

Mathematica as Equation Solver in Chemistry

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DEDICATED TO THE MEMORY OF PROF TOMISLAV CVITAŠ WHO WAS ALWAYS INTERESTED IN CHEMICAL EDUCATION

Abstract: We describe a graphical method for solving a wide range of algebraic equations in one unknown. The method can be used to solve problems in acid/base equilibria, properties of real gases, general equilibria, solubility products and chemical kinetics. The graphical method employs Mathematica software to solve equations by plotting two curves. This is different to current practices which use numerical (iterative) method or complex formulae.

The graphical method is easy to apply and requires minimal mathematical manipulations. It introduces students to the use of powerful computer algebra software. The method works not only for polynomial type equations (often encountered in acid/base or general equilibria or real gas equations), but also for non-polynomial equations involving exponential terms. The graphical method implemented by Mathematica represents a “graphing calculator”. The calculator is a general equilibrium solver for single equilibrium systems and allows students to calculate equilibrium concentrations without recourse to complex analytical formulae or numerical methods.

Keywords: teaching physical chemistry or general chemistry, calculator-based learning, computer algebra software.

INTRODUCTION

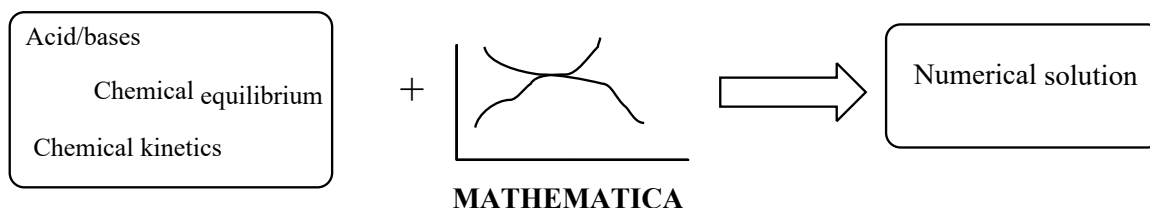
NONLINEAR equations in one unknown appear when teaching chemistry topics on acids and bases, solubility products, chemical equilibrium or chemical kinetics. The algebraic equations which quantify these chemical processes are often in the form of polynomials of the order > 4 which is generally solvable by numerical methods. Such approaches as discussed previously^[1–5] require mathematical or programming skills which entry level undergraduate students do not usually possess.

We describe a graphical method where mathematical manipulations are simple enough to be used in general chemistry teaching when real gases, chemical equilibria, solubility products or acid/base behavior are introduced and discussed. The method can be applied equally well in the classroom context (e.g. as a tutorial problem) or in the lab context (as analysis of experimental data). The method uses graphical representation (plot), rather than numerical, iterative methods or closed formulae and can be carried out with Mathematica software.

DISCUSSION

The graphical method described in this work updates and extends the earlier work.^[6–7] The update is interesting because it demonstrates that the method can be used not only for teaching real gases^[6] or chemical equilibrium,^[7] but also for teaching and learning of related topics e.g. acid/base systems and sparsely soluble salts. Furthermore, the method can be applied to some reactions in chemical kinetics. The update in this work also shows how to solve general problems which can be described by algebraic equations in one unknown (not necessarily of polynomial type). The one other update is to point out that the readout of the result can be achieved directly from computer screen by simply positioning of the cursor in Mathematica software. The example of the use of this graphical method (without Mathematica) on the example of real gas was described by Atkins *et al.*^[6] The graphical method described in this work is not obsolete as far as chemical education goes. It is included in the latest edition of the most widely used physical chemistry textbook.^[6]

The method can be conceptually summarized in the scheme below:



We illustrate the application of our method on several examples and provide corresponding Mathematica codes in the Appendix. In the initial step, the mathematical equation (in one unknown) is rearranged in such a way that the unknown variable (x) appears on both sides of the equation. This algebraic rearrangement is not unique, but different rearrangements lead to the same unique answer with the same precision. This rearrangement generates two expressions (labelled “l” for left and “r” for right in the code) containing the same variable x . The expressions correspond to two sides of the original equation which needs to be solved. The two expressions are then plotted as separate curves (functions of x) and the curves’ intersection point is sought. The value of x , determined at the intersection point satisfies the original equation and x is thus the solution desired. The range of x variable in the plot is adjusted by trial and error until the intersection point is located. This is achieved easily and quickly in Mathematica, simply by modifying the two numbers in Plot command which define the plot range e.g. in $\{x, 0, 1\}$. If the intersection point is not found in this range, the range is modified until it encompasses the intersection point e.g. $\{x, 0, 10\}$. Once the intersection is found, the range can be narrowed as much as desired to bracket the intersection point closely. Mathematica enables numerical readout of x coordinate of the intersection point directly from the computer screen, by placing cursor over the intersection point. The readout on the plot itself (on horizontal x axis) is of course also possible, but is less accurate or convenient. There are three important advantages of our method compared to numerical method or use of analytical formulae. The first advantage is that our method leads directly to the physically meaningful root (amongst several roots of higher order polynomial equation). In closed thermodynamic system, for a given set of initial (pre-equilibrium) concentrations only a single equilibrium state exists. Consequently, the resultant equilibrium concentrations are also unique which corresponds to the root found graphically. The second advantage is that the original equation requires little, if any algebraic manipulation. This is shown in the Example 2 below where one can keep the

unknown variable x in the denominator. To use standard, closed formulae one would need to rearrange the original

equation to match the solution formula. This reduces the burden of algebraic manipulations which may be necessary in preparation for using computer program when pursuing numerical solution method.^[1] The third advantage is that our method works in cases when analytical solution formulae do not exist.

Example 1

Calculate $[H^+]$ of the solution of acetic acid of concentration $C_a = 0.00001$ M which has ionization constant $K_a = 1.74 \times 10^{-5}$ M without using any approximations.^[2] The relevant equation is: $[H^+]^3 + K_a[H^+]^2 - (K_w + C_aK_a)[H^+] - K_wK_a = 0$. Rearranging the equation to get unknown $[H^+]$ on both sides of the equation gives $[H^+]^3 + K_a[H^+]^2 = (K_w + C_aK_a)[H^+] + K_wK_a$ where K_w is 10^{-14} M².

The relevant mathematical equation for this weak acid is then:

$$x^3 + 0.0000174x^2 = 0.0000174 \times 10^{-14} + x(10^{-14} + 0.00001 \times 0.0000174) \quad (1)$$

Plotting expressions: $x^3 + 0.0000174x^2$ and $0.0000174 \times 10^{-14} + x(10^{-14} + 0.00001 \times 0.0000174)$ as two curves representing two sides of Eq (1) and searching for their intersection gives Figure 1.

From Figure 1, x coordinate of the intersection point is $x = 7.15 \times 10^{-6}$ M which is the required $[H^+]$. This example shows that Mathematica’s graphical engine can readily handle very small numbers.

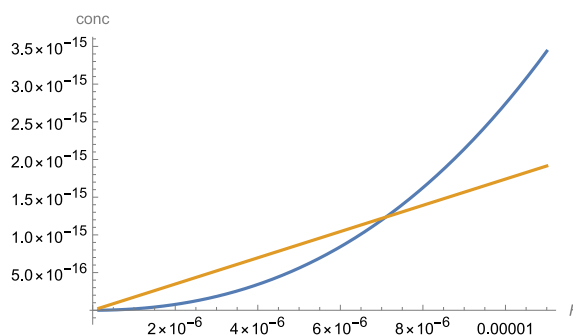


Figure 1. Plot of two expressions from each side of Eq (1).

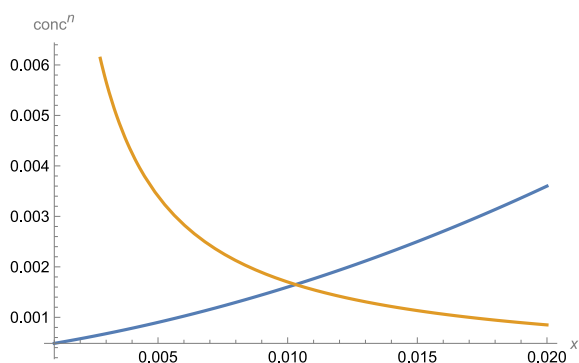


Figure 2. Plot of expressions on each side of (3) gives intersection at $x = 0.0105$ M.

