

Training module # WQ - 24

Basic Aquatic Chemistry
Concepts

New Delhi, October 1999

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with
HALCROW, TAHAL, CES, ORG & JPS

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1. Module context

This module deals with the basic aquatic chemistry concepts, which are relevant for water quality monitoring and assessment. 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 placing 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	<ul style="list-style-type: none">• Discuss the common water quality parameters• List important water quality issues
2.	Basic chemistry concepts ^a	WQ - 02	<ul style="list-style-type: none">• 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	<ul style="list-style-type: none">• Discuss about the concept of pH• Calculate pH

a- prerequisite

2. Module profile

Title	:	Basic Aquatic Chemistry Concepts
Target group	:	HIS function(s): Q2, Q3, Q5, Q6, Q7, Q8
Duration	:	1 session of 90 minutes
Objectives	:	After the training the participants will be able to: <ul style="list-style-type: none">• Understand equilibrium chemistry and ionisation constants• Understand basis of pH and buffers• Calculate different types of alkalinity
Key concepts	:	<ul style="list-style-type: none">• Chemical equilibrium• Ionisation constants• pH and buffers• Types of alkalinity• Activity and ionic strength
Training methods	:	Lecture, exercises and discussion
Training tools Required	:	Board, flipchart, OHS,
Handouts	:	As provided in this module,
Further reading and references	:	<ul style="list-style-type: none">• Chemistry for Environmental Engineering, C.N. Sawyer, P.L. McCarty and C.F. Parkin. McGraw-Hill, 1994

3. Session plan

No	Activities	Time	Tools
1	Preparations		
2	Introduction: <ul style="list-style-type: none"> Introduce the session Introduce the subject of chemical reactions and write a general ($A + B = C + D$) reversible reaction 	10 min	OHS
3	Equilibrium and Ionisation Constants: <ul style="list-style-type: none"> Introduce Le Chatelier's Principle and discuss it by referring to general reaction on flip-chart Introduce subject of simple reaction equilibrium constant (K) and define Discuss how K definition varies when multiple moles of reactants and products are involved Discuss ionisation constant (K) for ionisation of general salt 'AB' 	10 min	OHS, flip chart
4	The Ionisation of Water and pH <ul style="list-style-type: none"> Demonstrate how water ionises (check for understanding) Derive pH and pOH from K_w (check for understanding) Show how the pH of a neutral solution is 7 (check understanding) 	10 min	OHS
5	Acid-base Reactions in Water and Buffer Solutions: <ul style="list-style-type: none"> Show how pH can affect the chemical species present in water. Demonstrate by showing ammonia example Discuss buffer solutions and how they function Show how carbonic acid acts as a buffer in natural waters Discuss various forms of alkalinity Describe alkalinity titration and types of alkalinity in different samples 	20 min	OHS
6	Construction of Buffers <ul style="list-style-type: none"> Discuss buffers & their construction 	10 min	OHS
7	Ionic Strength & Activity <ul style="list-style-type: none"> Explain the effect of ionic concentration on activity 	10 min	OHS
8	Wrap up and Evaluation	20 min	Evaluation Sheets, Addl. handouts

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

Basic Aquatic Chemistry Concepts

- Chemical and ionic equilibria
- pH and ion product of water
- Ionisation of acids and bases
- Alkalinity relationships
- Buffers
- Activity coefficients and ionic strength

Le Chatelier's Principle:

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

Chemical Equilibria (1)

Consider the reaction:



The equilibrium constant (K) can be defined as:

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

[C] = concentration of C, [D] = concentration of D etc.

Chemical Equilibria (2)

- *For the reaction:*



- *The equilibrium constant (K) becomes:*

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

Ionisation Equilibria

- *When the solid AB is ionised, the equation is:*



- *The ionisation constant (K) is:*

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

Ionisation of Water (1)

- *Water ionises as follows:*



- *The ionisation constant (K) is:*

$$K_a = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

- $K_a = 1.8 \times 10^{-16}$ at 25°C

Ionisation of Water (2)

- As $[H_2O] = 55.5 \text{ moles/L} \approx \text{constant}$
- Replace $K_a \times [H_2O] = K_w = 10^{-14}$
- Where $K_w = \text{the ion product of water}$

$$[H^+][OH] = K_w = 10^{-14} \text{ at } 25^\circ\text{C}$$

Ionisation of Water (3)

- *The term 'p' is introduced to eliminate small powers of ten:*

$$p(x) = -\log_{10} (x)$$

$$p(10^{-14}) = -\log_{10} (10^{-14}) = 14$$

- *'p' is applied to the ionisation constant of water:*

$$-\log_{10} ([H^+][OH^-]) = -\log_{10} (K_w) = -\log_{10}(10^{-14})$$

Ionisation of Water (4)

- *which means that:*

$$\mathbf{pH + pOH = pK_w = 14}$$

- *Note the introduction of the term 'pH defined as:*

$$\mathbf{pH = -\log_{10}[H^+]}$$

Ionisation of Water (5)

- *For a neutral solution where $[H^+] = [OH^-]$:*

$$[H^+][OH^-] = [H^+][H^+] = [H^+]^2 = 10^{-14}$$

- *so:*

$$[H^+] = 10^{-7}$$

- *or:*

pH = 7 (ie: the pH of a neutral solution)

Acid-base Equilibria

- Definitions

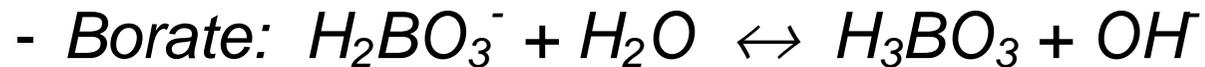
- *An acid yields a Hydrogen ion (H^+) when added to water*
- *A base yields a Hydroxide ion (OH^-) when added to water*

- Strong acids and bases completely dissociate in water:

- *Hydrochloric acid: $HCl \rightarrow H^+ + Cl^-$*
- *Sodium Hydroxide: $NaOH \rightarrow Na^+ + OH^-$*

Weak Acid and Conjugate Base

- Weak acids and bases partially dissociate, and
- Weak acids and bases are often paired:



Ionisation of Weak Acids

- K_a = ionisation constant for acids, e.g. Boric acid:

$$K_A = \frac{[H^+][H_2BO_3^-]}{[H_3BO_3]} = 10^{-9.24}$$

- K_b = ionisation constant for bases, e.g. Borate:

$$K_B = \frac{[OH^-][H_3BO_3]}{[H_2BO_3^-]} = 10^{-4.76}$$

pH Scale

- pH – Important points:
 - *the pH scale runs from 0 (acid) to 14 (alkali)*
 - *when pH is measured it is the negative logarithm of the hydrogen ion concentration that is being determined*
 - *an acidic solution (pH: 0 – 7) has a greater concentration of hydrogen ions than hydroxide ions*
 - *an alkaline solution (pH: 7 – 14) has a greater concentration of hydroxide ions than hydrogen ions*

