Mixed weak acid/base systems
Part II: Dosing estimation, aqueous phase

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Abstract

This paper develops algorithms whereby the mass of dosing chemical can be estimated to bring about a desired change in the state of an aqueous mixture of weak acid/bases. It is shown that the solution alkalinity for an aqueous mixture of weak acid/bases (relative to a selected solution reference state defined by selected weak acid/base reference species) can be expressed as the sum of the subsystem alkalinities, one for each weak acid/base (relative to the same selected weak acid/base reference species) plus a water subsystem alkalinity (relative to H_2O where $[H^+]=[OH^-]=10^{-7}$ moles/ℓ). Making use of weak acid/base subsystem and water subsystem alkalinities, relatively simple dosing estimation algorithms are developed and illustrated by some practical examples.

Introduction

In **Part I** of this series (Loewenthal *et al.*, 1989) it was shown that in characterising a solution containing a mixture of weak acid/bases the principal difficulty arises in determining the carbonate weak acid/base total species concentration. Total species concentrations of all the common weak acid/bases can be measured directly without undue difficulty, but not that of the carbonate weak acid/base, except if an inorganic carbon analyser is available.

In the absence of an inorganic carbon analyser, for the carbonate system only in solution, the literature records the establishment of the mass parameter alkalinity as alternative to the total carbonate species parameter. Measurement of alkalinity plus the pH of the solution provides sufficient information to calculate the total carbonate species concentration. The alkalinity measurement needs to be taken relative to a selected reference solution state. With **only the carbonate system present** in solution, procedures to identify the solution reference state have been developed, some semi-empirical, some based on prior pH experimental titrations; in this way, an alkalinity relative to the solution reference state can be measured and the total carbonate species concentration determined. However, for the carbonate subsystem only in solution, Gran (1952) had proposed an ingenious method which allows the $H_2CO_3^*$ alkalinity to be determined relative to the reference solution state without actually experimentally identifying the reference state.

With mixtures of weak acid/bases in solution, empirical or experimental identification of the reference solution state has been found to be well-nigh impossible so that only an approximate empirically defined alkalinity measurement could be made. To address this situation, in **Part I** a theoretical formulation of alkalinity for a mixture of weak acid/bases was developed, based on a reference solution state for the mixture with associated reference species. The Gran method was extended to such mixtures where one of the weak acid/bases was the carbonate system. Using the extended Gran method, an alkalinity measurement could be made. Knowing the total species concentration of each weak acid/base except that of the carbonate system; the measured alkalinity; and the pH of the solution, the total species concentration of the carbonate system could be derived and hence the solution characterised completely.

Having characterised a solution containing one or more weak acid/bases the next important aspect is that of **chemical conditioning** of the solution, that is, determining the chemical type and dosage to achieve a desired change in the chemical state of the solution.

Chemical conditioning is necessary in a wide spectrum of weak acid/base problems. Examples of such problems, categorised according to the phases in which the chemical reactions take place, aqueous, solid and gaseous, are as follows:

(1) ***Single-phase aqueous problems.*** pH/alkalinity/acidity adjustment of solutions by addition of weak or strong acids and bases, or salts of these (e.g. carbonate system in stabilisation of water supplies); assessment of transient solution states during which precipitation/dissolution or gas exchange takes place (e.g. kinetics of solid $CaCO_3$ precipitation, or dissolution of solid $CaCO_3$).

(2) ***Two-phase aqueous-gas equilibrium problems.*** Equilibrium between dissolved carbonate species, gaseous CO_2 and pH (e.g. in anaerobic digesters the effect due to changes in pH caused by changes in short-chain fatty acid concentration).

(3) ***Two-phase aqueous-solid equilibrium problems.*** Incongruent precipitation/dissolution (e.g. in chemical removal of SO_4^{2-}, aqueous-solid equilibrium of $BaCO_3$, $BaSO_4$ and $CaCO_3$); precipitation of $CaCO_3$ and $Mg(OH)_2$ (e.g. water softening); precipitation with changes in CO_2 (e.g. struvite precipitation in anaerobic digesters).

(4) ***Three-phase aqueous-solid-gas equilibrium problems.*** CO_2 stripping (e.g. CO_2 from dolomitic ground water with concomitant $CaCO_3$ precipitation); dissolution potential of solid $CaCO_3$ (e.g. redissolution of $CaCO_3$ after overdosing an anaerobic digester with lime and consequential precipitation of $CaCO_3$).

Two approaches to equilibrium chemical dosing estimation have developed, graphical and numerical. In the past, graphically-based solution procedures have found ready application in solving dosing problems in the carbonate single weak acid/base system, Loewenthal and Marais (1976; 1983) and Loewenthal *et al.* (1986). With the increasing availability of personal computers, computerised numerical procedures (algorithms), to obtain dosing estimates, are superseding the graphical procedures (Loewenthal *et al.*, 1988). However, graphical procedures still have a role to play in providing an understanding of the behaviour of these complex systems. With the even more complex systems of mixtures of weak acid/bases, computer-based numerical methods inevitably will become the norm. In this paper the principles of chemical dosing

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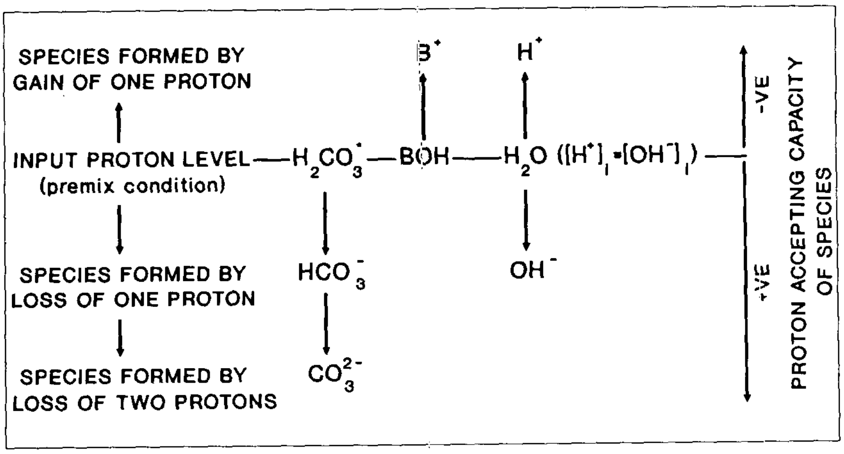

Figure 1
Proton level diagram for addition of $H_2CO_3^*$, and a strong base, BOH, to pure water

estimation in chemical conditioning will be set out in detail. Application of these principles will be restricted to (1) above, i.e. single-phase aqueous problems; two and three-phase problems will be addressed in future papers. Attention will be focused almost exclusively on the numerical algorithms to estimate dosages; graphical presentation will be used only to promote understanding of the basic tenets governing the solution procedures.

Dosing estimation — carbonate system only present

To date, dosing estimation procedures have been developed exclusively for situations where the carbonate system only is present in solution (Loewenthal and Marais, 1983; Loewenthal *et al.*, 1986). These dosing estimation procedures made use of the graphical approach. Below we will review these procedures when converted to a numerical approach, thereby to highlight the limitations in the present dosing estimation procedures.

Basic theory

In **Part I** it was shown that alkalinity or acidity is measured relative to some standard or reference solution state. Using the carbonate system as an example, the reference solution state is defined as the state created by addition to pure water of a selected carbonate species, called the reference species. Thus, addition of, for example, the selected reference species CO_3^{2-} creates the CO_3^{2-} reference solution state. Addition of a strong base or acid moves the state of the solution away from the reference solution state to a new state by an amount called the alkalinity or acidity respectively. Quantitatively, the alkalinity is the mass of strong acid (H^+) that needs to be added to the solution to return the state to the initial solution reference state, and the acidity as the mass of strong base (OH^-) to return the state to the initial solution reference state. The alkalinity and acidity were designated in terms of the reference species, in our example by CO_3^{2-} alkalinity (CO_3^{2-} alk) and CO_3^{2-} acidity respectively.

From the theoretical formulation for alkalinity and acidity, by considering the proton state (see Fig. 1), the alkalinity can be defined as the proton **accepting** capacity and the acidity as the proton **donating** capacity relative to the solution reference state. This definition does away with the previous definition in which alkalinity and acidity were defined in terms of H^+ and OH^- respectively. With the "new" definition, alkalinity and acidity become, as it were, opposite sides of the same coin; with respect to the selected reference solution state (with its associated reference species), the proton accepting capacity (alkalinity) equals the negative of the proton donating capacity (acidity), i.e. for our example CO_3^{2-} alk $= -CO_3^{2-}$ acidity. Thus, for the same reference solution state, the two designations alkalinity and acidity are not independent, the one being equal to the other, but of opposite sign.

This two-term system of designation is rooted in history and seems to have developed either from the H^+, OH^- approach, or to ensure that in their normal application the alkalinity and acidity both would give positive values. The two-term nomenclature is a continuous cause for confusion of users not intimately involved with the subject matter and complicates unnecessarily the dosing algorithms. Accepting a single-term nomenclature, because characterisation of the carbonate system virtually always commences with an alkalinity measurement, it would seem that the alkalinity designation should be preserved and the acidity one abandoned.

