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Short communication

General ion recruiting procedure for pH-based calculations

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Abstract

In this paper, a simple procedure is developed to numerically evaluate the total equivalents introduced by any buffer component in a solution. The same procedure calculates the corresponding derivative with respect to the hydrogen ion. The procedure is useful for generalising the pH calculation for any pH-dependent model with reduction of the model stiffness. It is also found to be useful to calculate total alkalinity and to simulate titration experiments for a solution with known buffer composition.

Keywords: Cations estimation; Equivalent concentration; pH; Mathematical modelling; Model stiffness; Simulation; Titration

Software availability

Title: General ion recruiting procedure, standalone programme TITRATION.EXE
Developer: Usama E. Zaher, BIOMATH – Department of Applied Mathematics, Biometrics and Process Control, Ghent University, Coupure Links 653, 9000 Gent, Belgium. Tel.: +32 9 264 5932; fax: +32 9 264 6220; E-mail: usama.zaher@biomath.ugent.be
First year available: 2004
Hardware requirements: IBM-compatible computer, Windows 95 or higher version;
Programme language: C++
Programme size: As code CPP 8 KB, h 3 KB, as compiled standalone programme: 561 KB, C++ code run associated with the simulation package WEST® (Hemmis NV, Kortrijk, Belgium).
Availability and cost: For scientific research purposes, the C++ code is available upon written request to the authors and signing an agreement on terms of use. Integrated with WEST®, to be ordered from (Hemmis NV, Kortrijk, Belgium). For the latter, the general procedure is already implemented for pH calculation with different models, an alkalinity calculator and a titrimetric analyser simulator.

1. Introduction

There are many pH-dependent models and applications. Examples of the International Water Association (IWA) models that consider chemical equilibrium to calculate the pH are the River Water Quality Model no.1, RWQM1, (Reichert et al., 2001) and the Anaerobic Digestion Model no.1, ADM1 (Batstone et al., 2002). Also, IWA's Activated Sludge Models: ASM1, ASM2, ASM2d and ASM3 (Henze et al., 2000) deal with proton consumption and alkalinity. Therefore, pH and alkalinity calculations are evident extensions for these models. However, solving the chemical equilibrium within these models, as a set of differential equations that describe the equilibrium reactions, introduces stiffness to the model since the chemical reactions are significantly faster compared to the biological reactions. As a result, the numerical solution of the model will be calculation intensive and a stiff solver is needed. However, stiff solvers are not always available in all simulation platforms. Also, stiff solvers are less robust and

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slower in handling dynamic inputs and simulating complex systems that mix continuous model functions with discontinuous functions, e.g. of discrete controllers (Rosen et al., 2005). Therefore, it is advantageous to reduce model stiffness by solving the fast reactions of a model, e.g. the chemical equilibria, directly by an algebraic solver. Then, an explicit (non-stiff) solver can be used for the whole model. An algebraic solution of the chemical equilibrium reactions was already successfully implemented for the determination of pH in modelling the SHARON advanced nitrogen removal processes (Hellinga et al., 1999; Volcke et al., 2002). The implementation used the iterative procedure of Newton–Raphson to directly solve the set of implicit algebraic equations of the chemical equilibria of the SHARON model. For the ADM1, Rosen et al. (2005) applied the same procedure to algebraically solve the chemical equilibrium as well as the fast dynamics of hydrogen uptake and transfer. They illustrated the reduction of the model stiffness and the increase of the simulation speed using the extended COST/IWA Benchmark Simulation Model (BSM2) (Jeppsson et al., 2004). BSM2 is a plant-wide model including the most common units in a treatment plant and uses ADM1 to model the sludge digester.

However, each model will have a different set of buffering components, e.g. whether phosphate is considered or not. The iterative procedure, as implemented in the above mentioned examples, requires symbolic derivation of the ion concentration algebraic equations and their derivatives. In this paper, the procedure is generalised to avoid the symbolic derivation and have both the ion concentrations and their derivative calculated numerically using a unique function. The general procedure is therefore suitable for pH calculations for any combination of buffer systems and is applicable with any model. Moreover, it is applicable for the calculation of the total alkalinity (net cation concentration) and the simulation of titration experiments. The general procedure, alkalinity calculation and titration simulation depend on the unique function that numerically calculates the equivalent concentration introduced to a solution by any buffer component. Real titration experiments are therefore used to validate this unique numerical calculation function.

