inorganic Analysis*, New York: John Wiley & Sons (1953).

117. Lundell, G. E. F. and Hoffman, J. I.: *Outline of Methods of Chemical Analysis*, New York: John Wiley & Sons (1951).

118. Nozaki, Y. and Tsunogai, S.: A Simultaneous Determination of Lead-210 and Polonium-210 in Sea Water, *Anal. Chim. Acta*, *64*, 209-216, (1973).

119. Schomaker, V. and Stevenson, D. P.: Some Revisions of the Covalent Radii and the Additivity Rule for the Lengths of

of Partially Ionic Single Covalent Bonds, *J. Am. Chem. Soc.*, *63*, (1) 37-40, (1941).

120. Bigliocca, C.; Girardi, F.; Pauly, J.; Sabbioni, E.; Meloni, S. and Provasoli, A.: Radiochemical Separations by Adsorption on Manganese Dioxide, *Anal. Chem.*, *39*, (13) 1634-1639, (1967).

121. Jenkins, S. F.: Effect of Selected Cation Concentration on Coagulation and Adhesion to Silica Surfaces of δ-MnO_2, *Environmental Science & Technology*, *7*, (1) 43-47, (1973).

122. Sipalo-Zuljevic, J. and Wolf, R. H. H.: Sorption of Lanthanum(III), Cobalt(II) and Iodide Ions at Trace Concentrations on Ferric Hydroxide, *Microchimica Acta*, 315-320, (1973).

123. Kolthoff, Elving and Sandell, *Treatise on Analytical Chemistry*, (Ch. 32, Hermann, J. A. and Suttle, J. F., Precipitation and Crystallization), New York: The Interscience Encyclopedia (1959).

124. Hermann, J. A.: Ph.D. Thesis, Univ. of N. Mex., Albuquerque, N. Mex., 1955.

125. Verwey, E. J. W.: The Electrical Double Layer and the Stability of Lyophobic Colloids, *Chem. Rev.*, *16*, 363-415, (1935).

GLOSSARY

Adsorption is the process by which a substance is taken up and becomes attached to the solid surface. The surface of a solid in contact with solution cannot be bare, it must be covered by either the solvent or the solute. Thus, adsorption can be viewed as a competition between solvent and solute for the surface and consequently the net work involved in adsorbing the solute at the expense of the solvent can be analysed. This work may be negative or positive and, as a result, adsorption itself may also be positive or negative. Positive adsorption means there is a net attraction force between the surface and solute and there is more solute near the surface than would correspond to a uniform distribution throughout all the solvent. Negative adsorption means that there is a net repulsion force, and hence there is more solvent adsorbed than solute. Specific ionic adsorption occurs when ions interact so strongly with the solid surface that they lose their solvation (at least in the direction toward the solid surface), penetrate into the inner layer and become fixed to the solid surface with their electric centers at the inner Helmholtz plane (see Grahame-Stern model of the electrical double layer). In contrast to the complicated case of specific adsorption, in which various types of short-range forces of interaction must be taken into account, the interaction of the solvated ions with the surface may be accounted for by ordinary long-range coulombic forces. The interaction of these ions with the solid surface is essentially independent of their chemical properties, except for their ionic charges. Such ions are therefore said to be non-specifically adsorbed. Positive non-specific adsorption implies electrostatic attraction of the ion toward the surface; negative non-specific adsorption implies electrostatic repulsion. Non-specifically adsorbed ions (or counter ions) are partly located in the outer Helmholtz plane and partly in the diffuse layer of the electrical double layer.

Adsorption isotherms. Since temperature affects adsorption so markedly, the effects of changing bulk concentration are best observed at constant temperature. Thus, for a given constant temperature, adsorption isotherms give the relationship between the quantity of solute adsorbed and the equilibrium concentration of the solute in solution.

