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Chapter

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Solutions and Solution Properties

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1.1 Introduction and Motivation

Crystallization is a separation and purification technique employed to produce a wide variety of materials. Crystallization may be defined as a phase change in which a crystalline product is obtained from a solution. A solution is a mixture of two or more species that form a homogeneous single phase. Solutions are normally thought of in terms of liquids, but solutions may include solids and even gases. Typically, the term solution has come to mean a liquid solution consisting of a solvent, which is a liquid, and a solute, which is a solid, at the conditions of interest. The term *melt* is used to describe a material that is solid at normal conditions and is heated until it becomes a molten liquid. Melts may be pure materials, such as molten silicon used for wafers in semiconductors, or they may be mixtures of materials. In that sense, a homogeneous melt with more than one component is also a solution, but it is normally referred to as a melt. A solution can also be gaseous; an example of this is a solution of a solid in a supercritical fluid.

Virtually all industrial crystallization processes involve solutions. The development, design, and control of any of these processes involve knowledge of a number of the properties of the solution. This chapter presents and explains solutions and solution properties and relates these properties to industrial crystallization operations.

1.2 Units

Solutions are made up of two or more components, of which one is the solvent and the other is the solute(s). There are a variety of ways to express the composition of a solution. If we consider the simple system of a solvent and a solute, its composition may be expressed in terms of mass fraction, mole fraction, or a variety of concentration units, as shown in Table 1.1. The types of units that are commonly used can be divided into those that are ratios of the mass (or moles) of solute to the mass (or moles) of the solvent, those that are ratios of the mass (or moles) of the solute to the mass (or moles) of the solution, and those that are ratios of the mass (or moles) of the solute to the volume of the solution.

While all three units are commonly used, it is important to note that use of units of type 3 requires knowledge of the solution density to convert these units into those of the other types. In addition, type 3 units must be defined at a particular temperature because the volume of a solution is a function of temperature. The best units to use for solution preparation are mass of solute per mass of solvent. These units have no temperature dependence, and solutions can be prepared simply by weighing each species. Table 1.1 Concentration Units

Type 1: Mass (or moles) solute/mass (or moles) solvent grams solute/100 grams solvent moles solute/100 grams solvent Molal: moles solute/1000 grams solvent lb_m solute/lb_m solvent moles solute/moles solvent Type 2: Mass (or moles) solute/mass (or moles) solution Mass fraction: grams solute/grams total Mole fraction: moles solute/moles total Type 3: Mass (or moles) solute/volume solution

Molar: moles solute/liter of solution grams solute/liter of solution lb_m solute/gallon solution

Conversion among mass (or mole) -based units is also simple. Example 1.1 demonstrates conversion of units of all three types.

1.3 Solubility of Inorganics

1.3.1 Basic Concepts

A solution is formed by the addition of a solid solute to a solvent. The solid dissolves, forming the homogeneous solution. At a given temperature, there is a maximum amount of solute that can dissolve in a given amount of solvent. When this maximum is reached, the solution is said to be saturated. The amount of solute required to make a saturated solution at a given condition is called the *solubility*.

Solubilities of common materials vary widely, even when the materials appear to be similar. Table 1.2 lists the solubility of a number of inorganic species (Mullen 1972; Myerson et al. 1990). The first five species all have calcium as the cation, but their solubilities vary over several orders of magnitude. At 20° C, the solubility of calcium hydroxide is 0.17 g/100 g water, while that of calcium iodide is 204 g/100 g water. The same variation can be seen in the six sulfates listed in Table 1.2. Calcium sulfate has a solubility of 0.2 g/100 g water at 20°C, while ammonium sulfate has a solubility of 75.4 g/100 g water.

The solubility of materials depends on temperature. In the majority of cases, the solubility increases with

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Jennifer Moffitt Schall and Allan S. Myerson

Example 1.1 Conversion of Concentration Units

Given: 1 molar solution of NaCl at 25°C Density of solution = 1.042 g/cm³

Molecular weight (MW) NaCl = 58.44 g/mol

Solution:

1 molar —	1 mol NaCl	1liter	58.44 g NaCl	1 cm ³
	liter of solution	1000 cm ³	mol NaCl	1.042 g
=	0.056 g NaCl g solution			
=	0.056 wt fractic	on NaCl =	5.6 wt% NaC]
<u>0</u>	$\frac{0.056 \text{ g NaCl}}{\text{g solution}} = \frac{1}{0}$	0.0).944 g wa)56 g NaCl iter + 0.056 g	NaCl
	= (0.059 g Na	Cl/g water	

 $0.056 \text{ wt fraction NaCl} = \frac{0.056 \text{ g NaCl}}{0.944 \text{ g water} + 0.056 \text{ g NaCl}}$

 $= \frac{\frac{0.056 \text{ g NaCl}}{58.44 \text{ g/mol NaCl}}}{\frac{0.056 \text{ g NaCl}}{58.44 \text{ g/mol NaCl}} + \frac{0.944 \text{ g water}}{18 \text{ g/mol water}}}$

= 0.018 mol fraction NaCl



Figure 1.1 Solubility of KNO_3 , $CuSO_4$, and NaCl in aqueous solution Source: Data from Mullen 1972.

increasing temperature, although the rate of the increase varies widely from compound to compound. The solubilities of several inorganics as a function of temperature are shown in Figure 1.1. Sodium chloride is seen to have a relatively weak temperature dependence, with the solubility changing from 35.7 to 39.8 g/100 g water over a 100°C range. Potassium nitrate, by contrast, changes from 13.4 to 247 g/100 g water over the same temperature range. This kind of information is very important in crystallization processes because it will determine the amount of cooling required to yield a given amount of product and whether cooling will provide a reasonable product yield.

