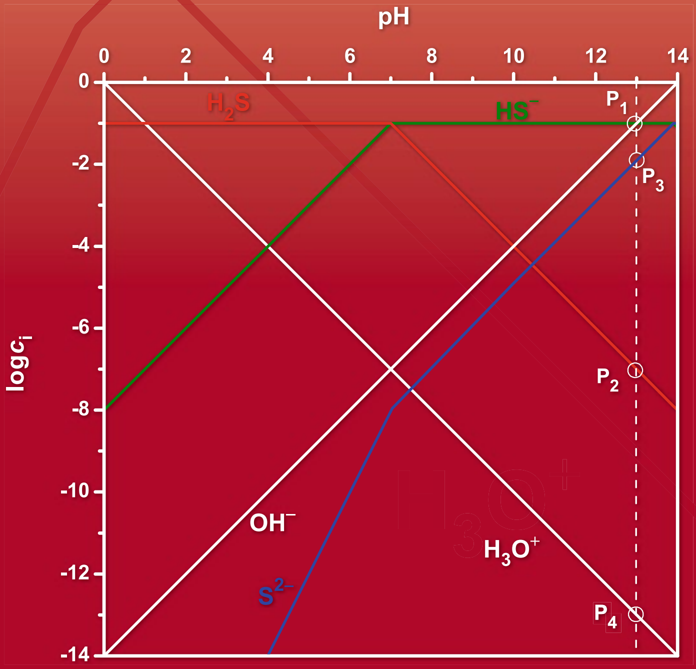
Heike Kahlert · Fritz Scholz

Acid-Base Diagrams



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This book is dedicated to Prof. Dr. Günter Henrion on the occasion of his 80th birthday. It is an expression of esteem for an inspirational teacher, who first sparked our love of pH-logc_i *diagrams during our chemistry studies at Humboldt University, Berlin.*

Heike Kahlert and Fritz Scholz

Preface

The understanding of acid–base equilibria is of basic importance for chemistry, and thus also for biochemistry, biology, environmental sciences, etc. Hardly any chemical technique, any biochemical process, any environmental phenomenon can be understood without a profound knowledge of the underlying acid–base equilibria on a quantitative basis. However, even for the simplest chemical systems the mathematical calculations can be rather complicated, and the desire will arise to describe the systems by well-chosen approximations. For all these requirements there is one powerful means, the so-called acid–base diagrams (pH-logc_{i} diagrams), which permit a simple presentation of the dependencies of the concentrations of all participating species as a function of pH of the aqueous solutions. With their help, it is easy to find the possible simplified equation which permits a straightforward calculation of special cases. These diagrams also permit the construction of titration diagrams. The present book is the result of the many years of teaching experience of the authors, during which they have learned what the usual problems of understanding are which students have in using these diagrams. The book has been written because there was no other textbook which presented the fundamentals and applications of pH-logc_{i} diagrams in the necessary depth *and* with the desired simplicity. It was not the goal to describe these diagrams comprehensively with all imaginable special cases, but the authors had the aim of giving clear and straightforward instruction on how to construct and use these tools for problem-solving. We hope that this book will guide students of chemistry, biochemistry, biotechnology, biology, pharmacy, physics, environmental sciences, geosciences, hydrology, medicine, etc. in their attempts to handle acid–base equilibria.

Greifswald
January 2013

Heike Kahlert
Fritz Scholz

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Introduction

1

Acid–base diagrams, better called pH-logc_i diagrams, are the most beneficial tools that have been developed to describe acid–base equilibria. They present the interrelations between the logarithm of all equilibrium concentrations c of the species i and the pH value of the solution. They make it possible to find the approximate pH of solutions of acids and bases and buffers without any math calculations. They can be applied to find out what approximations in the math calculations of the pH (or concentration of any species) are allowed under certain conditions. These acid–base diagrams can also be used to construct titration curves to extract the most important data, such as pH at the equilibrium point. Good training in the use of these diagrams is necessary for a wide range of science studies. This book provides the basics as well as a good number of applications.

pH-logc_i diagrams have several fathers (Fig. 1). The Danish chemist Niels Bjerrum introduced the coordination system in 1915 [1], the Swedish chemists H. Arnfelt [2] and G. A. Ölander [3] further developed them, and finally the Swedish chemists G. Hägg [4] and L. G. Sillén [5, 6] popularized them on an international scale. The latter led to these diagrams being called Hägg diagrams in Germany and Sillén diagrams in the USA [7].

This book provides a consistent presentation of material, and the reader can use it without consulting additional literature. Of course, there are a number of textbooks and monographs that can be consulted [7, 9–16], as well as a number of original journal papers.

The complete book is based on the acid–base theory of Brønsted (Brönsted) and Lowry, according to whom acids are proton donators and bases are proton acceptors. All other acid–base theories are not discussed here, and we refer to the respective literature [9, 17].

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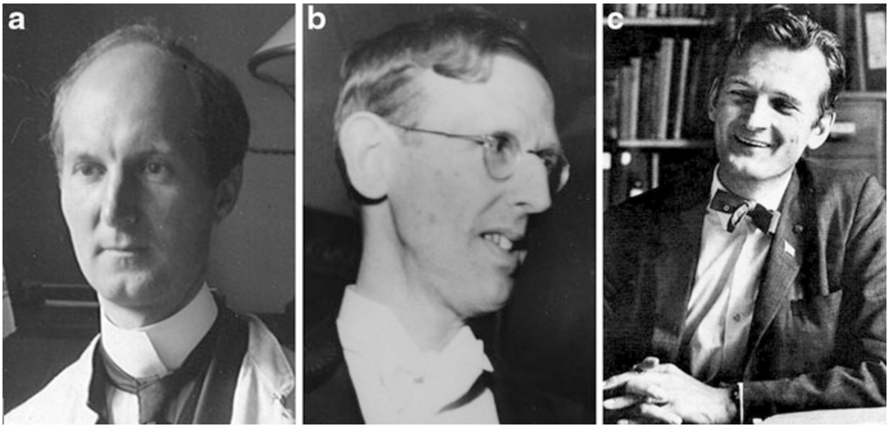

Fig. 1 **a** *Niels Bjerrum* (March 11, 1879, Copenhagen, Denmark – September 30, 1958, Copenhagen, Denmark). Bjerrum studied chemistry in Leipzig, Zurich, Paris and Berlin. He obtained a Ph.D. from the University of Copenhagen in 1908. From 1914 to 1949 he was Professor at the Royal Veterinary and Agricultural College in Copenhagen. His research concerned acid–base equilibria and electrolyte solutions. (Copyright Morten J. Bjerrum Reproduced from [8]). **b** *Gunnar Hägg* (December 14, 1903, Stockholm, Sweden – May 28, 1986, Uppsala, Sweden) studied chemistry in Stockholm, and in 1936 he became Professor in Uppsala. His main research area was X-ray diffraction. (Archive, University of Uppsala). **c** *Lars Gunnar Sillén* (July 11, 1916, Stockholm, Sweden – July 23, 1970, Danderyd/Stockholm) studied chemistry in Stockholm, and was a Professor of Inorganic Chemistry at the Royal Institute of Technology, Stockholm from 1950. At the beginning of his career he also did research in X-ray diffraction, but later he turned his interest to chemical solution equilibria and sea chemistry. Sillén was a pioneer in applying computer programs to the calculation of chemical equilibria, and his research group was most productive in providing new estimations of highly reliable equilibrium constants (Svenskt biografiskt lexikon)

Literature

1. Bjerrum N (1915) Sammlung chemisch und chemisch-technischer Vorträge 21:1
2. Arnfeld H (1937) Svensk Kemisk Tidskrift 49:96 (cited from: Hägg G (1950) Die theoretischen Grundlagen der analytischen Chemie. Birkhäuser, Basel)
3. Ölander A (1939) Kompendium i teoretisk kemi [Tekniska Högskolan Stockholm] (cited from: Hägg G (1950) Die theoretischen Grundlagen der analytischen Chemie. Birkhäuser, Basel)
4. Hägg G (1950) Die theoretischen Grundlagen der analytischen Chemie. Birkhäuser, Basel
5. Sillén LG, Lange PW, Gabrielson CO (1952) Problems in physical chemistry. Prentice Hall, New York
6. Sillén LG (1959) Graphical presentation of equilibrium data. Kapitel 8. In: Kolthoff IM, Elving PJ, Sandell EB (eds) Treatise on analytical chemistry. The Interscience Encyclopedia, New York
7. Butler JN (1998) Ionic equilibrium. Solubility and pH calculations. Wiley, New York
8. Scholz F (2011) Bjerrum, Niels. In: Bard AJ, Inzelt G, Scholz F (eds) Electrochemical dictionary. Springer, Berlin
9. Bliefert C (1978) pH-Wert-Berechnungen. Verlag Chemie, Weinheim
10. Seel F (1976) Grundlagen der Analytischen Chemie, 6th edn. Verlag Chemie, Weinheim

11. Blumenthal G (1993) Grundlagen der quantitativen chemischen Analyse. In: Kolditz L (ed) Anorganikum, 13th edn. Barth, Leipzig
12. Otto M (2011) Analytische Chemie, 4th edn. Wiley-VCH, Weinheim
13. Kotrlý S, Šůcha L (1985) Handbook of chemical equilibria in analytical chemistry. E. Horwood, Chichester
14. Šůcha L, Kotrlý S (1972) Solution equilibria in analytical chemistry. Van Nostrand Reinhold Comp, London
15. Inczedy J (1976) Analytical applications of complex equilibria. E. Horwood/Akadémiai Kiadó, Chichester/Budapest
16. Christian GD (2004) Analytical chemistry. Wiley, New York
17. Kahlert H (2012) Acid–base theories. In: Bard AJ, Inzelt G, Scholz F (eds) Electrochemical dictionary, 2nd edn. Springer, Berlin, pp 4–6

The Math Behind the pH-logc_i Diagrams

2

Figure 2 shows the coordination system as used for the construction of pH-logc_i diagrams of aqueous solutions.

In an aqueous solution of the acid HB, the following equilibria are established:

$$HB + H_2O \rightleftarrows B^- + H_3O^+ \tag{1}$$

$$H_2O + H_2O \rightleftarrows OH^- + H_3O^+ \tag{2}$$

The equilibrium (1) is characterized by the equilibrium constant K_a:

$$K_a = \frac{a^c_{B^-} a^c_{H_3O^+}}{a^c_{HB}} \tag{3}$$

This equilibrium constant is called *acidity constant*. It has no unit. The quantities a^c_i are the activities (to be more exact the *concentration activities*, hence the superscript c). They are related to the concentrations c_i in mol L^{-1} by the relationship:

$$a^c_i = c_i \gamma_i \times \frac{1}{c^*} \tag{4}$$

The activity coefficients γ_i can be understood as correction coefficients by which the concentrations have to be multiplied to fulfill the law of mass action. The quantity c^* is the concentration of the species in its reference state, that is, for concentration activities this is the concentration 1 mol L^{-1}. That quantity leads to unit-free activities. In fact, Eq. (3) also contains the activity of water; however, the *molar ratio activity* is $a^{mb}_{H_2O} = 1$, and it is not necessary to write this term. Because the activity coefficients approach 1 for diluted solutions, it is customary (and no bad approximation) to formulate the acidity constants on the basis of equilibrium *concentrations*, and Eq. (3) can be written as follows:

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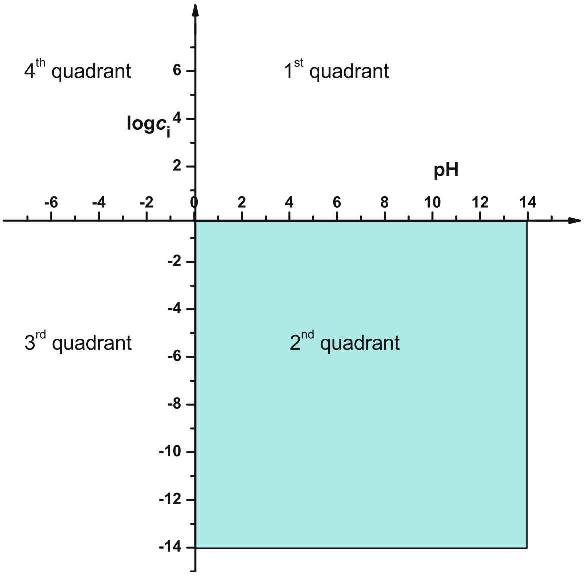


Fig. 2 Coordination system of pH-logc_i diagrams: normally, only the second quadrant (*the colored part*) is used, and constructed as a quadratic diagram because only that range of pH and logc_i is of significance in aqueous solutions

$$K_a = \frac{c_{B^-} c_{H_3O^+}}{c_{HB}} \tag{5}$$

The so defined acidity constant has a unit, here mol L^{-1}, which in calculations has the advantage that the units can be easily used for checking the general correctness of derived equations. For the sake of simplicity, in this book concentrations are used throughout, and the pH-logc_i diagrams are generally not applicable to activities. At concentrations higher than 10^{-3} mol L^{-1}, one needs to be always alert to the possibility that the activity coefficients may deviate from 1.0, which may considerably affect the pH.

