

Kinetic-based model for mixed weak acid/base systems

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Abstract

This paper describes the development of a simple kinetic model for mixed weak acid/base systems. In the model, the weak acid/base equilibria are formulated in terms of the kinetics of the forward and reverse reactions for the dissociation of the weak acid/bases. The parameter (compound) H^+ is also explicitly included in the model, so that pH can be calculated directly. The weak acid/bases included are water, carbonate, ammonium, phosphate and short-chain fatty acids. However, the approach used to develop the model is general, and can be applied to include any other weak acid/base of importance. Precipitation of $CaCO_3$ and gaseous exchange of CO_2 also have been included. The model and the approach on which it is based have been validated by comparing model predictions to those obtained from equilibrium-chemistry-based models; good correlation was obtained. Compared to the equilibrium chemistry approach to modelling mixed weak acid/base systems, the kinetic approach offers several advantages. In particular, the use of kinetics will facilitate integration of the weak acid/base model with other kinetic models (biological, chemical or physical). For example, the model presented here can be readily integrated with the existing biological kinetic models for wastewater treatment systems; to extend application of these models to situations where an estimate for pH is essential. Furthermore, by providing an estimate for pH and for the species making up the weak acid/bases, the model will simplify inclusion of chemical and physical processes, where these are of importance.

Introduction

To aid the design and operation of, and research into, conventional biological waste-water treatment systems, a variety of mathematical models has been developed. With few exceptions, these models have focused almost exclusively on the biologically mediated processes that lead to the removal of, or change in, the particular compounds of interest. For example, models for the activated sludge system have progressively included the biologically mediated processes of COD removal, nitrification, denitrification and biological excess phosphorus removal (Dold et al., 1980; 1991; Van Haandel et al., 1981; Henze et al., 1987; Wentzel et al., 1992; Henze et al., 1995). In this group of models, by focusing on the biological processes usually it is implicitly assumed that:

- The biological processes dominate the system response; and that
- chemical and physical processes (e.g. precipitation and gas stripping respectively) play an insignificant role compared to the biological processes and accordingly can be neglected,
- compounds not directly involved in the biological processes or not of interest, even though present, do not significantly influence the behaviour, and
- the biological processes take place within a regime of constant pH.

This has restricted application of these models to situations where the assumptions remain valid. For the activated sludge system treating municipal or similar types of waste waters, where the organics are present at relatively high concentrations compared to the nutrient (N & P) concentrations, these assumptions usually are valid. For example, in the nitrification of municipal waste

waters it usually is reasonable to assume that the biological processes dominate and that there is sufficient buffer capacity present to absorb the generation of hydrogen ions (H^+) and loss of CO_2 so that the pH does remain approximately constant; some of the models have included the parameter "alkalinity" to check that this condition is in fact true (e.g. Dold et al., 1991). However, in the treatment of a number of waste waters the assumptions are not valid and the models cannot be applied. For example, in the nitrification of waste waters with low buffer capacity and/or high N concentrations, or in the treatment of waste waters where the generation or utilisation of short-chain fatty acids (SCFA), e.g. acetic, propionic, is significant, the assumption that the pH remains essentially constant no longer can be accepted.

In particular, the models cannot be applied to situations where chemical and physical processes do play a significant role, and so cannot be neglected. For example, one such category of waste waters is that where the organics are present at relatively low concentrations compared to the nutrients. These waste waters, termed high nutrient, low organic carbon, are generated in a number of municipal waste treatment operations such as trickling filter effluents, anaerobic digester supernatants, activated sludge dewatering liquors, landfill leachates, septic tank effluents and waste sludge lagoon effluents. In the treatment of these waste waters, chemical and physical processes can be expected to play a significant role and no longer can be neglected; these processes and their interactions with each other and with the biological processes will have to be included in any model of these treatment systems. In other words, a model integrating the biological, physical and chemical processes of importance will be required. Deterministic models that quantitatively describe the stoichiometry and kinetics of the biological processes are well advanced, e.g. IAWQ Model No. 1 (Henze et al., 1987; Dold et al., 1991) and No. 2 (Henze et al., 1995). Similar models need to be developed for the chemical and physical processes, and integrated with the biological models. Models including chemical and physical processes will require that the pH parameter/compound is incorporated and accurately determined, as pH is of fundamental importance in these processes, significantly

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Received 31 December 1996; accepted in revised form 4 July 1997.

influencing them.

From the discussion above, it is evident that application of the existing biological models for waste-water treatment systems can be enhanced by including **pH as a parameter/compound**. Further, including the pH will facilitate the integration of chemical and physical processes into the biological models, and the development of independent physical/chemical models. Including the pH in turn will require that all the weak acid/bases present that influence the pH (e.g. carbonate system, SCFA) also will have to be included in some fashion. That is, weak acid/base chemistry must form an integral part of the models. This paper sets out the development of a model that describes mixed weak acid/base chemistry. In the development of this model, requirements were that it must be able to be readily integrated with:

- the existing biological models, so that the "background" chemistry within which the biological processes take place can be described;
- chemical and physical processes, so that it can form the basis for the development of models describing systems where these processes are of importance.

Scope of model

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 and water weak acid/bases dominate to such a degree that usually all other weak acid/bases can be neglected. In municipal waste waters, however, the ammonia and phosphate weak acid/bases are present and in anaerobic treatment systems additionally the SCFA (e.g. acetate, propionate) weak acid/bases are generated/utilised. All these weak acid/base systems may be present at such concentrations relative to the carbonate weak acid/base, that they exert a significant influence on the pH established. Accordingly, to include the pH parameter in models of waste-water treatment systems, the weak acid/bases that need to be considered are the water, carbonate, ammonia, phosphate and SCFA (represented by acetate). Any other weak acid/base system that significantly influences pH also can be included, by following the approach set out in this paper.

In incorporating these weak acid/base systems in a model, their chemical interactions in the aqueous phase would necessarily require inclusion. Furthermore, inclusion of the carbonate weak acid/base would require that the phase exchanges between the aqueous phase of this weak acid/base and the gaseous (via carbon dioxide exchange) and solid (via CaCO_3 precipitation or dissolution) phases must be included.

