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Water Topos: A 3-D Trend Surface Approach to
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Prologue: An Overview to Water Topos: A 3-D Trend Surface Approach to Viewing and Teaching Aqueous Equilibrium Chemistry

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P.1 Introduction

This book outlines a new approach to viewing and teaching aqueous equilibrium chemistry, a method that employs computer-generated trend surfaces (topos) to broadly summarize chemical process that can occur in water solutions.   Because water is essential to all life forms and the physiological processes on which they depend, the better our understanding of aqueous chemistry is, the better our ability to meet the ever-changing challenges with which we are faced.

Why should anyone be interested in learning a new approach to equilibrium? The "topos approach" provides a visual method of following systematic behavior in equilibrium chemistry as one changes the composition of a water solution.[1,2] Structures that arise on topo surfaces often prompt new questions about the underlying chemistry. Previously unperceived or uncharacterized trends may appear as dramatic ridges, plateaus, ramps or chasms on the surfaces themselves. New conceptual understandings often emerge in seeking their explanation. Every time we began working on a new chapter, we made new discoveries ourselves. We completely characterize a category of pH buffering that is only marginally found elsewhere in the chemical literature. One of our findings in metal ligand complexation was so counterintuitive that a number of faculty colleagues told us we must be wrong. We were forced to present them with experimental evidence from the laboratory to finally convince them of its correctness. (See Chapter 2.2 for the concept and its experimental proof.)

Each **Water Topos** chapter includes:

- A concept paper that forms its main body
- A fully-functioning Excel Workbook with embedded Visual Basic code that allows the user create colorful 3-D topo trend surfaces

- A PowerPoint lecture that can serve as a tutorial or be used directly in the classroom
- A teaching document with learning objectives, sample exercises and coordinated laboratory experiments
- Other supporting information files that provide additional background for introductory readers, derivation of chemical models and mathematical equations used in the chapter, and detailed descriptions of the numerical methods used to solve the equilibrium calculations

Much of this book's content should be helpful for introductory students who are unfamiliar with aqueous equilibrium concepts such as pH, solubility and oxidation/reduction. Other sections explore advanced topics that will challenge upper division chemistry majors and graduate students. While the material is theoretical in concept, the straight-forward application of the topos will prove widely useful in analytical chemistry, environmental chemistry, geochemistry, and biochemistry. Each chapter includes specific examples of such applications that will assist the reader in discovering his/her own potential uses of the topos.

It is important at the outset to note that the topics in this book are restricted to EQUILIBRIUM situations. Clearly, there is just as much to learn about KINETIC aspects of aqueous chemistry as well. Kinetics are, for the most part, omitted in the chapters that follow.

Traditionally, the "Big Four" subdivisions that comprise aqueous equilibrium chemistry pedagogy are: 1) acid-base equilibrium, 2) metal-ligand complexation equilibrium, 3) oxidation-reduction (redox) equilibrium, and 4) solubility equilibrium. The chapters in this book are grouped according to these major areas. All of them, however, share a "topos" approach in their exposition.

As used here, a topo is a 3-dimensional trend surface constructed above some form of composition grid. The grid axes allow two composition parameters to vary over a wide range of possible values, often close to the limit of any reasonable levels for their chemical components. The composition grid style changes from one equilibrium topic to the next. For acid-base and complexation discussions, the topos are titration-dilution grids. For redox analyses, the grid follows an oxidized form on one axis and its corresponding reduced form on the

other. For solubility of ionic salts, one axis follows the cation concentration while the other tracks the anion.

