

# Dynamical Approach to Multiequilibria Problems for Mixtures of Acids and Their Conjugated Bases

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**S** Supporting Information

**ABSTRACT:** Mathematical methods are described for the determination of steady-state concentrations of all species in multiequilibria systems consisting of several acids and their conjugated bases in aqueous solutions. The main example consists of a mixture of a diprotic acid  $H_2A$ , a monoprotic acid  $HB$ , and their conjugate bases. The reaction equations lead to a system of autonomous ordinary differential equations for the species concentrations. The traditional equilibrium approach is briefly reviewed. Single variable polynomials are determined that are satisfied by the equilibrium proton concentrations. The remaining species are then given explicitly by rational functions of these proton concentrations, the equilibrium constants, and the initial concentrations of the other species. A quintic polynomial was derived to determine the equilibrium proton concentration for the example system. It is shown to reduce to a quartic polynomial in the absence of the second acid  $HB$ . An alternative dynamical approach to the equilibrium problem is described that involves the formulation of the kinetic rate equations for each species, which together constitute a nonlinear system of ordinary differential equations. The equilibrium concentrations are determined by evolving the initial concentrations via this dynamical system to their steady state. This dynamical approach is particularly attractive because it can easily be extended to determine equilibrium concentrations for arbitrarily large multiequilibria systems. With the equations provided here and some knowledge of computing software, the fast and accurate computation of equilibrium concentrations becomes feasible for the education of upper-division undergraduate and graduate students as well as for the study of research problems. This dynamical method also serves to introduce students to nonlinear dynamical systems, which are essential for the study of dynamic problems in chemistry, for example, oscillatory reactions.

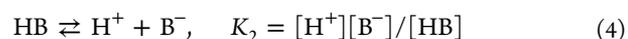
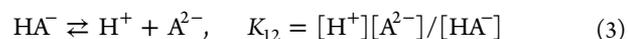
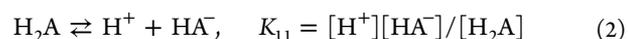
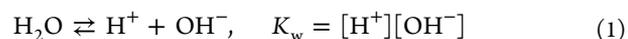
**KEYWORDS:** Upper-Division Undergraduate, Graduate Education/Research, Interdisciplinary/Multidisciplinary, Computer-Based Learning, Equilibrium, Mathematics/Symbolic Mathematics, Acids/Bases

<b>Multi-Component Equilibrium</b> Aqueous Solution of $m$ Acids $H_nX$ and their $n_m$ Conjugate Bases <b><math>(2 + \sum_m n_m + m)</math> Species <math>S_i</math></b>	
<b>Equilibrium Approach</b>  $(1 + \sum_m n_m)$ equil. eqs. $m$ mass balance eqs. 1 charge balance eq.	<b>Dynamical Approach</b>  one differential equation for each one of $(2 + \sum_m n_m + m)$ species
<b>Chemistry &amp; Mathematics: Synergy and New Science</b>	

Chemical equilibrium is a central and significant qualitative concept in all STEM (science, technology, engineering, and mathematics) fields, the quantitative determination of chemical equilibria is a core topic in STEM education,<sup>1–4</sup> and equilibrium is prominently featured as one of the 10 “big ideas” (level 1) of the general chemistry anchoring concepts content map (ACCM).<sup>5</sup> Discussion of simple acid–base equilibria, complexation reactions, phase distributions and precipitation reactions, and redox reactions can be found in standard introductory textbooks.<sup>6</sup> In contrast, the solution of multiequilibria problems is nontrivial and frequently involves assumptions, constraints, or both. The discussion of acid dissociation reactions has been a frequent topic in the *Journal*.<sup>7–13</sup> Parker and Breneman discussed diprotic acid equilibria<sup>14</sup> and titrations<sup>15</sup> using an iterative numerical method implemented using a spreadsheet. More recently, Baeza–Baeza and Garcia-Alvarez-Coque described a more general approach for the computation of the chemical species in multiequilibria systems.<sup>16,17</sup> From an educational perspective, analyses of multiequilibria present excellent opportunities for the synergistic integration of science and math education,<sup>18,19</sup> and such activities are very much in the spirit of the Next Generation

Science Standards<sup>20,21</sup> and its implications for college teaching.<sup>22,23</sup>

Stimulated by our interest in understanding aqueous solutions of sulfuric acid and bromate in the context of studies of Belousov–Zhabotinsky oscillating reactions,<sup>24,25</sup> we consider here the general case of the coupled equilibria given by the dissociation and equilibrium equations



Equations 1–4 describe mixtures of a diprotic acid  $H_2A$  (acid 1) with a monoprotic acid  $HB$  (acid 2) and their salts  $MHA$ ,  $M_2A$  and  $MB$ , where  $M$  represents an arbitrary singly charged, inert, nonaggregated metal cation and the corresponding dissociation constants are  $K_w$ ,  $K_{11}$ ,  $K_{12}$ , and  $K_2$ . The equilibrium constant  $K_w$  is the ionic product of water, the acidity constants

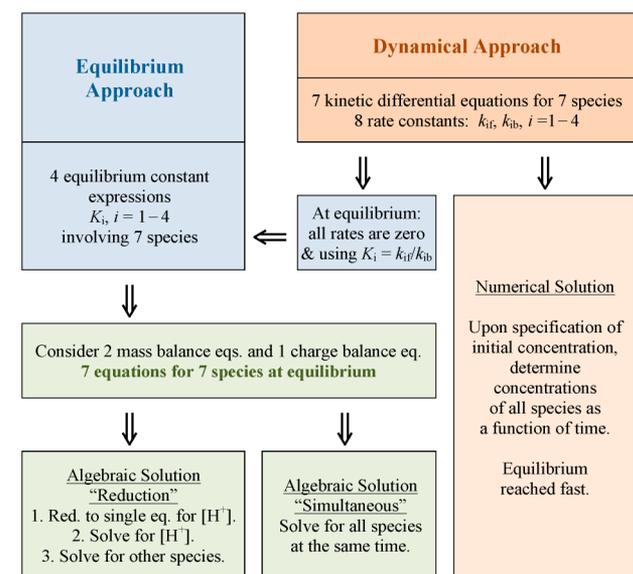
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Table 1. Numbers of Species and Equations