Example 2

Consider the sparsely soluble salt^[1,2] $\text{PbCl}_2(\text{s}) \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + 2\text{Cl}^{-}(\text{aq})$ with $K_{\text{sp}} = 1.75 \times 10^{-5} \text{ M}^3$. What is the molar solubility of PbCl_2 in solution which has $[\text{NaCl}] = 0.02 \text{ M}$? The relevant mathematical equation corresponding to $K_{\text{sp}} = [\text{Pb}^{2+}][\text{Cl}^{-}]^2$ is Eq (2):

$$x(2x + 0.02)^2 = 1.75 \times 10^{-5} \quad (2)$$

Rearranging Eq (2) we get

$$(2x + 0.02)^2 = \frac{1.75 \times 10^{-5}}{x} \quad (3)$$

We then plot the left hand side $(2x + 0.02)^2$ and the right hand side $\frac{1.75 \times 10^{-5}}{x}$ expressions of Eq (3) as separate functions. The intersection of the two curves gives molar solubility of PbCl_2 as $x = 0.0105 \text{ M}$ (Figure 2) which is the molar solubility sought.

Example 3

Consider the equilibrium: $2\text{H}_2(\text{g}) + \text{CO}(\text{g}) \rightleftharpoons 1/2\text{C}_2\text{H}_4(\text{g}) + \text{H}_2\text{O}(\text{g})$ with $K = 2.79$. If the initial pressures of H_2 and CO are 4 and 1 atm, respectively, find the equilibrium pressures in the system.^[5] We derive the mathematical equation (4) from the equilibrium equation $K = (p_{\text{C}_2\text{H}_4}^{1/2} p_{\text{H}_2\text{O}}) / (p_{\text{H}_2}^2 p_{\text{CO}})$ as

$$K = \frac{x \cdot \sqrt{\frac{x}{2}}}{(4 - 2x)^2 (1 - x)} = 2.79 \quad (4)$$

We then plot expression $2.79 \times (4 - 2x)^2 (1 - x)$ as a function of x and expression $x \cdot \sqrt{\frac{x}{2}}$ as a function of x . The intersection of the two curves gives the value of x as 0.947 atm as the solution (Figure 3). The equilibrium pressures can subsequently be calculated by plugging the 0.947 atm value into Eq (4). As a check of the obtained solution, the calculated equilibrium pressures are plugged into Eq (4) to give back the correct equilibrium constant of 2.79.

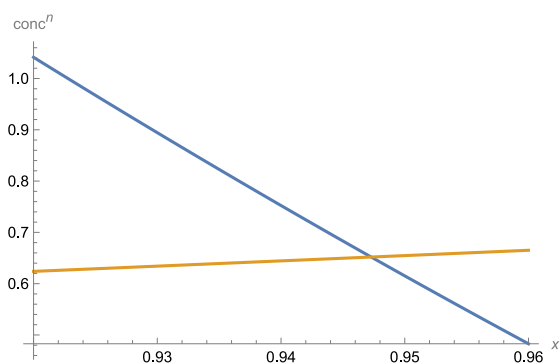


Figure 3. Plot equations on each side of Eq (4) gives intersection at $x = 0.947$ atm.

More examples of polynomial equations which originate when solving problems in acid/base chemistry are given by Bamdad.^[1] However, we also wish to demonstrate that our graphical method can also handle equations which are not simple polynomials. We do so on the example from chemical kinetics (Example 4).

