Technical Assistance
HYDROLOGY PROJECT

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Training module # WQ - 29

Advanced Aquatic Chemistry: solubility equilibria

New Delhi, October 1999

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with
HALCROW, TAHAL, CES, ORG & JPS

Table of contents

1. Module context

This module discusses theory of solubility equilibria. Modules in which prior training is required to complete this module successfully and other available, related modules in this category are listed in the table below.

While designing a training course, the relationship between this module and the others, would be maintained by keeping them close together in the syllabus and place them in a logical sequence. The actual selection of the topics and the depth of training would, of course, depend on the training needs of the participants, i.e. their knowledge level and skills performance upon the start of the course.

No.	Module title	Code	Objectives
1.	Basic water quality concepts	**WQ - 01**	• Discuss the common water quality parameters • List important water quality issues
2.	Basic chemistry concepts [a]	**WQ - 02**	• Convert units from one to another • Discuss the basic concepts of quantitative chemistry • Report analytical results with the correct number of significant digits.
3.	Understanding the hydrogen ion concentration (pH)[a]	**WQ -06**	• Discuss about the concept of pH • Calculate pH
4.	Basic Aquatic Chemistry Concepts[a]	**WQ – 24**	• Understand equilibrium chemistry and ionisation constants • Understand basis of pH and buffers

a - prerequisite

2. Module profile

Title : Advanced Aquatic Chemistry: solubility equilibria

Target group : HIS function(s): Q2, Q3, Q5, Q6, Q7, Q8

Duration : 1 session of 60 min

Objectives : After the training the participants will be able to:
- explain the principles of chemical equilibrium
- define solubility product and explain how this relates to water quality assessment
- define the octanol-water partition coefficient and explain how this relates to water quality assessment

Key concepts :
- Equilibrium chemistry
- Solubility equilibria
- Partition equilibria

Training methods : Lecture, open discussion and exercises

Training tools required : Board, OHS, flipchart

Handouts : As provided in this module

Further reading and references :
- Chemistry for Environmental Engineering, C.N. Sawyer, P. L. McCarty, G.E Parkin, 4th edition, McGraw-Hill, Inc. New York

3. Session plan

No	Activities	Time	Tools
1	***Preparations***		
2	***Introduction***: • Discuss importance of solubility concepts and limitations	10 min	OHS
3.	***Solubility product constant*** • Reversible reactions and equilibrium constants • Solubility of ionic solids • Example	15 min	OHS
4.	***Logarithmic concentration diagrams*** • Discuss pH vs solubility • Formation of complexes	15 min	OHS
5.	***Partition equilibrium*** • Discuss the use of the constants	5 min	OHS
6.	***Wrap up and evaluation***	15 min	Addl. handout

4. Overhead/flipchart master

OHS format guidelines

Type of text	Style	Setting
Headings:	OHS-Title	Arial 30-36, with bottom border line (not: underline)
Text:	OHS-lev1 OHS-lev2	Arial 24-26, maximum two levels
Case:		Sentence case. Avoid full text in UPPERCASE.
Italics:		Use occasionally and in a consistent way
Listings:	OHS-lev1 OHS-lev1-Numbered	Big bullets. Numbers for definite series of steps. Avoid roman numbers and letters.
Colours:		None, as these get lost in photocopying and some colours do not reproduce at all.
Formulas/ Equations	OHS-Equation	Use of a table will ease horizontal alignment over more lines (columns) Use equation editor for advanced formatting only

Solubility Equilibria

- Study of solubility equilibrium
- Solubility product constant
- Logarithmic concentration diagrams
- Partition equilibrium

Study of equilibrium relationships (1)

- *is an aid to understanding the fate of pollutants*
- *enables quantitative determinations of the relationships between species*
- *helps to evaluate how to treat pollution*

Study of equilibrium relationship (2)

- Limitations
  - *rivers, unlike laboratories, are subject to outside influences*
  - *no account is taken of the speed of the chemical reaction*
  - *equilibrium constants have not been derived for natural waters*