Acid	Number of New Species	Number of Equil Eqs	Balance Equations Mass
HOH, 0th acid	2 species: H <sup>+</sup> , OH <sup>-</sup>	1	0
H <sub>n</sub> X, mth acid	n + 1 new species: H <sub>n</sub> X, H <sub>n-1</sub> X <sup>-</sup> , ..., X <sup>n-</sup>	n	1 mass balance: [H <sub>n</sub> X] + [H <sub>n-1</sub> X <sup>-</sup> ] + ... [X <sup>n-</sup> ] = const
Mixture	Number of Species		Balance Equations Charge and Mass
H <sub>2</sub> O and m H <sub>n</sub> X	2 + ∑ <sub>m</sub> (n <sub>m</sub> + 1) = 2 + ∑ <sub>m</sub> n <sub>m</sub> + m	1 + ∑ <sub>m</sub> n <sub>m</sub>	1 + m

$K_{mn}$  describe the equilibria for the  $n$ th dissociation of  $n$ -protic acid  $m$ , and  $K_m$  describes the acidity constant for the first and only dissociation of a monoprotic acid  $m$  ( $K_m = K_{m1}$ ).

This specific problem is the backdrop for an interface with mathematical methods. It is a fundamental and general problem to determine the pH of an aqueous solution of  $m$  dissociating acids H<sub>n</sub>X containing  $(2 + \sum_m n_m + m)$  species (Table 1). In the traditional “equilibrium approach”, the definitions of the equilibrium constants are used  $(1 + \sum_m n_m)$  equations together with conservation of mass ( $m$  equations) and conservation of charge (1 equation) to determine the concentrations of the  $(2 + \sum_m n_m + m)$  species (Figure 1). For multiequilibria systems



**Figure 1.** Overview of approaches to solving H<sub>2</sub>A/HA<sup>-</sup>/A<sup>2-</sup>/HB/B<sup>-</sup> systems (7 species). The equilibrium constant  $K_i$  depends on the reaction rate constant  $k_{if}$  for the forward reaction and the reaction rate constant  $k_{ib}$  for the back reaction. See text for details.

there is no explicit solution to this system of equations and, thus, numerical methods must be employed. The system of  $(2 + \sum_m n_m + m)$  equations could be solved simultaneously for the concentrations of all species. Usually, however, the  $(2 + \sum_m n_m + m)$  equations are reduced to a single equation for one species (i.e., [H<sup>+</sup>]) and the concentrations of the other species are computed subsequently. We show that the proton concentration satisfies a single variable polynomial. We report a quintic polynomial (eq 22) whose positive root is the proton concentration [H<sup>+</sup>]<sub>ss</sub> at the stationary state (a.k.a. steady state) of H<sub>2</sub>A/HA<sup>-</sup>/A<sup>2-</sup>/HB/B<sup>-</sup> systems (7 species) and also discuss a quartic polynomial (eq 23) for the H<sub>2</sub>A/HA<sup>-</sup>/A<sup>2-</sup> systems (5 species). The desired positive root can be approximated using a variety of numerical methods.

An alternative dynamical approach to the equilibrium problem is to write the kinetic rate equations for each species, which together constitute a nonlinear system of ordinary differential equations. The equilibrium concentrations are determined by evolving the initial concentrations via this dynamical system to their steady state. General mass action kinetics theory<sup>26,27</sup> and the assumption of a stirred reactor lead to the system of ordinary differential equations (ODEs)

$$\begin{aligned} \frac{d[H^+]}{dt} = & k_{wf} - k_{wb}[H^+][OH^-] + k_{11f}[H_2A] \\ & - k_{11b}[H^+][HA^-] - k_{12b}[H^+][A^{2-}] + k_{12f}[HA^-] \\ & + k_{2f}[HB] - k_{2b}[H^+][B^-] \end{aligned} \quad (5)$$

$$\frac{d[OH^-]}{dt} = k_{wf} - k_{wb}[H^+][OH^-] \quad (6)$$

$$\frac{d[H_2A]}{dt} = -k_{11f}[H_2A] + k_{11b}[H^+][HA^-] \quad (7)$$

$$\begin{aligned} \frac{d[HA^-]}{dt} = & k_{11f}[H_2A] - k_{11b}[H^+][HA^-] + k_{12b}[H^+][A^{2-}] \\ & - k_{12f}[HA^-] \end{aligned} \quad (8)$$

$$\frac{d[A^{2-}]}{dt} = k_{12f}[HA^-] - k_{12b}[H^+][A^{2-}] \quad (9)$$

$$\frac{d[HB]}{dt} = -k_{2f}[HB] + k_{2b}[H^+][B^-] \quad (10)$$

$$\frac{d[B^-]}{dt} = k_{2f}[HB] - k_{2b}[H^+][B^-] \quad (11)$$

for the time-dependent concentrations of the species involved in the reactions 1–4. We will show how this system of differential equations can be formulated and describe how the steady-state solutions can be determined by solving this system of differential equations upon specification of the reaction rate constants and the initial concentrations. While the conceptual framework for this dynamical approach is somewhat more sophisticated than the equilibrium approach, it has several advantages: There is no need to reduce the system of equations to a simpler system (in contrast to solving the equilibrium equations); there are well-established numerical methods available for the computation of all species as functions of time; and the dynamical method scales easily with the addition of more types of acids. In addition and perhaps most importantly, the method lays the foundation for approaching dynamical problems in chemistry. These include oscillating chemical reactions, pattern formations in reaction-diffusion systems, and many more other processes in all areas of science and engineering.<sup>28–33</sup> Of course, the equilibrium approach is embedded in the dynamical approach. The conservation laws

correspond to invariant sets for the dynamical equations and the equilibrium constants are encoded in the rate constants.