Ammonia Toxicity

- Acid-base Reactions in Water

- *For the reaction:*



- *At high pH (alkaline conditions), the reaction produces more ammonia species (NH_3) which is toxic to fish*
 - *At low pH (acid conditions) the ammonium species (the relatively non-toxic, NH_4^+) predominates*

Ammonia Toxicity: Example

- $[\text{NH}_3] + [\text{NH}_4^+] = 0.2 \times 10^{-3} \text{M}$ (2.8 mg/L)
- Calculate NH_3 conc. at pH 7 & 9.5
 - $[\text{H}^+][\text{NH}_3]/[\text{NH}_4^+] = 10^{-9.26}$
 - At pH 7: $[\text{NH}_3]/[\text{NH}_4^+] = 10^{-2.26}$, $[\text{NH}_3] = 10^{-6} \text{M}$
= 0.014 mg NH_3 - N/L
 - At pH 9.5: $[\text{NH}_3]/[\text{NH}_4^+] = 10^{-0.24}$, $[\text{NH}_3] = 0.13 \times 10^{-3}$
= 1.8 mg NH_3 - N/L

Buffering of Natural Water (1)

- *A buffer solution is one which offers resistance to changes in pH*
- *Normally buffer solutions are made up of weak acids and their salts or weak bases and their salts*
- *In the laboratory they are used for calibration and ensuring that pH meters are reading correctly*

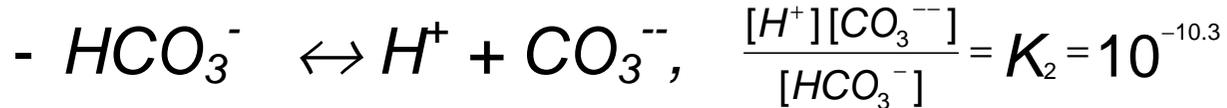
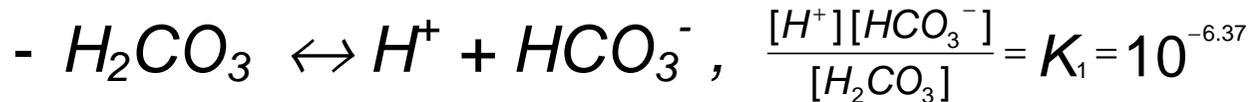
Buffering of Natural Water (2)

- *The ionisation of carbonic acid is common in natural waters:*



- *If acid is added it is taken up by HCO_3^- and so the pH of the water does not change significantly*
- *Once HCO_3^- is consumed, the pH can reduce rapidly with little further acid addition*

Buffering of Natural Water (3)



pH and Carbonate Species

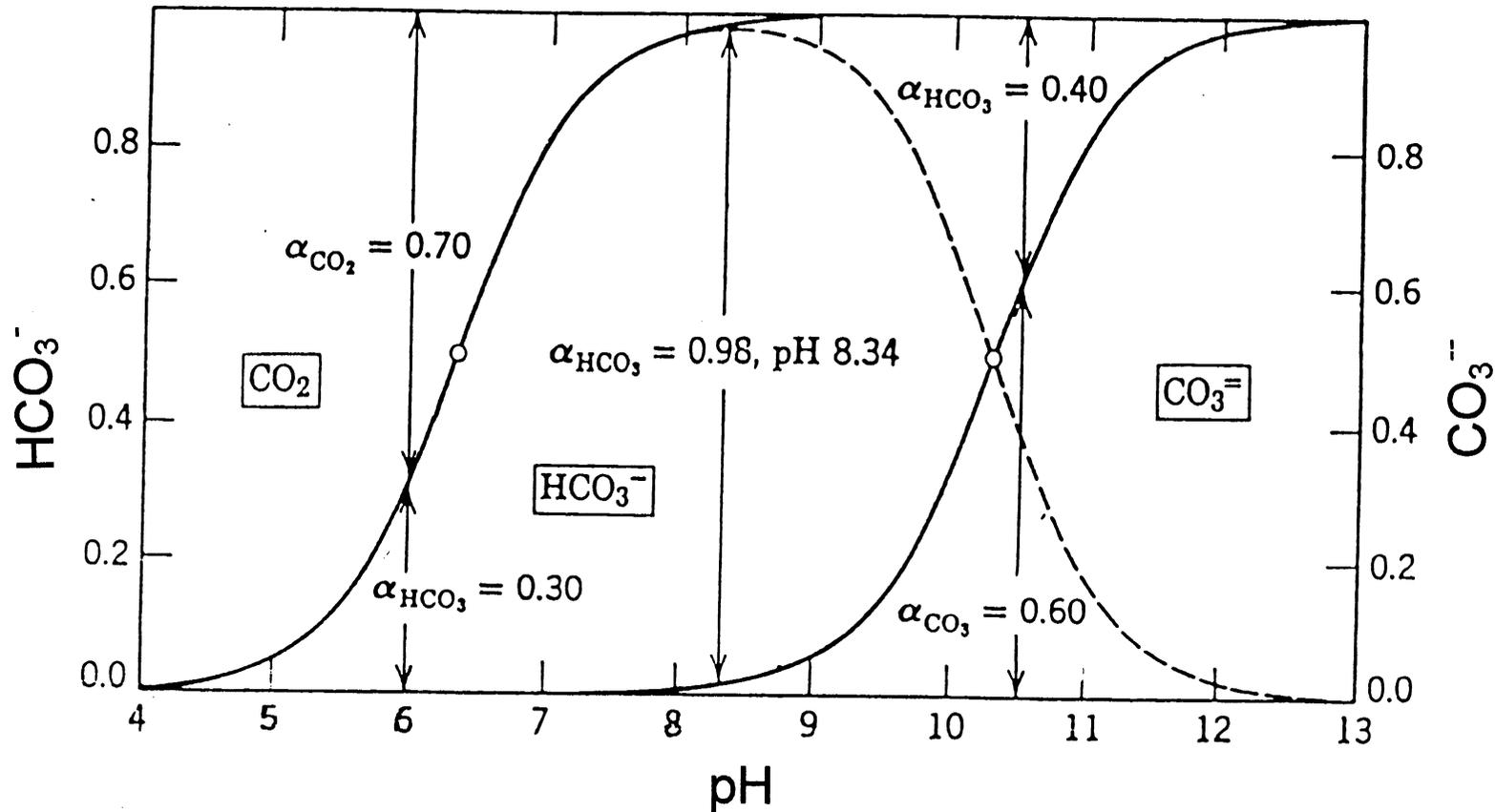


Fig 1 Carbonate species as a function of pH

Alkalinity Relationships

- Hydroxide alkalinity
 - *when pH is well above 10*
- Carbonate alkalinity
 - *when pH is > 8.3*
- Bicarbonate alkalinity
 - *when pH < 8.3*

