CALCULATIONS OF CHEMICAL EQUILIBRIUM WITH SYMBOLIC COMPUTATION

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Abstract

We show how a processor for symbolic computation can readily enable extensive calculations to describe the equilibria involving gases, the pH of an aqueous solution in the titration of a polyprotic acid, and complex ions as a function of concentration of ligand in aqueous solution.

Resumen

En el presente trabajo se muestra un procedimiento matemático para el cálculo simbólico de problemas de equilibrio químico de gases, equilibrio ácido base en disolución, incluyendo curvas de valoración de ácidos polipróticos, y equilibrio de formación de complejos metal ligando en medio acuoso.

Key words: chemical equilibrium, titration curve, stability constants, symbolic computation

Palabras claves: equilibrio químico, curva de valoración, constantes de equilibrio, cálculo simbólico

I.   INTRODUCTION

Chemical equilibrium is a fundamental concept of chemistry that has profound implications also in biochemistry, biology, geology and physiology. For many chemical reactions of great relevance to contemporary chemical applications such as in industrial and environmental chemistry, in the application of analytical methods and even in the use of pharmaceutical products, its proper comprehension plays a crucial role. For this reason this topic should be diligently addressed during chemical education -- it has ubiquitous applications in not only chemistry but all contexts of natural and human processes in atmospheric, aquatic or marine and terrestrial media. The comprehension by students of this topic must then be a major objective in introductory courses of chemistry.

Although pupils who study chemistry in secondary schools typically undergo an initial acquaintance with chemical equilibrium, in universities an expanded coverage is common for students of general chemistry whose interests lie in any scientific subject named above. Its comprehension is essential as a basis of understanding phenomena in any succeeding course of chemistry such as analytical, inorganic, organic or physical chemistry, but its quantitative aspects cause difficulty in teaching and learning [1,2], not only because of the underlying mathematics. Students tend to have problems with basic concepts of chemical equilibrium such as reaction quotient and equilibrium quotient, Le Châtelier's principle, concentrations at equilibrium, the

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extent of reaction and the rate of reaction[2]. Even when students score well on examinations, it is generally accepted that they do not necessarily understand thoroughly the fundamental concepts of chemical equilibrium [3].

An obstacle that is encountered by the students when approaching problems in chemical equilibrium is that some assumptions are commonly made to simplify the mathematical treatment of a problem. These assumptions and the conditions under they are roughly valid are generally poorly understood by students, which leads to serious gaps and misunderstandings of real chemical phenomena. Although the qualitative concepts make little demand on understanding, the quantitative implementation of those concepts becomes challenging because of the mathematical nature of the treatment: when the detailed mathematical manipulations might be circumvented with the use of appropriate electronic computers and mathematical software, a student is free to devote his attention to the principles and their application to solve problems that confront him. Here we illuminate the use of true mathematical software for symbolic computation to solve problems in chemical equilibrium; we illustrate the principal concepts and calculations at a level of general chemistry. In this way, a focus on chemical phenomena, which are what matter in the teaching of chemistry, is achieved. The mathematical concepts are of course important as a basis to approach the problems, but the tedious mathematical manipulation can be effected with a computer program under a direct and interactive control by a student so that that student can concentrate on the chemical phenomena without undue distraction by minor details of mathematical operations. The mathematical basis of chemical equilibrium otherwise imposes a barrier to its understanding and application, analogously to many other aspects of chemistry.

Almost every textbook of general chemistry published in the past century contains a more or less extensive -- and more or less approximate, or even incorrect -- treatment of chemical equilibrium. Our purpose here is not to duplicate such discussion but rather to emphasize how chosen mathematical software with a symbolic capacity to prepare for and to implement the inevitable succeeding numerical calculations produces a powerful edifying effect on a student through its algebraic, numerical and graphical capabilities. To introduce the principles and application of chemical equilibrium, we present three examples of chemical systems to which we apply symbolic computation. For this purpose we use a common mathematical computer program called *Maple* [4] to undertake unflinchingly the manipulations that anybody would choose to avoid by hand; with minimal effort we plot elaborate figures that greatly enhance the comprehension of the problems.

