
HYDROLYSIS OF UNIUNIVALENT SALTS IN AQUEOUS
SOLUTIONS. II. HYDROLYSIS OF WEAK ACID-
WEAK BASE WEAK-ELECTROLYTE SALTS†

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The previous paper of this series (Bulloff, 1961) dealt with electroneutrality-violation correction calculation for the weak acid-weak base strong-electrolyte case in essentially weakly acidic or basic, but not near-neutral solutions. In near-neutral solutions, the common-ion effect of the ions of water itself adds another factor affecting the electroneutrality balance of solute ions. In this paper, the recursive iterative technique is applied so that all the material and charge balances are reconciled whatever the origin of initial inconsistencies in formulations. The weak-electrolyte case considered here is the most complicated of the thirteen uniunivalent solute cases.

The generality of the recursive approach is illustrated by presenting a calculation conducted by progressive minimization of mass discrepancies in contrast to the previous calculation for the simpler strong-electrolyte case which was converged by reduction of electroneutrality discrepancies. Comparison of calculations for the two weak acid-weak base cases indicates how simpler cases may be treated by simpler calculation cycles and more complicated ones by use of more inclusive cycles.

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UNIUNIVALENT SOLUTE CASES

At introductory levels, students encounter the expression for water:

$$K_w = [H^+][OH^-] = 1 \times 10^{-14}, \quad (1)$$

weak acids, HA, where A^- is the anion:

$$K_{HA} = [H^+][A^-]/[HA], \quad (2)$$

and weak bases, BOH, where B^+ is the cation:

$$K_{BOH} = [B^+][OH^-]/[BOH].$$

These weak electrolyte cases, treated by an ionization constant, differ from the strong electrolyte cases whose essentially complete dissociation makes it possible to take the concentration of solute species as that of the whole solute, as in the instances of the strong-acid case, HX, the strong-base case, M^+OH^- , and the strong-salt case, M^+X^- , where,

$$\{HX\} = [H^+] = [X^-]; \{M^+OH^-\} = [M^+] = [OH^-]; \{M^+X^-\} = [M^+] = [X^-]. \quad (4)$$

Where strong-electrolyte salts contain the anions or cations of weak-electrolyte acids or bases, as in the cases B^+X^- , M^+A^- , and B^+A^- , there are involved the aforementioned ionization constants. Conformable pedagogic presentation of the properties of the ions in terms of hydrolysis constants (Ricci, 1952 [A]):

$$K_{hb^+} = [BOH][H^+]/[B^+] = K_w/K_{BOH}; K_{ha^-} = [HA][OH^-]/[A^-] = K_w/K_{HA}; K_{hb^+a^-} = [HA][BOH]/[A^-][B^+] = K_w/K_{HA}K_{BOH}, \quad (5)$$

has the weakness that the last case differs from the other two, and that the actual equations:



are inchoately normalized to:



not only implicitly assuming that:

$$K_{HA} = K_{BOH}; a = b; [B^+] = [A^-]; [BOH] = [HA]; [H^+] = [OH^-], \quad (8)$$

but also yielding an expression in which a most important factor, the pH of the solution, is not directly accessible. In addition, the unwonted treatment of a pair of ions as a molecular electrolyte (Ricci, 1952 [A]) for all cases:

$$K_{HA} \neq K_{BOH}, \quad (9)$$

creates a violation of the electroneutrality corollary of the Law of Conservation of Matter (Bulloff, 1961).

For the weak-electrolyte salt cases, MX, BX, MA, and BA, the ionization constants:

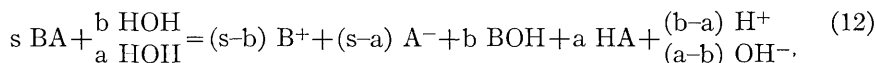
$$K_{MX} = [M^+][X^-]/[MX]; K_{BX} = [B^+][X^-]/[BX]; K_{MA} = [M^+][A^-]/[MA]; K_{BA} = [B^+][A^-]/[BA], \quad (10)$$

make the introduction and use of hydrolysis constants:

$$K_{hBX} = K_{BX}K_w/K_{BOH} = [BOH][H^+]/[BX]; K_{hMA} = K_{MA}K_w/K_{HA} = [HA][OH^-]/[MA]; K_{hBA} = K_{BA}K_{hb^+a^-} = K_{BA}K_w/K_{HA}K_{BOH} = [HA][BOH]/[BA], \quad (11)$$

without unwonted normalizations impossible. It is perhaps fortunate that in elementary teaching weak salts are largely neglected. Their consideration can involve as many as three kinds of mass or charge conservation violation, unless either expressions too sophisticated for introductory courses are used, or some simple means of pointing out the limitations of simple expressions is adopted, and an elementary means of showing correction is presented.

Of these cases, as in the strong-salt series, again the weak acid-weak base one is the most difficult, involving as it does, the inchoate normalization of:



to:



which not only denies direct access to pH evaluation, but which also bars direct evaluation of other anion or cation concentrations. Thus this case is one in which the definitiveness and power of the calculations of concern here can be effectively illustrated. Since (1) governs in aqueous solutions, if its requirements are reconciled with those of all solutes and solute species present, then all other discrepancies thereon dependent will also be reconciled.