Thus, the model must take cognizance of three phases, i.e.:

- **Single-phase aqueous systems**
 - Aqueous mixed weak acid/base systems including water, carbonate, phosphate, ammonia and SCFA species, the non-carbonate systems without phase changes.
- **Two-phase systems**
 - Solid/aqueous
 - Chemical precipitation of CaCO_3
 - Gas/aqueous
 - Exchange between dissolved carbonate species and gaseous CO_2 .

The above must then be integrated to give a model for:

- **Three-phase systems**
 - Solid/liquid/gas

Equilibrium-based approach to modelling mixed weak acid/base chemistry

Conventionally, in working with mixed weak acid/base systems one is confronted with three types of problems (Loewenthal et al., 1989), viz.:

- estimation of the concentrations of the species of each of the weak acid/base systems, called characterisation;
- estimation of the amount and type of chemicals to be added/removed to change the pH and species concentration to desired values, called dosing estimation; or conversely,
- estimation of the final state of a water after addition/removal of a known amount of a specified chemical to/from a known initial state.

Including weak acid/base chemistry in models for application to waste-water treatment systems would encompass elements of all three types of problems. Both numerical and graphical solution procedures to address these types of problems have been developed (e.g. Loewenthal et al., 1989; 1991). These procedures are based on equilibrium chemistry. The basis for these procedures will be described *briefly* below, to assess their potential for use; the intention is not to provide an exhaustive review, the reader is referred to the cited texts for details.

In addition to water a weak acid/base will dissociate; for example, consider the weak acid/base HA:



The degree of dissociation will depend on the pH, dissociation constants, the total species concentration of the weak acid/base and the ionic strength of the solution. Conventionally, it is accepted that the rate of dissociation is so rapid that the weak acid/base is at equilibrium, with the rates of the forward and reverse dissociation reactions being equal. Accepting the equilibrium condition, by using equilibrium chemistry the weak acid/base individual species concentrations can be formulated in terms of total species concentration, dissociation constants and pH (Loewenthal et al., 1989). Thus, if the total species concentrations of each of the weak acid/bases present are known and the pH has been measured, then the concentrations of the dissociated and undissociated species for each of the weak acid/bases can be calculated via the appropriate dissociation and mass balance equations. With each of the weak acid/base species determined, the solution is completely characterised.

Thus, to completely characterise the solution, the pH and total species concentrations of all the weak acid/bases are required. Usually the pH is available via potentiometric pH measurement; total species concentrations for each of the weak acid/bases in solution can be measured by conventional wet chemical techniques (e.g. ammonia, phosphate, SCFA) or by specialised techniques such as chromatography (e.g. SCFA) and inorganic carbon analyser (total carbonate species). However, measurement of total carbonate (C_T) using the inorganic carbon analyser presents problems - the instrument is highly specialised, difficult to operate and only available in large laboratories. Furthermore, measurements of C_T with this instrument are very likely to be in

error, due to CO_2 loss/gain on sampling. The practical difficulties in measuring C_T have led to the development using equilibrium chemistry of a substitute parameter, H_2CO_3^* alkalinity; if H_2CO_3^* alkalinity and pH are known, C_T can be determined (Loewenthal and Marais, 1976; Loewenthal et al., 1986). Methods to determine H_2CO_3^* alkalinity from a total alkalinity titration of solutions containing only the carbonate weak acid/base and mixtures of weak acid/bases have been developed (Gran, 1952; Loewenthal et al., 1989; Moosbrugger et al., 1992). The H_2CO_3^* alkalinity has the merit that CO_2 loss does not affect its value (provided that carbonate precipitation does not take place).

Accordingly, with mixtures of weak acid/bases in solution, provided the appropriate measurements (pH, total species concentrations, total alkalinity, and hence H_2CO_3^* alkalinity) are available, through the use of equilibrium chemistry it is possible to completely characterise the solution. Having characterised the solution, the next important aspect is to determine the chemical type and dosage to achieve a final desired state (also called dosing estimation) or conversely to determine the final state of a water after addition/removal of a known amount of a specified chemical; both these problems are collectively termed chemical conditioning. **In chemical conditioning the principle difficulty is that the pH does not change in a simple stoichiometric fashion** with changes in concentrations of the weak acid/bases, that is, with addition or removal of strong or weak acid/base species. To overcome this problem, chemical conditioning estimation procedures have been developed using equilibrium chemistry (e.g. Loewenthal et al., 1991). In terms of these procedures, it is recognised that the solution alkalinity does change in a simple stoichiometric fashion with chemical dosing, as do the total species concentrations of the weak acid/bases. Knowing the solution alkalinity and the total species concentration of each weak acid/base, the pH can be calculated from equilibrium chemistry, or, knowing the pH and all capacity parameters except one (e.g. one total species concentration), the unknown capacity parameter can be calculated from equilibrium chemistry.

From the above, for aqueous systems where only chemical and physical processes take place, by using an equilibrium-based chemistry approach that includes the concepts of alkalinity, chemical conditioning problems can be largely resolved. This would suggest that a similar approach may be successful for integrating weak acid/base chemistry into the kinetically based biological models. In concept this approach would be as follows: Solution alkalinity would be included as a compound in the model. Any kinetic transformation would act on the compounds and the solution alkalinity, changing their concentrations. Knowing the new solution alkalinity and total species concentrations of all the weak acid/base systems present (e.g. SCFA, ammonium, phosphate, carbonate), the pH can be calculated using equilibrium chemistry. The calculated pH then can be used to speciate the weak acid/bases, i.e. determine the concentrations of the individual species making up the weak acid/base (e.g. NH_4^+ and NH_3 making up the ammonia/ammonium weak acid/base). The kinetic transformations, the rates of which depend on the concentrations of individual weak acid/base species, then act on the compounds (including the weak acid/base species) and the solution alkalinity. The cycle is repeated at every time/space step until a "steady state" solution is reached (i.e. constant compound concentrations and pH for the time/space step). However, although in concept this approach is feasible, it does present practical difficulties in implementation:

- The equilibrium-based chemical conditioning algorithms have been developed for situations where the total species concentration of a single or few weak acid/bases is changed in a simple fashion by adding or removing species; in the integrated weak acid/base chemistry and biological models, a number of different processes will act on the total species concentrations of a number of weak acid/bases simultaneously. This makes solution of the equilibrium-based algorithms difficult.
- In the equilibrium-based chemical conditioning algorithms, the reference species for the solution alkalinity have to be carefully selected, so that the solution alkalinity stays constant or changes in a simple stoichiometric fashion with dosing (Loewenthal et al., 1991). However, in the integrated models to be developed it may not prove possible to select reference species *ab initio*, since there is no surety as to which species will change. Furthermore, the species that do change will vary from situation to situation, so that new reference species would have to be selected for each particular case, an undesirable event. Lastly, processes may act on both the dissociated and undissociated weak acid/base species simultaneously so that selection of the correct reference species may not be obvious, or even possible.
- Combining equilibrium chemistry with kinetic-based models is neither convenient nor efficient: The repeated calculations necessary to reach a "steady state" solution between the kinetics and equilibrium chemistry probably would cause any solution procedure to be unacceptably slow; in fact, there is not even surety that a "steady state" solution would be reached.

Due to the difficulties with the traditional equilibrium-chemistry-based approach to modelling weak acid/base systems, as described above, it was decided to develop a new approach.

Development of kinetic model for mixed weak acid/base systems

As an alternative to the traditional equilibrium-chemistry-based models for mixed weak acid/base systems, a kinetic-based model would seem to offer considerable advantages: Using a kinetic-based modelling approach will resolve the difficulties identified above with the equilibrium chemistry approach; in particular, a kinetic-based model would expedite integration with the existing biological models, and extension to include chemical and physical processes, both important requirements identified for the model. In this section, the development of such a kinetic-based model for mixed weak acid/bases is described - aqueous phase mixed weak acid/base chemistry; CaCO_3 precipitation; and CO_2 exchange.

Aqueous phase weak acid/base chemistry

From the discussion in the previous sections above, it is evident that the principle requirement for a mixed weak acid/base chemistry model is that the pH is accurately determined. In a kinetic-based modelling approach, H^+ is included explicitly in the model as a compound (in mole units); pH can be calculated directly from H^+ via $\text{pH} = -\log(\text{H}^+) = -\log f_m[\text{H}^+]$. Further, all weak acid/base species that significantly influence the pH are included as compounds (in mole units), and weak acid/base equilibria are described in terms of the kinetics of the forward and reverse

reactions for the dissociation of these weak acid/bases. For example, consider the dissociation for the ammonium/ammonia weak acid/base. The dissociation equation is given by:



The rate of the forward reaction is:

$$r_f = K_f(\text{NH}_4^+) = K_f f_m [\text{NH}_4^+] \quad (3a)$$

$$= K_f' [\text{NH}_4^+] \quad (3b)$$

where:

- r_f = rate of forward reaction
- K_f = specific rate constant for the forward reaction
- () = activity
- f_m = monovalent activity coefficient (see Loewenthal et al., 1989)
- [] = molar concentration
- K_f' = apparent specific rate constant for the forward reaction

and the rate of the reverse reaction is:

$$r_r = K_r (\text{NH}_3)(\text{H}^+) = K_r [\text{NH}_3] f_m [\text{H}^+] \quad (4a)$$

$$= K_r' [\text{NH}_3][\text{H}^+] \quad (4b)$$

where:

- r_r = rate of reverse reaction
- K_r = specific rate constant for the reverse reaction
- K_r' = apparent specific rate constant for the reverse reaction.

The dissociation equation for the ammonia/ammonium weak acid/base can be represented by these two half-reactions and both kinetic equations are included in the model as separate processes. Similarly, the kinetics of the forward and reverse dissociation equations for all weak acid/bases of importance are included. The apparent specific rate constants of the forward and reverse dissociation reactions are selected such that the rates are so rapid that equilibrium can be considered to be reached effectively instantaneously. Further, the **relative** values for the apparent specific rate constants will determine what that equilibrium condition will be. Thus, through careful selection of the apparent specific rate constants of the forward and reverse reactions for all the weak acid/base dissociation reactions, the concentrations of all the weak acid/bases' species will effectively be at a "pseudo-equilibrium", and their "equilibrium" concentrations can be made to correspond to those determined by true equilibrium chemistry. Since H^+ (and correspondingly pH) is included as a compound in the model, and also is included in the kinetic equations for the dissociation reactions, its value at the "pseudo-equilibrium" also will be calculated. If any of the weak acid/base species is added or removed from solution (including H^+), the kinetic equations for the forward and reverse dissociation reactions will cause the relative species concentrations (including H^+) to readjust very rapidly (effectively instantaneously) to the new condition. Since all the weak acid/bases have the species H^+ in common, all would be influenced and so readjust. In this manner a new "pseudo-equilibrium" condition is established.

The values of the apparent specific rate constants for the forward and reverse reactions that give rise to weak acid/base species concentrations that correspond to true equilibrium

chemistry can be determined from the equilibrium constant. For the same ammonia/ammonium system, from the law of mass action, at equilibrium:

$$r_f = r_r \quad (5a)$$

$$K_f' [\text{NH}_4^+] = K_r' [\text{NH}_3] [\text{H}^+] \quad (5b)$$

$$K_f' / K_r' = [\text{NH}_3] [\text{H}^+] / [\text{NH}_4^+] = K_n' \quad (5c)$$

where:

- K_n' = apparent equilibrium constant for the ammonium system.

Since the forward and reverse dissociation reactions are very rapid, the rate of the reactions cannot be measured. However, from a practical point of view, the exact actual value for the reaction rate is of little importance. In selecting values for the apparent specific rate constants, to ensure the reactions are effectively instantaneous, one of the rate constants (K_f') was given a very high theoretical value (new "equilibrium" achieved in < 10 s). To ensure that the kinetically established equilibrium corresponds to true equilibrium chemistry, the value for the other rate constant (K_r') was calculated through the relationship with the apparent equilibrium constant, Eq. (5c).