Alkalinity Titration (1)

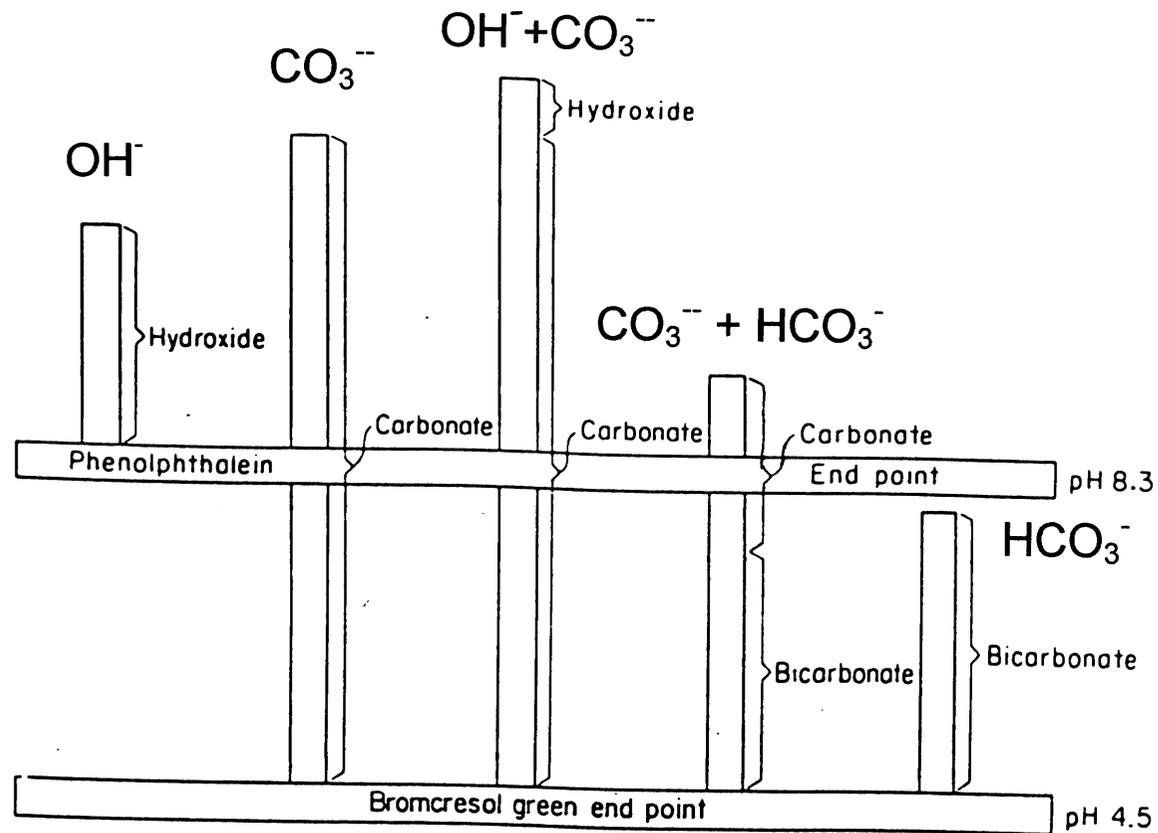


Fig 2 Titration of samples containing various forms of alkalinity

Alkalinity Titration (2)

Result of titration	Hydroxide alkalinity	Carbonate alkalinity	Bicarbonate alkalinity
$P = 0$	0	0	T
$P < 1/2 T$	0	2P	$T - 2P$
$P = 1/2 T$	0	2P	0
$P > 1/2 T$	$2P - T$	$2(T - P)$	0
$P = T$	T	0	0

*Key: P-phenolphthalein alkalinity, T-total alkalinity

Construction of Buffers

- $K = [H^+][A^-] / [HA]$
- $pH = pK + \log \{[A^-] / [HA]\}$
- Select a weak acid, HA, and its conjugate base, A⁻, whose pK is close to required buffer pH
 - *Calculate ratio of [A⁻] and [HA]*
- Molarity determines strength of the buffer

Construction of Buffers: Example

- Required acetate buffer, pH = 5, molarity 0.05
pK acetic acid = 4.74
 - $pH = pK + \log \{[A^-] / [HA]\}$
 - *Therefore $\log\{[(Na)acetate] / [Acetic acid]\} = 0.26$*
 - *$[(Na)acetate] / [Acetic acid] = 1.82$*
 - *$[Acetic acid] + [(Na)acetate] = 0.05$*
 - *Acetic acid = 0.0177 and (Na)acetate = 0.0323 moles/L*

Activity Coefficient

- Dilute solutions
 - *activity of ions = molar concentration*
- Concentrated solutions
 - *activity of ions = activity coefficient (γ) x molar conc*
- $\log \gamma = -0.5Z^2(\sqrt{\mu}/(1 + \sqrt{\mu}))$
 - *where Z = ion charge and μ = ionic strength*

Ionic Strength

- Aggregate property, depends on all dissolved species

$$\mu = \frac{1}{2} \sum C_i Z_i^2$$

C_i is the molar conc of i th ion & Z_i its charge

- Ionic strength is also = 2.5×10^{-5} x TDS (mg/L)

5. Evaluation sheets

6. Handout

Basic Aquatic Chemistry Concepts

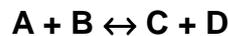
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- Alkalinity relationships
- Buffers
- Activity coefficients and ionic strength

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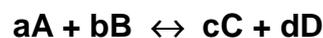
The equilibrium constant (*K*) can be defined as:

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

[C] = concentration of C, *[D]* = concentration of D etc.