Equilibrium Constant

- All Equilibrium reactions have an Equilibrium constant
- For the reaction:

$$aA + bB \Leftrightarrow cC + dD$$

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

- K is the equilibrium constant

Solubility Product Constant (1)

- For an ionic solid dissolving in water:

$$\underline{\mathbf{AB}} \Leftrightarrow \mathbf{A^{+} + B^{-}}$$

$$K = \frac{\left[A^{+}\right]\left[B\right]}{\left[\underline{AB}\right]}$$

- or

$$K = \frac{\left[A^{+}\right]\left[B^{-}\right]}{K_1}$$

Solubility Product Constant (2)

- Definition of Solubility Product for an ionic solid dissolving in water:

$$\mathbf{KK_1 = [A^+]\ [B^-] \ = \ K_{sp}}$$

- K_{sp} is the solubility product constant

Solubility Product Constant (3)

$\underline{AgCl} \leftrightarrow Ag^+ + Cl^-$ K_{sp} (at 25°C) = 3×10^{-10}

$\underline{BaSO_4} \leftrightarrow Ba^{2+} + SO_4^{2-}$ K_{sp} (at 25°C) = 1×10^{-10}

$\underline{Ca\ CO_3} \leftrightarrow Ca^{2+} + CO_3^{2-}$ K_{sp} (at 25°C) = 5×10^{-9}

$\underline{MgCO_3} \leftrightarrow Mg^{2+} + CO_3^{2-}$ K_{sp} (at 25°C) = 4×10^{-5}

$\underline{Mg(OH)_2} \leftrightarrow Mg^{2+} + 2OH^-$ K_{sp} (at 25°C) = 9×10^{-12}

Example: Solubility of $CaCO_3$

- $\underline{CaCO_3} \leftrightarrow Ca^{++} + CO_3^{--}$
- If p moles of $CaCO_3$ goes in solution, conc of each ion will be p moles
- $p \text{ X } p = K_{sp} = 5 \text{ X } 10^{-9}$

  $p^2 = 5 \text{ X } 10^{-9}$

  $p = 7 \text{ x } 10^{-5}$ moles/L
- Solubility = $7 \text{ X } 10^{-5}$ moles/L X 100g/mole = 0.007 g/L

Logarithmic concentration diagram (1)

- $[Mg^{++}]\,[OH^-]^2 = 9 \times 10^{-12}$
  - *Substituting* $10^{-14}/[H^+]$ *for* $[OH^-]$ *and taking logarithms:*
  - $\log[Mg^{++}] = 16.95 - 2pH$

pH	**$\log[Mg^{++}]$**
6	+4.95
8	+0.95
10	-3.05

Logarithmic concentration diagram (2)