Using this kinetic-based approach to weak acid/base chemistry, a model was developed for aqueous mixtures of the carbonate, ammonium, phosphate and SCFA (represented by acetate) weak acid/bases. This model is illustrated in matrix format (Henze et al., 1987) in Table 1; values for the stoichiometric and kinetic constants are listed in Table 2. **The approach is general, and can be applied to include any weak acid/base in the model.**

Kinetics of calcium carbonate (CaCO_3) precipitation

Since the carbonate weak acid/base system is included in the model and plays a crucial role in establishing the pH, processes/reactions influencing the concentration of carbonate species also need to be included. One such process is the precipitation of CaCO_3 . For surface-controlled processes, the rate of CaCO_3 precipitation can be formulated by following the theory of Koutsoukos et al. (1980): For many sparingly soluble salts $\text{M}_{v^+} \text{A}_{v^-}$, the rate of crystallisation can be expressed by an equation of the form (Koutsoukos et al., 1980):

$$\frac{d}{dt} \text{M}_{v^+} \text{A}_{v^-} = -k' s [([M^{m^+}]^{v^+} [A^{a^-}]^{v^-})^{1/v} - ([M^{m^+}]_0^{v^+} [A^{a^-}]_0^{v^-})^{1/v}]^n \quad (6)$$

where:

- $[M^{m^+}]$, $[A^{a^-}]$ and $[M^{m^+}]_0$, $[A^{a^-}]_0$ are the concentrations in mole units of crystal lattice ions in solution at time t and at equilibrium respectively. At equilibrium $[M^{m^+}]_0^{v^+} [A^{a^-}]_0^{v^-} = K_{sp}'$ where K_{sp}' is the apparent solubility product of the salt.
- k' is the apparent precipitation rate constant
- s is proportional to the total number of available growth sites on the added seed material
- v^+ is the total number of cationic species
- v^- is the total number of anionic species
- $v = v^+ + v^-$
- The number n is determined experimentally and equals 2 for a number of divalent sparingly soluble salts

TABLE 1 MATRIX REPRESENTATION OF THE KINETIC MODEL FOR AN AQUEOUS MIXTURE OF WEAK ACID/BASE SYSTEMS. PRECIPITATION OF CaCO ₃ AND EXCHANGE OF CO ₂ HAVE ALSO BEEN INCLUDED. (NOTE THAT THE CONCENTRATION OF THE COMPOUND CO ₂ (g) IS KEPT CONSTANT; IT IS INCLUDED IN THE MATRIX ONLY FOR CONTINUITY)																	
Compound→ Process↓	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	Rate	
	NH ₄ ⁺	NH ₃	H ₂ CO ₃ * HCO ₃ ⁻	HCO ₃ ⁻	CO ₃ ²⁻	CO ₂ (g)	H ⁺	OH ⁻	H ₃ PO ₄	H ₂ PO ₄ ⁻	HPO ₄ ²⁻	PO ₄ ³⁻	HA	A ⁻	Ca ²⁺		
Forward dissociation of NH ₄ ⁺	-1	1					1									K' _{in} [NH ₄ ⁺]	
Reverse dissociation of NH ₄ ⁺	1	-1					-1									K' _{rn} [NH ₃][H ⁺]	
Forward dissociation of H ₂ CO ₃ *			-1	1			1									K' _{fel} [H ₂ CO ₃ *]	
Reverse dissociation of H ₂ CO ₃ *			1	-1			-1									K' _{rel} [HCO ₃ ⁻][H ⁺]	
Forward dissociation of HCO ₃ ⁻				-1	1		1									K' _{fec} [HCO ₃ ⁻]	
Reverse dissociation of HCO ₃ ⁻				1	-1		-1									K' _{rec2} [CO ₃ ²⁻][H ⁺]	
Dissolution of CO ₂			1			-1										K' _{feo2} [CO ₂ (g)]	
Expulsion of CO ₂ from solution			-1			1										K' _{reo2} [H ₂ CO ₃ *]	
Forward dissociation of H ₃ PO ₄							1	-1	1							K' _{fp1} [H ₃ PO ₄]	
Reverse dissociation of H ₃ PO ₄							-1	1	-1							K' _{fp1} [H ₂ PO ₄ ⁻][H ⁺]	
Forward dissociation of H ₂ PO ₄ ⁻							1		-1	1						K' _{fp2} [H ₂ PO ₄ ⁻]	
Reverse dissociation of H ₂ PO ₄ ⁻							-1		1	-1						K' _{fp2} [HPO ₄ ²⁻][H ⁺]	
Forward dissociation of HPO ₄ ²⁻							1			-1	1					K' _{fp3} [HPO ₄ ²⁻]	
Reverse dissociation of HPO ₄ ²⁻							-1									K' _{fp3} [PO ₄ ³⁻][H ⁺]	
Forward dissociation of HA							1						-1	1		K' _{fa} [HA]	
Reverse dissociation of HA							-1						1	-1		K' _{ra} [A ⁻][H ⁺]	
Forward dissociation of water							1	1								K' _{fw}	
Reverse dissociation of water							-1	-1								K' _{rw} [H ⁺][OH ⁻]	
Precipitation of CaCO ₃					-1										-1	K' _{rcac03} ([Ca ²⁺] ^{1/2} [CO ₃ ²⁻] ^{1/2} ·K' _{spCaCO3}) ^{1/2}	
Units	mol/l	mol/l	mol/l	mol/l	mol/l	mol/l	mol/l	mol/l	mol/l	mol/l	mol/l	mol/l	mol/l	mol/l	mol/l	mol/l	

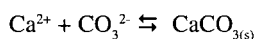
TABLE 2a
KINETIC CONSTANTS FOR WEAK ACID/BASES IN MIXED WEAK ACID/BASE MODEL (TABLE 1);
 f_m, f_d AND f_i ARE MONO-, DI- AND TRIVALENT ACTIVITY COEFFICIENTS RESPECTIVELY,
SEE LOEWENTHAL ET AL.(1989); FOR pK VALUES, SEE TABLE 2c