Chemisorption. When it is established that chemical bonds are formed between sorbate and sorbent (see "sorption"), the process is called chemisorption. When the rate of reaching equilibrium with respect to chemisorption is very slow and greatly affected by temperature, then we speak of activated adsorption.

Coprecipitation is the carrying down by the precipitate of a soluble substance (coprecipitant) from its unsaturated solution (i.e., the ion product of the coprecipitant is less than its solubility product). The mechanisms by which coprecipitation occurs are: adsorption, solid solution formation (incorporation) and occlusion (entrapment).

Crystal lattice refers to the arrangement of atoms, molecules or ions of a crystal in the form of a space lattice.

Diffuse layer. Positive non-specific adsorption implies electrostatic attraction of the ion toward the solid; negative non-specific adsorption implies electrostatic repulsion. The non-specifically adsorbed ions are not all located in the inner layer, some are contained in a three-dimensional region, the diffuse layer (sometimes called Gouy layer), which extends from the inner layer into the bulk of the solution. The origin of the diffuse character of this region is thermal agitation, which provides a disordering force opposed to the ordering coulombic forces of attraction and repulsion

Electrical double layer refers to the interfacial region formed at the crystal surface in contact with an electrolyte solution, regardless of the actual structural complexity of the phase boundary. A more descriptive term would be electrochemical multilayer, since (a) the forces which lead to its formation include, in addition to long-range electrostatic forces, shorter-range forces of types usually considered molecular or chemical, and (b) the interfacial region consists of not two, but at least three, and sometimes more, distinct subregions or layers. The double layer consists of three main parts: (a) the solid phase; and on the solution side of the interface, (b) an immobile inner layer only a few molecular diameters thick located next to the solid surface, and (c) an outer or diffuse layer, which is really a three-dimensional region extending into the bulk of the solution.

Gouy-Chapman model of the electrical double layer. The electrical double layer consists of excess ions (or electrons) present on the solid phase and an equivalent amount of ionic charge of opposite sign distributed in the solution phase near the interface. The charge on the solid "wall" is treated as a surface charge smeared out uniformly over the surface. The space charge in the solution is considered to be built up by unequal distribution of point-like ions. The solvent is treated as a continuous medium, influencing the double layer only through its dielectric constant. The Gouy-Chapman theory predicts that the potential across the double layer drops exponentially from the "wall" into the bulk of the solution.

Grahame-Stern model of the electrical double layer. The first evaluation of the amounts of solutes adsorbed, based on experimental data using the Stern model, is due to Grahame. According to Grahame, the locus of the electrical centers of specifically adsorbed ions is called the inner Helmholtz plane (iHp). Occasionally, the iHp is referred to simply as the Helmholtz plane. The imaginary plane passing through the centers of the closest approaching solvated ions is known as the outer Helmholtz plane (oHp). The oHp is sometimes called the Gouy plane. The non-specifically adsorbed (solvated) ions are not all located at the oHp; some are located in the diffuse (Gouy) layer which extends from the oHp into the bulk of the solution.

Ion exchange. Adsorption by ion exchange may take place: (a) between the lattice ions and foreign ions, in which case specific properties of the foreign ions are of the greatest importance, or (b) between counter ions, in which case electrical forces play the predominant role.

Inner layer is the immobile layer of adsorbed ions, solvent molecules and, sometimes, other neutral molecules on the solution side of the interface. It is also sometimes called compact, rigid, Helmholtz or Stern layer.

Interface and interphase. An interface formed by two phases is the apparent two-dimensional surface of contact of these two phases. It is an apparent surface because in reality when two phases meet, there is a region in which there is a continuous transition from the properties of one phase to the properties of the other. If one aims to refer specifically to this three-dimensional transition region, then it is more appropriate to use the term interphase.

Isomorphism. Two compounds are isomorphous if their internal crystal structure is similar. That is, (a) they have the same type chemical formulas, (b) the sizes of their components relative to one another are about the same and (c) the component atoms are joined together by similar-type bonds.

Lattice ions refer to precipitate component ions.

