

**Supporting Information (10 pages)**

**Dynamical Approach to Multi-Equilibria Problems for Mixtures of Acids and Their Conjugated Bases**

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**Table S3. Equilibrium Concentrations of Malate Solutions, Dilute Malic Acid, and of Malic Acid/Malate Buffers**

$[\text{H}_2\text{A}]_0$	$[\text{HA}^-]_0$	$[\text{H}^+]$	$[\text{H}_2\text{A}]$	$[\text{HA}^-]$	$[\text{A}^{2-}]$	pH
<b>HA<sup>-</sup> Salt Hydrolysis</b>						
0.00	1.00	5.28E-05	1.16E-01	0.767319	0.116367	4.28
0.00	0.30	5.24E-05	3.47E-02	0.229521	0.0347657	4.28
0.00	0.10	5.26E-05	1.16E-02	7.67E-02	1.17E-02	4.28
0.00	0.03	5.21E-05	3.46E-03	2.30E-02	3.51E-03	4.28
0.00	0.01	5.16E-05	1.14E-03	7.67E-03	1.19E-03	4.29
0.00	3.00E-03	4.89E-05	3.25E-04	2.30E-03	3.74E-04	4.31
0.00	1.00E-03	4.37E-05	9.60E-05	9.64E-04	1.40E-04	4.36
0.00	3.00E-04	3.29E-05	2.13E-05	2.24E-04	5.42E-05	4.48
0.00	1.00E-04	2.16E-05	4.32E-06	6.98E-05	2.59E-05	4.67
0.00	3.00E-05	1.15E-05	5.75E-07	1.74E-05	1.20E-05	4.94
0.00	1.00E-05	5.72E-06	6.81E-08	4.14E-06	5.79E-06	5.24
<b>H<sub>2</sub>A Acid Dissociation</b>						
1.00	0.00	1.85E-02	9.82E-01	1.85E-02	7.99E-06	1.73
0.30	0.00	1.00E-02	2.90E-01	1.00E-02	7.93E-05	2.00
0.10	0.00	5.74E-03	9.43E-02	5.72E-03	7.98E-06	2.24
0.03	0.00	3.06E-03	2.69E-02	3.05E-03	7.90E-06	2.51
0.01	0.00	1.71E-03	8.30E-03	1.69E-03	7.93E-06	2.77
3.00E-03	0.00	8.69E-04	2.14E-03	8.53E-04	7.80E-06	3.06
1.00E-03	0.00	4.49E-04	5.59E-04	4.33E-04	7.72E-06	3.35
3.00E-04	0.00	2.00E-04	1.07E-04	1.86E-04	7.36E-06	3.70
1.00E-04	0.00	8.80E-05	1.88E-05	7.44E-05	6.77E-06	4.06
3.00E-05	0.00	3.32E-05	2.15E-06	2.25E-05	5.37E-06	4.48
1.00E-05	0.00	1.34E-05	2.36E-07	6.12E-06	3.65E-06	4.87
<b>H<sub>2</sub>A/HA<sup>-</sup> Buffer</b>						
0.01	1.00	5.50E-05	1.23E-01	7.75E-01	1.13E-01	4.26
0.01	0.30	6.02E-05	4.12E-02	2.37E-01	3.13E-02	4.22
0.01	0.10	7.75E-05	1.85E-02	8.30E-02	8.56E-03	4.11
0.01	0.03	1.45E-04	1.13E-02	2.72E-02	1.49E-03	3.84
0.01	0.01	3.48E-04	9.88E-03	9.89E-03	2.28E-04	3.46
0.01	3.00E-03	8.45E-04	9.19E-03	3.77E-03	3.55E-05	3.07
0.01	1.00E-03	1.32E-03	8.69E-03	2.29E-03	1.39E-05	2.88
0.01	3.00E-04	1.58E-03	8.43E-03	1.86E-03	9.36E-06	2.80
0.01	1.00E-04	1.66E-03	8.35E-03	1.75E-03	8.40E-06	2.78
0.01	3.00E-05	1.69E-03	8.32E-03	1.71E-03	8.01E-06	2.77
0.01	1.00E-05	1.70E-03	8.30E-03	1.70E-03	7.97E-06	2.77

Malic acid is a diprotic acid with  $pK_1 = 3.46$  and  $pK_2 = 5.10$ .