Process	Specific rate constants					
	Forward dissoc. reaction		Reverse dissoc. reaction		Equilibrium constant	
	Symbol	Value	Symbol	Value	Symbol	Value
Ammonia $\text{NH}_4^+ \rightleftharpoons \text{NH}_3 + \text{H}^+$	K'_{fn}	$K'_{rn} \cdot K'_n$	K'_{in}	$10^{12} (/s)$	K'_n	10^{-pK_n}
Carbonate 1 $\text{H}_2\text{CO}_3^* \rightleftharpoons \text{HCO}_3^- + \text{H}^+$	K'_{fc1}	$K'_{rc1} \cdot K'_{c1}$	K'_{ic1}	$10^7 (/s)$	K'_{c1}	$10^{-pK_{c1}/f_m^2}$
Carbonate 2 $\text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+$	K'_{fc2}	$K'_{rc2} \cdot K'_{c2}$	K'_{ic2}	$10^{10} (/s)$	K'_{c2}	$10^{-pK_{c2}/f_d}$
Phosphate 1 $\text{H}_3\text{PO}_4 \rightleftharpoons \text{H}_2\text{PO}_4^- + \text{H}^+$	K'_{fp1}	$K'_{rp1} \cdot K'_{p1}$	K'_{ip1}	$10^8 (/s)$	K'_{p1}	$10^{-pK_{p1}/f_m^2}$
Phosphate 2 $\text{H}_2\text{PO}_4^- \rightleftharpoons \text{HPO}_4^{2-} + \text{H}^+$	K'_{fp2}	$K'_{rp2} \cdot K'_{p2}$	K'_{ip2}	$10^{12} (/s)$	K'_{p2}	$10^{-pK_{p2}/f_d}$
Phosphate 3 $\text{HPO}_4^{2-} \rightleftharpoons \text{PO}_4^{3-} + \text{H}^+$	K'_{fp3}	$K'_{rp3} \cdot K'_{p3}$	K'_{ip3}	$10^{15} (/s)$	K'_{p3}	$10^{-pK_{p3} \cdot f_d / (f_i \cdot f_m)}$
SCFA $\text{HA} \rightleftharpoons \text{A}^- + \text{H}^+$	K'_{fa}	$K'_{ra} \cdot K'_a$	K'_{ia}	$10^7 (/s)$	K'_a	$10^{-pK_a/f_m^2}$
Water $\text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{H}^+$	K'_{fw}	$K'_{rw} \cdot K'_w$	K'_{iw}	$10^{10} (/s)$	K'_w	$10^{-pK_w/f_m^2}$

TABLE 2b
CONSTANTS FOR CO₂ EXCHANGE AND CaCO₃ PRECIPITATION IN MIXED WEAK ACID/BASE MODEL (TABLE 1);
FOR pK VALUES, SEE TABLE 2c

Process	Constants			
	Description	Symbol	Value	Units
CaCO ₃ precipitation $\text{Ca}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{CaCO}_{3(s)}$	Specific rate of ppt	$K'_{rc\text{CaCO}_3}$	0.0171	/s
	Equilibrium constant	$K'_{sp\text{CaCO}_3}$	$10^{-pK_{sp\text{CaCO}_3}/f_d^2}$	-
CO ₂ exchange $\text{CO}_{2\text{gas}} \rightleftharpoons \text{H}_2\text{CO}_3^*$	Dissolution of CO ₂	$K'_{rc\text{CO}_2}$	$K'_{rc\text{CO}_2} \cdot K'_{eq\text{CO}_2}$	/s
	Expulsion of CO ₂	$K'_{rc\text{CO}_2}$	10^4	/s
	Equilibrium constant	$K'_{eq\text{CO}_2}$	$K_{H,\text{CO}_2} \cdot RT$	-
	Henry's law constant	K_{H,CO_2}	$10^{-pK_{H,\text{CO}_2}}$	mol/l·atm
	Universal gas constant	R	$8.20575 \cdot 10^{-2}$	l·atm/K·mol

Applying this equation to the precipitation of CaCO₃, where:



and $v^+ = 1$, $v^- = 1$ and $v = 2$, then:

$$\frac{d}{dt} [\text{CaCO}_3] = -k'_c s [[\text{Ca}^{2+}]^{1/2} [\text{CO}_3^{2-}]^{1/2} - K'_{sp}]^2 \quad (7)$$

In Eq. (7), accepting that no seed material has been added, the rate no longer depends on the available number of growth sites (s) so that the rate constant k'_c 's can be replaced by a single precipitation rate constant $K'_{rc\text{CaCO}_3}$. This equation can also be derived by using the hypothesis of Davies and Jones (Benjamin et al., 1976; Sturrock et al., 1976) and, accordingly, has been accepted for use in the model, see Tables 1 and 2. The equation applies only to the

TABLE 2c VALUES FOR pK CONSTANTS IN MIXED WEAK ACID/BASE MODEL (TABLES 2a AND 2b) (T IS TEMPERATURE IN KELVIN)	
pK constant	Formulation
1940s Database (Loewenthal and Marais, 1976; Loewenthal et al., 1989)	
pK _n	2 835.8/T - 0.6322 + 0.00123•T
pK _{c1}	3 404.7/T - 14.8435 + 0.03279•T
pK _{c2}	2 902.4/T - 6.498 + 0.02379•T
pK _{p1}	799.3/T - 4.5535 + 0.01349•T
pK _{p2}	1 979.5/T - 5.3541 + 0.01984•T
pK _{p3}	12.023
pK _a	1 170.5/T - 3.165 + 0.0134•T
pK _{spCaCO3}	0.01183•T + 8.03
1980s Database (Friend and Loewenthal, 1992)	
pK _{c1}	356.309 + 0.0609196•T - 21 834.4/T - 126.834•logT + 1.68492•10 ⁶ /T ²
pK _{c2}	107.887 + 0.0325285•T - 5 151.79/T - 38.9256•logT + 563 714/T ²
pK _{H,CO2}	-2 025.3/T - 0.0104•T + 11.365
pK _w	14.00

precipitation of CaCO₃ and not to the dissolution; in the model the equation is valid only if $[Ca^{2+}]^{1/2} [CO_3^{2-}]^{1/2} > K'_{sp}$ - this condition must be checked.