2. Procedure

The structure of the general pH function consists of three functions (pH, DeltaH and SubDeltaH) that work together in the hierarchy depicted in Fig. 1. The innovation in this paper is that the function SubDeltaH at the bottom of the hierarchy has a general form that calculates the equivalent concentration (δ_{sub}) introduced by a buffer component regardless of its type, being mono-, di-, triprotic or even higher in case of organic compounds. Also, the function has a general form that allows to calculate the derivative of the equivalent concentration (δ'_{sub}) that is needed in the nonlinear solution of the charge balance using the Newton–Raphson iterative procedure. In bottom-up direction according to Fig. 1, the development of the general procedure is illustrated in the following sections.

2.1. Algorithm

The equivalent concentration introduced by mono-, di- and triprotic buffers is evaluated symbolically as a function of total buffer concentration C_{T}, acidity constants K_{ai} and the hydrogen ion concentration H^+ according to Eqs. (1)–(3). The symbolic evaluation shows that the δ_{sub} is evolving systematically with the number of ions N.

$$\delta_{\mathrm{sub},N=1} = \frac{K_{\mathrm{a1}}C_{\mathrm{T}}}{\mathrm{H}^+ + K_{\mathrm{a1}}} \tag{1}$$

$$\delta_{\mathrm{sub},N=2} = \frac{K_{\mathrm{a1}}C_{\mathrm{T}}\mathrm{H}^+ + 2K_{\mathrm{a1}}K_{\mathrm{a2}}C_{\mathrm{T}}}{\mathrm{H}^{+^2} + K_{\mathrm{a1}}\mathrm{H}^+ + K_{\mathrm{a1}}K_{\mathrm{a2}}} \tag{2}$$

$$\delta_{\mathrm{sub},N=3} = \frac{K_{\mathrm{a1}}C_{\mathrm{T}}\mathrm{H}^{+^2} + 2K_{\mathrm{a1}}K_{\mathrm{a2}}C_{\mathrm{T}}\mathrm{H}^+ + 3K_{\mathrm{a1}}K_{\mathrm{a2}}K_{\mathrm{a3}}C_{\mathrm{T}}}{\mathrm{H}^{+^3} + K_{\mathrm{a1}}\mathrm{H}^{+^2} + K_{\mathrm{a1}}K_{\mathrm{a2}}\mathrm{H}^+ + K_{\mathrm{a1}}K_{\mathrm{a2}}K_{\mathrm{a3}}} \tag{3}$$

