The pH of very dilute solutions of strong acids – a calculation for a medical or biomedical class involving the application of simple numerical skills

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Abstract: This paper presents the solution to a calculation of the pH of a very dilute solution of a strong acid or base, taking into account the effect of the hydronium or hydroxyl ions generated from the ionisation of the strong acid or base on the ionisation of water, as a second very weak acid. To be solved successfully, this calculation involves the concepts of conservation of charge, pH and the application of the general solution to a quadratic equation. Such an exercise involves the application of skills in basic numeracy, and can provide a core of understanding that can prepare students for many different sorts of calculations that represent real-life problems in the medical and biological sciences. A programme is presented in C++ which enables the work of students to be individualised so that each student in a class can work through a slightly different pH calculation, in such a way that a class supervisor can quickly check each student's result for accuracy. This exercise is presented as a potential means of enabling students to undertake and master similar types of calculations involving simple or more complex equilibria.

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Numeracy is an important component of the mastery of both medical and biomedical science. Recently, Nusbaum (2006) has drawn attention to the relevance of basic mathematical knowledge, defined therein as "a knowledge of algebra, statistics, and overall numeracy", to the mastery of medical concepts. However, little attention has been paid to this idea in recent years. In particular, many students have considerable difficulty in understanding pH and related calculations using the Henderson-Hasselbalch equation (Martin, 2012). Presented below is a calculation involving the concepts of conservation of charge, pH and the application of the general solution to a quadratic equation to compute the pH values of very dilute solutions of a strong acid. Such an exercise in numeracy can provide a core of understanding that can prepare students for many different sorts of calculations that represent real-life problems in medical and biological sciences.

As a simple extension of the concept of pH, there is widespread confusion by students and teaching staff on how to calculate the pH of solutions of strong acids of concentrations approximating those due to the hydronium ions resulting from the self-ionisation of water:

$$2H_2O \leftarrow\rightarrow H_3O^+ + OH^-$$

The ion product of water (K_w) is generally represented by the logarithm of its value to the base 10, ($\log_{10}K_w$) and this latter value has been determined by a variety of methods to be around -13.994 at 25°C (Marshall and Frank, 1981). The ionisation of water is highly temperature-dependent because of the associated large enthalpy change of 55.65 kJ mol^{-1} (Cerutti, Ko, McCurdy and Hepler, 1978). Table 1 presents a partial list of the values for $\log_{10}K_w$. as determined by Marshall and Frank, 1981:

temperature (°C)	$\log_{10}K_w$
0	-14.938
25	-13.995
50	-13.275
75	-12.712
100	-12.265

At 25°C, the expected pH resulting from the ionisation of pure water will be the value for $--\log_{10}K_w/2$, that is, pH 6.998. Concentrations of a strong acid around 1 x 10^{-7} M will therefore add additional hydronium ions in the same concentration range as those derived from the self-ionization of water, partially, but not completely, suppressing that ionisation. So calculation of the resulting pH is not a straightforward matter for

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the average student. The first-guess answer of ~pH 7 is intuitively incorrect, as this would result from self-ionization of water alone, and does not also take account of the contribution from hydronium ions originating from the presence of the added strong acid. Students are often bogged down in how to further approach this problem to achieve a correct solution.

An accurate approach requires the use of an equality of charge equation. This is presented below with reference to the specific instance of the ionisation of very dilute hydrochloric acid. It indicates that the concentration of the totality of positively charged ions (that is, hydrogen ions, $[H_3O^+]$) is equal to the concentration of the totality of negatively-charged ions (that is, hydroxyl ions plus chloride ions, namely $[OH^-] + [Cl^-]$):

$$[OH^-] + [Cl^-] - [H_3O^+] = 0$$ - equation I(A)

This equation could equally apply to the ionization of any strong acid in dilute solution.

An equivalent conservation of charge equation for ions in a solution of a dilute base can also be written. For example, that for sodium hydroxide in solution is:

$$[Na^+] + [H_30^+] - [OH^-] = 0$$ - equation I(B)

In this equation, the concentration of the totality of positively charged ions is represented by the concentration of sodium ions and hydrogen ions, ($[Na^+] + [H_30^+]$) which is clearly equal to the concentration of the totality of negatively-charged ions (that is, hydroxyl ions ($[OH^-]$). Again, this equation could equally apply to the ionisation of any strong base in dilute solution.

Equations such as these appear to be absent from many other (and erroneous) attempts to solve the problem of the pH of very dilute solutions of strong acids or bases.