II.   EXAMPLES

i. A gaseous system

The reaction of nitrogen and hydrogen to produce ammonia is an important reaction both biologically and industrially:

$$3H_2(g) + N_2(g) \Leftrightarrow 2NH_3(g)$$
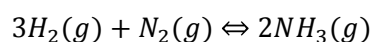
Its reaction quotient is

$$Q = \frac{p_{NH_3}{}^2}{p_{H_2}{}^3 p_{N_2}}$$

which has a value 4.07 x 10^{-5} bar^{-2} for the gaseous system in equilibrium at 723 K.

What would be the composition at equilibrium for this system given the initial composition P_{N2} = 1.0 bar and P_{H2} = 3.4 bar ?

Given the value of the equilibrium quotient at this temperature, we generate a system of equations as a basis to calculate the partial pressures of these gases at equilibrium. The equations for the partial pressures of each substance at equilibrium are stated as an initial pressure plus a change multiplied by a stoichiometric coefficient. The change x expresses the variation of the partial pressures that must occur such that the composition of the system conforms to the value of the equilibrium quotient. Here follow the steps in a computation of the solution for the specified initial composition. A line justified left, beginning with > and containing letters in roman font is an input statement or command to the *Maple* processor, and the resulting output line containing letters in italic font, if any, is centred just below that input line in each case.

> `K[p] := p[NH3]^2/(p[H2]^3*p[N2]) = evalf(4.07*10^(-5), 3)/bar^2;`

$$K_p := \frac{p_{NH3}^2}{p_{H2}^3\, p_{N2}} = \frac{0.0000407}{bar^2}$$

> `eq1 := p[N2] = (1.0 - x)*bar;`

$$eq1 := p_{N2} = (1.0 - x)\, bar$$

> `eq2 := p[H2] = (3.4 - 3*x)*bar;`

$$eq2 := p_{H2} = (3.4 - 3\, x)\, bar$$

> `eq3 := p[NH3] = (2*x)*bar;`

$$eq3 := p_{NH3} = 2\, x\, bar$$

> `sol := solve({eq1,eq2,eq3,K[p]}, {x,p[H2],p[NH3],p[N2]}):`
> `evalf(sol[1], 3);`

$$\{x = 0.0193\,, p_{H2} = 3.34\ bar\,, p_{N2} = 0.981\ bar\,, p_{NH3} = 0.0386\ bar\,\}$$

The former four equations set the stage for the critical calculation of the partial pressures of the substances at equilibrium. The solution, in the fifth command, of those four simultaneous and non-linear equations yields results in four sets corresponding to the roots of a quartic equation. Three of these sets are directly discarded because they contain negative or complex values of pressures; the acceptable solution is displayed in the last line. Attempting manually such a solution would be a major undertaking requiring substantial algebraic skill and a duration of tedious calculation that has nothing to do with understanding the problem; that understanding is essential in preparing the four equations, and, with mathematical software that can handle algebraic quantities, the solution is produced almost instantaneously. In this calculation, we carry explicitly the units attached to each intrinsic quantity, because the symbolic software is equally capable of carrying either numbers or numbers with their units through an entire calculation, including making conversions between units when appropriate. Hence the material of chemical significance advances to the fore, and the arithmetical details recede into the background.

