Mixed weak acid/base systems
Part 1 — Mixture characterisation

by RE Loewenthal*, GA Ekama and GvR Marais
Department of Civil Engineering, University of Cape Town, Rondebosch 7700, South Africa.

Abstract

Characterisation of the carbonate system in aqueous solution requires measurement *inter alia* of the alkalinity associated with an equivalent carbonic acid solution, a solution state usually identified by an estimated end point pH value. To overcome difficulties in end point estimation Gran developed a technique for alkalinity determination that does not depend on the end point. Characterisation of the carbonate system in mixtures of weak acid/bases again requires an alkalinity measurement but now no end point can be estimated. In this paper the Gran approach is extended to the carbonate system in mixtures of weak acid/base systems. The extension requires a generalisation of the concepts of alkalinity and acidity and the development of a consistent nomenclature. The extended method has been tested experimentally using a number of made-up mixtures of the carbonate, phosphate, acetate and ammonia systems and the alkalinity results have been found to be within one per cent of the expected values.

Introduction

In the aqueous environment, weak acids and bases play an important role in establishing the pH and damping pH changes. In terrestrial waters the carbonate system is the dominating one, to such a degree that other weak acid/base systems are usually neglected. In municipal waste waters, however, in addition to the carbonate system, the phosphate and ammonia systems are present, and in anaerobic waste treatment processes sulphides and short-chain fatty acid systems (e.g. acetate and propionate) are generated. All these systems may be present in such large concentrations relative to the carbonate system, that they exert a significant influence on the pH established.

In working with these weak acid/base systems one is confronted with two problems, viz.

- estimation of the concentrations of the species of each of the weak acid/base systems, called **characterisation**; and
- estimation of chemicals to be added to change the pH and species concentrations to desired values, called **dosing estimation**.

In this paper we will consider **characterisation**, and in *Part 2* **dosing estimation**.

Review

A *weak* acid/base dissociates in solution; the degree of dissociation depends on the pH, dissociation constant(s), the total species concentration of the weak acid/base system and the ionic strength of electrolyte. If the *total species* concentration of each system in a mixture of weak/base systems is known, then for any *selected pH*, the concentration of each of the dissociated and undissociated species can be calculated theoretically via the dissociation and mass balance equations governing each system. These equations can be expressed graphically, by the so-called log species-pH diagrams. The diagrams (Fig. 1) can be constructed rapidly, using approximate graphical methods, and allow rapid solution of the species concentration for any selected pH, with sufficient accuracy for most practical purposes (Loewenthal and Marais, 1976 and Loewenthal *et al.*, 1986). There is an extensive literature on weak acid/base systems, particularly the carbonate system. The reader can refer to Loewenthal and Marais (1976) for a critical review.

The species evaluation procedure above is possible only *if pH and total weak acid/base species concentration of each system are known.* Usually the pH is available via potentiometric pH measurements; total species concentration for each of the weak acid/base systems in solution can be determined either by wet chemical methods (e.g. ammonia, sulphide, sulphate, phosphate and total short-chain fatty acids); or by special techniques such as chromatography (e.g. individual short-chain fatty acids); or by inorganic carbon analyser (total carbonate species). However, a problem arises with the carbonate system: the inorganic carbon analyser is a highly specialised instrument available only in larger laboratories; and the carbonate system is unusual in that it can exist in three phases, gaseous, aqueous and solid — exchange of CO_2 between the aqueous and gas phases and/or precipitation or dissolution of calcium carbonate may cause that, subsequent to sampling, the state of the sample as measured (i.e. pH and total aqueous carbonate species concentration) may differ significantly from the state of the sample as taken. As a consequence, alternative methods of measurement needed to be developed to characterise the carbonate system in water *as sampled.*

With *only the carbonate system present*, an alternative to the total species concentration measurement was developed, based on the concept of alkalinity/acidity. The carbonate system exists in solution as dissolved CO_2 gas (always associated with a fixed ratio of carbonic acid H_2CO_3 giving a total concentration of $H_2CO_3^*$); bicarbonate (HCO_3^-); and carbonate (CO_3^{2-}) ions. If either CO_2 gas, a bicarbonate or carbonate salt is added to pure water, the species added, called the *reference species*, dissolves and dissociates to form all three of the carbonate species in proportions determined by the dissociation constants and the mass concentration of the reference species added; this solution is called an *equivalent solution.* Associated with the equivalent solution is a pH called the *equivalence point.* This equivalence point (commonly called an "end point pH") is almost universally used in a titration to establish when the equivalent solution state has been attained.

For the carbonate system three equivalent solutions can be formed, by adding either CO_2, HCO_3^- or CO_3^{2-} to water. If a strong base (acid) is added to any of the respective equivalent solutions, the pH changes away from that at the equivalence point. The mass of base (acid) added is called the *alkalinity (acidity)* relative to the equivalent solution. This alkalinity (acidity) is determined experimentally by titrating back to the equivalent solution with a standard strong acid (base). In this fashion, for example, we obtain total, phenolphthalein and caustic alkalinities respectively, by titrating with a strong acid

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* To whom all correspondence should be addressed.

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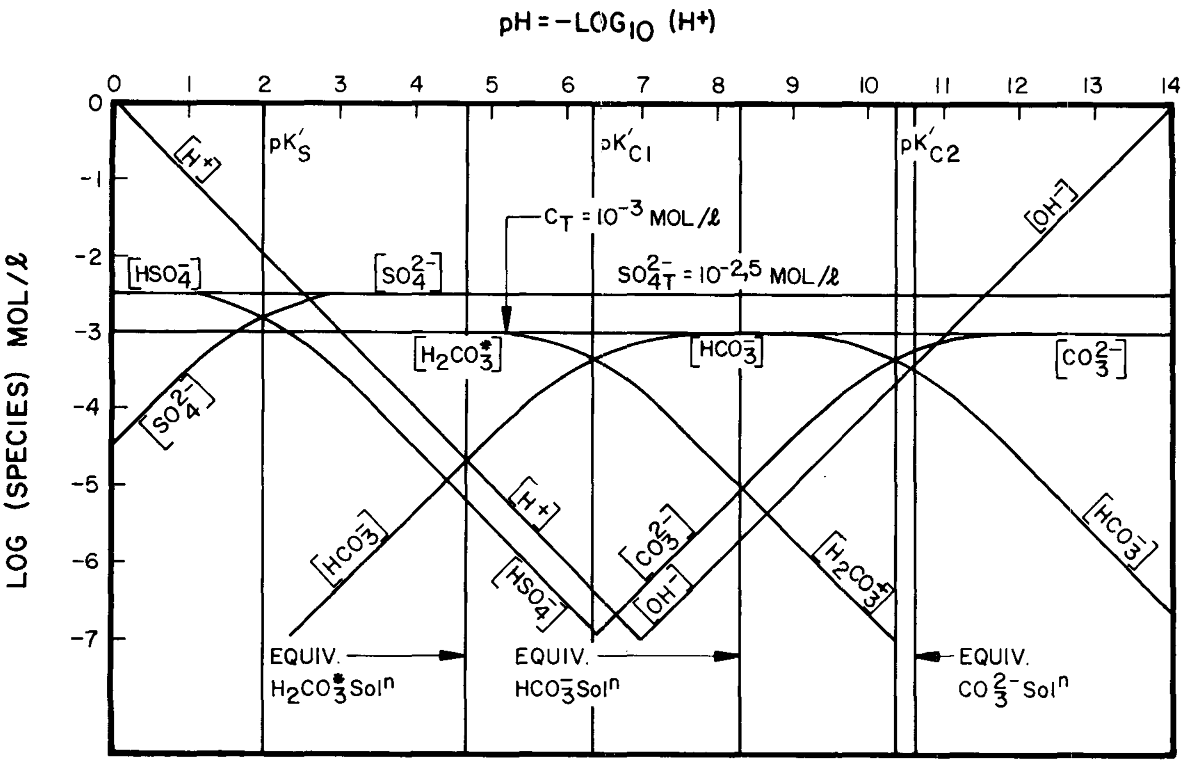

Figure 1

Log species-pH diagram for the carbonate and sulphate weak acid/base systems for total carbonate and sulphate species concentrations of $10^{-3,0}$ *and* $10^{-2,5}$ *mol/ℓ respectively. Note* pK' *values for the carbonate system are* $pK'_{C1} = 6,3$ *and* $pK'_{C2} = 10,3$ *and that for the sulphate system* $pK'_S = 2,0$*. The* $H_2CO_3^*$*,* HCO_3^- *and* CO_3^{2-} *equivalent solutions for the carbonate system are at pH values 4,7, 8,2 and 10,6 respectively.*

down from a higher pH to the respective equivalence points for the $H_2CO_3^*$, HCO_3^- and CO_3^{2-} equivalent solutions. Similarly we obtain mineral, carbon dioxide and total acidities by titrating with a strong base up from a lower pH to the respective equivalence points for $H_2CO_3^*$, HCO_3^- and CO_3^{2-} equivalent solutions. These alkalinities and acidities are mass parameters and theoretically are formulated in terms of partial sets of the carbonate weak acid/base species concentrations ($H_2CO_3^*$, HCO_3^-, CO_3^{2-}) and the water species (H^+, OH^-). The various alkalinities, acidities and total carbonate species concentration (C_T) are interrelated so that if one alkalinity or acidity can be determined and the sample pH measured, the others, and C_T, can be calculated via these relationships. Hence with the pH and *one* alkalinity or acidity measurement the carbonate system is completely characterised (Loewenthal and Marais, 1976; Loewenthal *et al.*, 1986).

From a practical point of view the alkalinity associated with the carbonic acid equivalent solution — the so-called total alkalinity — is the most useful. The total alkalinity is independent of the $H_2CO_3^*$ concentration, and therefore is not affected by loss or gain of CO_2 with the result that it can be measured even if there is a loss of CO_2 between sampling and measurement. However, the experimental measurement does present a problem in that the *equivalence point* depends on C_T so that CO_2 loss does affect the equivalence point (Loewenthal and Marais, 1976). Fortunately the equivalence point lies in a pH region of low buffering capacity so that slight errors in the equivalence point estimation (usually based on rules developed from experience) do not give rise to significant errors in the total alkalinity except when the alkalinity is low. Because the exact end point is not crucial, for many purposes the colorimetric method for end point titration has been adequate, and indeed the only feasible approach in the past when pH meters were not generally available. With the availability of pH meters the end point may be determined with greater accuracy by plotting pH-titration curves, but even here a relatively high error can result if the total alkalinity is low (Loewenthal *et al.*, 1986).

To overcome the difficulties associated with the end point titration, Gran (1952) proposed a method for determining alkalinity that does not depend on a titration to the equivalence point; in fact the titration is always taken well past the end point pH. Briefly, consider a titration past the total alkalinity equivalence point (i.e. below pH ≈ 4,6). Below pH ≈ 4 any further changes in pH will depend virtually only on the mass concentration of strong acid added i.e. the changes become independent of the carbonate weak acid/base system. Gran developed a function (First Gran function) which, in this pH region (pH < 4,0), gives a linear relationship between the function value and the volume of titrant added (Fig. 2). The linear section is extrapolated to intersect the titrant volume axis; the point of intersection defines the volume of titrant required to reach the equivalent solution state; from this volume the total alkalinity is calculated. When the carbonate system only is present Gran's method has been demonstrated to give accurate results even when the alkalinity (as $CaCO_3$) is as low as 1 mg/ℓ (Loewenthal *et al.*, 1986).

When the carbonate system *and* other weak acid/base systems are present in solution, the equivalence point of the *mixture* usually cannot be estimated from previous experience (as it can be with the carbonate system only present) because the other weak acid/base systems may influence the end point pH. For mixtures, in general, no exact method is available to carry out a titration to the end point pH; only approximate methods are available for some mixtures, e.g. procedures by McCarthy (1964) and in Standard Methods (1985), for a mixture of the carbonate and short-chain fatty acids systems.

Due to the difficulties with the equivalence point titration approach in mixed systems, an alternative approach has been put forward based on charge balance, originally proposed by Ricci (1952) and developed by Poncelet *et al.* (1985). The charge balance approach requires the total species concentration of all the weak acid/base systems other than the carbonate; a complete analysis of ionic species present in the water (with the exception of HCO_3^- and CO_3^{2-}); and the pH of the sample. The sum of the concentrations of HCO_3^- and CO_3^{2-} is then determined from the difference between the sum of the charges of the cationic and anionic species, and, knowing pH, C_T can be determined. However, the carbonate system is present nearly always in trace quantities compared to the strong salt ionic species, with the result that even small errors in the concentrations of the strong salt species can give rise to gross error in the determination of C_T.

In this paper a method is proposed for evaluating the carbonate system in a mixed system by extending the Gran approach and it is shown that, provided the total species concentrations of all the weak acid/base systems *except* the carbonate system are known, an alkalinity relative to a preselected equivalent solution of the mixed system can be determined accurately experimentally, and knowing the pH of the sample, C_T can be determined; and hence the mixed system can be completely characterised.

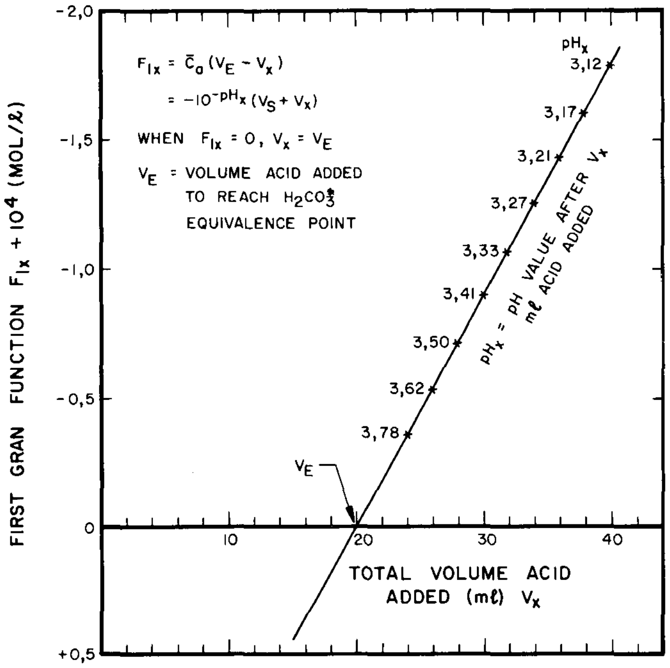

Figure 2

Plot of the first Gran function (F_{1x}) versus acid added demonstrating the method to determine the volume of acid required to reach the $H_2CO_3^*$ equivalent solution (Data from Table 1).

