

Hyperquad simulation and speciation (HySS): a utility program for the investigation of equilibria involving soluble and partially soluble species

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Contents

Abstract	311
1. Introduction	312
2. Structure of the hyperquad simulation and speciation (HySS) program	313
3. Discussion	315
4. Availability	318
Acknowledgements	318
References	318

Abstract

Hyperquad simulation and speciation (HySS) is a computer program written for the Windows operating system on personal computers which provides (a) a system for simulating titration curves and (b) a system for providing speciation diagrams. The calculations relate to equilibria in solution and also include the possibility of formation of a partially soluble

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precipitate. There are no restrictions as to the number of reagents that may be present or the number of complexes that may be formed. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The calculation of the concentrations of species in chemical equilibrium is important in a very wide variety of applications. Two main lines of approach have been used. For gas-phase equilibria it is convenient to minimise the free energy of the system by adjusting the partial pressures of the reagents, using either stoichiometries based on explicit chemical reactions or a nonstoichiometric approach in which chemical reactions are not used explicitly [1]. This follows from the fact that there are extensive databases of standard free energies of formation for compounds in the gas phase, and the fact that (for ideal-gas mixtures) there is a simple relationship between the chemical potential of a species, its standard free energy of formation and its partial pressure (or mol fraction).

For equilibria in solution, which we regard as generalised acid–base equilibria, it is usual to measure the equilibrium constants for the individual reactions and to calculate the species' concentrations by solving the equations of mass-balance. This approach was pioneered in the programs HALTAFALL [2] and COMICS [3]. In fact HALTAFALL could also handle solid–solution and gas–solution equilibria and the authors of that program expounded very clearly the principles involved in all of these calculations. However, we note that it has been shown [4] how a set of standard free energy data may be obtained from equilibrium constant data, which can then be used in a conventional free-energy minimisation algorithm. Such methods have been applied to biological systems [5] and to multiphase equilibria [6]. Information on the program EQS4WIN, which incorporates some of these extensions, is available at <http://www.mathtrek.com/>.

Many speciation programs using the equilibrium constant approach have been written. Comparisons of some of them were published first in 1977 [7] and then in 1984 [8]. De Robertis et al. [9] have given a good bibliography up to 1986 and another comparison paper appeared in 1988 [10]. Other programs not cited by those authors or which were published more recently include: EQUIL [11], RAMESES [12–14], CSMC [15], SYSTAB [16], ESTA [17], INSOL [18], CHEMEQL (which runs on an Apple MacIntosh and is available at <http://www.eawag.ch/soft/chemeql.htm>) [19] and HYPHEN [20].

The motivation for writing a new program was to utilise the facilities offered by the Windows operating system to provide users with a greater degree of flexibility than had been previously possible in respect of both input and output and to make the program very easy to use. The starting point was our earlier program HYPHEN [20] which handles only equilibria in solution; the present program has the added option of including solid–solution equilibria.

2. Structure of the hyperquad simulation and speciation (HySS) program

At the centre of any calculation the concentrations of the free reagents, $[A]$, $[B]$ etc., are determined by solving the equations of mass-balance

$$T_A = [A] + \sum_i a_i \beta_i [A]^{a_i} [B]^{b_i} \dots + \sum_j p_j C_j$$

$$T_B = [B] + \sum_i a_i \beta_i [A]^{a_i} [B]^{b_i} \dots + \sum_j q_j C_j$$

where A , B , etc. are reagents, a , b , ... p , q , etc. are stoichiometric indices, β represents equilibrium constants and the quantities C represent molar concentrations of insoluble species (quantity of solid divided by the volume of the solution) if any are present. The device of representing the quantity of an insoluble substance as a concentration was used in HALTAFALL [2]. Associated with each insoluble there is a solubility product.