Example 4

This example considers kinetics of a reversible 1st order reaction $\text{A} \rightleftharpoons \text{P}$. While this particular example is better suited for upper-level undergraduates, it is given here to demonstrate that our method can be applied to equations other than polynomials. The relationship giving dependence of concentration of A as a function of time (A_t) in $\text{A} \rightleftharpoons \text{P}$ reaction is well known^[8,9] and is given as (5). A_e is the equilibrium concentration of A and k_f and k_r are rate constants for the forward and reverse reactions, respectively. We assume that initially only A is present with known concentration A_0 . Upon rearranging (5) we get (6). Since A_e is fixed for a given initial concentration and temperature we can derive (7) and (8) which relate concentrations of A_{t1} and A_{t2} at times t_1 and t_2 ($t_2 > t_1$). Eq (8) is a simplified form of Eq (7) with reduced number of terms.

$$\frac{A_t - A_e}{A_0 - A_e} = e^{-(k_f + k_r)t} \quad (5)$$

$$A_e = \frac{A_t - A_0 e^{-(k_f + k_r)t}}{1 - e^{-(k_f + k_r)t}} \quad (6)$$

$$\frac{A_{t1} - A_0 e^{-(k_f + k_r)t1}}{1 - e^{-(k_f + k_r)t1}} = \frac{A_{t2} - A_0 e^{-(k_f + k_r)t2}}{1 - e^{-(k_f + k_r)t2}} \quad (7)$$

$$A_{t1} + (A_{t2} - A_0) e^{-(k_f + k_r)t1} = A_{t2} + (A_{t1} - A_0) e^{-(k_f + k_r)t2} \quad (8)$$

Selecting suitable times (t_1 and t_2) and the corresponding concentrations (A_{t1} and A_{t2}) we apply our method to solve Eq (8) and obtain $(k_f + k_r)$. Using the value

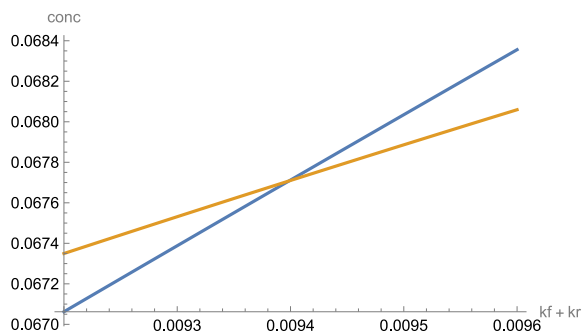


Figure 4. Plot for equilibrium equation (8) gives $k_f + k_r = 0.0094 \text{ s}^{-1}$.

of $(k_f + k_r)$ we can then get the remaining parameters k_f , k_r and K as per Eqs (9–11). Expression (9) is well known and combining it with Eq (5) and Eq (6) gives Eq (10).

$$K = \frac{A_0 - A_e}{A_e} = \frac{k_f}{k_r} \quad (9)$$

$$K = \frac{A_t - A_0}{A_0 e^{-(k_f + k_r)t} - A_t} \quad (10)$$

Selecting a certain time t and the corresponding concentration A_t we use Eq (10) to calculate K . Knowing K and $(k_f + k_r)$ we can finally obtain k_f , k_r and A_e from (11)

$$k_r = \frac{(k_f + k_r)}{K + 1} \quad k_f = \frac{K(k_f + k_r)}{K + 1} \quad A_e = \frac{A_0}{1 + K} \quad (11)$$

The method described in this Example 4 is suitable for very slow $A \rightleftharpoons P$ reactions when the equilibrium state cannot be reached and measured in the practical time period. This implies that K cannot be estimated accurately. We use the experimental data for esterification reaction in which 4-hydroxybutanoic acid gets converted into lactone derivative.^[8] We select the following experimental data for lactonization reaction: $A_0 = 0.1823 \text{ M}$, $A_{t1} = 0.1324 \text{ M}$, $A_{t2} = 0.0788 \text{ M}$, $t_1 = 50 \text{ min}$, $t_2 = 160 \text{ min}$. The application of our method and Eq (8) gives $k_f + k_r = 0.0094 \text{ s}^{-1}$ from Figure 4. Eq (8) is not a polynomial equation, but our method works well. The method can be applied to multiple experimental data points in this reaction^[8] in order to get the average value of $k_f + k_r$. However, as mentioned earlier, we only wanted to demonstrate the applicability of our method to non-polynomial type equations like Eq (8).