Using the concept of reference solution state, for the reference species $H_2CO_3^*$, HCO_3^- and CO_3^{2-} and total carbonate species concentration (C_T) the following alkalinity and C_T equations were developed (**Part I**):

$$H_2CO_3^* \text{ alk} = 2[CO_3^{2-}]+[HCO_3^-]+[OH^-]-[H^+] \tag{1}$$

$$HCO_3^- \text{ alk} = [CO_3^{2-}]-[H_2CO_3^*]+[OH^-]-[H^+] \tag{2}$$

$$CO_3^{2-} \text{ alk} = -2[H_2CO_3^*]-[HCO_3^-]+[OH^-]-[H^+] \tag{3}$$

$$C_T = [H_2CO_3^*]+[HCO_3^-]+[CO_3^{2-}] \tag{4}$$

where:
[ ] = concentration (mol/ℓ)

Subtracting Eq. (3) from Eq. (1)

$$H_2CO_3^* \text{ alk} - CO_3^{2-} \text{ alk} = 2\,C_T \tag{5}$$

Adding Eqs. (1) and (3)

$$H_2CO_3^* \text{ alk} + CO_3^{2-} \text{ alk} = 2HCO_3^- \text{ alk} \tag{6}$$

In **Part I** it was shown that if any two **independent** parameters from $H_2CO_3^*$ alk, HCO_3^- alk, CO_3^{2-} alk, C_T and pH are known the others can be determined.

The basic measurements in characterisation are pH and one capacity parameter, almost always $H_2CO_3^*$ alkalinity. In solving dosing problems, the values of **two capacity parameters** are required, for reason that the capacity parameters change in a simple stoichiometric fashion with dosing whereas pH does not. It is necessary therefore to develop equations to determine other capacity parameters from $H_2CO_3^*$ alkalinity and pH:

From the pH measurement, which is formulated in terms of the activity of H^+ [i.e. (H^+)], the molar concentration of H^+ (i.e. $[H^+]$) can be determined from:

$$[H^+] = \frac{1}{f_m} 10^{-pH} \tag{7}$$

where:

f_m = monovalent activity coefficient.

Knowing $[H^+]$ and $H_2CO_3^*$ alkalinity, an expression linking these with the CO_3^{2-} alkalinity (acidity) can be derived from the equilibrium equations describing the carbonate system (Loewenthal *et al.*, 1986) i.e.:

$$CO_3^{2-} \text{ alk} = -CO_3^{2-} \text{ acidity}$$

$$= -H_2CO_3^* \text{ alk} \left[\frac{1+2\times 10^{(pK_1'-pH)}}{1+2\times 10^{(pH-pK_2')}} \right] + 10^{(pH-pK_w')} - 10^{-pH} \tag{8}$$

where:

$$pK_1' = -\log K_1' \text{ and } K_1' = \frac{K_1}{f_{HCO_3^-}} = \frac{(H^+)[HCO_3^-]}{[H_2CO_3^*]} \tag{9a}$$

$$pK_2' = -\log K_2' \text{ and } K_2' = \frac{K_2 f_{HCO_3^-}}{f_{CO_3^{2-}}} = \frac{(H^+)[CO_3^{2-}]}{[HCO_3^-]} \tag{9b}$$

$$pK_w' = -\log K_w' \text{ and } K_w' = \frac{K_w}{f_{OH^-}} = (H^+)[OH^-] \tag{9c}$$

$f_{HCO_3^-}$, $f_{CO_3^{2-}}$, f_{OH^-} = activity coefficients for HCO_3^-, CO_3^{2-}, OH^- species respectively

K_1, K_2, K_w = equilibrium constants (for determination of values see Loewenthal *et al.*, 1986); K_1 and K_2 are in mol/ℓ and K_w in $(mol/ℓ)^2$.

Knowing two capacity parameters, CO_3^{2-} alk and $H_2CO_3^*$ alk, the other capacity parameters, i.e. C_T and HCO_3^- alk, can be derived, if required, from Eqs. (5) and (6) respectively. Historically, $H_2CO_3^*$ alk and CO_3^{2-} acidity (i.e.—CO_3^{2-} alk) were the two capacity parameters usually selected. It is likely that these two were selected because they are expressed with respect to the solution states defined by the most and least protonated species respectively and hence usually will give rise to positive numerical values.

Changes in capacity parameters with dosing

Whereas the individual dissolved species concentrations (i.e. $[H_2CO_3^*]$, $[HCO_3^-]$, $[CO_3^{2-}]$, $[H^+]$ and $[OH^-]$) change in a rather complex fashion with chemical dosing, the capacity parameters, $H_2CO_3^*$ alkalinity, HCO_3^- alkalinity, CO_3^{2-} alkalinity and C_T, change in a simple stoichiometric fashion. The changes with dosing are as follows:

$$\Delta H_2CO_3^* \text{ alk} = 2[CO_3^{2-}]_{added} + [HCO_3^-]_{added} + [OH^-]_{added} - [H^+]_{added} \tag{10}$$

$$\Delta HCO_3^- \text{ alk} = [CO_3^{2-}]_{added} - [CO_2]_{added} + [OH^-]_{added} - [H^+]_{added} \tag{11}$$

$$\Delta CO_3^{2-} \text{ alk} = -2[CO_2]_{added} - [HCO_3^-]_{added} + [OH^-]_{added} - [H^+]_{added} \tag{12}$$

$$\Delta C_T = [CO_2]_{added} + [HCO_3^-]_{added} + [CO_3^{2-}]_{added} \tag{13}$$

where:

Δ = an increase in the parameter value (mol/ℓ)

[ ] = species concentration (mol/ℓ).

Tabular representation of Eqs. (10) to (13) is shown in Table 1 for addition of X mol/ℓ of either CO_2, HCO_3^-, CO_3^{2-}, OH^- or H^+.

Dosing estimation

In solutions containing only the carbonate system, chemical conditioning problems in the aqueous phase devolve into the following two categories:

- Final solution state for a specified initial state and a specified chemical dose and chemical dosage type.
- Chemical dose for specified chemical dosage type and specified initial and final solution states.

Solution procedures for the two basic conditioning problems in the aqueous phase are set out below. In the procedures, units of mol/ℓ should be used.

Final state for a specified initial state and specified dosing

The initial state of the water is given, invariably by $H_2CO_3^*$ alk and pH. The chemical dosage type and amount are specified and the final state of the solution is required to be determined. The solution procedure is carried out in four steps:

(1) For known (measured) values of the **two** independent parameters of the raw water, usually pH and $H_2CO_3^*$ alk, calculate the corresponding value for the third parameter, CO_3^{2-} alk, using Eq. (8).

(2) Calculate the changes in the two capacity parameters (i.e. $\Delta H_2CO_3^*$ alk and ΔCO_3^{2-} alk) for the dosage applied, Eqs. (10) and (12).

(3) Calculate the final values for $H_2CO_3^*$ alk and CO_3^{2-} alk after dosing, from:

$H_2CO_3^*$ alk (final) = $H_2CO_3^*$ alk (initial) + $\Delta H_2CO_3^*$ alk
CO_3^{2-} alk (final) = CO_3^{2-} alk (initial) + ΔCO_3^{2-} alk

(4) Determine the final pH from the final $H_2CO_3^*$ alk and CO_3^{2-} alk values, Eq. (8). The final pH cannot be determined directly from Eq. (8) as the equation cannot be written down with pH only on the left hand side. Instead, an iterative method of successive approximation is used as follows:

> A pH is selected and substituted into Eq. (8) together with the known $H_2CO_3^*$ alk and the equation is solved for CO_3^{2-} alk. The calculated CO_3^{2-} alk is compared with that determined in (3) above; if the value is higher then pH is decreased, if lower then pH is increased. The new pH and known $H_2CO_3^*$ alk are substituted back into Eq. (8). This procedure is repeated until the calculated CO_3^{2-} alk and that determined in (3) above are equal (within the limits required).

Dosage of a specified chemical for specified initial and final states

The initial and final states of the water are given, the initial state invariably by $H_2CO_3^*$ alk and pH values and the final state by pH. The dosage type is specified but the mass of dosage is to be determined. The solution procedure is carried out in seven steps:

(1) For known (measured) values of the two independent parameters of the water, usually pH and $H_2CO_3^*$ alk, calculate the corresponding value for the third parameter CO_3^{2-} alk, using Eq. (8).

(2) Select a capacity parameter the value of which is unaffected by the chemical dosage type specified, see Eqs. (10) to (13) and Table 1, i.e. $H_2CO_3^*$ alk for CO_2 ($H_2CO_3^*$) addition, CO_3^{2-} alk for CO_3^{2-} addition, HCO_3^- alk for HCO_3^- addition and C_T for strong acid/base addition.

(3) Determine the initial value of the capacity parameter selected in (2) above. If capacity parameter selected is:

(i) $H_2CO_3^*$ alk, the value is known from measurement,
(ii) CO_3^{2-} alk, the value is known from (1) above,
(iii) HCO_3^- alk or C_T, the value is calculated from Eq. (6) or Eq. (5) respectively using the known values for $H_2CO_3^*$ alk and CO_3^{2-} alk.

After dosing the final value for this capacity parameter equals the initial value [see (2) above].

(4) Select a capacity parameter that **will change** with dosing, see Eqs. (10) to (13) and Table 1, i.e. $H_2CO_3^*$ alk for addition of CO_3^{2-}, HCO_3^- or strong acid/base, CO_3^{2-} alk for addition of CO_2($H_2CO_3^*$). Initial values of these two parameters are known, $H_2CO_3^*$ alk from measurement, CO_3^{2-} alk from (1) above.

(5) Calculate the final values of $H_2CO_3^*$ alk and CO_3^{2-} alk from the specified final pH and the final value of the capacity parameter in (3) above (i.e. the capacity parameter for which the initial and final values remain the same) using Eqs. (1) to (6).

(6) Calculate the change in the capacity parameter selected in (4) above ($H_2CO_3^*$ alk or CO_3^{2-} alk), i.e. the final value determined in (5) minus the initial value determined in (1).

(7) Determine the mass concentration of chemical dosage from the change in the capacity parameter [from (6) above] and the relevant equation from Eqs. (10) to (13).

The computational sequences outlined above are simple but the calculations are laborious. A computer program to solve these algorithms has been developed (Loewenthal *et al.*, 1988). Although the procedures above have been applied to resolving dosing problems with the carbonate system only present, the approach in fact can be applied with little modification to any **single** weak acid/base system in solution, differing only in that the initial alkalinity is not known but instead is determined from the measured initial total species concentration and pH.