$$K_j = [A]^{p_j} [B]^{q_j} \dots$$

Initially it is assumed that there is no precipitate present and the free concentrations are calculated with the C terms omitted from the equations of mass-balance. If there is the possibility of the formation of a precipitate the concentration product is compared with the corresponding K_j . If it is larger not only is the C term included, but an additional equation is added to the set

$$\ln K_j = p_j \ln[A] + q_j \ln[B] \dots$$

and the free concentrations are recalculated. When a solid is present the set of mass-balance and solubility equations is solved, according to the Newton–Raphson method, by iteratively solving the set of linear equations

$$\begin{bmatrix} \frac{\partial T_A}{\partial [A]} [A] & \frac{\partial T_A}{\partial [B]} [B] & \dots & \frac{\partial T_A}{\partial C_j} & \dots \\ \frac{\partial T_B}{\partial [A]} [A] & \frac{\partial T_B}{\partial [B]} [B] & \dots & \frac{\partial T_B}{\partial C_j} & \dots \\ \dots & \dots & \dots & \dots & \dots \\ \frac{\partial \ln K_j}{\partial [A]} [A] & \frac{\partial \ln K_j}{\partial [B]} [B] & \dots & \frac{\partial \ln K_j}{\partial C_j} & \dots \\ \dots & \dots & \dots & \dots & \dots \end{bmatrix} \begin{bmatrix} \Delta[A] \\ [A] \\ \Delta[B] \\ [B] \\ \dots \\ \frac{\Delta C_j}{C_j} \\ \dots \end{bmatrix} = \begin{bmatrix} \Delta T_A \\ \Delta T_B \\ \dots \\ \Delta \ln K_j \\ \dots \end{bmatrix}$$

Now, because $\partial T_A / \partial T_B = (\partial \ln K_j / \partial [A]) [A] = p_j$, etc. the matrix of coefficients is symmetric and we can use the numerically stable [21] Choleski factorisation for the solution whether or not a precipitate has formed: when a solid has dissolved the corresponding row and column of the equations will simply be omitted.

A further complication can arise in a speciation calculation since it is possible to specify either the analytical concentration, T_A , or the free concentration $[A]$ of any reagent. For example, the pH may be specified rather than T_H . In that case the corresponding equation of mass balance is omitted and the given value of that free concentration is used to solve the remaining set.

The numerical process just outlined is encoded in FORTRAN subroutines compiled to a dynamic link library (DLL). This DLL is called from the program HySS which is written in 16-bit Visual Basic 4 (VB4). The VB4 code handles all the data input and output while the DLL performs only numerical processing, thus permitting the use of the Windows operating system (Windows 3.xx or Windows95) while retaining the speed advantage of compiled FORTRAN for the computationally intensive task. HySS provides an integrated environment for setting up a calculation, performing it and creating speciation diagrams, etc. There are no limits imposed on the numbers of reagents, complexes or partially soluble products that may be present. Three types of calculation may be performed. (i) simulation of a titration curve, (ii) calculation of species' concentrations for a range of conditions and (iii) speciation for a single set of conditions (single data points).

Data is input by on-screen editing of two forms. The model form allows equilibrium constants, solubility products and/or stoichiometric coefficients to be entered. This form is common to all three types of calculation. The appearance of the conditions form varies a little with circumstances. If the titration simulation option is chosen, the user enters values for the initial and final volumes and for the concentrations of reagents in the burette, but if the fixed volume option is chosen only that volume need be given. The analytical concentration of any reagent may be set by entering the amount of that reagent initially present in the reaction vessel and in that case calculated initial and final concentrations will be shown on the screen. Alternatively, in a speciation calculation¹ the initial and final p[reagent] values may be entered; for example, specifying the initial and final pH will define the range over which the speciation calculation is to be performed. For single data point calculations there is a separate form for entering either the analytical concentration of a reagent or the p[reagent] value. Any number of single points can be entered. All this data will normally be stored in a file. Thus, a complete set of data may be entered by recalling it from a file. In addition, Hyperquad data can also be imported.

The main calculations are initiated by choosing a graph to draw or by creating a table of concentrations. There are up to eight types of graph that may be drawn, but which types are available depends on the set of conditions chosen. Thus, for a titration simulation in which all the reagents' analytical concentrations are given, the x -axis may be titrant volume, pH (if one reagent is the hydrogen ion) or p[reagent]. The y -axis may show the concentrations of the species relative to the analytical concentration of one of the reagents or it may show the logarithms of the

¹ It is possible to specify p[reagent] also in a titration simulation, but this possibility should only be used with great caution as it may result in a physically impossible simulation.

absolute concentrations. In the last case the user may choose which species' concentrations are to appear on the graph.

The graphs are drawn in Windows Metafile format so that they can be copied to the clipboard or saved in a.WMF file. Each curve may be labelled by dragging the chemical formula for the species to a suitable point on the screen. The table of concentrations gives the free concentrations of the reagents and the concentrations of the species in the form of a tab-separated table which can be pasted to the clipboard or saved in a .TSV file. In either case the table data can be imported into most spreadsheet-type programs for the purpose of doing other calculations (such as finding cumulative concentrations) or creating other graphs. The number of points in a table or graph is selectable from 21, 51, 101, 201, 401 or 901; choosing the smallest number will result in very fast calculations, but a larger number will be used when preparing graphs for publication.