Carbon dioxide (CO₂) exchange

In solution the carbonate weak acid/base consists of four species, viz. CO₂ dissolved; carbonic acid (H₂CO₃); bicarbonate (HCO₃⁻); and carbonate (CO₃²⁻). The ratio CO₂ dissolved: H₂CO₃ is fixed and equal to 99.76 : 0.24 at 25°C and is independent of pH and ionic strength. Accordingly, these two species are dealt with as a single combined species, H₂CO₃^{*} (Stumm and Morgan, 1970), i.e.:

$$[H_2CO_3^*] = [CO_2 \text{ dissolved}] + [H_2CO_3] \quad (8)$$

The CO₂ dissolved, and hence H₂CO₃^{*}, tends to equilibrium with the partial pressure of CO₂ (gas) outside the liquid, i.e.:



or equivalently:



This gives rise to CO₂ exchange at the liquid/gas interface, resulting in loss or gain of H₂CO₃^{*} in the solution, and accordingly in total carbonate species concentration. Thus, CO₂ loss or gain would need to be included in the model. This can be done by following the same approach used for the weak acid/base dissociation reactions, i.e. by modelling separately the rate of the forward and reverse reactions in Eq. (9b). For the forward reaction:

$$r_f = K'_{rcO_2} [CO_2 (g)] \quad (10)$$

where:

r_f = rate of forward reaction, Eq. (9b)
 K'_{rcO_2} = apparent specific rate constant for forward reaction.

Similarly, for the reverse reaction:

$$r_r = K'_{rcO_2} [H_2CO_3^*] \quad (11)$$

where:

r_r = rate of reverse reaction, Eq. (9b)
 K'_{rcO_2} = apparent specific rate constant for reverse reaction.

The approach of modelling the forward and reverse reactions separately has been used to include CO₂ exchange in the model, see Table 1. Note that in the model the concentration of CO₂(g) is kept constant; the CO₂(g) is included as a compound in the model only for continuity. The constant concentration of CO₂(g) can be calculated from the partial pressure of CO₂ using Dalton's law of partial pressure (Stumm and Morgan, 1970):

$$[CO_2 (g)] = pCO_2/RT \quad (12)$$

where:

pCO_2 = partial pressure of CO₂ (atm)
 R = universal gas constant
 = 8.20575 · 10⁻² (l atm/K/mol)
 T = temperature in Kelvin

In Eqs. (10) and (11) values are required for the apparent specific rate constants for the forward (K'_{rcO_2}) and reverse (K'_{rcO_2}) reactions respectively. For the cases to be examined in this paper (see later), only the equilibrium condition will be considered so that exact values for the specific rate constants are not required; the only requirement is that equilibrium must be reached by the end of the simulation. However, the relative values for K'_{rcO_2} and K'_{rcO_2} are important since the relative values will establish the equilibrium concentration of H₂CO₃^{*}. At equilibrium:

$$r_f = r_r \quad (13)$$

Substituting Eqs. (10) and (11) into Eq. (13) and rearranging gives:

$$\frac{K'_{rCO_2}}{K'_{rCO_2}} = \frac{[H_2CO_3^*]}{[CO_2(g)]} = K'_{eqCO_2} \quad (14a)$$

where:

K'_{eqCO_2} = apparent equilibrium constant for CO_2 exchange

From Eq. (14a):

$$K'_{rCO_2} = K'_{eqCO_2} \cdot K'_{rCO_2} \quad (14b)$$

Thus, if K'_{eqCO_2} is known, by selecting a value for K'_{rCO_2} the relative value for K'_{rCO_2} can be calculated and the correct equilibrium condition will be established giving the correct equilibrium concentration of $[H_2CO_3^*]$. What is required is to determine a value for K'_{eqCO_2} . This can be done by noting that at equilibrium (Stumm and Morgan, 1970):

$$K'_{H,CO_2} = K'_{eqCO_2} / RT \quad (14c)$$

where:

K'_{H,CO_2} = Henry's law constant for CO_2 (mol/l/atm)
 $K'_{eqCO_2} = K'_{D,CO_2}$
 K'_{D,CO_2} = distribution (mass law) constant

Values for the variation in Henry's law constant for CO_2 (K'_{H,CO_2}) with temperature are available in the literature (Friend and Loewenthal, 1992), see Table 2c). From K'_{H,CO_2} , the equilibrium constant (K'_{eqCO_2}) can be calculated using Eq. (14c), and for a selected value for K'_{rCO_2} , K'_{rCO_2} can be calculated using Eq. (14b). Values for K'_{rCO_2} and K'_{rCO_2} used in the simulations are listed in Table 2.

A near identical formulation for CO_2 exchange can be derived from the theories of interphase mass transfer; here the rate of change in the bulk liquid concentration is considered to be proportional to the product of a mass transfer rate constant times a concentration driving force:

$$\frac{dC_L}{dt} = K_{LA} (C_e - C_L) \quad (15)$$

where:

K_{LA} = overall liquid phase mass transfer rate coefficient (d^{-1})
 C_e = equilibrium concentration in the bulk liquid
 C_L = actual concentration in the bulk liquid

With exchange to the atmosphere, from Dalton's and Henry's laws (Stumm and Morgan, 1970), the dissolved CO_2 equilibrium concentration (C_{eCO_2}) is given by:

$$C_{eCO_2} = K_{H,CO_2} \rho CO_2 \quad (16)$$

Substituting the equilibrium CO_2 concentration from Eq. (16) into Eq. (15) and accepting that $C_L = [H_2CO_3^*]$, the rate of exchange of CO_2 is:

$$\frac{dH_2CO_3^*}{dt} = K_{LA,CO_2} (K_{H,CO_2} \cdot \rho CO_2 - [H_2CO_3^*]) \quad (17)$$

This equation is identical to the sum of the forward and reverse reaction rates used in the model (Table 1), substituting for $[CO_2(g)]$ from Eq. (12) and accepting from Eqs. (14b) and (14c) that $K'_{rCO_2} = K'_{H,CO_2} \cdot RT \cdot K'_{rCO_2}$ and that $K'_{rCO_2} = K'_{LA,CO_2}$.