Chemical Equilibria (2)

- *For the reaction:*



- *The equilibrium constant (*K*) becomes:*

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

Ionisation Equilibria

- *When the solid AB is ionised, the equation is:*



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Ionisation of Water

- Water ionises as follows:



- The ionisation constant (K) is:

$$K_a = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

- $K_a = 1.8 \times 10^{-16}$ at 25°C
- As $[\text{H}_2\text{O}] = 55.5$ moles/L \approx constant
- Replace $K_a \times [\text{H}_2\text{O}] = K_w = 10^{-14}$
- Where K_w = the ion product of water

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- so:

$$[\text{H}^+] = 10^{-7}$$

- or:

$$pH = 7 \text{ (ie: the pH of a neutral solution)}$$

Acid-base Equilibria

- Definitions
 - *An acid yields a Hydrogen ion (H^+) when added to water*
 - *A base yields a Hydroxide ion (OH^-) when added to water*
- Strong acids and bases completely dissociate in water:
 - *Hydrochloric acid: $HCl \rightarrow H^+ + Cl^-$*
 - *Sodium Hydroxide: $NaOH \rightarrow Na^+ + OH^-$*

Weak Acid and Conjugate Base

- Weak acids and bases partially dissociate, and
- Weak acids and bases are often paired:
 - *Boric acid: $H_3BO_3 \leftrightarrow H^+ + H_2BO_3^-$*
 - *Borate: $H_2BO_3^- + H_2O \leftrightarrow H_3BO_3 + OH^-$*

Ionisation of Weak Acids

- K_a = ionisation constant for acids, e.g. Boric acid:

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Ammonia Toxicity

- Acid-base Reactions in Water
 - *For the reaction:*
$$NH_3 + H^+ \leftrightarrow NH_4^+$$
 - *At high pH (alkaline conditions), the reaction produces more ammonia species (NH_3) which is toxic to fish*
 - *At low pH (acid conditions) the ammonium species (the relatively non-toxic, NH_4^+) predominates*

Ammonia Toxicity: Example

- $[\text{NH}_3] + [\text{NH}_4^+] = 0.2 \times 10^{-3} \text{M}$ (2.8 mg/L)
- Calculate NH_3 conc. at pH 7 & 9.5
 - $\frac{[\text{H}^+][\text{NH}_3]}{[\text{NH}_4^+]} = 10^{-9.26}$
 - At pH 7: $\frac{[\text{NH}_3]}{[\text{NH}_4^+]} = 10^{-2.26}$, $[\text{NH}_3] = 10^{-6} \text{M} = 0.014 \text{ mg NH}_3 - \text{N/L}$
 - At pH 9.5: $\frac{[\text{NH}_3]}{[\text{NH}_4^+]} = 10^{-0.24}$, $[\text{NH}_3] = 0.13 \times 10^{-3} = 1.8 \text{ mg NH}_3 - \text{N/L}$

Buffering of Natural Water (1)

- A buffer solution is one which offers resistance to changes in pH
- Normally buffer solutions are made up of weak acids and their salts or weak bases and their salts
- In the laboratory they are used for calibration and ensuring that pH meters are reading correctly

Buffering of Natural Water (2)

- The ionisation of carbonic acid is common in natural waters:

$$\text{H}_2\text{CO}_3 \leftrightarrow \text{H}^+ + \text{HCO}_3^-$$
- If acid is added it is taken up by HCO_3^- and so the pH of the water does not change significantly
- Once HCO_3^- is consumed, the pH can reduce rapidly with little further acid addition

Buffering of Natural Water (3)

- $\text{H}_2\text{O} + \text{CO}_2 \leftrightarrow \text{H}_2\text{CO}_3$
- $\text{H}_2\text{CO}_3 + \text{CaCO}_3 = \text{Ca}^{++} + 2\text{HCO}_3^-$
- $\text{H}_2\text{CO}_3 \leftrightarrow \text{H}^+ + \text{HCO}_3^-$, $\frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = K_1 = 10^{-6.37}$
- $\text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{--}$, $\frac{[\text{H}^+][\text{CO}_3^{--}]}{[\text{HCO}_3^-]} = K_2 = 10^{-10.3}$

Alkalinity Relationships

- Hydroxide alkalinity
 - when pH is well above 10
- Carbonate alkalinity
 - when pH is > 8.3
- Bicarbonate alkalinity
 - when pH < 8.3

Alkalinity Titration

Result of titration	Hydroxide alkalinity	Carbonate alkalinity	Bicarbonate alkalinity
P = 0	0	0	T
P < 1/2 T	0	2P	T - 2P
P = 1/2 T	0	2P	0
P > 1/2 T	2P - T	2(T - P)	0
P = T	T	0	0

*Key: P-phenolphthalein alkalinity, T-total alkalinity

Construction of Buffers

- $K = [H^+][A^-] / [HA]$
- $pH = pK + \log \{[A^-] / [HA]\}$
- Select a weak acid, HA, and its conjugate base, A⁻, whose pK is close to required buffer pH
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- Required acetate buffer, pH = 5, molarity 0.05 pK acetic acid = 4.74
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 - $[Acetic acid] + [(Na)acetate] = 0.05$
 - Acetic acid = 0.0177 and (Na)acetate = 0.0323 moles/L

Activity Coefficient

- Dilute solutions
 - activity of ions = molar concentration
- Concentrated solutions
 - activity of ions = activity coefficient (γ) x molar conc
- $\log \gamma = -0.5Z^2(\sqrt{\mu}/(1 + \sqrt{\mu}))$
 - where Z = ion charge and μ = ionic strength

Ionic Strength

- Aggregate property, depends on all dissolved species

$$\mu = \frac{1}{2} \sum C_i Z_i^2$$

C_i is the molar conc of ith ion & Z_i its charge
- Ionic strength is also = $2.5 \times 10^{-5} \times \text{TDS (mg/L)}$

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 the ratio of H_2S and HS^- at pH7 if:
 $\text{H}_2\text{S} \longleftrightarrow \text{HS}^- + \text{H}^+, K_a = 10^{-7}$
-

2. Calculate different forms of alkalinity if $\text{P} = 100 \text{ mg/L}$ and $\text{T} = 160 \text{ mg/L}$
-

- 3.(a) Calculate pH of buffer if 500 mL of 0.05M solutions of H_2PO_4^- and HPO_4^{2-} each are mixed, if $\text{H}_2\text{PO}_4^- \longleftrightarrow \text{HPO}_4^{2-} + \text{H}^+, K_a = 10^{-7.2}$

- (b) What is the molarity of the buffer
-

Questions and Answers

1. Calculate the ratio of H_2S and HS^- at pH7 if:
 $\text{H}_2\text{S} \longleftrightarrow \text{HS}^- + \text{H}^+, K_a = 10^{-7}$
-