Alkalinity and acidity in single systems

The concentrations of weak acid/base species in solution in water are governed by equilibrium dissociation reactions for the weak acid/base system and the water, and a mass balance of the weak acid/base concentrations. For example, for the aqueous carbonate (i.e. carbonate-water) system, the weak acid dissociation equilibrium and mass balance equations are:

For the carbonate species:

$$(H^+)[HCO_3^-] / [H_2CO_3^*] = K_1/f_m = K_1' \qquad (1)$$

$$(H^+)[CO_3^{2-}] / [HCO_3^-] = K_2 \cdot f_m / f_d = K_2' \qquad (2)$$

and for the water species:

$$(H^+)[OH^-] = K_w / f_m = K_w' \qquad (3)$$

The sum of the carbonate species must equal the total carbonate species concentration:

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

where $[H_2CO_3^*]$ = the sum of molecularly dissolved carbon dioxide $[CO_2]_{aq}$, and carbonic acid, $[H_2CO_3]$, mol/ℓ, these two having a virtually fixed ratio with regard to each other thereby allowing expression in terms of the composite $H_2CO_3^*$ (Loewenthal and Marais, 1976).
C_T = total carbonate species concentration, mol/ℓ
K_1, K_2, K_1', K_2' = thermodynamic and apparent dissociation equilibrium constants respectively for the carbonate system
K_w, K_w' = thermodynamic and apparent ion product constants respectively for water system
f_m, f_d = monovalent and divalent activity coefficients (see Appendix 1)
[ ], ( ) = molar mass and active mass (activity) respectively.

Note that $(H^+) = f_m[H^+]$ in Eqs. 1 to 3 above; (H^+) is used in the equations because its numerical value is obtained from a pH measurement — the pH is measured in terms of the activity of H^+ from, $-\log_{10}(H^+) = pH$, i.e. $(H^+) = 10^{-pH}$.

Thus the carbonate-water system is defined by four equations incorporating six unknown parameters; hence two parameters need to be measured to characterise the system.

It is always necessary to measure two parameters to characterise a single weak acid/base in water. This is true irrespective of whether the weak acid/base is mono or multiprotic, i.e. has one or more dissociations. One measurement is related to the water species, the other to the weak acid/base introduced into the water. Measurement related to the water species invariably is via a pH measurement to give (H^+) and hence $[H^+]$. Measurement of the weak acid/base introduced usually is via the total species concentration, but in the case of the carbonate system the difficulties associated with the measurement of C_T prompted the development of a related mass parameter, an alkalinity or acidity. For any weak acid/base system it is permissible to substitute an alkalinity or acidity for the total species although usually this measurement will involve more effort than that for the total species.

In mixtures of weak acid/bases again one measurement relating to the water and one relating to each of the weak acid/base systems is required for characterisation. Now water itself is in fact a weak acid/base and accepting this the number of parameters to be measured is equal to the total number of weak acid/bases making up the solution.

When the mixed system does *not* include the carbonate system, then characterisation of the mixed system is straightforward, because the total species concentrations and the pH can be measured. However, when the mixture includes the carbonate system, which is the usual situation, then the determination of the carbonate system again must take place via an alkalinity/acidity measurement. The problem now is that an alkalinity/acidity measurement will include alkalinities and acidities due to the other weak acid/base systems. In order to utilise alkalinity and acidity in the characterisation of mixed weak acid/base systems in water, it is necessary therefore to understand exactly what we mean by the terms alkalinity or acidity and to define these terms unambiguously.

Definition of alkalinity (acidity)

Alkalinity (acidity) is the proton (i.e. hydrogen ion) accepting (donating) capacity of the solution of mixed acid/base systems in water relative to some reference state.

Reference states: If the solution is pure water, the reference state is $[H^+] = [OH^-] = 10^{-7}$ mol/ℓ – the "solution" of pure water forms the ***equivalent solution***. Associated with this reference state (or equivalent solution) is the pH = 7,0 (at 25°C) called the equivalence point. The equivalence point provides the practical means for identifying the reference state and for pure water it is particularly effective, because the equivalent solution lies in a region of extremely low buffer capacity. This results in rapid pH changes for small additions of acid or base around pH 7 so that both the equivalent solution state and the acid or base to be added to achieve this state can be accurately determined. If a mass of weak acid or base, or the salt of a weak acid or base, is added to the pure water, the solution formed defines the new reference state (or equivalent solution) and the pH established forms the new equivalence point. For example, the addition of any one of the carbonate weak acid/base system reference species i.e. carbon dioxide, bicarbonate or carbonate, to pure water gives rise to equivalent solutions of $H_2CO_3^*$, HCO_3^- or CO_3^{2-} respectively, each with its associated equivalence point (Fig. 1).

Because weak acids and bases dissociate only partially in solution, an equivalent solution will always contain both dissociated and undissociated weak acid/base species (in addition to the water species H^+ and OH^-). The relative concentrations of these species will depend on whether the equivalent solution is formed by addition of the weak acid or base or its salt to water, the mass added and the dissociation constant(s) for the weak acid/base system. An equation linking these species, and forming a reference level equation for the equivalent solution, can be formulated from a proton balance (Loewenthal and Marais, 1976). For example, if the equivalent solution is obtained by adding carbon dioxide to pure water, the reference species are $H_2CO_3^*$ and the pure water species (in which the hydrogen and hydroxyl ion concentrations $[H^+]_i$ and $[OH^-]_i$ are equal, i.e. $[H^+]_i = [OH^-]_i$, where i denotes initial or pure water species). **These reference species specify the input proton state.** In solution, partial dissociation of $H_2CO_3^*$ takes place and HCO_3^- and CO_3^{2-} species are formed by the release of one and two protons respectively; of the protons released, a fraction will increase the hydrogen ion concentration from the initial concentration $[H^+]_i$ and a fraction will react with OH^- (to form H_2O) so that the equilibrium equation for the water species is satisfied, i.e. $[OH^-](H^+) = K_w'$ (Eq.3). The total carbonate species in the system, C_T, is now

$$C_T = [CO_2]_{added} = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}].$$

The proton changes induced can be visualised readily by using the tabular technique set out below (Loewenthal and Marais, 1976):

Species formed by gain of one proton		H^+
↑		↑
Input species proton level (reference species)	—— $H_2CO_3^*$ ——	H_2O ($[H^+]_i = [OH^-]_i$)
	↓	↓
↓		
Species formed by loss of one proton	HCO_3^-	OH^-
↓	↓	
Species formed by loss of two protons	CO_3^{2-}	

A proton balance equation is now set up by noting that the sum of protons gained by species relative to the input proton level must equal the sum of the protons lost, i.e.

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

Noting that in pure water the hydrogen and hydroxyl ion concentrations are equal, i.e. $[H^+]_i - [OH^-]_i = 0$, then

$$[H^+] = 2[CO_3^{2-}] + [HCO_3^-] + [OH^-] \cdot$$

and rearranging terms

$$2[CO_3^{2-}] + [HCO_3^-] + [OH^-] - [H^+] = 0 \qquad (5)$$

Eq. 5 defines the state of the equivalent $H_2CO_3^*$ solution with an associated equivalence point defined by pH = $-\log(H^+)$.

Alkalinity and acidity: If a strong base (e.g. NaOH) is added to the equivalent (reference state) $H_2CO_3^*$ solution above, the pH will increase above the equivalence point and the mass concentration of base added is called the alkalinity (i.e. the proton accepting capacity) with respect to the equivalent solution. This alkalinity can be measured by titrating the solution with standard strong acid back to the equivalence point of the equivalent solution; the mass concentration of strong acid (titrant) added is equal to the base added, i.e. equal to the alkalinity of the solution. Similarly, if a strong acid is added to an equivalent solution, the pH will drop below the equivalence point and the acid added is called the acidity (i.e. the proton donating capacity) relative to the equivalent solution. Acidity can be measured by titrating the solution with standard strong base back to the equivalence point of the equivalent solution.

Equations for the alkalinities and acidities in respect of each of the equivalent solutions of the carbonate-water system can be formulated in terms of the concentrations of weak acid/base species and the hydrogen and hydroxyl ions by using proton balances as outlined above. As as example, equations for alkalinity and acidity relative to an $H_2CO_3^*$ equivalent solution are formulated as follows: If pH is *above* the $H_2CO_3^*$ equivalence point, we consider the solution a mixture of $H_2CO_3^*$, a *strong* base, BOH and pure H_2O. The reference species are $H_2CO_3^*$, BOH and H_2O ($[H^+]_i = [OH^-]_i$); these specify the input proton levels. After mixing, weak acid/base species will form which have either gained or lost protons relative to the input proton level as depicted below:

$$\begin{array}{llll}
\text{Species formed by gain of one proton} & & B^+ & H^+ \\
\uparrow & & \uparrow & \uparrow \\
\text{Input proton level} — & H_2CO_3^* — & BOH — & H_2O\ ([H^+]_i = [OH^-]_i) \\
\text{(premix condition)} & & & \\
\downarrow & \downarrow & & \downarrow \\
\text{Species formed by loss of one proton} & HCO_3^- & & OH^- \\
\downarrow & \downarrow & & \\
\text{Species formed by loss of two protons} & CO_3^{2-} & &
\end{array}$$

(With regard to the strong base, BOH, it dissociates completely to B^+ by *losing* one OH^- relative to BOH. Alternatively, B^+ species can be visualised as being formed by *gaining* one H^+ relative to BOH).

The proton balance gives:

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

Note that [BOH] added is the alkalinity and equal to $[B^+]$; and for pure water $[H^+]_i - [OH]_i = 0$. Inserting these in the above equation yields the equation for the $H_2CO_3^*$ alkalinity in terms of the species concentrations present in the water i.e.

$$H_2CO_3^*\text{ alkalinity} = [B^+] = 2[CO_3^{2-}] + [HCO_3^-] + [OH^-] - [H^+] \qquad (6)$$

(The nomenclature defining the different alkalinities and acidities for the carbonate-water system, that is, expressing alkalinities and acidities relative to the input reference species, was first introduced by Loewenthal and Marais (1976). This nomenclature can be applied to *any* aqueous system *in which only one weak acid/base system is introduced.* For example, H_3PO_4 alkalinity (acidity) will be alkalinity (acidity) of a phosphate-pure water solution relative to the H_3PO_4 reference species i.e. relative to the H_3PO_4 equivalent solution).

If pH is *below* the $H_2CO_3^*$ equivalence point, we consider the solution a mixture of $H_2CO_3^*$, pure H_2O and a strong acid (say HCl). Again using a proton balance and noting that [HCl] added = $[Cl^-]$, the $H_2CO_3^*$ acidity equation is derived:

$$H_2CO_3^*\text{ acidity} = [Cl^-] = -2[CO_3^{2-}] - [HCO_3^-] - [H^+] + [OH^-] \qquad (7)$$

In a similar fashion alkalinity and acidity equations relative to the HCO_3^- and CO_3^{2-} equivalent solutions are obtained; these are given below:

$$HCO_3^-\text{ alkalinity} = -[H_2CO_3^*] + [CO_3^{2-}] + [OH^-] - [H^+] \qquad (8a)$$

$$HCO_3^-\text{ acidity} = [H_2CO_3^*] - [CO_3^{2-}] - [OH^-] + [H^+] \qquad (8b)$$

$$CO_3^{2-}\text{ alkalinity} = -2[H_2CO_3^*] - [HCO_3^-] + [OH^-] - [H^+] \qquad (9a)$$

$$CO_3^{2-}\text{ acidity} = 2[H_2CO_3^*] + [HCO_3^-] - [OH^-] + [H^+] \qquad (9b)$$

It was pointed out earlier that the $H_2CO_3^*$ alkalinity is generally the most useful. Accordingly C_T (Eq. 4) is replaced by the $H_2CO_3^*$ alkalinity (Eq. 6) so that Eqs. 1, 2, 3 and 6 now define the carbonate-water system.

It is important to note from Eq. 4 and Eqs. 6 to 9, that C_T and the various alkalinities and acidities are interrelated. For example:

$$H_2CO_3^*\text{ alkalinity} + CO_3^{2-}\text{ acidity} = 2\,C_T \qquad (10)$$

$$H_2CO_3^*\text{ alkalinity} - CO_3^{2-}\text{ acidity} = 2HCO_3^-\text{ alkalinity} \qquad (11)$$

These and other interrelationships are depicted graphically in Fig. 3 (see Loewenthal and Marais, 1976 and Loewenthal *et al.*, 1986 for detailed treatment). Hence once one alkalinity or acidity value is available, and the pH of the sample is known, the system is defined and the other alkalinities, acidities and C_T can be calculated. Use of these related parameters greatly simplifies problem solving. For example in water stabilisation the CO_3^{2-} acidity is calculated from $H_2CO_3^*$ alkalinity and pH and serves as a pivotal parameter in resolving dosage problems (Loewenthal *et al.*, 1986).

As an example of another weak acid/base system consider the phosphate system. The H_3PO_4 alkalinity and PO_4^{3-} acidity can be derived with the aid of the proton balance approach i.e.

$$H_3PO_4\text{ alkalinity} = [H_2PO_4^-] + 2[HPO_4^{2-}] + 3[PO_4^{3-}] + [OH^-] - [H^+] \qquad (12)$$

$$PO_4^{3-}\text{ acidity} = +3[H_3PO_4] + 2[H_2PO_4^-] + [HPO_4^{2-}] + [H^+] - [OH^-] \qquad (13)$$

In the same fashion alkalinities and acidities relative to the weak acid/base reference species for $H_2PO_4^-$, HPO_4^{2-}, NH_4^+, NH_3, HAc, and Ac^- can be developed:

$$\begin{aligned}
H_2PO_4^-\text{ alkalinity} &= [HPO_4^{2-}] + 2[PO_4^{3-}] + [OH^-] - [H^+] - [H_3PO_4] \\
&= -\,H_2PO_4^-\text{ acidity} \qquad (14)
\end{aligned}$$

$$\begin{aligned}
HPO_4^{2-}\text{ acidity} &= [H_2PO_4^-] + 2[H_3PO_4] + [OH^+] - [PO_4^{3-}] - [OH^-] \\
&= -\,HPO_4^{2-}\text{ alkalinity} \qquad (15)
\end{aligned}$$

$$\begin{aligned}
NH_4^+\text{ alkalinity} &= [NH_3] + [OH^-] - [H^+] \\
&= -\,NH_4^+\text{ acidity} \qquad (16)
\end{aligned}$$

$$\begin{aligned}
NH_3\text{ acidity} &= [NH_4^+] + [H^+] - [OH^-] \\
&= -\,NH_3\text{ alkalinity} \qquad (17)
\end{aligned}$$

$$\begin{aligned}
HAc\text{ alkalinity} &= [Ac^-] + [OH^-] - [H^+] \\
&= -\,HAc\text{ acidity} \qquad (18)
\end{aligned}$$