More than one weak acid/base in solution

When more than one weak acid/base is in solution, application of approaches similar to the ones set out above leads to cumbersome and complex algorithms. Furthermore, it is difficult to cast the solution procedure into a general method, or a set of methods. However, reinterpreting the theoretical formulation of alkalinity, by shifting the focus of interest from the reference solution state to the individual weak acid/bases making up the state, conditioning procedures can be developed which are simple and powerful. The basis for these procedures is developed in the section below.

TABLE 1
EFFECT OF ADDITION OF X moles/ℓ OF A PARTICULAR DOSING CHEMICAL ON THE CAPACITY PARAMETERS, $H_2CO_3^*$ alk, CO_3^{2-} alk (= $-CO_3^{2-}$ acidity), HCO_3^- alk AND TOTAL CARBONATE SPECIES CONCENTRATION (C_T)

Addition of X mol/ℓ	Δ $H_2CO_3^*$ alk	Δ CO_3^{2-} alk	Δ HCO_3^- alk	Δ C_T
CO_2 ($H_2CO_3^*$)	0	-2X	-X	+X
CO_3^{2-}	+2X	0	+X	+X
HCO_3^-	+X	-X	0	+X
OH^-	+X	+X	+X	0
H^+	-X	-X	-X	0

Solution and subsystem alkalinities

Consider the theoretical formulation of $H_2CO_3^*$ alkalinity for a water containing only the carbonate weak acid/base system in solution. In **Part I** it was shown that addition of $H_2CO_3^*$ only to pure water makes up the $H_2CO_3^*$ **solution reference state,** the species added (i.e. $H_2CO_3^*$) being called the **reference species.** Addition of a molar mass of say a monoprotic strong base, BOH, changes the state of the solution away from the reference state imparting an **alkalinity** to the water relative to the reference state. We have seen that by adding the strong base we have imparted a proton accepting capacity to the solution relative to the solution reference state. This is evident from formulation of the alkalinity from the proton level diagram, shown in Fig. 1.

At equilibrium the positive and negative changes in protons should be equal, i.e.:

$$[B^+]+[H^+]-[H^+]_i = 2[CO_3^{2-}]+[HCO_3^-]+[OH^-]-[OH]_i$$

where:

i denotes initial pure water species; and

[ ] = concentration (mol/ℓ).

Now in pure water $[H^+]_i = [OH^-]_i = 10^{-7}$ mol/ℓ so that these two parameters cancel in the equation above, and solving for B^+, the $H_2CO_3^*$ alkalinity equation is obtained, i.e.:

$$H_2CO_3^* \text{ alkalinity} = [B^+] = 2[CO_3^{2-}]+[HCO_3^-]+[OH^-]-[H^+] \qquad (14)$$

Referring to Fig. 1 and Eq. (14) it can be appreciated that the $H_2CO_3^*$ alkalinity can be expressed as the **sum of two alkalinities,** i.e. an alkalinity, or proton accepting capacity, due to:

- the carbonate subsystem, $[HCO_3^-]+2[CO_3^{2-}]$, relative to the $H_2CO_3^*$ reference species
- dissolved water subsystem, $[OH^-]-[H^+]$, relative to H_2O reference species with $[H^+]_i = [OH^-]_i$.

In effect one may look upon the alkalinity of the solution to have arisen from changes away from the reference **carbonate weak acid/base species** ($H_2CO_3^*$) and from the reference **water weak acid/base species** (H_2O where $[H^+]_i = [OH^-]_i$). That is, we may look on the solution to be made up of two weak acid/base subsystems, the carbonate weak acid/base subsystem and water weak acid/base subsystem respectively, i.e. the classical carbonate weak acid/base in solution [as expressed by Eq. (14)] is now viewed as a mixture of two weak acid/base subsystems. Expressing the alkalinity **due to a subsystem** with respect to its reference species, as Alk **(reference species)** we may write:

$$H_2CO_3^* \text{ alk} = \text{Alk } H_2CO_3^* + \text{Alk } H_2O \qquad (15)$$

where:

Alk $H_2CO_3^*$ = alkalinity of carbonate subsystem with respect to the reference species $H_2CO_3^*$ $= 2[CO_3^{2-}]+[HCO_3^-]$, and

Alk H_2O = alkalinity of water subsystem with respect to the reference species H_2O with $[H^+]_i = [OH^-]_i$ $= [OH^-]-[H^+]$

The two alkalinity terms on the right-hand side of Eq. (15) henceforth will be designated as **carbonate subsystem alkalinity** and **water subsystem alkalinity** respectively to distinguish these from the **solution alkalinity** on the left-hand side of Eq. (15). Thus, the solution alkalinity includes both these partial alkalinities, i.e.:

Solution alkalinity = carbonate subsystem alkalinity + water subsystem alkalinity.

This approach can be applied to any number of weak acid/bases in solution. If there were "n" weak acid/base subsystems in solution, then we could write:

$$\text{Solution alkalinity} = \sum_{j=1}^{n} \text{Alk}_j + \text{Alk } H_2O \qquad (16)$$
$$= -\text{solution acidity}$$

where:

Alk_j = subsystem alkalinity for the j^th weak acid/base subsystem relative to its selected reference species.

From **Part I** the general definition of alkalinity can be stated as follows:

> **Alkalinity of a solution is the proton accepting capacity relative to a selected reference state. Associated with this alkalinity is an acidity which, relative to the same selected reference state, equals the negative alkalinity.**

The solution alkalinity can be redefined with **equal exactitude** and **complete equivalence** in terms of the subsystem alkalinities and water subsystem alkalinity as follows:

Alkalinity of a solution (system) (For uniformity with the term "subsystem" as used in the definition, it is perhaps useful to define the solution alkalinity as a system alkalinity) **is the sum of the alkalinities due to the individual weak acid/bases (subsystems) in the solution relative to their respective selected reference species, plus the water subsystem alkalinity.**

Note that, because we have seen that relative to the same reference species the acidity is the negative of alkalinity, the definition above for solution alkalinity applies also for solution acidity except that the term alkalinity(ies) is replaced by acidity(ies). As an example, in **Part I** Eq. (24), for the weak acid/base subsystems carbonate, phosphate, ammonium and water with reference species $H_2CO_3^*$, H_3PO_4, NH_4^+ and H_2O respectively, we can write:

$$H_2CO_3^*/H_3PO_4/NH_4^+ \text{ alkalinity}$$

$$= \text{Alk } H_2CO_3^* + \text{Alk } H_3PO_4 + \text{Alk } NH_4^+ + \text{Alk } H_2O \qquad (17a)$$

$$= \{2[CO_3^{2-}]+[HCO_3^-]\} + \{3[PO_4^{3-}] + 2[HPO_4^{2-}]+[H_2PO_4^-]\} + \{[NH_3]\} + \{[OH^-]-[H^+]\} \qquad (17b)$$

$$= -H_2CO_3^*/H_3PO_4/NH_4^+ \text{ acidity} \qquad (17c)$$

$$= -\text{Acid } H_2CO_3^* - \text{Acid } H_3PO_4 - \text{Acid } NH_4^+ - \text{Acid } H_2O \tag{17d}$$

However, because for the same reference species the acidity is simply the negative alkalinity, the solution alkalinity and subsystem alkalinity terms will be retained and the solution acidity and subsystem acidity terms discarded.

In the subsystem approach to alkalinity, the water subsystem **is always present.** Accordingly, in this paper when we speak of a **mixture** of weak acid/base subsystems **we refer only to the non-water subsystems.**

Subsystem reference species

For each weak acid/base subsystem added to water, the **subsystem** alkalinity can be formulated with any of its species as the selected reference species. For example, the monoprotic ammonium weak acid/base subsystem contains two species, NH_3 and NH_4^+ ; either of the two species NH_3 or NH_4^+ , can be selected as reference species. Relative to the selected reference species, an equation for the subsystem alkalinity is readily derived from the proton balance of the subsystem, as was done in Fig. 1 for the carbonate subsystem (see also **Part I**).

With NH_4^+ as reference species, the proton accepting capacity or subsystem alkalinity is:

$$\text{Alk } NH_4^+ = [NH_3] \tag{18a}$$

because one proton is **accepted** by NH_3 to form the reference species NH_4^+ . Similarly with NH_3 as reference species

$$\text{Alk } NH_3 = -[NH_4^+] \tag{18b}$$

because one proton is **donated** by NH_4^+ (i.e. negatively accepted) to form the reference species NH_3.