The topo approach to aqueous equilibrium is computationally intense. In a standard equilibrium calculation, an answer is sought for just a single solution setting or maybe a before-and-after comparison. For the construction of a topo surface, a calculation must be done for each point in the composition grid array. The trend surfaces included in the chapters that follow are typically grids of 37 x 37 or 40 x 37 or 40 x 40 points, necessitating 1,369 or 1,517 or 1,681 computations, respectively. A sample titration/dilution grid as used in the acid-base chapters appears as Figure P.1.
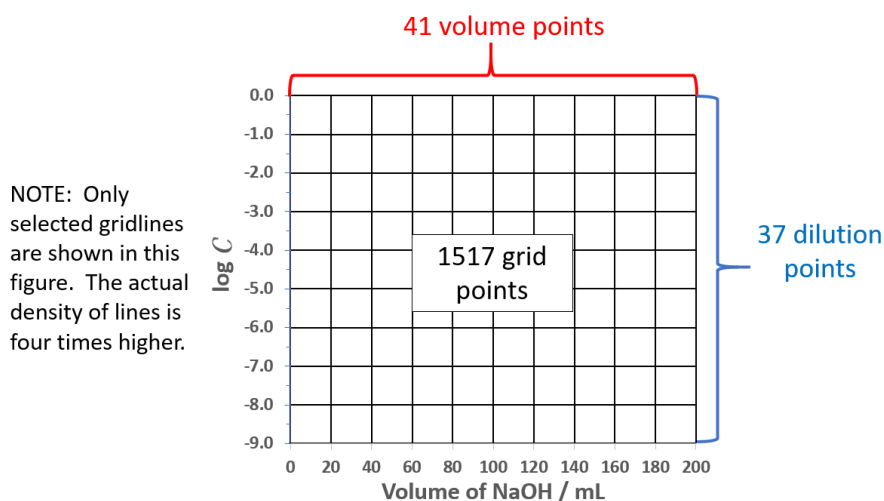
Figure P.1. A sample titration/dilution composition grid for an acid-base system's topos.

Included in each chapter is a downloadable Excel workbook that contains Visual Basic macros that can perform these massive computations for all grid points. Data arrays within the workbook's spreadsheets contain the concentration for each species of interest as well as associated partition information for each grid point. Achieving these results requires sophisticated numerical methods to solve the higher order, nonlinear equation sets, many of which have no closed form solutions. Most run times are 20 – 40 seconds, thus, live runs can even be done in a classroom setting. For the interested reader, the strategy employed in each macro is described in detail in an associated downloadable file.

The output of each modeling exercise is a series of 3-dimensional topo surfaces that present a visual summary of system trends. Each topo appears in two forms: 1) a bent-wire framework that depicts the 3-D shape of the surface within a 3-walled box (Figure P.2, Panel a), and 2) a contour map version that allows one to read an unequivocal (x, y)-grid location for any surface feature (Figure P.2, Panel b).
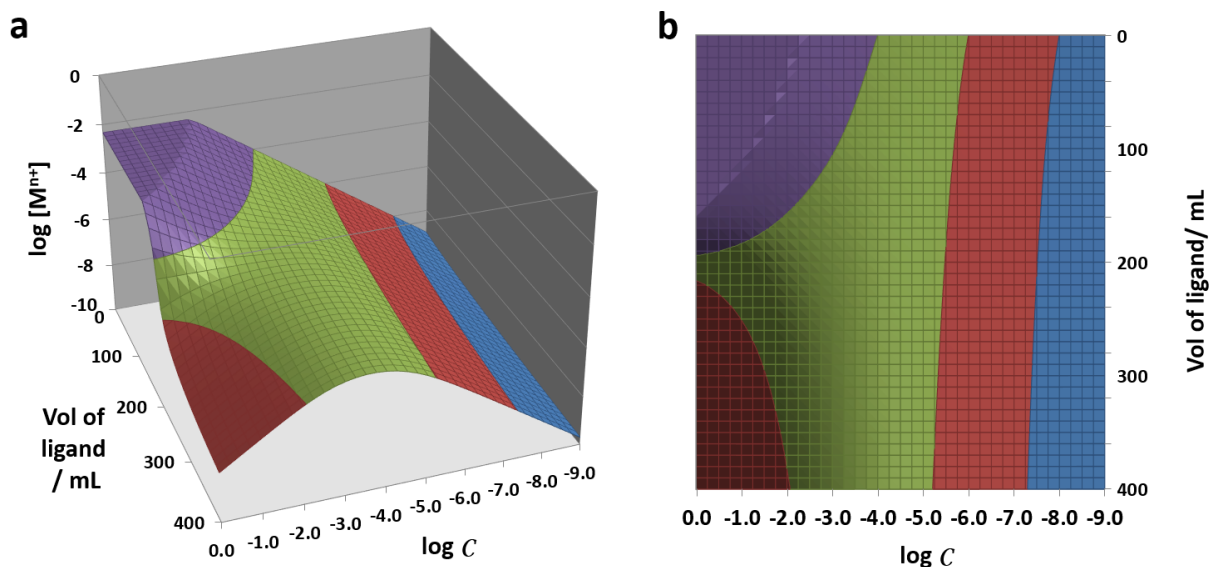
Figure P.2. The two topo presentation formats. a) wire-frame; b) contour map.