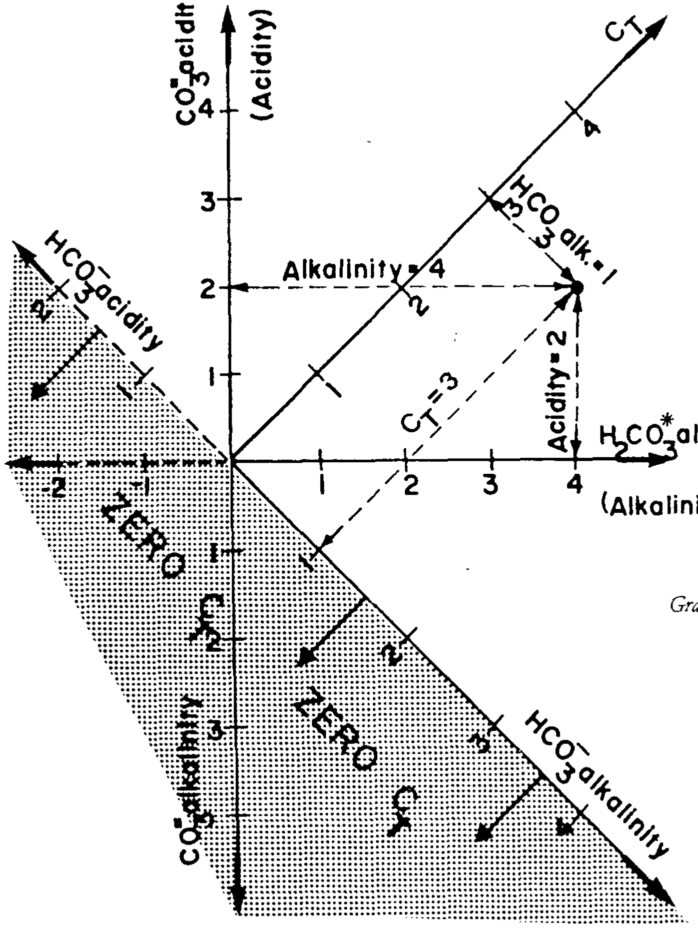

Figure 3
Graphical representation of interdependence between mass parameters for the carbonate system;

$$
\begin{aligned}
Ac^- \text{ acidity} &= [HAc] + [H^+] - [OH^-] \\
&= -\ Ac^- \text{ alkalinity} \qquad (19)
\end{aligned}
$$

The interrelationships between the various alkalinities and acidities of all weak acid/base systems are similar to those of the carbonate-water system; for example:

i) from Eqs. 12 and 13
H_3PO_4 alkalinity + PO_4^{3-} acidity = 3 P_T (20)
where P_T is the total phosphate species concentration

ii) from Eqs. 14 and 15
$H_2PO_4^-$ alkalinity + HPO_4^{2-} acidity = P_T (21)

iii) from Eqs. 16 and 17
NH_4^+ alkalinity + NH_3 acidity = N_T (22)
where N_T is the total ammonium species concentration

iv) from Eqs. 18 and 19
HAc alkalinity + Ac^- Acidity = A_T (23)
where A_T is the total acetate species concentration.

Note, from Eqs. 10, 20, 22 and 23, that the sum of the alkalinity, defined in terms of the most protonated species, and the acidity, defined in terms of the least protonated species, equals the number of dissociations times the total species concentration.

Alkalinity and acidity in mixed systems

Consider an aqueous solution made up by addition of masses of different weak acid/bases, of carbonic acid ($H_2CO_3^*$) (via CO_2 addition), phosphoric acid (H_3PO_4), acetic acid (HAc) and ammonium (by addition of NH_4Cl). In terms of our earlier discussion these input species become the reference species and the mixture in solution would define an equivalent solution with an associated equivalence point. If a strong base is added to this equivalent solution the pH will increase above the equivalence point and then theoretically the proton accepting capacity of the solution — an alkalinity — could be determined experimentally by titrating with standard strong acid back to the equivalence point.

The theoretical alkalinity equation for the mixture above is obtained from a proton balance in a fashion similar to that for the various alkalinities and acidities of the carbonate and other single weak acid/base systems discussed above. As a first example consider an equivalent solution formed by addition of $[H_2CO_3^*]$, $[H_3PO_4]$, [HAc] and $[NH_4^+]$ to pure water. Assume that the pH of the solution is raised by addition of a strong base, BOH. The mass of strong base BOH added is then the "alkalinity" of the mixed weak acid/base system with respect to the reference state which is the equivalent solution of the mixture of carbonic ($H_2CO_3^*$), phosphoric (H_3PO_4) and acetic (HAc) acids and ammonium chloride (NH_4Cl) originally added to the pure water. An equation for this "alkalinity" with respect to the reference state is formulated via the proton changes of species relative to the input proton levels as set out below:

$$\begin{tikzcd}
\text{Species formed by gain of one proton} & & & & & B^+ & H^+ \\
\text{Input proton level (reference species)} \arrow[u] \arrow[d] & H_2CO_3^* \arrow[r, dash] \arrow[d] & H_3PO_4 \arrow[r, dash] \arrow[d] & HAc \arrow[r, dash] \arrow[d] & NH_4^+ \arrow[r, dash] \arrow[d] & BOH \arrow[u] \arrow[r, dash] & H_2O \arrow[u] \arrow[d] \\
\text{Species formed by loss of one proton} \arrow[d] & HCO_3^- \arrow[d] & H_2PO_4^- \arrow[d] & Ac^- & NH_3 & & OH^- \\
\text{Species formed by loss of two protons} \arrow[d] & CO_3^{2-} & HPO_4^{2-} \arrow[d] & & & & \\
\text{Species formed by loss of three protons} & & PO_4^{3-} & & & &
\end{tikzcd}$$

Proton balance relative to the reference species gives:

$$[B^+] + [H^+] = 2[CO_3^{2-}] + [HCO_3^-] + 3[PO_4^{3-}] + 2[HPO_4^{2-}] + [H_2PO_4^-] + [Ac^-] + [NH_3] + [OH^-]$$

Solving for the net strong base in the solution, $[B^+]$, gives the required equation for alkalinity, called the $H_2CO_3^*/H_3PO_4/HAc/NH_4^+$ alkalinity:

$$H_2CO_3^*/H_3PO_4/HAc/NH_4^+ \text{ alkalinity} = 2[CO_3^{2-}] + [HCO_3^-] + 3[PO_4^{3-}] + 2[HPO_4^{2-}] + [H_2PO_4^-] + [Ac^-] + [NH_3] + [OH^-] - [H^+] \qquad (24)$$

The nomenclature for alkalinity, as written in the left hand side of Eq. 24, is consistent with that for a solution made up by the addition of only one weak acid/base system, that is, the alkalinity is named after the reference species introduced to make up the equivalent solution. In the same way the $H_2CO_3^*/H_3PO_4/HAc/NH_4^+$ *acidity* can be derived by adding carbonic ($H_2CO_3^*$), phosphoric (H_3PO_4) and acetic (HAc) acids and ammonium chloride (NH_4Cl) to pure water, then adding a mass of strong acid (HCl) and doing a proton balance, gives:

$$H_2CO_3^*/H_3PO_4/HAc/NH_4^+ \text{ acidity} = -2[CO_3^{2-}] - [HCO_3^-] - 3[PO_4^{3-}] - 2[HPO_4^{2-}] - [H_2PO_4^-] - [Ac^-] - [NH_3] - [OH^-] + [H^+] = -H_2CO_3^*/H_3PO_4/HAc/NH_4^+ \text{ alkalinity} \qquad (25)$$

Note that the $H_2CO_3^*/H_3PO_4/HAc/NH_4^+$ alkalinity is not equal to the sum of the individual system alkalinities (Eqs. 6, 12, 16 and 18). The difference is that in Eq. 24 the water terms $[OH^-]$ and $[H^+]$ occur only once instead of four times when summing the 4 individual alkalinities. (The alkalinity due to the water, being an inevitable component in either a single or mixture of added weak acid/bases, suggests that the alkalinity of the solution should be broken down into alkalinity components associated with the weak acid/bases added plus the alkalinity component associated with the water species. The separation of alkalinity into components is developed further in the next paper and forms the basis for devising simple procedures for dosing estimations).

In the carbonate/phosphate/acetate/ammonium/water mixture there are five systems (four weak acid/bases and the water) with the result that five independent measurements need to be made to completely characterise the mixed system. Of the five, three are total species concentration measurements of the phosphate, acetate and ammonia systems (i.e. P_T, A_T and N_T) and can be measured readily and accurately; the fourth is $[H^+]$ via the pH for the water system. The fifth measurement is for the carbonate system, where an alkalinity measurement is substituted for C_T. This alkalinity is defined in terms of a particular set of reference species of the carbonate, phosphate, acetate and ammonium systems. From this alkalinity measurement, the total carbonate species concentration C_T can be calculated (the method is set out below). In this fashion the mixed system can be completely characterised. Once this is achieved, then the various species concentration of each of the carbonate, phosphate, acetate, ammonia and water systems can be calculated for any pH via the equilibrium equations, or determined graphically via the log species-pH diagram (Fig. 4), using the procedure described by Loewenthal and Marais (1976).

In the mixture above we selected the equivalent solution to comprise a mixture of $H_2CO_3^*$, H_3PO_4, HAc and NH_4^+ added to water. However, we could have selected any one of the species of each of the weak acid/base systems as the reference species to make up the equivalent solution. Taking the input proton level of the selected species of each system, a corresponding alkalinity or acidity equation can be formulated relative to the selected reference species making up the equivalent solution. For example, in Eqs. 24 and 25 we took the most protonated species of each system as the reference input species; we could have taken the least protonated species and deduce the associated alkalinity and acidity, i.e.

$$CO_3^{2-}/PO_4^{3-}/Ac^-/NH_3 \text{ acidity} = 2[H_2CO_3^*] + [HCO_3^-] + 3[H_3PO_4] + 2[H_2PO_4^-] + [HPO_4^{2-}] + [HAc] + [NH_4^+] + [H^+] - [OH^-] = -CO_3^{2-}/PO_4^{3-}/Ac^-/NH_3 \text{ alkalinity} \qquad (26)$$

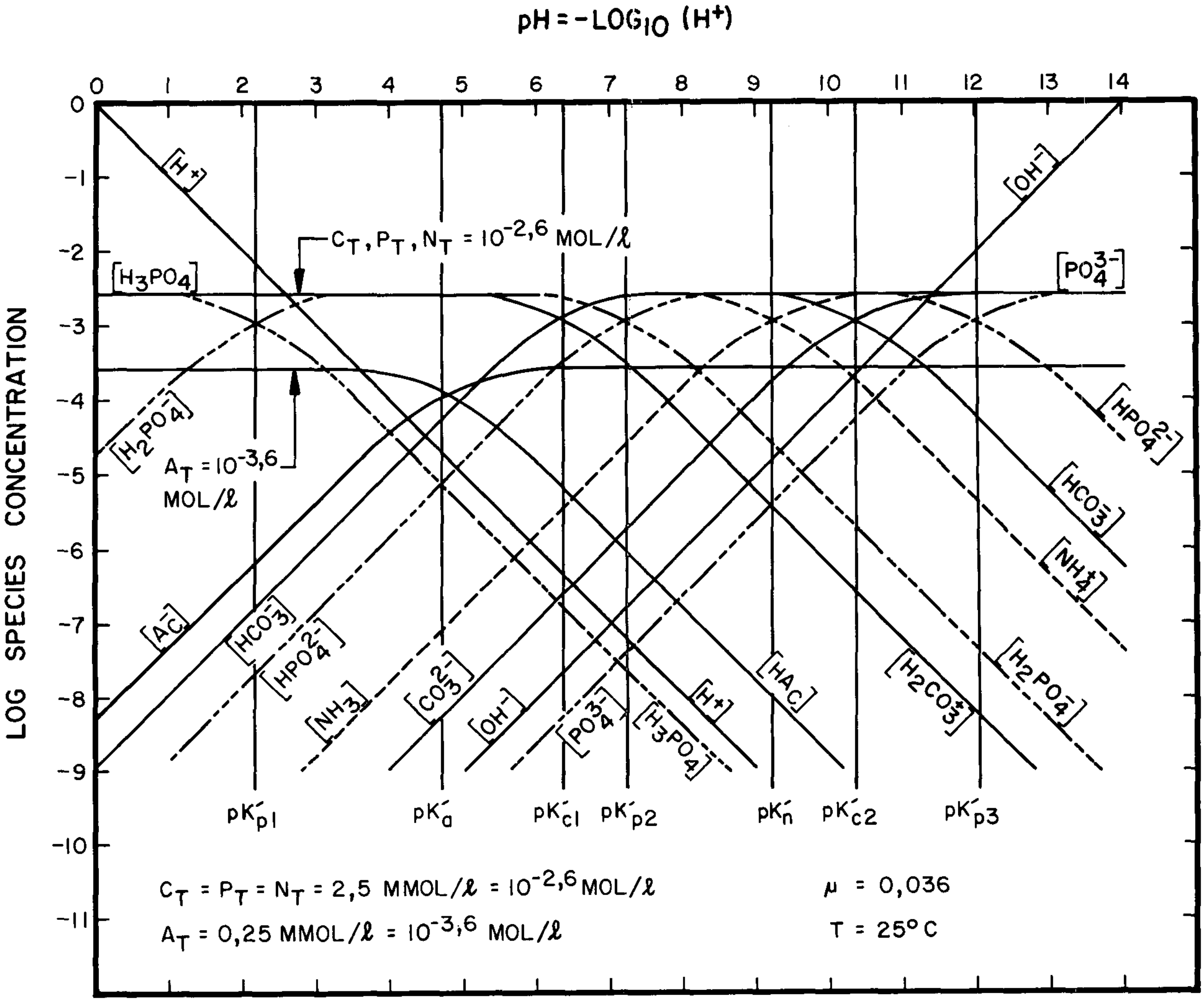

Figure 4

Log species-pH diagram for a mixture of carbonate, phosphate, acetate and ammonium systems at total species concentrations of $10^{-2,6}$, $10^{-2,6}$, $10^{-3,6}$ and $10^{-2,6}$ mol/ℓ respectively at 25 °C. pK values of the systems given in Table 2 (Note that Fig. 4 is valid for multiprotic acid species only down to a log species concentration of about −6; below this concentration the slopes of the lines are affected by secondary dissociation effects (Butler, 1964). The lines were drawn beyond their point of validity to facilitate labelling).