For a diprotic subsystem (for example the carbonate subsystem with species $H_2CO_3^*$, HCO_3^- and CO_3^{2-}) there will be a subsystem alkalinity relative to each of the three reference species $H_2CO_3^*$, HCO_3^- and CO_3^{2-} :

$$\text{Alk } H_2CO_3^* = 2[CO_3^{2-}] + [HCO_3^-] \tag{19a}$$

$$\text{Alk } HCO_3^- = [CO_3^{2-}] - [H_2CO_3^*] \tag{19b}$$

$$\text{Alk } CO_3^{2-} = -2[H_2CO_3^*] - [HCO_3^-] \tag{19c}$$

Similarly for a triprotic subsystem (for example the orthophosphate subsystem with species H_3PO_4, $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-}) there will be four subsystem alkalinities:

$$\text{Alk } H_3PO_4 = 3[PO_4^{3-}] + 2[HPO_4^{2-}] + [H_2PO_4^-] \tag{20a}$$

$$\text{Alk } H_2PO_4^- = 2[PO_4^{3-}] + [HPO_4^{2-}] - [H_3PO_4] \tag{20b}$$

$$\text{Alk } HPO_3^{2-} = [PO_4^{3-}] - [H_2PO_4^-] - 2[H_3PO_4] \tag{20c}$$

$$\text{Alk } PO_4^{3-} = -[HPO_4^{2-}] - 2[H_2PO_4^-] - 3[H_3PO_4] \tag{20d}$$

From the above it is apparent that subsystem alkalinity equations can be developed for any of the subsystem species selected as reference species. In most cases it is convenient to select the **most protonated** species as reference species and to formulate the subsystem alkalinities relative to these. Once reference species have been selected for each subsystem, these reference species also serve as reference species for the **solution alkalinity.**

For the water subsystem, we accept H_2O with $[H^+]_i = [OH^-]_i$ as reference species. Accordingly there will be only one subsystem alkalinity equation:

$$\text{Alk } H_2O = [OH^-] - [H^+] \tag{21}$$

Interrelationships between subsystem alkalinities

The difference between a subsystem alkalinity with respect to its selected reference species, and a subsystem alkalinity with respect to the next lower protonated reference species, equals the total species concentration of the weak/acid base. For example, for the phosphate subsystem with total species concentration P_T:

$$\text{Alk } H_3PO_4 - \text{Alk } H_2PO_4^- = P_T \tag{22a}$$

$$\text{Alk } H_2PO_4^- - \text{Alk } HPO_4^{2-} = P_T \tag{22b}$$

$$\text{Alk } HPO_4^{2-} - \text{Alk } PO_4^{3-} = P_T \tag{22c}$$

From Eqs. (22a) to (22c), if the reference species relative to which the subsystem alkalinities are defined are 'n' protons apart, the difference between the respective subsystem alkalinities is 'n' times the total species concentration. For example, considering the phosphate subsystem:

$$\text{Alk } H_3PO_4 - \text{Alk } H_2PO_4^- = P_T \quad (n=1) \tag{23a}$$

$$\text{Alk } H_3PO_4 - \text{Alk } HPO_4^{2-} = 2P_T \quad (n=2) \tag{23b}$$

$$\text{Alk } H_3PO_4 - \text{Alk } PO_4^{3-} = 3P_T \quad (n=3) \tag{23c}$$

Graphical presentations of the relationships between subsystem alkalinities with different reference species, and total species concentration for mono- and diprotic weak acid/bases are shown in Figs. 2a and 2b respectively. These plots illustrate that for each weak acid/base subsystem, if values are known for two independent parameters (subsystem alkalinities with respect to two sets of reference species and/or with respect to one set of reference species plus total species concentration), then all the remaining subsystem parameters can be determined. Similar plots can be constructed for triprotic weak acid/bases.

pH and subsystem alkalinities and total species concentration

From basic equilibrium chemistry, for any weak acid/base in solution, if total species concentration and the pH [i.e. (H^+)] are known then the distribution of the species of the weak acid/base for that pH can be determined via equilibrium equations. Knowing the species concentrations, the various subsystem alkalinities for that weak acid/base can be formulated and calculated. Similarly for a mixture of weak acid/bases, the respective subsystem alkalinities can be calculated for each weak acid/base for any pH. Knowing the subsystem alkalinities and the water subsystem alkalinity, the solution alkalinity can be determined and the solution characterised completely. Alternatively, if pH and a subsystem alkalinity are known, the total species concentration for the subsystem can be determined. The same situation applies for each subsystem in a mixture of weak acid/bases. Thus, if pH is known only one subsystem alkalinity for each of the subsystems in solution need be known to characterise the solution. The relationships between pH and water subsystem alkalinity, and between pH and weak acid/base subsystem alkalinity and total species concentration, are developed below.

For the water subsystem, an expression linking water subsystem alkalinity (Alk H_2O) to pH is developed as follows:

For the water subsystem, the equilibrium expression is given by (Loewenthal *et al.,* 1986):

$$(H^+)(OH^-) = K_W \tag{24}$$

where:

K_W = thermodynamic ion product constant for water subsystem

$$= (H_2O) \times K$$
$$= 55{,}5 \times 1{,}8 \times 10^{-16}$$
$$= 10^{-14}\ (\text{mol}/\ell)^2$$

The relationships linking activity ( ) to molar concentration [ ] are given by:

$$(H^+) = f_{m1}\,[H^+] \tag{25a}$$
$$(OH^-) = f_{m2}\,[OH^-] \tag{25b}$$

where:

$f_{m1} = f_{m2}$ = monovalent activity coefficient (see **Part I, Appendix 1** for determination).

Substituting Eq. (25b) into Eq. (24) gives:

$$(H^+)[OH^-] = K_w/f_{m2} = K_w' \tag{26}$$

where:

K_w' = apparent ion product constant for water subsystem.

The water subsystem alkalinity expression is given by Eq. (21) i.e.:

$$\text{Alk } H_2O = [OH^-]-[H^+]$$

Substituting Eqs. (25a) and (26) into the Alk H_2O equation gives:

$$\text{Alk } H_2O = \frac{K_w'}{(H^+)} - \frac{(H^+)}{f_{m1}} \tag{27}$$

Noting that:

$$pH = -\log (H^+),\ \text{and} \tag{28a}$$

$$pK_w' = -\log K_w' \tag{28b}$$

then:

$$\text{Alk } H_2O = 10^{pH-pK_w'} - \frac{10^{-pH}}{f_{m1}} \tag{29}$$

where all units are in terms of moles, i.e. for $pK_w' = 14$, Alk H_2O has units, mol/ℓ. Thus, for the water subsystem, Alk H_2O can be determined directly from pH.

For a monoprotic subsystem, HA, with a total species concentration of A_T moles/ℓ, the equilibrium expression is:

$$(H^+)(A^-)/(HA) = K_a \tag{30}$$

where:

( ) denotes activity.

K_a = equilibrium constant (mol/ℓ).

The subsystem alkalinity equations relative to the most and least protonated species respectively are:

$$\text{Alk HA} = [A^-] \tag{31}$$

$$\text{Alk } A^- = -[HA] \tag{32}$$

and the subsystem total species concentration A_T is given by:

$$A_T = [HA]+[A^-] \tag{33}$$

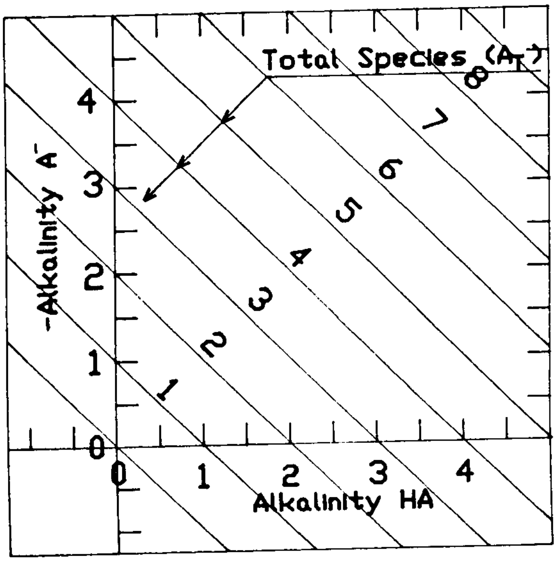

Figure 2a
Graphical illustration of interrelationships between subsystem alkalinities and total species concentration for the general monoprotic weak acid/base, with species HA and A^- and total species concentration A_T

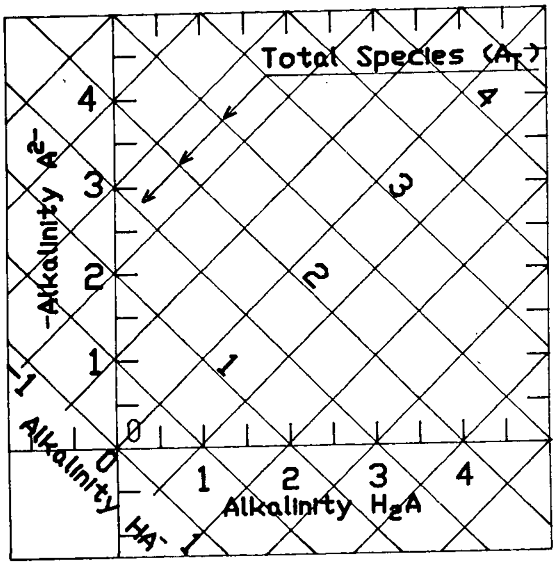

Figure 2b
Graphical illustration of interrelationships between subsystem alkalinities and total species concentration for the general diprotic weak acid/base, with species H_2A, HA^- and A^{2-} and total species concentration A_T

TABLE 2

RELATIONSHIPS BETWEEN SUBSYSTEM ALKALINITIES, TOTAL SPECIES CONCENTRATION AND pH FOR MONOPROTIC, DIPROTIC AND TRIPROTIC WEAK ACID/BASE SUBSYSTEMS, AND FOR THE WATER SUBSYSTEM. [ALL CONCENTRATIONS AND ACTIVITIES ARE IN mol/ℓ, ALL K AND K' VALUES ARE mol/ℓ EXCEPT K_w AND K'_w WHICH ARE $(mol/ℓ)^2$]