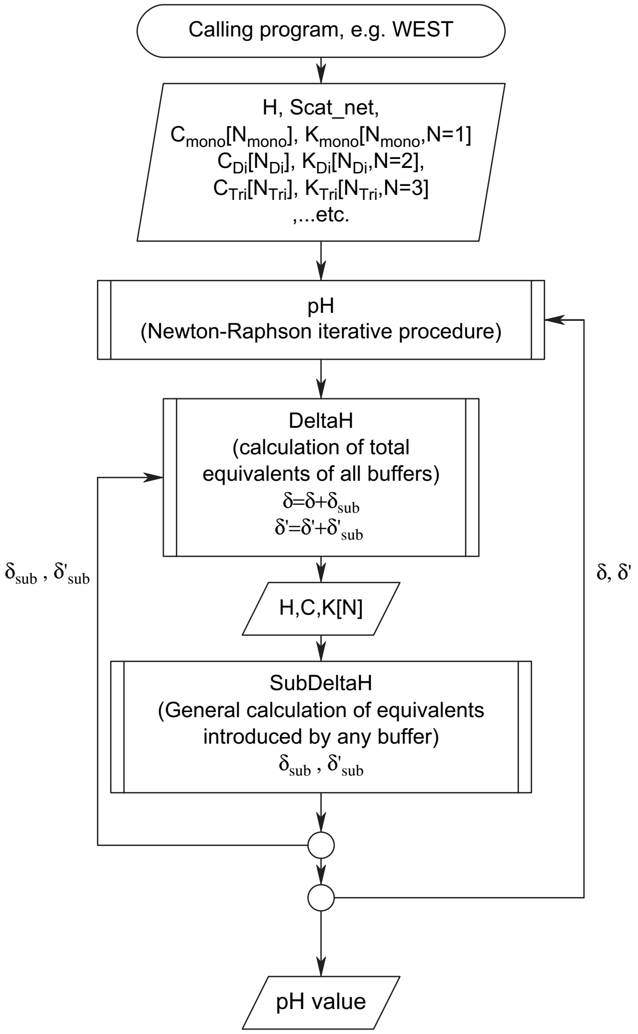


Fig. 1. General ion recruiting procedure for pH calculation.

Similarly, the derivative with respect to H^+, δ'_{sub}, is systematic with the number of ions N according to Eqs. (4)–(6).

$$\delta'_{\text{sub},N=1} = -\frac{K_{a1}C_T}{(H^+ + K_{a1})^2} \tag{4}$$

$$\delta'_{\text{sub},N=2} = \frac{K_{a1}C_T}{H^{+^2} + K_{a1}H^+ + K_{a1}K_{a2}} - \frac{(K_{a1}C_TH^+ + 2K_{a1}K_{a2}C_T)(2H^+ + K_{a1})}{\left(H^{+^2} + K_{a1}H^+ + K_{a1}K_{a2}\right)^2} \tag{5}$$

$$\delta'_{\text{sub},N=3} = \frac{(2K_{a1}C_TH^+ + 2K_{a1}K_{a2}C_T)}{H^{+^3} + K_{a1}H^{+^2} + K_{a1}K_{a2}H^+ + K_{a1}K_{a2}K_{a3}} - \frac{\left(K_{a1}C_TH^{+^2} + 2K_{a1}K_{a2}C_TH^+ + 3K_{a1}K_{a2}K_{a3}C_T\right)\left(3H^{+^2} + 2K_{a1}H^+ + K_{a1}K_{a2}\right)}{\left(H^{+^3} + K_{a1}H^{+^2} + K_{a1}K_{a2}H^+ + K_{a1}K_{a2}K_{a3}\right)^2} \tag{6}$$

2.2. Ion recruiting

The complexity of δ_{sub} and δ'_{sub} functions increases with the increase of the number N of ions introduced by a buffer component. Moreover, for organic buffer components that have more than 3 dissociation steps the functions will be more complex and difficult to evaluate symbolically. The general ion recruiting procedure presented in Fig. 2 evaluates the δ_{sub} and δ'_{sub} numerically and avoids the inclusion of complex equations in the pH calculation. Also, with its generality it avoids the inclusion of conditional if statements that would have been needed to select the appropriate formula for each buffer. Accordingly, the implementation of this procedure significantly improves the calculation speed and simplifies the programming code. For a buffer B that has N dissociation reactions, the input to the procedure in Fig. 2 is the hydrogen ion concentration H (mol/l), the total concentration of B (mol/l) and a vector with N acidity constants $K[i]$. The procedure iterates N times to calculate the terms num, denom, diffnum1 and diffnum2, according to Fig. 2. Then the δ_{sub} and δ'_{sub} can be calculated for the buffer by rearranging those terms according to Eqs. (7) and (8).

$$\delta_{\text{sub},B_j} = \frac{\sum_{i=1}^{N} \text{num}_{i,B_j}}{\text{denom}_{B_j}} \tag{7}$$

$$\delta'_{\text{sub},B_j} = \frac{\sum_{i=1}^{N} \text{diffnum1}_{i,B_j}}{\text{denom}_{B_j}} - \frac{\sum_{i=1}^{N} \text{num}_{i,B_j} \times \text{diffnum2}_{i,B_j}}{\left(\text{denom}_{B_j}\right)^2} \tag{8}$$