Then again in Eqs. 24 and 25 we could have selected $H_2PO_4^-$ instead of H_3PO_4 as the reference species to give:

$$H_2CO_3^*/H_2PO_4^-/HAc/NH_4^+ \text{ alkalinity} = 2[CO_3^{2-}] + [HCO_3^-] + 2[PO_4^{3-}] + [HPO_4^{2-}] - [H_3PO_4] + [Ac^-] + [NH_3] + [OH^-] - [H^+]$$
$$= - H_2CO_3^*/H_2PO_4^-/HAc/NH_4^+ \text{ acidity} \qquad (27)$$

When the carbonate system only is present in water, it was shown previously that one can choose any of the carbonate species i.e. $H_2CO_3^*$, HCO_3^- or CO_3^{2-} as the reference species for the equivalent solution as a basis for an alkalinity or acidity determination. In working with the carbonate system it is necessary always to know with which alkalinity or acidity one is concerned. The same care must be taken also in a mixed weak acid/base system — it is necessary always to distinguish between the alkalinities and acidities based on different sets of reference species. Furthermore, just as in the carbonate-water system there are relationships linking the 3 different alkalinities and acidities and the total carbonate species concentration, so also in the mixed system there are relationships linking the alkalinities and acidities of different sets of reference species and the total species concentrations. For example:

$$H_2CO_3^*/H_3PO_4/HAc/NH_4^+ \text{ alkalinity (Eq. 24)} - H_2CO_3^*/H_2PO_4^-/Hac/NH_4^+ \text{ alkalinity (Eq. 27)} = P_T \qquad (28)$$

$$H_2CO_3^*/H_3PO_4/HAc/NH_4^+ \text{ alkalinity (Eq. 24)} + CO_3^{2-}/PO_4^{3-}/Ac^-/NH_3 \text{ acidity (Eq. 26)} = 2C_T + 3P_T + A_T + N_T \qquad (29)$$

Clearly in a mixture of weak acid/base systems a large number of alkalinities and acidities can be formulated each having a selected set of reference species. However from a practical point of view the set that is most amenable to measurement would be the best one to use for characterisation. For reasons described in Appendix 2 this is the $H_2CO_3^*/H_2PO_4^-/HAc/NH_4^+$ alkalinity as defined by Eq. 27.

Alkalinity measurement using Gran's method

Up to this stage we have considered the theoretical structure of alkalinity and acidity of one or more weak acid/base systems in water. Now we need to measure these. The basis for any such a measurement is the mass of acid or base to be added to establish the relevant equivalent solution state. The usual means whereby this state has been identified has been to estimate by some means the associated equivalence point (end point pH), and titrate until this pH is attained. However, in mixtures of weak acid/base systems a practical difficulty arises with the equivalence point: It is not known *ab initio*; it cannot be estimated from experience because it depends on the reference species selected; it can vary widely depending on the type and relative concentrations of weak acid/base systems present; and it cannot necessarily be estimated from a pH-titration curve because the equivalent point may be hidden in one of the numerous regions of high buffer capacity afforded by one of the weak acid/base systems. However, we will show now that the alkalinity to the equivalent solution *can* be measured via the Gran approach without requiring the equivalence point to be known.

Gran's function for the $H_2CO_3^*$ alkalinity for the carbonate-water system

Gran (1952) developed a method for determining any of the alkalinities and acidities of the carbonate system relative to the respective equivalent solutions without requiring knowledge of the respective equivalence points. Up to the present Gran's method has found application principally for determining the $H_2CO_3^*$ alkalinity; to explain his method we propose therefore to develop it taking the $H_2CO_3^*$ alkalinity determination as our model.

Assume a strong acid titration has been performed to the $H_2CO_3^*$ equivalence point. If $\bar{C}_a$ is the H^+ molarity of the strong acid and V_E is the volume of strong acid added to reach the equivalence point in litres, the mass of $H_2CO_3^*$ alkalinity (i.e. $MH_2CO_3^*$ alkalinity) in moles is:

$$MH_2CO_3^*\ \text{alkalinity} = V_E\bar{C}_a \qquad \text{(mol)} \qquad (30)$$

Hence the original sample $H_2CO_3^*$ alkalinity is:

$$\begin{aligned} H_2CO_3^*\ \text{alkalinity} &= MH_2CO_3^*\ \text{alkalinity}/V_s \\ &= V_E\bar{C}_a/V_s \qquad (\text{mol}/\ell) \qquad (31) \end{aligned}$$

where V_s = sample volume in ℓ.

In doing the titration to the equivalence point, after adding V_x litres of strong acid, the *mass* of alkalinity remaining i.e. $MH_2CO_3^*$ alkalinity$_x$, is:

$$\begin{aligned} MH_2CO_3^*\ \text{alkalinity}_x &= V_E\bar{C}_a - V_x\bar{C}_a \qquad (32) \\ &= \bar{C}_a(V_E - V_x) \qquad \text{(mol)} \end{aligned}$$

The mass of $H_2CO_3^*$ alkalinity remaining ($MH_2CO_3^*$ alkalinity$_x$) also is given by the concentration of $H_2CO_3^*$ alkalinity remaining times the combined volume of the sample and acid added i.e.

$$MH_2CO_3^*\ \text{alkalinity}_x = H_2CO_3^*\ \text{alkalinity}_x . (V_s + V_x) \qquad (33)$$

Defining the mass of $H_2CO_3^*$ alkalinity remaining as a Gran function F'_{1x}, we obtain from Eqs. 32 and 33:

$$\begin{aligned} F'_{1x} &= \bar{C}_a(V_E - V_x) \qquad (34) \\ &= H_2CO_3^*\ \text{alkalinity}_x . (V_s + V_x) \qquad (35) \end{aligned}$$

Now the concentration of $H_2CO_3^*$ alkalinity remaining is found from the $H_2CO_3^*$ alkalinity concentration equation (Eq. 6) i.e.

$$\begin{aligned} H_2CO_3^*\ \text{alkalinity}_x = {} & [HCO_3^-]_x + 2[CO_3^{2-}]_x + \\ & [OH^-]_x - [H^+]_x \qquad (36) \end{aligned}$$

Substituting Eq. 36 into Eq. 35 for the $H_2CO_3^*$ alkalinity$_x$, yields Gran's complete first function F'_{1x} (with respect to the hydrogen ion concentration):

$$\begin{aligned} F'_{1x} &= \bar{C}_a(V_E - V_x) \qquad (34) \\ &= \{[HCO_3^-]_x + 2[CO_3^{2-}]_x + [OH^-]_x - \\ &\quad [H^+]_x\} \cdot (V_s + V_x) \qquad (37) \end{aligned}$$

Eq. 34 indicates that Gran's complete first function (Eq. 37) should be linear with respect to the volume of acid added V_x throughout the titration. That this is indeed so can be demonstrated taking a bicarbonate solution of which the C_T concentration is known as an example. To facilitate the calculation of F'_{1x} for incremental V_x values from the measured pH, the $[HCO_3^-]_x$ and $[CO_3^{2-}]_x$ concentrations are replaced by expressions in terms of pH_x, C_T and the apparent dissociation constants for the carbonate system K'_{c1} and K'_{c2}, and the $[OH^-]_x$ and $[H^+]_x$ concentrations by expressions in terms of pH_x and the apparent dissociation constant for water K'_w. (Note that the apparent dissociation constants are used because the solution constituents are defined in terms of mass concentration rather than activity except for the hydrogen ion, which is defined in terms of activity) i.e.

$$[HCO_3^-]_x = \frac{10^{-pK'_{c1}}}{(10^{-pH_x} + 10^{-pK'_{c1}})} \cdot \frac{C_TV_s}{V_s + V_x} \qquad (38a)$$

$$[CO_3^{2-}]_x = \frac{10^{-pK'_{c1} - pK'_{c2}}}{10^{-pH_x}(10^{-pH_x} + 10^{-pK'_{c1}})} \cdot \frac{C_TV_s}{V_s + V_x} \qquad (38b)$$

$$[OH^-]_x = 10^{pH_x - pK'_w} \qquad (38c)$$

$$[H^+]_x = (H^+)_x/f_m = 10^{-pH_x}/f_m \qquad (38d)$$

where f_m = the monovalent ion activity coefficient (see Appendix 1).

Multiplying Eq. 37 by f_m, Gran's complete first function (F_{1x}) is obtained i.e.

$$\begin{aligned} F_{1x} &= f_mF'_{1x} = f_m\bar{C}_a(V_E - V_x) \qquad (39) \\ &= f_m[HCO_3^-]_x(V_s + V_x) + 2f_m[CO_3^{2-}]_x(V_s + V_x) \\ &\quad + f_m[OH^-]_x(V_s + V_x) - f_m[H^+]_x(V_s + V_x) \\ &= L_x + 2.M_x + N_x - O_x \qquad (40) \end{aligned}$$

$$\text{where } L_x = \frac{f_m \cdot 10^{-pK'_{c1}}}{(10^{-pH_x} + 10^{-pK'_{c1}})} \cdot C_T V_s \qquad (40a)$$

$$M_x = \frac{f_m \cdot 10^{-pK'_{c1} - pK'_{c2}}}{10^{-pH_x}(10^{-pH_x} + 10^{-pK'_{c1}})} \cdot C_T V_s \qquad (40b)$$

$$N_x = f_m \cdot 10^{pH_x - pK'_w} \cdot (V_s + V_x) \qquad (40c)$$

$$O_x = 10^{-pH_x} \cdot (V_s + V_x) \qquad (40d)$$

The significance of the complete Gran function value is that it represents the alkalinity remaining at the different stages of the titration.

Now consider the bicarbonate solution of ionic strength $\mu = 0{,}010$ with a total carbonate species concentration $C_T = 10^{-3}$ mol/ℓ. The pH of this solution is 8,22 and its $H_2CO_3^*$ alkalinity is 10^{-3} mol/ℓ. A sample of 200 mℓ of the solution is taken for the Gran titration and the molarity of the standard strong acid added is 0,010 mol/ℓ. Because the $H_2CO_3^*$alkalinity is known, the volume of acid added to reach the equivalence point can be calculated from a rearranged Eq. 31 i.e. $V_E = 10^{-3}.200/0{,}01 = 20$ mℓ. Hence from Eq. 34 the Gran function value should be zero when the volume of acid added $V_x = V_E = 20$ mℓ. In this theoretical calculation of the Gran titration, 2 mℓ of strong acid are added at a time and after each addition the pH is calculated. From the pH thus obtained, the Gran function values are calculated with the aid of Eq. 40. These are listed in Table 1 and are shown plotted against acid added in Fig. 5 in which the Gran function value is given on the vertical axis with decreasing values *upwards*. Clearly the line is linear from the beginning of the titration. The initial function value is $+ 1{,}806.10^{-4}$ mol and with each addition of 2 mℓ strong acid the function value decreases by $0{,}1806.10^{-4}$ mol. After 10 additions of 2 mℓ i.e. 20 mℓ of strong acid, the function value is zero as expected. Hence the intersection point of the function with the acid added (horizontal) axis gives the volume of acid required to establish the equivalent state of the $H_2CO_3^*$ solution. In this example the equivalence point pH theoretically is 4,70. Adding

TABLE 1

CALCULATION OF THE VALUES OF THE SIMPLIFIED (EQ. 41) AND COMPLETE (EQ. 40) FIRST GRAN FUNCTIONS (F_{1x}) AS A TITRATION OF A 200 mℓ SAMPLE OF A 10^{-3} mol/ℓ BICARBONATE SOLUTION (WITH IONIC STRENGTH $\mu = 0{,}010$) PROCEEDS WITH THE SEQUENTIAL ADDITION OF 2 mℓ OF 10^{-2} mol/ℓ STRONG ACID (SEE FIG. 5).

Acid Added (ℓ)	Sample volume plus acid added (ℓ)		Bicarbonate contribution (mol x10^{-4})†	Carbonate contribution (mol x10^{-4})	Hydroxyl contribution (mol x10^{-4})	Hydrogen contribution simplified (Gran function*) (mol x10^{-4})	Complete** Gran function (mol x10^{-4})
V_x	$V_s + V_x$	$p(H^+)$	L_x	$2.M_x$	N_x	O_x	$L_x + 2.M_x + N_x - O_x$
0,000	0,200	8,216	+ 1,7657	+ 0,0370	+ 0,0033	− 0,0000	+ 1,8061
0,002	0,202	7,262	+ 1,6255	+ 0,0038	+ 0,0004	− 0,0001	+ 1,6296
0,004	0,204	6,910	+ 1,4451	+ 0,0015	+ 0,0002	− 0,0003	+ 1,4465
0,006	0,206	6,676	+ 1,2646	+ 0,0008	+ 0,0001	− 0,0004	+ 1,2651
0,008	0,208	6,484	+ 1,0843	+ 0,0004	0,0001	− 0,0007	+ 1,0841
0,010	0,210	6,309	+ 0,9040	+ 0,0002	0,0000	− 0,0010	+ 0,9033
0,012	0,212	6,133	+ 0,7240	+ 0,0001	0,0000	− 0,0016	+ 0,7226
0,014	0,214	5,942	+ 0,5442	+ 0,0001	0,0000	− 0,0024	+ 0,5419
0,016	0,216	5,712	+ 0,3654	+ 0,0000	0,0000	− 0,0042	+ 0,3612
0,018	0,218	5,377	+ 0,1897	+ 0,0000	0,0000	− 0,0091	+ 0,1806
0,020	0,220	4,702	+ 0,0437	+ 0,0000	0,0000	− 0,0437	+ 0,0000
0,022	0,222	4,066	+ 0,0103	+ 0,0000	0,0000	− 0,1909	− 0,1806
0,024	0,224	3,786	+ 0,0054	+ 0,0000	0,0000	− 0,3666	− 0,3612
0,026	0,226	3,617	+ 0,0037	+ 0,0000	0,0000	− 0,5455	− 0,5418
0,028	0,228	3,497	+ 0,0028	+ 0,0000	0,0000	− 0,7252	− 0,7224
0,030	0,230	3,405	+ 0,0023	+ 0,0000	0,0000	− 0,9053	− 0,9030
0,032	0,232	3,330	+ 0,0019	+ 0,0000	0,0000	− 1,0855	− 1,0836
0,034	0,234	3,267	+ 0,0016	+ 0,0000	0,0000	− 1,2658	− 1,2642
0,036	0,236	3,212	+ 0,0014	+ 0,0000	0,0000	− 1,4462	− 1,4448
0,038	0,238	3,165	+ 0,0013	+ 0,0000	0,0000	− 1,6267	− 1,6254
0,040	0,240	3,123	+ 0,0012	+ 0,0000	0,0000	− 1,8072	− 1,8060

* F_{1x} (simplified $= -(f_m [H^+])(V_s + V_x) = -10^{-pH_x}(V_s + V_x) = -O_x$

** F_{1x} (complete) $= \{f_m [HCO_3^-]_x + 2f_m [CO_3^{2-}]_x + f_m [OH^-] - 10^{-pH}\} (V_s + V_x) = L_x + 2.M_x + N_x - O_x$.

† Function value in mol multiplied by 10^{+4}.