SUBSYSTEM	Equilibrium Eqs	pH/Alk/total species concentration Eqs*
Monoprotic HA/A^-	$\dfrac{(H^+)[A^-]}{[HA]} = K_1/f_m$** $= K'_1$	$\text{Alk } HA = -\text{Alk } A^-/W$ $\text{Alk } HA = A_T/(1+W)$
Diprotic $H_2CO^*_3/$ $HCO^-_3/$ CO^{2-}_3	$\dfrac{(H^+)[HCO^-_3]}{[H_2CO^*_3]} = K'_1$ $\dfrac{(H^+)[CO^{2-}_3]}{[HCO^-_3]} = K_2 \cdot f_m/f_d$** $= K'_2$	$\text{Alk } H_2CO^*_3 = (\dfrac{1+2X}{1+2W})\ (-\text{Alk } CO^{2-}_3)$ $\text{Alk } H_2CO^*_3 = (\dfrac{1+2X}{1+W+X})\ C_T$ $\text{Alk } H_2CO^*_3 = (\dfrac{1+2X}{W-X})\ (-\text{Alk } HCO^-_3)$
Triprotic $H_3PO_4/$ $H_2PO^-_4/$ $HPO^{2-}_4/$ PO^{3-}_4	$\dfrac{(H^+)[H_2PO^-_4]}{[H_3PO_4]} = K'_1$ $\dfrac{(H^+)[HPO^{2-}_4]}{[H_2PO^-_4]} = K'_2$ $\dfrac{(H^+)[PO^{3-}_4]}{[HPO^{2-}_4]} = K_3 \cdot f_d/f_t$** $= K'_3$	$\text{Alk } H_3PO_4 = (\dfrac{1+2X+3XY}{2+X+3W})\ (-\text{Alk } PO^{3-}_4)$ $\text{Alk } H_3PO_4 = (\dfrac{1+2X+3XY}{1+W+X+XY}) \cdot P_T$ $\text{Alk } H_3PO_4 = (\dfrac{1+2X+3XY}{W-X-2XY}) \cdot (-\text{Alk } H_2PO^-_4)$ $\text{Alk } H_2PO^-_4 = (\dfrac{-W+X+2XY}{2+X+3W}) \cdot (-\text{Alk } PO^{3-}_4)$
Water	$(H^+)[OH^-] = K_w/f_m$ $= K'_w$	$\text{Alk } H_2O = 10^{pH-pK'_w} - \dfrac{10^{-pH}}{f_m}$

$* \ W = 10^{pK'_1-pH}$

$X = 10^{pH-pK'_2}$

$Y = 10^{pH-pK'_3}$

$pK' = -\log K'$

** f_m, f_d and f_t = mono, di and trivalent activity coefficients.

In the subsystem alkalinity equations the subsystem species concentrations are expressed in molar form. However, the hydrogen ion species, H^+, is expressed through the pH (i.e. via the activity of H^+). Accordingly, Eq. (30) is modified to provide consistency, i.e.

$$(H^+)[A^-]/[HA] = K_a/f_m = K'_a \qquad (34)$$

where:

f_m = activity coefficient for monovalent ions
K'_a = apparent equilibrium constant (mol/ℓ).

Substituting for [HA] and [A^-] from Eqs. (31) and (32) into Eqs. (33) and (34) and rearranging yields:

$$A_T = \text{Alk HA} - \text{Alk } A^-\text{, and} \qquad (35)$$

$$\text{Alk HA} = -\text{Alk } A^- \times K'_a/(H^+)$$

$$= -\text{Alk } A^- \times 10^{pH-pK'_a} \qquad (36)$$

where:
pK'_a = $-\log K'_a$
(all units are in terms of moles).

From Eq. (36), if any two of the three parameters Alk HA, Alk A^- and pH, are known, the third can be calculated. Eqs. (35) and (36) can be combined to give an equation for subsystem alkalinity in terms of total species concentration, A_T, and pH, i.e.:

$$\text{Alk HA} = A_T \times 10^{pH-pK'_a}/(1 + 10^{pH-pK'_a}) \qquad (37)$$

Relationships for the general monoprotic weak acid/base, linking pH to two subsystem alkalinities and to total species concentration, are given in Table 2.

The interrelationships between pH and the various subsystem alkalinities can be illustrated graphically. However, whereas the interrelationships between the subsystem alkalinities and total species concentrations are general [Fig. 2(a) and 2(b)], the relationships between pH and the subsystem alkalinities depend upon the value of the equilibrium constant. For illustrative purposes, consider the monoprotic ammonia weak acid/base subsystem. For the plot, Alk NH_4^+ and Alk NH_3 form the axes. Substituting the equilibrium constant for the ammonia subsystem at 20°C (pK'_a = 9,19) into Eq. (36) (NH_4^+ ≡ HA; NH_3 ≡ A^-), the plots for a series of selected pH values are radiating straight lines through the origin (Fig. 3).

Fig. 3 is in effect a Deffeyes type diagram (Deffeyes 1965; Loewenthal and Marais, 1976; Loewenthal *et al.,* 1986). However, it differs from the normal Deffeyes diagram in that the axes are now two subsystem alkalinities; we will call this type of plot a subsystem Deffeyes diagram. By using two subsystem alkalinities as axes the pH lines now pass through the origin; this arises because these parameters include only subsystem species. In the normal Deffeyes diagrams the **solution** alkalinities relative to the most and least protonated species serve as axes and these include subsystem species plus water subsystem species ([H^+] and [OH^-]); this causes that pH lines do not pass through the origin.

Linear relationships between subsystem alkalinities, total species concentration and pH also can be developed for the di- and triprotic weak acid/bases.

For the general diprotic weak acid/base with species [H_2A], [HA^+] and [A^{2-}] and total species concentration A_T:

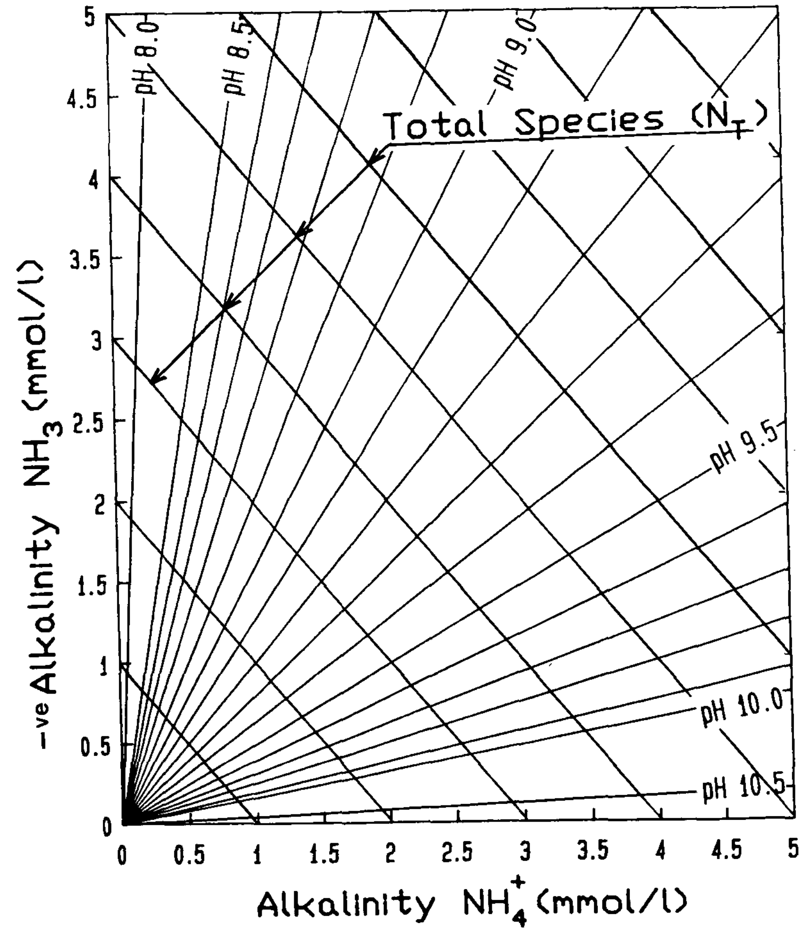

Figure 3
Subsystem Deffeyes diagram for the ammonia weak acid/base subsystem (with species, NH_3 and NH_4^+) at 20°C (pK'_a = 9,19)

$$2\,A_T = \text{Alk } H_2A - \text{Alk } A^{2-} \quad (38)$$

$$\text{Alk } H_2A = \frac{1 + 2 \times 10^{pH-pK'_2}}{1 + 2 \times 10^{pK'_1-pH}} \times (-\text{Alk } A^{2-}) \quad (39)$$

$$\text{Alk } H_2A = \frac{1 + 2 \times 10^{pH-pK'_2}}{10^{pK'_1-pH} - 10^{pH-pK'_2}} \times (-\text{Alk } HA^{-}) \quad (40)$$

$$\text{Alk } H_2A = \frac{1 + 2 \times 10^{pH-pK'_2}}{1 + 10^{pH-pK'_2} + 10^{pK'_1-pH}} \times (A_T) \quad (41)$$

where all units are in terms of moles.

Specific equations for the diprotic carbonate weak acid/base subsystem are given in Table 2.

For the triprotic weak acid/base, the only one likely to be encountered in normal conditioning applications is the phosphate subsystem. Equations for the various relationships of this subsystem are listed in Table 2. Of particular importance for solving dosing problems is the equation linking subsystem alkalinity to total species concentration and pH, i.e.:

$$\text{Alk } H_3PO_4 = \frac{(1 + 2X + 3XY)}{1 + W + X + XY} \times P_T \quad (42)$$

where:

$W = 10^{pK'_1-pH}$

$X = 10^{pH-pK'_2}$

$Y = 10^{pH-pK'_3}$

(all units are in terms of moles).

Changes in capacity parameters with dosing

In determining the change in the capacity parameters with dosing (in alkalinities and total species concentration), clear distinction must be made between the **subsystem** parameters and **solution** parameters as these change very differently with dosing.

Subsystem parameters

For the subsystem parameters, the following generalisations can be identified:

- Subsystem alkalinities change in a complex fashion with dosing (due to change in pH).
- Total species concentrations for all subsystems except that including the dosing type remain constant with dosing.
- Total species concentration for the subsystem including the dosing type increases by the amount of dosage chemical added.