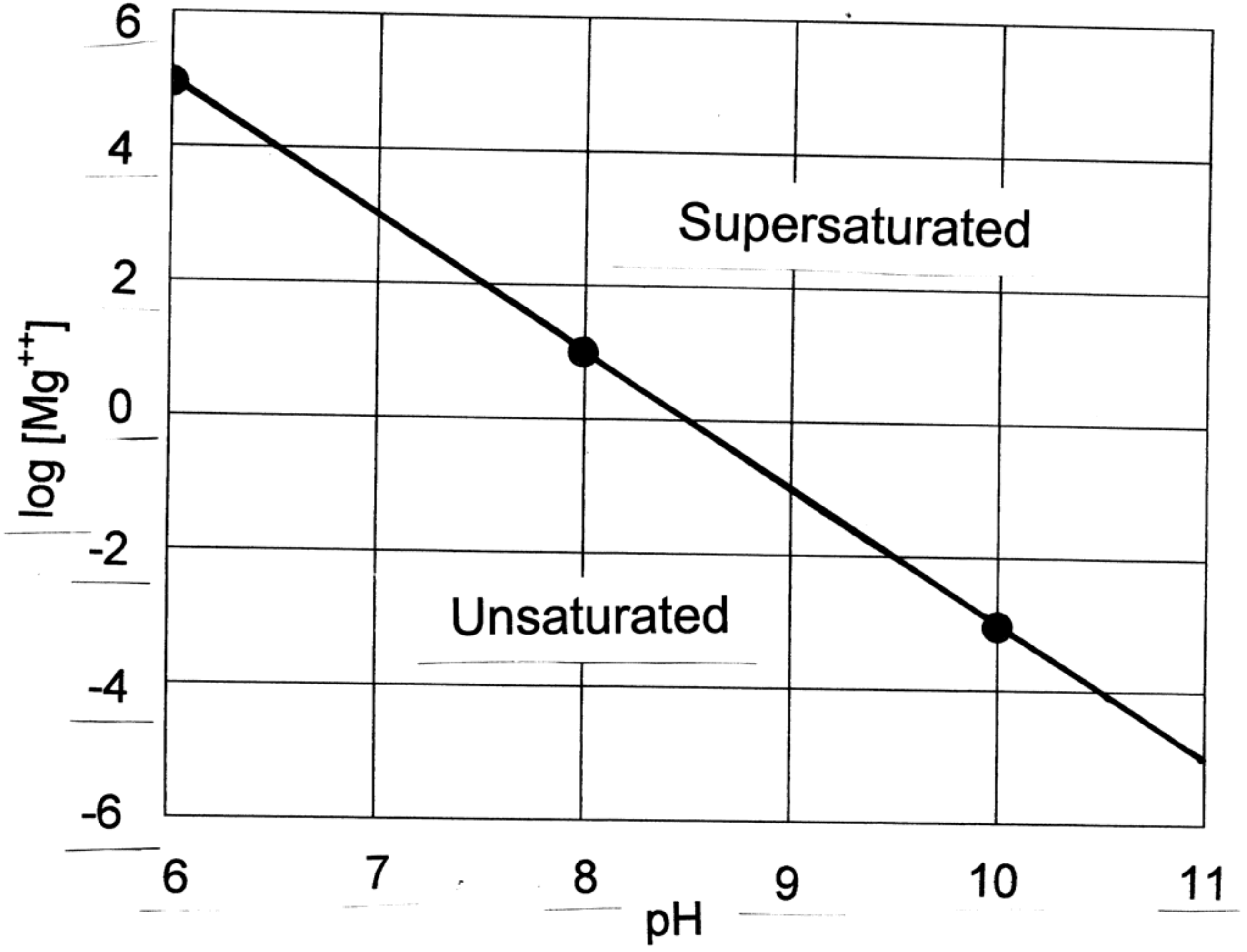

Figure 1 Logarithmic concentration diagram

Complex Formation (1)

- Solubility increases if one of the ions forms complexes
  - $\underline{Zn(OH)_2} \leftrightarrow Zn^{++} + 2OH^-$ $K_{sp} = 8 \times 10^{-18}$
  - $Zn^{++} + OH^- \leftrightarrow ZnOH^+$ $K_1 = 1.4 \times 10^4$
  - $ZnOH^+ + OH^- \leftrightarrow Zn(OH)_2$ $K_2 = 1 \times 10^6$
  - $Zn(OH)_2 + OH^- \leftrightarrow Zn(OH)_3^-$ $K_3 = 1.3 \times 10^4$
  - $Zn(OH)_3^- + OH^- \leftrightarrow Zn(OH)_4^{--}$ $K_4 = 1.9 \times 10^1$

Complex Formation (2)