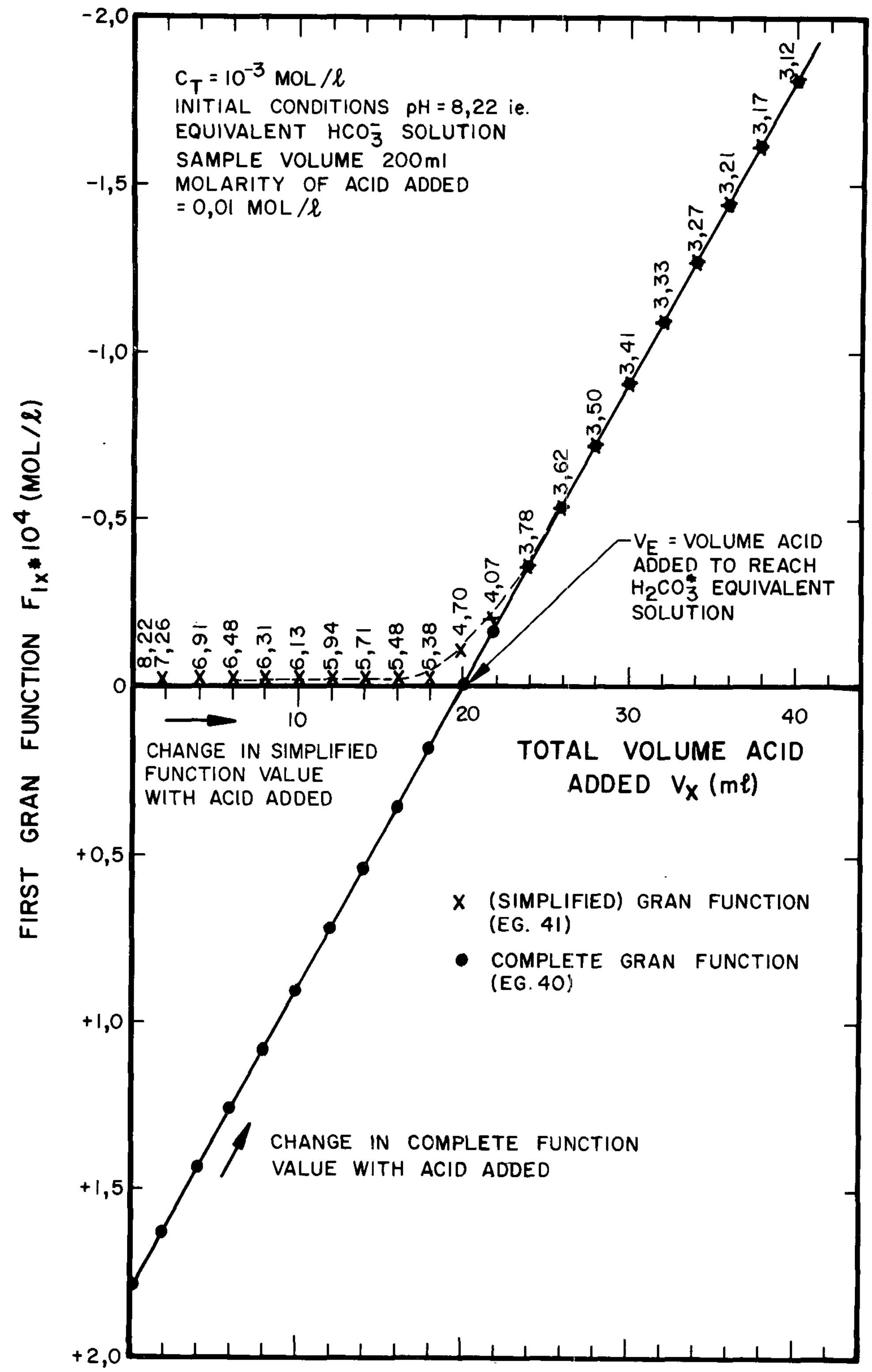

Figure 5

"Simplified" and "Complete" first Gran function versus cumulative acid added plot for a titration of 200 mℓ equivalent HCO_3^- solution of 10^{-3} mol/ℓ carbonate species concentration for sequential 2 mℓ 0,010 mol/ℓ strong acid added. Note complete Gran function line (Eq. 41) is linear throughout the titration but the simplified Gran function line is linear only in the pH range 3 to 4. Complete function line confirms that extrapolation of the simplified Gran function line to the horizontal axis ($F_{1x} = 0$) gives the volume of acid added to reach the $H_2CO_3^*$ equivalence point (V_E = 20 mℓ).

more strong acid incrementally, the function value continues to change by $0,1806.10^{-4}$ mol for every 2 mℓ acid added and after a further 20 mℓ acid added, the function value is $-1,806.10^{-4}$ mol and pH 3,12.

The above example demonstrates that Gran's complete function is linear with respect to acid added, as Eq. 34 suggests. However to utilise the complete function, C_T needs to be known. Usually C_T is ***not*** known; indeed the purpose of doing the titration is to determine C_T from the $H_2CO_3^*$ alkalinity. Hence at the time of the titration, the terms L_x and M_x cannot be determined. Omitting these two terms, as well as N_x (because for initial sample pH < 9, it contributes negligibly to the function value, see Table 1) we are left with the simplified Gran function i.e.

$$F_{1x} = -O_x = -10^{-pH_x} \cdot (V_s + V_x) \qquad (41)$$

For the titration above, the simplified Gran function values in Table 1 are given by the O_x term, and are plotted in Fig. 5 versus acid added. The simplified Gran function line is not linear. From Fig. 5 it can be seen that up to about 16 mℓ of acid added, the F_{1x} value is very small and plots horizontally. From 16 to 24 mℓ of acid added, the F_{1x} value begins to increase sharply and for more than 24 mℓ of acid added, F_{1x} increases at a constant rate for every further 2 mℓ of acid added. Furthermore, the sloping linear section of the simplified function line falls directly on, and has the same slope as, the complete function line. Hence, if a straight line is drawn through the sloping section of the simplified function values between pH say 3,21 and 3,78 and extrapolated, the extrapolated simplified function line intersects the horizontal axis at 20 mℓ, as for the complete Gran function line. Therefore the $H_2CO_3^*$ alkalinity can be determined from only the pH readings and the volumes of acid added in the pH range 3 to 4.

The reason why the simplified and complete Gran function values are identical in the pH range 3 to 4, is that the contribution of the bicarbonate and carbonate species to the alkalinity in this pH range is negligible (the bicarbonate and carbonate concentrations are more than two orders of magnitude lower than the hydrogen ion concentration, see Fig. 1 and Table 1) and the alkalinity in this pH range is provided solely by the hydrogen ion species.

It is useful to note that if a Gran titration is done on a sample of pure water the complete Gran function includes only the $[OH^-]$ and $[H^+]$ terms and the Gran plot commences at the origin of the plot ($f_{1x} = 0$, $V_x = 0$) with pH = 7,0 (Fig. 6). If a ***strong*** base of known molarity is added to the water sample prior to doing the Gran titration, again only $[OH^-]$ and $[H^+]$species are involved. The plot now commences on the F_{1x} axis on the positive region (below the horizontal V_x axis) and where it intersects the V_x axis (i.e. at V_E) defines the volume of strong base added to the water prior to doing the titration (Fig. 6). From the definition of alkalinity this concentration of strong base added is equivalent to the alkalinity.

Influence of sulphate

Sulphate is a weak acid/base and when present in water forms sulphate and bisulphate species in accordance with the following equilibrium reaction and equation:

$$H^+ + SO_4^= \rightleftarrows HSO_4^- \qquad (42)$$

i.e.

$$(H^+)[SO_4^{2-}]/[HSO_4^-] = K_s' \qquad (43)$$

where K_s' = apparent dissociation constant for the sulphate system
= K_s/f_m
K_s = dissociation constant
= $10^{-1,99}$ at 25°C (see Table 2)
f_m = monovalent ion activity coefficient.

Because of the low K value for the sulphate system (pK = 1,99), virtually all the species of the system will be in the sulphate form

TABLE 2

WEAK ACID DISSOCIATION CONSTANTS AT 25°C (EXPRESSED AS THEIR NEGATIVE LOG VALUE pK_a) AND THEIR TEMPERATURE DEPENDENCY, FOR THE CARBONATE, PHOSPHATE, SHORT-CHAIN FATTY ACIDS ACETATE AND PROPIONATE, AMMONIUM, SULPHATE AND HYDROGEN SULPHIDE SYSTEMS. $pK = \frac{A}{T} - B + CT$ WHERE T IS IN KELVIN. (HELGESON, 1967)

Weak acid		pK 25°C	A	B	C
Water	pK_w	14,000			
Carbonate	pK_{c1}	6,352	3404,7	14,8435	0,03279
	pK_{c2}	10,329	2902,4	6,4980	0,02379
Henry's constant†,	pK_{CO_2}	1,47	− 1760,0	− 9,619	− 0,00753
Phosphate	pK_{p1}	2,148	799,3	4,5535	0,01349
	pK_{p2}	7,198	1979,5	5,3541	0,01984
	pK_{p3}	12,023	———	not given	———
Short-chain fatty acids:					
Acetate	pK_{fa}	4,756	1170,5	3,165	0,0134
Propionate	pK_{fp}	4,874	1213,3	3,3860	0,01406
Ammonium	pK_n	9,245	2835,8	0,6322	0,00123
Sulphate	pK_s	1,99		not sensitive between 5 and 40°C	
Hydrogen sulphide	pK_h	6,99	1351,90	− 0,0992	0,00792

† $[H_2CO_3^*] = K_{CO_2} \cdot P_{CO_2}$

for pH > 3. With all the species in the sulphate form, the sulphate system affords no buffer capacity. Hence for most practical water treatment purposes, where pH adjustments above 4 are required, the sulphate system can be, and in fact is, ignored. By ignoring the sulphate system it is assumed that the reference species for the system is SO_4^{2-}. However, when determining $H_2CO_3^*$ alkalinity using the Gran function, the sulphate system commences to have a significant effect in the pH range 3 to 4. This effect, on the $H_2CO_3^*$ alkalinity determination via the Gran titration, is examined below.

The alkalinity of the carbonate-sulphate-water system with respect to the $H_2CO_3^*$ and SO_4^{2-} reference species is:

$$H_2CO_3^*/SO_4^{2-} \text{ alkalinity} = 2[CO_3^{2-}] + [HCO_3^-] + [OH^-] - [H^+] - [HSO_4^-] \qquad (44)$$

from which the simplified Gran function (i.e. ignoring species of negligible concentrations at pH < 4) is:

$$F_{1x} = \{-(H^+)_x - [HSO_4^-]_x\}(V_s + V_x) \qquad (45)$$
$$= f_m\bar{C}_a(V_E - V_x) \qquad (46)$$

In order that Eq. 45 is useful for calculating Gran function values from measured pH_x and V_x values, the $[HSO_4^-]_x$ term needs to be replaced with known terms. This is done by substituting a rearrangement of Eq. 43 for $[HSO_4^-]_x$ into Eq. 45 i.e.

$$F_{1x} = \{-(H^+)_x - f_m(H^+)_x[SO_4^{2-}]/K_S'\}(V_s + V_x)$$
$$= -C_S(H^+)_x(V_s + V_x)$$
$$= f_m\bar{C}_a(V_E - V_x)$$

where $C_S = (1 + f_m[SO_4^{2-}]/K_S')$ (47)

Now referring to a log species - pH diagram for the carbonate system (with $C_T = 10^{-3}$ mol/ℓ) (Fig. 1), for pH > 3, the $[H^+]$ and $[HSO_4^-]$ lines are parallel; the ratio $[H^+]/[HSO_4^-]$ is constant and hence from Eq. 43, $[SO_4^{2-}]$ is constant. Because $[SO_4^{2-}]$ is constant for pH > 3, C_S also is constant for pH > 3.

Knowing that C_S is constant and comparing the simplified Gran function excluding sulphate (Eq. 41) with that including sulphate (Eq. 47), it can be seen that only the slope of the function is changed from $f_m\bar{C}_a$ without sulphate to $f_m\bar{C}_a/C_S$ with sulphate. **However the intercept with the horizontal axis, which gives the volume of acid added to reach the equivalent solution, is not changed.** Hence the $H_2CO_3^*$ alkalinity determined from the intersection value V_E will be the same irrespective of whether sulphate is present or not. Interpreted graphically in Fig. 5, the presence of sulphate causes the complete Gran function line, and hence also the linear section of the simplified function between pH 3 and 4, to rotate about the intercept with the horizontal axis (at V_E = 20 mℓ in Fig. 5) in an anti-clockwise direction; the higher the sulphate concentration the greater the degree of rotation. (The increase in slope of the Gran function with increase in sulphate concentration has been used by Loewenthal and Marais (1983) to determine the single ion activity of the hydrogen ions in solutions with very high sulphate concentrations such as sea water).

Extended Gran function for alkalinity measurement of mixed weak acid/base systems

In a solution composed of the carbonate system plus a number of other weak acid/base systems, provided the *lowest* dissociation constant (pK) for the other systems is not less than the *lowest* dissociation constant for the carbonate system, pK_{C1} (i.e. not < 6,3) then in the region of pH < 4 these systems will be in their completely protonated form and therefore cannot absorb protons. For mixtures of weak acid/base systems which conform to this proviso, the total alkalinity of the mixed system can be obtained by using the Gran function for the carbonate system only (Eq. 41) developed above. However, if a weak acid/base system

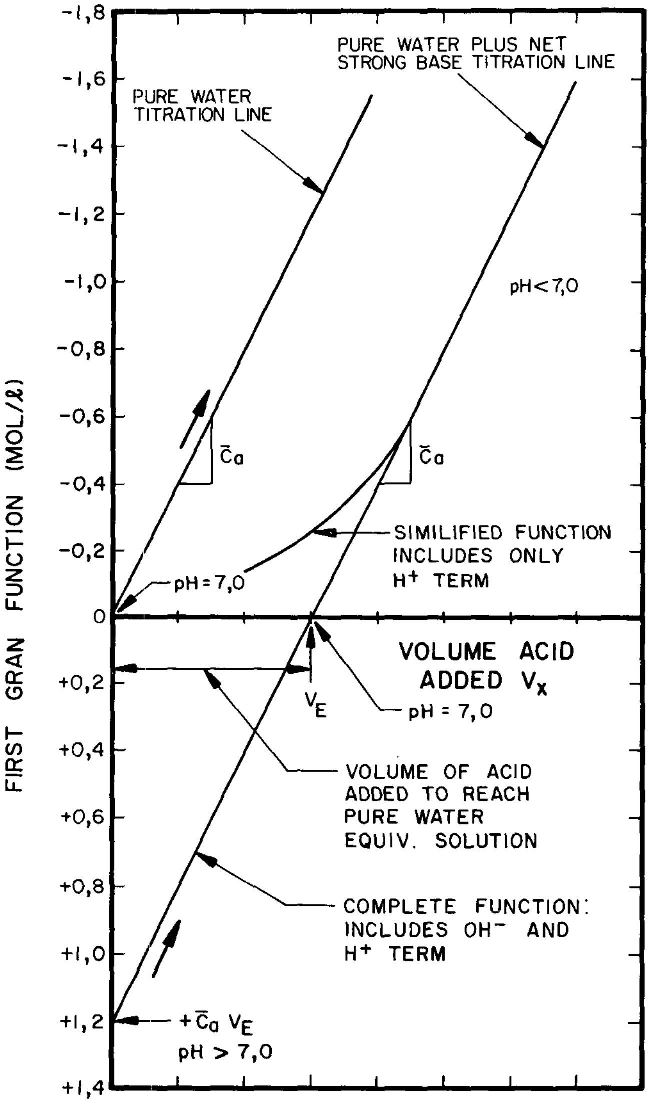

Figure 6

First Gran function versus volume acid added for a pure water sample (initial pH = 7,0) and a pure water plus net strong base sample (initial pH > 7,0). Note that for the pure water sample the initial function value is 0,0 because titration commences at pure water equivalent solution but for the pure water plus net strong base the initial function value is > 0 and pH > 7,0 and the function value equals 0 ($V_x = V_E$) when the volume of acid added equals the net strong base added i.e. the pure water equivalent solution again is reached (i.e. pH = 7,0).

with a dissociation constant (pK) value less than about 6 is present, then it is not completely associated in the region pH < 4 with the result that it acts as a pH buffer and the simplified Gran function for the carbonate system only (Eq. 41) no longer is valid. This situation arises when the mixture includes, for example, the short-chain fatty acids, the pK values of which are around 4,6, and the phosphate system, the lowest pK value of which is 2,15 (Table 2). To overcome the problem of alkalinity measurement of mixtures of weak acid/base systems, some of which have pK values between 2 and 6, the Gran function can be extended to incorporate the buffering actions of such weak acid/base systems. This extension is presented below.