The purpose of constructing a pH-logc_i diagram is to display the logarithm of the concentrations of all chemical species as a function of pH. In the case of a mono basic acid HB in water, the following species have to be considered: HB, B^-, H_2O, H_3O^+ and OH^-. In this book, the solvated proton will be always written as H_3O^+, although more complex hydrates such as $H_5O_2^+$, $H_7O_3^+$ and $H_9O_4^+$ may even more precisely describe it. Because water is the main constituent of aqueous solutions, and the concentration of water is practically constant, it is not necessary to display it in the diagrams (see Sect. 4.4.1). The concentration activity of H_3O^+ determines the pH of a solution:

$$\mathrm{pH} = -\log a^{c}_{H_3O^+} = -\log\left(c_{H_3O^+}\gamma_{H_3O^+} \times \frac{1}{c^*}\right) \tag{6}$$

The symbol p stands for "–log." It was introduced in 1909 by the Danish chemist Søren Peter Lauritz Sørensen (Fig. 3) [1]. Initially, Sørensen used to write p_H^+; however, this was not generally accepted, and people wrote pH instead.

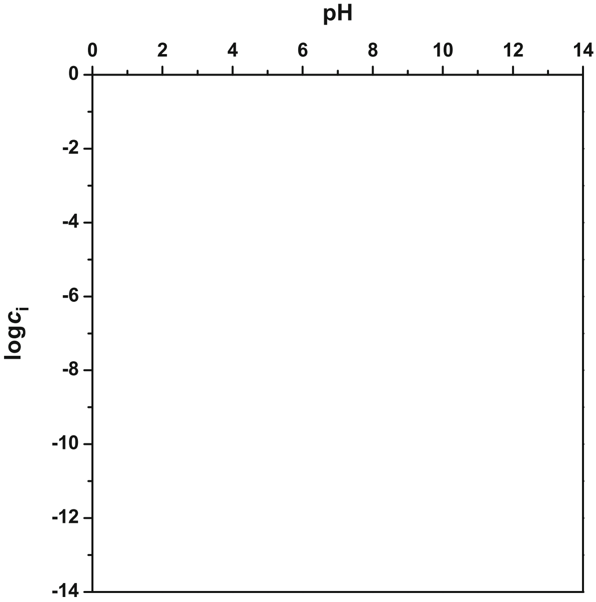
Fig. 3 Søren Peter Lauritz Sørensen (January 9, 1868, Havrebjerg, Denmark – February 12, 1939, Charlottenlund, Denmark)

In line with the suggestions of the International Union of Pure and Applied Chemistry, pH is not written in italics, although it is a symbol of a physical quantity [2]. For a long time, it was believed that Sørensen had chosen “p” as a symbol for “power” (“Potenz” in German); however, a recent historical study has revealed that he used it simply as a symbol for a variable [3], standing for the H^+ concentration C_p or $10^{-\mathrm{p}}$. In modern style this is: $c_{\mathrm{H_3O^+}} = 10^{-\mathrm{pH}}$! Nowadays, the definition $\mathrm{pX} = -\log c_\mathrm{X}$ is generally used in chemistry for a species X, and also for various equilibrium constants, e.g., $\mathrm{p}K_\mathrm{a} = -\log K_\mathrm{a}$ (see further down; here, K has to be written in italics). The equilibria (1) and (2) connect the activities (concentrations) of all species (HB, B^-, $\mathrm{H_2O}$, $\mathrm{H_3O^+}$, and OH^-) with each other, i.e., it is impossible to change the activity of one species without affecting all others. Hence, it makes sense to display these relations in a diagram. In aqueous solutions the range of pH values from 0 to 14 is of special importance, as the pH of real solutions usually falls within these limits. Although pH values below 0 and above 14 are in principle possible, such limitation of the diagrams is well reasoned. Similarly, the range of concentrations c_i can be limited, because only those between 1 mol L^{-1} and 1.0×10^{-14} mol L^{-1} are of any importance in real solutions (of course, there may be special cases with concentrations above 1 mol L^{-1}, but then the deviations of the activity coefficient from 1.0 will be very remarkable, and special calculations are necessary). Hence, on the logc_i axis, the range from 0 to -14 will be plotted in the diagrams. This logc_i range and the mentioned pH range (0–14) are situated in the 2nd quadrant of the coordination system shown in Fig. 2. Since usually data in this quadrant will be of interest, it is normal to construct a quadratic diagram as displayed in Fig. 4.

The relation between $\log c_{\mathrm{H_3O^+}}$ and pH, as well as that between $\log c_{\mathrm{OH^-}}$ and pH, are the same for all acid–base systems, because these quantities are related to each other by the equilibrium (2), the autoprotolysis of water. Also here, the pH will be approximately calculated using the concentration:

$$\mathrm{pH} = -\log c_{\mathrm{H_3O^+}} \tag{7}$$

Fig. 4 This is the quadratic diagram with the range of pH and logc_i values important in aqueous solution



Although this equation is not completely correct from the point of view of physical chemistry, it suffices for our purpose. The equilibrium constant of the autoprotolysis (2) is

$$K_w = a^c_{H_3O^+} a^c_{OH^-} \tag{8}$$

and it can be approximately described by concentrations as follows:

$$K_w = c_{H_3O^+} c_{OH^-} \tag{9}$$

K_w is called the ion product of water. It is a temperature-dependent quantity. At 25 °C it holds that: $-\log K_w = pK_w = 13.995$. Equation (7) defines a straight line in the pH-logc_i diagram (cf. Fig. 5).

Equation (9) can be rearranged by using 10^{-14} mol^2 L^{-2} for K_w:

$$K_w = c_{H_3O^+} c_{OH^-} = 10^{-14}\ \text{mol}^2\ \text{L}^{-2} \tag{10}$$

$$c_{OH^-} = \frac{K_w}{c_{H_3O^+}} \tag{11}$$

$$\log c_{OH^-} = \log K_w - \log c_{H_3O^+} \tag{12}$$

$$-\log c_{OH^-} = -\log K_w - (-\log c_{H_3O^+}) \tag{13}$$

$$pOH = pK_w - pH \tag{14}$$

Equation (14) also describes a straight line in the pH-logc_i diagram. This is the so-called OH^- line (cf. Fig. 6).

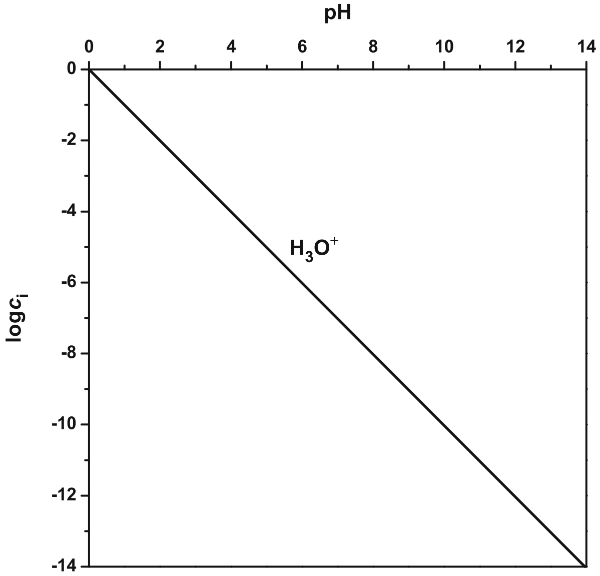


Fig. 5 The pH-logc_i diagram with the H_3O^+ line of water

Figure 6 displays only the components H_3O^+ and OH^-. These species are part of the two acid–base systems H_3O^+/ H_2O and H_2O/OH^-. H_3O^+ is the strongest acid which can exist in water, and OH^- is the strongest base in water. In the case of all acids HB which are stronger than H_3O^+ in water, the equilibrium (1) is so much shifted to the right side that one can claim a complete conversion to H_3O^+ and B^-, although in chemical equilibria "complete" never means 100 % and, at least theoretically, a certain concentration of HB will be always present. Bases which are much stronger than OH^- in water will be almost "completely" converted to HB and OH^- according to the reaction

$$B^- + H_2O \rightleftarrows HB + OH^- \tag{15}$$

This leads to the effect that all acids which are much stronger than H_3O^+ appear to be of the same strength of acidity, i.e., concentration of H_3O^+ (provided they have equal analytical concentrations of HB). All bases which are much stronger than OH^- will appear also to be of the same strength, i.e., exhibiting the same concentrations of OH^- (at equal analytical concentrations of B^-). This phenomenon is known as the levelling effect of water. It is customary to classify acids and bases according to their strength; however, one should remember that any such classification is arbitrary.

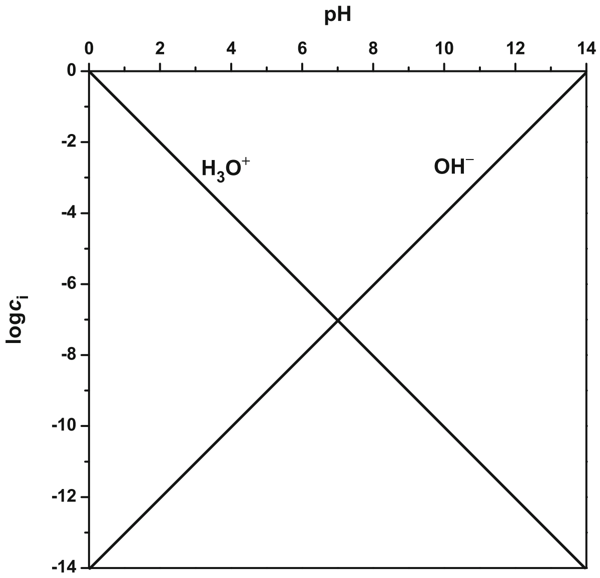


Fig. 6 The pH-logc_i diagram with the H_3O^+ and OH^- lines of water

It certainly makes sense to designate acids which are stronger than H_3O^+ in water as *very strong acids*, and their corresponding bases as *very weak bases*. It is impossible to define a strict border line above which acids are very strong: the reason is that there is no way to define the pK_a value of H_3O^+ in water on a strict thermodynamic basis [4]. Similarly, no pK_b value can be defined for OH^-. Nevertheless it is reasonable to assume that the pK_a of H_3O^+ is near to 0 (more precisely, slightly below zero) and the pK_a of H_2O near to 14 (more precisely, slightly above) (see Sect. 4.4.1). Thus, distinguishing very strong, strong, moderately strong, weak and very weak acids is only possible with soft borders (see Fig. 7):

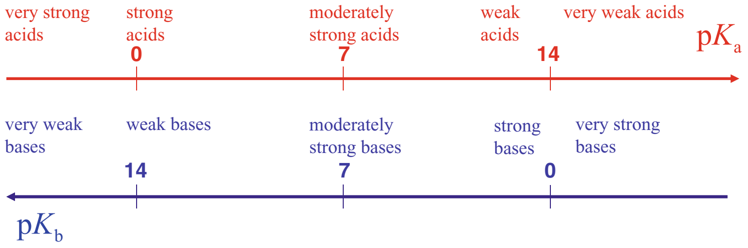


Fig. 7 Classification of acids and bases according to their strength in water

Since the calculation of pK_a values according to Eq. (3) is based on the transfer of a proton from HB to H_2O, it is the basicity of H_2O that determines the strength of an acid in water. Hence, all pK_a values defined by Eq. (3) are valid for water only, and in other solvents different pK_a values have to be used [5]. Table 1 gives a number of pK_a values of acids in water.