2

Table 1.2 Solubilities of Inorganics at 20°C

Compound	Chemical formula	Solubility (g anhydrous/ 100 g H₂O)
Calcium chloride	CaCl ₂	74.5
Calcium iodide	Cal ₂	204
Calcium nitrate	Ca(NO ₃) ₂	129
Calcium hydroxide	Ca(OH) ₂	0.17
Calcium sulfate	CaSO ₄	0.20
Ammonium sulfate	(NH ₄) ₂ SO ₄	75.4
Copper sulfate	CuSO ₄	20.7
Lithium sulfate	Li ₂ SO ₄	34
Magnesium sulfate	MgSO ₄	35.5
Silver sulfate	Ag ₂ SO ₄	0.7
<i>Source:</i> Based on data fr	om Mullen 1972 and	Mverson et al. 1990.



Figure 1.2 Solubility of calcium hydroxide in aqueous solution *Source*: Data from Myerson et al. 1990.

In sparingly soluble materials, solubility can also decrease with increasing temperature. A good example of this is the calcium hydroxide-water system shown in Figure 1.2.

The solubility of a compound in a particular solvent is part of the system phase behavior and can be described graphically by a phase diagram. In phase diagrams of solid-liquid equilibria, the mass fraction of the solid is usually plotted versus temperature. An example is Figure 1.3, which shows the phase diagram for the magnesium sulfate–water system. This system demonstrates another common property of inorganic solids, the formation of hydrates. A *hydrate* is a solid formed on crystallization from water that contains water molecules as part of its crystal structure. The chemical formula of a hydrate indicates the number of moles of water present per mole of the solute species by listing a stoichiometric number and water after the dot in the chemical formula. Many compounds that form hydrates form several hydrates with varying amounts of Cambridge University Press 978-0-521-19618-5 — Handbook of Industrial Crystallization Edited by Allan S. Myerson , Deniz Erdemir , Alfred Y. Lee Excerpt

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Solutions and Solution Properties



Figure 1.3 Phase diagram for MgSO₄·H₂O *Source*: Reprinted with permission of the publisher from R. M. Felder and

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water. From the phase diagram (Figure 1.3) we can see that $MgSO_4$ forms four stable hydrates ranging from 12 mol of water/mol $MgSO_4$ to 1 mol of water/mol of $MgSO_4$. As is usual with hydrates, as the temperature rises, the number of moles of water in the stable hydrate declines, and at some temperature, the anhydrous material is the stable form.

The phase diagram contains much useful information. Referring to Figure 1.3, the line *abcdef* is the solubility or saturation line that defines a saturated solution at a given temperature. Line *ab* is the solubility line for the solvent (water) because when a solution in this region is cooled, ice crystallizes out and is in equilibrium with the solution. Point *b* marks what is known as the *eutectic composition*. If the solution is cooled at this composition (0.165 wt fraction MgSO₄), both ice and MgSO₄ will separate as solids. The rest of the curve from *b* to *f* represents the solubility of MgSO₄ as a function of temperature. If we were to start with a solution at 100°F and 27.5 wt% MgSO₄ (point *A* in Figure

1.3) and cool that solution, the solution would be saturated at the point where a vertical line from A crosses the saturation curve, which is at 80°F. If the solution were cooled to 60°F as shown at point D, the solution will have separated at equilibrium into solid MgSO₄·7H₂O and a saturated solution of the composition corresponding to point C.

The phase diagram also illustrates a general practice concerning hydrate solubility. The solubilities of compounds that form hydrates are usually given in terms of the anhydrous species. This saves much confusion when multiple stable hydrates can exist but requires that care be taken when performing mass balances or preparing solutions. Example 1.2 illustrates these types of calculations.

Phase diagrams can be significantly more complex than the example presented in Figure 1.3 and may involve additional stable phases and/or species. A number of references discuss these issues in detail (Gordon 1968; Rosenberger 1981). **Cambridge University Press** 978-0-521-19618-5 — Handbook of Industrial Crystallization Edited by Allan S. Myerson , Deniz Erdemir , Alfred Y. Lee Excerpt More Information

Jennifer Moffitt Schall and Allan S. Myerson

Example 1.2 Calculations Involving Hydrates

Given solid MgSO₄·H₂O, prepare a saturated solution of MgSO₄ at 100°F.

(a) Looking at the phase diagram (Figure 1.3), the solubility of MgSO₄ at 100°F is 0.31 wt. fraction MgSO₄ (anhydrous), and the stable phase is MgSO₄·7H₂O. First, calculate the amount of MgSO₄ (anhydrous) necessary to make a saturated solution at 100°F.