2.3. Calculation of total equivalents

Referring to Fig. 1, the function DeltaH iterates to pass buffer components one by one to SubDeltaH and calculates the cumulative sum of the total equivalents introduced by all buffer components. Some important aspects need to be considered for the general application of the procedure. The net cation (ions of strong bases minus ions of strong acids) concentration is known and passed with the DeltaH arguments so that it will be added to the δ-value but not to its derivative, the derivative of the cation concentration is zero. For consideration of OH^-, the water buffer is passed to the DeltaH function as a mono-protic buffer with acidity constant $K_w^{\dagger} = K_w/[H_2O]$ and $[H_2O] = 55.5$ mol/l, K_w is the acidity constant of water. Weak bases (e.g. ammonia) can also be considered to calculate the net equivalent sum. This can even be achieved without changing the SubDeltaH function by passing on the total concentration of the weak base with a negative sign together with its base constant K_b rather than the acidity constant K_a. Note that $K_b = K_w/K_a$.

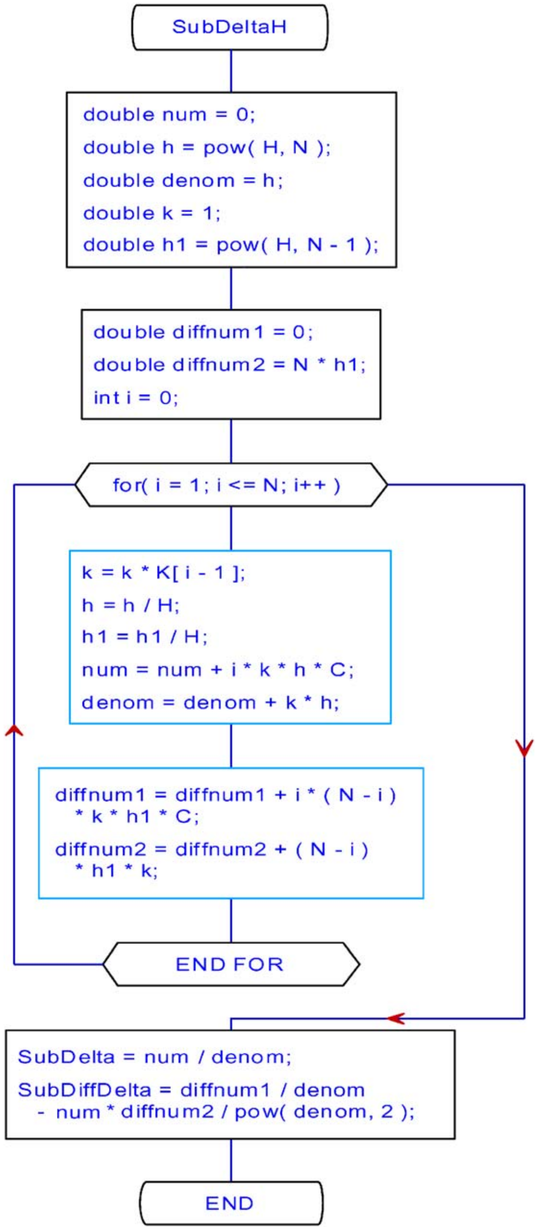
3. Application

3.1. pH calculation

The calculated δ and δ' are used to calculate the pH that maintains the charge balance of the buffer mixture. When the buffer components in the solution are known and the pH is unknown, the Newton–Raphson procedure, Fig. 1, iterates to correct a previous H-value according to Eq. (9) till an accepted tolerance is reached, i.e. till δ/δ' is less than a specified tolerance. Accordingly the pH is calculated as the $-\log_{10} H$.