Solution parameters

For the solution parameters the following generalisations can be identified:

- Solution alkalinities that **include** the dosage type as a reference species do not change with dosing. For example, $H_2CO_3^*/H_3PO_4/NH_4^+$ alkalinity does not change for addition of $CO_2(H_2CO_3^*)$, H_3PO_4 or NH_4^+.
- Solution alkalinities that **do not include** the dosage type as a reference species change in a simple stoichiometric fashion with dosing, given by:

$$\Delta\text{Solution alkalinity} = (\text{number of protons for reference species of the subsystem including dosing type} - \text{number of protons for dosing type}) \times \text{mass of dose added} \quad (43)$$

For example, if X moles of $CO_2(H_2CO_3^*)$ are added to a solution with reference species CO_3^{2-}, H_3PO_4 and NH_4^+, then:

$$\Delta CO_3^{2-}/H_3PO_4/NH_4^+ \text{ alkalinity} = (0-2) \times X = -2X \text{ mol}$$

If X moles of CO_3^{2-} are added to a solution with reference species $H_2CO_3^*$, H_3PO_4 and NH_4^+, then:

$$\Delta H_2CO_3^*/H_3PO_4/NH_4^+ \text{ alkalinity} = (2-0) \times X = 2X \text{ mol}$$

or, if Y moles of HCO_3^- are added to this solution:

$$\Delta H_2CO_3^*/H_3PO_4/NH_4^+ \text{ alkalinity} = (2-1) \times Y = Y \text{ mol}$$

Changes in **solution** alkalinities with dosing are summarised in Table 3 for an aqueous system containing the carbonate, phosphate and ammonia subsystems.

Dosing estimation algorithms using solution and subsystem parameters

In all the dosing algorithms, the initial total species concentration for each subsystem and the initial pH are required. From characterisation: In mixtures, (1) that do not include the carbonate subsystem, total species concentration for each subsystem and the solution pH will be known; (2) that include the carbonate subsystem, a solution alkalinity relative to a selected set of reference species, the total species concentrations of all the subsystems (except that of the carbonate subsystem) and the solution pH will be known. For the purposes of generalisation, in (2) the total species concentration for the carbonate subsystem should be calculated, see **Part I** for method. Also, the relevant pK values for the subsystems should be calculated, see **Part I** for method. **All units should be in terms of moles.**

Algorithms for resolving chemical conditioning problems are developed from two basic tenets:

- Solution alkalinity equals the sum of the subsystem alkalinities plus the water subsystem alkalinity, see Eq. (16).
- **Solution** alkalinities either remain constant or change in a simple stoichiometric fashion with chemical dosing, see Eq. (43). Note that subsystem alkalinities do **not** change in a stoichiometric fashion with chemical dosing.

The manner in which the above tenets are applied to resolve dosing problems will differ depending on the nature of the dosing problem. Earlier we have seen that essentially two types of dosing problems arise, determination of:

TABLE 3
EFFECT OF ADDITION OF X moles/ℓ ON *SOLUTION* ALKALINITY PARAMETERS IN AN AQUEOUS SYSTEM CONTAINING THE CARBONATE, PHOSPHATE AND AMMONIA SUBSYSTEMS

Dosing chemical (X moles/ℓ added)	$\Delta H_2CO_3^*/H_3PO_4/$ NH_4^+ alk	$\Delta HCO_3^-/H_2PO_4^-/$ NH_3 alk	$\Delta CO_3^{2-}/PO_4^{3-}/$ NH_3 alk
CO_2 ($H_2CO_3^*$)	0	-X	-2X
HCO_3^-	+X	0	-X
CO_3^{2-}	+2X	+X	0
H_3PO_4	0	-X	-3X
$H_2PO_4^-$	+X	0	-2X
HPO_4^{2-}	+2X	+X	-X
PO_4^{3-}	+3X	+2X	0
NH_4^+	0	-X	-X
NH_3	+X	0	0
OH^-	+X	+X	+X
H^+	-X	-X	-X

- Chemical dose for specified chemical dosage type and specified initial and final solution states.
- Final state for a specified initial state and specified chemical dosage and dosage type.

Dosing for specified initial and final states and dosing type

From characterisation we will know the initial pH and the total species concentrations of each subsystem. We are required to determine the mass of specified chemical to add to the solution to give a specified final pH.

The form of the solution algorithm will differ depending on whether the specific dosing type is a strong acid (base) or weak acid/base species: (1) if a strong acid or base is added then each subsystem total species concentration does not change; (2) if a weak acid/base species is added the **total species concentration** of the subsystem that includes the dosage species will change and those for the other subsystems will stay constant. For example, for a water containing the carbonate and phosphate subsystems (with total species concentrations C_T and P_T respectively), if a strong base is dosed, C_T and P_T remain constant; if CO_3^{2-} is dosed C_T will increase but P_T will remain constant; if both HCO_3^- and PO_4^{3-} are dosed both C_T and P_T will increase.

Dosing with a strong acid or base

Dosing with a strong acid or base will not change the total species concentrations of the subsystems. Consequently, for each of the subsystems the final subsystem *alkalinity* can be determined from the initial total species concentration and the specified final pH. The step by step procedure is as follows:

(1) Select a set of reference species, one reference species for each weak acid/base subsystem. There is complete freedom in selection of the reference species but for each weak acid/base subsystem it is convenient to select the most protonated species as reference species for the subsystem alkalinity capacity parameter. The set of reference species for all the weak acid/base subsystems serves as reference species for solution alkalinity.

(2) Calculate the initial subsystem alkalinity [with the reference species selected in (1) above] for each weak acid/base from its total species concentration and the initial pH; for monoprotic weak acid/bases use Eq. (37), for diprotic Eq. (41) and triprotic Eq. (42), with the relevant pK values. Calculate the initial water subsystem alkalinity from the pH, Eq. (29).

(3) Calculate the initial solution alkalinity from the sum of the initial subsystem alkalinities plus the initial water subsystem alkalinity, Eq. (16).

(4) Repeat steps (2) and (3) with the final pH and the initial total species concentrations to obtain the **final solution alkalinity**; total species concentrations do not change with dosing.

(5) Determine the strong acid dosage from the difference between initial and final solution alkalinity.

Dosing with a weak acid/base species

For any dosing problem we have seen that the total species concentration of each of the subsystems plus the solution pH will be known. Dosing with a weak acid/base species, the total species concentrations of all the subsystems remain the same in the final state as in the initial state **except** the subsystem that includes the dosing type. Consequently for each subsystem (except the one including the dosing type) the final **subsystem** alkalinity can be determined from their initial total species concentration and final pH (see Table 2 for appropriate equations). For the subsystem that includes the dosing type, the dosing species must be selected as reference species; this (1) fixes the reference species and the initial solution alkalinity can be calculated if it is not available, and (2) ensures that the **solution** alkalinity does not change with dosing. The final **subsystem** alkalinity for the subsystem including the dosing type can be determined from the **solution** alkalinity and from the final subsystem alkalinities for all the other subsystems. This enables the change in total species concentration for the subsystem containing dosing type to be determined and accordingly the dose required. To solve for the dosing:

(1) Select the set of reference species, one for each subsystem. For the subsystem that includes the dosing type species select the dosing type species as reference species. (For example, if a water contains the carbonate, phosphate and ammonia subsystems, if the dosing chemical is HPO_4^{2-} the reference species for the phosphate subsystem must be HPO_4^{2-} ; if CO_2 then the reference species for the carbonate system must be $H_2CO_3^*$). Since this reference species also serves as reference species for solution alkalinity, by selecting the dosing type species as reference species the **solution** alkalinity does not change with dosing [See Eq. (17a), where addition of say H_3PO_4 will not change the $H_2CO_3^*$ /H_3PO_4/NH_4^+ alkalinity].

For each of the remaining subsystems there is complete freedom in the selection of reference species. However, as noted earlier it is usual to select the most protonated species as reference species for the subsystems alkalinity. (Freedom in the selection of reference species for subsystems not of the dosing type might not apply in solving solid-liquid phase problems, for example in solving struvite (Mg $NHPO_4$) precipitation).

(2) Calculate the initial subsystem alkalinity for each subsystem from the initial total species concentration and initial pH; Eq. (37) for monoprotic weak acid/base, Eq. (41) for diprotic weak acid/base, Eq. (42) for triprotic weak acid/base. Calculate the initial water subsystem alkalinity from initial pH, Eq. (29).

(3) Calculate the initial **solution** alkalinity from the sum of the initial subsystem alkalinities plus the initial water subsystem alkalinity, Eq. (16). **From (1) the solution alkalinity does not change with dosing.**

(4) For all the subsystems (except the one that includes the dosing type species) their final **subsystem** alkalinities are determined from the initial total species concentration and the final pH; total species concentrations for these subsystems do not change. For monoprotic weak acid/base use Eq. (37), for diprotic Eq. (41) and triprotic Eq. (42). For the water subsystem alkalinity, the final subsystem alkalinity is determined from the final pH, Eq. (29).

(5) For the **subsystem** containing the dosing type the final **subsystem** alkalinity cannot be calculated directly because for this subsystem the final total species concentration changes with dosing. It is calculated indirectly as follows:

The **solution** alkalinity for the selected set of reference species does not change [see (1) above], hence, the dosing species final **subsystem** alkalinity can be found from:

$$\text{Solution alkalinity} = \text{Alk (dosing subsystem)} + \text{Alk } H_2O + \Sigma \text{ Alk (remaining subsystems)},$$

i.e.

$$\text{Alk (dosing subsystem)} = \text{Solution alkalinity} - \text{Alk } H_2O - \Sigma \text{ Alk (remaining subsystems)}.$$

(6) Having calculated the final subsystem alkalinity for the subsystem with the chemical dosing type (i.e. the value after dosing), the final total species concentration for this subsystem is calculated from the relationship linking the final subsystem total species concentration to final subsystem alkalinity and final pH, see Table 2.

(7) The mass of chemical dose to be applied is calculated as the change in total species concentration between initial and final states for the subsystem containing the chemical dosage type.