 $0.31 = x_{f} = \frac{\text{weight MgSO}_{4}(g)}{\text{weight MgSO}_{4}(g) + \text{weight H}_{2}O(g)}$

Using a basis:

For 1000 g H_2O , the weight of MgSO₄ (g) needed to make a saturated solution is 449 g MgSO₄ (anhydrous). (b) Because the stable form of the MgSO₄ available is MgSO₄·7H₂O, to do this, we need to know the molecular masses of MgSO₄, H₂O, and MgSO₄·7H₂O. These are 120.37 g/gmol and 246.48 g/gmol, respectively.

$$x_{MgSO_4} = \frac{\text{wt of MgSO}_4 \text{ in the hydrate}}{\text{wt of MgSO}_4 \cdot 7\text{H}_2\text{O}} = \frac{120.37}{246.48} = 0.488$$
$$x_{H_2O} = \frac{\text{wt of H}_2\text{O in the hydrate}}{\text{wt of MgSO}_4 \cdot 7\text{H}_2\text{O}} = \frac{126.11}{246.48} = 0.512$$

Mass balances:

Total weight = wt H_2O + wt of MgSO₄ in the hydrate 0.31(total weight) = wt of MgSO₄ in the hydrate 0.69(total weight) = wt of H₂O in the hydrate + wt of H₂O solvent

First, we will examine the total mass balance. Because we are using a basis of 1000 g of H_2O , and the weight of MgSO₄ in the hydrate is equal to the weight of MgSO₄ (anhydrous) calculated in (a), the total weight of our system is 1449 g.

By substituting the mole fraction expressions into the species material balances, we can solve for the amount of MgSO₄·7H₂O needed to make a saturated solution at 100°F.

 $0.31(1449 \text{ g}) = 0.488(\text{wt of MgSO}_4 \cdot 7\text{H}_2\text{O})$ wt of MgSO₄ \cdot 7H₂Og = 920 g $0.69 (1449 g) = wt H_2 O solvent + 0.512 (wt of MgSO_4 \cdot 7H_2 O)$ $0.69(1449 \,\text{g}) = \text{wt H}_2\text{O solvent} + 0.512(920 \,\text{g})$ wt H₂O solvent = 529 g

Therefore, to make a saturated solution of MgSO₄ at 100°F starting with MgSO₄·7H₂O, we need to add 920 g of the hydrate to 529 g of H₂O.

1.3.2 Sparingly Soluble Species: Dilute Solutions

As we saw in Section 1.3.1, the solubility of materials varies according to their chemical composition and with temperature. Solubility is also affected by the presence of additional species in the solution, by the pH, and by the use of different solvents (or solvent mixtures). When discussing inorganic species, the solvent is usually water, whereas with organics, the solvent can be water or a number of organic solvents or solvent mixtures.

If we start with a sparingly soluble inorganic species such as silver chloride and add silver chloride to water in excess of the saturation concentration, we will eventually have equilibrium between solid AgCl and the saturated solution. The AgCl is, like most of the common inorganics, an electrolyte and dissociates into its ionic constituents in solution. The dissociation reaction can be written as

$$\operatorname{AgCl}(s) \leftrightarrow \operatorname{Ag}^+ + \operatorname{Cl}^-$$
 (1.1)

The equilibrium constant for this reaction can be written as

$$K = \frac{a_{\rm Ag^+} a_{\rm Cl^-}}{a_{\rm AgCl}} \tag{1.2}$$

where *a* denotes the activities of the species. If the solid AgCl is in its stable crystal form and at atmospheric pressure, it is at a standard state and will have an activity of 1. The equation can then be written as

$$K_{sp} = a_{Ag^+} a_{Cl^-} = (\gamma_{Ag^+} m_{Ag^+}) (\gamma_{Cl^-} m_{Cl^-})$$
(1.3)

where γ is the activity coefficient of the species and *m* represents the concentration in solution of the ions in molal units. For sparingly soluble species such as AgCl, the activity coefficient can be assumed to be unity (using the asymmetric convention for activity coefficients), so that Equation (1.3) reduces to

$$K_{sp} = (m_{Ag^+})(m_{Cl^-})$$
 (1.4)

This equation represents the solubility product of silver chloride. Solubility products are generally used to describe the solubility and equilibria of sparingly soluble salts in aqueous solutions. Solubility products of a number of substances are given in Table 1.3. It is important to remember that use of solubility product relations based on concentrations assumes that the solution is saturated, in equilibrium, and ideal (the activity coefficient is equal to 1). It is therefore an approximation, except with very dilute solutions of one solute.

Equation (1.4) can be used for electrolytes in which there is a 1:1 molar ratio of the anion and cation. For an electrolyte that consists of univalent and bivalent ions, such as silver sulfate, which dissociates into 2 mol of silver ions for each mole of sulfate ions, the solubility product equation would be written as

$$K_{sp} = (m_{Ag^+})^2 (m_{SO_4^{2-}}) \tag{1.5}$$

In the dissociation equation, the concentration of the ions of each species is raised to the power of the species' stoichiometric number.

The solubility product principle enables simple calculations to be made of the effect of other species on the solubility of a given substance and may be used to determine the species that Cambridge University Press 978-0-521-19618-5 — Handbook of Industrial Crystallization Edited by Allan S. Myerson , Deniz Erdemir , Alfred Y. Lee Excerpt <u>More Information</u>