The compositions at equilibrium of this and two other mixtures are made visual in the plot in Figure 1.
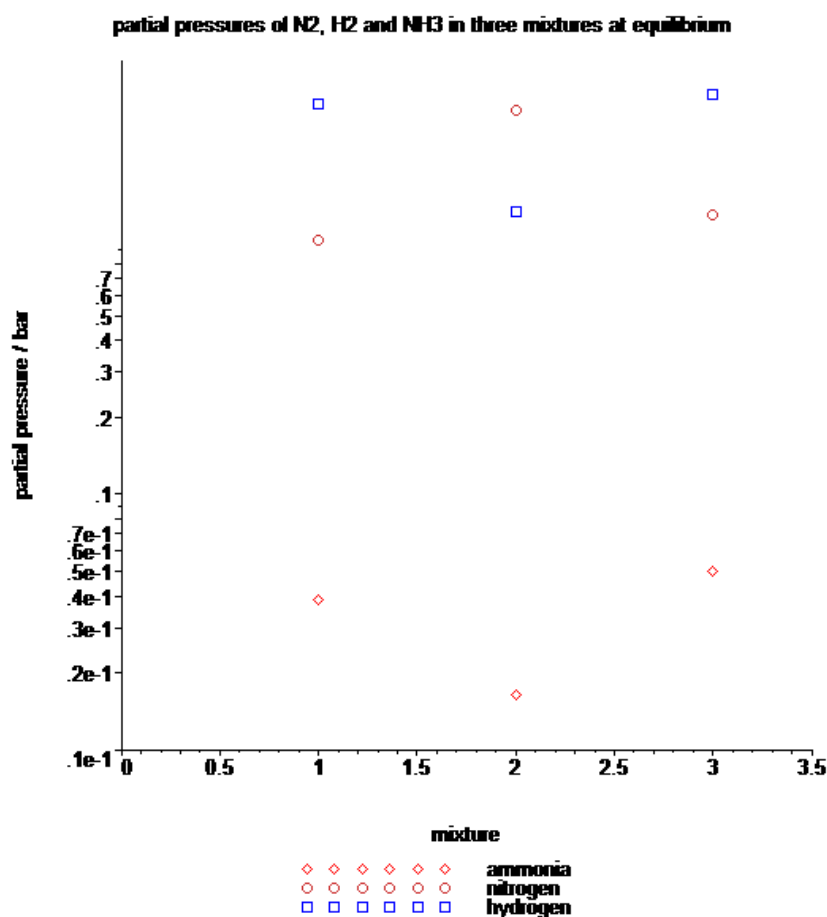
Figure 1. Partial pressures at equilibrium of three mixtures of disparate compositions in the system of N_2, H_2 and NH_3 at 723 K.

This figure shows how, for the same chemical system, these mixtures exist at equilibrium in multiple and disparate compositions. Although the individual pressures of the components of this system vary widely, over the large ordinate scale of the plot, their collective values conform to a particular condition called the equilibrium quotient, here expressed as K_P. What is important to assert is that this equilibrium quotient is the quantity that displays constancy, not the composition of the mixture, because, as seen here, multiple compositions of the system satisfy the value 4.07×10^{-5} bar^{-2} for the reaction quotient of the system at chemical equilibrium at 723 K.

ii. Titration of a polyprotic acid

Even when instrumental analysis is the standard approach to a quantitative determination of chemical elements or compounds, a titration remains a primary method of evaluating the potency of standard solutions. The titration of an acid with a base provides a textbook example in analytical chemistry of the variation of pH during a chemical reaction; for this purpose the calculation of a curve for the titration of a monoprotic acid with a monoprotic base might be practicable as a tedious manual calculation, whereas an analogous calculation for a diprotic acid might strain the limit of human patience, even when approximations, possibly severe, are invoked. Here we generate the titration curve of a tetraprotic acid, pyrophosphoric acid $H_4P_2O_7$, which has

scarcely any precedent in the literature but which requires no strenuous effort with the use of symbolic mathematical software. A sample of $H_4P_2O_7$ (concentration 0.10 mol L^{-1} , volume 10 mL) as analyte is to be titrated with NaOH (0.10 mol L^{-1}) as titrant. To treat this problem, we must know all equilibrium quotients applicable to the dissociation of this acid as well as any other pertinent relation. The successive ionizations of this acid and the reported corresponding values [5] of pK$_a$, formally applicable at ionic strength 0.10 mol L^{-1} and 298.15 K, appear in table 1.

Table I. Dissociation equilibria of pyrophosphoric acid and their pK$_a$

Equilibrium	pK$_a$
$H_4P_2O_7(aq) \Leftrightarrow H^+(aq) + H_3P_2O_7{}^{2-}(aq)$	0.70
$H_3P_2O_7{}^-(aq) \Leftrightarrow H^+(aq) + H_2P_2O_7{}^{2-}(aq)$	2.19
$H_2P_2O_7{}^{2-}(aq) \Leftrightarrow H^+(aq) + HP_2O_7{}^{3-}(aq)$	6.80
$HP_2O_7{}^{3-}(aq) \Leftrightarrow H^+(aq) + P_2O_7{}^{4-}(aq)$	9.59

To undertake the necessary calculation, we state these dissociation equilibria as equations identified by names to which the equations are assigned. The letter *P* serves to represent the pyrophosphate ion so that *H4P* serves both as a symbol to identify a chemical species $H_4P_2O_7$ and to denote its concentration, i.e. [$H_4P_2O_7$], and analogously for other species; *Ka1* denotes the equilibrium quotient for the first acid dissociation in Table 1, and analogously for the other quotients.

