



Chemical Education

A CHIMIA Column

Sillén diagrams are of great practical value in teaching acid-base chemistry

Teaching Acid-Base Equilibria by Using Log-log Diagrams

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Abstract: The purpose of this column consists in illustrating the utility of log-log diagrams for the graphical determination of the pH value of acid-base systems in dilute aqueous solution. This methodology allows to tackle systems going well beyond the case of mono- or diprotic acids, providing fast and accurate estimations of the pH. It is also argued that the use of so-called *Sillén* diagrams affords a better understanding of complex acid-base systems.

Keywords: Acid-base equilibria · Distribution diagrams · *Sillén* diagrams · Graphical pH determination

Acid-base equilibria, viewed in terms of the Brønsted-Lowry definition,^[1] constitute a classical topic in general chemistry. They are crucial not only because of the quintessential importance of acids^[2] but also because they provide an ideal playground for the discussion and understanding of chemical equilibrium in (mostly) dilute solutions. Consequently, virtually all textbooks on general chemistry will feature a specific chapter devoted to acid-base equilibria. However, the depth of the corresponding mathematical treatment is very often affected by approximations. This usually leads to a set of simple equations used for the calculation of the pH value for solutions of strong or weak acid and bases depending on their concentration and dissociation constants. Correspondingly, students will often focus on learning these equations by heart, thereby missing the chance of a more thorough understanding of the chemistry governing acid-base equilibria. To a certain degree, this is reasonable, given the relative complexity of a rigorous treatment of even the simple dissociation equilibrium of a monoprotic weak acid HA, such as e.g. acetic acid. In fact, in order to exactly compute $[H^+]$ for a corresponding solution, one needs a cubic equation (eq. 1) in $[H^+]$, whereas a diprotic acid H_2A will lead to a fourth-order polynomial in $[H^+]$ (eq. 2).^[3]

$$[H^+]^3 + K_a[H^+]^2 - (K_w + [A]_{\text{tot}}K_a)[H^+] - K_wK_a = 0 \quad (1)$$

$$[H^+]^4 + K_{a1}[H^+]^3 - ([A]_{\text{tot}}K_{a1} - K_{a1}K_{a2} + K_w)[H^+]^2 - (K_w + 2[A]_{\text{tot}}K_{a2})K_{a1}[H^+] - K_{a1}K_{a2}K_w = 0 \quad (2)$$

For polyprotic acids the situation is even more complex and clearly out of reach for manual solutions and calling for computational ones.^[4] On the other hand, graphical representations, e.g. in form of distribution diagrams may help in visualizing which species deriving from a specific dissociation of a polyprotic acid will be present in relevant concentrations with respect to the total concentration of the acid at a defined pH. Fig. 1 shows such a diagram for the triprotic acid H_3PO_4 .

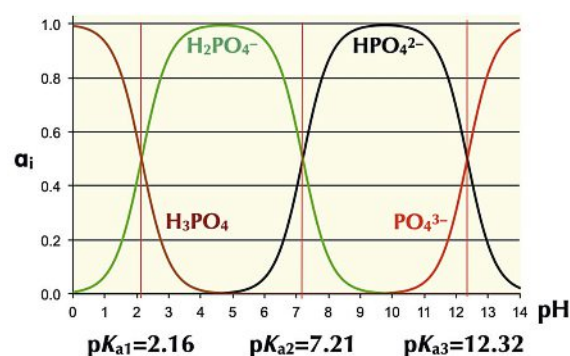


Fig. 1. Distribution diagram – α_i as functions of pH – for H_3PO_4 .

The curves in such a diagram represent the mole fraction α_i of a certain species i as a function of pH and are derived from expressions such as e.g.:

$$\alpha_0 = \frac{[PO_4^{3-}]}{[PO_4]_{\text{tot}}} = \frac{K_{a1}K_{a2}K_{a3}}{[H^+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3}} \quad (3)$$

$$\alpha_3 = \frac{[H_3PO_4]}{[PO_4]_{\text{tot}}} = \frac{[H^+]^3}{[H^+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3}} \quad (4)$$

This kind of distribution (or speciation) diagram is clearly useful when it comes to judging, for example, which dissociation equilibrium will be relevant at which pH. So for the case of H_3PO_4 , a relatively strong acid with $pK_{a1} = 2.16$, it is evident that the second and third dissociation will be relevant at pH values above ca. 5 and ca. 10, respectively, meaning that H_3PO_4 in a not too dilute solution essentially behaves as a monoprotic acid and can be quantitatively treated as such.