Table 1.3 Solubility Products

Substance	Solubility Product at 25°C
Aluminum hydroxide	3.70×10^{-15}
Barium carbonate	2.58×10^{-9}
Barium chromate	1.17×10^{-10}
Barium fluoride	1.84×10^{-7}
Barium iodate monohydrate	1.67×10^{-9}
Barium sulfate	1.08×10^{-10}
Calcium carbonate (calcite)	3.36×10^{-9}
Calcium fluoride	3.45×10^{-11}
Calcium iodate hexahydrate	7.10×10^{-7}
Calcium oxalate monohydrate	2.32×10^{-9}
Calcium sulfate	4.93×10^{-5}
Cupric iodate monohydrate	6.94×10^{-8}
Cupric oxalate	4.43×10^{-10}
Cuprous bromide	6.27×10^{-9}
Cuprous chloride	1.72×10^{-7}
Cuprous iodide	1.27×10^{-12}
Ferric hydroxide	2.79×10^{-39}
Ferrous hydroxide	4.87×10^{-17}
Lead carbonate	7.40×10^{-14}
Lead sulfate	2.53×10^{-8}
Lithium carbonate	8.15×10^{-4}
Magnesium carbonate	6.82×10^{-6}
Magnesium fluoride	5.16×10^{-11}
Magnesium hydroxide	5.61×10^{-12}
Magnesium oxalate dehydrate	4.83×10^{-6}
Manganese carbonate	2.24×10^{-11}
Silver bromate	5.38×10^{-5}
Silver iodide	8.52×10^{-17}
Zinc hydroxide	3.00×10^{-17}
Source: Data from Weast 1975.	

will precipitate in an electrolyte mixture. One simple result of applying the solubility product principle is the common ion effect. This is the effect caused by the addition of an ionic species that has an ion in common with the species of interest. Because the solubility of a species is given by the product of the concentration of its ions, when the concentration of one type of ion increases, the concentration of the other must decline, or the overall concentration of that compound must decline. We can illustrate this simply by using our previous example of silver

Solutions and Solution Properties

chloride. The solubility product of silver chloride at 25°C is 1.56 $\times 10^{-10}$. This means that at saturation we can dissolve 1.25 $\times 10^{-5}$ mol of AgCl/1000 g of water. If, however, we were to start with a solution that has a concentration of 1×10^{-5} molal NaCl (hence 1×10^{-5} molal Cl⁻), the solubility product equation would be written in the form

$$K_{\rm sp} = (m_{\rm Ag^+})(m_{\rm Cl^-}) = (x_{\rm Ag^+})(x_{\rm Cl^-} + 1 \times 10^{-5})$$
 (1.6)

$$K_{sp} = x^2 + 10^{-5}x \tag{1.7}$$

where *x* is the amount of AgCl that can dissolve in the solution. Solving Equation (1.7) results in $x = 0.725 \times 10^{-5}$ molal. The common ion effect has worked to decrease the solubility of the compound of interest. It is important to remember that this is true only for very dilute solutions. In more concentrated solutions, the activity coefficients are not unity, and more complex electrical effects and complexation may occur. This is discussed in detail in Section 1.3.3.

Another use of solubility products is the determination, in a mixture of slightly soluble materials, as to what material is likely to precipitate. This is done by looking at all the ion concentrations and calculating their products in all possible combinations. These are then compared with the solubility products that must already be known. This is useful in situations where scale formation is of interest or in determining the behavior of slightly soluble mixtures.

1.3.3 Concentrated Solutions

Unfortunately, like all easy-to-use principles, the solubility product principle is not generally applicable. At higher concentrations, electrical interactions, complex formation, and solution nonideality make the prediction of the effect of ionic species on the solubility of other ionic species much more complicated.

In Section 1.3.2 we used the solubility product principle to calculate the effect of a common ion on the solubility of a sparingly soluble species. The common ion effect, however, is completely dominated by a more powerful effect when a large concentration of another electrolyte is present. In fact, the solubility of sparingly soluble materials increases with increasing ion concentration in solution. This is called the *salt effect* and is illustrated in Figures 1.4 through 1.6, where we see the increase in solubility of AgCl as a function of increasing concentrations of added electrolytes. We see this effect in both added salts with a common ion and without. This effect can also be induced by changing the pH of the solution because this changes the ion content of the solution.

The solubility of many inorganics in aqueous solution is available in the book by Linke and Seidell (1965). This reference also contains the solubilities of electrolytes in the presence of other species. For example, Figure 1.7 shows the solubility of NaCl as a function of NaOH concentration. As a general rule, the solubility of most inorganics in water is available as a function of temperature. What is more difficult to find is the effect of other species on the solubility. If several other species are present, the data will usually not be available. Given this situation, there are two alternatives. The first is to measure the solubility at the conditions and composition of interest. Experimental

5

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Figure 1.4 Solubility of AgCl in aqueous CaSO₄ solution at 25°C Source: Data from Linke and Seidell 1965.



Figure 1.6 Solubility of AgCl in aqueous CaCl₂ solution *Source:* Data from Linke and Seidell 1965.

methods for solubility measurement will be discussed in Section 1.4.6. The second alternative is to calculate the solubility. This is a viable alternative when thermodynamic data are available for the pure components (in solution) making up the multicomponent mixture. An excellent reference for calculation techniques in this area is the *Handbook of Aqueous Electrolyte Thermodynamics* by Zemaitis et al. (1986). A simplified description of calculation techniques is presented later in Section 1.3.3.

Solution Thermodynamics. As we have seen previously, for a solution to be saturated, it must be at equilibrium with the solid solute. Thermodynamically, this means that the chemical potential of the solute in the solution is the same as the chemical potential of the species in the solid phase.

$$\mu_{i_{\text{solid}}} = \mu_{i_{\text{solution}}} \tag{1.8}$$

If the solute is an electrolyte that completely dissociates in solution (strong electrolyte), Equation (1.8) can be rewritten as

$$\mu_{i_{\text{solid}}} = \nu_c \mu_c + \nu_a \mu_a \tag{1.9}$$

where v_c and v_a are the stoichiometric numbers, and μ_c and μ_a are the chemical potentials of the cation and anion,



Figure 1.5 Solubility of AgCl in aqueous NaNO₃ solution at 30°C *Source*: Data from Linke and Seidell 1965.