> **eq[acid1] := Ka1 = H*H3P/H4P;**

$$eq_{acid1} := Ka1 = \frac{H\,H3P}{H4P}$$

> **eq[acid2] := Ka2 = H*H2P/H3P;**

$$eq_{acid2} := Ka2 = \frac{H\,H2P}{H3P}$$

> **eq[acid3] := Ka3 = H*HP/H2P;**

$$eq_{acid3} := Ka3 = \frac{H\,HP}{H2P}$$

> **eq[acid4] := Ka4 = H*P/HP;**

$$eq_{acid4} := Ka4 = \frac{H\,P}{HP}$$

The ion product of water and two other relations must be taken into account. The equation for material balance states that the analytical concentration of pyrophosphoric acid in the analyte solution must be equal to the sum of the concentrations of all pyrophosphate species present in the system. Another relation is the equation for charge balance or electroneutrality that states that the sum of concentrations of cationic species must equal the sum of concentrations of anionic species. These three corresponding equations follow.

> **eq[water] := Kw=H*OH;**

$$eq_{water} := Kw = H\,OH$$

> **eq[material] := CnP = H4P + H3P + H2P + HP + P;**

$$eq_{material} := CnP = H4P + H3P + H2P + HP + P$$

> `eq[charge] := H + Na = OH + H3P + 2*H2P + 3*HP + 4*P;`

$$eq_{charge} := H + Na = OH + H3P + 2\,H2P + 3\,HP + 4\,P$$

In the equation for charge balance the symbol *Na* refers to the concentration of the added base, sodium hydroxide. We proceed to substitute in equations to obtain an expression for the concentration of H⁺ in terms of known or measurable quantities.

> `HP := solve(eq[acid4], HP);`

$$HP := \frac{H\,P}{Ka4}$$

> `H2P := solve(eq[acid3], H2P);`

$$H2P := \frac{H^2\,P}{Ka3\,Ka4}$$

> `H3P := solve(eq[acid2], H3P);`

$$H3P := \frac{H^3\,P}{Ka2\,Ka3\,Ka4}$$

> `H4P := solve(eq[acid1], H4P);`

$$H4P := \frac{H^4\,P}{Ka1\,Ka2\,Ka3\,Ka4}$$

> `P := solve(eq[material], P);`

$$P := \frac{CnP\,Ka1\,Ka2\,Ka3\,Ka4}{H^4 + H^3\,Ka1 + H^2\,Ka1\,Ka2 + H\,Ka1\,Ka2\,Ka3 + Ka1\,Ka2\,Ka3\,Ka4}$$

> `OH := solve(eq[water], OH);`

$$OH := \frac{Kw}{H}$$

All variables *H4P*, *H3P*, *H2P*, *HP*, *P* and *OH* thus become expressed in the equation for charge balance in terms of the dissociation quotients and the concentration of added base.

> `eq[charge];`

$$H = \frac{Kw}{H} + \frac{H^3\,CnP\,Ka1}{H^4 + H^3\,Ka1 + H^2\,Ka1\,Ka2 + H\,Ka1\,Ka2\,Ka3 + Ka1\,Ka2\,Ka3\,Ka4}$$
$$+ \frac{2\,H^2\,CnP\,Ka1\,Ka2}{H^4 + H^3\,Ka1 + H^2\,Ka1\,Ka2 + H\,Ka1\,Ka2\,Ka3 + Ka1\,Ka2\,Ka3\,Ka4}$$
$$+ \frac{3\,H\,CnP\,Ka1\,Ka2\,Ka3}{H^4 + H^3\,Ka1 + H^2\,Ka1\,Ka2 + H\,Ka1\,Ka2\,Ka3 + Ka1\,Ka2\,Ka3\,Ka4}$$
$$+ \frac{4\,CnP\,Ka1\,Ka2\,Ka3\,Ka4}{H^4 + H^3\,Ka1 + H^2\,Ka1\,Ka2 + H\,Ka1\,Ka2\,Ka3 + Ka1\,Ka2\,Ka3\,Ka4} - Na$$

The analytical concentration, *CnP*, of pyrophosphoric acid and the concentration, *Na*, of the added base are expressible in terms of the initial volume *V0* and added volume *V* of the base solution.