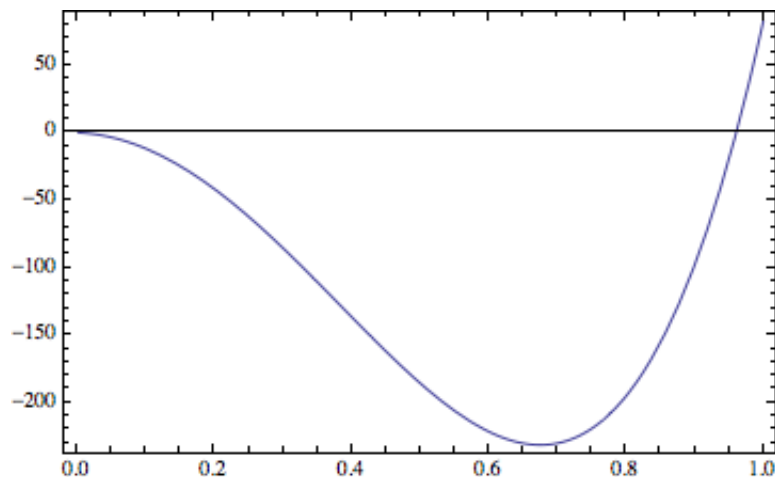
**Table S4. Equilibrium Concentrations of Solutions of Sulfuric Acid (1.0 M) and Bromate Salt (0.1 M) as a Function of the Acidity Constant  $K_2$  of Bromic Acid**

$pK_2$	$[H^+]$	pH	$[BrO_3^-]$	$[HBrO_3]$
-2.0	1.008	-0.003	0.099	0.001
-1.8	1.007	-0.003	0.098	0.002
-1.6	1.006	-0.003	0.098	0.002
-1.4	1.005	-0.002	0.096	0.004
-1.2	1.003	-0.001	0.094	0.006
-1.0	1.000	0.000	0.091	0.009
-0.8	0.995	0.002	0.086	0.014
-0.6	0.989	0.005	0.080	0.020
-0.4	0.981	0.008	0.072	0.028
-0.2	0.971	0.013	0.062	0.038
0.0	0.960	0.018	0.051	0.049
0.2	0.949	0.023	0.040	0.060
0.4	0.939	0.027	0.030	0.070
0.6	0.931	0.031	0.021	0.079
0.8	0.924	0.034	0.015	0.085
1.0	0.920	0.036	0.010	0.090
1.2	0.916	0.038	0.006	0.094
1.4	0.914	0.039	0.004	0.096
1.6	0.913	0.040	0.003	0.097
1.8	0.912	0.040	0.002	0.098
2.0	0.911	0.040	0.001	0.099

Acidity constants of sulfuric acid  $pK_{11} = -3$  and  $pK_{12} = +2$ .  
Case highlighted in yellow is exemplified in Figures 2 and 3.

### Addendum A, Solving the Quartic and Quintic Polynomials

When using Newton's method to approximate the root of the quintic polynomial eq. 22 describing the multi-equilibria in solutions of bromate ( $B^-$ ) in aq. sulfuric acid ( $H_2A$ ) as in Figure S6, the starting point for the iteration is important. For starting values larger than 0.7 the Newton iterations converge to the root near 0.96. However, for smaller positive starting points, the iteration converges to the largest negative root, which is close to zero. This example illustrates the necessity to choose starting values that converge to the desired positive root. A general algorithm might implement bisection until a root is trapped in a small interval and then switch to Newton's method to rapidly refine the approximation. More detailed accounts are available in textbooks on numerical methods. For practical applications to equilibrium concentrations, appropriate starting values can be easily found by trial and error or by inspection of a computer generated graph.



**Figure S6.** Part of the graph of the quintic polynomial eq. 22 describing the multi-equilibria in solutions of bromate ( $B^-$ ) in aq. sulfuric acid ( $H_2A$ ) for the set of equilibrium constants  $K_{11} = 10^3$ ,  $K_{12} = 10^{-2}$ , and  $K_2 = 1$  and initial concentrations  $[H_2A]_0 = 1.0$  M and  $[B^-]_0 = 0.1$  M ( $\alpha = 0.1$ ,  $\beta = 1$ ,  $\gamma = 0.1$ ) is depicted.