P.2 Part 1 - Acid-base systems

There are three chapters dealing with acid-base systems. The acids considered in these chapters fall under the classic Arrhenius definition of compounds who give rise to the hydronium ion, H_3O^+, in solution.

Chapter 1.1 focuses on pH titration surfaces. The acid-base composition grid uses the x-axis to designate the volume of base titrant that has been added, while the y-axis tracks overall dilution of the reagents. Topo surfaces plotted above this grid show cliffs where equivalence points are reached (*i.e.*, equal amounts of acid and base are present) and plateaus where pH-buffering occurs (*i.e.,* the pH is stable against changes in either titrant volume or dilution). It is easy to demonstrate how sufficient dilution eventually erodes a buffer's effectiveness, how the simplified Henderson-Hasselbalch[2] equation for calculating a buffer's pH eventually breaks down, and how the titration curves beyond that point are

reminiscent of a dilute strong acid/dilute strong base titration curve. At sufficient dilution, the buffer properties of a system are a function of $\mathcal{K}_w$, *i.e.*, the H_3O^+ and OH^- concentrations of the solvent water itself.

Chapter 1.2 explores the concept of buffer capacity over the same titration/dilution composition grid. While pH is independent of the volume of a sample, buffer capacity is not. The more sample one has, the higher the buffer capacity it contains. This chapter details the changes in buffer capacity during a titration as a function of the volume of base added, a viewpoint not traditionally addressed in acid-base studies. The difference between this new viewpoint and traditional pH vs. buffer capacity plots is illustrated with side-by-side topo surfaces for comparison. The buffer capacity surfaces also reveal the meaning of buffer capacity for conditions rarely considered – strong acid solutions, strong base solutions and extremely dilute systems.

Chapter 1.3 presents 3-D species distribution diagrams for the titration/dilution composition grid. These surfaces provide visual images of the regions under which each species predominates in the system. It makes it easy to predict what form or forms will be important for a specific set of conditions. Species distributions are normally plotted only as a function of pH. We provide here an alternative perspective, that is, species distributions as a function of volume of base added and dilution. Again, side by side comparisons of the two presentation styles is useful in enhancing an understanding of this topic. Real world situations are more akin to the volume of base/dilution approach than the pH approach. The dilution aspects of species distributions have rarely been addressed in the literature.

P.3 Part 2 - Metal-ligand complexation systems

Two chapters treat metal-ligand complexation concepts. As with acid-base systems, they employ a titration-dilution grid for most topos. The x-axis represents the total analytical concentration of metal on the x-axis and the overall dilution of a system is on the y-axis. The most interesting z-axis from which to construct topos is the one that records the equilibrium activity of free metal. Other topos are built from metal and ligand speciation distributions.