As an illustration, we studied two examples with both the equilibrium approach and the dynamic approach. For the dissociation of the diprotic acid  $H_2A$  described by equilibria 1–3, we present results for the pH values of malate solutions, of dilute malic acid, and of malic acid/malate buffer solutions. In the second example, we analyze a timely research problem related to the Belousov–Zhabotinsky oscillating reaction.<sup>34,35</sup> Belousov–Zhabotinsky reactions (BZR) comprise all metal-catalyzed bromate oxidations of organic polyacids (citric acid, malonic acid, etc.) in highly acidic media, and these reactions are *the* prototypical nonlinear chemical systems.<sup>28–33</sup> The desire to understand the precise mechanisms of oscillating chemical reactions provided strong incentives to study the chemistry of bromous acid.<sup>24,25,36</sup> The need to obtain accurate equilibrium concentrations for the  $H_2SO_4/BrO_3^-$  system motivated the work reported here, and we studied a typical  $H_2SO_4/BrO_3^-$  mixture as a function of the  $K_a(HBrO_3)$  value.

## ■ GENERAL EQUILIBRIUM APPROACH TO STEADY-STATE DETERMINATION

### Single Variable Polynomials for Equilibrium Proton Concentrations

The mathematically most satisfying approach to the equilibrium concentrations is the determination of a single variable polynomial whose (positive) root can be used to determine all the species concentrations at equilibrium. While the method is viable for an arbitrary number of acids, it is illustrated here for the  $H_2A/HA^-/A^{2-}/HB/B^-$  system (eqs 1–4).

The analysis begins with the coupled equilibrium equations and, for the case of two acids, these are eqs 1–4. Note that the proton concentration appears in every one of these equations and that each of these equations would be a linear relation between two other species if the proton concentration were treated as a parameter. This observation is the key to a general procedure for determining all the concentrations systematically.

The second ingredient required for the computation of the steady-state concentrations are the equations for balance of charge and mass.<sup>16</sup> For the example given by eqs 1–4, the charge balance is

$$[OH^-] + [HA^-] + 2[A^{2-}] + [B^-] - [H^+] = [HA^-]_0 + 2[A^{2-}]_0 + [B^-]_0 = \alpha \quad (12)$$

where the terms involving anion concentrations account for the positive charges of the counterions of the salts of acids  $H_2A$  and  $HB$  and  $\alpha$  is simply a name given to the sum of the initial concentrations that appears on the right-hand side. The mass balances of groups A and B, respectively, are given by

$$[H_2A] + [HA^-] + [A^{2-}] = [H_2A]_0 + [HA^-]_0 + [A^{2-}]_0 = \beta \quad (13)$$

$$[HB] + [B^-] = [HB]_0 + [B^-]_0 = \gamma \quad (14)$$

where again  $\beta$  and  $\gamma$  are names assigned to the right-hand sides of these equations. Note that all the balance equations are linear in the unknown species concentrations.

The general procedure proceeds in a few simple steps. As discussed in the introduction, there are exactly the same numbers of equations (that is, equilibrium equations and balance equations) as unknown species. For the example, there

are three balance equations (eqs 12–14) and four equilibrium constant expressions (eqs 1–4) and seven unknown concentrations. By treating the proton concentration as a parameter in the equilibrium constant expressions and ignoring the charge balance equation, the remaining equations are a system of linear equations for the remaining unknown concentrations. This set of equations can be solved explicitly by the usual procedure of Gaussian elimination (by hand for a small number of acids or by symbolic computation in general). The result is an explicit expression for each unknown concentration (except for  $[H^+]$ ) as a rational function of the unknown proton concentration  $[H^+]$ , the equilibrium constants, and the expressions  $\beta$  and  $\gamma$  of initial concentrations. These expressions are substituted into the charge balance equation thus producing a single equation for the unknown proton concentration. When we gather terms with a common denominator and then equate the numerator to zero, this procedure produces the desired single variable polynomial for the unknown proton concentration. Once this concentration is approximated as the positive root of this polynomial, its value is used to determine the remaining unknown concentrations by substitution into the previously computed rational expressions.

### $H_2A/HA^-/A^{2-}/HB/B^-$ System

There are four equilibrium constant expression equations, two mass balance equations, and the conservation of charge for the seven species  $H_2A$ ,  $HA^-$ ,  $A^{2-}$ ,  $HB$ ,  $B^-$ ,  $OH^-$ ,  $H^+$ . Treating  $[H^+]$  as a parameter and solving the linear system of four equilibrium equations and the two mass balance equations for the remaining six parameters gives the rational expressions for the solution. After solving the linear system with the proton concentration treated as a parameter we obtain the expressions

$$[OH^-] = K_w/z \quad (15)$$

$$[H_2A] = \frac{\beta z^2}{z^2 + K_{11}z + K_{11}K_{12}} \quad (16)$$

$$[HA^-] = \frac{K_{11}\beta z}{z^2 + K_{11}z + K_{11}K_{12}} \quad (17)$$

$$[A^{2-}] = \frac{K_{11}K_{12}\beta}{z^2 + K_{11}z + K_{11}K_{12}} \quad (18)$$

$$[HB] = \frac{z\gamma}{z + K_2} \quad (19)$$

$$[B^-] = \gamma - \frac{z\gamma}{z + K_2} \quad (20)$$

where we write for simplicity  $z = [H^+]_{ss}$  for the proton concentration at the stationary state.