AT pH7, $[\text{H}^+] = 10^{-7}$

Since $\frac{[\text{HS}^-][\text{H}^+]}{[\text{H}_2\text{S}]} = 10^{-7}$

$$\frac{[\text{HS}^-][10^{-7}]}{[\text{H}_2\text{S}]} = 10^{-7} \quad \text{or} \quad \frac{[\text{HS}^-]}{[\text{H}_2\text{S}]} = 1$$

2. Calculate different forms of alkalinity if $P = 100 \text{ mg/L}$ and $T = 160 \text{ mg/L}$
-

Since $P > \frac{1}{2} T$

Hydroxide alkalinity	=	$2P - T = 40 \text{ mg/L}$
Carbonate alkalinity	=	$2(T - P) = 120 \text{ mg/L}$
Bicarbonate alkalinity	=	0 mg/L

- 3.(a) Calculate pH of buffer if 500 mL of 0.05M solutions of H_2PO_4^- and HPO_4^{2-} each are mixed, if $\text{H}_2\text{PO}_4^- \longleftrightarrow \text{HPO}_4^{2-} + \text{H}^+, K_a = 10^{-7.2}$

- (b) What is the molarity of the buffer
-

(a) $\text{pH} = \text{pK} + \log \left\{ \frac{[\text{A}^-]}{[\text{AH}]} \right\}$
 $= 7.2 + \log \{0.025 / 0.025\} = 7.2 + 0 = 7.2$

(b) $\text{Molarity} = 0.025 + 0.025 = 0.05$

8. *Main text*

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Basic Aquatic Chemistry Concepts

1. Introduction

In order to understand aquatic chemistry it is necessary to be familiar with certain principles which dictate how chemical species react when dissolved in water. This module discusses some of these principles, in particular those concerned with chemical equilibria and its relation to the ionisation of species and pH.

2. Chemical Equilibrium

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



This means that the reaction is reversible (indicated by \leftrightarrow) 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 molar concentration of C, [D] is the molar concentration of D etc.

Where different numbers of molecules are involved, the reaction becomes:



The equilibrium constant (K) for the reaction is then defined as:

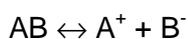
$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

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 environment) 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. This concept will be discussed later in this module.

3. Ionisation Equilibria

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



The equilibrium for this equation can be written as:

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

where $[A^+]$ and $[B^-]$ represent concentrations of the species in solution and $[AB]$ represents the concentration of the solid (or solute).

Because 'K' also describes the ionisation of 'AB', it can be called the 'ionisation constant' of the species. This ionisation constant concept can also be applied to the ionisation of any molecule which dissociates into its constituent ions.

4. Ion Product of Water

Under normal circumstances, water dissociates into its component ions, namely hydrogen (H^+) and hydroxide (OH^-) ions as follows:



And the ionisation constant is given by:

$$K_a = \frac{[H^+][OH^-]}{[H_2O]}$$

where $K_a = 1.8 \times 10^{-16}$ mole/L at 25 °C

The concentration of the species ' $[H_2O]$ ' in the above equation is largely unchanged after ionisation and = 55.5 moles/L. The above equation, therefore, can be written as:

$$[H^+][OH^-] = K_w = 10^{-14} \text{ (at } 25^\circ\text{C)}$$

where K_w = the ion product of water

To eliminate the very small powers of ten in the above equation it is useful to introduce the following terminology:

$$p(x) = -\log_{10} (x)$$

which means that:

$$p(10^{-14}) = -\log_{10} (10^{-14}) = 14$$

This can be applied to the ionisation equation of water at 25 °C:

$$-\log_{10} ([H^+][OH^-]) = -\log_{10} (K_w) = -\log_{10} (10^{-14})$$

$$pH + pOH = pK_w = 14$$

Note that the term pH has now been introduced which is defined as:

$$\text{pH} = -\log_{10}[\text{H}^+]$$

For a neutral solution, that is one where the concentration of $[\text{H}^+]$ ions is equal to the concentration of $[\text{OH}^-]$ ions:

$$[\text{H}^+] = [\text{OH}^-]$$

therefore: $[\text{H}^+][\text{OH}^-] = [\text{H}^+][\text{H}^+] = [\text{H}^+]^2 = 10^{-14}$

and $[\text{H}^+] = 10^{-7}$

or: $\text{pH} = 7$ (i. e: the pH of a neutral solution)

From the above, it can be seen that:

- the pH scale runs from 0 (acid) to 14 (alkali)
- that when pH is measured it is actually the negative logarithm of the hydrogen ion concentration that is being determined
- that an acidic solution (pH: 0 – 7) has a greater concentration of hydrogen ions than hydroxide ions
- that an alkaline solution has a greater concentration of hydroxide ions than hydrogen ions

5. Ionisation of Acids and Bases

The classical definition of acids and bases is given as:

- An *acid* is a compound that yields a hydrogen ion (H^+) when it is added to water.
- A *base* is a compound that yields a hydroxide ion (OH^-) when it is added to water.

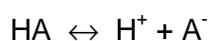
Strong acids and bases completely dissociate in water:

- Hydrochloric acid (strong acid): $\text{HCl} \rightarrow \text{H}^+ + \text{Cl}^-$
- Sodium Hydroxide (strong base): $\text{NaOH} \rightarrow \text{Na}^+ + \text{OH}^-$

Weak acids and bases only partially dissociate in water. A weak acid often has a paired or 'conjugate' base, and vice versa. For example, boric acid is a weak acid, and borate is its conjugate base.

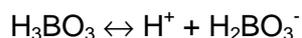
- Boric acid (weak acid): $\text{H}_3\text{BO}_3 \leftrightarrow \text{H}^+ + \text{H}_2\text{BO}_3^-$
- Borate (weak base): $\text{H}_2\text{BO}_3^- + \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{BO}_3 + \text{OH}^-$

The general equation for an acid can be written:



$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

The value of K_a is defined for each different acid , e.g. for Boric Acid (H_3BO_3):



$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{[H^+][H_2BO_3^-]}{[H_3BO_3]} = 10^{-9.24}$$

Values for some common weak acids are given in Table 1.