Table 1 pK_a values of acids in water. Most data are from Ref. [10]

Acid–base pair	pK_a values [ionic strength][a] (25 °C)
$HClO_4/ClO_4^-$	ca. –10
HI/I^-	ca. –10
HBr/Br^-	ca. –9
HCl/Cl^-	ca. –7
H_2SO_4/HSO_4^-	−3 [0]
HNO_3/NO_3^-	−1.34 [0]
$C_2O_4H_2/C_2O_4H^-$ (oxalic acid/hydrogenoxalate)	1.271
HSO_4^-/SO_4^{2-}	1.99 [0], 1.55 [0.1]
$H_3PO_4/H_2PO_4^-$	2.148 [0], 2.0 [0.1]
$[Fe(H_2O)_6]^{3+}/[Fe(H_2O)_5OH]^{2+}$	2.19 [0], 2.83 [0.1]
HF/F^-	3.17 [0], 2.92 [01], 2.96 [1.0]
$HCOOH/HCOO^-$ (formic acid/formate)	3.752
$C_2O_4H^-/C_2O_2^{2-}$ (hydrogenoxalate/oxalate)	4.266
H_3CCOOH/H_3CCOO^- (acetic acid/acetate)	4.756
$[Al(H_2O)_6]^{3+}/[Al(H_2O)_5OH]^{2+}$	4.99 [0], 5.69 [0.1]
H_2CO_3/HCO_3^-	6.35 [0], 6.16 [0.1], 6.02 [1.0]
H_2S/HS^-	7.02 [0], 6.83 [0.1], 6.61 [1.0]
$H_2PO_4^-/HPO_4^{2-}$	7.199[0], 6.72 [0.1], 6.46 [1.0]
NH_4^+/NH_3	9.244 [0], 9.29 [0.1], 9.40 [1.0]
HCN/CN^-	9.21 [0], 9.01 [0.1], 8.95 [1.0]
$[Fe(H_2O)_6]^{2+}/[Fe(H_2O)_5OH]^+$	9.5 [0]

(continued)

Table 1 (continued)

Acid–base pair	pK_a values [ionic strength][a] (25 °C)
HCO_3^-/CO_3^{2-}	10.33 [0], 10.0 [0.1], 9.57 [1.0]
HPO_4^{2-}/PO_4^{3-}	12.35 [0], 11.74 [0.1], 10.79 [3.0]
HS^-/S^{2-}	13.9 [0], 13.8 [1.0][b]
NH_3/NH_2^-	ca. 23

[a] The ionic strength can affect the pK_a values. Normally those data are tabulated which are extrapolated for an ionic strength of zero

[b] For the second protolysis stage of hydrogen sulfide, even pK_a values of 16 and 18 are given in the literature

▶ A closer look at the data in Table 1 shows that the pK_a values of very strong acids (pK_a below 0) and very weak acids (pK_a larger than 14) are not given with the high precision of acids with pK_a values between 0 and 14. The reason is that for the very strong acids, the activities of HB and for the very weak acids, the activities of B^- are extremely small, and a precise experimental determination is difficult. Thus, these pK_a values are not known with very high precision.

Another interesting feature is exhibited by hydrofluoric acid (HF): in comparison to HCl, HBr, and HI the pK_a value of HF is surprisingly large (-4 would probably be a better understandable value). This can be easily explained with the following equilibria:

(a) $HF + H_2O \rightleftarrows F^- + H_3O^+$,

(b) $F^- + H_3O^+ \rightleftarrows [F^- H_3O^+]$.

The species $[F^- H_3O^+]$ is a very stable ion pair having no net charge. The pK_a value is calculated according to $K_a = \frac{a_{F^-} a_{H_3O^+}}{a_{HF}}$ using the activities of fluoride ions, hydronium ions, and HF. For the latter, however, the classical experimental data (potentiometry, conductometry) do not distinguish between HF and the ion pair $[F^- H_3O^+]$, and thus a too large pK_a value results. This value does not reflect the real tendency of HF to transfer a proton to water [6]. The reason for the high stability of the ion pair is the small radius of the fluoride ion, which leads to a strong coulomb interaction with the hydronium ion.

The table also shows pK_a values of metal-aqua ions. At first glance, it may be surprising that metal-aqua ions are Brønsted acids. However, it is easy to understand that the coordinated water molecules are affected by the positively charged metal ions. This weakens the O–H bonds in the coordinated water, and thus the proton of coordinated water molecules is more easily transferred to a free water molecule than a proton from a free water molecule to another free water molecule. The formation of hydroxo complexes from metal-aqua complexes is of immense importance: the hydroxo complexes have a strong tendency to undergo condensation reactions leading to dimeric, trimeric, oligomeric complexes, finally even to the formation of insoluble metal oxide hydrates. The driving force for these condensation reactions is the entropy gain by releasing water molecules. These reactions have shaped the world. Before the rise of photosyntheses on earth, the atmosphere did not contain free oxygen, and the ocean held large amounts of dissolved iron(II) ions. Oxidation by the oxygen formed in photosyntheses oxidized iron(II) to iron(III), and the iron(III)-aqua ions formed hydroxo complexes which then underwent condensations until finally iron(III) oxide hydrates, and later iron(III) oxide were formed and deposited. Fifty-eight percent of all oxygen ever formed on earth was thus used for iron(III) deposition! The interesting relationships between pK_a values of metal-aqua ions and metal ion radii, etc. are described elsewhere [7].

For depicting the functions

$$\log c_{\mathrm{HB}} = f(\mathrm{pH}) \tag{16}$$

and

$$\log c_{\mathrm{B^-}} = f(\mathrm{pH}) \tag{17}$$

in the pH-logc_i diagram (Fig. 6), it is necessary to derive appropriate equations. This requires the law of mass action (5) $K_a = \frac{c_{\mathrm{B^-}} c_{\mathrm{H_3O^+}}}{c_{\mathrm{HB}}}$, and an equation connecting the quantities c_{HB} and $c_{\mathrm{B^-}}$. According to the reaction (1), $\mathrm{HB} + \mathrm{H_2O} \rightleftarrows \mathrm{B^-} + \mathrm{H_3O^+}$, the acid can be present in solution either as HB or as $\mathrm{B^-}$. Using concentrations in the unit mol $\mathrm{L^{-1}}$, i.e., number of particles (amount in mol) per volume, the following equation must hold for the overall concentration C°_{HB}:

$$C^{\circ}_{\mathrm{HB}} = c_{\mathrm{HB}} + c_{\mathrm{B^-}} \tag{18}$$

Relations of that kind will be called here “amount balances.” The *overall* concentration C°_{HB} has to be carefully distinguished from *equilibrium* concentrations, such as c_{HB} and $c_{\mathrm{B^-}}$: equilibrium concentrations give the concentration of certain species following establishment of equilibrium (in the case of acid–base reactions, that establishment is almost instantaneous, i.e., extremely fast). Thus, equilibrium concentrations are the *real* concentrations of species. *Overall* concentrations are often also called *analytical* concentrations, because they can be determined with classical methods of analysis, such as titrations. It is important to understand that Eq. (18) is only correct when using amount concentrations (molarities), i.e., when giving the concentrations in mol $\mathrm{L^{-1}}$. When using mass concentrations, e.g., in g $\mathrm{l^{-1}}$, Eq. (18) would be wrong, as HB has a larger mass than $\mathrm{B^-}$.

Here follows the derivation of the two functions (16) and (17):

$$K_\mathrm{a} = \frac{c_{\mathrm{B}^-}\, c_{\mathrm{H_3O}^+}}{c_\mathrm{HB}} \quad (5)$$

$$C^{\circ}_\mathrm{HB} = c_\mathrm{HB} + c_{\mathrm{B}^-} \quad (18)$$

Acid HB $\log c_\mathrm{HB} = f(\mathrm{pH})$ (16)	Base B^- $\log c_{\mathrm{B}^-} = f(\mathrm{pH})$ (17)
$K_\mathrm{a} = \frac{\left(C^{\circ}_\mathrm{HB} - c_\mathrm{HB}\right) c_{\mathrm{H_3O}^+}}{c_\mathrm{HB}}$ (19)	$K_\mathrm{a} = \frac{c_{\mathrm{B}^-}\, c_{\mathrm{H_3O}^+}}{C^{\circ}_\mathrm{HB} - c_{\mathrm{B}^-}}$ (25)
$K_\mathrm{a} c_\mathrm{HB} = C^{\circ}_\mathrm{HB} c_{\mathrm{H_3O}^+} - c_\mathrm{HB} c_{\mathrm{H_3O}^+}$ (20)	$K_\mathrm{a} C^{\circ}_\mathrm{HB} - K_\mathrm{a} c_{\mathrm{B}^-} = c_{\mathrm{B}^-} c_{\mathrm{H_3O}^+}$ (26)
$K_\mathrm{a} c_\mathrm{HB} + c_\mathrm{HB} c_{\mathrm{H_3O}^+} = C^{\circ}_\mathrm{HB} c_{\mathrm{H_3O}^+}$ (21)	$K_\mathrm{a} C^{\circ}_\mathrm{HB} = c_{\mathrm{B}^-} c_{\mathrm{H_3O}^+} + K_\mathrm{a} c_{\mathrm{B}^-}$ (27)
$c_\mathrm{HB} = \frac{C^{\circ}_\mathrm{HB} c_{\mathrm{H_3O}^+}}{c_{\mathrm{H_3O}^+} + K_\mathrm{a}}$ (22)	$c_{\mathrm{B}^-} = \frac{K_\mathrm{a} C^{\circ}_\mathrm{HB}}{c_{\mathrm{H_3O}^+} + K_\mathrm{a}}$ (28)
$c_\mathrm{HB} = \frac{C^{\circ}_\mathrm{HB}}{1 + \frac{K_\mathrm{a}}{c_{\mathrm{H_3O}^+}}}$ (23)	$c_{\mathrm{B}^-} = \frac{C^{\circ}_\mathrm{HB}}{1 + \frac{c_{\mathrm{H_3O}^+}}{K_\mathrm{a}}}$ (29)
with $\frac{K_\mathrm{a}}{c_{\mathrm{H_3O}^+}} = \frac{10^{-\mathrm{p}K_\mathrm{a}}}{10^{-\mathrm{pH}}} = 10^{\mathrm{pH}-\mathrm{p}K_\mathrm{a}}$ (24) follows	with $\frac{c_{\mathrm{H_3O}^+}}{K_\mathrm{a}} = \frac{10^{-\mathrm{pH}}}{10^{-\mathrm{p}K_\mathrm{a}}} = 10^{-\mathrm{pH}+\mathrm{p}K_\mathrm{a}}$ (30) follows
$\log c_\mathrm{HB} = \log C^{\circ}_\mathrm{HB} - \log\left(1 + 10^{\mathrm{pH}-\mathrm{p}K_\mathrm{a}}\right)$ (31)	$\log c_{\mathrm{B}^-} = \log C^{\circ}_\mathrm{HB} - \log\left(1 + 10^{-\mathrm{pH}+\mathrm{p}K_\mathrm{a}}\right)$ (32)

Equations (31) and (32) describe curves in the pH-logc_i diagram which strongly resemble that of a hyperbola. In the following discussions the curves will be called hyperbolas, although this is mathematically not fully correct. The two hyperbolas will be designated as the HB line and the B^- line. It is also good to write the species names at the hyperbola in the diagram. Giving there c_HB and c_{B^-} would be wrong, as the logarithms of concentrations are plotted there.