When these expressions (eqs 15–20) are substituted into the charge balance equation, we obtain the equation

$$-z + \frac{K_w}{z} - \alpha + \frac{K_{11}\beta(z + 2K_{12})}{z^2 + zK_{11} + K_{11}K_{12}} + \gamma - \frac{z\gamma}{z + K_2} = 0 \quad (21)$$

and the desired quintic polynomial

$$\begin{aligned}
 & z^5 + (K_{11} + K_2 + \alpha)z^4 + (K_{11}(K_{12} + K_2 + \alpha - \beta) \\
 & + K_2(\alpha - \gamma) - K_w)z^3 \\
 & + (K_{11}(-K_w + K_{12}(K_2 + \alpha - 2\beta) + K_2(\alpha - \beta - \gamma)) \\
 & - K_{12}K_w)z^2 + K_{11}(K_2K_w + K_{12} \\
 & (K_w + K_2(-\alpha + 2\beta + \gamma)))z - K_{11}K_{12}K_2K_w = 0 \quad (22)
 \end{aligned}$$

whose positive root is the proton concentration at the stationary state,  $z = [\text{H}^+]_{\text{ss}}$ .

The quartic eq 23 describing the  $\text{H}_2\text{A}/\text{HA}^-/\text{A}^{2-}$  system can be obtained from the quintic eq 22 by setting  $\gamma = 0$ .

$$\begin{aligned}
 & z^4 + (K_{11} + \alpha)z^3 + (-K_w + K_{11}(K_{12} + \alpha - \beta))z^2 \\
 & - K_{11}(K_w - K_{12}\alpha + 2K_{12}\beta)z - K_{11}K_{12}K_w = 0 \quad (23)
 \end{aligned}$$

### Solving the Quartic and Quintic Polynomials

While quartic polynomial equations may be solved exactly using Cardano's formula,<sup>37</sup> the resulting expressions for the roots are cumbersome and generally not used for practical calculations. Instead, roots are approximated using numerical methods. As an example, the *Mathematica*<sup>38,39</sup> code shown in Figure 2 may

```

K11 = 1.0 × 103;
K12 = 1.0 × 10-2;
K2 = 1.0;
Kw = 1.0 × 10-14;
α = 0.1;
β = 1;
γ = 0.1;
a1 = K11 + K2 + α;
a2 = -Kw + K11 (K12 + K2 + α - β) + K2 (α - γ);
a3 = -K2 Kw + K11 (-Kw + K12 (K2 + α - 2 β) + K2 (α - β - γ));
a4 = -K11 (K2 Kw + K12 (Kw + K2 (-α + 2 β + γ)));
a5 = -K11 K12 K2 Kw;
ans = NSolve[z5 + a1 z4 + a2 z3 + a3 z2 + a4 z + a5, z]
{ {z → -1000.99}, {z → -1.05147}, {z → -0.0197866},
  {z → -5. × 10-15}, {z → 0.960357} }

```

**Figure 2.** Relevant section of a *Mathematica* notebook for the approximation of the five roots of the quintic polynomial eq 22 describing the multiequilibria in solutions of bromate ( $\text{B}^-$ ) in aq sulfuric acid ( $\text{H}_2\text{A}$ ) for the set of equilibrium constants  $K_{11} = 10^3$ ,  $K_{12} = 10^{-2}$ , and  $K_2 = 1$  and initial concentrations  $[\text{H}_2\text{A}]_0 = 1.0 \text{ M}$  and  $[\text{B}^-]_0 = 0.1 \text{ M}$  ( $\alpha = 0.1$ ,  $\beta = 1$ ,  $\gamma = 0.1$ ). The command `NSolve` uses a numerical method to approximate the roots. The positive root  $z \approx 0.96$  is the desired proton concentration.

be used to find the five roots of eq 22. Of course, the use of a computer algebra system is not necessary. The desired root may be approximated by a simple bisection method, by Newton's method, or by many other well-known numerical methods. All these can be carried out by hand, with a calculator, or by writing a simple computer program using available software. Newton's method is the best choice for simplicity and speed of convergence. A guess  $z_0$  is made for the approximate root of the equation  $p(z) = 0$  and the iteration process  $z_{k+1} = z_k - p(z_k)/p'(z_k)$  is carried out (where  $p'$  denotes the derivative of  $p$ ) until two consecutive iterates differ by some preassigned tolerance. The convergence to a root is very rapid. Indeed, if the initial guess is not too far from the desired positive root, then the error in approximating the root for each iteration is proportional to the square of the error of the previous iterate. For the example of Figure 2, an initial guess of  $z = 1.0$  results in

the iterates 0.963892, 0.960389, 0.960357, and 0.960357. High accuracy is reached after three iterations.

### DYNAMICAL APPROACH TO MULTIEQUILIBRIA

In this section, we describe and discuss an alternative to the general equilibrium approach: the dynamical approach. We begin with a description of the formulations of the differential eqs 5–11 and then describe mathematical methods to find the equilibrium concentrations.

