The pH of very dilute solutions of weak acids – a calculation involving the application of numerical skills to the solution of a cubic equation

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Abstract: This paper presents the solution to a calculation of the pH of a very dilute solution of a weak acid, taking into account the effect of the hydroxonium ions generated from the ionization of the acid on the ionization of water, also a very weak acid. To be solved successfully, this calculation involves the concepts of conservation of charge, pH, equilibria and the application of the general solution to a cubic equation. Such an exercise requires the application of skills in algebra, and can provide a core of understanding that can prepare advanced students for many different sorts of calculations that represent real-life problems in the chemical sciences. A programme is presented in C++ which enables the work of students to be individualized 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 the application of complex algebra to problems related to equilibria and solution dynamics.

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Numeracy is an important component of the mastery of chemical sciences. Yates (2002) has drawn attention to the relevance of mathematical knowledge to the mastery of concepts in physical chemistry.[1] However, insufficient attention has been paid to this idea in recent years. In particular, many students, especially those who are more familiar with the biological sciences, have considerable difficulty in understanding pH and related calculations using the Henderson-Hasselbalch equation.[2] Presented below is a calculation involving the concepts of conservation of charge, pH and the application of the general solution to a cubic equation to compute the pH values of very dilute solutions of a weak 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 advanced chemical sciences.

The present author has recently drawn attention to this in relation to the teaching of medical sciences and has developed software appropriate to the rapid solution of the quadratic function that results from the derivation of a non-approximate solution to the problem of the pH of very dilute solutions of strong acids and bases.[3] In the present paper, these concepts are further extended to the much more complex problem of the pH of a dilute solution of a weak acid. The approach that will be described here could be extended with facility to the corresponding problem of the pH of a dilute solution of a weak base.

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 acids of concentrations approximating those due to the hydroxonium ions resulting from the self-ionization of water:

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

Simplifying this equation by replacing the hydroxonium ion (H_3O^+) with the (more conventionally used) hydrogen ion (H^+):

$$H_2O \underset{K_w'}{\leftarrow\rightarrow} H^+ + OH^-$$

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An equivalent equation for the ionization of any weak (or for that matter, strong) acid (AcH) can be written:

$$AcH \xleftrightarrow[K_a]{} H^+ + Ac^-$$

These reaction equations can be rearranged to the following equilibrium equations:

$K_w' = [H^+]*[OH^-]$ …….. I

$K_a = [H^+]*[Ac^-] / [AcH]$ …….. II

We can also write the conservation equation:

$[Ac_{total}] = [AcH] + [Ac^-]$ …….. III

and a balance of charge equation:

$[H^+] – [OH^-] – [Ac^-] = 0$ …….. IV

Equations I to IV can now be combined to express $[H^+]$ in terms of K_a, K_w' and $[Ac_{total}]$:

$[H^+]^3 + K_a*[H^+]^2 – [H^+]*(K_w' + K_a * [Ac_{total}]) – K_a*K_w' = 0$ …….. V

Equation V is a cubic equation in the form:

$AX^3 + BX^2 + CX + D = 0$

Where:

$A = 1$

$B = K_a$

$C = –(K_w' + K_a*[Ac_{total}])$

$D = – K_a* K_w'$

$X = [H^+]$

Several methods have been developed for the exact solution to a cubic equation. In the author's opinion, the most facile of these to apply generally to any cubic equation is found at the site: http://www.1728.org/cubic2.htm.

The method outlined at that site involves initially calculating two variables, ***f*** and **g**, defined as follows:

$$f = \frac{(3C/A) – (B^2/A^2)}{3}$$

$$g = \frac{(2B^3/A^3) – (9BC/A^2) + (27D/A)}{27}$$

A derivative variable, $\boldsymbol{h}$, is then defined as:

$\boldsymbol{h} = (g^2/4) + (f^3/27)$

If $\boldsymbol{h} > 0$, which is the case for the solution of all pH problems of the type covered in this present paper, then there are three real roots. These are determined by defining parameters $\boldsymbol{i}$, $\boldsymbol{j}$, $\boldsymbol{K}$, $\boldsymbol{L}$, $\boldsymbol{M}$, $\boldsymbol{N}$ and $\boldsymbol{P}$ as follows:

$\boldsymbol{i} = ((\boldsymbol{g}^2/4) - \boldsymbol{h})^{1/2}$

$\boldsymbol{j} = \boldsymbol{i}^{1/3}$

(NOTE: The following trigonometric functions are in radians)

$\boldsymbol{K} = \text{arc cosine } (-(\boldsymbol{g} / 2\boldsymbol{i}))$

$\boldsymbol{L} = -\boldsymbol{j}$

$\boldsymbol{M} = \text{cosine } (\boldsymbol{K}/3)$

$\mathbf{N} = 3^{1/2} * \text{sine } (\boldsymbol{K}/3)$

$\boldsymbol{P} = -(\boldsymbol{b}/3\boldsymbol{a})$

Then these parameters can be used to compute the three real roots ($\boldsymbol{X_1}$, $\boldsymbol{X_2}$ and $\boldsymbol{X_3}$) of the cubic equation:

$\boldsymbol{X_1} = (2\boldsymbol{j} * \text{cosine } (\boldsymbol{K}/3)) - (\mathbf{B}/3\mathbf{A})$

$\boldsymbol{X_2} = \boldsymbol{L} * (\mathbf{M} + \mathbf{N}) + \boldsymbol{P}$

$\boldsymbol{X_3} = \boldsymbol{L} * (\mathbf{M} - \mathbf{N}) + \boldsymbol{P}$

In practice, $\boldsymbol{X_1}$ always turns out to be positive, while $\boldsymbol{X_2}$ and $\boldsymbol{X_3}$ are negative. As $[H^+]$ cannot be negative, the hydrogen ion concentration is in practice equal to $\boldsymbol{X_1}$. From this, the resulting pH can be calculated.