> `VT := V0 + V;`

$$VT := V0 + V$$

> `Na := CNaOH*V/VT;`

$$Na := \frac{CNaOH\ V}{V0 + V}$$

> `CnP := C0P*V0/VT;`

$$CnP := \frac{C0P\ V0}{V0 + V}$$

> `eq[charge];`

$$H = \frac{Kw}{H}$$

$$+ \frac{H^3\ C0P\ V0\ Ka1}{(V0 + V)\,(H^4 + H^3\ Ka1 + H^2\ Ka1\ Ka2 + H\ Ka1\ Ka2\ Ka3 + Ka1\ Ka2\ Ka3\ Ka4)}$$

$$+ \frac{2\ H^2\ C0P\ V0\ Ka1\ Ka2}{(V0 + V)\,(H^4 + H^3\ Ka1 + H^2\ Ka1\ Ka2 + H\ Ka1\ Ka2\ Ka3 + Ka1\ Ka2\ Ka3\ Ka4)}$$

$$+ \frac{3\ H\ C0P\ V0\ Ka1\ Ka2\ Ka3}{(V0 + V)\,(H^4 + H^3\ Ka1 + H^2\ Ka1\ Ka2 + H\ Ka1\ Ka2\ Ka3 + Ka1\ Ka2\ Ka3\ Ka4)}$$

$$+ \frac{4\ C0P\ V0\ Ka1\ Ka2\ Ka3\ Ka4}{(V0 + V)\,(H^4 + H^3\ Ka1 + H^2\ Ka1\ Ka2 + H\ Ka1\ Ka2\ Ka3 + Ka1\ Ka2\ Ka3\ Ka4)}$$

$$- \frac{CNaOH\ V}{V0 + V}$$

The latter complete expression defines the concentration of H$^+$ ions in terms of known quantities -- equilibrium quotients, initial concentration of the acid and added volume of the base solution. We can thus calculate the concentration of H$^+$, and thereby the pH, at any stage of the titration. In Figure 2 we simulate the titration for this problem.
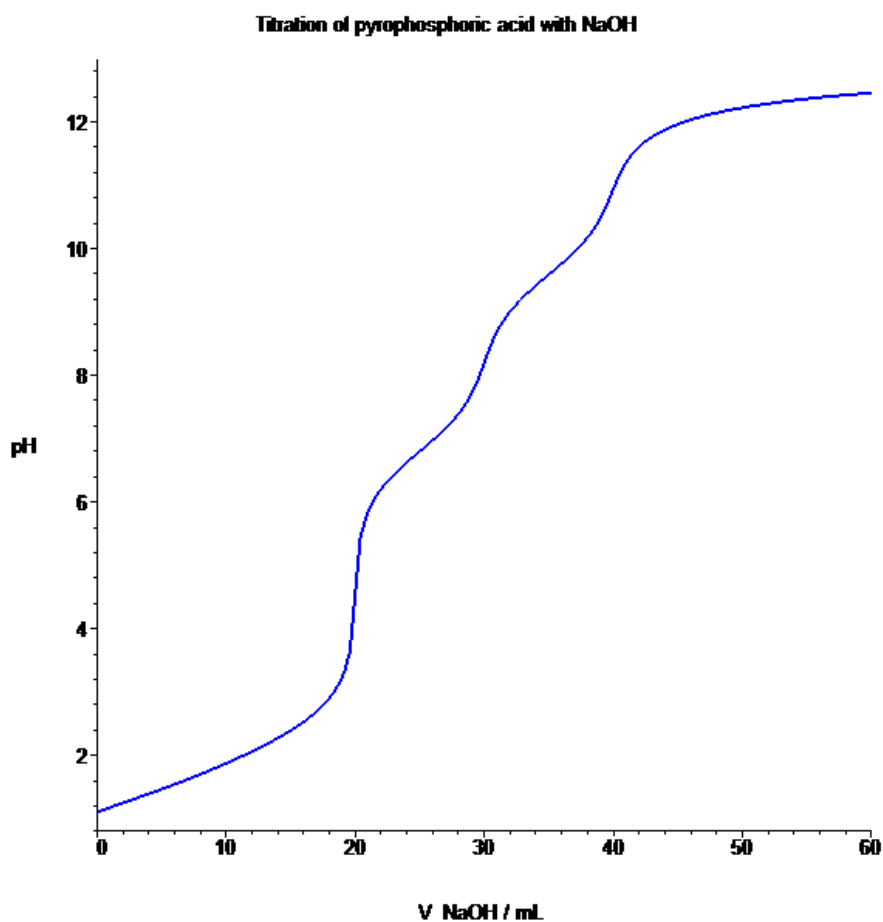
Figure 2. pH as a function of volume of NaOH solution added to a solution of pyrophosphoric acid.