#### Formulation of the Autonomous Ordinary Differential Equations

The kinetic differential equations describe the reaction rates of the species in the mixture, that is, the time rate of change of the concentrations of the species as a function of the concentrations of all other species according to mass action kinetics theory.<sup>26,27</sup> There will be two equations for  $[\text{H}^+]$  and  $[\text{OH}^-]$  and  $(n_m+1)$  equations for the  $(n_m+1)$  new species ( $\text{H}_m\text{X}$ ,  $\text{H}_{m-1}\text{X}^-$ , ...,  $\text{X}^{n-}$ ) for each  $n$ -protic acid  $m$  (Table 1). The right-hand side of the differential equation for  $d[\text{S}]/dt$  for each species  $S$ , contains one positive and one negative term for the two elemental reactions that increase or decrease the concentration of the species in every equilibrium reaction involving species  $S$ . Each of these terms is taken to be the product of a reaction rate constant  $k_i$  and the concentrations of all substrates of the reaction, that is, this approach assumes a reaction order of one for every substrate involved in the elemental reaction. The concentration of water does not change for practical purposes and it is included in  $k_{\text{wf}}$ . For example, the diprotic acid  $\text{H}_2\text{A}$  is involved in one equilibrium only (eq 2), and hence, the equation for  $d[\text{H}_2\text{A}]/dt$  (eq 7) contains just two terms: the term  $-k_{11f}[\text{H}_2\text{A}]$  accounts for the depletion of  $\text{H}_2\text{A}$  upon forward reaction  $\text{H}_2\text{A} \rightarrow \text{H}^+ + \text{HA}^-$  and the term  $+k_{11b}[\text{H}^+][\text{HA}^-]$  accounts for the reformation of  $\text{H}_2\text{A}$  upon backward reaction  $\text{H}^+ + \text{HA}^- \rightarrow \text{H}_2\text{A}$ . On the other hand, the proton is involved in all four equilibria (eqs 1–4) and  $d[\text{H}^+]/dt$  thus contains eight terms (eq 5).

Every equilibrium reaction is described by two reaction rate constants, one reaction rate constant  $k_f$  for the forward reaction and one reaction rate constant  $k_b$  for the backward reaction. These reaction rate constants are related via the equilibrium constant  $K$  by  $K = k_f/k_b$ . We refer to the reaction rate constants of reactions 1 – 4 using the subscript of the respective equilibrium constant and appending either "f" or "b" for forward and backward. Hence, the reaction rate constants  $k_{\text{wf}}$  and  $k_{\text{wb}}$  describe the autoionization of water (eq 1). We refer to the reaction rate constants for the forward and backward reactions of the first dissociation of  $\text{H}_2\text{A}$  (acid 1, eq 2) as  $k_{11f}$  and  $k_{11b}$ , respectively, and to the reaction rate constants for the forward and backward reactions of the second dissociation of  $\text{H}_2\text{A}$  (eq 3) as  $k_{12f}$  and  $k_{12b}$ , respectively. Similarly,  $k_{2f}$  and  $k_{2b}$  are the reaction rate constants for the forward and backward reactions, respectively, of the dissociation of  $\text{HB}$  (acid 2, eq 4).

In the present context, we are interested in the determination of the concentrations of all species at equilibrium, not the transient kinetics of reaching the equilibrium. Hence, once the equilibrium constants are specified, we can freely choose in each case either the forward or backward reaction rate constant and then use the equation  $K = k_f/k_b$  to determine the other. Of course, the determination of the reaction rate constants is a difficult and important problem for other applications (vide infra).

```

diffequations =
{Hp'[t] == kwf - kwb Hp[t] OHm[t] + k11f H2A[t] - k11b Hp[t] HAm[t] - k12b Hp[t] A2m[t] + k12f HAm[t] +
  k2f HB[t] - k2b Hp[t] Bm[t],
 OHm'[t] == kwf - kwb Hp[t] OHm[t],
 H2A'[t] == - k11f H2A[t] + k11b Hp[t] HAm[t],
 HAm'[t] == k11f H2A[t] - k11b Hp[t] HAm[t] + k12b Hp[t] A2m[t] - k12f HAm[t],
 A2m'[t] == k12f HAm[t] - k12b Hp[t] A2m[t],
 HB'[t] == - k2f HB[t] + k2b Hp[t] Bm[t],
 Bm'[t] == k2f HB[t] - k2b Hp[t] Bm[t]};
species = {Hp, OHm, H2A, HAm, A2m, HB, Bm};
Kw = 10^-14;
K11 = 10^3;
K12 = 10^-2;
K2 = 10^0;
backwardrateconstants = {kwb -> kwf/Kw, k11b -> k11f/K11, k12b -> k12f/K12, k2b -> k2f/K2};
diffequationsb = diffequations /. backwardrateconstants;
forwardrateconstants = {kwf -> 10^-3, k11f -> 10^2, k12f -> 10^2, k2f -> 10^2};
odes = diffequationsb /. forwardrateconstants;
initialconcentrations = {Hp[0] == 10^-7, OHm[0] == 10^-7, H2A[0] == 1.0, HAm[0] == 0.0, A2m[0] == 0,
  HB[0] == 0.0, Bm[0] == 0.1};
odeswithinitialdata = Union[odes, initialconcentrations];
timeend = 1;
approximation = NDSolve[odeswithinitialdata, species, {t, 0, timeend}];
{Hpa, OHma, H2Aa, Hama, A2ma, HBa, Bma} = species /. approximation[[1]];
finalconcentrations = {Hpa[t], OHma[t], H2Aa[t], Hama[t], A2ma[t], HBa[t], Bma[t]} /. {t -> timeend};
pHfinal = -Log[10, Hpa[timeend]];
Print["Hfinal = ", Hpa[timeend], ", OHmfinal = ", OHma[timeend], ", H2Afinal = ", H2Aa[timeend],
  ", HAmfinal = ", Hama[timeend], ", A2mfinal = ", A2ma[timeend], ", HBafinal = ", HBa[timeend],
  ", Bmafinal = ", Bma[timeend], ", and pHfinal = ", pHfinal, "."]
Hfinal = 0.960357, OHmfinal = 1.04128×10^-14, H2Afinal = 0.000949558, HAmfinal = 0.988755,
  A2mfinal = 0.0102957, HBafinal = 0.0489889, Bmafinal = 0.0510111, and pHfinal = 0.0175672.