As can be seen from Fig. 8, each hyperbola has two branches which quickly convert to almost linear lines. Only in the vicinity of pH = pK_a do the hyperbola

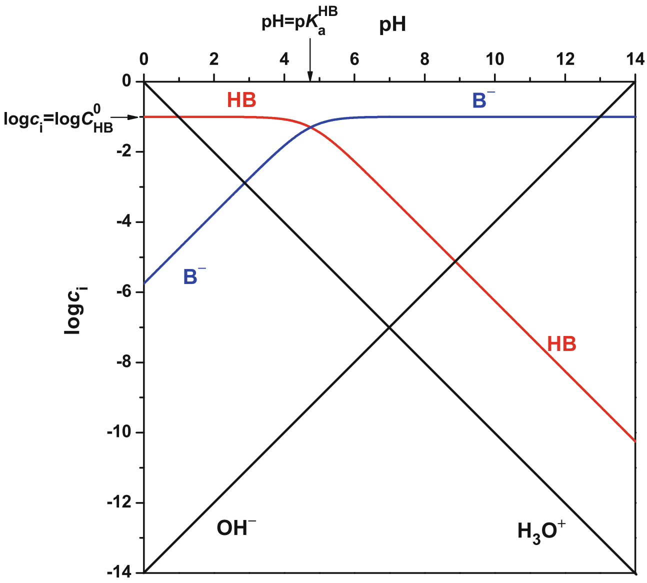
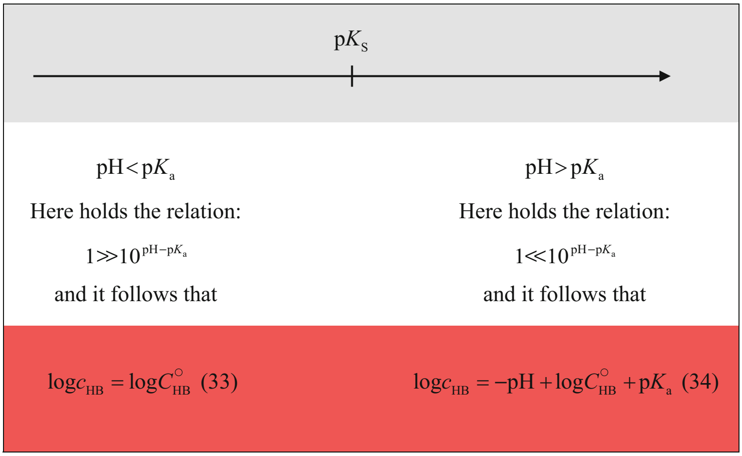


Fig. 8 The pH-logc_i diagram with the lines of H_3O^+, OH^-, HB and B^- for acetic acid with $C^{\circ}_{HB} = 0.1$ mol L^{-1} and p$K_a = 4.75$

have a pronounced curvature. This makes it possible to use the asymptotes instead of the hyperbola. In order to do so, the equations of the asymptotes need to be derived. In order to find the asymptotes of the hyperbola described by Eq. (31), it is necessary to study what term in $(1 + 10^{pH-pK_a})$ will dominate in the two pH ranges, below and above pK_a :

$$\log c_{HB} = \log C^{\circ}_{HB} - \log\left(1 + 10^{pH-pK_a}\right) \tag{31}$$



pK_S

pH < pK_a

Here holds the relation:

$1 \gg 10^{pH-pK_a}$

and it follows that

$\log c_{HB} = \log C^{\circ}_{HB}$ (33)

pH > pK_a

Here holds the relation:

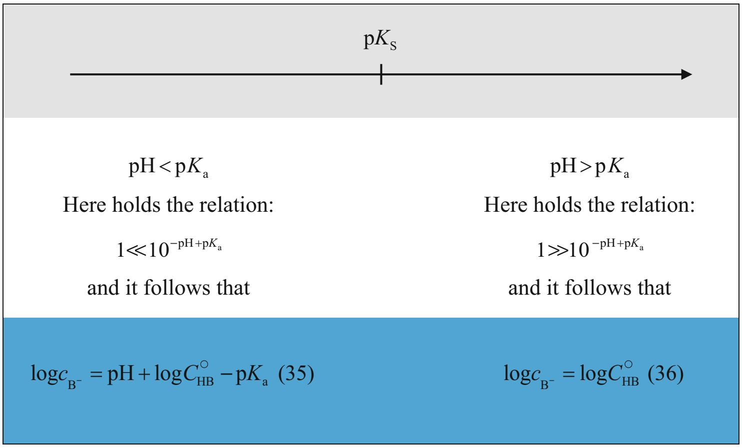
$1 \ll 10^{pH-pK_a}$

and it follows that

$\log c_{HB} = -pH + \log C^{\circ}_{HB} + pK_a$ (34)

Analogously, it is possible to find the asymptotes of the hyperbola described by Eq. (32) by anlysis of the two terms in $(1 + 10^{-\mathrm{pH}+\mathrm{p}K_a})$:

$$\log c_{B^-} = \log C^{\circ}_{HB} - \log\left(1 + 10^{-\mathrm{pH}+\mathrm{p}K_a}\right) \tag{32}$$



pH < pK_a
Here holds the relation:
$1 \ll 10^{-\mathrm{pH}+\mathrm{p}K_a}$
and it follows that

$$\log c_{B^-} = \mathrm{pH} + \log C^{\circ}_{HB} - \mathrm{p}K_a \quad (35)$$

pH > pK_a
Here holds the relation:
$1 \gg 10^{-\mathrm{pH}+\mathrm{p}K_a}$
and it follows that

$$\log c_{B^-} = \log C^{\circ}_{HB} \quad (36)$$

In most cases it is not necessary to plot the hyperbolas, but it is sufficient to display the asymptotes, i.e., the simple line Eqs. (33), (34), (35) and (36) within the limits of their validity! Figure 9 shows such a pH-logc_i diagram.

Looking at Fig. 9 can prompt the following question: how is it possible that the concentration of B^- so strongly varies in the range pH $<$ pK_a whereas that of HB is constant, if Eq. (18) $C^{\circ}_{HB} = c_{HB} + c_{B^-}$ holds true? The answer is: (a) in the entire range pH $<$ pK_a, both concentrations vary, and that of HB *appears* to be constant only because the asymptote (33) is displayed, and (b) because the logarithm of c_{B^-} is plotted, a straight line with the slope +1 follows, but — with the exception of the vicinity of pH = pK_a — very small concentrations c_{B^-} are involved, and thus it follows that $\log c_{HB} \approx \log C^{\circ}_{HB}$ is a good approximation.

The philosophy of pH-logc_i diagrams:

1. The diagrams show the single acid–base systems, e.g., those of water and HB, *independent* of each other and *no* interaction is taken into consideration.
2. From the diagrams one can find (a) the approximate equilibrium concentrations of all species at any pH, and, the other way round, (b) the approximate pH of solutions having specified equilibrium concentrations of certain species. The determined data are approximate, because the interactions between the single acid–base systems are not taken into account.

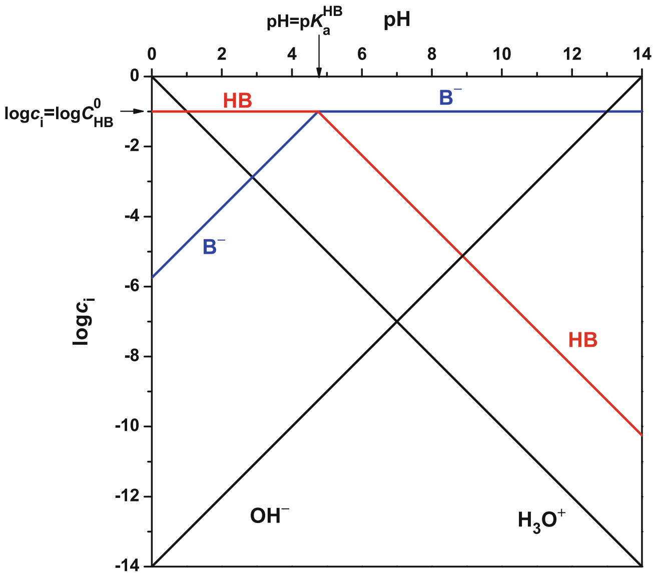


Fig. 9 The pH-logc_i diagram with the H_3O^+ line, the OH^- line and the asymptotes of HB and B^- for acetic acid with $C^{\circ}_{HB} = 0.1$ mol L^{-1} and p$K_a = 4.75$

▶ The crossing point of the HB and B^- lines is the so-called *buffer point*: an acid–base buffer is a solution which has the capability of keeping its pH value rather unaffected by additions of acids or bases. The pH of buffer solutions can be calculated as follows. Finding the logarithm of Eq. (5) $K_a = \frac{c_{B^-} c_{H_3O^+}}{c_{HB}}$ gives $\log K_a = \log c_{H_3O^+} + \log \frac{c_{B^-}}{c_{HB}}$, i.e., $\log c_{H_3O^+} = \log K_a + \log \frac{c_{HB}}{c_{B^-}}$ or $\mathrm{pH} = \mathrm{p}K_a - \lg \frac{c_{HB}}{c_{B^-}}$. This equation is frequently called *buffer equation* or also the *Henderson–Hasselbalch Equation* because the physiologists L. J. Henderson [8] and K. A. Hasselbalch [9] derived it. Clearly, it is nothing else but a form of the law of mass action (Eq. 5). At a concentration ratio $\frac{c_{B^-}}{c_{HB}} = 1$, the buffer has a pH equal to the pK_a of the involved acid. At that point, the buffer has also his largest capacity to minimize the effect of added acids and bases, i.e., the largest *buffer capacity* $\beta = \frac{dn}{d(\mathrm{pH})}$. Here, $\frac{dn}{d(\mathrm{pH})}$ is the first derivative of the function $n = f(\mathrm{pH})$ in which n is the amount of added H_3O^+ or OH^-. Thus, the buffer capacity is the reciprocal value of the slope of the dependence of the pH as function of added amounts of H_3O^+ or OH^-. The buffer capacity decreases for $\frac{c_{B^-}}{c_{HB}} < 1$ and $1 < \frac{c_{B^-}}{c_{HB}}$, and an acceptable buffer capacity can be realized only in the range $0.1 \le \frac{c_{B^-}}{c_{HB}} \le 10$, i.e., in the range $(\mathrm{p}K_a - 1) \le \mathrm{pH} \le (\mathrm{p}K_a + 1)$. The pH of buffers depends not only on the ratio $\frac{c_{B^-}}{c_{HB}}$, but the buffer capacity depends also on the overall concentration of the acid and base forms $C^{\circ} = c_{B^-} + c_{HB}$.