Validation of kinetic-based model

The validity of the kinetic-based model, and of the approach on which it is based need to be tested. This was done by applying the model to chemical conditioning problems. In the past, solving chemical conditioning problems has been achieved by using equilibrium chemistry procedures (e.g. Loewenthal and Marais, 1976, 1983; Loewenthal et al., 1986; 1991). These procedures have been extensively evaluated against a wide range of experimental data. Accordingly, to evaluate the model developed here using the kinetic-based approach, the predictions were compared to the values calculated using the equilibrium-chemistry-based approach of Loewenthal and co-workers. The solution procedures of Loewenthal and co-workers have been used to solve chemical conditioning problems in:

• **Systems dominated by the carbonate weak acid/base system** (Loewenthal and Marais, 1976; Loewenthal et al., 1986; 1988; Friend and Loewenthal, 1992):

- pH/alkalinity/acidity adjustment in stabilisation of water supplies;
- assessment of transient states during which precipitation/dissolution or gas exchange takes place; and
- precipitation of $CaCO_3$ in water softening.

• **Systems containing a mixture of weak acid/base systems** (Loewenthal et al., 1991):

Dosing estimation for the two basic problems in the aqueous phase, i.e.:

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

Chemical conditioning problems for both types of systems have been used to evaluate the model. All model predictions were made using the computer program AQUASIM (Reichert, 1994; Reichert et al., 1995).

Systems dominated by the carbonate weak acid/base system

Examples obtained from Loewenthal et al. (1986) were used to test the model. The results obtained using the kinetic-based model (in AQUASIM) were compared with the results obtained from the equilibrium-based graphical solution procedure using the Modified Caldwell Lawrence (MCL) diagrams (Loewenthal et al., 1986) and from the equilibrium-based computer programs STASOFT I (Loewenthal et al., 1988) and STASOFT III (Friend and Loewenthal, 1992). The MCL diagrams are based on equilibrium constants derived from data obtained in the 1940s, while the equilibrium constants used in STASOFT III are based on data obtained in the 1980s; STASOFT I includes the option to use either set of equilibrium constants. To evaluate the kinetic model, results from the MCL diagrams, STASOFT I and the

TABLE 3a: EXAMPLE 1 RESULTS OBTAINED USING EQUILIBRIUM CONSTANTS FROM THE 1940s DATABASE				
Parameter	Units	Kinetic model	MCL	STASOFT I
H ₂ CO ₃ * alkalinity	mg/l as CaCO ₃	75.9	75	75.9
Ca ²⁺	mg/l as CaCO ₃	95.9	95	95.9
pH		8.13	8.13	8.12
CaCO ₃ precipitation potential	mg/l as CaCO ₃	4.1	5	4.1

TABLE 3b: EXAMPLE 1 RESULTS OBTAINED USING EQUILIBRIUM CONSTANTS FROM THE 1980s DATABASE				
Parameter	Unit	Kinetic model	STASOFT I	STASOFT III
H ₂ CO ₃ * alkalinity	mg/l as CaCO ₃	74.3	74.9	74.2
Ca ²⁺	mg/l as CaCO ₃	94.3	94.9	94.2
pH		7.97	8.00	7.94
CaCO ₃ precipitation potential	mg/l as CaCO ₃	5.7	5.1	5.7

TABLE 4a: EXAMPLE 2 RESULTS OBTAINED USING EQUILIBRIUM CONSTANTS FROM THE 1940s DATABASE				
Parameter	Unit	Kinetic model	MCL	STASOFT I
H ₂ CO ₃ * alkalinity	mg/l as CaCO ₃	120	120	120
Ca ²⁺	mg/l as CaCO ₃	100	100	100
pH		7.97	7.95	7.96
Ca(OH) ₂ dose	mg/l as CaCO ₃	257.5	270	265.3

TABLE 4b: EXAMPLE 2 RESULTS OBTAINED USING EQUILIBRIUM CONSTANTS FROM THE 1980s DATABASE				
Parameter	Unit	Kinetic model	STASOFT I	STASOFT III
H ₂ CO ₃ * alkalinity	mg/l as CaCO ₃	120	120	120
Ca ²⁺	mg/l as CaCO ₃	100	100	100
pH		7.78	7.84	7.77
Ca(OH) ₂ dose	mg/l as CaCO ₃	253.1	264.0	253.6

kinetic model were compared using the same 1940s-based equilibrium constants, and the results from STASOFT I, STASOFT III and the kinetic model were compared using the same 1980s-based equilibrium constants.

Example 1: Assessment of initial state

Analysis of a water gives alkalinity = 80 mg/l, Ca²⁺ = 100 mg/l (both as CaCO₃), pH = 8.6, ionic strength (μ) = 0.005 (TDS = 200 mg/l) and T = 20°C. Determine the saturation state of the water and the mass of concentration of CaCO₃ which potentially can precipitate from the water (see Tables 3a and b).

The results obtained using the kinetic-based model compare very well with those obtained using the equilibrium-chemistry-based MCL diagrams, STASOFT I and STASOFT III.

Example 2: Calcium softening using lime

Analysis of a water gives: H₂CO₃* alkalinity = 300 mg/l, calcium = 280 mg/l (both as CaCO₃), pH = 7.2, μ = 0.01 (TDS = 400 mg/l) and temperature 20°C. Determine the Ca(OH)₂ dose to soften the water to Ca²⁺ = 100 mg/l (as CaCO₃) (see Tables 4a and b).

Again results from all calculations correlate closely.

Example 3: Determining the final state of an underground water after three-phase equilibrium is attained

Analysis of an underground water to be pumped to the surface, gives H₂CO₃* alkalinity = 320 mg/l, calcium = 210 mg/l (both as CaCO₃), pH = 7.4, μ = 0.02 (TDS = 800 mg/l) and temperature 15°C. The water is exposed to air. Determine the chemical state of the water after it has (1) achieved equilibrium with air, and (2)

TABLE 5.1a: EXAMPLE 3 RESULTS OBTAINED USING EQUILIBRIUM CONSTANTS FROM THE 1940s DATABASE AFTER EQUILIBRIUM WITH AIR			
Parameter	Unit	Kinetic model	MCL
H ₂ CO ₃ * alkalinity	mg/l as CaCO ₃	320	320
Ca ²⁺	mg/l as CaCO ₃	210	210
pH		8.95	8.83
CaCO ₃ precipitation potential	mg/l as CaCO ₃	55.6	50
CO ₂ expelled	mg/l as CaCO ₃	86.1	80