```

**Figure 3.** Relevant section of a *Mathematica* notebook for the computation of multiequilibria in solutions of bromate ( $\text{Br}^-$ , a.k.a. BM) in aq sulfuric acid ( $\text{H}_2\text{A}$ ) for the set of equilibrium constants  $K_{11} = 10^3$ ,  $K_{12} = 10^{-2}$ , and  $K_2 = 1$  and initial concentrations  $[\text{H}_2\text{A}]_0 = 1.0 \text{ M}$  and  $[\text{Br}^-]_0 = 0.1 \text{ M}$  ( $\alpha = 0.1$ ,  $\beta = 1$ ,  $\gamma = 0.1$ ).  $\text{Hfinal} \approx 0.96$  is the equilibrium proton concentration  $[\text{H}^+]_{\text{ss}}$  and the concentrations of all other species also are listed.

### Numerical Determination of Steady-State Concentrations

An effective method for determining the steady-state concentrations for a given set of initial concentrations is the use of a numerical method (for example, Euler's method or the Runge–Kutta method<sup>40</sup>) to approximate the solutions of the kinetic differential equations forward in time until the computed concentrations remain unchanged up to some prespecified accuracy over some prespecified time interval. In general, forward numerical integration of a system of differential equations does not guarantee that a steady state is reached; but, in practice, the method is effective for acid dissociation problems because the kinetic equations are expected to have unique steady states for each choice of initial concentrations and the steady states are reached exponentially fast in the numerical integration. Euler's method is the simplest choice. It involves the computation of the concentrations of each species  $S$  at time  $t + \Delta t$  based on its concentrations at time  $t$  via  $[S(t + \Delta t)] = [S(t)] + \Delta t \cdot d[S]/dt$ . This numerical method can easily be implemented in simple programming languages (i.e., Basic, C) or in a spreadsheet program (i.e., Excel).

For all numerical computations in this paper, we used  $k_{\text{wf}} = 10^{-3}$ ,  $K_{\text{w}} = 10^{-14}$ ,  $k_{11\text{f}} = 10^2$ ,  $k_{12\text{f}} = 10^2$ , and  $k_{2\text{f}} = 10^2$ . In addition, all runs used the initial concentrations  $[\text{H}^+] = [\text{OH}^-] = 10^{-7}$  for the dissociation of water. The remaining initial settings are specified in Tables and Figures.

While we approximated solutions of the system of differential equations using the *Mathematica*<sup>38</sup> solver *NDSolve*,<sup>41</sup> other commercial mathematical software could be used and these include, for example, *Matlab*<sup>42</sup> and *ode45* or *Maple*<sup>43</sup> and

*dsolve*. A simple *Mathematica* code block and its output are shown in Figure 3 for the same case exemplified in Figure 2.

### RESULTS FOR CASE STUDIES

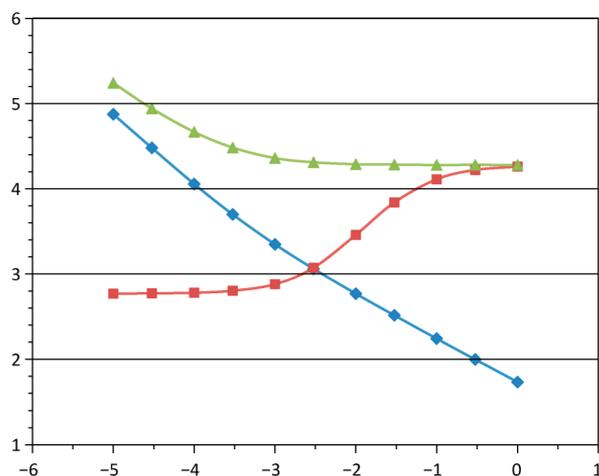
Two examples are presented in this section to illustrate the mathematical methods for the evaluations of the  $\text{H}_2\text{A}/\text{HA}^-/\text{A}^{2-}$  and  $\text{H}_2\text{A}/\text{HA}^-/\text{A}^{2-}/\text{HB}/\text{B}^-$  multiequilibria. The data were computed both by direct numerical approximations of the positive solutions of polynomials of eqs 22 and 23 and by numerical integration of the differential eqs 5–11. The results are shown in Figures 4 and 5 and tables of the computed data are given as Supporting Information.

