

# HYDROLYSIS OF UNIUNIVALENT SALTS IN AQUEOUS SOLUTIONS. I—THE HYDROLYSIS OF WEAK ACID-WEAK BASE STRONG-ELECTROLYTE SALTS†

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## *Introduction*

Solution theory taught in beginning analytical chemistry courses has to be restricted to explanations that sophomore-level students can follow. The explanation usually given is based on Arrhenius' theory of ionization. It applies with the precision needed to the laboratory examples commonly chosen except for the case of weak acid-weak base salts. The hydrolytic constants derived for this case present an explanation that postulates equal hydrolysis for anions and cations in contradiction of the fact that it is applied to systems where the acid and base ionization constants may differ by orders of magnitude (Glasstone, 1949, 1950). It may not be generally known that this involves a violation of the Law of Conservation of Matter.

## *Electrical Neutrality of Electrolyte Solutions*

The behavior of an electrolyte, BA, of variant degree of dissociation, for dilute solutions, can be represented by the Arrhenius' theory formulation:



For solutions where the concentration of a solute species, e.g.,  $c_{\text{B}^+}$ , can be taken as equal to its activity, e.g.,  $a_{\text{B}^+}$ , the expression  $[\text{B}^+]$  is employed, in units of moles per liter. Such expressions are generally limited to dilute solutes, except that where the solvent is one but slightly affected in activity by the interactions considered, they may also be used. Thus, for (1),

$$[\text{HOH}] = \text{constant} = \text{about } 55.5 \text{ moles/liter.} \tag{2}$$

In the solution for which (1) describes the essential solute-solvent interaction, the constituents B, A, H, and OH are each present as three different species, e.g., B atoms occur in BA,  $\text{B}^+$ , and BOH. By the Law of Conservation of Matter, the concentration of the constituent B,  $\{\text{B}\}$ , is:

$$\{\text{B}\} = [\text{BA}] + [\text{B}^+] + [\text{BOH}]. \tag{3}$$

Similarly,

$$\{\text{A}\} = [\text{BA}] + [\text{A}^-] + [\text{HA}], \tag{4}$$

$$\{\text{H}\} = [\text{HOH}] + [\text{H}^+] + [\text{HA}], \tag{5}$$

and,

$$\{\text{OH}\} = [\text{HOH}] + [\text{OH}^-] + [\text{BOH}]. \tag{6}$$

†Presented before Section G, Ohio Academy of Science Meeting, Yellow Springs, Ohio, April 22, 1960.

Then, since the Law is holding,

$$\{\text{HOH}\} = \{\text{H}\} = \{\text{OH}\}, \quad (7)$$

and,

$$\{\text{BA}\} = \{\text{B}\} = \{\text{A}\}. \quad (8)$$

Since, by (7), it follows from (5) and (6) that:

$$[\text{HOH}] + [\text{OH}^-] + [\text{BOH}] = [\text{HOH}] + [\text{H}^+] + [\text{HA}], \quad (9)$$

then,

$$[\text{BOH}] + [\text{OH}^-] = [\text{HA}] + [\text{H}^+]. \quad (10)$$

Since, by (8), it follows from (3) and (4) that:

$$[\text{BA}] + [\text{A}^-] + [\text{HA}] = [\text{BA}] + [\text{B}^+] + [\text{BOH}], \quad (11)$$

then,

$$[\text{HA}] + [\text{A}^-] = [\text{BOH}] + [\text{B}^+]. \quad (12)$$

Adding (10) and (12),

$$[\text{BOH}] + [\text{HA}] + [\text{OH}^-] + [\text{A}^-] = [\text{BOH}] + [\text{HA}] + [\text{H}^+] + [\text{B}^+]. \quad (13)$$

Cancellation in (13) gives:

$$[\text{OH}^-] + [\text{A}^-] = [\text{H}^+] + [\text{B}^+]. \quad (14)$$

Assuming that electrons obey the Law of Conservation of Mass, and that their charge is unitary, (14) expresses what has been postulated as an independent Law of Electrical Neutrality of Electrolyte Solutions (Griffith, 1921-2).

#### *Violation of the Electrical Neutrality Law*

For the hydrolysis of a strong salt of a weak acid, HA, and a weak base, BOH, (1) is usually written:



For a strong electrolyte, in dilute solution, for any  $\{\text{BA}\}$ ,

$$[\text{BA}] = 0. \quad (16)$$

Because of (2), it is possible to express the ionization constant of water as:

$$[\text{H}^+] [\text{OH}^-] = K_w = 1 \times 10^{-14}. \quad (17)$$

The net hydrolytic reaction indicated in (15) can be expressed by the summation,



which assumes that both ions can be correlated despite the fact that each actually reacts with water separately.

For the reaction assumed in (18), the reaction constant, taken to be the actual hydrolysis constant  $K_{h_{BA}}$ , is expressed as:

$$K_{h_{BA}} = [\text{BOH}] [\text{HA}] / [\text{B}^+] [\text{A}^-], \quad (19)$$

with  $[\text{HOH}]$  eliminated as a separate term by using (2) as in (17). Since multiplying the denominator and numerator of (19) by the quantity  $[\text{H}^+] [\text{OH}^-]$  would leave its value unchanged,

$$K_{h_{BA}} = ([\text{BOH}] / [\text{B}^+] [\text{OH}^-]) ([\text{HA}] / [\text{H}^+] [\text{A}^-]) ([\text{H}^+] [\text{OH}^-]), \quad (20)$$

and

$$K_{h_{BA}} = K_w / K_{\text{BOH}} K_{\text{HA}}, \quad (21)$$

where  $K_{\text{BOH}}$  is the ionization constant of the weak base as usually defined,

$$K_{\text{BOH}} = [\text{B}^+] [\text{OH}^-] / [\text{BOH}], \quad (22)$$

where  $K_{\text{HA}}$  is the ionization constant of the weak acid as usually defined,

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

and  $K_w$  is as defined in (17).