The power of modern computer algebra software used on a modern laptop computer is such that graphical method (plot) provides solution whose accuracy matches numerical/closed formula method. This is in itself an important learning experience for students and an encouragement to use and explore computer algebra software further.

The limitation of our method is that it requires some very basic familiarity with Mathematica software. The advantage is that it does not require writing programs using numerical analysis or complicated formulae as earlier methods do.^[1–5,10] Programming, the use of numerical (iterative) methods and complicated formulae, tax the average student's mathematical knowledge and consumes the time which can more profitably be spent on learning chemistry concepts.

CONCLUSION

The use of computer algebra software in teaching and learning chemistry (e.g. Maple, Matlab or Mathematica) has become widespread with the increasing power of personal computers. It is therefore beneficial for students to encounter such software early in their study of chemistry and apply it to solving standard problems encountered in learning general chemistry. This will encourage them to use this type of software later on, should they continue to study chemistry at upper undergraduate level. Many problems in chemical equilibria or acid/base reactions presented when teaching general chemistry level are artificially designed in such a way as to avoid the need to solve polynomial equations of degrees higher than two. The fact that there are no general, analytical solutions to equations in one unknown of the order > 4 limits the selection of tutorial problems even further. Our method overcomes these limitations without making heavy demands on student's mathematical background. Furthermore, drawing graphs to obtain numerical values of various parameters is a staple diet of teaching chemical kinetics in general chemistry subject, so our method fits well into what students are already using and learning.^[10]

Mathematica software also provides numerical solutions of the equations discussed in this work. See for example web sites **A** and **B**:

A

<https://www.wolfram.com/mathematica/new-in-10/enhanced-algebraic-computation/find-chemical-equilibrium-for-networks-of-reaction.html>

B

<https://mathematica.stackexchange.com/questions/98329/how-to-get-the-coordinates-of-the-intersection-of-two-lines-from-a-listlineplot>.

However, using these numerical Mathematica codes requires students learn a lot more about Mathematica syntax. The purpose of our work was to provide a universal equation solver with minimal effort which can be used and understood by 1st year chemistry students and not as an introduction to Mathematica capabilities. 1st year chemistry students often do not have extensive background in mathematics or computing.

To demonstrate direct numerical approach using Mathematica we utilized numerical function called: `ResourceFunction["CurveIntersection"]`. This function was used to obtain all numerical solutions directly in Examples 2 and 3 (see Appendix). The numerical results matched graphical results. However, `ResourceFunction["CurveIntersection"]` does not always work as indicated by the message on site B and as shown by our Example 4 where this numerical function does not work either.

APPENDIX

Mathematica code for Example 1 (graphical solution)

```
l=x^3+0.0000174*x^2
r=x*(10^(-14)+0.00001*0.0000174)+0.0000174*10^(-14)
Plot[{l,r},{x,0.00011,0.00015},AxesLabel->{H,conc}]
```

Mathematica code for Example 2 (graphical solution)

```
l=(2*x+0.02)^2
r=1.7*10^(-5)/x
Plot[{l,r},{x,0.001,0.02},AxesLabel->{x,conc}]
```

Mathematica code for Example 2 (numerical solution)

```
ResourceFunction["CurveIntersection"][{y==(2x+0.02)^2,y==1.7*(10^(-5))/x},{x,y}]
```

Mathematica code for Example 3 (graphical solution)

```
l=2.79*((4-2*x)^2)*(1-x)
r=Sqrt[x/2]*x
Plot[{l,r},{x,0.92,0.96},AxesLabel->{x,conc}]
```

Mathematica code for Example 3 (numerical solution)

```
ResourceFunction["CurveIntersection"][{y==2.79*((4-2x)^2)*(1-x),y==Sqrt[x/2]*x},{x,y}]
```

Mathematica code for Example 4 (graphical solution)

```
l=0.1324+(0.0788-0.1823)*Exp[-a*50]
r=0.0788+(0.1324-0.1823)*Exp[-a*160]
Plot[{l,r},{a,0.0092,0.0096},AxesLabel->{a,conc}]
```

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