#### $\text{H}_2\text{A}/\text{HA}^-/\text{A}^{2-}$ Equilibria: Malic Acid and Malate Systems

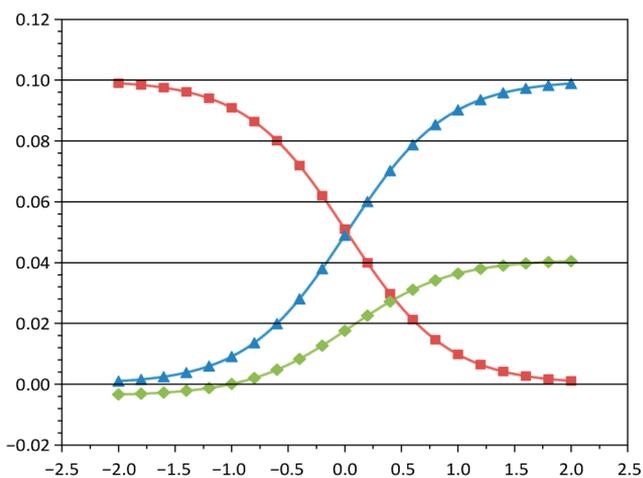
As a case study of a diprotic acid  $\text{H}_2\text{A}$ , we present results for the pH values of malate solutions, of dilute malic acid, and of malic acid/malate buffer solutions (Figure 4, Table S3). Malic acid ( $\text{HO}_2\text{C}-\text{CH}_2-\text{CH}(\text{OH})-\text{CO}_2\text{H}$ , 2-hydroxybutanedioic acid, 2-hydroxysuccinic acid) is a diprotic acid with  $\text{p}K_1 = 3.46$  ( $K_1 = 3.48 \times 10^{-4} \text{ mol/L}^{44} = K_{11}$ ) and  $\text{p}K_2 = 5.10$  ( $K_2 = 8.0 \times 10^{-6} \text{ mol/L} = K_{12}$ ).<sup>14,45,46</sup> The results for the malate solutions ( $[\text{HA}^-]_0 \neq 0$ ;  $[\text{H}_2\text{A}]_0 = [\text{A}^{2-}]_0 = 0$ ) exactly reproduce the numerical solutions reported by Parker and Breneman (Table 1 in ref 14), and our application to the buffered system illustrates the greater flexibility of the present approach.

#### $\text{H}_2\text{A}/\text{HA}^-/\text{A}^{2-}/\text{HB}/\text{B}^-$ Equilibria: Sulfuric Acid/Bromate Systems

The bromine chemistry of the Belousov–Zhabotinsky reaction involves hydrobromic acid  $\text{HBr}$ , hypobromous acid  $\text{HOBr}$ , bromous acid  $\text{HOBrO}$ , and bromic acid  $\text{HBrO}_3$ . It has been



**Figure 4.** pH-Values (y-axis) of malate solutions (green, triangles) as a function of  $\log([\text{HA}^-]_0)$  (x-axis), of dilute malic acid (blue, diamonds) as a function  $\log([\text{H}_2\text{A}]_0)$ , and of malic acid/malate buffer solutions (red, squares) as a function  $\log([\text{HA}^-]_0)$  with  $[\text{H}_2\text{A}]_0 = 0.01$ . All concentrations in mol/L.



**Figure 5.** Equilibrium pH value (green, diamonds) and equilibrium concentrations  $[\text{BrO}_3^-]$  (red, squares) and  $[\text{HBrO}_3]$  (blue, triangles) of solutions of dilute aqueous  $\text{H}_2\text{SO}_4$  containing bromate (y-axis) are shown as a function of the value of the acid dissociation constant  $K_a(\text{HBrO}_3)$  (x-axis). Initial concentrations:  $[\text{H}_2\text{SO}_4]_0 = 1.0$  M and  $[\text{BrO}_3^-]_0 = 0.1$  M.

assumed that bromic acid is dissociated under BZR conditions even though the acidity of bromic acid has not been well established. Experimental  $\text{p}K_a(\text{HBrO}_3)$  values of 1.87,<sup>47</sup> 0.7,<sup>48</sup> and  $-0.29$ <sup>49</sup> were reported, and most recently, Cortes and Faria concluded that  $\text{p}K_a(\text{HBrO}_3) < -0.5$ .<sup>50</sup> It is important<sup>24,25</sup> to firmly establish  $\text{p}K_a(\text{HBrO}_3)$  because this value affects the kinetics of the BZR reaction.

Mixtures of sulfuric acid ( $\text{H}_2\text{A} = \text{H}_2\text{SO}_4$ ) and bromate salts ( $\text{B}^- = \text{BrO}_3^-$ ) were studied to illustrate the power of both approaches to solve multiequilibria cases described by eqs 1–4. We employed acidity constants  $\text{p}K_{11} = -3$  and  $\text{p}K_{12} = +2$  for the first and second dissociations of sulfuric acid.<sup>51,52</sup> Computations were performed for initial concentrations  $[\text{H}_2\text{SO}_4]_0 = 1.0$  M and  $[\text{BrO}_3^-]_0 = 0.1$  M as a function of the acidity of bromic acid ( $\text{p}K_a(\text{HBrO}_3) = \text{p}K_2: -2$  to 2). Numerical data are tabulated in Supporting Information and the results are illustrated in Figure 5. Figure 5 shows in a

compelling fashion that the assumption of complete dissociation of bromic acid is no longer warranted as soon as  $\text{p}K_a(\text{HBrO}_3)$  drops below  $\text{p}K_{12}$  by one unit. Moreover, any degree of protonation of bromate affects the pH value of the solution and therefore all reaction rates that depend on bromate and/or pH are tied to the precise value of  $\text{p}K_a(\text{HBrO}_3)$ .

## MULTIEQUILIBRIA IN EDUCATION

The examples show that the mathematical methods allow for the fast and accurate determination of concentrations in buffered systems, and it is this feature that makes the equations broadly applicable in undergraduate education. The explorations of  $\text{H}_2\text{A}/\text{HA}^-/\text{A}^{2-}$  and  $\text{H}_2\text{A}/\text{HA}^-/\text{A}^{2-}/\text{HB}/\text{B}^-$  multiequilibria provide a wealth of educational opportunities. We envision a matrix of modes of engagement depending on the abilities of the students and the desired learning aims in chemistry and/or mathematics. To describe these modes, we classify the students' abilities in chemistry and mathematics depending on their abilities to perform tasks at an "applied", "advanced", or "intensive" level.