Chapter 2.1 covers systems that are restricted to systems with solely 1:1 metal complexes in them exclusive of the hydroxy complexes that are always present in aqueous media. EDTA is used as an illustrative ligand that meets this constraint. The main objective of the chapter is to introduce the reader to the notion of metal ion buffering. Similar to the well-known pH buffering, metal ion buffering is characterized by situations in which the concentration of metal ion is stable against additions of reagents (metal ion or ligand) or dilution. Two separate types of metal ion buffering are identified: 1) mass action metal ion buffering, and 2) precipitate metal ion buffering.

Chapter 2.2 deals with systems in which higher stoichiometries of mononuclear complexes are present – 1:2, 1:3, 1:4, etc. This chapter contains a very counterintuitive behavior that we have named "metal ion anti-buffering". Under the right circumstances – a system with higher stoichiometries and excess ligand compositions – the activity of free metal will actually increase as the overall system is diluted. A copper(II) ethylenediamine system was employed to experimentally demonstrate this behavior. As a sample was diluted by a factor of 1318x, the activity of free Cu(II) rose a factor of 102x. This gives an overall result that is 135,000 times higher (the anti-buffering factor) than one might expect.

1.4 Part 3 - Redox systems

For redox systems, a new composition grid is used to portray the Nernst equation and the change of half-cell voltages as electrochemical cells operate over a wide range of possible solution concentrations. One grid axis holds the activity of the oxidized species; the other holds the activity of the reduced species. Calculated potentials for a given composition are plotted as the z-coordinate to form Nernst topo surfaces.

Chapter 3.1 is an initial treatment of Nernst topos. The design of these surfaces dramatizes the importance of the E^o value over most solution compositions, namely, they are mostly flat. Paths across the topos trace compositional changes that occur as redox reactions take place. Then, pairs of surfaces are stacked to track the progress of a galvanic cell undergoing discharge. Next, there is a topo with oppositely trending reaction paths that explain the theory behind concentration cells. Finally, the visual effect of each variable in the Nernst equation on a topo surface's appearance is discussed.

Chapter 3.2 is a stand-alone chapter for a specific application of Nernst topo surfaces. It supplies a visual rationale to why batteries deliver a fairly constant voltage until they suddenly die. It explains why your laptop computer tells you to save you files when battery life is short!

1.5 Part 4 - Solubility of ionic salts

Solubility equilibrium can involve solutes that are solids, liquids or gases. Solids, by themselves, can be ionic salts, molecular solids or covalent networks.

Chapter 4.1 centers on the solubility of ionic salts. It opens with the traditional way in which the solubility of ionic salts is taught – a simple $\mathcal{K}_{sp}$ expression.[4] This is an inadequate description of the rich chemistry that can occur with the solution phenomenon. Ion pairing, hydrolysis reactions, dissolved aqueous complexes and polynuclear species are all possibilities. This chapter extends the simple $\mathcal{K}_{sp}$ case topos to ever more complicated systems. The composition grids employed in this chapter contain the analytical concentration of the anion on the y-axis and the analytical concentration of the cation on the x-axis. A modified definition of solubility is required for advanced surfaces because dissolved forms are more than just the bare component ions.

1.6 Numerical Methods and Excel Macros

The exploration and construction of the 3-dimensional topo surfaces described above necessitated the development of numerical techniques and computer programs to implement. We elected to code the programs as Visual Basic macros embedded within MicroSoft Excel workbooks. This was done so that any reader who has an operating version of MicroSoft Office need not purchase additional software. As supplied, the programs efficiently calculate the equilibrium activities/concentrations of all species in a specified system for each point in the composition grid. Run times are typically less than two minutes. Once the equilibrium solution has been found, the workbooks populate data arrays whose contents are immediately displayed in colorful 3-D topos. With Excel it is easy to rotate the trend surfaces around all three axes to explore the nature of any surface feature. These tools provide a rich framework for investigating aqueous equilibria in its full measure.

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