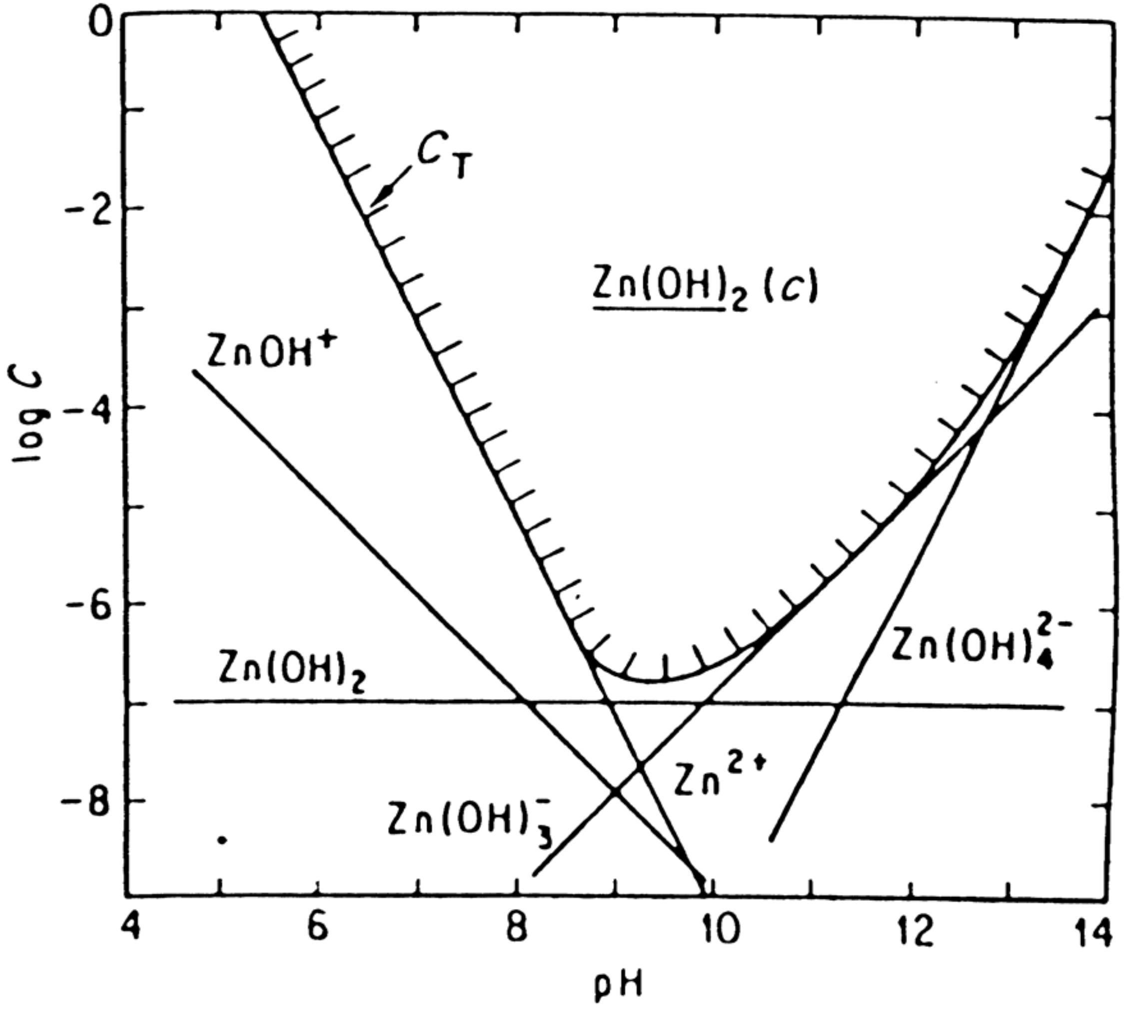

Figure 2 Solubility of zinc

Partition equilibrium

- Partition of organics between solid and liquid phases
- K_{ow} is the octanol-water partition coefficient

$$K_{ow} = \frac{\text{conc. in octanol } \left(\mu g/\ell\right)}{\text{conc. in water } \left(\mu g/\ell\right)}$$

- Higher value indicates larger proportion in solid phase

5. Evaluation sheets

6. Handout

Solubility Equilibria

- Study of solubility equilibrium
- Solubility product constant
- Logarithmic concentration diagrams
- Partition equilibrium

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Equilibrium Constant

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- K is the equilibrium constant

$$K = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

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- For an ionic solid dissolving in water:

$$AB \Leftrightarrow A^+ + B^-$$

$$K = \frac{\lfloor A^+ \rfloor \lfloor B \ \rfloor}{[AB]}$$

- or

$$K = \frac{\lfloor A^+ \rfloor \lfloor B^- \rfloor}{K_1}$$

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- Definition of Solubility Product for an ionic solid dissolving in water:

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  $p = 7 \times 10^{-5}$ moles/L
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  - *$\log[Mg^{++}] = 16.95 - 2pH$*

pH	**Log[Mg^{++}]**
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Partition equilibrium

- Partition of organics between solid and liquid phases
- K_{ow} is the octanol-water partition coefficient

$$K_{ow} = \frac{\text{conc.in octanol}(\mu g/\ell)}{\text{conc.in water}(\mu g/\ell)}$$

- Higher value indicates larger proportion in solid phase

Add copy of Main text in chapter 8, for all participants.

7. Additional handout

These handouts are distributed during delivery and contain test questions, answers to questions, special worksheets, optional information, and other matters you would not like to be seen in the regular handouts.

It is a good practice to pre-punch these additional handouts, so the participants can easily insert them in the main handout folder.

Questions

1. Calculate solubility of CaF_2 in distilled water $K_{sp} = 3 \times 10^{-11}$

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2. What will be the effect on the above solubility if the water contains calcium hardness? Will it increase or decrease?

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3. A water sample contains 10^{-4} moles/L Zn at a pH of 8.5. Will it precipitate or dissolve zinc? Use Figure 2 of the handout to give your answer.

Questions and Answers

1. Calculate solubility of CaF_2 in distilled water $K_{sp} = 3 \times 10^{-11}$

Assume solubility = p moles/L

Therefore $p^3 = 3 \times 10^{-9}$

Or $p = 1.4 \times 10^{-3}$ moles/L

2. What will be the effect on the above solubility if the water contains calcium hardness? Will it increase or decrease?

It will decrease

3. A water sample contains 10^{-4} moles/L Zn at a pH of 8.5. Will it precipitate or dissolve zinc? Use Figure 2 of the handout to give your answer.

It will precipitate zinc

8. Main text

Contents

Advanced Aquatic Chemistry: solubility equilibria

1. Introduction

A knowledge of basic equilibrium chemistry is useful to the environmental chemist dealing with water pollution problems. This is because equilibrium chemistry:

- is an aid to the understanding of the fate of pollutants discharged into water
- enables quantitative determinations to be made of the relationships between various species present in polluted and natural waters
- helps to evaluate how best to treat contaminated waters

However it is important to understand that the concepts detailed below are, in most cases simplifications of what goes in the dynamic and multi-species systems which make up natural waters. Further limitations are imposed by:

- the fact that unlike laboratory experiments, natural systems are subject to outside influences (e.g., sunlight)
- the fact that no account is taken of the kinetics (speed) of the reactions considered some of which may be very slow (such as some oxidation-reduction reactions) whilst some are very fast (certain acid-base reactions)
- the lack of accurate equilibrium constants for reactions in natural waters

Even given the above limitations, however, the concepts of equilibrium chemistry can indicate whether certain reactions are likely, the direction in which these reactions are likely to proceed and the relative position of the equilibrium with respect to the reactants and products.

2. Chemical Equilibrium

It is possible to write the an equation for a theoretical chemical equilibrium as follows:

$$A + B \leftrightarrow C + D$$

This means that the reaction is reversible and that the species C and D are in equilibrium with the species A and B. It is possible to disturb this equilibrium by a number of means including increasing the concentration of one of the species involved in the reaction. When this is done, Le Chatelier's principle states that:

> *'A reaction, at equilibrium, will adjust itself in such a way as to relieve any force, or stress, that disturbs the equilibrium'*

This means, for example, that if the concentration of, say, D is increased, the reaction will tend to move to the left thus producing more of the species A and B.

This leads to the concept of the equilibrium constant (K) for a reaction which is defined as:

$$K = \frac{[C][D]}{[A][B]}$$

where the [C] is the concentration of C, [D] is the concentration of D etc.