$$H_i = H_{i-1} - \frac{\delta}{\delta'} \tag{9}$$

This procedure was successfully implemented to simulate the pH in a lab-CSTR digester (Zaher et al., 2004), using the ADM1 model. The results agreed with the pH measurements. Applying this procedure for pH simulation reduced the model stiffness and improved the simulation speed. Also, with this improvement it was possible to simulate the digester pH in a plant-wide model (Zaher, 2005) using ADM1 to model the anaerobic digester and ASM1 to model the activated sludge plant. The generalised procedure is therefore applicable to the specific BSM2 plant-wide model (Jeppsson et al., 2004) and can be used if desired to extend the plant-wide simulation with pH calculation for more buffers. For instance, the general pH calculation procedure will be useful when using BSM2 to benchmark the control system of a plant designed for phosphorous removal. The generalised procedure has the same effect on the simulation speed as the traditional procedure that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SubDeltaH

double num = 0;
double h = pow( H, N );
double denom = h;
double k = 1;
double h1 = pow( H, N - 1 );

double diffnum1 = 0;
double diffnum2 = N * h1;
int i = 0;

for( i = 1; i <= N; i++ )
    k = k * K[ i - 1 ];
    h = h / H;
    h1 = h1 / H;
    num = num + i * k * h * C;
    denom = denom + k * h;

    diffnum1 = diffnum1 + i * ( N - i )
      * k * h1 * C;
    diffnum2 = diffnum2 + ( N - i )
      * h1 * k;
END FOR

SubDelta = num / denom;
SubDiffDelta = diffnum1 / denom
  - num * diffnum2 / pow( denom, 2 );