### **Addendum B, *Formulation of the Autonomous Ordinary Differential Equations***

An earlier, longer version of this section contained the following paragraph at the end:

“Once all reaction rates are specified, the mathematical theory of ordinary differential equations ensures that for each choice of the initial concentrations there is a unique solution of the kinetic model equations that exists for some interval of time beyond the initial time, which we may always take to be the origin of the temporal variable. In the case of acid dissociation, physical intuition suggests that the transient reaction proceeds to a steady state of constant species concentrations while all transient concentrations remain bounded. The boundedness assumption, which can also be checked directly from the system of differential equations, ensures that each physically realistic solution of the differential equation model exists for all positive time.”

### **Proof that Eq. 23 Has Exactly One Real Positive Root**

Descartes's rule of signs (Wang, X. A Simple Proof of Descartes's Rule of Signs. *The Amer. Math. Monthly* **2004**, *111*, 525-526) can be used to demonstrate that the quartic eq. 23 has exactly one positive real root (which is  $[H^+]$  at equilibrium). This rule states that the maximum number of real positive roots is equal to the number of sign changes in the list of nonzero coefficients of the polynomial written in order of descending powers. Recall the quartic polynomial

$$z^4 + (K_{11} + \alpha)z^3 + (-K_w + K_{11}(K_{12} + \alpha - \beta))z^2 - K_{11}(K_w - K_{12}\alpha + 2K_{12}\beta)z - K_{11}K_{12}K_w = 0 \quad (\text{eq. 23}).$$

To determine that there is exactly one positive real root (which is  $[H^+]$  at equilibrium), apply Descartes' rule of signs, which states that the maximum number of real positive root is equal to the number of times the signs change in the list of nonzero coefficients of the polynomial written in order of descending powers. For example, the coefficient list of the polynomial,  $a_1z^2 + a_2z + a_3$  is  $\{a_1, a_2, a_3\}$ , and the number of real roots is equal to the number of sign changes going down the list. Applying this to eq. 23, the coefficient list is  $\{1, K_{11} + \alpha, K_{11}(K_{12} + \alpha - \beta) - K_w, K_{12}(K_{12}\alpha - 2K_{12}\beta - K_w), -K_{11}K_{12}K_w\}$ . Substituting for  $\alpha$  and  $\beta$ , we find that  $1 > 0$ ,  $K_{11} + \alpha = K_{11} + [HA^-]_0 + 2[A^{2-}]_0 + [B^-]_0 > 0$ ,  $-K_{11}K_{12}K_w < 0$ , and  $K_{11}(K_{12}\alpha - 2K_{12}\beta - K_w) = K_{11}(K_{12}(-2[H_2A]_0 - [HA^-])) - K_w < 0$ . But, the sign of the coefficient  $S_1 := K_{11}(K_{12} + \alpha - \beta) - K_w = K_{11}(K_{12} + [A^{2-}]_0 - [H_2A]_0) - K_w$  is undetermined. The list of signs of the coefficients becomes  $\{+, +, S_1, -, -\}$ . Thus there is only one sign change independent of the sign of  $S_1$ . Therefore, the application of Descartes' rule of signs shows that eq. 23 has at most 1 real positive root.

**Quartic Polynomial vs. Iterative Methods.** The combination of equilibrium constant expression eqs. 1 – 3 with the charge and mass balance eqs. 12 and 13 (absence of HB and B<sup>-</sup>) allows to express the proton concentration of an aqueous solution of the salt MHA as a function of [HA<sup>-</sup>] via

$$[H^+] = \sqrt{\frac{K_{11}K_{12}[HA^-] + K_{11}K_w}{[HA^-] + K_{11}}}. \quad (\text{eq. S1})$$

The derivation of this equation is provided below.

Parker and Breneman employed eq. S1 in their iteration method.<sup>14</sup> This equation relates the equilibrium concentrations of [H<sup>+</sup>] and [HA<sup>-</sup>]. The corresponding steady state concentrations are approximated with the method of successive approximation.<sup>6b</sup> To begin the process, a tolerance  $\tau$  is specified, the approximation [HA<sup>-</sup>]<sub>1</sub> = [HA<sup>-</sup>]<sub>0</sub> is made and eq. S1 is used to determine [H<sup>+</sup>]<sub>1</sub>. The concentrations [H<sub>2</sub>A]<sub>1</sub> and [A<sup>2-</sup>]<sub>1</sub> are computed in accordance with eqs. 2 and 3, respectively, using the concentrations [H<sup>+</sup>]<sub>1</sub> and [HA<sup>-</sup>]<sub>1</sub>. For,  $i = 1, 2, 3, \dots$ , the new concentration [HA<sup>-</sup>]<sub>i+1</sub> is determined via eq. 13 as [HA<sup>-</sup>]<sub>i+1</sub> = [HA<sup>-</sup>]<sub>0</sub> - [A<sup>2-</sup>]<sub>i</sub> - [H<sub>2</sub>A]<sub>i</sub>, and so on until |[HA<sup>-</sup>]<sub>i+1</sub> - [HA<sup>-</sup>]<sub>i</sub>| <  $\tau$ . Eq. S1 expresses the proton concentration as a function of [HA<sup>-</sup>] and describes the pH of an aqueous solution of the salt MHA. Similarly, one can derive the equations