Figure 1.7 Solubility of NaCl in aqueous NaOH solution *Source:* Data from Linke and Seidell 1965.

respectively. The chemical potential of a species is related to the species activity by

$$\mu_i(T) = \mu_{(aq)}^0(T) + RT\ln(a_i)$$
(1.10)

where a_i is the activity of species i, $\mu^0_{(aq)}$ is an arbitrary reference state chemical potential, R is the gas constant, and T is temperature. The activity coefficient is defined as

$$\gamma_i = \frac{a_i}{m_i} \tag{1.11}$$

where m_i is the concentration in molal units. In electrolyte solutions, because of the condition of electroneutrality, the charges of the anion and cation will always balance. When a salt dissolves, it will dissociate into its component ions. This has led to the definition of a mean ionic activity coefficient and mean ionic molality defined as

$$\gamma_{+} = \left(\gamma_{c}^{\nu_{c}} \gamma_{a}^{\nu_{a}}\right)^{1/\nu} \tag{1.12}$$

$$m_{\pm} = (m_c^{\nu_c} m_a^{\nu_a})^{1/\nu} \tag{1.13}$$

where v_c and v_a are the stoichiometric number of ions of each type present in a given salt. The chemical potential for a salt can be written as

6

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$$\mu_{\text{salt}(aq)} = \mu_{(aq)}^0 + \nu RT \ln(\gamma_{\pm} m_{\pm})^{\nu}$$
(1.14)

where $\mu^0_{(aq)}$ is the sum of the two ionic standard-state chemical potentials, and v is the stoichiometric number of moles of ions in 1 mole of solid. In practice, experimental data are usually reported in terms of mean ionic activity coefficients. As we discussed earlier, various concentration units can be used. We have defined the activity coefficient on a molal scale. On a molar scale, it is

$$y_i = \frac{a_i(c)}{c_i} \tag{1.15}$$

where y_i is the molar activity coefficient, and c_i is the molar concentration. We can also define the activity coefficient on a mole fraction scale as

$$f_i = \frac{a_i(x)}{x_i} \tag{1.16}$$

where f_i is the activity coefficient, and x_i the mole fraction. Converting activity coefficients from one type of unit to another is neither simple nor obvious. Equations that can be used for this conversion have been developed and include (Zemaitis et al. 1986)

$$f_{\pm} = (1.0 + 0.01 M_s vm) \gamma_{\pm} \tag{1.17}$$

$$f_{\pm} = \frac{\rho + 0.001c(\nu M_s - M)}{\rho_0} y_{\pm}$$
(1.18)

$$\gamma_{\pm} = \frac{\rho - 0.001 cM}{\rho_0} y_{\pm} = \left(\frac{c}{m\rho_0}\right) y_{\pm}$$
 (1.19)

$$y_{\pm} = (1 + 0.001 mM) \left(\frac{\rho}{\rho_0}\right) \gamma_{\pm} = \left(\frac{m\rho_0}{c}\right) \gamma_{\pm}$$
(1.20)

where v = stoichiometric number = $v_+ + v_-$

 ρ = solution density

 ρ_0 = solvent density

M = molecular weight of the solute

 M_s = molecular weight of the solvent

Solubility of a Pure-Component Strong Electrolyte. Calculation of the solubility of a pure-component solid in solution requires that the mean ionic activity coefficient be known along with a thermodynamic solubility product (a solubility product based on activity). Thermodynamic solubility products can be calculated from standard-state Gibbs free energy of formation data. If, for example, we wish to calculate the solubility of KCl in water at 25°C,

$$\mathrm{KCl} \leftrightarrow \mathrm{K}^+ + \mathrm{Cl}^-$$
 (1.21)

the equilibrium constant is given by

$$K_{sp} = \frac{a_{\mathrm{K}^+} a_{\mathrm{Cl}^-}}{a_{\mathrm{KCl}}} = (\gamma_{\mathrm{K}^+} m_{\mathrm{K}^+}) (\gamma_{\mathrm{Cl}^-} m_{\mathrm{Cl}^-}) = \gamma_{\pm}^2 m_{\pm}^2 \qquad (1.22)$$

The equilibrium constant is related to the Gibbs free energy of formation by the relation

Solutions and Solution Properties

$$K_{sp} = \exp\left(\frac{-\Delta G_{f^0}}{RT}\right) \tag{1.23}$$

The free energy of formation of KCl can be written as

$$\Delta G_{f^0} = \Delta G_{f^0 K^+} + \Delta G_{f^0 Cl^-} - \Delta G_{f^0 KCl}$$
(1.24)

Using data from the literature, one finds (Zemaitis et al. 1986)

$$\Delta G_{f^0} = -1282 \text{ cal/gmol} \tag{1.25}$$

so that

 $K_{sp} = 8.704$

(1.26)

Employing this equilibrium constant and assuming an activity coefficient of 1 yields a solubility concentration of 2.95 molal. This compares with an experimental value of 4.803 molal (Linke and Seidell 1965). Obviously, assuming an activity coefficient of unity is a very poor approximation in this case and results in a large error.