3. Discussion

The main novelty in HySS is the complete flexibility with which the conditions may be specified for speciation calculations and the simple interface to other Windows applications, such as word-processors or spreadsheets, for the results of the calculations. Also, the titration simulation option can be used effectively in didactic situations.

The diagrams produced by HySS have been arranged with particular care so that they can be used in manuscripts destined for publication. In particular, the two standard diagram sizes of width 16.5 and 8.25cm are suitable for direct reproduction in one and two-column A4 journal pages, as recommended by the American Chemical Society. Also, properly written chemical formulae can be placed where desired on the diagrams by means of simple mouse-controlled operations. The diagrams can also be stored as Windows Metafiles which, being vector-graphics files, allow arbitrary resizing to be performed. The figures shown in this paper are examples of standard HySS diagrams.

HySS is supplied with seven specimen data files which illustrate the various ways in which the program can be run. Fig. 1 shows a HySS plot for a simulated titration of acetic acid (methanoic acid) with alkali, with concentrations on a logarithmic scale. Although this may be considered to be the simplest possible speciation diagram it illustrates points which have didactic utility: the pH at half neutralisation, where $[\text{AcOH}] = [\text{AcO}^-]$, is equal to $\text{p}K_{\text{a}}$ for the weak acid; the concentration of the undissociated acid mirrors the concentration of hydrogen ions; the concentration of the acetate ion reaches 100% at the titration end point.

Fig. 2 shows the HySS plot for a simulated titration of phosphoric acid with strong base. In this case the y -axis shows the concentrations as a percentage of the total phosphate. The diagram illustrates an example of well separated end-points: at each end-point one of the phosphate moieties reaches a maximum in concentration.

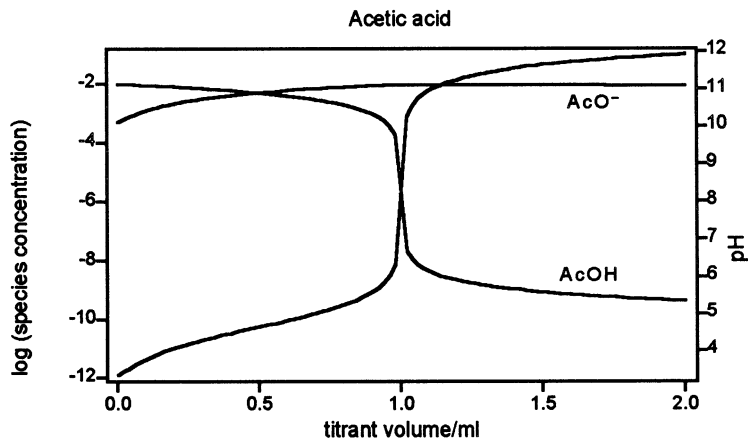


Fig. 1. Simulated titration curve of 10 ml 0.01 M acetic acid with 0.1 M KOH and $\log_{10}(\text{concentration}/\text{mol dm}^{-3})$ of acetic acid (AcOH) and acetate (AcO^-).

Fig. 3 shows the results of a speciation calculation for the beryllium–malonate system as a function of pH. This plot includes the formation of an insoluble hydroxide at high pH. HySS was used extensively in the study of this system as an aid to finding the best experimental conditions for the titrations [22].

Fig. 4 shows a simulated titration of silver salts with aqueous ammonia. Initially the silver is all in the form of insoluble AgCl and AgBr. With the addition of ammonia the AgCl dissolves with the formation of $[\text{Ag}(\text{NH}_3)_2]^+$ but then little AgBr dissolves under these conditions—it is well known that AgBr only dissolves in concentrated ammonia solution.