The Water Effect

Taking (1) into account, for $[\text{H}^+]$ in HX, instead of (4), there has to be employed:

$$[\text{H}^+] = 0.5 [(4K_w + \{\text{HX}\}^2)^{0.5} + \{\text{HX}\}]. \quad (14)$$

Table 1 indicates the magnitude of the corrections to (4) for various solute concentrations of HX. Though such correction may not be large, it can lead to corrections larger for certain solute species concentrations than are usually the basis for modern theory treatments of electrolyte problems in preference to Arrhenius theory treatments. Thus table 1 is important, as is its counterpart for strong bases.

TABLE I
[H⁺] in HX solutions

$\{\text{HX}\},^6 [\text{H}^+]_{(4)}$	$[\text{H}^+]_{(14)}$	$[\text{OH}^-]_{(1)}$	$[\text{H}^+] + [\text{OH}^-]$
10^{-4}	1.000001×10^{-4}	1×10^{-10}	1.000002×10^{-4}
10^{-5}	1.000100×10^{-5}	1.00×10^{-9}	1.000200×10^{-5}
10^{-6}	1.009975×10^{-6}	9.9750×10^{-9}	1.019950×10^{-6}
10^{-7}	1.618034×10^{-7}	6.18034×10^{-8}	2.236068×10^{-7}
10^{-8}	1.051249×10^{-8}	9.51249×10^{-8}	2.002598×10^{-7}
10^{-9}	1.005013×10^{-7}	9.95013×10^{-8}	2.000026×10^{-7}
10^{-10}	1.000500×10^{-7}	9.99500×10^{-8}	2.000000×10^{-7}
0	1×10^{-7}	1×10^{-7}	2×10^{-7}

Similarly to (14), for the weak acid HA, there is obtained:

$$[\text{H}^+] = 0.5 \{ (4K_w + [\text{A}^-]^2)^{0.5} + [\text{A}^-] \}, \quad (15)$$

equivalent to alternative expressions that may be derived via (2), in that H^+ cannot be expressed in terms of only $\{\text{HA}\}$. Attempts at solution give equations dependent on:

$$[\text{H}^+]^3 + K_{\text{HA}}[\text{H}^+]^2 - (K_{\text{HA}}[\text{HA}] + K_w)[\text{H}^+] - K_w K_{\text{HA}} = 0, \quad (16)$$

(Griffith, 1921-2; Park, 1953) which are either intrinsically difficult or redundant or else approximate (Ricci, 1952[B]; Nightingale, 1957) or which have to be evaluated from tables (Park, 1953). The recursive calculations are simpler, and students can use them more easily. These latter do not require separate consideration of weak-base solutes.

Among the eight salt solute cases, the expressions for exact solutions of $[\text{H}^+]$ in terms of evaluable quantities are even more recondite (Ricci, 1952[A,B]; Bishop, 1960; Bruckenstein, 1959), and the calculations illustrated below are thereby relatively more attractive.

THE RECURSIVE ITERATIVE APPROACH

For BA Solutions, by the Law of Conservation of Mass:

$$\{BA\} = [BA] + [B^+] + [BOH] = [BA] + [A^-] + [HA], \quad (17)$$

and:

$$\{BA\} - [BA] = [B^+] + [BOH] = [A^-] + [HA]. \quad (18)$$

By electroneutrality corollary:

$$[B^+] + [H^+] = [A^-] + [OH^-], \quad (19)$$

(18) gives:

$$[H^+] = 0.5 [(4K_w + q^2)^{0.5} + q]; \quad OH^- = 0.5[(4K_w + q^2)^{0.5} - q]. \quad (21)$$

(21) can be related to table 1 as follows:

$$q = \{H^+\} = [H^+]_{(14)} - [OH^-]; \quad [H^+] + [OH^-] = 2[H^+] - q. \quad (22)$$

Thus, if there is assumed a value of $[H^+]$, say, $[H^+]_1$, then the assumption fixes values $[OH^-]_1$ and q_1 . It then becomes possible to determine assumed values for all the other solute species in a BA solution.

Rearranging (2) and (3), and subtracting, via (20):

$$([B^+][OH^-]/K_{BOH}) - ([H^+][A^-]/K_{HA}) = [BOH] - [HA] = q, \quad (23)$$

and, since:

$$[A^-] = [H^+] - [OH^-] + [B^+] = q + [B^+], \quad (24)$$

then,

$$[B^+] = q K_{BOH} (K_{HA} + [H^+]) / (K_{HA}[OH^-] - K_{BOH} [H^+]);$$

$$[A^-] = a K_{HA} (K_{BOH} + [OH^-]) / (K_{HA}[OH^-] - K_{BOH} [H^+]) \quad (25)$$