The calculation of mean ionic activity coefficients can be complex, and a number of methods are available. Several references describe these various methods (Robinson and Stokes 1970; Guggenheim 1986; Zemaitis et al. 1986). The method of Bromley (1972, 1973, 1974) can be used up to a concentration of 6 molal and can be written as

$$log\gamma_{\pm} = \frac{A|z^{+}z^{-}|\sqrt{I}}{1+\sqrt{I}} + \frac{(0.06+0.6B)|z^{+}z^{-}|I}{\left(1+\frac{1.5}{|z^{+}z^{-}|}I\right)^{2}} + BI \quad (1.27)$$

where γ_{\pm} = activity coefficient

A = Debye-Hückel constantz = number of charges on the cation or anion I = ionic strength, which is $\frac{1}{2}\sum_{i}m_{i}z_{i}^{2}$ B = constant for ion interaction

Values for the constant B are tabulated for a number of systems (Zemaitis et al. 1986). For KCl, B = 0.0240. Employing Equation (1.27), γ_+ can be calculated as a function of *m*. This must be done until the product $\gamma_{+}^2 m^2 = K_{sp}$. For the KCl-water system at 25°C, γ_+ is given as a function of concentration in Table 1.4 along with $\gamma_{\pm}^2 m^2$. You can see that the resulting calculated solubility is approximately 5 molal, which compares reasonably well with the experimental value of 4.8 molal.

Electrolyte Mixtures. Calculation of the solubility of mixtures of strong electrolytes requires knowledge of the thermodynamic solubility product for all species that can precipitate and requires using an activity coefficient calculation method that takes into account ionic interactions. These techniques are well described by Zemaitis et al. (1986), but we will discuss a simple case in this section.

The simplest case would be a calculation involving a single possible precipitating species. A good example is the effect of HCl on the solubility of KCl. The thermodynamic solubility product K_{sp} for KCl is defined as

$$K_{sp} = (\gamma_{K^+} m_{K^+})(\gamma_{Cl^-} m_{Cl^-}) = \gamma_{\pm}^2 m^2$$
(1.28)

7

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Table 1.4 Calculated Activity Coefficients for KCl in Water at 25°C

<i>m</i> (molality)	γ+	γ±m		
0.01	0.901	8.11×10^{-6}		
0.1	0.768	5.8×10^{-3}		
1.0	0.603	0.364		
1.5	0.582	0.762		
2.0	0.573	1.31		
2.5	0.569	2.02		
3.0	0.569	2.91		
3.5	0.572	4.01		
4.0	0.577	5.32		
4.5	0.584	6.91		
5.0	0.592	8.76		
Note: $K_{sp} = 8.704$ from Gibbs free energy of formation.				

ce: Data from Zemaitis et

In the preceding example, we obtained K_{sp} from the Gibbs free energy data and used this to calculate the solubility of KCl. Normally for a common salt, solubility data are available. K_{sp} is therefore obtained from the experimental solubility data and activity coefficients. Using the experimental KCl solubility at 25°C (4.8 molal) and the Bromley activity coefficients yields $K_{sp} = 8.01$. If we wish to calculate the KCl solubility in a 1 molal HCI solution, we can write the following equations:

$$\frac{(\gamma_{\rm K^+} m_{\rm K^+})(\gamma_{\rm Cl^-} m_{\rm Cl^-})}{K_{sp}} = 1$$
(1.29)

$$\begin{array}{l} z_{\rm K^+} m_{\rm K^+} + z_{\rm H^+} m_{\rm H^+} = z_{\rm Cl^-} m_{\rm Cl^-} + z_{\rm Cl^-} m_{\rm Cl^-} \\ ({\rm from \ KCl}) \ ({\rm from \ HCl}) \ ({\rm from \ HCl}) \ ({\rm from \ HCl}) \end{array} \tag{1.30}$$

Equations (1.29) and (1.30) must be satisfied simultaneously for a fixed value of 1 molal HCI.

Using Bromley's method for multicomponent electrolytes,

$$\log \gamma_i = \frac{-Az_i^2 \sqrt{I}}{I + \sqrt{I}} + F_i \tag{1.31}$$

where $A = H \ddot{u} ckel$ constant

I = ionic strength

i = any ion present

 z_i = number of charges on ion i

 F_i = an interaction parameter term

$$F_i = \sum B_{ij} z_{ij}^2 m_j \tag{1.32}$$

where *j* indicates all ions of opposite charge to *i*

$$z_{ij} = \frac{z_i + z_j}{2} \tag{1.33}$$

where m_i = molality of ion j

8



Figure 1.8 Calculated versus experimental KCI solubility in aqueous HCI solution at 25°C

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$$B_{ij} = \frac{(0.06 + 0.6B)|z_i z_j|}{\left[1 + (1.5/|z_i z_i|)I\right]^2} + B$$
(1.34)

Employing these equations, the activity coefficient for K⁺ and Cl⁻ are calculated as a function of KCl concentration at a fixed HCI concentration of 1 molar. These values, along with the molalities of the ions, are then substituted into Equation (1.29) until it is an equality (within a desired error). The solubility of KCl in a 1 molal solution of HCl is found to be 3.73 molal, which compares with an experimental value of 3.92 molal. This calculation can then be repeated for other fixed HCl concentrations. Figure 1.8 compares the calculated and experimental values of KCl solubility over a range of HCl concentrations. Unfortunately, many systems of interest include species that form complexes, intermediates, and undissociated aqueous species. This greatly increases the complexity of solubility calculations because of the large number of possible species. In addition, mixtures with many species often include a number of species that may precipitate. These calculations are extremely tedious and time consuming to do by hand or to write a specific computer program for each application. Commercial software is available for calculations in complex electrolyte mixtures. ProChem, part of the OLI Toolkit developed by OLI Systems, Inc. (Cedar Knolls, NJ), is an excellent example. The purpose of the package is to simultaneously consider the effects of the detailed reactions as well as the underlying species interactions that determine the actual activity coefficient values. Only by such a calculation can the solubility be determined.