This particular approach outlined above is also convenient for turning the paradigm for solving a cubic equation into a programme for doing this in C++. Such a programme is appended to this paper in the Appendix.

As shown in the Appendix to this paper, it is a straightforward matter to write software in a high-level language such as C++ to calculate the pH of very dilute solutions of a strong or weak acid using the above approach. Moreover, this can be readily extended to the case of a strong or weak base, although that is left to the reader to develop. A compiled version of the present 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 individualized so that a specific student can work through a pH calculation, using specific values for the ionization constant of water and a specific molarity and K_a value for the weak (or for that matter, strong) acid. A supervisor can quickly check the resulting calculation using the resulting programme without having to compute the correct result *de novo*.

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 and programme-writing skills to quite complex calculations. Complex equilibria of many sorts apply widely in all branches of the chemical sciences – for example in an isothermal homogeneous continuous flow stirred tank reactor.[4] The successful completion of the above calculation of the pH of dilute solutions of a weak acid involves the application of procedures such as the general solution to a cubic equation and the concept of conservation of charge. It is submitted that this type of calculation exercise is an effective approach to assisting students of chemistry to make progress in development and extension of basic computing concepts that will provide them with the opportunity later to successfully master many similar or substantially more complex problems.

Within the fields of general and biological chemistry, one of the problems in which the above concepts may be readily applied is that of the pH of distilled water, standing in the open. The electrical conductivity of ultra-pure water increases substantially when exposed to the atmosphere as a consequence of the dissolution of carbon dioxide gas.[5] Moreover, the chemical nature of carbon dioxide in water is complicated by its presence as dissolved CO_2 as well as carbonic acid:

$$CO_2 + H_20 \longleftrightarrow H_2CO_3$$

The attainment of this equilibrium is slow, unless catalysed by an enzyme such as carbonic anhydrase. Hence, the time-dependence of changes in pH and conductivity in ultrapure water exposed to different partial pressures of CO_2 at different temperatures could provide further insight into the relevant kinetics and equilibria of carbon dioxide in dilute solution. Such an experimental exercise falls outside the scope of this paper, but is presented to illustrate but one of many potential applications of the equations considered herein.

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Appendix

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

```
#include <iostream.h>
#include <math.h>
#include <stdio.h>
#include <math.h>
#include <stdio.h>

void main()
{
        long double a, b, c, d, f, g, h, l, i, J, j, k, X1, dc, am, pH, kw, pK, kA, p=0.3333333333333333333;
        char cha = 'n', peekay = 'n';

cout << "\nThis program (by Peter Barling) calculates pH for very \n" ;
cout << "\ndilute solutions of a weak acid.\n\n" ;
cout << "\nThe dissociation constant of water at 0 degrees C is 0.1153 x 10^-14.";
cout << "\nThe dissociation constant of water at 25 degrees C is 1.0116 x 10^-14.";
cout << "\nThe dissociation constant of water at 37 degrees C is 2.2418 x 10^-14.";
cout << "\nThe dissociation constant of water at 50 degrees C is 5.3088 x 10^-14.";
cout << "\nThe dissociation constant of water at 75 degrees C is 19.4089 x 10^-14.";
cout << "\nThe dissociation constant of water at 100 degrees C is 54.3250 x 10^-14.\n";
cout << "Enter the dissociation constant of water (without the 10^-14): ";
cin  >> dc;
kw = 0.00000000000001 * dc;
cout << "\nThe pK for acetic acid is 4.75 at 25 deg. C\n";
cout << "and for carbonic acid is 6.35 at 25 deg. C. and 6.10 at 37 deg. C\n";
cout << "\nEnter pK of your chosen acid: ";
cin >> pK;

do
        {
        if (peekay == 'Y' || peekay == 'y')
        {cout << "\nEnter pK of your chosen acid: ";
        cin >> pK;
        }
        cout << "\nEnter molarity of acid in normal notation (e.g. 0.0000001):";
        cin  >> am;
        kA = 1/(pow (10, pK));
        a = 1;
        b = kA;
        c = -(kw + (kA*am));
        d = -kA*kw;
        cout << "\n";
```

```
            f = ((3*(c/a)) - ((pow(b,2))/(pow(a,2))))/3;
            g = ((2*(pow(b,3))/(pow(a,3)) - (((9*b)*c)/pow(a,2)) + ((27*(d/a))))) /27;
            h = (((pow(g,2))/4)+((pow(f,3)))/27);
            I = ((pow(g,2))/4 - h);
            i = pow(I,0.5);
            j = pow(i,p);
            J = -g/(2*i);
            k = acos(J);


            cout << “RESULT:\n”;
            X1 = (2*j*cos(k/3)) - (b/(3*a));
            pH = -log10(X1);
            cout << “pH = “ << pH << “\n”;

            cout << “\n\nDo you wish to continue with another calculation? \n”;
            cout << “\nIf so, enter a *Y*”;
            cout << “\nIf not, enter a *N* :”;
            cin >> cha;
            if (cha == ‘Y’ || cha == ‘y’)
            {cout << “\n\nDo you wish to change to another value for pK? \n”;
            cout << “\nIf so, enter a *Y*”;
            cout << “\nIf not, enter a *N* :”;
            cin >> peekay;
            }
            }
while (cha == ‘Y’ || cha == ‘y’);

            cout << “\nFINISHED!”;
            cout << endl;
}
```