By expressing the mole fractions α_i in logarithmic form, one obtains, e.g. for the concentration of A^{2-} in the case of a diprotic acid H_2A :

$$\log[A^{2-}] = \log[A]_{\text{tot}} - \log\left(\frac{[H^+]^2}{K_{a1}K_{a2}} + \frac{[H^+]}{K_{a2}} + 1\right) \quad (5)$$

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Expressions of this kind are now the basis for plotting $\log C$ ($\log[\text{species}]$) as a function of pH, thereby obtaining a log-log diagram of the type illustrated in Fig. 2 for the triprotic system of aspartic acid as a specific example. Such a diagram is often called a *Sillén* diagram honouring the name of the Swedish chemist Lars Gunnar Sillén who contributed in popularizing log-log diagrams.^[6]

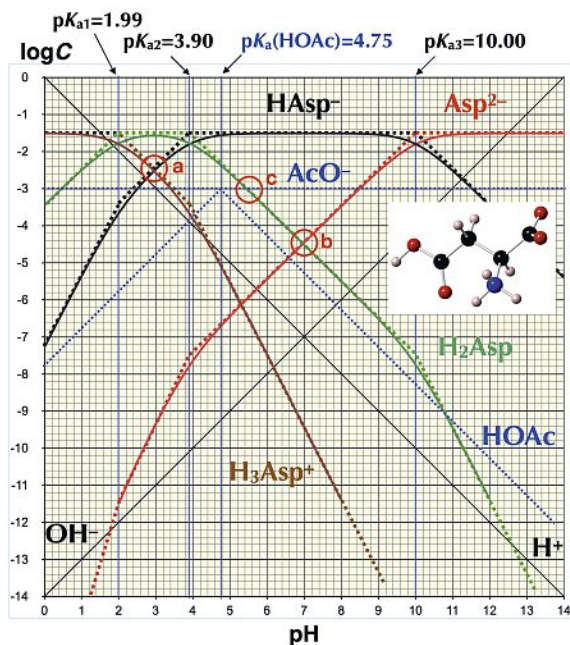
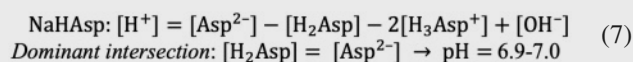
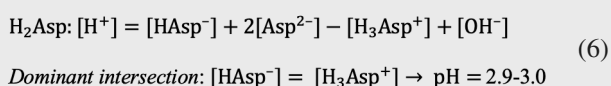


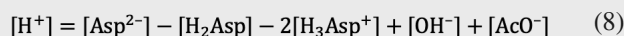
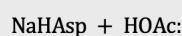
Fig. 2. Sillén diagram for aspartic acid, $[\text{Asp}]_{\text{tot}} = 0.03 \text{ M}$ ($\log[\text{Asp}]_{\text{tot}} = -1.5$). Solid curves are calculated, dotted linear segments are approximations. Red circles indicate the dominant intersection in the case of a solution prepared from H_2Asp (a), NaHAsp (b), and NaHAsp and acetic acid, HOAc , at 0.001 M (c), respectively (*vide infra*).

It can be shown that the curves in a *Sillén* diagram may be approximated by linear segments of slope 0, +1, -1, +2, -2, etc., as recognizable in Fig. 2. Hence, a *Sillén* diagram may be constructed “by hand”. Note that the greater deviations from the calculated curves occur at pH values close to the corresponding $\text{p}K_a$ values, where also slope changes occur, the maximum error being 0.3 on the logarithmic scale, i.e. a factor of 2 in concentration at $\text{pH} = \text{p}K_a$. The diagram can now be used for the – mostly quite accurate – estimation of the pH of a solution, not only of a simple monoprotic acid, but also of more complex systems, including mixtures of different acids, given that the total concentrations of the involved species are known. In order to do this, one needs to formulate the so-called *proton condition* (in German: *Protonenherkunftsgleichung*, PHG). This accounts for all contributions to $[\text{H}^+]$ (equilibrium concentration) deriving from deprotonations/protonations of all involved species including water. With the *proton condition* in hand, one can identify in the diagram the intersection of two dominant species (*dominant intersection*), i.e. by neglecting all other species occurring there in lower concentrations, thus allowing for an estimation of the pH value of the corresponding solution. In the case of a solution of e.g. aspartic acid (H_2Asp), or sodium aspartate (NaHAsp), respectively, the *proton conditions* and the *dominant intersections* read as follows:



The estimated pH values of 2.9–3.0 and 6.9–7.0, respectively, correspond quite well to the calculated ones of 3.02 and 6.95.^[4] The slightly underestimated pH value in the former case is mainly due to the rather close proximity of the H^+ line to the *dominant intersection*, meaning that $[\text{H}^+]$ cannot be totally neglected.