A good example of the complexity of these calculations can be seen when looking at the solubility of $Cr(OH)_3$. Simply assuming the dissociation reaction

$$Cr(OH)_3 \leftrightarrow Cr^{3+} + 3OH^-$$
 (1.35)

and calculating a solubility using the K_{sp} obtained from Gibbs free energy of formation lead to serious error. This is because a

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Table 1.5 Calculated Results for Cr(OH) ₃ Solubility at 25°C				
Equilibrium const	ant	K (mol/kg)		
H ₂ O		9.94×10^{-15}		
CrOH ⁺²		1.30×10^{-10}		
Cr(OH) ₂ ⁺		2.72×10^{-9}		
$Cr(OH)_3(aq)$		2.03×10^{-6}		
Cr(OH) ₃ (crystal)		6.44×10^{-31}		
Cr(OH) ₄ ⁻		1.67×10^{-5}		
$Cr_2(OH)_2^{+4}$		2.35×10^{-5}		
Cr ₃ (OH) ₄ ⁺⁵		2.52×10^{-7}		
Liquid-phase pH =	10	lonic strength = 1.01×10^{-2}		
Species	Moles	Activity coefficient		
H ₂ O	55.5	1.0		
H^+	1.22×10^{-10}	0.904		
OH ⁻	1.00×10^{-4}	0.000		
	1.00 / 10	0.902		
Cr ⁺³	2.21×10^{-18}	0.397		
Cr ⁺³ CrOH ⁺²	2.21×10^{-18} 9.32×10^{-13}	0.397 0.655		
Cr^{+3} $CrOH^{+2}$ $Cr(OH)_2^+$	2.21×10^{-18} 9.32×10^{-13} 1.65×10^{-8}	0.397 0.655 0.899		
Cr^{+3} $CrOH^{+2}$ $Cr(OH)_{2}^{+}$ $Cr(OH)^{3}(aq)$	2.21×10^{-18} 9.32×10^{-13} 1.65×10^{-8} 6.56×10^{-7}	0.397 0.655 0.899 1.0		
Cr^{+3} $CrOH^{+2}$ $Cr(OH)_{2}^{+}$ $Cr(OH)^{3}(aq)$ $Cr(OH)_{4}^{-}$	2.21×10^{-18} 9.32×10^{-13} 1.65×10^{-8} 6.56×10^{-7} 3.95×10^{-6}	0.397 0.655 0.899 1.0 0.899		
Cr^{+3} $CrOH^{+2}$ $Cr(OH)_{2}^{+}$ $Cr(OH)^{3}(aq)$ $Cr(OH)_{4}^{-}$ $Cr_{2}(OH)_{2}^{+4}$	2.21×10^{-18} 9.32×10^{-13} 1.65×10^{-8} 6.56×10^{-7} 3.95×10^{-6} 2.98×10^{-21}	0.397 0.655 0.899 1.0 0.899 0.185		
Cr^{+3} $CrOH^{+2}$ $Cr(OH)_{2}^{+}$ $Cr(OH)^{3}(aq)$ $Cr(OH)_{4}^{-}$ $Cr_{2}(OH)_{2}^{+4}$ $Cr_{3}(OH)_{4}^{+5}$	1.00×10^{-18} 2.21×10^{-18} 9.32×10^{-13} 1.65×10^{-8} 6.56×10^{-7} 3.95×10^{-6} 2.98×10^{-21} 4.48×10^{-22}	0.397 0.655 0.899 1.0 0.899 0.185 0.0725		
Cr^{+3} $CrOH^{+2}$ $Cr(OH)_{2}^{+}$ $Cr(OH)^{3}(aq)$ $Cr(OH)_{4}^{-}$ $Cr_{2}(OH)_{4}^{+5}$ $Cr_{3}(OH)_{4}^{+5}$	2.21×10^{-18} 9.32×10^{-13} 1.65×10^{-8} 6.56×10^{-7} 3.95×10^{-6} 2.98×10^{-21} 4.48×10^{-22} 1.00×10^{-2}	0.397 0.655 0.899 1.0 0.899 0.185 0.0725 0.898		
$ Cr^{+3} CrOH^{+2} Cr(OH)_2^+ Cr(OH)^3(aq) Cr(OH)_4^- Cr_2(OH)_4^{+4} Cr_3(OH)_4^{+5} CI^- Na^- $	$\begin{array}{c} 2.21 \times 10^{-18} \\ 9.32 \times 10^{-13} \\ 1.65 \times 10^{-8} \\ 6.56 \times 10^{-7} \\ 3.95 \times 10^{-6} \\ 2.98 \times 10^{-21} \\ 4.48 \times 10^{-22} \\ 1.00 \times 10^{-2} \\ 1.01 \times 10^{-2} \end{array}$	0.397 0.655 0.899 1.0 0.899 0.185 0.0725 0.898 0.898		

number of other dissociation reactions and species are possible. These include $Cr(OH)_3$ (undissociated molecule in solution), $Cr(OH)_4^-$, $Cr(OH)_2^+$, $Cr_2(OH)_2^{4+}$, and $Cr_3(OH)_4^{5+}$.