Where different numbers of molecules are used, this formula becomes:

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

where a, b, c, d are the number of molecules of species A, B, C and D involved in the reaction.

The above equations give good results for salts, acids and bases when concentrations are low (as they mostly are in aquatic environmental chemistry) but become progressively less accurate as the concentration of the species increases. This is due to the fact that the ‘activity’ of the ions – a concept thought to be associated with ion interactions – needs to be taken into account at higher ion concentrations.

3. Solubility Product

For an ionic solid AB, which dissolves in water (or any solvent) a general equation can be written as follows:

$\underline{AB} \leftrightarrow A^+ + B^-$

The underscore represents solid or precipitated material.

The equilibrium for this equation can be treated as though the equilibrium were homogeneous in nature. It can be written as:

$$K = \frac{[A^+][B^-]}{[\underline{AB}]}$$

where [ ] represents molar concentrations of the species.

However, the concentration of the solid can be regarded as constant in equilibrium calculations, since the rate of dissolution of the solid at equilibrium condition is equal to the rate deposition of the ions. Therefore:

$$K = \frac{[A^+][B^-]}{[\underline{K_1}]}$$

where K_1 is a constant

or:

$KK_1 = [A^+]\,[B^-] = K_{sp}$ (replacing two constants with a new constant K_{sp})

The constant K_{sp} is called the solubility-product constant (sometimes simply the solubility constant) and is a measure of the extent of dissolution of a solid when it is dissolved. Tables of solubility product constants are available in the chemical literature and, for solutes which produce the same number of ions upon dissolution, can be compared to ascertain relative solubilities.

Examples of solubility product constants are:

$AgCl \leftrightarrow Ag^+ + Cl^-$ K_{sp} (at 25°C) = 3×10^{-10}
$BaSO_4 \leftrightarrow Ba^{2+} + SO_4^{2-}$ K_{sp} (at 25°C) = 1×10^{-10}
$Ca\,CO_3 \leftrightarrow Ca^{2+} + CO_3^{2-}$ K_{sp} (at 25°C) = 5×10^{-9}
$MgCO_3 \leftrightarrow Mg^{2+} + CO_3^{2-}$ K_{sp} (at 25°C) = 4×10^{-5}
$Mg(OH)_2 \leftrightarrow Mg^{2+} + 2OH^-$ K_{sp} (at 25°C) = 9×10^{-12}

From the above solubility product constants it can be seen that magnesium carbonate ($MgCO_3$) is the most soluble followed by calcium carbonate ($CaCO_3$), silver chloride ($AgCl$) and finally barium sulphate ($BaSO_4$) being the least soluble.

Example

Calculate the solubility of $CaCO_3$ in mg/L in pure water.

Assume that the solubility of $CaCO_3$ is p moles/L. Therefore the concentrations of both calcium and carbonate ions would be p moles/L each. Writing the equilibrium expression one obtains:

$p^2 = 5 \times 10^{-9}$ or $p = 7 \times 10^{-5}$ moles/L
or Solubility = 7×10^{-5} moles/L X 100g/mole X 1000 mg/g = 7 mg/L

Note that the solubility of a compound would be different in case the water contains any of the ions released by dissolution of the compound or if one of the released ions enters into a reaction with other constituents in the water. In the above example, if the water contains carbonate ion from any other source, say presence of sodium carbonate, the solubility of calcium carbonate would be lesser or if the carbonate ion obtained from dissolution of calcium carbonate is converted to bicarbonate, the solubility would be higher.

For environmental chemists the solubility product constant is a useful aid to understanding the fate of chemical species discharged to water bodies and, in particular, whether they are likely to be present as dissolved substances or solid particles.

4. Logarithmic Concentration Diagrams

Logarithmic concentration diagrams are useful in understanding solubility equilibrium of compounds when the water contains ions, which affect its solubility. Consider the case of solubility of $Mg(OH)_2$. The solubility is a function of hydroxyl ion concentration in water or its pH.