Final state for a specified initial state and specified chemical dosage

For problems of this type the form of the solution algorithm will be the same, irrespective of whether the dosing type is a strong acid/base or weak acid/base species. This arises because in both instances the initial and final total species concentrations for each of the subsystems are known. If a strong acid/base is added the subsystem total species concentrations do not change and equal the initial values. If a weak acid/base species is added, the total species concentration of the subsystem that includes the dosage species will increase by an amount equal to the molar mass of dosing chemical added; hence because the dosage is specified the final total species concentration for this subsystem can be determined directly. The final total species concentrations of the remaining subsystems do not change from the initial known values. The problem is to determine the final pH (i.e. the final state) after the prescribed dosing; this requires an iterative procedure. The dosing algorithm is as follows:

(1) Select a reference species for each subsystem. There is freedom in selecting each subsystem reference species, but again it is advisable to select the most protonated species for the subsystem alkalinity. These reference species also serve as reference species for **solution** alkalinity.

(2) Calculate the initial subsystem alkalinity for each subsystem with selected reference species from initial subsystem total species concentrations and initial pH, monoprotic Eq. (37), diprotic Eq. (41) and triprotic Eq. (42); specific relationships for selected subsystems are listed in Table 2. Calculate initial water subsystem alkalinity from the initial pH, Eq. (29).

(3) Calculate the initial **solution** alkalinity from initial subsystem alkalinities, and initial water subsystem alkalinity, using Eq. (16).

(4) Calculate the change in **solution** alkalinity for reference species selected in (1) due to the prescribed dosing type and amount. The change in **solution** alkalinity is stoichiometric

and is determined from the equations for the carbonate, phosphate and ammonia subsystems in solution as set out in Table 3, or generally from the proton changes as set out in Eq. (43).

(5) Calculate the final solution alkalinity as the initial value [determined in step (3)] plus the change [determined in step (4)].

(6) Calculate the final subsystem total species concentration for the subsystem of the dosage type as equal to the initial concentration plus the applied dosage.

(7) Determine the final pH. This is done by successive approximation as follows:

> The equation for the final **solution** alkalinity is written down in terms of the sum of the final **subsystem** alkalinities plus the water subsystem alkalinity [Eq. (16)]; each of the subsystem alkalinity terms is replaced by the expression linking the subsystem alkalinity to subsystem total species concentrations and pH [monoprotic weak acid/base subsystem, Eq. (37), diprotic, Eq. (41), triprotic, Eq. (42)] and the water subsystem alkalinity term by the expression linking it to pH [Eq. (29)]. Final subsystem total species concentrations are known and substituted into the equation. A final pH is selected and substituted into the equation and the solution alkalinity obtained. This calculated value is compared with the known final solution alkalinity value [from step (5) above]. If the calculated solution alkalinity exceeds the known value then the selected pH is decreased ; alternatively if the calculated solution alkalinity is less than the known value then the selected pH is increased.

This procedure is repeated until the calculated and known solution alkalinities agree to within some specified value. This successive approximation technique will always give a result because the solution alkalinity changes monotonically with pH.

Application

In this section we will apply the algorithms that use solution and subsystem parameters, as developed above, to solve a number of selected problems in mixtures of weak acid/bases.

Dosing for specified initial and final states and dosing type

Dosing with strong acid or base

Example 1: A water has carbonate, ammonium and phosphate weak acid subsystems present in solution, with C_T = 5,0 mmol/ℓ, N_T = 4,0 mmol/ℓ and P_T = 3,0 mmol/ℓ, ionic strength (μ) = 0,01 and temperature = 20°C. We are required to determine the strong base required to adjust pH from 6,50 to 8,50. Prior to using the dosing algorithm, convert total species concentrations to mol/ℓ.

- $C_T = 5 \times 10^{-3}$ mol/ℓ
  $N_T = 4 \times 10^{-3}$ mol/ℓ
  $P_T = 3 \times 10^{-3}$ mol/ℓ

Also, the relevant pK values need to be calculated, as follows:

- Calculate the mono-, di- and trivalent activity coefficients (f_m, f_d and f_t respectively) at 20°C by substituting μ = 0,01 and Z = 1, Z = 2 and Z = 3 into the Davies equation (Eq. 1.1 in **Appendix 1** of **Part I**) and determining the activity coefficients, f_m—0,90, f_d = 0,65 and f_t = 0,38.

- Determine equilibrium thermodynamic constants at 20°C for the carbonate, ammonium and phosphate subsystems in terms of moles (from Table 2, **Part I**):

  Carbonate subsystem:
  pK_{c1} = 6,38; pK_{c2} = 10,38
  Ammonium subsystem:
  pK_{a1} = 9,41
  Phosphate subsystem:
  pK_{p1} = 2,13; pK_{p2} = 7,21; pK_{p3} = 12,02

- Adjust thermodynamic equilibrium constants for activity coefficient effects to obtain the apparent constants, pK', as shown in **Part I:**

  Carbonate system:
  pK'_{c1} = 6,33; pK'_{c2} = 10,24
  Ammonium system:
  pK'_{a1} = 9,36
  Phosphate system:
  pK'_{p1} = 2,08; pK'_{p2} = 7,07; pK'_{p3} = 11,79

The dosing algorithm solution is as follows:

(1) Select reference species, one reference species for each weak acid/base subsystem; it is usual to select the most protonated speies for each weak acid/base subsystem as reference species, i.e. we select H_3PO_4, $H_2CO_3^*$ and NH_4^+ as reference species.

(2) Calculate initial subsystem alkalinity for each weak acid/base; equations for Alk H_3PO_4, Alk $H_2CO_3^*$, Alk NH_4^+ in terms of total species concentrations and pH are listed in Table 2, and the equation for Alk H_2O in terms of pH is given by Eq. (29). In the respective equations for Alk H_3PO_4, Alk $H_2CO_3^*$, Alk NH_4^+ and Alk H_2O insert the respective total species concentrations ($P_T = 3 \times 10^{-3}$, $C_T = 5 \times 10^{-3}$ and $N_T = 4 \times 10^{-3}$ all mol/ℓ) and initial pH (pH = 6,50) giving

Alk H_3PO_4 (initial)	= $3{,}636 \times 10^{-3}$ mol/ℓ
Alk $H_2CO_3^*$ (initial)	= $2{,}984 \times 10^{-3}$ mol/ℓ
Alk NH_4^+ (initial)	= $0{,}006 \times 10^{-3}$ mol/ℓ
Alk H_2O (initial)	= $-0{,}000 \times 10^{-3}$ mol/ℓ

(3) Calculate the initial solution alkalinity from the sum of the initial subsystem alkalinities plus the water subsystem alkalinity, i.e.:

$H_3PO_4/H_2CO_3^*/NH_4^+$ alk (initial)
= Alk H_3PO_4 (initial) + Alk $H_2CO_3^*$ (initial) + Alk NH_4^+ (initial) + Alk H_2O (initial)
= $[3{,}636 + 2{,}984 + 0{,}006 + (-0{,}000)] \times 10^{-3}$
= $6{,}626 \times 10^{-3}$ mol/ℓ.

(4) Repeat steps (2) and (3) with specified final pH (pH = 8,50) and the initial total species concentration (these do not change with dosing) to determine the final subsystem alkalinities and hence the final solution alkalinity, i.e.:

$H_3PO_4/H_2CO_3^*/NH_4^+$ alk (final)
$= \text{Alk } H_3PO_4 \text{ (final)} + \text{Alk } H_2CO_3^* \text{ (final)} + \text{Alk } NH_4^+ \text{ (final)} + \text{Alk } H_2O \text{ (final)}$
$= [5{,}894+5{,}056+0{,}485+0{,}003] \times 10^{-3}$
$= 11{,}438 \times 10^{-3}$ mol/ℓ.

(5) Determine the strong base dosage from the difference between initial and final solution alkalinities, i.e.:
Dosage $= H_3PO_4/H_2CO_3^*/NH_4^+$ alk (final) $- H_3PO_4/H_2CO_3^*/NH_4^+$ alk (initial)
$= [11{,}438 - 6{,}626] \times 10^{-3}$
$= 4{,}812 \times 10^{-3}$ mol/ℓ.

Dosing with weak acid/base

Example 2: For the raw water in Example 1, determine the carbonate (CO_3^{2-}) dosage to adjust pH from 6,50 to 8,50.

- Convert total species concentration to mol/ℓ as in preliminary steps to Example 1.
- Determine apparent equilibrium constants for the weak acid subsystems as set out in the preliminary steps to Example 1.

(1) Select the reference species, one for each subsystem. For the subsystem that includes the dosing type species (i.e. carbonate subsystem) select the dosing species (i.e. CO_3^{2-}) as reference species; for the remaining weak acid/base subsystems we arbitrarily select PO_4^{3-} and NH_3 as reference species (H_3PO_4 and NH_4^+ also could have been selected, as in Example 1).

(2) Calculate the initial subsystem alkalinity for each subsystem; substitute the initial pH (pH = 6,5) and initial subsystem total species concentrations into the respective equations for Alk CO_3^{2-}, Alk PO_4^{3-} and Alk NH_3 listed in Table 2, and the initial pH into Eq. (29) for Alk H_2O. This gives

Alk CO_3^{2-} (initial) $= -7{,}016 \times 10^{-3}$ mol/ℓ
Alk PO_4^{3-} (initial) $= -5{,}363 \times 10^{-3}$ mol/ℓ
Alk NH_3 (initial) $= -3{,}994 \times 10^{-3}$ mol/ℓ
Alk H_2O (initial) $= -0{,}000 \times 10^{-3}$ mol/ℓ

(3) Calculate the initial solution alkalinity from the sum of the initial subsystem alkalinities plus water subsystem alkalinity. This solution alkalinity does not change with dosing:

$PO_4^{3-}/CO_3^{2-}/NH_3$ alk (initial) $= -16{,}373 \times 10^{-3}$ mol/ℓ
$= PO_4^{3-}/CO_3^{2-}/NH_3$ alk (final)

(4) For all the subsystems except the carbonate subsystem (i.e. the system that includes the dosing species), calculate the **final** subsystem alkalinities from the final specified pH (pH = 8,50) and the known total species concentrations (equal to the initial values), i.e.