Let us now determine the pH of a solution prepared from both sodium aspartate and acetic acid, being their total concentrations $[\text{Asp}]_{\text{tot}} = 0.03 \text{ M}$ and $[\text{OAc}]_{\text{tot}} = 0.001 \text{ M}$. The original *Sillén* diagram for the aspartic acid system must be completed by the estimated curves for acetic acid (blue dotted lines in Fig. 2). Next, the *proton condition* for this new system must be formulated and the *dominant intersection* must be identified:



The exactly computed pH value for such a solution is 5.45,^[4] again confirming the accuracy of the graphical approach, which usually lies within at most ± 0.1 pH units.

The didactic value of the graphical methodology resides in the visualization of even rather complex acid-base systems at equilibrium. The formulation of the *proton condition* and its use for the determination of the *dominant intersection*, and hence the pH value, requires the ability to first locate an approximate pH range pertinent to the solution under scrutiny. This, in turn, must be based on a proficiency in comparing and judging the relative relevance of specific equilibria in the concert of a number of interdependent ones. Thus, the systematic use of *Sillén* diagrams greatly contributes in acquiring these skills.

- [1] For the original contributions, see: a) J.N. Brønsted, *Recl. Trav. Chim. Pays-Bas* **1923**, 42, 718–728. b) T.M. Lowry, *Trans. Faraday Soc.* **1924**, 20, 13–15, <https://doi.org/10.1002/recl.19230420815>.
- [2] «La définition de l'acide est, à vrai dire, la clef de la Chymie» noted Louis Bernard Guyton de Morveau (Baron) in Vol. 1 of the *Encyclopédie Méthodique: Chymie, Pharmacie et Métallurgie*, published in Paris in **1786!**
- [3] In equations (1) and (2), K_a , K_{a1} , and K_{a2} are the equilibrium constants for the dissociation of HA , H_2A , and HA^- , respectively, $[\text{A}]_{\text{tot}}$ is the total concentration of the corresponding acid and K_w is the equilibrium constant for the water autoprotolysis.
- [4] I.G.R. Gutz (University of São Paulo, Brasil) published a very useful and exhaustive software named *CurTiPot*, available as freeware: https://www.iq.usp.br/gutz/Curtipot_.html.
- [5] For a comprehensive treatment, see: a) H. Kahlert, F. Scholz, *Acid-Base Diagrams*, Springer, Heidelberg, **2013**, available also in German as *Säure-Base-Diagramme*. b) R. de Levie, *Aqueous Acid-Base Equilibria and Titrations*, Oxford Chemistry Primers, Oxford University Press, Oxford, **1999**. See also, e.g.: c) J. Kovac, *J. Chem. Educ.* **2012**, 89, 905–909. d) A. Gambi, R. Toniolo, *ChemTexts* **2016**, 2:9 (DOI 10.1007/s40828-016-0029-1). e) J.N. Butler, *Ionic Equilibrium – Solubility and pH Calculations*, Wiley, New York, 1998. f) R. de Levie, *Critical Reviews in Analytical Chemistry* **1997**, 27, 51–76.
- [6] Niels Bjerrum introduced the use of log-log representations in his theory of acidimetry and alkalimetry as early as 1914. See: a) N. Bjerrum, in *Sammlung chemischer und chemisch-technischer Vorträge*, W. Herz, F.B. Ahrens, Eds., Enke, Stuttgart, **1915**, Vol. XXI, pp. 1–128. For selected Sillén's contributions, see e.g.: b) L.G. Sillén in *Treatise on Analytical Chemistry*, I.M. Kolthoff, P.J. Elving, E.B. Sandell, Eds., Part 1, Vol. 1, Chapter 8, pp. 277–317, The Interscience Encyclopedia, New York, **1959**. c) L.G. Sillén, P.W. Lange, C.O. Gabrielson, *Problems in Physical Chemistry*, Prentice-Hall, New York, **1952**, Chapter 8, pp. 193–235. See also d) G. Hägg, *Die theoretischen Grundlagen der analytischen Chemie*, 2nd edition, Springer Basel AG (Birkhäuser), Basel, **1962**.