Literature

1. Sørensen SPL (1909) Compt Rend Lab Carlsberg 8:1 and 396
2. Cohen ER, Cvitas T, Frey JG et al (eds) (2007) IUPAC quantities, units and symbols in physical chemistry, 3rd edn. RSC, Cambridge, UK, p 70
3. Nørby JG (2000) Trends Biochem Sci 25:36–37
4. Henrion G, Scholz F, Schmidt W, Zettler M (1982) Z phys Chem (Leipzig) 263:634–636
5. Himmel D, Goll SK, Leito I, Krossing I (2010) Angew Chem 263:7037–7040
6. Giguere PA (1979) J Chem Educ 56:571–575
7. Tytko KH (1979) Chem unserer Zeit 13:184–194
8. Scholz F (2012) Henderson, Lawrence Joseph. In: Bard AJ, Inzelt G, Scholz F (eds) Electrochemical dictionary, 2nd edn. Springer, Berlin, p 451
9. Scholz F (2012) Hasselbalch, Karl Albert. In: Bard AJ, Inzelt G, Scholz F (eds) Electrochemical dictionary, 2nd edn. Springer, Berlin, p 446
10. Kotrlý S, Šůcha L (1985) Handbook of chemical equilibria in analytical chemistry. E. Horwood Ltd., Chichester

Constructing pH-logc_i Diagrams

3

3.1 Monobasic Acids

The construction of the pH-logc_i diagram of a monobasic acid HB is shown stepwise in Figs. 10, 11, 12, 13, and 14. The acid has an overall concentration C_{HB}° and a given pK_a^{HB} value:

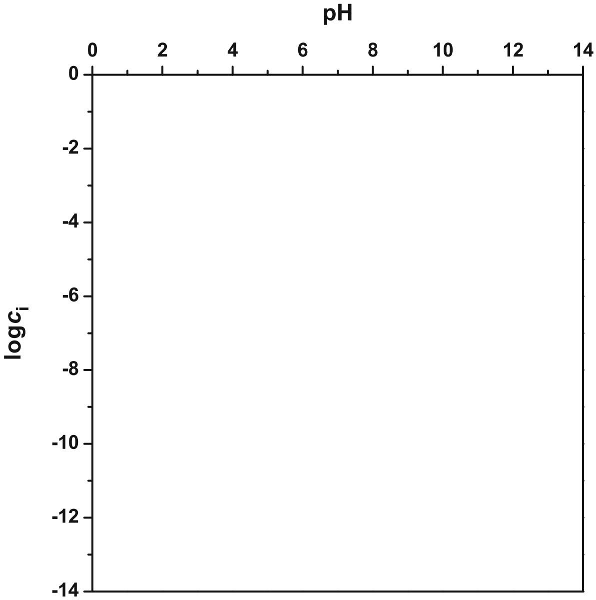


Fig. 10 The coordination system of the pH-logc_i diagram

H. Kahlert and F. Scholz, *Acid-Base Diagrams*,
DOI 10.1007/978-3-642-37902-4_3,

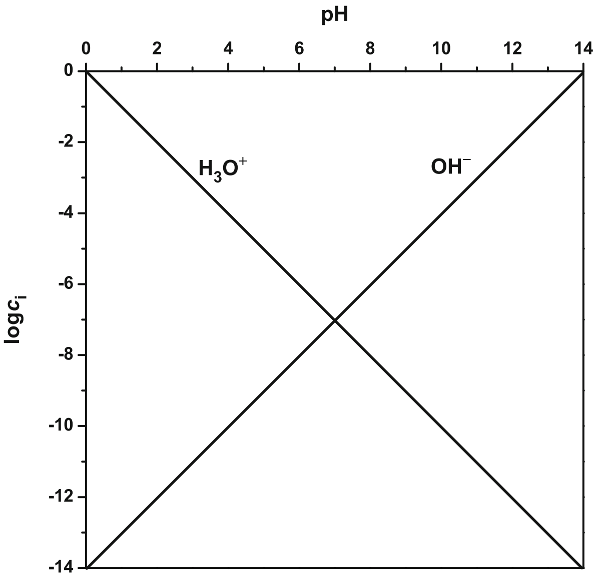


Fig. 11 Plotting the H_3O^+ and OH^- lines of the water system

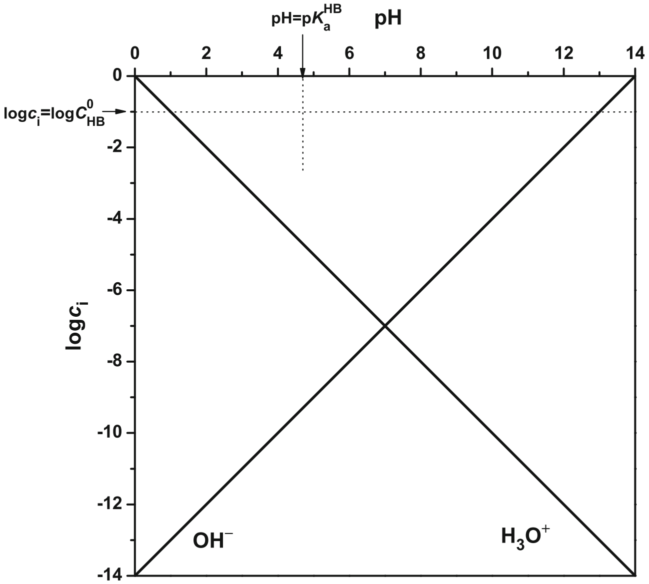


Fig. 12 Marking the coordinates $\log c_i = \log C_{HB}^{O} = -1$ and pH $=$ p$K_a = -4.75$, using here the example of acetic acid with $C_{HB}^{O} = 10^{-1}$ mol L^{-1}

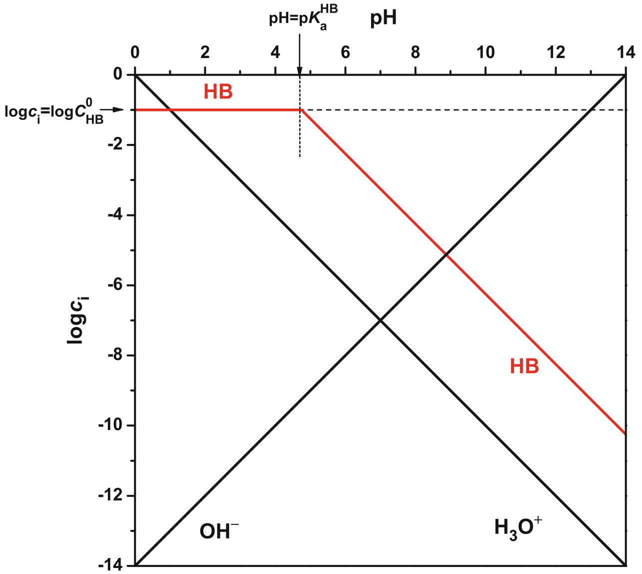


Fig. 13 Plotting the two asymptotes of HB with Eq. (33) for pH $<$ pK_a and Eq. (34) for pH $>$ pK_a. Example: acetic acid with $C^{\circ}_{HB} = 0.1$ mol L^{-1} and p$K_a = 4.75$

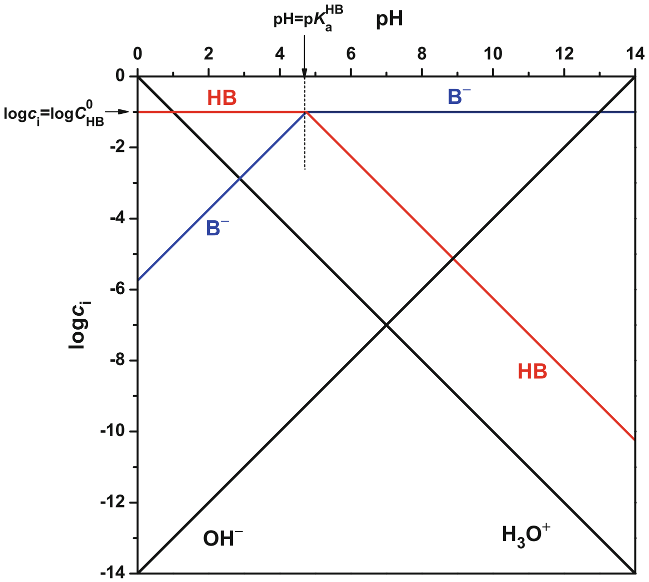


Fig. 14 Plotting the two asymptotes of B⁻ with Eq. (35) for pH $<$ pK_a and Eq. (36) for pH $>$ pK_a. Example: acetic acid with $C^{\circ}_{HB} = 0.1$ mol L^{-1} and p$K_a = 4.75$

3.2 Dibasic Acids

In the case of dibasic acids H_2B, the following two protolysis reactions have to be considered:

$$H_2B + H_2O \rightleftarrows HB^- + H_3O^+ \tag{37}$$

$$HB^- + H_2O \rightleftarrows B^{2-} + H_3O^+ \tag{38}$$

The equilibrium equation (37) is characterized by the following law of mass action:

$$K_{a1} = \frac{c_{HB^-} c_{H_3O^+}}{c_{H_2B}} \tag{39}$$

and equilibrium equation (38) by:

$$K_{a2} = \frac{c_{B^{2-}} c_{H_3O^+}}{c_{HB^-}} \tag{40}$$

As an analogy to Eq. (18), the following amount balance has to be formulated:

$$C^{\circ}_{H_2B} = c_{H_2B} + c_{HB^-} + c_{B^{2-}} \tag{41}$$

The mathematical equations of the functions are given in the Appendix. The pH-logc_i diagram can be easily constructed by plotting the line equations for the pH ranges separated by the pK_a values (see Appendix). The construction is analogous to that of monobasic acids, with the following specificity. The asymptote of H_2B has the slope -2 in the range pH $>$ pK_{a2}, that is, in the range where B^{2-} is the dominating species. The asymptote of B^{2-} has the slope +2 in the range pH $<$ pK_{a1}, that is, where H_2B is dominating. The stepwise construction of the diagram is illustrated in Figs. 15, 16, 17, 18, and 19.