Table 1 Ionisation constants for common weak acids (25°C)

Acid	Equilibrium Equation	K_a	K_a	p K_a	Significance
Acetic	$CH_3COOH \leftrightarrow H^+ + CH_3COO^-$	1.8×10^{-5}	$10^{-4.74}$	4.74	Organic Wastes
Ammonium	$NH_4^+ \leftrightarrow H^+ + NH_3$	5.56×10^{-10}	$10^{-9.26}$	9.26	Nutrient, fish toxicity
Boric	$H_3BO_3 \leftrightarrow H^+ + H_2BO_3^-$	5.8×10^{-10}	$10^{-9.24}$	9.24	Nitrogen Analysis
Carbonic	$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$	4.3×10^{-7}	$10^{-6.37}$	6.37	Buffering, precipitation
	$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$	4.7×10^{-11}	$10^{-10.33}$	10.33	
Hydrocyanic	$HCN \leftrightarrow H^+ + CN^-$	4.8×10^{-10}	$10^{-9.32}$	9.32	Toxicity
Hydrogen Sulphide	$H_2S \leftrightarrow H^+ + HS^-$	9.1×10^{-8}	$10^{-7.04}$	7.04	Odours, corrosion
	$HS^- \leftrightarrow H^+ + S^{2-}$	1.3×10^{-13}	$10^{-12.89}$	12.89	
Hypochlorous	$HOCl \leftrightarrow H^+ + OCl^-$	2.9×10^{-8}	$10^{-7.54}$	7.54	Disinfection
Phenol	$C_6H_5OH \leftrightarrow H^+ + C_6H_5O^-$	1.2×10^{-10}	$10^{-9.92}$	9.92	Tastes, industrial waste
Phosphoric	$H_3PO_4 \leftrightarrow H^+ + H_2PO_4^-$	7.5×10^{-3}	$10^{-2.12}$	2.12	Analytical buffer Plant nutrient
	$H_2PO_4^- \leftrightarrow H^+ + HPO_4^{2-}$	6.2×10^{-8}	$10^{-7.21}$	7.21	
	$HPO_4^{2-} \leftrightarrow H^+ + PO_4^{3-}$	1.3×10^{-13}	$10^{-12.32}$	12.32	

Many weak acids have corresponding (conjugate) weak bases. The base dissociates to form OH^- when added to water. For these weak bases, an ionization constant K_b can also be defined. For Boric Acid, the corresponding weak base is Borate, which has the following reaction:



The ionization constant for a weak base (K_b) is defined:

$$K_b = \frac{[HA][OH^-]}{[A^-]} = \frac{[H_3BO_3][OH^-]}{[H_2BO_3^-]} = 10^{-4.76}$$

Water (H_2O) is not included in the constant.

Values for some common weak bases are given in Table 2.

Table 2 Ionization constants for some common weak bases (25°C)

Acid	Equilibrium Equation	K_b	K_b	PK_b	Significance
Acetate	$CH_3COO^- + H_2O \leftrightarrow CH_3COOH + OH^-$	5.56×10^{-10}	$10^{-9.264}$	9.26	Organic Wastes
Ammonia	$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$	1.8×10^{-5}	$10^{-4.74}$	4.74	Nutrient, fish toxicity
Borate	$H_3BO_3 + H_2O \leftrightarrow H_3BO_3^- + OH^-$	1.72×10^{-5}	$10^{-4.76}$	4.76	Nitrogen Analysis
Carbonate	$CO_3^{2-} + H_2O \leftrightarrow HCO_3^- + OH^-$ $HCO_3^- + H_2O \leftrightarrow H_2CO_3 + OH^-$	2.13×10^{-4} 2.33×10^{-8}	$10^{-3.67}$ $10^{-7.63}$	3.67 7.63	Buffering, precipitation
Calcium Hydroxide	$CaOH^+ \leftrightarrow Ca^{2+} + OH^-$	3.5×10^{-2}	$10^{-1.46}$	1.46	Softening
Magnesium Hydroxide	$MgOH^+ \leftrightarrow Mg^{2+} + OH^-$	2.6×10^{-3}	$10^{-2.59}$	2.59	Softening

It is often useful to know that, for a weak acid and its associated base:

$$pK_a + pK_b = 14$$

which is the same as:

$$K_a K_b = K_w = 10^{-14}$$

So for boric acid, for example:

$$pK_a = 9.24 \text{ (from tables)}$$

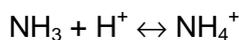
And for borate:

$$pK_b = 4.76 \text{ (from tables)}$$

Thus, it can be seen that:

$$9.24 + 4.76 = 14$$

Acid-base reactions are very important in water quality chemistry. For example, the toxicity of ammonia to fish is affected by the reaction below, which is itself affected by pH of the water:



At high pH (alkaline conditions), the reaction tends to produce more ammonia species (NH_3) which is toxic to fish, whereas at low pH (acid conditions) the ammonium species (the relatively non-toxic, NH_4^+) predominates.

Example 1

A eutrophic lake water sample contains 2.8 mg NH₃-N (NH₃ + NH₄⁺)/L. High pH values are likely to occur due to photosynthetic activity. Determine the concentration of NH₃ specie at pH 7 and 9.5. Water quality standards for fish culture specify that NH₃ concentration should not exceed 1.5 mg/L.

Solution

$$2.8 \text{ mg NH}_3 - \text{N/L} = 2.8 \text{ mg NH}_3 - \text{N/L} \times 1\text{g}/10^3 \text{ mg} \times 1 \text{ mole}/14 \text{ g NH}_3 - \text{N} = 0.2 \times 10^{-3} \text{ mole/L}$$

From Table 1:

$$[\text{H}^+][\text{NH}_3]/[\text{NH}_4^+] = 10^{-9.26}$$

At pH 7:

$$10^{-7} \times [\text{NH}_3]/[\text{NH}_4^+] = 10^{-9.26}$$

$$\text{and } [\text{NH}_3] + [\text{NH}_4^+] = 0.2 \times 10^{-3}$$

$$\text{or: } [\text{NH}_3]/[\text{NH}_4^+] = 10^{-2.26}$$

$$\text{or: } [\text{NH}_3] = 10^{-6} \text{ mole/L} = 0.014 \text{ mg/L}$$

At pH 9.5:

$$10^{-9.5} \times [\text{NH}_3]/[\text{NH}_4^+] = 10^{-9.26}$$

$$\text{and } [\text{NH}_3] + [\text{NH}_4^+] = 0.2 \times 10^{-3}$$

$$\text{or: } [\text{NH}_3]/[\text{NH}_4^+] = 10^{0.24}$$

$$\text{or: } [\text{NH}_3] = 0.13 \times 10^{-3} \text{ mole/L} = 1.8 \text{ mg/L}$$

The maximum limit is likely to exceed.

6. Buffering of Natural Water

A buffer solution is one which offers resistance to changes in pH. Normally, buffer solutions are made up of weak acids and their salts or weak bases and their salts. In the laboratory they are used for calibrating pH meters.