Consider a solution comprising the carbonate, phosphate, acetate and ammonium systems, the pK values of which are listed in Table 2. We stated earlier that a large number of equations for alkalinity can be formulated by selecting various combinations of reference species, one from each of the weak acid/base systems. For the carbonate, phosphate, acetate and ammonium systems the alkalinity parameter most useful for measurement is the one using the $H_2CO_3^*$, $H_2PO_4^-$, HAc, NH_4^+ reference species in pure water (Appendix 2). A Gran function for determining this alkalinity is formulated by following the procedure described above for the carbonate system only:

The mass of $H_2CO_3^*/H_2PO_4^-/HAc/NH_4^+$ alkalinity remaining after adding $V_x\ \ell$ of strong acid to a sample of $V_s\ \ell$ is given by the alkalinity concentration remaining times the sum of the sample and acid added volumes i.e.

$$(H_2CO_3^*/H_2PO_4^-/HAc/NH_4^+ \text{ alkalinity})_x \cdot (V_s + V_x) = V_E\bar{C}_a - V_x\bar{C}_a = \bar{C}_a(V_E - V_x) \tag{48}$$

Hence the alkalinity in the sample before titration, i.e. $V_x = 0$, is:

$$H_2CO_3^*/H_2PO_4^-/HAc/NH_4^+ \text{ alkalinity} = \frac{\bar{C}_a V_E}{V_s} \tag{49}$$

The theoretical formulation for $H_2CO_3^*/H_2PO_4^-/HAc/NH_4^+$ alkalinity is given by Eq. 27. Referring to the log species – pH plot in Fig. 4, for the carbonate, phosphate, acetate and ammonia systems, in the region pH < 4, the species $[CO_3^{2-}]$, $[HCO_3^-]$, $[HPO_4^{2-}]$, $[PO_4^{3-}]$, $[NH_3]$ and $[OH^-]$ all have negligible concentrations compared with $[H_3PO_4]$, $[Ac^-]$ and $[H^+]$. Hence for pH < 4, Eq. 27 reduces to:

$$H_2CO_3^*/H_2PO_4^-/HAc/NH_4^+ \text{ alkalinity} = -[H^+] - [H_3PO_4] + [Ac^-]$$

Consequently the alkalinity concentration remaining after adding $V_x\ \ell$ of strong acid is given by:

$$H_2CO_3^*/H_2PO_4^-/HAc/NH_4^+ \text{ alkalinity}_x = -[H^+]_x - [H_3PO_4]_x + [Ac^-]_x$$

Substituting this simplified alkalinity equation into Eq. 48 yields:

$$(-[H^+] - [H_3PO_4]_x + [Ac^-]_x) \cdot (V_s + V_x) = \bar{C}_a(V_E - V_x) \tag{50}$$

For this Gran function to be useful for construction a Gran plot from pH_x and V_x measurements, the $[H^+]_x$ concentration needs to be expressed in terms of pH_x and the concentrations $[H_3PO_4]_x$ and $[Ac^-]_x$ need to be expressed in terms of pH_x and the respective measureable total species concentration P_T and A_T i.e.

$$[H^+]_x = 10^{-pH_x}/f_m \tag{38d}$$

$$[H_3PO_4]_x \approx \frac{10^{-pH_x}}{10^{-pH_x} + 10^{-pK'_{p1}}} \cdot \frac{P_T V_s}{V_s + V_x} \tag{51}$$

and

$$[Ac^-]_x = \frac{10^{-pK_a}}{10^{-pH_x} + 10^{-pK'_a}} \cdot \frac{A_T V_s}{V_s + V_x} \tag{52}$$

where K'_a and K'_{p1} = acetate and first phosphate apparent weak acid dissociation constants respectively.

The derivation of Eqs. 51 and 52 is given in Appendix 3.

Substituting Eqs. 51 and 52 into Eq. 50 and multiplying through by the monovalent ion activity coefficient f_m (for consistency with the original Gran function, Eq. 40) gives a useful form for the Gran function for a mixed weak acid/base system comprising carbonate, phosphate, acetate and ammonium for $H_2CO_3^*/H_2PO_4^-/HAc/NH_4^+$ reference species:

$$\begin{aligned} F_x &= f_m\bar{C}_a(V_E - V_x) \\ &= -f_m[H^+]_x(V_s + V_x) - f_m[H_3PO_4]_x(V_s + V_x) \\ &\quad + f_m[Ac^-]_x(V_s + V_x) \\ &= -O_x - Q_x + R_x \end{aligned} \tag{53}$$

where

$$O_x = (10^{-pH_x}) \cdot (V_s + V_x) \tag{41}$$

$$Q_x = \frac{f_m P_T 10^{-pH_x}}{10^{-pH_x} + 10^{-pK'_{p1}}} \cdot V_s \tag{54a}$$

$$R_x = \frac{f_m A_T 10^{-pK'_a}}{10^{-pH_x} + 10^{-pK'_a}} \cdot V_s \tag{54b}$$

For the purposes of ready identification, Eq. 53 is termed the *extended* Gran function F_x.

To obtain an extended Gran plot, F_x values are calculated for a set of pH_x and V_x values and plotted against V_x. In the region $pH_x < 4$ the plot will be linear; if extrapolated to intersect the V_x axis, i.e. where $F_x = 0$, the point of intersection defines the value of V_E. Substituting V_E into Eq. 49 gives the $H_2CO_3^*/H_2PO_4^-/HAc/NH_4^+$ alkalinity of the sample.

Characterisation of mixed systems

To characterise a mixture of carbonate, phosphate, acetate and ammonium systems requires five measurements, one for the water and one for each of the four weak acid/base systems introduced. The water system measurement is supplied by the sample pH, i.e. pH_0 and P_T, A_T and N_T by chemical analyses; C_T is found via the $H_2CO_3^*/H_2PO_4^-/HAc/NH_4^+$ alkalinity, a measurement that in itself requires P_T and A_T. Calculation of C_T from the five measurements is as follows: From Eq. 27:

$$\begin{aligned}\{2[CO_3^{2-}] + [HCO_3^-]\} &= H_2CO_3^*/H_2PO_4^- / HAc/NH_4^+ \\ &\text{alkalinity} - \{2[PO_4^{3-}] + [HPO_4^{2-}] - H_3PO_4]\} \\ &- \{[Ac^-]\} - \{[NH_3]\} - \{[OH^-]\} - [H^+]\} \\ &= Y \end{aligned} \qquad (55)$$

Each of the weak acid/base species concentration in Eq. 55 can be determined by inserting expressions in terms of the respective total species concentrations and the pH of the sample, pH_0. These expressions are obtained from the respective mass balance and equilibrium equations, as shown below.

For the phosphate system, in the region $4 \leq pH_0 \leq 10$ the values of the terms $2[PO_4^{3-}]$ and $[H_3PO_4]$ are completely negligible compared with $[HPO_4^{2-}]$ (Fig. 4), so that *if the original sample pH (pH_0) is in this region,* the term $\{[PO_4^{3-}] + [HPO_4^{2-}] - [H_3PO_4]\}$ in the alkalinity equation above is closely approximated by $[HPO_4^{2-}]$, where:

$$[HPO_4^{2-}] \approx \frac{P_T 10^{-pK'_{p2}}}{10^{-pH_0} + 10^{-pK'_{p2}}} = U \qquad (56)$$

For the acetate system:

$$[Ac^-] = \frac{A_T 10^{-pK'_a}}{10^{-pH_0} + 10^{-pK'_a}} = V \qquad (57)$$

For the ammonium system:

$$[NH_3] = \frac{N_T 10^{-pK'_n}}{10^{-pH_0} + 10^{-pK'_n}} = W \qquad (58)$$

For the water system:

$$[OH^-] - [H^+] = 10^{pH_0 - pK'_w} - 10^{-pH_0} / f_m = X \qquad (59)$$

For the carbonate system:

$$\{[HCO_3^-] + 2[CO_3^{2-}]\} = $$

$$C_T \cdot (1 + 10^{pK'_{c1} - pH_0} + 10^{pH_0 - pK'_{c2}}) = Y \qquad (60)$$

The total carbonate species concentration can now be determined by equating Eqs. 55 and 60 from which:

$$C_T = \frac{(1 + 10^{pK'_{c1} - pH_0} + 10^{pH_0 - pK'_{c2}}}{(1 + 2.10^{pH_0 - pK'_{c2}})} \cdot Y \qquad (61)$$

where $Y = (H_2CO_3^*/H_2PO_4^-/HAc/NH_4^+ \text{ alkalinity}) - U - V - W - X$ and U, V, W and X are given Eqs. 56 to 59 respectively.

The procedures for calculating C_T might appear formidable but can be readily accomplished by means of a short computer program. Alternatively, in the second paper of this series a simple graphical procedure will be presented that *inter alia* allows a rapid solution for C_T.

Experimental verification

The validity of the method described above for characterising mixtures of weak acid/base systems from *inter alia* an alkalinity measurement with respect to a selected set of reference species was checked experimentally by making up a number of mixtures of known masses of weak acids and salts. The weak acid/base systems selected were the carbonate, phosphate, acetate and ammonium systems. The mixtures were made up by combining different volumes of standard 0,010 M solutions of $Na_2CO_3$for the carbonate system, KH_2PO_4 for the phosphate system, NaAc for the acetate system and NH_4Cl for the ammonium system. These solutions were prepared with carbon dioxide free distilled water, and in mixing the solutions, care was exercised to avoid CO_2 dissolution. This was necessary in order to obtain an accurate initial pH value for the mixture with respect to the known total carbonate species added. The $H_2CO_3^*/H_2PO_4^-/HAc/NH_4^+$ alkalinity of the mixtures was determined from a Gran titration. The phosphate and acetate total species concentrations required for the $H_2CO_3^*/H_2PO_4^-/HAc/NH_4^+$ alkalinity calculation were not measured, but were calculated from their respective input masses because in practice, these concentrations can be obtained accurately by direct measurement. Fifteen Gran titrations were conducted. For all of these tests, the measured $H_2CO_3^*/H_2PO_4^-/HAc/NH_4^+$ alkalinity agreed within 1% of the expected alkalinity calculated from the input species. From the measured $H_2CO_3^*/H_2PO_4^-/HAc/NH_4^+$ alkalinity and initial pH of the mixture, the total carbonate species concentrations can be calculated. In those tests where the initial pH was recorded, the total carbonate species concentration C_T was calculated. The calculated C_T agreed to within 2% of the expected value from the input carbonate species.

As an example of the characterisation procedure, the details and calculations for a test in which the initial pH was recorded, are set out below.

Example

A mixture of carbonate, phosphate, acetate and ammonia systems was prepared by mixing 20 mℓ of each of the 0,010 M standard solution of Na_2CO_3, KH_2PO_4 and NH_4Cl with 40 mℓ of the 0,010 M standard standard acetate solution making a total sample volume of 100 mℓ. The initial pH (pH_0) was 8,07 and from the input masses, the total species concentrations for the carbonate, phosphate, acetate and ammonia systems were 2,00, 2,00, 4,00 and 2,00 mmol/ℓ respectively. The $H_2CO_3^*/H_2PO_4^-/HAc/NH_4^+$ alkalinity is given by 2,00 mmol/ℓ CO_3^{2-} from the carbonate system plus 4,00 mmol/ℓ Ac^- from the acetate system giving 2.2,00 + 4,00 = 8,00 mmol/ℓ; the phosphate and ammonia systems do not contribute to $H_2CO_3^*/H_2PO_4^-/HAc/NH_4^+$ alkalinity because the species added to the mixture are the reference species. The temperature and ionic strength of the mixture was 25°C and 0,014 respectively. The 100 mℓ sample was titrated with 0,0983 mol/ℓ standard HCl acid. The pH values recorded after sequential additions of acid during the Gran titration are listed in Table 3.

TABLE 3

AN EXAMPLE OF A GRAN TITRATION FOR DETERMINATION OF THE $H_2CO_3^*/H_2PO_4^-/HAc/NH_4^+$ ALKALINITY OF A MIXTURE OF CARBONATE, PHOSPHATE, ACETATE AND AMMONIUM WEAK ACID/BASE SYSTEMS GIVING pH READINGS FOR INCREMENTS OF ACID ADDED. THE CALCULATED O_x, Q_x and R_x FROM WHICH THE EXTENDED GRAN FUNCTION VALUES F_x (EQ. 53) ARE DETERMINED ARE ALSO GIVEN.