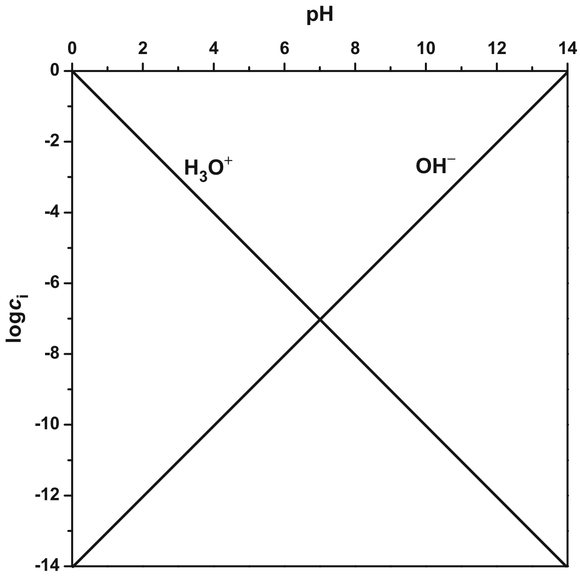


Fig. 15 Plotting the coordination system with the H_3O^+ and OH^- lines of water

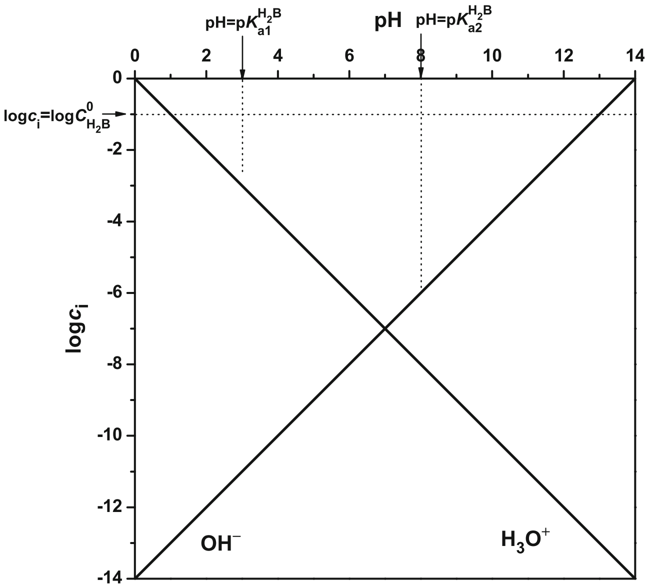


Fig. 16 Marking the coordinates, here for the example of an acid with $\log c_\mathrm{i} = \log C^\mathrm{O}_{\mathrm{H_2B}} = -1$, $\mathrm{pH} = \mathrm{p}K_{\mathrm{a1}} = 3$ and $\mathrm{pH} = \mathrm{p}K_{\mathrm{a2}} = 8$

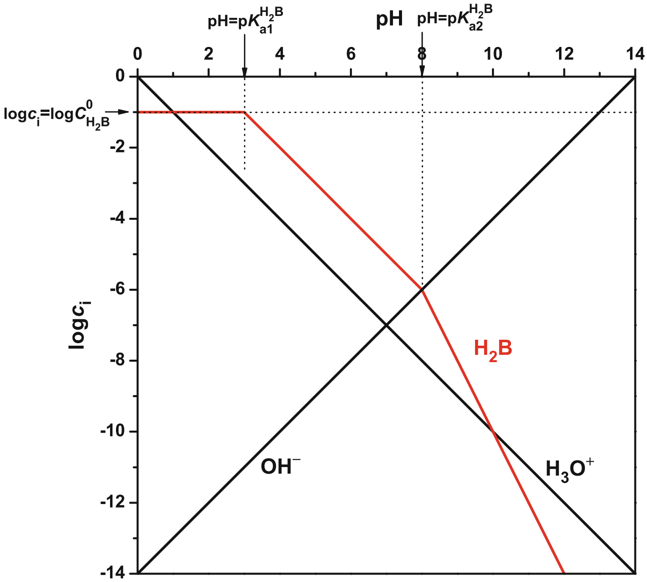


Fig. 17 Plotting the three lines of H_2B in the ranges $pH < pK_{a1}$, $pK_{a1} < pH < pK_{a2}$ and $pH > pK_{a2}$. Example: acid with $\log C^{O}_{H_2B} = -1$, $pK_{a1} = 3$ and $pK_{a2} = 8$

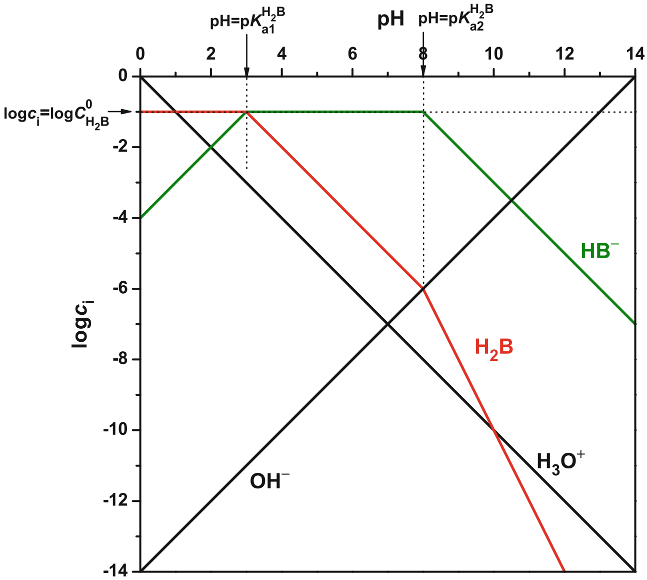


Fig. 18 Plotting the three lines of HB^- in the ranges $pH < pK_{a1}$, $pK_{a1} < pH < pK_{a2}$ and $pH > pK_{a2}$. Example: acid with $\log C^{O}_{H_2B} = -1$, $pK_{a1} = 3$ and $pK_{a2} = 8$

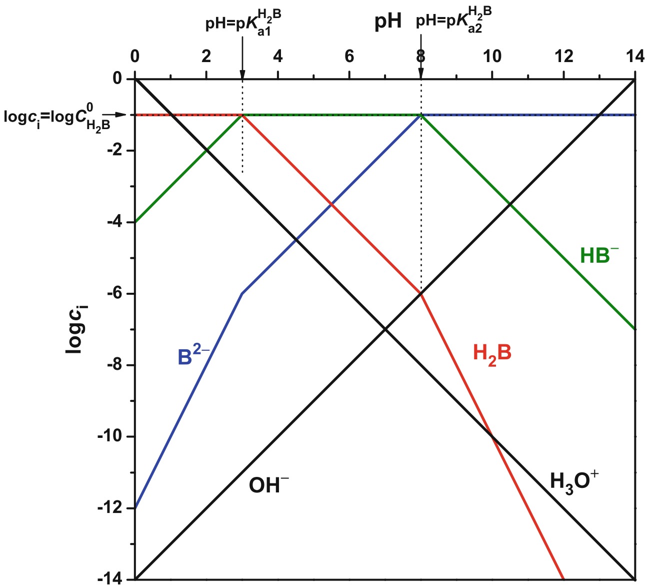


Fig. 19 Plotting the three lines of B^{2-} in the ranges $pH < pK_{a1}$, $pK_{a1} < pH < pK_{a2}$ and $pH > pK_{a2}$. Example: acid with $\log C^{\circ}_{H_2B} = -1$, $pK_{a1} = 3$ and $pK_{a2} = 8$

3.3 Tribasic Acids

For H_3B, the following protolysis equilibria have to be written:

$$H_3B + H_2O \rightleftarrows H_2B^- + H_3O^+ \tag{42}$$

$$H_2B^- + H_2O \rightleftarrows HB^{2-} + H_3O^+ \tag{43}$$

$$HB^{2-} + H_2O \rightleftarrows B^{3-} + H_3O^+ \tag{44}$$

The mathematical equations of the functions are given in the Appendix. The diagram can be constructed in analogy to the previous examples (Figs 15 to 19).

Figures 20, 21, 22, 23, 24 and 25 show the construction of the diagram and the lines of the different species. The line of H_3B has the slope −2 in the range $pK_{a2} < pH < pK_{a3}$ (HB^{2-} is dominating here). For $pH > pK_{a3}$ (B^{3-} is dominating) the slope is −3, which is not visible in the diagram because of the limited range of $\log c_i$ and pH (it is outside the used quadrant).

The line of H_2B^- has the slope −2 in the range $pH > pK_{a3}$ (where B^{3-} is dominating).

The line of HB^{2-} has the slope +2 in the range $pH < pK_{a1}$ (where H_3B is dominating).

The line of B^{3-} has the slope +3 for $pH < pK_{a1}$ (H_3B is dominating). In the given example, this line is situated outside the range of the diagram. In the range $pK_{a1} < pH < pK_{a2}$ the slope is +2 (H_2B^- is dominating).

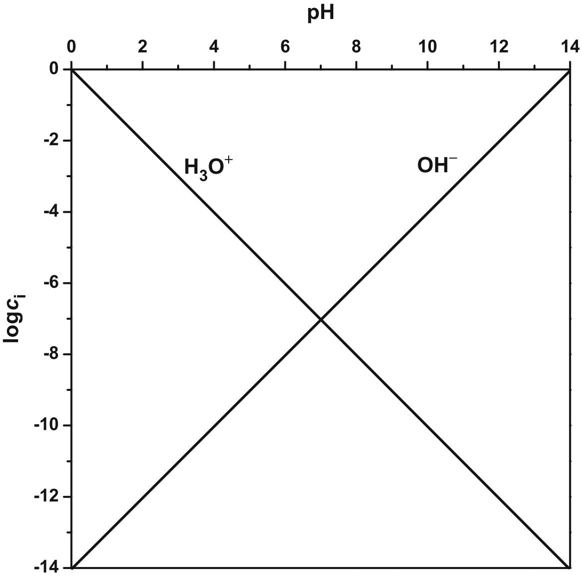


Fig. 20 Plotting the coordination system with the H_3O^+ and OH^- lines of water

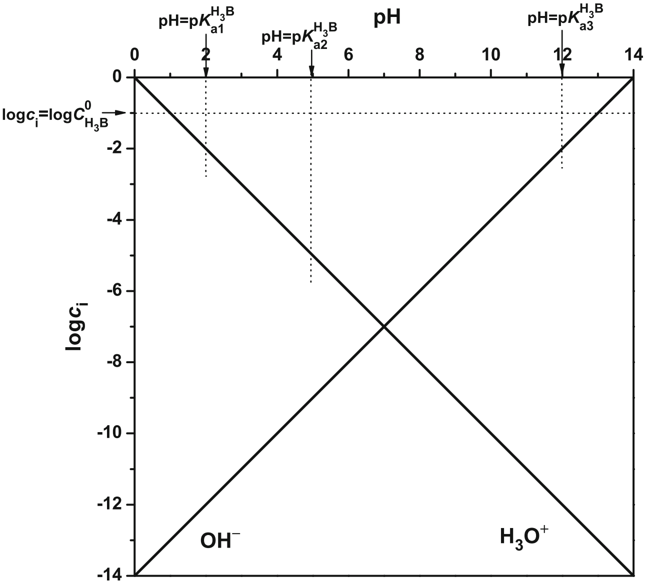


Fig. 21 Marking the coordinates, here for an acid with $\log c_\mathrm{i} = \log C^\mathrm{O}_\mathrm{H_3B} = -1$, $\mathrm{pH} = \mathrm{p}K_\mathrm{a1} = 2$, $\mathrm{pH} = \mathrm{p}K_\mathrm{a2} = 5$ and $\mathrm{pH} = \mathrm{p}K_\mathrm{a3} = 12$

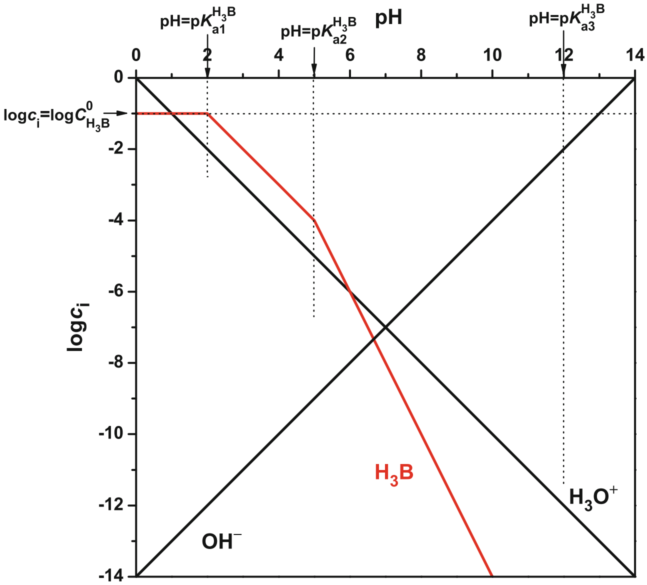


Fig. 22 Plotting the three lines of H_3B in the ranges $pH < pK_{a1}$, $pK_{a1} < pH < pK_{a2}$ and $pK_{a2} < pH < pK_{a3}$. The line of H_3B for $pH > pK_{a3}$ is situated outside the range of the diagram. Example: $\log C^{O}_{H_3B} = -1$, $pK_{a1} = 2$, $pK_{a2} = 5$ and $pK_{a3} = 12$