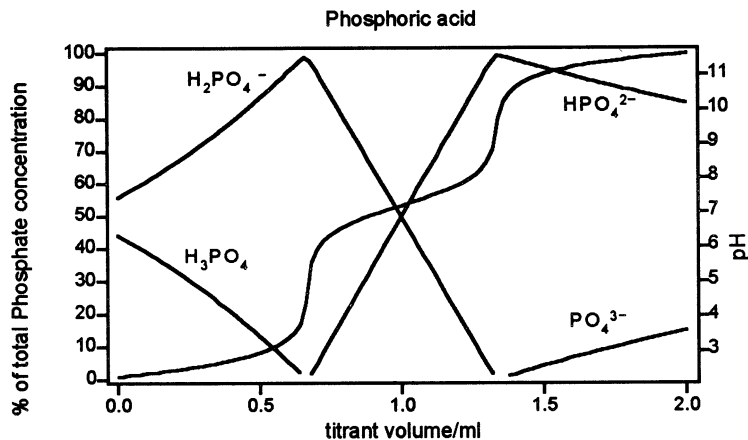


Fig. 2. Simulated titration curve of 10 ml 0.01 M phosphoric acid with 0.15 M KOH and %formation of H_3PO_4 , H_2PO_4^- , HPO_4^{2-} and PO_4^{3-} .

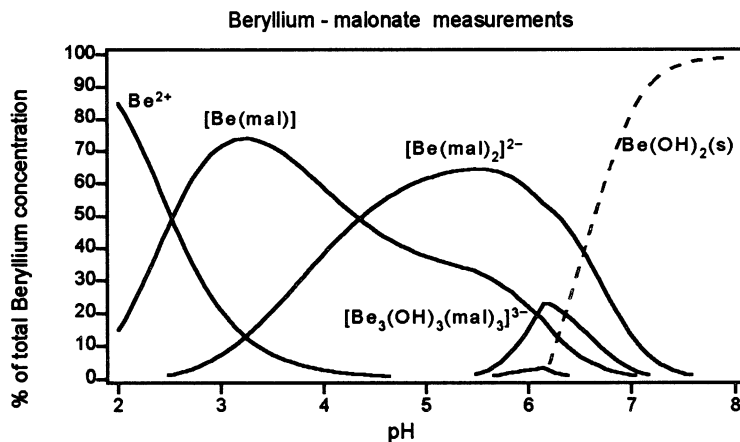


Fig. 3. Percentage formation of complexes of beryllium with malonate (mal) as a function of pH. $T_{\text{Be}} = 2$ mM, $T_{\text{mal}} = 4$ mM. The insoluble beryllium hydroxide is shown as $\text{Be}(\text{OH})_2(\text{s})$.

The set of sample data files also includes the following systems.

- A simulation of a titration of Ni^{2+} –glycinate with alkali. In this case the end-points overlap so much that they cannot be seen individually.
- A simulation of a titration of Ni^{2+} –histidinate–prolinate with alkali. This example illustrates the formation of mixed complexes.
- Speciation calculations for the biofluids present in brain and muscle. These calculations involve eight reagents: Mg^{2+} , Na^+ , K^+ , H^+ , Cl^- , phosphate, phosphocreatine and ATP, and a total of 22 possible complexes. The calculations were used to set up a model for the in vivo measurement of Mg^{2+} concentrations in brain and muscle tissues from ^{31}P -NMR measurements which

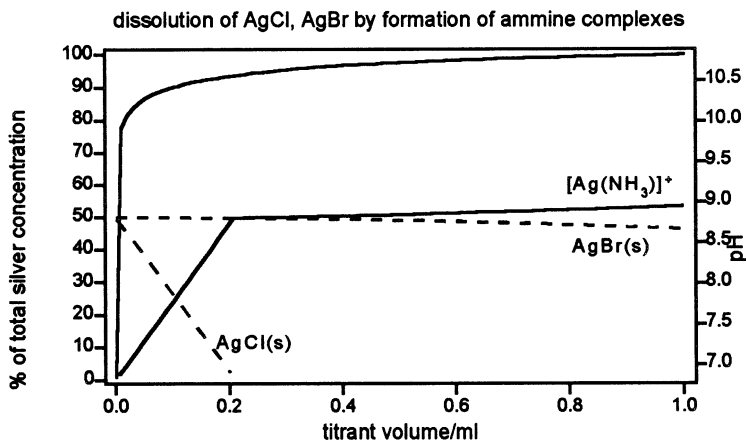


Fig. 4. Simulated titration curve of 1 ml 2 mM Ag^+ , 1 mM Cl^- and 1 mM Br^- with 0.1 M NH_3 .

can be used to derive the concentrations of the various phosphorus-containing species [23].

4. Availability

Hyss-lite may be downloaded free of charge by visiting <http://www.chim1.unifi.it/group/vacsab/hyss.htm>

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