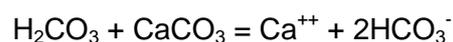
Natural waters also normally possess a buffering capacity; that is they have the ability, due to the salts, acids and alkalis that they naturally contain, to resist pH changes. The capacity of a water to neutralise acid is called alkalinity.

Rain water, as it travels through the atmosphere, dissolves carbon dioxide to yield poorly ionised carbonic acid:

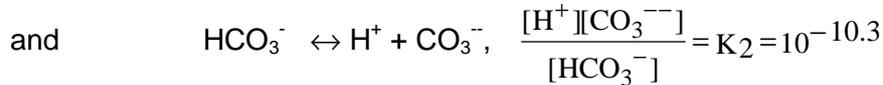
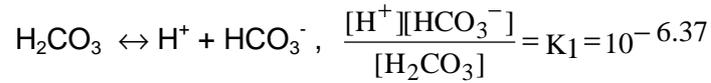


Carbon dioxide may also be dissolved as the water percolates through the soil, where carbon dioxide is available as the end product of microbial degradation of organic matter.

Carbonic acid is a diprotic acid. It contains two ionisable hydrogen ions. It reacts with soil and rock minerals to form soluble bicarbonates:



Carbonic acid, bicarbonates and carbonates exist in equilibrium with each other according to the following ionisation and equilibrium relations:



The hydrogen ion concentration, which appears in both the equilibrium equations, controls the relative concentrations of the three carbonate species. Figure 1 shows the distribution of the three species as a function of pH according to the above equations.

Note that:

- at pH 11.5 and higher carbonate species predominates
- at pH 10.3 concentrations of carbonate and bicarbonate species are equal
- at pH 8.3, phenolphthalein end point, bicarbonate species predominates, which reduces with decreasing pH
- at pH 4.5, bromocresol green or the alkalinity titration end point, carbonic acid or carbon dioxide species predominate

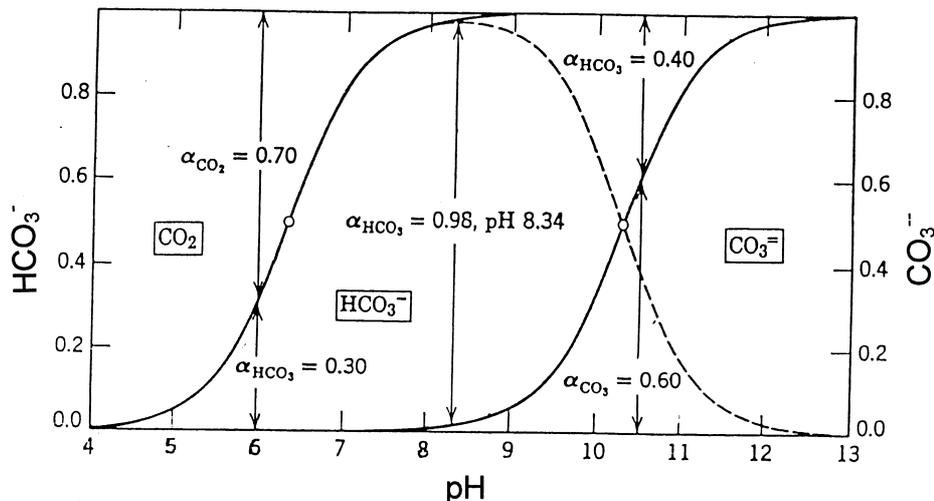


Fig 1 Carbonate species as a function of pH

If acid is added to a water at neutral or near neutral pH, the hydrogen ions (H^+) will be taken up by the bicarbonate ions (HCO_3^-) to produce more neutral carbonic acid (H_2CO_3). Assuming that the bicarbonate is not totally consumed, the addition of acid will cause only a slight increase in the hydrogen ion concentration of the water. Therefore the pH, which is a measure of hydrogen ion concentration, will also not change significantly. It is worth noting, however, that once nearly all the bicarbonate is consumed, and the buffering capacity is nullified, a relatively small addition of acid may cause a large pH change.

The above effect occurs when acid rain (rain made acidic by passing through atmospheric pollution such as sulphur dioxide) is continually deposited in a lake containing bicarbonate species. At first when this occurs, the lake water pH is unaltered due to the natural buffering capacity of the dissolved bicarbonate. However, once this buffering capacity is consumed, the lake rapidly becomes acidic and unable to support certain forms of life.

Similarly, addition of an alkali will shift the equilibrium towards carbonate specie and the pH will increase only slightly. Only when nearly all the bicarbonate is consumed there will be a significant increase in the pH value.

7. Alkalinity Relationships

The alkalinity of a water is a measure of its capacity to neutralize acid. Bicarbonates represent the major form of alkalinity in natural waters. Other salts of weak acids, such as borates, silicates and phosphates, which may be present in small amounts, would also contribute to alkalinity. Salts of organic acids, for example, humic acid, which is quite resistant to biological oxidation, would also add to alkalinity.

For all practical purposes, the alkalinity in natural waters may be classified as, hydroxide, carbonate and bicarbonate alkalinity.

Hydroxide alkalinity: Water having pH well above 10 would have significant amount of hydroxide alkalinity. At a lower pH value, say the phenolphthalein end point, the hydroxide alkalinity may be taken to be insignificant.

Carbonate alkalinity: Water having pH higher than 8.5 may have carbonate alkalinity. When the pH is lowered to 8.3 exactly one-half of the carbonate alkalinity is neutralised.

Bicarbonate alkalinity: Water having pH less than 8.3 would have only bicarbonate alkalinity.

The above concepts, in relation to titration of water samples with an acid to phenolphthalein and bromocresol green end points are illustrated in Figure 2. The distribution of various forms of alkalinity in samples may be calculated as described in Table 3.