$$[H^+]^2 - 2[H^+]( [H_2A]_0 - H_2A ) - K_w + K_{11}[H_2A] = 0, \quad (\text{eq. S2})$$

$$2[H^+]^3[A^{2-}] + (K_{11}[A^{2-}] - K_{11}K_{12})[H^+]^2 - K_wK_{11}K_{12} = 0, \quad (\text{eq. S3})$$

for the proton concentration of aqueous solutions of the diprotic acid H<sub>2</sub>A or of the salt M<sub>2</sub>A; respectively. Derivations of these equations also are given below.

We emphasize that eqs. S1, S2, and S3 (respectively) provide the proton concentration as a function of the *equilibrium* concentration of [HA<sup>-</sup>], [H<sub>2</sub>A], or [A<sup>2-</sup>] (respectively). In marked contrast, eqs. 22 and 23 provide the proton concentration at equilibrium based solely on the knowledge of the equilibrium constants and *initial* concentrations.

**Derivation of Eq. S1 with  $[\text{HA}^-]_0 \neq 0$ ,  $[\text{H}_2\text{A}]_0 = 0$ ,  $[\text{A}^{2-}]_0 = 0$  (Parker's eq. 5)**

In the absence of HB and its conjugate base, and for the special case where  $[\text{A}^{2-}]_0 = [\text{H}_2\text{A}]_0 = 0$ , eqs. 12 and 13 take the form

$$[\text{H}^+] + [\text{HA}^-]_0 = [\text{OH}^-] + [\text{HA}^-] + 2[\text{A}^{2-}], \quad (\text{eq. 12a})$$

$$[\text{H}_2\text{A}] + [\text{HA}^-] + [\text{A}^{2-}] = [\text{HA}^-]_0. \quad (\text{eq. 13a})$$

Replacement of  $[\text{HA}^-]_0$  in eq. 12a by eq. 13a yields

$$[\text{H}_2\text{A}] - [\text{A}^{2-}] + [\text{H}^+] - [\text{OH}^-] = 0. \quad (\text{eq. P5})$$

Recall the reaction constant equation forms of Eq. 1 – 3:

$$K_w = [\text{OH}^-][\text{H}^+], \quad K_{11} = \frac{[\text{HA}^-][\text{H}^+]}{[\text{H}_2\text{A}]}, \quad K_{12} = \frac{[\text{A}^{2-}][\text{H}^+]}{[\text{HA}^-]}.$$

Substitution of  $[\text{H}_2\text{A}] = \frac{[\text{HA}^-][\text{H}^+]}{K_{11}}$ ,  $[\text{A}^{2-}] = \frac{K_{12}[\text{HA}^-]}{[\text{H}^+]}$  and  $[\text{OH}^-] = \frac{K_w}{[\text{H}^+]}$  into eq. P5 yields

$$\frac{[\text{HA}^-][\text{H}^+]}{K_{11}} - \frac{K_{12}[\text{HA}^-]}{[\text{H}^+]} + [\text{H}^+] - \frac{K_w}{[\text{H}^+]} = 0.$$

By multiplying by  $[\text{H}^+]$  and rearranging the last equation is recast in this form

$$([\text{HA}^-] + K_{11})[\text{H}^+]^2 = K_{12}[\text{HA}^-] + K_w.$$

Finally solving for  $[\text{H}^+]$ , we find that

$$[\text{H}^+] = \sqrt{\frac{K_{11}K_{12}[\text{HA}^-] + K_{11}K_w}{[\text{HA}^-] + K_{11}}}. \quad (\text{eq. S1})$$