It can be shown that use of the expression (21), commonly employed in college teaching, by virtue of the inadequacy of (18), leads to a general violation of the electric neutrality rule and of the basic laws underlying it, for the general condition,

$$K_{\text{HA}} \neq K_{\text{BOH}}. \quad (24)$$

A general expression for this inequality could be readily derived, but it is more complicated than would be desired for sophomore instruction (Griffith, 1921-2). Demonstrating the inequality by a selected example is more simple and has the advantage of providing a starting point for the rapid calculation of an instructive correction.

Alpha-naphthylaminium barbiturate seems an apt choice for a sample calculation. For alpha-naphthylamine:

$$K_{\text{BOH}} = K_b = 9.9 \times 10^{-11} \cong 1 \times 10^{-10}, \quad (25)$$

and for barbituric acid,

$$K_{\text{HA}} = K_a = 1.05 \times 10^{-4} \cong 1 \times 10^{-4}. \quad (26)$$

Assuming a solution 0.001 M in this salt, by (21),

$$K_{h_{BA}} = 1, \quad (27)$$

and, by (19),

$$[\text{A}^-] = [\text{B}^+] = [\text{BOH}] = [\text{HA}] = 0.0005 \text{ M}. \quad (28)$$

This result follows from the usual calculations used in solution problems. However, from (23),

$$[\text{H}^+] = 0.001 \text{ M}, \quad (29)$$

and from (22), or via (17),

$$[\text{OH}^-] = 10^{-10} \text{ M}, \quad (30)$$

on using the values of (28). Thus, there is an excess of 0.0001 mole of positive charge per liter of solution, a fantastic discrepancy.

*Minimization of Electrical Neutrality Violation*

There are two approaches to avoiding the discrepancies that arise for the general case (24) when (21) is used. One approach is to replace (18) by an expression in which the separate hydrolysis of  $B^+$  and of  $A^-$  is taken account of in the correlation; this leads to quadratic equations that are simple algebraically, accurate in principle, but require manipulations too complicated arithmetically for slide-rule manipulation or for average sophomore performance (personal communication, Dr. P. M. Williamson). The other approach is that of correcting the discrepancy by a numerical minimization technique. This technique could be expressed generally in the form of a single recursive series formula. (General iterative functions applicable to computer programming have been derived, and will be reported elsewhere). Again, using an example, that already taken, offers a simpler means of indicating the actual technique.

From (28-30)

$$[B^+] + [H^+] = [A^-] + [OH^-] + 0.0001. \quad (31)$$

If one-half of the excess positive charge is equally distributed by adding half of it to  $[A^-]$  and subtracting half of it from  $[B^+]$ , then, by (19),

$$[B^+] = [HA] = 0.00045 \text{ M}, \quad (32)$$

and,

$$[A^-] = [BOH] = 0.00055 \text{ M}. \quad (33)$$

The same results could be derived by use of (12) and its antecedents. By (23), for these first corrected values (32) and (33),

$$[H^+] = 8.18 \times 10^{-5} \text{ M} \quad ([OH^-] = 1.22 \times 10^{-10} \text{ M}). \quad (34)$$

From (28-30),

$$[B^+] + [H^+] = [A^-] + [OH^-] = 0.0000182. \quad (35)$$

TABLE I

*Hydrolysis of 0.001 M BA,  $K_a = 10^{-4}$ ,  $K_b = 10^{-10}$ , strong salt tabulation of effect of corrections for electrical neutrality violation*

Quantity	Uncorrected	First Cycle Correction	Second Cycle	Third Cycle
$[HA] = [B^+]$	0.0005	0.00045	0.000459	0.0004576
$[BOH] = [A^-]$	0.0005	0.00055	0.000541	0.0005424
$[H^+] \times 10^{+4}$	1.	0.818	0.848	0.845
$[OH^-] \times 10^{+10}$	1.	1.22	1.18	1.19
Charge Discrepancy*	$+1 \times 10^{-4}$	$-1.82 \times 10^{-5}$	$+2.8 \times 10^{-6}$	$-3 \times 10^{-7}$

\*In units of  $6.0268 \times 10^{23}$  electron charges.

The discrepancy of (31) has been reduced about fivefold, and it has been changed in sign. The cycle (32-35) can be repeated, with due regard for alternation of signs, to reduce the discrepancy to as small an amount as may be desired. Table I shows the progress made by further pursuit of such calculation.

### Summary

It has been shown that for the case of weak acid-weak base strong salts, where the ionization constants of the acid and base involved differ appreciably, the hydrolysis constant usually derived from simple Arrhenius' theory gives an inadequate and contradictory description of the solutes in dilute solution. The rule that electrolyte solutions are electrically neutral can be derived from the Law of Conservation of Matter, and can be applied to simple arithmetic recursive correction of the usual description to produce corrections of a desired order of accuracy. Its application is sufficiently simple and rapid, and the concepts involved are fundamental enough that it can be applied to elementary teaching.

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