Macrocomponent refers to a precipitate component which is a major constituent of the precipitate.

Microcomponent (or impurity) refers to coprecipitated ions or molecules, since they are usually present in minute amount in the precipitate.

Molecular adsorption refers to adsorption of non-electrolytes (molecules) involving van der Waals' forces, and also the adsorption of ion pairs, which appears to involve the simultaneous occupation of adjacent sites by a foreign cation and anion.

Non-specific adsorption. (See "adsorption")

Occlusion is defined as the entrapment of counter ions by the rapidly growing solid phase.

Paneth-Fajans-Hahn rules of adsorption of ions on crystal lattices

1. An ion is strongly adsorbed on an equivalent compound of the salt type only when it forms a difficultly soluble or weakly ionized compound with the oppositely charged ions of the lattice.
2. The adsorption of a cation is increased by adsorbed anions, that is, by charging the surface negatively, and is decreased by adsorbed cations, that is, by charging the surface positively.
3. The converse of "2": The adsorption of anions is increased by adsorbed cations and is decreased by adsorbed anions. The effect on the adsorption of a given ion in both "2" and "3" increases with increasing adsorption of the foreign ion.

Postprecipitation. In postprecipitation, the main precipitate comes down first; a precipitate of another substance comes down later from its supersaturated solution.

Potential-determining ions are those that carry a charge to the solid phase.

Potential drop across the electrical double layer. There are three potentials of particular interest. One is at the surface of the particle itself and measures the total potential of the double layer. This is called psi, ψ, and is sometimes distinguished as

ψ_0. Those ions whose concentrations determine ψ_0 are called potential-determining ions. Another is at the boundary between the Stern and the Gouy part of the double layer and is known as ψ_δ (Stern potential). The third is at the boundary between the solvent molecules adhering to the particle in its motion and that which can move with respect to it. This plane of shear (or slipping plane) essentially separates the water of hydration from free water. The potential at this plane is called the zeta potential, ζ (or Gouy potential or electrokinetic potential). The zeta potential includes only that part of the diffuse layer which is not within a firmly bound solvent layer nor within crevices and hollows.

Precipitation is the process of forming a precipitate from solution by the addition of a reagent (precipitant). The process involves formation of nuclei, growth of nuclei, growth of crystallites and/or coagulation of colloidal particles. Supersaturation is the driving force of precipitate formation.

Simultaneous precipitation occurs when, for all of the substances precipitated, the individual ion products have exceeded the solubility product constant.

Solid solution formation. If, due to similarity in size and structure, the adsorbed phase is miscible with and diffuses into the host phase, then a solid solution is formed.

Sorption is a very general term to designate the movement of a component from one phase to another, particularly when this other phase is solid. We can say "the dye is sorbed by the precipitate", in this case the dye is the sorbate and the precipitate is the sorbent. If it is established that the sorbate is only on the surface of the precipitate, then we speak of adsorption.

Stern model. Stern considered the possibility of specific adsorption of the ions and that these and a certain fraction of those ions that are attracted by purely coulombic forces, are located in a plane at a distance δ from the "wall" of the solid. He then applied the Gouy-Chapman theory to those ions in the diffuse layer. Thus the potential falls linearly from the "wall" to the plane at distance δ, but exponentially from δ into the bulk of the solution. Stern also assumed that the Langmuir adsorption isotherm relates the concentration of adsorbed ions to their concentration in the solution.

Van der Waals' forces. These are short-range forces which decrease in intensity as the inverse sixth power of the distance between the atoms. There are several types. One is the dipole-dipole interaction, as typified by a hydrogen bond. A second involves the interaction between a dipole and a molecule into which it induces a dipole. This is known as an induction or Debye force. A third is known as dispersion or London force, which strongly depends on the polarizability of molecules. The force is due to instantaneous dipoles created in atoms or molecules by the motion of electrons. The dipoles tend to be synchronized, so that a net attractive potential is found.