**Derivation of Eq. S2 with  $[\text{HA}^-]_0 = 0$ ,  $[\text{H}_2\text{A}]_0 \neq 0$ ,  $[\text{A}^{2-}]_0 = 0$**

In the absence of HB and its conjugate base, and for the special case where  $[\text{A}^{2-}]_0 = [\text{HA}^-]_0 = 0$ , eqs. 12 and 13 take the form

$$[\text{OH}^-] + [\text{HA}^-] + 2[\text{A}^{2-}] = [\text{H}^+], \quad (\text{eq. 12b})$$

$$[\text{H}_2\text{A}] + [\text{HA}^-] + [\text{A}^{2-}] = [\text{H}_2\text{A}]_0. \quad (\text{eq. 13b})$$

Rearranging eq. 13b and substituting this result into eq. 12b, we obtain the equation

$$[\text{A}^{2-}] = [\text{H}_2\text{A}]_0 - [\text{H}_2\text{A}] - [\text{HA}^-],$$

$$[\text{OH}^-] - [\text{HA}^-] + 2([\text{H}_2\text{A}]_0 - [\text{H}_2\text{A}]) = [\text{H}^+].$$

Also from the definition of the rate constants of Eqs. 1 – 2

$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]}, \quad [\text{HA}^-] = \frac{K_{11}[\text{H}_2\text{A}]}{[\text{H}^]}.$$

By substitution into the preceding equation, we find that

$$\frac{K_w}{[\text{H}^+]} - \frac{K_{11}[\text{H}_2\text{A}]}{[\text{H}^+]} + 2([\text{H}_2\text{A}]_0 - [\text{H}_2\text{A}]) = [\text{H}^+].$$

Multiplying by  $[\text{H}^+]$  and rearranging yields the desired result

$$[\text{H}^+]^2 - 2[\text{H}^+]([\text{H}_2\text{A}]_0 - [\text{H}_2\text{A}]) - K_w + K_{11}[\text{H}_2\text{A}] = 0. \quad (\text{eq. S2})$$

**Derivation of Eq. S3 with  $[\text{HA}^-]_0 = 0$ ,  $[\text{H}_2\text{A}]_0 = 0$ ,  $[\text{A}^{2-}]_0 \neq 0$**

In the absence of HB and its conjugate base, and for the special case where  $[\text{H}_2\text{A}]_0 = [\text{HA}^-]_0 = 0$ , eqs. 12 and 13 take the form

$$[\text{OH}^-] + [\text{HA}^-] + 2[\text{A}^{2-}] - [\text{H}^+] = 2[\text{A}^{2-}]_0, \quad (\text{eq. 12c})$$

$$[\text{H}_2\text{A}] + [\text{HA}^-] + [\text{A}^{2-}] = [\text{A}^{2-}]_0. \quad (\text{eq. 13c})$$

Substituting eq. 13c into 12c yields

$$[\text{H}^+] = [\text{OH}^-] - 2[\text{H}_2\text{A}] - [\text{HA}^-] = [\text{H}^+].$$

Recall the reaction constant equation forms of Eq. 1 – 3

$$K_w = [\text{OH}^-][\text{H}^+], K_{11} = \frac{[\text{HA}^-][\text{H}^+]}{[\text{H}_2\text{A}]}, K_{12} = \frac{[\text{A}^{2-}][\text{H}^+]}{[\text{HA}^-]}.$$

Substitution of  $[\text{OH}^-] = \frac{K_w}{[\text{H}^+]}$ ,  $[\text{HA}^-] = \frac{[\text{A}^{2-}][\text{H}^+]}{K_{12}}$ , and  $[\text{H}_2\text{A}] = \frac{[\text{HA}^-][\text{H}^+]}{K_{11}}$  into the preceding equation gives us the result

$$\frac{K_w}{[\text{H}^+]} - 2 \frac{[\text{H}^+]^2[\text{A}^{2-}]}{K_{11}K_{12}} - \frac{[\text{A}^{2-}][\text{H}^+]}{K_{12}} = [\text{H}^+].$$

Multiplying by  $K_{11}K_{12}[\text{H}^+]$  and rearranging gives the final result

$$2[\text{H}^+]^3[\text{A}^{2-}] + (K_{11}[\text{A}^{2-}] - K_{11}K_{12})[\text{H}^+]^2 - K_wK_{11}K_{12} = 0. \quad (\text{eq. S3})$$