With regard to the skill level in mathematics, students at the applied level would solve problems using symbolic mathematics software (perhaps Mathematica Notebooks or Excel spreadsheets) with code provided by the instructor (for instance, the code in Figures 2 and 3). Advanced students might write code to solve instructor provided equations on a platform of their choice. These more mathematically inclined students might also serve as formal or informal undergraduate teaching assistants in the instruction of the entire class in computer laboratories. Math-intensive students might pursue the development of new mathematical methods to explore the properties of the kinetic differential equations in alternative ways.

The chemistry competency levels can be defined with similar criteria. At the first level, a student would explore multiequilibria problems for a specified system. What is the pH of a solution of  $\text{H}_2\text{A}$ ? How does the pH depend on  $[\text{H}_2\text{A}]_0$ ? How does the pH differ if the second dissociation is neglected or considered? Similar questions can be explored for solutions of the salts and for common-ion buffered systems. At the second level, the student might explore several systems, perform comparative analyses to discover patterns and correlations, and learn about the construction of structure–activity relationships. At the third level, the student would explore new systems with desired and predicted properties. How can one fine-tune the acid dissociation constants of an organic dioic acid  $\text{H}_2\text{A}$  and what would be the consequences for its solution chemistry? And, of course, how can one synthesize this new acid and measure its acidity?

It is recommended that instructors integrate chem-math cross-disciplinary content in their own contexts beginning with relatively simple, specific, and well-defined modules on multiequilibria. The success of any curriculum innovation ultimately depends on the acceptance of the new curriculum by the students, and this acceptance must be earned with explanations of clearly defined goals, with carefully planned, transparent changes to the course organization (computer lab component), and with precise instructions about carefully developed assignments. With the basic elements of the cross-disciplinary module in place, extensions to higher levels of chemistry and/or mathematics will present themselves naturally as individual students will seek more intensive engagement according to their talents.

## CONCLUSIONS

Mathematical methods have been described for the determination of steady-state concentrations of all species in the multiequilibria system of eqs 1–4, i.e., mixtures of diprotic acid  $H_2A$  and monoprotic acid  $HB$  and of salts of their conjugate bases using both the traditional equilibrium approach and the dynamical approach.

In the equilibrium approach, the quintic polynomial of eq 22 was derived to determine the equilibrium proton concentration  $[H^+]_{ss}$  based on the knowledge of all equilibrium constant expressions, the equilibrium constants, and the initial concentration. The quintic polynomial of eq 22 reduces to the quartic polynomial of eq 23 in the absence of the second acid  $HB$ . All other steady-state concentrations were computed from  $[H^+]_{ss}$ .

In the dynamical approach, we formulated a system of autonomous ordinary differential eqs 5–11 for the time-dependent concentrations of the species involved in the reactions 1–4 and described numerical methods for the simultaneous determination of the steady-state concentrations of all species based on the equilibrium constants and the initial concentrations.

With the equations provided here and some elemental knowledge of computing software, the fast and accurate computation of equilibrium concentrations becomes feasible for graduate students working on research problems as well as for the education of graduate and upper-division undergraduate students.

The multiequilibria system described by eqs 1–4 allows for the analysis of the most important buffers in chemistry and biology. The methods were illustrated by analyses of solutions of malic acid, malate, and common-ion buffered malic acid. In the context of Belousov–Zhabotinsky oscillating reactions, we studied bromate-buffered sulfuric acid solutions as a function of the acidity constant of bromic acid.

The state determination via the numerical solution of the system of differential equations is particularly attractive because this method can be extended to (much) larger multiequilibria systems with relative ease. For example, the additional consideration of a third acid  $H_nC$  and its  $n$  conjugate base(s)  $H_{n-k}C^{k-}$  ( $k \leq n$ ) merely requires the addition of  $n + 1$  differential equations for  $d[H_{n-k}C^{k-}]/dt$  for the new species  $H_nC$ ,  $H_{n-1}C^-$ , ...,  $C^{n-}$ , the addition of  $2n$  terms to the differential equation for  $d[H^+]/dt$ , and the knowledge of  $n$  additional values  $K_{3n}$  of the third acid  $H_nC$ . Moreover, and perhaps most importantly, the knowledge and the skills gained in formulating kinetic models lay the foundation for approaching dynamical problems in chemistry.<sup>28–33</sup> The differential equations describing the dynamical systems contain *twice as many reaction rate constants* (forward and backward reactions) *than there are equilibrium constants* in the equilibrium approach. If one is only interested in the determination of the concentrations of all species *at equilibrium*, then one can freely choose one of the reaction rate constants for every reaction  $\rho$  and use the respective equation  $K_\rho = k_{f\rho}/k_{b\rho}$  to determine the other reaction rate constant for a given reaction  $\rho$  (as we have done here). On the other hand, if one is interested in the transient kinetics of *reaching* the equilibrium, or, more generally, of reaching a stable oscillation or chaotic invariant set, then it no longer suffices to know only the *ratios* of the forward and backward reactions (i.e., the equilibrium constants) and one must also know one of the reaction rate constants for

each elemental reaction. Research and/or education efforts in this direction require more advanced methods in chemistry (determination of reaction rate constants) but essentially the same mathematical methods described here. We will report on the dynamic approach to mechanistic studies of oscillating chemical reactions in the future.

## ASSOCIATED CONTENT

### Supporting Information

Tables of equilibrium concentrations of the solutions of Figures 4 and 5, a graph of the quintic polynomial eq 22 for the case depicted in Figures 2 and 3 and a discussion of the choice of the starting value in Newton's method, proof that eq 23 has exactly one real positive root, and a comparison of the quartic polynomial to iterative methods. This material is available via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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