Presented below are the equations required to compute the pH values of hydrochloric acid or of sodium hydroxide, both at concentrations of 1×10^{-7} M. Apart from the use of equation I(A) or I(B) respectively, the remaining equations are standard and assume that $\log_{10}K_w = -13.995$, for the sake of simplicity:

$$[H_3O^+]*[OH^-] = 1.0116*10^{-14}$$ - equation II

$$[Cl^-] = 1*10^{-7}$$ - equation III(A) for ionization of HCl

or: $[Na^+] = 1*10^{-7}$ - equation III(B) for ionization of NaOH

Appendix 1 section (a) presents the solution of equations I, II and III(A) to give an accurate value for $[H^+]$ in a solution of hydrochloric acid (1×10^{-7} M) in pure water. The resulting pH is calculated to be 6.7897.

Similarly, when this exercise is modified to compute the pH value of NaOH at a concentration of 1×10^{-7} M, using equations I, II and III(B), the resulting pH is calculated to be 7.2054. This calculation is presented as Appendix I section (b).

It is a simple matter to write software in any high-level language to calculate the pH of very dilute solutions of a strong acid and/or strong base using the above approach, by simply generalizing equation III. Presented in Appendix II is such a programme written in Microsoft Visual C++ version 6 for a DOS window. A compiled version of this simple programme can be obtained from the Author on request.

In this programme, K_w can be selected as $1.011*10^{-14}$, i.e. $\log_{10}K_w = -13.995$, its value at 25°C. However, the software will permit calculations at temperatures other than 25°C by allowing manual entry of a specific alternative values for $\log_{10}K_w$.

Using this approach, the work of students can be individualised so that a specific student can work through a pH calculation, using specific values for the ionisation constant of water and specific molarities of acid. A supervisor can quickly check the resulting calculation using a simple programme such as the one illustrated in the Appendix II.

By undertaking and mastering such calculations, students will get a thorough introduction to the concept of pH, of complex equilibria, and to the application of basic numeracy to simple calculations. Complex equilibria of many sorts apply widely in medicine – for example, in the unlikely field of immune-epidemiology (Reluga, Medlock and Perelson, 2008). The successful completion of the above calculation of the pH of dilute solutions of a strong acid or base involves the application of simple equations such as the general solution to a quadratic equation and the concept of conservation of charge. It is submitted that this type of calculation exercise is an effective approach to assisting medical and science students to make progress in development and extension of basic concepts of numeracy that will provide them with the opportunity later to successfully master many similar but simple problems in biology and medicine.

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Appendix I

Section (a). The calculation of pH for a solution of hydrochloric acid of 1 x 10^{-7} M and K_w = 1.011*10^{-14}, i.e. $\log_{10}K_w = -13.9952$.

$[OH^-] + [Cl^-] - [H_3O^+] = 0$ - conservation of charge equation I(A)

$[H_3O^+]*[OH^-] = 1.0116*10^{-14}$ - equation II

$[Cl^-] = 1*10^{-7}$ - equation III(A)

From equations I and III:

$[Cl^-] = 1*10^{-7} = [H_3O^+] - [OH^-]$ - equation IV

From equation II:

$$[OH^-] = \frac{1.0116*10^{-14}}{[H_3O^+]}$$ - equation V

Substituting in equation IV the right hand side of equation V for [OH-]:

$$1*10\text{-}7 = [H_3O^+] - \frac{1.0116*10^{-14}}{[H_3O^+]}$$ - equation VI

Multiplying equation VI by $[H_3O^+]$ on both sides and rearranging:

$[H_3O^+]^2 - 1*10^{-7}*[H_3O^+] – 1.0116*10^{-14} = 0$ - equation VII

This is now an equation expressed in the form of a general quadratic equation:

$ax^2 + bx + c = 0$

where in this instance:

$a = 1$

$b = -1*10^{-7}$

$c = -1.0116*10^{-14}$

$x = [H_3O^+]$

The roots of this general quadratic equation are:

$$x = \frac{- b +/- ((b^2 – 4a*c)^{\wedge 0.5})}{2a}$$

Therefore:

$$[H_3O^+] = \frac{1*10^{-7} +/- ((1*10^{-14} + 4*1.0116*10^{-14})^{\wedge 0.5})}{2}$$

As $[H_3O^+]$ cannot be negative:

$$[H_3O^+] = \frac{1 + (5.0464^{\wedge 0.5}) * 10^{-7}}{2}$$

So:

$[H_3O^+] = 1.624322 \times 10^{-7}$

i.e. the resulting pH = 6.78963

Section (b). The calculation of pH for a solution of sodium hydroxide of 1 x 10^{-7} M and $K_w = 1.011*10^{-14}$, i.e. $\log_{10}K_w = -13.9952$.