According to solubility equilibrium expression:

$$[Mg^{++}]\,[OH^-]^2 = 9 \times 10^{-12}$$

Substituting $10^{-14}/[H^+]$ for $[OH^-]$ and taking logarithms, the following expression is obtained:

$$\log[Mg^{++}] = 16.95 - 2pH$$

This is an equation to a straight line when $\log[Mg^{++}]$ is plotted against pH value. By substituting different values for pH in the equation values of $\log[Mg^{++}]$ can be obtained:

pH	$\log[Mg^{++}]$
6	+4.95
8	+0.95
10	-3.05

Figure 1 shows a plot of the above relation. Note that as the pH increases from 6 to 10 the solubility decreases from $10^{4.95}$ moles/L to $10^{-3.05}$ moles/L. Further, it can be concluded that waters having pH and $\log[Mg^{++}]$ values plotting to the right of the line are supersaturated and precipitation will take place. Similarly, the waters plotting to the left of the line are undersaturated.

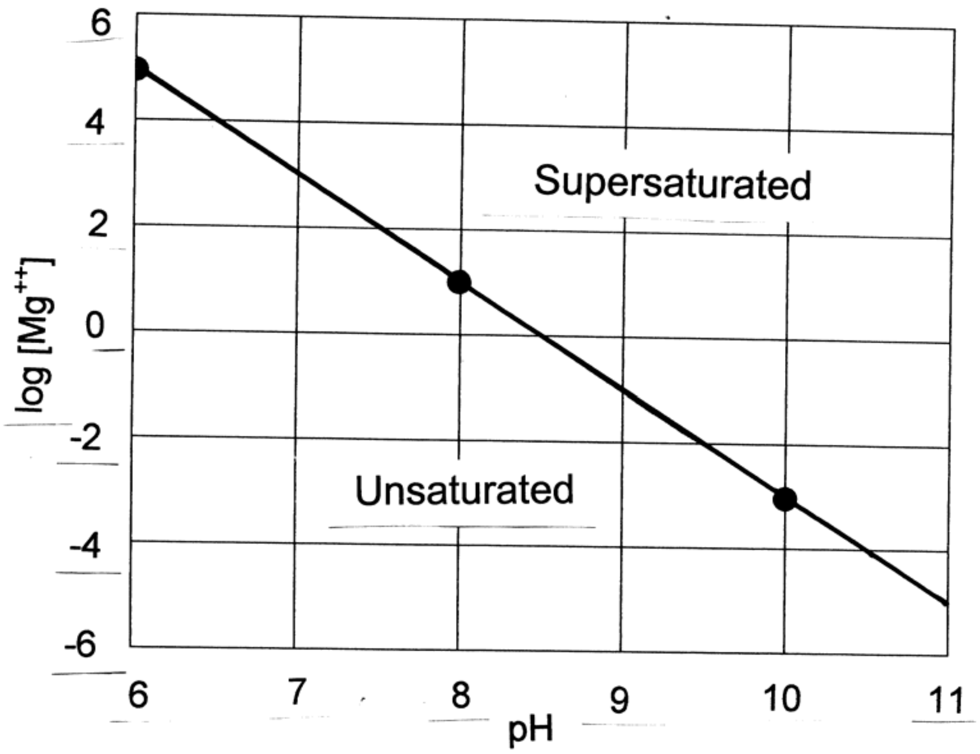

Figure 1 Logarithmic concentration diagram

5. Complex formation

The total solubility of a compound increases if one of the ions start forming complexes with another specie present in the water or with the hydroxide or hydrogen ion contributed by the solvent water. The case of $Zn(OH)_2$ will be used as an illustration, which undergoes the following reactions:

$\underline{Zn(OH)_2} \leftrightarrow Zn^{++} + 2OH^-$ $K_{sp} = 8 \times 10^{-18}$
$Zn^{++} + OH^- \leftrightarrow ZnOH^+$ $K_1 = 1.4 \times 10^4$
$ZnOH^+ + OH^- \leftrightarrow Zn(OH)_2$ $K_2 = 1 \times 10^6$
$Zn(OH)_2 + OH^- \leftrightarrow Zn(OH)_3^-$ $K_3 = 1.3 \times 10^4$
$Zn(OH)_3^- + OH^- \leftrightarrow Zn(OH)_4^{--}$ $K_4 = 1.9 \times 10^1$

It is seen that as the solid zinc hydroxide goes into solution, the Zn ion is consumed to make 4 different hydroxide complexes in step-wise reactions. The dissolution continues till each of the 4 complexing reactions and the solubility product reaction attains equilibrium.