END
```

Fig. 2. General procedure of ion recruiting for calculation of total equivalents and derivatives effected by a buffer component.

uses algebraic equations for ion concentrations and therefore would lead to the same improvement of the ADM1 and BSM2 simulation speed as achieved by Rosen et al. (2005).

3.2. Total alkalinity calculation

If the pH and the buffer composition are known, the procedure can be implemented to calculate the total alkalinity Z, Eq. (10).

$$Z = \delta - H \tag{10}$$

The procedure was used to calculate the influent net cation concentration in an upflow anaerobic sludge bed reactor with known influent pH and concentrations of phosphorous, acetate, bicarbonate and cyanide buffers (Zaher, 2005).

3.3. Titration simulation

The same procedure can also be implemented to simulate titration curves. At different pH steps, the acid volume V_a that needs to be added to shift the equilibrium at each pH can be calculated according to Eq. (11).

$$V_a = \frac{V_s}{N_a - H}(H - \delta) \tag{11}$$

where V_s is the sample volume and N_a is the acid normality (i.e. the concentration of the acid in equivalents).

The procedure was applied to simulate titration experiments of mono-, di- and triprotic buffers, Fig. 3. The figure shows the fit of the simulation results to the experimental data without any parameter estimation, i.e. using the standard values of acidity constants. The left pane of the figure shows the results obtained by titrating acetate and lactate mixtures and the right pane shows the results for titrating bicarbonate and phosphorus mixtures. Each point of the measured titration curve can be considered as an experimental validation of the numerical procedure of the function SubDeltaH, the main innovation of the work presented in this paper.

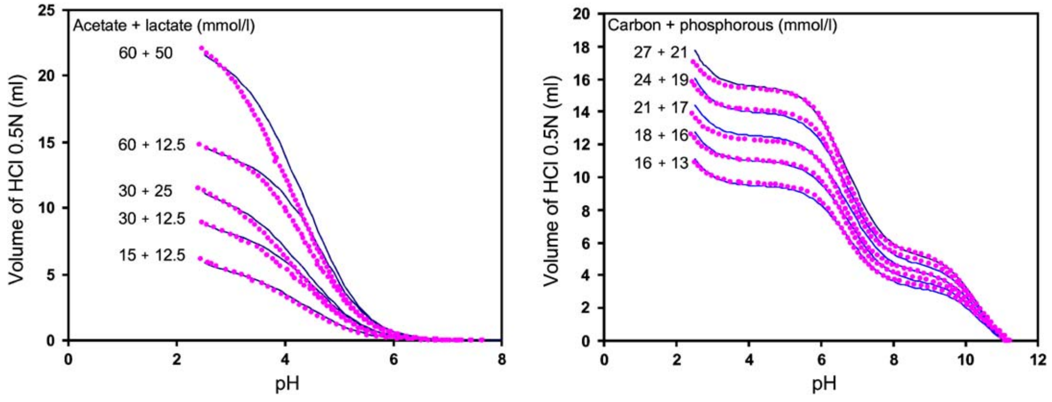

Fig. 3. Validation of the calculation and titration simulation with real titration experiments, ● data — simulation.

4. Conclusion

The systematic evolution of the equivalent concentrations (δ_{sub}) and the corresponding *H*-derivatives (δ'_{sub}) with the buffer types and the number of their ions was implemented in a general procedure "SubDeltaH". A higher level function "DeltaH" can arrange the properties of any group of buffers (including the water buffer) and iterate calling "SubDeltaH" to calculate the total equivalents (δ) and *H*-derivative (δ'). This generalisation was useful to simplify different calculation and simulation procedures that are dependent on the charge balance and pH. It reduces the stiffness of pH-dependent models, thus improving the simulation speed. It was used to calculate the net cation concentration (total alkalinity) of a sample given a known buffer composition and pH. Also, it is useful for the simulation of titration experiments.

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References

Batstone, D.J., Keller, J., Angelidaki, R.I., Kalyuzhnyi, S.V., Pavlostathis, S.G., Rozzi, A., Sanders, W.T.M., Siegrist, H., Vavilin, V.A., 2002. Anaerobic Digestion Model no 1. IWA publishing, London, UK, 77 pp.

Hellinga, C., van Loosdrecht, M.C.M., Heijnen, J.J., 1999. Model based design of a novel process for nitrogen removal from concentrated flows. Mathematical and Computer Modelling of Dynamical Systems 5, 351–371.

Henze, M., Gujer, W., Mino, T., van Loosdrecht, M.C.M., 2000. Activated Sludge Models: ASM1, ASM2, ASM2d and ASM3. Scientific and Technical Report No. 9. IWA Publishing, London, UK.

Jeppsson, U., Rosen, C., Alex, J., Copp, J., Gernaey, K.V., Pons, M.-N., Vanrolleghem, P.A., 2004. Towards a benchmark simulation model for plant-wide control strategy performance evaluation of WWTPs. In: Proceedings of the Sixth International Symposium on Systems Analysis and Integration Assessment (WATERMATEX 2004), Beijing, China, November 3–5, 2004, pp. 285–293.

Reichert, P., Borchardt, D., Henze, M., Rauch, W., Shanahan, P., Somlyódy, L., Vanrolleghem, P.A., 2001. River Water Quality Model No. 1. Scientific and Technical Report No. 12. IWA Publishing, London, UK.

Rosen, C., Vrecko, D., Gernaey, K.V., Jeppsson, U., 2005. Implementing ADM1 for benchmark simulations in Matlab/Simulink. In: Proceedings of the First International Workshop on the IWA Anaerobic Digestion Model No. 1, Lyngby, Copenhagen, Denmark, September 4–6, 2005, pp. 11–18.

Volcke, E.I.P., Hellinga, C., Van Den Broeck, S., van Loosdrecht, M.C.M., Vanrolleghem, P.A., 2002. Modelling the SHARON process in view of coupling with Anammox. In: Proceedings of the First IFAC International Scientific and Technical Conference on Technology, Automation and Control of Wastewater and Drinking Water Systems (TiASWiK'02), Gdansk-Sobieszewo, Poland, June 19–21, 2002, pp. 65–72.

Zaher, U., Rodríguez, J., Franco, A., Vanrolleghem, P.A., 2004. Conceptual approach for ADM1 application. In: Ujang, Z., Henze, M. (Eds.), Selected Proceedings of the IWA International Conference held in Kuala Lumpur, Malaysia, 9–10 December 2003. Water and Environment Management Series (WEMS), pp. 249–258.

Zaher, U., 2005. Modelling and Monitoring the Anaerobic Digestion Process in View of Optimisation and Smooth Operation of WWTP's. PhD thesis, Ghent University, Ghent, Belgium, 346 pp. <http://biomath.ugent.be/publications/download/zaherusama_phd.pdf>.