$[Na^+] + [H_30^+] - [OH^-] = 0$ - conservation of charge equation I(B)

$[H_3O^+]*[OH^-] = 1.0116*10^{-14}$ - equation II

$[Na^+] = 1*10^{-7}$ - equation III(B)

From equations I and III:

$[Na^+] = 1*10^{-7} = [OH^-] - [H_3O^+]$ - equation IV

From equation II:

$[OH^-] = \frac{1.0116*10^{-14}}{[H_3O^+]}$ - equation V

Substituting in equation IV the right hand side of equation V for $[OH^-]$:

$1*10^{-7} = \frac{1.0116*10^{-14}}{[H_3O^+]} - [H_3O^+]$ - equation VI

Multiplying equation VI by $[H_3O^+]$ on both sides and rearranging:

$[H_3O^+]^2 + 1*10^{-7}*[H_3O^+] - 1.0116*10^{-14} = 0$ - equation VII

This is now an equation expressed in the form of a general quadratic equation:

$ax^2 + bx + c = 0$

where in this instance:

$a = 1$

$b = 1*10^{-7}$

$c = -1.0116*10^{-14}$

$x = [H_3O^+]$

The roots of this general quadratic equation are:

$$x = \frac{-b +/- ((b^2 - 4a*c)^{\wedge 0.5})}{2a}$$

Therefore:

$$[H_3O^+] = \frac{-1*10^{-7} +/- ((1*10^{-14} - 4*1.0116*10^{-14})^{\wedge 0.5})}{2}$$

As $[H_3O^+]$ cannot be negative:

$$[H_3O^+] = \frac{-1 + (5.0464^{\wedge 0.5})}{2} * 10^{-7}$$

So:

$[H_3O^+] = 0.62321 \times 10^{-7}$

i.e. the resulting pH = 7.2054

Appendix II. A programme written in Microsoft Visual C++ version 6 for a DOS window to calculate the pH of a very dilute solution of a strong acid.

```
//Calculates pH for very dilute solutions of a fully ionized acid or alkali
#include <iostream.h>
#include <math.h>
#include <stdio.h>
        double am, ch, pH, msq, rh, sqr, kw, dc;
        char cha, stuff = 'S';
void main()
{
        cout  << "\nThis program (by Peter Barling) calculates pH for very \n" ;
        cout  << "\ndilute solutions of a fully ionized acid or alkali.\n\n" ;
        cout  << "\nThe dissociation constant of water at 0 degrees C is 0.1153 x 10^-14.\n\n";
        cout  << "\nThe dissociation constant of water at 25 degrees C is 1.0116 x 10^-14.\n\n";
        cout  << "\nThe dissociation constant of water at 37 degrees C is 2.2418 x 10^-14.\n\n";
        cout  << "\nThe dissociation constant of water at 50 degrees C is 5.3088 x 10^-14.\n\n";
        cout  << "\nThe dissociation constant of water at 75 degrees C is 19.4089 x 10^-14.\n\n";
        cout  << "\nThe dissociation constant of water at 100 degrees C is 54.3250 x 10^-14.\n\n";
        cout  << "\nNow set your value for the dissociation constant (without the 10^-14).\n\n";
        cin   >> dc;
        kw = 0.00000000000001 * dc;
        do {
        do {
        cout  << "\nDo you want to work with a strong acid or a strong base? (enter <A> or <B>):\n\n";
        cin  >> stuff;
        }
        while (stuff != 'A' && stuff != 'B');
        cout  << "\nEnter molarity of the strong " <<stuff<< " in normal notation (e.g. 0.0000001):\n\n";
        cin  >> am;
        msq = am*am;
        rh = msq + kw*4;
        sqr = pow(rh, 0.5);
        if (stuff == 'B') am = am*-1;
        ch= (am + sqr)/2;
        pH = -log10(ch);
```

```
        printf("\npH is:  %2.5f",pH);
        cout  << "\n\n";
        cout  << "\n\nDo you wish to continue with
another calculation? \n";
        cout  << "\nIf so, enter a *Y*\n";
        cha = 'N';
        cin  >> cha;
        }
        while (cha == 'Y' || cha == 'y');

        cout  << endl;
```