Calculation of the solubility of $Cr(OH)_3$ as a function of pH using HCl and NaOH to adjust the pH requires taking into account all species, equilibrium relationships, mass balances, and electroneutrality, as well as calculation of the ionic activity coefficients. The results of such a calculation (employing Prochem) is shown in Table 1.5 and Figures 1.9 and 1.10. Table 1.5 shows the results obtained at a pH of 10. Figure 1.9 gives the solubility results obtained from a series of calculations and also shows the concentration of the various species, whereas Figure 1.10 compares the solubility obtained with that calculated from a solubility product. The solubility results obtained by the simple solubility product calculation are orders of magnitude less than those obtained by the complex calculation, demonstrating the importance of considering all possible species in the calculation.

Solutions and Solution Properties



Figure 1.9 Chrome hydroxide solubility and speciation versus pH at 25°C Source: Reproduced from J. F. Zemaitis, Jr., D. M. Clark, M. Rafal, and N. C. Scrivner (1986), *Handbook of Aqueous Electrolyte Thermodynamics*, p. 284. Used by permission of the American Institute of Chemical Engineers © 1986 AIChE.



Figure 1.10 Chrome solubility versus pH *Source*: Reproduced with permission of OLI Systems, Inc.

1.4 Solubility of Organics

In crystallization operations involving inorganic materials, we virtually always employ water as the solvent, thus requiring solubility data on inorganic water systems. Because most inorganic materials are ionic, this means that dissociation reactions, ionic interactions, and pH play a major role in determining the solubility of a particular inorganic species in aqueous solution. When dealing with organic species (or inorganics in nonaqueous solvents), a wide variety of solvents and solvent mixtures usually can be employed. The interaction between the solute and

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Figure 1.11 Solubility of hexamethylenetetramine in different solvents *Source:* Reprinted with permission from S. Decker, W. P. Fan, and A. S. Myerson, Solvent selection and batch crystallization, *Ind. Eng. Chem. Fund.* 1986; 25:925. Copyright © 1986, American Chemical Society.



Figure 1.12 Solubility of adipic acid in different solvents *Source:* Reprinted with permission from S. Decker, W. P. Fan, and A. S. Myerson, Solvent selection and batch crystallization, *Ind. Eng. Chem. Fund.* 1986; 25:925. Copyright © 1986, American Chemical Society.

the solvent determines the differences in solubility commonly observed for a given organic species in a number of different solvents. This is illustrated in Figures 1.11 and 1.12 for hexamethylene tetramine and adipic acid in several different solvents. In the development of crystallization processes, this can be a powerful tool. In many cases the solvent chosen for a particular process is an arbitrary choice made in the laboratory with no thought of the downstream processing consequences. Frequently, from a chemical synthesis or reaction point of view, a number of different solvents could be used with no significant change in product yield or quality. This means that the solubility and physical properties of the solvent (solubility as a function of temperature, absolute solubility, and vapor pressure) should be evaluated so that the solvent that provides the best characteristics for the crystallization step is chosen. This requires that the process-development engineers be in contact with the synthetic organic chemists early in process development. In this section we will describe the basic principles required to estimate and

10

calculate the solubility of an organic solute in different solvents and explain how to assess mixed solvents.

1.4.1 Thermodynamic Concepts and Ideal Solubility

As we have shown previously, the condition for equilibrium between a solid solute and a solvent is given by the relation

$$\mu_{i_{\text{solid}}} = \mu_{i_{\text{solution}}} \tag{1.36}$$

A thermodynamic function known as the *fugacity* can be defined as

$$\mu_i - \mu_i^0 = RT \ln\left(\frac{f_i}{f_i^0}\right) \tag{1.37}$$

Comparing Equation (1.10) with Equation (1.37) shows us that the activity $a_i = f_i/f_i^0$. Through a series of manipulations, it can be shown that for phases in equilibrium (Prausnitz et al. 1986),

$$f_{i_{\text{solid}}} = f_{i_{\text{solution}}} \tag{1.38}$$

Equation (1.38) will be more convenient for us to use in describing the solubility of organic solids in various solvents. The fugacity is often thought of as a "corrected pressure" and reduces to pressure when the solution is ideal. Equation (1.38) can be rewritten as

$$f_{2_{\text{solid}}} = \gamma_2 x_2 f_2^0 \tag{1.39}$$

where f_2 = fugacity of the solid

 x_2 = mole fraction of the solute in the solution

 f_2^0 = standard state fugacity

 γ_2 = activity coefficient of the solute

or

$$x_2 = \frac{f_{2_{\text{solid}}}}{\gamma_2 f_2^0} \tag{1.40}$$

Equation (1.40) is a general equation for the solubility of any solute in any solvent. We can see from this equation that the solubility depends on the activity coefficient and on the fugacity ratio f_2/f_2^0 . The standard state fugacity normally used for solid–liquid equilibrium is the fugacity of the pure solute in a subcooled liquid state below its melting point. We can simplify Equation (1.40) further by assuming that our solid and subcooled liquid have small vapor pressures. We can then substitute vapor pressure for fugacity. If we further assume that the solute and solvent are chemically similar so that $\gamma_2 = 1$, then we can write

$$x_2 = \frac{P_{2_{\text{solid solute}}}^s}{P_{2_{\text{subcooled liquid solute}}}^s} \tag{1.41}$$

Equation (1.41) gives the ideal solubility. Figure 1.13, an example phase diagram for a pure component, illustrates several points. First, we are interested in temperatures below the triple point because we are interested in conditions where the solute is a solid. Second, the subcooled liquid pressure is obtained by extrapolating the liquid-vapor line to the correct temperature.