V_x mℓ	pH_x	O_x mmol.10^3	Q_x mmol.10^3	R_x mmol.10^3	F_x $-O_x-Q_x+R_x$
0,0	8,07	–	–	–	–
8,1	3,65	24,2	4,8	28,8	-0,2
8,2	3,595	27,5	5,5	25,6	-7,3
8,3	3,525	32,5	6,4	22,0	-16,7
8,4	3,465	37,2	7,3	19,4	-25,1
8,5	3,412	42,0	8,2	17,2	-33,0
8,6	3,369	46,4	9,0	15,7	-39,8
8,7	3,320	52,0	10,0	14,1	-48,0
8,8	3,267	58,8	11,3	12,5	-57,6
8,9	3,217	66,1	12,5	11,2	-67,4
9,0	3,176	72,7	13,7	10,2	-76,1
9,1	3,137	79,6	14,9	9,4	-85,1
9,2	3,107	85,4	15,8	8,8	-92,4
9,3	3,070	93,0	17,1	8,1	-102,1
9,4	3,038	100,2	18,3	7,5	-111,0
9,5	3,010	107,0	19,3	7,0	-119,0

Determination of the $H_2CO_3^*/H_2PO_4^-/HAc/NH_4^+$ alkalinity from the titration data is demonstrated step-wise below:

- Calculate the monovalent ion activity coefficient f_m: Substitute $\mu = 0{,}014$ and $Z = 1$ into the Davies equation (Eq. 1.1 in Appendix 1) which gives $\log f_m = -0{,}0511$ and $f_m = 0{,}889$.
- Calculate the apparent dissociation constants for the phosphate and acetate systems at 25°C. For the phosphate system the first equilibrium constant $pK_{p1} = 2{,}148$ (Table 2); the apparent value is given by $pK'_{p1} = pK_{p1} + \log f_m = 2{,}148 + (-0{,}051) = 2{,}097$. For the acetate system, the dissociation constant $pK_a = 4{,}756$; the apparent value is given by $pK'_a = pK_a + \log f_m = 4{,}756 + (-0{,}051) = 4{,}705$.
- Calculate the contributions of the three terms O_x, Q_x and R_x of the extended Gran function from the pH_x and V_x observations using Eqs. 41, 54a and 54b respectively. Add these (taking due cognisance of the sign) to give the extended Gran function value F_x (Eq. 53). These calculations are listed in Table 3.
- Plot F_x versus V_x from the data in Table 3 and extrapolate the linear section of the plot to $F_x = 0$, i.e. to intersect the V_x axis; this plot is shown in Fig. 7 (top).
- Determine the volume of acid added to reach the equivalent solution, V_E, from the graph; this is given by the intersection point of the extrapolated line with the horizontal axis, i.e. $V_E = 8{,}11$ mℓ. The V_E value can also be obtained by a linear least squares regression analysis of F_x on V_x. A regression analysis on the data in Table 3 yields the best straight line as $F_x = 695{,}56 - 85{,}72\ V_x$ with a correlation coefficient squared (R^2) of 0,999. From this $V_E = 695{,}56/85{,}72 = 8{,}11$ mℓ.
- Calculate the $H_2CO_3^*/H_2PO_4^-/HAc/NH_4^+$ alkalinity from Eq. 49, i.e.

$$H_2CO_3^*/H_2PO_4^-/HAc/NH_4^+ \text{ alkalinity} = \bar{C}_a V_E / V_s$$
$$= 0{,}0983.8{,}11/100 \text{ mol}/\ell$$
$$= 7{,}97 \text{ mmol}/\ell.$$

The accuracy of the titration is obtained by comparing the measured alkalinity value of 7,97 mmol/ℓ with that calculated from the constituents of the mixed acid/base solution i.e. 8,00 mmol/ℓ. Thus in this particular titration the measured alkalinity is within 0,3% of the true value. In 15 similar titrations, the largest error obtained was 1,0%. Generally the indications are that very accurate results can be obtained with the method, provided the parameters that are required for the determination such as P_T, A_T, pH_x and V_x are accurately made. A sensitivity analysis for errors in the measurement of the various parameters required in the Gran function calculation indicated for example, that a 10% error in the measurement of P_T has a negligible effect on the determination; this is because the phosphate system term (Q_x) is numerically small compared to the pH term (O_x) (Table 3). However, the magnitude of the error does depend on the relative total species concentrations of the different systems making up the mixture.

Having determined the $H_2CO_3^*/H_2PO_4^-/HAc/NH_4^+$ alkalinity, the calculation of the total carbonate species C_T is set out step-wise below.

- Calculate the divalent ion activity coefficient f_d: Substitute $\mu = 0{,}014$ and $Z = 2$ into the Davies equation (Eq. 1.1 in Appendix 1) which gives $\log f_d = -0{,}205$ and $f_d = 0{,}624$.
- Calculate the apparent dissociation constants pK'_{c1} and pK'_{c2} for the carbonate, pK'_{p2} for the phosphate, pK'_n for the ammonium and pK'_w for the water systems i.e. from Table 2

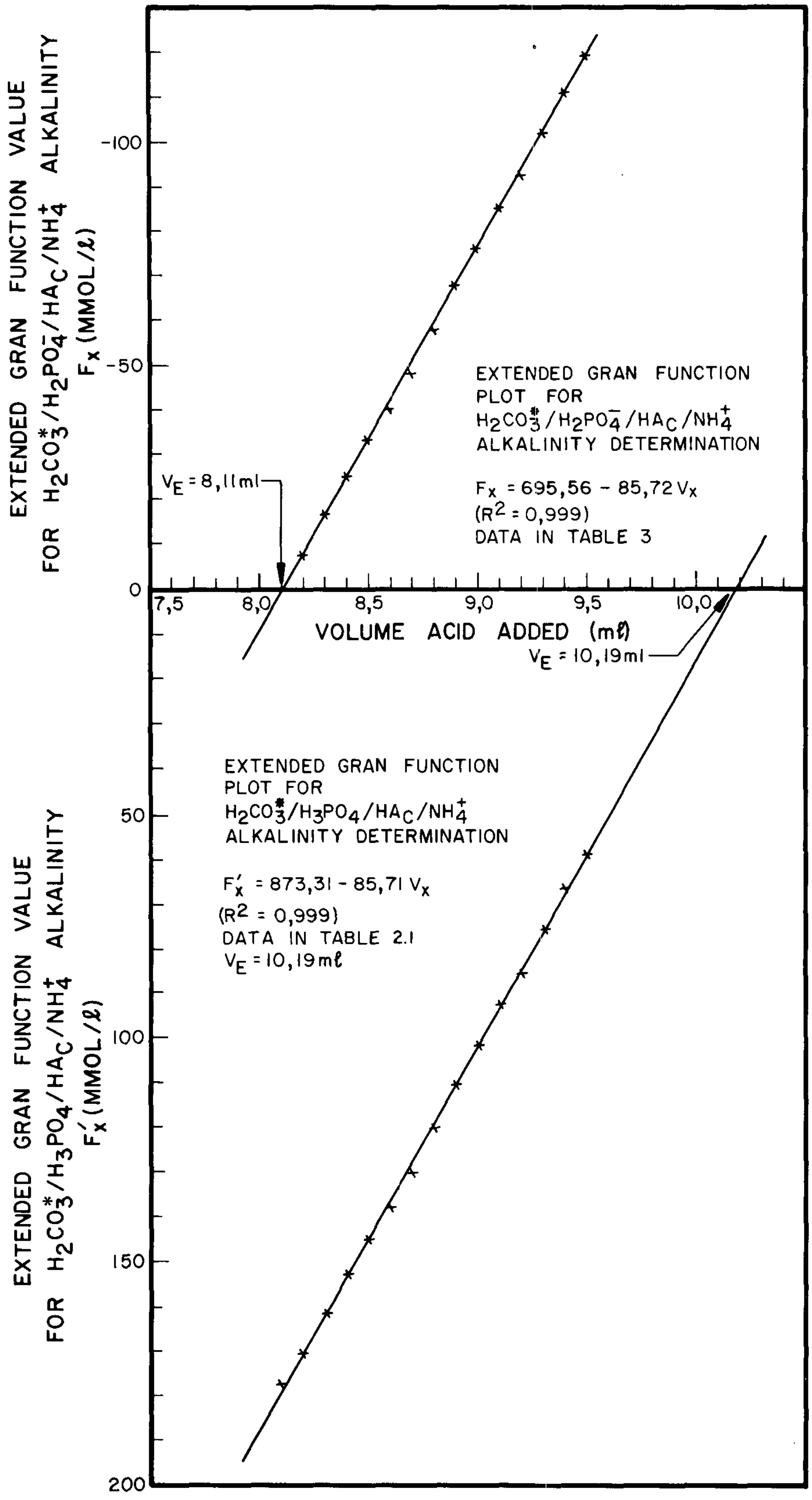

Figure 7

Extended Gran function versus cumulative acid added plot for a made-up mixture of carbonate, phosphate, acetate and ammonia systems at 2,2, 4,2 mmol/ℓ total species concentrations respectively for the $H_2CO_3^*/H_2PO_4^-/HAc/NH_4^+$ *(top) and* $H_2CO_3^*/H_3PO_4/HAc/NH_4^+$ *(bottom) alkalinities respectively. Note that 8,11 and 10,9 mℓ acid are required to reach* $H_2CO_3^*/H_2PO_4^-/HAc/NH_4^+$ *and* $H_2CO_3^*/H_3PO_4/HAc/NH_4^+$ *equivalent solutions (*V_E*) respectively and that the slopes of the two lines are equal. Data in Tables 3 and 2.1*

$$pK'_{c1} = pK_{c1} + \log f_m = 6{,}352 + (-0{,}051) = 6{,}301$$
$$pK'_{c2} = pK_{c2} - \log f_m + \log f_d = 10{,}329 - (-0{,}051) + (-0{,}205) = 10{,}175$$
$$pK'_{p2} = pK_{p2} - \log f_m + \log f_d = 7{,}198 - (-0{,}051) + (-0{,}205) = 7{,}044$$
$$pK'_n = pK_n + \log f_m = 9{,}245 + (-0{,}051) = 9{,}194$$
$$pK'_w = pK_w + \log f_m = 14{,}000 + (-0{,}051) = 13{,}949$$

- Calculate the respective alkalinity contributions of the phosphate, acetate, ammonium and water systems to the $H_2CO_3^*/H_2PO_4^-/HAc/NH_4^+$ *alkalinity* at the measured pH of 8,07, i.e.

  for the phosphate system $U = 1{,}83$ mmol/ℓ (from Eq. 56)
  for the acetate system $V = 4{,}00$ mmol/ℓ (from Eq. 57)
  for the ammonium system $W = 0{,}14$ mmol/ℓ (from Eq. 58)
  for the water system $X = 0{,}00$ mmol/ℓ (from Eq. 59)
- Hence the alkalinity of the carbonate system is:

  $$Y = (H_2CO_3^*/H_2PO_4^-/HAc/NH_4^+ \text{ alkalinity}) - U - V - W - X = 7{,}97 - 1{,}83 - 4{,}00 - 0{,}14 - 0{,}00 = 2{,}00 \text{ mmol}/\ell$$
- Knowing the alkalinity of the carbonate system Y, C_T is calculated from Eq. 61 i.e.

  $C_T = 1{,}0090.2{,}00 = 2{,}02$ mmol/ℓ.

The accuracy of the characterisation procedure is obtained by comparing the measured C_T with that expected i.e. 2,00 mmol/ℓ. Hence in this particular test the C_T determination is within 1,0% of the true value. In the other tests where the initial pH value for the solution was measured, the largest error was 2,0%. This indicates that for practical purposes sufficiently accurate results can be obtained with the characterisation procedure set out in this paper.

As for the carbonate system only, the total carbonate species concentration C_T obtained with the characterisation procedure set out in this paper is the value *at the time the pH of the mixture is taken*. Consequently, great care must be exercised that no calcium carbonate precipitation/dissolution or CO_2 evolution/dissolution takes place between the time the sample is taken and the pH_0 is measured. Once pH_0 has been measured, CO_2 exchange no longer affects the characterisation results because the reference species for the carbonate system are $H_2CO_3^*$ species; also if the titration is done into the sample container any $CaCO_3$ precipitate formed after the pH is measured will redissolve at the low pH range of the Gran titration and hence also will not affect the characterisation results.

Conclusions

The objective of this paper was to develop a theoretical structure that would allow mixtures of weak acid/base systems, which include the carbonate system, to be characterised. For reasons of practicality, an alkalinity measurement needs to be made when the carbonate system is present either as the only weak acid/base system or included in a mixture of weak acid/base systems. For the carbonate system only, the alkalinity measurement usually is relatively simple; the alkalinity measured is the $H_2CO_3^*$ or total alkalinity which is the alkalinity associated with the equivalent carbonic acid ($H_2CO_3^*$) solution, a solution state which is identified by a pH value called the $H_2CO_3^*$ equivalence point or end point pH; although some difficulties can be encountered when estimating the end point pH, generally it is sufficiently accurate to obtain this from empirical rules of thumb or from a pH titration curve. However, for mixtures of weak acid/base systems which include the carbonate system, end point pH estimation no longer is possible, and a different approach has to be followed.

Gran (1952) developed a method for determining the $H_2CO_3^*$ alkalinity where the carbonate system only is present, without requiring the end point pH to be known. In this paper this method has been extended to mixtures of weak acid/base systems that include the carbonate system. This extension requires a generalisation of the concepts of alkalinity and acidity and the development of a consistent nomenclature for naming these. Important conclusions from this extension are:

- Alkalinity (acidity) is defined as the proton (i.e. hydrogen ion) accepting (donating) capacity of the solution of mixed acid/base systems in water relative to some reference solution state.
- The reference state, also called the equivalent solution state, is defined in terms of a selected set of reference species, one species from each of the weak acid/base systems (in water) making up the mixture.
- The alkalinity (or acidity) is named after the particular set of reference species selected e.g. the $H_2CO_3^*/H_2PO_4^-/HAc/NH_4^+$ alkalinity (acidity) is the alkalinity (acidity) associated with $H_2CO_3^*$, $H_2PO_4^-$, HAc and NH_4^+ reference species of the carbonate, phosphate, acetate and ammonium systems respectively in a mixture of these four weak acid/base systems.
- Theoretically there is complete freedom in selecting the set of reference species, but practically a particular set will be superior to other sets because it leads to more accurate measurement of the associated alkalinity (acidity).
- For the same mixture of weak acid/base systems, alkalinity (acidity) with respect to one set of reference species is related to the alkalinity (acidity) with respect to another set of reference species via the total species concentrations of the weak acid/base systems making up the mixture, i.e. an alkalinity or acidity with respect to one set can be converted to an alkalinity or acidity with respect to another set (In the second paper of this series, this conversion will be shown to be of crucial importance in solving dosing problems).
- To characterise a mixture of weak acid/base systems, the number of measurements to be made are one for the water, which is the pH, and one for each of the weak acid/base systems which usually is the total species concentration, except for the carbonate system. For the carbonate system the total carbonate species concentration measurement is replaced by an alkalinity measurement associated with a particular set of reference species.
- The set of reference species that provides the most accurate alkalinity measurement of a mixture of carbonate, phosphate, acetate and ammonium systems, and hence the most accurate for characterisation of the mixture, is the $H_2CO_3^*/H_2PO_4^-/HAc/NH_4^+$ alkalinity.
- The $H_2CO_3^*/H_2PO_4^-/HAc/NH_4^+$ alkalinity is measured by means of a Gran titration in which the $H_2CO_3^*/H_2PO_4^-/HAc/NH_4^+$ equivalent solution pH (i.e. end point pH) is not required to be known and pH values versus acid added are recorded in the pH range 3 to 4; and calculated by means of the extended Gran function from the pH versus acid added data.
- For calculating the alkalinity from the Gran function for the carbonate system alone, only pH readings versus acid added in the pH range 3 to 4 are required to be known. For calculating the alkalinity from the *extended* Gran function for *mixtures* of weak acid/base systems, the total species concentrations of those systems which exert buffer capacity in the pH range 3 to

4 and the activity of the hydrogen ion are also required to be known: For example, to calculate the alkalinity of a mixture of carbonate, phosphate, acetate and ammonium systems, the total phosphate and acetate species concentrations need to be known because these systems exert buffer capacity in the pH range 3 to 4; the total ammonium species concentration does not need to be known because this system does not exert buffer capacity in this pH range. The activity of H^+ can be estimated from the Davies equation provided the TDS < 2 500 mg/ℓ.