Why do there seem to be only three end points, each marked with a point of inflection or steep segment of the curve that implies a large increase of pH for a small added volume of base? What happens is that the first dissociation of pyrophosphoric acid has pK_a 0.70 and the initial pH of the solution is 1.1. At this stage the pyrophosphoric acid is almost completely dissociated; for this reason no end point appears at $V = 10$ mL that would correspond to the removal of the first proton from the undissociated acid.

In the preceding treatment in this section, we simply state equations for essentially the conservation of material and net charge, for the successive ionic dissociations of a polyprotic acid, and then solve for quantities of interest, to build progressively an extensive expression for the concentration of hydrogen ion, leading to pH, at any stage of the titration. Imagine trying to undertake manually this calculation! Although the form of the terms of the ultimate expression is fairly transparent -- once the result has been obtained, a manual derivation of this expression is at least tedious and prone to error. Within an approximation of the use of molar concentrations instead of activities, the ultimate expression is exact, whereas in a manual calculation some approximation to lessen the extent of the expression applicable at a particular stage would be almost obligatory. Moreover, what the titration curve displayed in a still or dead manner on the printed page fails to convey is the temporal progress of the display of the curve in an actual titration, whether by manual means or with an automatic titrimeter connected to a pH meter. The simulation of this curve in a computer display can be readily animated, to maintain the sense of

pH varying with time as basic titrant is progressively added at a constant rate to the acidic analyte solution. Even if a student is not required to calculate manually, point by point, the progress of the curve across the page, the visual impact of such an animation is a worthy result of this exercise; such an animation makes clear to any student the nature of the process in a way that utterly fails with a still curve. Through this example, we appreciate profoundly the application of the algebraic, numerical and graphical capabilities of mathematical software for the purpose of teaching and learning vital concepts of chemistry.

iii. Complex ions

The other example that we select to illustrate a calculation of chemical equilibrium pertains to inorganic chemistry. The information in Table 2 pertains to chemical equilibria involving the formation of complexes of copper(II) ion with ammonia in aqueous solution [6].

Table 2. Equilibria in the formation of complex ions of copper(II) with ammonia and their corresponding equilibrium quotients

Complex formation equilibrium	log K
$Cu(aq) + NH_3(aq) \Leftrightarrow Cu(NH_3)^{2+}(aq)$	4.04
$Cu(NH_3)^{2+}(aq) + NH_3(aq) \Leftrightarrow Cu(NH_3)_2{}^{2+}(aq)$	3.43
$Cu(NH_3)_2{}^{2+}(aq) + NH_3(aq) \Leftrightarrow Cu(NH_3)_3{}^{2+}(aq)$	2.80
$Cu(NH_3)_3{}^{2+}(aq) + NH_3(aq) \Leftrightarrow Cu(NH_3)_4{}^{2+}(aq)$	1.48

How the fraction of each copper species varies as a function of the concentration of ammonia is the objective of this calculation. To solve this problem we first define a quantity denoted a that expresses the fraction of a particular metal species:

$$\alpha = \frac{concentration\ of\ a\ particular\ metal\ species}{Sum\ of\ the\ concentrations\ of\ all\ metal\ species} = \frac{x}{CnCu}$$