Alk PO_4^{3-} (final) $= -3{,}106 \times 10^{-3}$ mol/ℓ
Alk NH_3 (final) $= -3{,}515 \times 10^{-3}$ mol/ℓ
Alk H_2O (final) $= 0{,}003 \times 10^{-3}$ mol/ℓ

(5) Calculate final subsystem alkalinity for the dosing subsystem (carbonate subsystem) from

Alk (dosing subsystem)
= solution alkalinity − Alk H_2O − ΣAlk (remaining subsystems)
Alk CO_3^{2-} (final)
$= PO_4^{3-}/CO_3^{2-}/NH_3$ alk (final) − Alk H_2O (final) − [Alk PO_4^{3-} (final) + Alk NH_3 (final)]
$= [-16{,}373 - 0{,}003 - [-3{,}106 - 3{,}515] \times 10^{-3}$
$= -9{,}755 \times 10^{-3}$ mol/ℓ

(6) Determine final total species concentration for the subsystem including the dosing type (i.e. the carbonate subsystem). To do this, first determine final Alk $H_2CO_3^*$ from the relationship linking Alk $H_2CO_3^*$ with pH (i.e. pH = 8,5) and Alk CO_3^{2-} listed in Table 2. This gives Alk $H_2CO_3^*$ (final) $= 9{,}975 \times 10^{-3}$ mol/ℓ.

Hence, from Eq. (38):

C_T(final) = [Alk $H_2CO_3^*$ (final) − Alk CO_3^{2-} (final)]/2
$= 9{,}865 \times 10^{-3}$ mol/ℓ

(7) Calculate the mass of CO_3^{2-} dosage from the change in total carbonate species concentration between the initial and final state, i.e.:

CO_3^{2-} dosage $= C_T\text{(final)} - C_T\text{(initial)}$
$= [9{,}865 - 5{,}00] \times 10^{-3}$
$= 4{,}865 \times 10^{-3}$ mol/ℓ

Final state for a specified initial state and specified chemical dose

Example 3: For the raw water in Example 1, determine the final pH for a carbonate (CO_3^{2-}) dosage of 4,865 mmol/ℓ (i.e. the dosage determined in Example 2 to give a prescribed pH = 8,50).

- Convert total species concentrations to mol/ℓ as in preliminary steps to Example 1.
- Determine apparent equilibrium constants for the weak acid/base subsystems as set out in the preliminary steps to Example 1.

(1) Select the reference species, one for each subsystem; it is usual to select the most protonated species as the reference species for each subsystem, i.e. we select H_3PO_4, $H_2CO_3^*$ and NH_4^+ as reference species.

(2) Calculate the initial subsystem alkalinity for each subsystem with selected reference species, as in step (2), Example 1, giving:

Alk H_3PO_4 (initial) $= 3{,}636 \times 10^{-3}$ mol/ℓ
Alk $H_2CO_3^*$ (initial) $= 2{,}984 \times 10^{-3}$ mol/ℓ
Alk NH_4^+ (initial) $= 0{,}006 \times 10^{-3}$ mol/ℓ
Alk H_2O (initial) $= -0{,}000 \times 10^{-3}$ mol/ℓ

(3) Calculate the initial solution alkalinity from the sum of the initial subsystem alkalinities, plus water subsystem alkalinity, using Eq. (16), i.e.:

$H_3PO_4/H_2CO_3^*/NH_4^+$ alk (initial)
= Alk H_3PO_4 (initial) + Alk $H_2CO_3^*$ (initial) + Alk NH_4^+ (initial) + Alk H_2O (initial)
$= [3{,}636 + 2{,}984 + 0{,}006 - 0{,}000] \times 10^{-3}$
$= 6{,}626 \times 10^{-3}$ mol/ℓ

(4) Determine the change in **solution** alkalinity with dosing, from Table 3 for the carbonate, phosphate and ammonia subsystems in solution, or, from the general equation [Eq. (43)] with dosing type as CO_3^{2-} and reference species for the subsystem including dosing type (i.e. carbonate subsystem) as $H_2CO_3^*$, i.e.:

$$\begin{aligned}\Delta H_3PO_4/H_2CO_3^*/NH_4^+ \text{ alk} &= (2-0) \times 4{,}865 \text{ mmol/}\ell \\ &= 9{,}730 \text{ mmol/}\ell \\ &= 9{,}730 \times 10^{-3} \text{ mol/}\ell\end{aligned}$$

(5) Calculate the final **solution** alkalinity as the initial value (determined in step 3) plus the change (determined in step 4), i.e.:

$$\begin{aligned}H_3PO_4/H_2CO_3^*/NH_4^+ \text{ alk (final)} &= [6{,}626 + 9{,}730] \times 10^{-3} \\ &= 16{,}356 \times 10^{-3} \text{ mol/}\ell\end{aligned}$$

(6) Calculate the final subsystem total species concentration for the subsystem including the dosage type (i.e. the carbonate subsystem) from:

$$\begin{aligned}C_T\text{(final)} &= C_T \text{ (initial)} + \text{applied dosage} \\ &= 5{,}00 + 4{,}865 \\ &= 9{,}865 \text{ mmol/}\ell \\ &= 9{,}865 \times 10^{-3} \text{ mol/}\ell\end{aligned}$$

(7) Determine final pH by successive approximation as follows: Write down the equation for final solution alkalinity in terms of the final subsystem alkalinities, i.e.:

$$\begin{aligned}&H_3PO_4/H_2CO_3^*/NH_4^+ \text{ alk (final)} \\ &= \text{Alk } H_3PO_4 \text{ (final)} + \\ &\quad \text{Alk } H_2CO_3^* \text{ (final)} + \text{Alk } NH_4^+ \text{ (final)} + \\ &\quad \text{Alk } H_2O \text{ (final)}\end{aligned}$$

Replace each subsystem alkalinity term by the expression linking subsystem alkalinity to total species concentration and pH [monoprotic weak acid/base subsystem Eq. (37), diprotic Eq. (41), triprotic Eq. (42)]; replace Alk H_2O term by expression linking it to pH [Eq. (29)], i.e.:

$$H_3PO_4/H_2CO_3^*/NH_4^+ \text{ alk (final)}$$

$$= \frac{(1+2X+3XY)}{(1+W+X+XY)} \times P_T +$$

$$\frac{(1+2X)}{(1+X+W)} \times C_T + \frac{1}{(1+W)} \times N_T +$$

$$(10^{pH-pK'_w} - \frac{10^{-pH}}{f_m})$$

where:

$W = 10^{pK'_1-pH}$

$X = 10^{pH-pK'_2}$

$Y = 10^{pH-pK'_3}$

f_m = monovalent activity coefficient (see **Part I, Appendix 1**).

Substitute relevant pK' values and final total species concentrations ($P_T = 3{,}0 \times 10^{-3}$ mol/ℓ, $C_T = 9{,}865 \times 10^{-3}$ mol/ℓ, $N_T = 4{,}0 \times 10^{-3}$ mol/ℓ) into the above equation. Select a pH value (e.g. pH = 7,0) and calculate $H_3PO_4/H_3CO_3^*/NH_4^+$ alk (final). Compare this calculated value ($12{,}530 \times 10^{-3}$ mol/ℓ for pH = 7,0) with that determined in step (5) above ($16{,}356 \times 10^{-3}$ mol/ℓ). Since the calculated value is less than that determined in step (5), increase in pH and substitute back into the equation.

The above procedure is repeated *until* the calculated solution alkalinity equals the value determined in step (5) above. This gives the final pH, equal to 8,50.

Discussion

When it was attempted to apply the classical solution alkalinity/acidity/pH approach (used in solving dosing problems with the carbonate system only present in solution) to situations where more than one weak acid/base was present, the solution procedures became specific to each mixture and were very cumbersome. It became apparent that the difficulty in this approach arose from viewing the solution state *in toto* and developing the capacity parameter equations for this solution. By shifting the focus of interest to the weak acid/base subsystems making up the solution, and developing capacity parameter equations for each subsystem, with the solution capacity parameters equal to the sum of the relevant subsystem capacity parameters of the individual weak acid/base subsystems, it was found that relatively simple algorithms for dosing could be developed. These algorithms are general, applying to any single or mixture of weak acid/bases in solution. The algorithms also lend themselves very readily to computerised solution procedures.

In developing the dosing algorithms it became evident that the use of the terms alkalinity **and** acidity as explicit descriptive parameters was unnecessary and a cause for confusion, because for the same reference solution state the acidity was equal to the alkalinity, but of opposite sign. Since an alkalinity measurement is a "normal" one whenever the carbonate subsystem is present, the alkalinity term was retained as a capacity parameter; the acidity term accordingly was discarded.

The terms alkalinity and acidity developed from very practical considerations. Even though they have been defined quantitatively in terms of a reference solution state, there still exists confusion in the minds of many users as to what the terms actually mean, illustrated by, for example, a definition for alkalinity relative to $H_2CO_3^*$ reference solution state and one for acidity relative to CO_3^{2-} reference solution state. In this paper we have emphasised the inseparability of alkalinity and acidity with respect to the same reference solution state and hence discarded the acidity term. However, even retaining only the alkalinity term creates a restricted image in the mind of the user. It would be most desirable to separate out the true concept of alkalinity from that conjured up in the mind of the user. For this reason, the authors suggest that in future development, instead of the term alkalinity, the term **proton accepting capacity** (defined relative to some proton reference state) be used. The proton donating capacity will be simply the negative of the proton accepting capacity relative to the same proton reference state. This approach will remove completely a confusion often encountered, that the term alkalinity is associated with an alkaline state and the term acidity with an acidic state. The work in this paper has shown that one may have a proton accepting or proton donating capacity in the alkaline or acidic region depending only on the selection of the reference solution state.

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