- For characterisation, *all* the total species concentrations of the weak acid/base systems of interest need to be known.
- The sulphate-bisulphate system influences the Gran titration results but not the alkalinity value that is calculated from these results.
- Using a number of made-up mixtures of carbonate, phosphate, acetate and ammonium systems, the extended Gran titration method was tested and found to give alkalinity values within 1% of the expected values, and total carbonate species concentrations within 2% of the expected values.
- The characterisation procedure set out in this paper, gives the total carbonate species concentration at the time the pH of the sample is taken. Consequently, for this procedure, like that for the carbonate system only, care must be exercised that CO_2 evolution/dissolution and/or $CaCO_3$ precipitation/dissolution does not take place between the time the sample is taken and the pH is measured. Once the pH has been measured, the CO_2 exchange no longer affects the results because the reference species for the carbonate system for determining the alkalinity are the $H_2CO_3^*$ species. Neither will $CaCO_3$ precipitation, provided the full sample is titrated in the sample container.

This paper has been concerned only with characterisation of mixed weak acid/base systems. In the next paper, the theoretical structure developed so far will be extended and applied to deal effectively with the problem of dosing estimation, to obtain a desired state in mixed weak acid/base systems, e.g. a specified pH by addition of one or more strong or weak acids or bases.

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Appendix 1

Calculation of activity coefficients with the aid of the Davies equation

In low salinity waters (TDS ⩽2 500 mg/ℓ) activity coefficients of ions can be determined from the Debye-Hückel theory or some modification of it. The most widely used modification of this theory is that by Davies (Butler, 1964); viz.

$$\log f_i = -AZ_i^2 \left(\frac{\mu^{1/2}}{1 + \mu^{1/2}} - 0{,}3\,\mu\right) \qquad (1.1)$$

where f_i = activity coefficient for ionic species i, written as f_m and f_d for mono and divalent ions respectively
μ = ionic strength
= $^1/_2\, \Sigma\, C_i\, Z_i^2$
C_i = concentration of the i^{th} ionic species, mol/ℓ
Z_i = charge of the i^{th} species, equal to 1 for mono and 2 for divalent ions
A = temperature dependant constant
= $1{,}825.10^6(78{,}3.T)^{-1{,}5}$
= 0,504 at 25°C
T = temperature in Kelvin.

To calculate the ionic strength, μ, requires a complete analyses of the water. However, the activity coefficients determined from the Davies equation are not very sensitive to ionic strength so that an approximate estimate of μ from empirical methods is usually sufficient. Two empirical equations are available (Kemp, 1971), i.e.

- $\mu \approx 2{,}5.10^{-5}.(\text{TDS} - 20)$

where TDS = total inorganic dissolved solids, mg/ℓ.

- $\mu = 1{,}68.10^{-4}.\text{SC}$

where SC = specific conductance, in mS/m.
(1 mS/m = 10 μ mho/cm)

The ionic strength of the solution in the example described in the body of the paper (Fig. 5 and Table 1) is μ = 0,010. For this ionic strength, the monovalent ion activity coefficient f_m at 25°C is:

$$\log f_m = -0{,}504(1)^2\,\{0{,}010^{1/2}/(1 + 0{,}010^{1/2}) - 0{,}3.0{,}010\} = -0{,}0443$$

$$\text{Hence } f_m = 10^{-0{,}0443} = 0{,}903$$

and the divalent ion activity coefficient f_d is

$$\log f_d = -0{,}504(2)^2\,\{0{,}010^{1/2}/(1 + 0{,}010^{1/2}) - 0{,}3.0{,}010\} = -0{,}1772$$

$$\text{Hence } f_d = 10^{-0{,}1772} = 0{,}665$$

Appendix 2

Reason for using $H_2PO_4^-$ and not H_3PO_4 as the reference species for the phosphate system in alkalinity measurement in mixed weak acid/base systems

It was stated that for reasons of practicality, the $H_2CO_3^*/H_3PO_4/HAc/NH_4^+$ alkalinity is *not* a convenient and accurate alkalinity parameter to measure in a mixture of carbonate, phosphate, acetate and ammonium systems. The reason for this arises from the presence of the term $[H_2PO_4^-]_x$ in the extended Gran function, a term which has very high numerical values compared to the other terms for this alkalinity. Hence not only is an error in the P_T measurement magnified but the Gran plot can now give a poor estimate of V_E. This is illustrated for the titration data of the example listed in Table 3 in the paper.

The $H_2CO_3^*/H_3PO_4$ / HAc/NH_4^+ alkalinity is given by Eq. 24. Referring to the log species-pH diagram for the carbonate, phosphate, acetate and ammonium systems shown in Fig. 4, it can be seen that, except for $[H^+]$, $[H_2PO_4]$ and $[Ac^-]$, the other species concentrations appearing in Eq. 24 have negligible concentrations at $pH < 5$ and therefore can be ignored. The alkalinity therefore reduces to:

$$H_2CO_3^*/H_3PO_4/HAc/NH_4^+ \text{ alkalinity} = -[H^+] + [H_2PO_4^-] + [Ac^-] \qquad (2.1)$$

Following the same reasoning that was applied in the development of the $H_2CO_3^*/H_2PO_4^-/HAc/NH_4^+$ alkalinity (Eqs. 48 to 54), the *mass* of $H_2CO_3^*/H_3PO_4/HAc/NH_4^+$ alkalinity remaining after adding V_x *ℓ* of strong acid to a sample of V_s *ℓ*, is given by the product of the concentration of alkalinity remaining and the sum of the volume of the sample and acid added, i.e.

$$H_2CO_3^*/H_3PO_4/HAc/NH_4^+ \text{ alkalinity}_x.(V_s + V_x) = \bar{C}_a(V_E - V_x) \qquad (2.2)$$

Substituting Eq. 2.1 into Eq. 2.2 and multiplying through by the monovalent ion activity coefficient f_m gives the required Gran function F_x' i.e.

$$F_x' = \{-f_m[H^+]_x + f_m[H_2PO_4^-]_x + f_m[Ac^-]_x\}(V_s + V_x) = -O_x + S_x + R_x \qquad (2.3)$$

where

$$O_x = 10^{-pH_x}(V_s + V_x) \qquad (mol) \qquad (41)$$

$$S_x = \frac{f_m P_T\, 10^{-pK_{p1}'}}{10^{-pH_x} + 10^{-pK_{p1}'}} \cdot V_s \qquad (mol) \qquad (2.4)$$

$$R_x = \frac{f_m A_T\, 10^{-pK_a'}}{10^{-pH_x} + 10^{-pK_a'}} \cdot V_s \qquad (mol) \qquad (54b)$$

The derivation of the term S_x follows identically that of R_x in Eq. 54b (Appendix 3) i.e. for $pH < 6$:

$$P_{Tx} \approx [H_3PO_4]_x + [H_2PO_4^-]_x \qquad (3.1)$$

where

$$P_{Tx} = P_T V_s/(V_s + V_x) \qquad (3.2)$$

and

P_T = total phosphate species concentration prior to titration.

From Eq. 3.3 (in Appendix 3):

$$[H_3PO_4]_x = (H^+)_x \cdot [H_2PO_4^-]_x / K_{p1}' \qquad (2.5)$$

and substituting Eq. 2.5 for $[H_3PO_4]_x$ and Eq. 3.2 for P_{Tx} in Eq. 3.1, multiplying through by f_m, rewriting K_{p1}' and $(H^+)_x$ in p-notation and rearranging yields

$$S_x = f_m\,[H_3PO_4]_x(V_s + V_x) = \frac{f_m P_T\, 10^{-pK_{p1}'}}{10^{-pH_x} + 10^{-pK_{p1}'}} \cdot V_s \qquad (2.6)$$

The calculation of the terms O_x, S_x and R_x for the V_x and pH_x values observed in the titration given in the example in the paper is listed in Table 2.1. Comparing these terms with the terms of the $H_2CO_3/H_2PO_4^-/HAc/NH_4^+$ alkalinity extended Gran function it can be seen that O_x and R_x are unchanged as expected but S_x, the term associated with the phosphate system, is 20 times larger than Q_x. The high S_x values produce high values for the extended Gran function F_x' about 5 times higher. In a plot of F_x' versus V_x (Fig. 7 bottom), the points lie far below the horizontal V_x axis. To obtain V_E at the intersection point with the horizontal axis (where $F_x' = 0$) from such a plot requires a long extrapolation, which can lead to significant errors. It may be thought that the problem can be overcome by including more data from pH values above 4 and/or below 3. However, the titration should be restricted to $3 < pH < 4$ because at $pH > 4$, the carbonate system still exerts some buffer capacity and at $pH < 3$, the changes in pH for acid added become very small and therefore subject to increasing error.

A solution to the problem is to replace the H_3PO_4 reference species of the phosphate system with $H_2PO_4^-$, as was done in the development of Eq. 53. This replaces the S_x term (Eq. 2.6) by Q_x (Eq. 54a). Now + $[H_3PO_4]_x$ appears in the extended Gran function instead of − $[H_2PO_4^-]_x$ (Eq. 53). The contribution of the H_3PO_4 species to the alkalinity is of approximately the same

TABLE 2.1
EXTENDED GRAN FUNCTION CALCULATION FROM MEASUREMENTS OF pH FOR INCREMENTAL VOLUMES OF ACID ADDED GIVING THE CALCULATED O_x, S_x and R_x VALUES FOR THE $H_2CO_3^* / H_3PO_4 / HAc / NH_4^+$ ALKALINITY (COMPARE WITH TABLE 3).

V_x mℓ	pH_x	O_x mmol.10^3	S_x mmol.10^3	R_x mmol.10^3	F'_x $-O_x + S_x + R_x$
0,0	8,07	–	–	–	–
8,1	3,65	24,2	172,9	28,8	177,5
8,2	3,595	27,5	172,3	25,6	170,4
8,3	3,525	32,5	171,4	22,0	161,1
8,4	3,465	37,2	170,5	19,4	152,7
8,5	3,412	42,0	169,5	17,2	144,8
8,6	3,369	46,4	168,7	15,7	138,0
8,7	3,320	52,0	167,7	14,1	129,8
8,8	3,267	58,8	160,5	12,5	120,2
8,9	3,217	66,1	165,2	11,2	110,4
9,0	3,176	72,7	164,1	10,2	101,6
9,1	3,137	79,6	162,9	9,4	92,7
9,2	3,107	85,4	161,9	8,8	85,3
9,3	3,070	93,0	160,7	8,1	75,7
9,4	3,038	100,2	159,5	7,5	68,8
9,5	3,010	107,0	158,4	7,0	58,4

magnitude as that of the other species in the extended Gran function. The improvement can be seen comparing Q_x in Table 3 with S_x in Table 2.1.

Appendix 3

Formulation of equations for O_x (Eq. 54a) and R_x (Eq. 54b) in the extended Gran function equation (Eq. 53).

The objective is to write each of the terms $[H_3PO_4]_x$ and $[Ac^-]_x$ in Eq. 53 as functions of the measured pH_x and known total species concentrations P_T and A_T respectively.

For f_m $[H_3PO_4]_x$:

For pH values below 6, the $[H_2PO_4^-]$ and $[PO_4^{3-}]$ concentrations are more than an order of magnitude lower than the $[H_2PO_4^-]$ and $[H_3PO_4]$ concentrations (Fig. 4) so that for these pH values, the total phosphate species concentration, P_{Tx}, very closely approximates to:

$$P_{Tx} \approx [H_3PO_4]_x + [H_2PO_4^-]_x \qquad (3.1)$$

where P_{Tx} = the total phosphate species concentration in the sample after addition of V_x ℓ strong acid,

$$= P_T . V_s / (V_s + V_x) \qquad (3.2)$$

P_T = total phosphate species concentration in the sample prior to titration.

Writing $[H_2PO_4^-]$ in terms of $(H^+)_x$ and $[H_3PO_4]_x$ using the first dissociation equation for the phosphate weak acid/base system:

$$[H_2PO_4^-]_x = K'_{p1} \cdot [H_3PO_4]_x / (H^+)_x \qquad (3.3)$$

Substituting for $[H_2PO_4^-]_x$ from Eq. 3.3, and for P_{Tx} from Eq. 3.2, into Eq. 3.1 and simplifying yields:

$$[H_3PO_4]_x = \frac{P_T.(H^+)_x}{(H^+)_x + K'_{p1}} \cdot \frac{V_s}{V_s + V_x}$$

Multiplying through by the monovalent ion activity coefficient f_m and rewriting (H^+) and K_{p1} in p-notation gives the required expression:

$$f_m\ [H_3PO_4]_x = \frac{10^{-pH_x}}{10^{-pH_x} + 10^{-pK'_{p1}}} \cdot \frac{f_m P_T V_s}{V_s + V_x} \quad \text{(mol)} \qquad (51)$$

For f_m $[Ac^-]_x$:

A similar approach to that above is now applied to the acetate system. The total acetate species concentration in the titrate after addition of V_x ℓ strong acid, A_{Tx}, is:

$$A_{Tx} = [HAc]_x + [Ac^-]_x \qquad (3.4)$$
$$= A_T . V_s (V_s + V_x) \qquad (3.5)$$

where A_T = total acetate species concentration in the sample prior to titration.

Writing $[HAc]_x$ in terms of $(H^+)_x$ and $[Ac^-]_x$ using the equilibrium equation for this species gives:

$$[HAc]_x = (H^+)_x . [Ac^-]_x / K'_a \qquad (3.6)$$

Substituting for $[HAc]_x$ from Eq. 3.6, and for A_{Tx} from Eq. 3.5, into Eq. 3.4 yields:

$$[Ac^-]_x = \frac{A_T K'_a}{(H^+)_x + K'_a} \cdot \frac{V_s}{V_s + V_x}$$

Multiplying through by f_m and rewriting $(H^+)_x$ and K'_a in p-notation gives the required expression:

$$f_m[Ac^-]_x = \frac{10^{-pK'_a}}{10^{-pH_x} + 10^{-pK'_a}} \cdot \frac{f_m A_T V_s}{V_s + V_x} \text{ (mol)} \quad (52)$$