The sum of the concentrations of all metal species is equal to the analytical concentration of copper(II) in solution, denoted *CnCu*. From this definition of a, we proceed to express all equilibrium expressions as equations, supplemented by the equation for material balance.

```
> eq1 := K1 = (CuNH3)/((Cu)*(NH3));
```
$$eq1 := K1 = \frac{CuNH3}{Cu\ NH3}$$
```
> eq2 := K2 = (CuNH32)/((CuNH3)*(NH3));
```
$$eq2 := K2 = \frac{CuNH32}{CuNH3\ NH3}$$
```
> eq3 := K3 = (CuNH33)/((CuNH32)*(NH3));
```
$$eq3 := K3 = \frac{CuNH33}{CuNH32\ NH3}$$
```
> eq4 := K4 = (CuNH34)/((CuNH33)*(NH3));
```

$$eq4 := K4 = \frac{CuNH34}{CuNH33\ NH3}$$

> **`eq[materialCu] := CnCu = Cu + CuNH3 + CuNH32 + CuNH33 + CuNH34;`**

$$eq_{materialCu} := CnCu = Cu + CuNH3 + CuNH32 + CuNH33 + CuNH34$$

As in the case of the titration of pyrophosphoric acid, we proceed to substitute the equations so that an expression for each species becomes expressed as a function of the known formation quotients and the concentration of ammonia. After obtaining this relation, quantity a becomes expressed for each species; for instance, a for $Cu(NH_3)_2^{2+}$ is

> **`alpha := x -> x/(CnCu);`**

$$\alpha := x \rightarrow \frac{x}{CnCu}$$

> **`alpha(CuNH32);`**

$$\frac{K2\ K1\ NH3^2}{1 + K1\ NH3 + K2\ K1\ NH3^2 + K3\ K2\ K1\ NH3^3 + K4\ K3\ K2\ K1\ NH3^4}$$

In Figure 3 we plot these a quantities as a function of pNH_3, to depict how the fraction of each species varies with the concentration of ammonia; in the legend of the figure, *L* denotes NH_3 as a ligand of the indicated number.
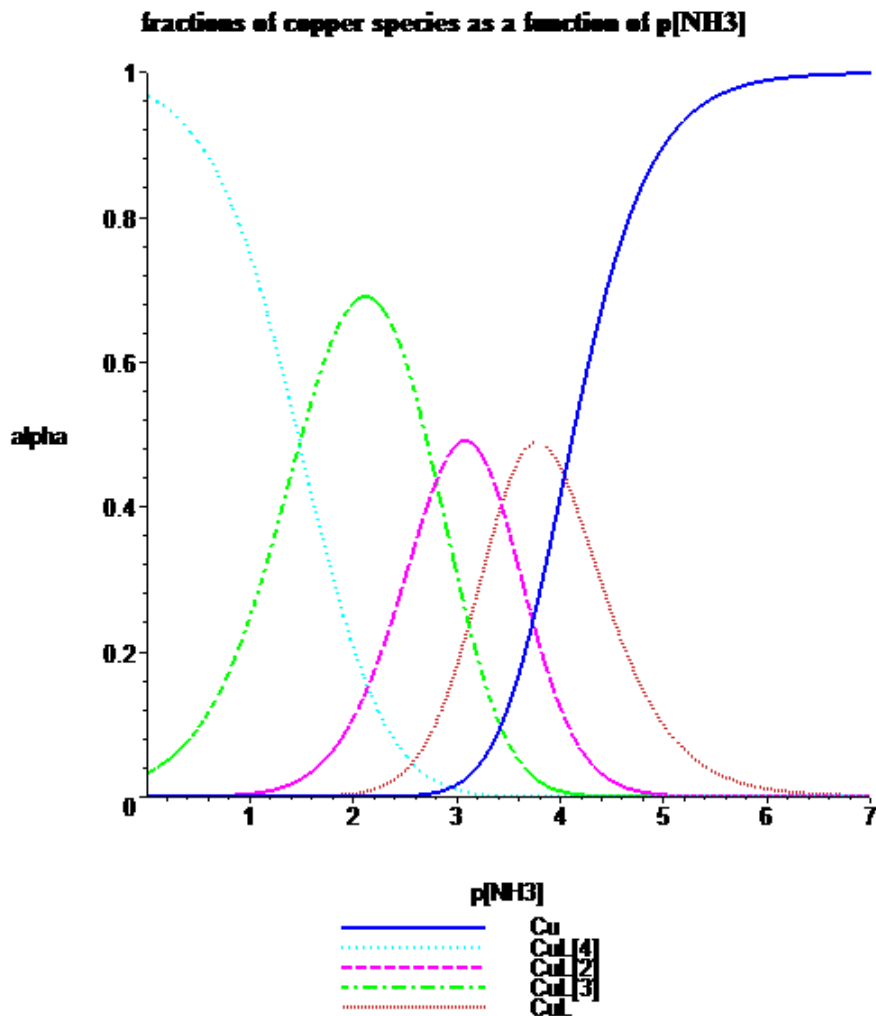
Figure 3. Fraction of copper(II) species as a function of pNH_3