These equations can be written in the form of logarithmic concentration and pH relations as described in the earlier section. Then each species of Zn can be plotted as shown in Figure 2. The total solubility,C_T, at any pH can be obtained by summing the ordinates of each plotat that pH value.

Note that the solubility of total Zn first decreases with increase in pH and then it again increases. The minimum solubility occurs at pH 9.4 and is equal to $10^{-6.8}$ moles/L.

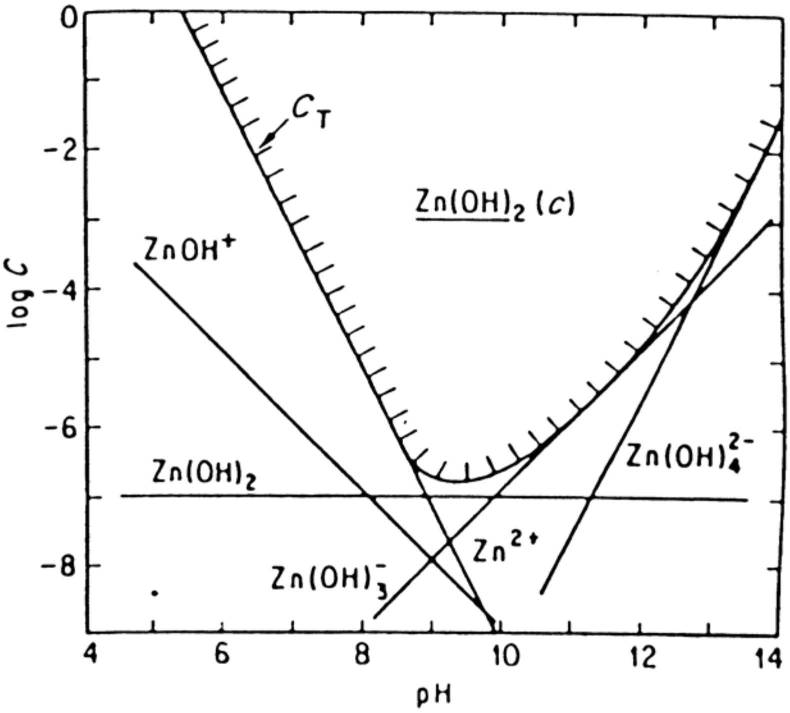

Figure 2 Solubility of zinc

6. Partition Equilibrium

One of the aspects of equilibrium chemistry, which is particularly important when dealing with water pollution, is that of the partition of contaminants between solid and liquid phases of the water body. In this way, it is often possible to be more definite about the fate of pollutants when they are discharged to the aquatic environment.

For organic chemicals, a useful way of estimating the relative amounts of a particular compound which may be present in the liquid and solid phases of surface water is provided by the so-called octanol-water partition coefficient which is defined as follows:

(for a particular organic chemical)

$$Kow = \frac{\text{conc. in octanol } (\mu g/\ell)}{\text{conc. in water } (\mu g/\ell)}$$

This coefficient, for which tables are available in the literature, can be used in concert with the solubility of the chemical in water to predict how the chemical is likely to be partitioned between the water and solid phases when discharged to surface waters. Thus, the higher the value of Kow is the greater the proportion of the chemical in the solid phase is likely to be.

Attempts have also been made to determine the partitioning of other chemicals, particularly metals, either theoretically or empirically. Such partition coefficients, whilst helpful at times, normally relate to quite strictly-defined conditions and are not, therefore, generally useful. Reference should be made to the surface water quality literature for further information in this regard.