Thus, the assumption $[H^+]_1$ also fixes $[B^+]_1$ and $[A^-]_1$; via (2), (3), (10), or (11), and (17), there are fixed: $[HA]_1$, $[BOH]_1$, $[BA]_1$, and $\{BA\}_1$, providing that the denominators of (25) have been positive, a requirement for an initial assumption that:

$$[H^+]_1 < (K_{HA} K_{hb+})^{0.5}. \quad (26)$$

According as to whether the $\{BA\}_1$ value derived from assuming $[H^+]_1$ is larger (or smaller) than the given $\{BA\}$ value, to minimize the difference, m_1 , a smaller $[H^+]$ value, say, $[H^+]_2$ must then be assumed. In such iteratively minimized further assumption, $[H^+]_{2, 3, 4, \dots, n'}$ there can be computed a set of concentrations $[H^+]_n$, $[OH^-]_n$, $[A^-]_n$, $[B^+]_n$, $[HA]_n$, $[BOH]_n$, $[BA]_n$, of accuracy as great as is desired, as $\{BA\}_n$ is made to approach actual $\{BA\}$.

The magnitude of the corrections so effected can be estimated by comparison with values obtained directly from (11) or (10), e.g., $[B^+]_0$, $[A^-]_0$, etc., as below.

Illustrative Calculation

Given:

$$\{BA\} = 10^{-4} \text{ M}, \quad K_{HA} = 10^{-4}, \quad K_{BOH} = 10^{-10}, \quad K_{BA} = 10^{-4}, \quad (27)$$

then from:

$$K_{hBA} = 10^{-4}, \quad K_{HA}K_{hb+} = 10^{-8}, \quad (28)$$

$$[BOH]_0 = [HA]_0 = 6.18034 \times 10^{-5}; \quad [BA]_0 = 3.81966 \times 10^{-5}, \quad (29)$$

and, by (26):

$$[H^+]_1 < 10^{-4}, \quad \text{say } 5 \times 10^{-5}, \quad (30)$$

and by (10):

$$[B^+]_0 = [A^-]_0 = 6.18034 \times 10^{-5}; \quad [BA]_0 = 3.81966 \times 10^{-5}, \quad (31)$$

and by (17),

$$\{BA\}_0 = 1.618034 \times 10^{-4}, \quad (32)$$

so that there is a mass discrepancy,

$$m_0 = +6.18034 \times 10^{-4}. \quad (33)$$

From (1) and (17) (26), by (30):

$$\begin{aligned} [\text{OH}^-]_1 &= 2 \times 10^{-10}; \quad q = 5 \times 10^{-5}; \quad [\text{B}^+] = 5 \times 10^{-5}; \quad [\text{A}^-] = 1 \times 10^{-4}; \\ [\text{BOH}]_1 &= 1 \times 10^{-4}; \quad [\text{HA}]_1 = 5 \times 10^{-5}; \quad [\text{BA}]_1 = 5 \times 10^{-5}; \\ \{\text{BA}\}_1 &= 2 \times 10^{-4}; \quad m_1 = 1 \times 10^{-4}. \end{aligned} \quad (34)$$

With this result, an improved assertion (iteration) of:

$$[\text{H}^+]_2 = 3 \times 10^{-5}, \quad (35)$$

is possible, and for subsequent iterations convergence occurs as is shown in table 2. After the use of (35), the rate of change of mass discrepancy m_n with change of assumed $[\text{H}^+]_n$ can be used to secure more convergent recursive progress. In the six cycles shown in table 2, the mass discrepancy is reduced 99.9 percent while in $[\text{BA}]$, $[\text{B}^+]$, and in $[\text{HA}]$, errors corrected are about 263 percent of the actual values. Further correction would be small; it would start with:

$$[\text{H}^+]_7 = 3.819124 \times 10^5. \quad (36)$$

TABLE 2

Successive cycles of calculation, n , for correction of Law of Conservation of Mass Violation, m , in 0.0001 M BA, $K_{\text{BA}} = 10^{-4}$, $K_{\text{HA}} = 10^{-4}$, $K_{\text{BOH}} = 10^{-10}$, typical weak acid-weak base weak-electrolyte solution

n	0	1	2	3	4	5	6 ^(a)
$\times 10^5$							
$[\text{H}^+]_n$	—	5	3	4	3.8	3.82	3.8186 ^a
$[\text{B}^+]_n = [\text{HA}]_n$	6.18	5	1.3	2.67	2.33	2.365	2.35985
$[\text{BOH}]_n = [\text{A}^-]_n$	6.18	10	4.3	6.67	6.13	6.181	6.17757
$[\text{BA}]_n$	3.82	5	0.56	1.77	1.43	1.462	1.45781
$\{\text{BA}\}_n$	1.62	20	6.16	11.11	9.89	10.008	9.99523
m_n	+6.2	+10	-3.04	+1.11	-0.11	+0.008	-0.00477
$m_n/[\text{H}^+]_n$	—		6.5	4.2	6.1	5.9	9.1

^(a)The correct value of $[\text{H}^+]_n$ is more nearly 3.819124.

SUMMARY

A calculation has been given illustrative of the application of recursive mass discrepancy correction by convergent iteration of a sort sufficiently elementary for introductory pedagogical use. The techniques illustrated can be generally applied to calculations of solute species concentrations in electrolyte solutions.

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