Table 3 Alkalinity Relationships*

Result of titration	Hydroxide alkalinity	Carbonate alkalinity	Bicarbonate alkalinity
P = 0	0	0	T
P < 1/2 T	0	2P	T - 2P
P = 1/2 T	0	2P	0
P > 1/2 T	2P - T	2(T - P)	0
P = T	T	0	0

*Key: P-phenolphthalein alkalinity, T-total alkalinity

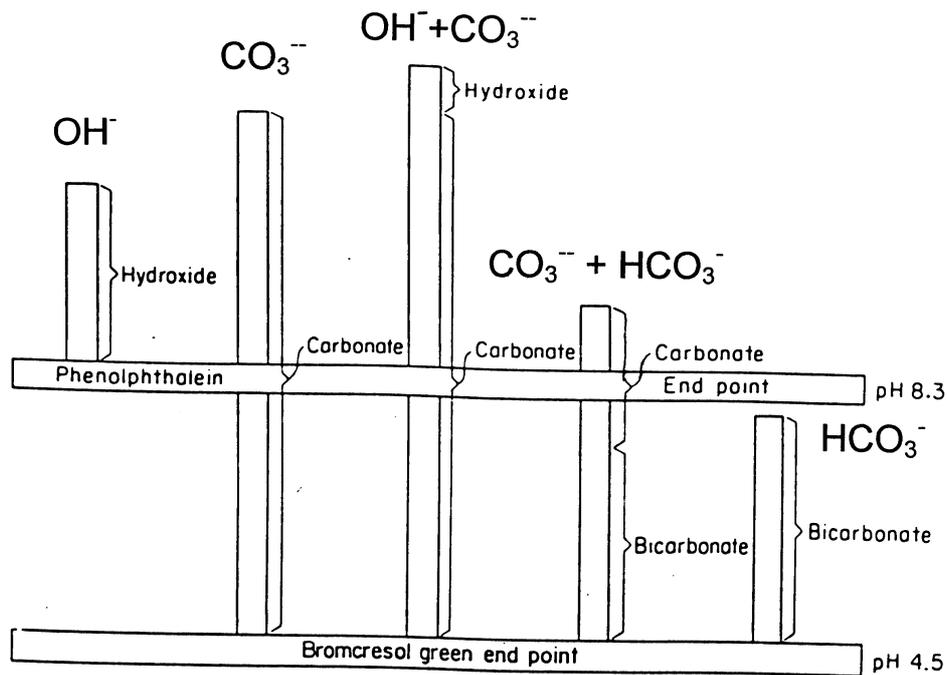


Fig 2 Titration of samples containing various forms of alkalinity

Example 2

Calculate the hydroxide alkalinity of water at pH 11 and 9. Express the result in terms of mg CaCO₃/L

Solution

At pH 11:

$$[\text{OH}^-] = 10^{-3} \text{ mole/L} \times 1\text{eq/1 mole} \times 50\text{g CaCO}_3/1\text{eq} \times 10^3\text{mg/1g} = 50 \text{ mg CaCO}_3/\text{L}$$

At pH 9:

$$[\text{OH}^-] = 10^{-5} \text{ mole/L} \times 1\text{eq/1 mole} \times 50\text{g CaCO}_3/1\text{eq} \times 10^3\text{mg/1g} = 0.5 \text{ mg CaCO}_3/\text{L}$$

Example 3

The phenolphthalein and total alkalinity of a water sample is 40 and 120 mg as CaCO₃/L, respectively. Calculate the different forms of alkalinity in the sample.

Solution

Since $P < 1/2 T$, from Table 3 the different forms of alkalinity are: hydroxide = 0, carbonate = 80 mg as CaCO₃/L and bicarbonate = 40 mg as CaCO₃/L

8. Construction of Buffers

The following relation is obtained by taking logarithm of the equilibrium expression for ionisation of a weak acid and rearranging:

$$\text{pH} = \text{pK} + \log\{[\text{A}^-]/[\text{HA}]\}$$

If the pK value is known (for example, Table 1), a buffer of predetermined pH value can be constructed by suitably proportioning the molar concentrations of the acid and its conjugate base.

Example 4

Calculate the quantities of acetic acid (AH) and sodium acetate (A⁻) required to construct 500 mL of a 0.05 molar acetate buffer of pH 5. The pK value for acetic acid is 4.74.

Solution

$$\text{pH} = \text{pK} + \log\{[\text{A}^-]/[\text{HA}]\}$$

Substituting in the above equation one obtains:

$$5 = 4.74 + \log\{[\text{A}^-]/[\text{HA}]\} \quad \text{or} \quad \log\{[\text{A}^-]/[\text{HA}]\} = 0.26 \quad \text{or} \quad [\text{A}^-]/[\text{HA}] = 1.82$$

Since molarity is 0.05: $[\text{HA}] + [\text{A}^-] = 0.05$

Therefore $[\text{HA}] + 1.82[\text{HA}] = 0.05$
or $[\text{HA}] = 0.0177$ and $[\text{A}^-] = 0.0323$ moles/L

For 500mL buffer: HA = 0.0088 and A⁻ = 0.0161 moles

Note that:

- In constructing a buffer of a given pH, select an acid or a base whose pK value is close to the pH value of the buffer, preferably within 1 pH unit range. The difference between pK and pH should never be more than 1.5 units. This will ensure that the pH variation is minimal when an acid or alkali is neutralised.
- It is also important to ensure that the selected compounds for constructing the buffer do not enter into any side reaction with the system, which is to be buffered.
- The molarity of buffer indicates the strength or the neutralising capacity of the buffer, i.e., the quantity of acid or alkali that it can neutralise without resulting in significant change in pH.

9. Activity Coefficients and Ionic Strength

As solutions of ionised materials become more concentrated, their quantitative effect in equilibrium relationships becomes progressively less. Thus, the effective concentration, or activity, of ions is decreased below that of the actual molar concentration. The activity of an ion or molecule can be found by multiplying its molar concentration by an activity coefficient, γ .

The activity coefficient is related to the ionic strength, μ , which is defined as

$$\mu = \frac{1}{2} \sum C_i Z_i^2$$

where C_i is the molar concentration of the i th ion and Z_i its charge and the summation extends over all the ions in solution.

The ionic strength can also be approximated by multiplying TDS in mg/L by 2.5×10^{-5} .

The activity coefficient is calculated by

$$\log \gamma = -0.5 Z^2 (\sqrt{\mu} / (1 + \sqrt{\mu}))$$

where Z is the charge on the ion for which the activity coefficient is being determined.

Example 5

Calculate the activity coefficients and activities of each ion in a solution containing 0.01 M MgCl_2 and 0.02 M Na_2SO_4 .

Solution

Setup a calculation table:

Ion	C	Z	CZ^2
Mg^{2+}	0.01	+2	0.04
Na^+	0.04	+1	0.04
Cl^-	0.02	-1	0.02
SO_4^{2-}	0.02	-2	<u>0.08</u>
		Σ	<u>0.18</u>

Calculate ionic strength:

$$\mu = \frac{1}{2} \sum C_i Z_i^2 = 1/2 \times 0.18 = 0.09$$

Calculate activity coefficients and activity for various ions:

$$\log \gamma = -0.5 Z^2 (\sqrt{\mu} / (1 + \sqrt{\mu})) = 0.115 Z^2$$

Ion	γ	γC
Mg^{2+}	0.35	0.0035
Na^+	0.77	0.031
Cl^-	0.35	0.015
SO_4^{2-}	0.77	0.007