TABLE 5.1b: EXAMPLE 3 RESULTS OBTAINED USING EQUILIBRIUM CONSTANTS FROM THE 1980s DATABASE AFTER EQUILIBRIUM WITH AIR			
Parameter	Unit	Kinetic model	STASOFT III
H ₂ CO ₃ * alkalinity	mg/l as CaCO ₃	320	320
Ca ²⁺	mg/l as CaCO ₃	210	210
pH		8.95	8.92
CaCO ₃ precipitation potential	mg/l as CaCO ₃	67.4	67.3
CO ₂ expelled	mg/l as CaCO ₃	86.1	83.6

TABLE 5.2a: EXAMPLE 3 RESULTS OBTAINED USING EQUILIBRIUM CONSTANTS FROM THE 1940s DATABASE AFTER EQUILIBRIUM WITH AIR AND SOLID CaCO ₃ IN SOLUTION.				
Parameter	Unit	Kinetic model	MCL	STASOFT I
H ₂ CO ₃ * alkalinity	mg/l as CaCO ₃	142.3	140	142.2
Ca ²⁺	mg/l as CaCO ₃	31.9	30	32.2
pH		8.62	8.52	8.59
CaCO ₃ precipitated	mg/l as CaCO ₃	178.1	180	177.8
CO ₂ expelled	mg/l as CaCO ₃	240.5	245	240.8

TABLE 5.2b: EXAMPLE 3 RESULTS OBTAINED USING EQUILIBRIUM CONSTANTS FROM THE 1980s DATABASE AFTER EQUILIBRIUM WITH AIR AND SOLID CaCO ₃ IN SOLUTION				
Parameter	Unit	Kinetic model	STASOFT I	STASOFT III
H ₂ CO ₃ * alkalinity	mg/l as CaCO ₃	133.1	134.5	131.8
Ca ²⁺	mg/l as CaCO ₃	23.1	24.5	21.8
pH		8.59	8.56	8.56
CaCO ₃ precipitated	mg/l as CaCO ₃	188.4	185.5	188.2
CO ₂ expelled	mg/l as CaCO ₃	249.7	247.8	-

attained equilibrium with air and solid CaCO₃ in solution (see Tables 5.1a and b; and 5.2a and b respectively).

Note that STASOFT I cannot be used to predict the transient state of the water after equilibrium with air, and so cannot be included in the comparison in Tables 5.1a and b.

Systems containing a mixture of weak acid/base systems

Examples from Loewenthal et al. (1991) were used to validate the model. The results obtained using the kinetic-based model in AQUASIM were compared with those obtained using the equilibrium-based algorithms from Loewenthal et al. (1991).

TABLE 6: EXAMPLE 4 RESULTS OBTAINED USING THE KINETIC MODEL AND THE EQUILIBRIUM-CHEMISTRY-BASED ALGORITHMS OF LOEWENTHAL ET AL. (1991)			
Parameter	Unit	Kinetic model	Equilibrium algorithm
H ₃ PO ₄ /H ₂ CO ₃ */NH ₄ ⁺ alkalinity	mol/l	0.01142	0.011438
OH ⁻ dose	mol/l	0.004812	0.004812

TABLE 7: EXAMPLE 5 RESULTS OBTAINED USING THE KINETIC MODEL AND THE EQUILIBRIUM-CHEMISTRY-BASED ALGORITHMS OF LOEWENTHAL ET AL. (1991)			
Parameter	Unit	Kinetic model	Equilibrium algorithm
H ₃ PO ₄ /H ₂ CO ₃ */NH ₄ ⁺ alkalinity	mol/l	0.01634	0.016356
pH		8.52	8.50

Example 4: Chemical dose for specified dosage type and specified initial and final solution states

A water has carbonate, ammonium and phosphate weak acid subsystems present in solution, with $C_T = 0.005$ mol/l, $N_T = 0.004$ mol/l and $P_T = 0.003$ mol/l, ionic strength (μ) = 0.01 and temperature = 20°C. Determine the strong base required to adjust pH from 6.50 to 8.50 (see Table 6).

Example 5: Final state for a specified initial state and a specified chemical dose and dosage type

For the raw water in Example 4, determine the final pH for a carbonate (CO₃²⁻) dosage of 0.004865 mol/l (see Table 7).

In both Examples 4 and 5, very good agreement is obtained between results from the kinetic-based model and the equilibrium-based algorithms of Loewenthal *et al.* (1991).

Closure

In this paper a kinetic model has been developed for mixtures of weak acid/bases in solution. The model includes pH as a compound/parameter, and is based on the kinetics of the forward and reverse reactions for the dissociation of the weak acid/bases. The weak acid/bases included in the model are water, carbonate, ammonium, phosphate and short-chain fatty acids. However, the approach used to develop the model is general, and can be applied to include any other weak acid/bases of importance. Precipitation of CaCO₃ and gaseous exchange of CO₂ also have been included. The model and the approach on which it is based have been validated by comparing model predictions to those obtained from equilibrium chemistry-based models; good correlation was obtained. Compared to the traditional equilibrium chemistry approach to modelling aqueous mixtures of weak acid/bases, the kinetic approach offers several advantages. In particular, the kinetic approach will expedite integration of the weak acid/base model with other kinetic models. For example, the model presented here can be readily integrated with the existing biological kinetic models for waste-water treatment systems, to extend application of these models to situations where the pH does not remain constant and the changes in pH influence the behaviour.

Furthermore, by providing an estimation for the pH, the weak acid/base model will greatly simplify the inclusion of chemical (e.g. precipitation/dissolution) and/or physical (e.g. CO₂ and NH₃ gas exchange) processes, either in an independent chemical/physical model, or in the existing biological models. Chemical and physical processes are of increasing importance in wastewater treatment systems; for example, in chemical or combined chemical/biological P removal in activated sludge systems, in treatment of waste waters with high nutrient (N & P) and low organic carbon such as anaerobic digester supernatants, sludge dewatering liquors and trickling filter effluents.

Acknowledgements

This research was supported jointly by the Water Research Commission and the Foundation for Research Development and the results are published with their permission.

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