This plot shows how the concentration of each species containing Cu in the equilibria defined in table 2 varies with the concentration of ammonia as Cu^{2+} becomes progressively converted to $Cu(NH_3)_4^{2+}$ from right to left in the figure. As expected, when the concentration of ammonia is small, such as at $pNH_3 = 7$, unassociated Cu^{2+} and the first complex $Cu(NH_3)^{2+}$ are the only species present; as the concentration of ammonia increases, the more associated species become predominant until eventually, at $pNH_3 < 0$ or $[NH_3] > 1$ mol L^{-1}, the concentration of NH_3 is sufficiently large that the only species present is $Cu(NH_3)_4^{2+}$.

The method developed here to form the equations that define the values of a of each species is readily extensible to further coordination numbers, for example to treat $Co(NH_3)_6^{3+}$, involving simply generating the additional equations for the additional complex ions in the same manner as above. The graph depicting the distribution of all species as a function of concentration of the ligand then contains further curves; the individual colouring of each curve, or the style of the line in the absence of colour, makes each one distinct and readily separate from other curves. Just as the algebra for the multiple stages of acidic dissociation of pyrophosphoric acid and the derived titration curve pose no problem for the algebraic processor (*Maple* for these calculations), so the algebra for the multiple stages of complexation of Cu^{2+} is managed directly and without approximation, for the purpose of creating Figure 3 that accurately illustrates the distribution of copper(II) species as a function of concentration of NH_3 ligand.

III.   CONCLUSION

In this essay we explain how problems of chemical equilibrium in general, analytical and inorganic chemistry become readily tractable through the use of mathematical software for symbolic computation, hence maximizing the chemical significance and minimizing the human labour in the solution of these problems. All calculations are performed within an approximation of the use of concentration rather than thermodynamic activity or fugacity, but that usage, despite its prospectively severe inaccuracy, is standard practice in general chemistry; the additional complications of activity coefficients are typically left to advanced courses in analytical and physical chemistry.

Chemical education should be concerned with a description of the actual natural phenomena that are studied. The present advanced development of mathematical software and its ready accessibility by students leaves unjustifiable the partial comprehension of real chemical systems and assumptions, their consequences in the approach to a solution of a real problem and the misleading ideas of students regarding basic concepts of chemical equilibrium [3].

The use of symbolic computation allows a student to understand profoundly the real chemical problem in a system at chemical equilibrium. It lets him or her focus on the chemistry; on understanding the mathematical language and relations of the system, the types of problems that one can solve become greatly extended so that the comprehension of this entire topic is enhanced. The teaching and learning of mathematics, not merely its application to the solution of chemical problems, is greatly facilitated through the use of software for symbolic computation [7], and an interactive electronic textbook especially designed for these purposes with particular reference to chemistry emphasizes the mathematical principles and concepts and their implementation for chemical applications throughout a large range of mathematics that any professor of chemistry

would expect his students to learn and to understand [8]. When students of chemistry are introduced to the use of mathematical software, typically through courses in calculus that are taken concurrently with general chemistry, these students can naturally apply their acquired skills with the software to the solution of chemical problems such as those in our examples here. Alternatively, the instructors of courses in general chemistry can provide, during their lectures or tutorial periods, demonstrations through the use of this software to simulate titrations and to illustrate other aspects of chemical equilibrium such as those that we present here.

Additional examples, including chemical equilibria in other acid-base systems, solubility of salts and formation of complex ions, and a substantial mathematical development of these systems with plots both still and animated and with solved exercises, are available in an original Maple worksheet that is freely accessible from the *Maple Application Centre* [9].

Acknowledgement

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