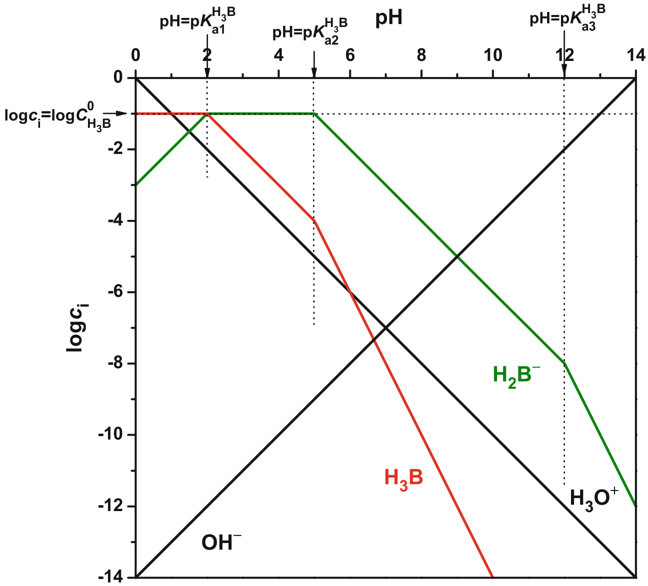


Fig. 23 Plotting the lines of H_2B^- in the ranges $pH < pK_{a1}, pK_{a1} < pH < pK_{a2}, pK_{a2} < pH < pK_{a3}$ and $pH > pK_{a3}$. Example: $\log C^{O}_{H_3B} = -1$, $pK_{a1} = 2$, $pK_{a2} = 5$ and $pK_{a3} = 12$

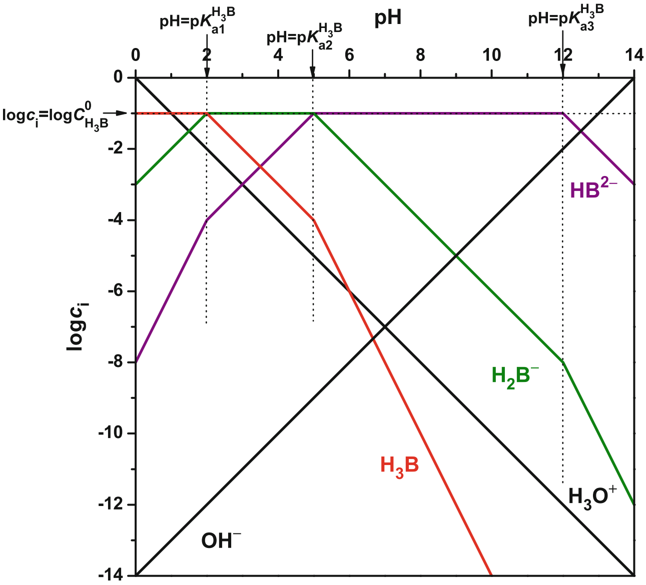


Fig. 24 Plotting the lines of HB^{2-} in the ranges $pH < pK_{a1}, pK_{a1} < pH < pK_{a2}, pK_{a2} < pH < pK_{a3}$ and $pH > pK_{a3}$. Example: $\log C_{H_3B}^{\circ} = -1$, $pK_{a1} = 2$, $pK_{a2} = 5$ and $pK_{a3} = 12$

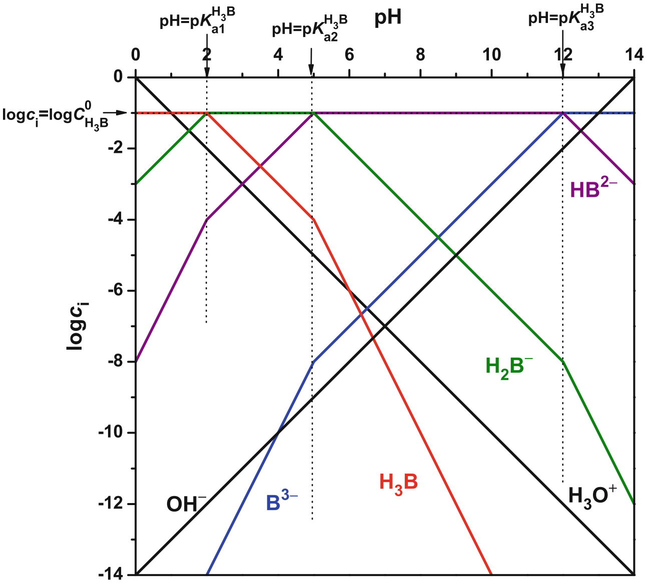


Fig. 25 Plotting the lines of B^{3-} in the ranges $pK_{a1} < pH < pK_{a2}$, $pK_{a2} < pH < pK_{a3}$ and $pH > pK_{a3}$. The line for $pH < pK_{a1}$ is situated outside the range of the coordination system. Example: $\log C_{H_3B}^{\circ} = -1$, $pK_{a1} = 2$, $pK_{a2} = 5$ and $pK_{a3} = 12$

3.4 Tetrabasic Acids

In case of a tetrabasic acid H_4B the following protolysis equilibria are established:

$$H_4B + H_2O \rightleftarrows H_3B^- + H_3O^+ \tag{45}$$

$$H_3B^- + H_2O \rightleftarrows H_2B^{2-} + H_3O^+ \tag{46}$$

$$H_2B^{2-} + H_2O \rightleftarrows HB^{3-} + H_3O^+ \tag{47}$$

$$HB^{3-} + H_2O \rightleftarrows B^{4-} + H_3O^+ \tag{48}$$

The mathematical equations of the functions are given in the Appendix. The plotting of all species in the diagram can be made with the help of the line equations given in the Appendix. Following the procedures for the mono- to tribasic acids, this is stepwise made in Figs. 26, 27, 28, 29, 30, and 31.

The line of H_4B has the slope -2 in the range $\mathrm{p}K_{a2} < \mathrm{pH} < \mathrm{p}K_{a3}$ (H_2B^{2-} is dominating). The slope is -3 in the range $\mathrm{p}K_{a3} < \mathrm{pH} < \mathrm{p}K_{a4}$ (HB^{3-} is dominating). Sometimes, also in the example shown in Fig. 27, the concentrations of B^{4-} are so small in the range $\mathrm{pH} > \mathrm{p}K_{a4}$ that the line is situated outside the range of the diagram. There the line has a slope of -4.

The line of H_3B^- has a slope of -2 for $\mathrm{p}K_{a3} < \mathrm{pH} < \mathrm{p}K_{a4}$ (HB^{3-} is dominating). For $\mathrm{pH} > \mathrm{p}K_{a4}$ (B^{4-} is dominating) the slope is -3. In some cases (e.g., example in Fig. 28) that line is already outside the range of the diagram.

The line of H_2B^{2-} has a slope of +2 in for $\mathrm{pH} < \mathrm{p}K_{a1}$ where H_4B is dominating. For $\mathrm{pH} > \mathrm{p}K_{a4}$, the slope is -2 (B^{4-} is dominating).

The line of HB^{3-} has a slope of +3 for $\mathrm{pH} < \mathrm{p}K_{a1}$ where H_4B is the dominating species. In the range $\mathrm{p}K_{a1} < \mathrm{pH} < \mathrm{p}K_{a2}$, the slope is +2. Here, H_3B^- is dominating.

The line of B^{4-} has a slope of +4 for $\mathrm{pH} < \mathrm{p}K_{a1}$ where H_4B is dominating. However, the concentrations of B^{4-} are so small in that range that they are outside the range of the diagram. In the range $\mathrm{p}K_{a1} < \mathrm{pH} < \mathrm{p}K_{a2}$, i.e., the range where H_3B^- dominates, the slope is +3, and for $\mathrm{p}K_{a2} < \mathrm{pH} < \mathrm{p}K_{a3}$ the slope is +2 (H_2B^{2-} is dominating).

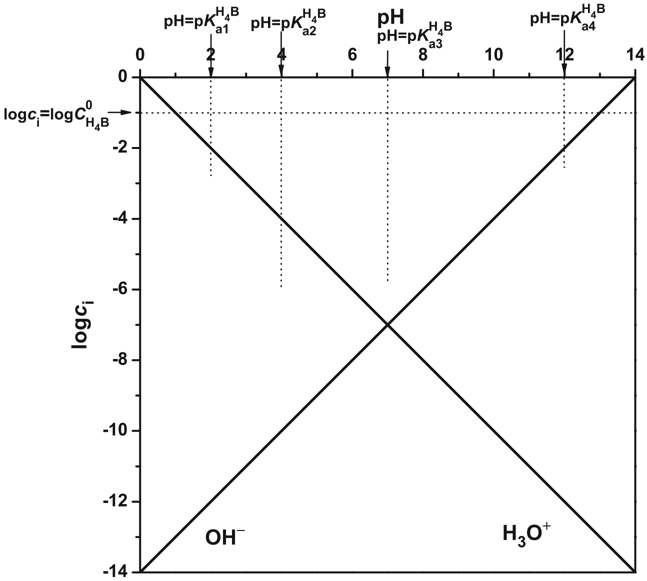


Fig. 26 Plotting the coordination system with the H_3O^+ and OH^- lines of water, and marking the coordinates, here for an example of an acid with $\log c_i = \log C^{O}_{H_4B} = -1$, $pH = pK_{a1} = 2$, $pH = pK_{a2} = 4$, $pH = pK_{a3} = 7$ and $pH = pK_{a4} = 12$

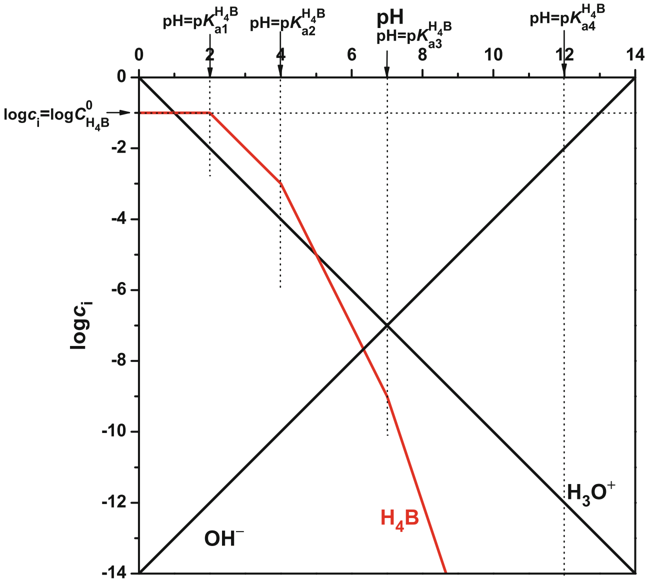


Fig. 27 Plotting the lines of H_4B for $pH < pK_{a1}$, $pK_{a1} < pH < pK_{a2}$, $pK_{a2} < pH < pK_{a3}$ and $pK_{a3} < pH < pK_{a4}$. The line of H_4B for $pH > pK_{a4}$ is situated outside the plotted range. Example: acid with $\log C^{O}_{H_4B} = -1$, $pK_{a1} = 2$, $pK_{a2} = 4$, $pK_{a3} = 7$ and $pK_{a4} = 12$

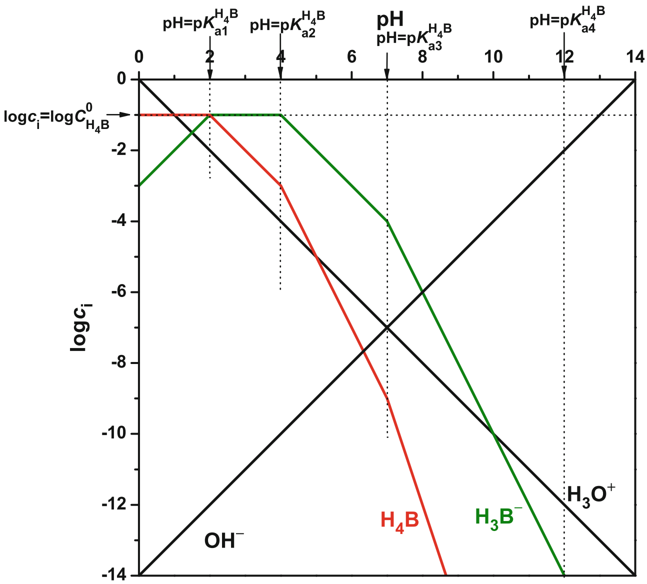


Fig. 28 Plotting the lines of H_3B^- for $pH < pK_{a1}$, $pK_{a1} < pH < pK_{a2}$, $pK_{a2} < pH < pK_{a3}$ and $pK_{a3} < pH < pK_{a4}$. Example: acid with $\log C^{\mathrm{O}}_{\mathrm{H_4B}} = -1$, $pK_{a1} = 2$, $pK_{a2} = 4$, $pK_{a3} = 7$ and $pK_{a4} = 12$

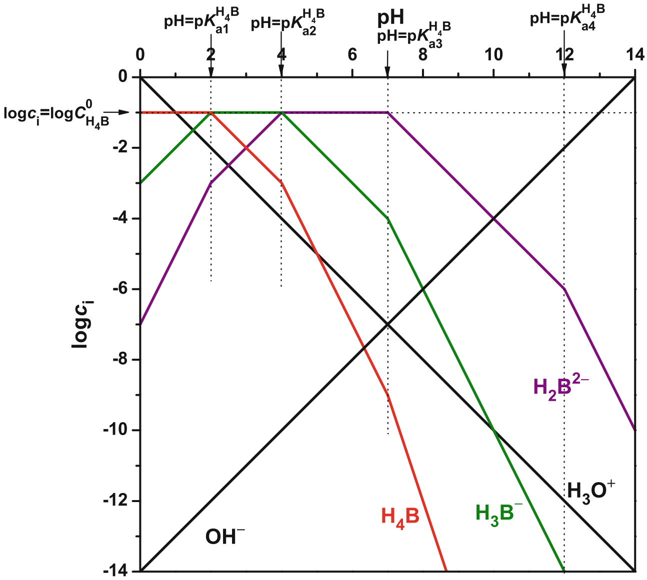


Fig. 29 Plotting the lines of H_2B^{2-} for $pH < pK_{a1}$, $pK_{a1} < pH < pK_{a2}$, $pK_{a2} < pH < pK_{a3}$, $pK_{a3} < pH < pK_{a4}$ and $pH > pK_{a4}$. Example: acid with $\log C^{\mathrm{O}}_{\mathrm{H_4B}} = -1$, $pK_{a1} = 2$, $pK_{a2} = 4$, $pK_{a3} = 7$ and $pK_{a4} = 12$

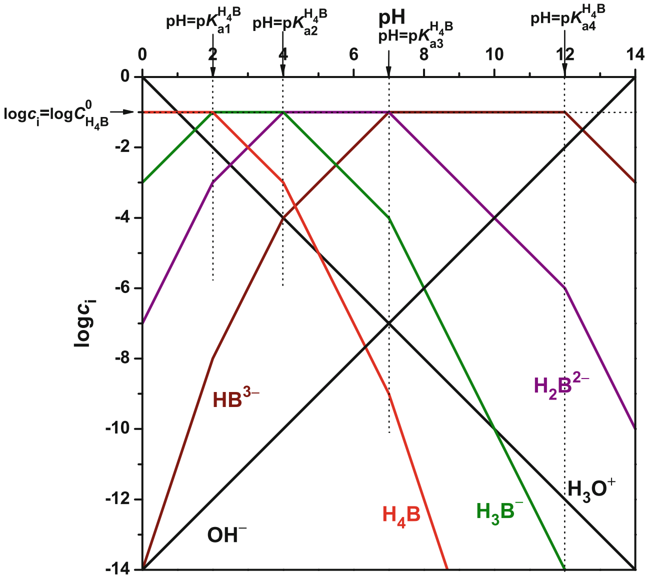


Fig. 30 Plotting the lines of HB^{3-} for pH < pK_{a1}, pK_{a1} < pH < pK_{a2}, pK_{a2} < pH < pK_{a3}, pK_{a3} < pH < pK_{a4} and pH > pK_{a4}. Example: acid with $\log C^{\circ}_{H_4B} = -1$, p$K_{a1} = 2$, p$K_{a2} = 4$, p$K_{a3} = 7$ and p$K_{a4} = 12$

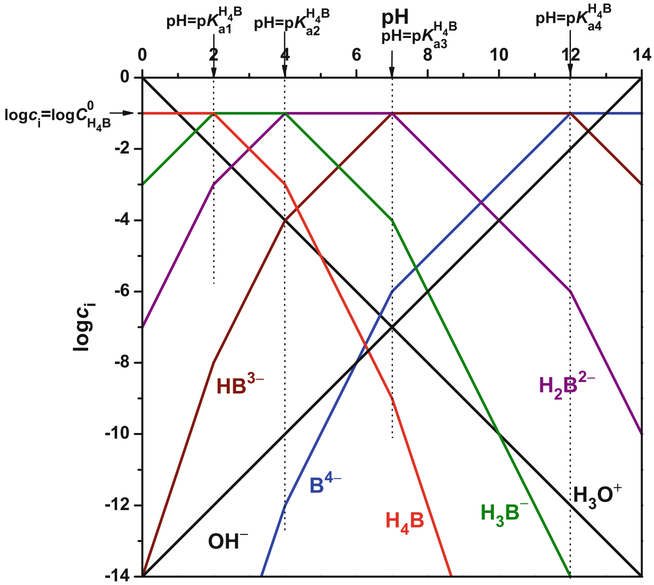


Fig. 31 Plotting the lines of B^{4-} for pK_{a1} < pH < pK_{a2}, pK_{a2} < pH < pK_{a3}, pK_{a3} < pH < pK_{a4} and pH > pK_{a4}. Example: acid with $\log C^{\circ}_{H_4B} = -1$, p$K_{a1} = 2$, p$K_{a2} = 4$, p$K_{a3} = 7$ and p$K_{a4} = 12$

The Application of pH-logc_i Diagrams for Graphical Estimation of the pH of Solutions and for the Derivation of Useful Simplified Equations

4

For the derivation of equations that allow an approximative calculation of pH values, it is again necessary to refer to the reactions of a monobasic acid HB in water:

$$HB + H_2O \rightleftarrows B^- + H_3O^+ \tag{1}$$

$$H_2O + H_2O \rightleftarrows OH^- + H_3O^+ \tag{2}$$

The following quantities have to be considered: c_{HB}, c_{B^-}, $c_{H_3O^+}$ and c_{OH^-}. Mathematics demand for the determination of n variables to have a system of n independent equations that do not contradict each other. Hence, four such equations are needed here. These are the already introduced Eq. (5) for the acidity constant, Eq. (9) for the ion product of water, Eq. (18) for the amount balance, and Eq. (49) for the charge balance:

$$\boldsymbol{K_a = \frac{c_{B^-} c_{H_3O^+}}{c_{HB}}} \tag{5}$$

$$\boldsymbol{K_w = c_{H_3O^+} c_{OH^-}} \tag{9}$$

$$\boldsymbol{C^{\circ}_{HB} = c_{HB} + c_{B^-}} \tag{18}$$

$$\boldsymbol{c_{H_3O^+} = c_{OH^-} + c_{B^-}} \tag{49}$$

▶ In the case of the reaction of a cation acid, for example, NH_4^+, with water, the following reactions have to be written:

$$HB^+ + H_2O \rightleftarrows B + H_3O^+ \tag{1*}$$

$$H_2O + H_2O \rightleftarrows OH^- + H_3O^+ \tag{2}$$

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(The asterisk marks equations that are only slightly different from the form without asterisk.)

From these two equations follows:

$$c_{H_3O^+} = c_{OH^-} + c_B \tag{49*}$$

because, according to Eq. (1*), one neutral particle B is formed per one H_3O^+, and one HB^+ cation is lost.

Combining Eqs. (5), (9), (18), and (49) and rearranging them gives a polynomial equation of degree 3 (cubic equation) with respect to H_3O^+:

$$\begin{tikzcd}
K_w = c_{H_3O^+} c_{OH^-} \ (9) \arrow[r] & c_{OH^-} = \dfrac{K_w}{c_{H_3O^+}} \ (11) \arrow[r, "\text{inserting (11) in (49)}"] & c_{H_3O^+} = \dfrac{K_w}{c_{H_3O^+}} + c_{B^-} \ (50) \\
K_a = \dfrac{c_{B^-} c_{H_3O^+}}{c_{HB}} \ (5) \arrow[r] & c_{HB} = \dfrac{c_{B^-} c_{H_3O^+}}{K_a} \ (51) \arrow[r, "\text{inserting (51) in (18)}"] & C^{\circ}_{HB} = \dfrac{c_{B^-} c_{H_3O^+}}{K_a} + c_{B^-} \ (52) \arrow[dll] \\
c_{B^-} = \dfrac{C^{\circ}_{HB}}{\dfrac{c_{H_3O^+}}{K_a} + 1} \ (53) \arrow[r, "\text{inserting (53) in (50)}"] & c_{H_3O^+} = \dfrac{K_w}{c_{H_3O^+}} + \dfrac{C^{\circ}_{HB}}{\dfrac{c_{H_3O^+}}{K_a} + 1} \ (54) \arrow[dl] & \\
c^2_{H_3O^+} = K_w + \dfrac{C^{\circ}_{HB} c_{H_3O^+}}{\dfrac{c_{H_3O^+} + K_a}{K_a}} \ (55) \arrow[r] & c^2_{H_3O^+} \left(\dfrac{c_{H_3O^+} + K_a}{K_a} \right) = K_w \left(\dfrac{c_{H_3O^+} + K_a}{K_a} \right) + C^{\circ}_{HB} c_{H_3O^+} \ (56) \arrow[d] & \\
 & \dfrac{c^3_{H_3O^+} + K_a c^2_{H_3O^+}}{K_a} = \dfrac{K_w c_{H_3O^+} + K_a K_w}{K_a} + C^{\circ}_{HB} c_{H_3O^+} \ (57) \arrow[d] & \\
 & c^3_{H_3O^+} + K_a c^2_{H_3O^+} = K_w c_{H_3O^+} + K_a K_w + K_a C^{\circ}_{HB} c_{H_3O^+} \ (58) \arrow[d] & \\
 & 0 = c^3_{H_3O^+} + K_a c^2_{H_3O^+} - \left(K_a C^{\circ}_{HB} + K_w \right) c_{H_3O^+} - K_a K_w \ (59) &
\end{tikzcd}$$

In the case of polybasic acids, the number of equilibria increases, as does the number of mathematical equations. Finally, this leads to equations of the degree 4 for a dibasic acid, degree 5 for a tribasic acid, etc.

The equations for a simple base B^- are analogously:

$$B^- + H_2O \rightleftarrows HB + OH^- \tag{15}$$

$$H_2O + H_2O \rightleftarrows OH^- + H_3O^+ \tag{2}$$

The following four variables have to be considered: $c_{HB}, c_{B^-}, c_{H_3O^+}$ and c_{OH^-}. The four equations necessary for further derivations are Eq. (60) for the base constant of B^-, Eq. (9) for the ionic product of water, and the equations for amount and charge balances:

$$\boldsymbol{K_b = \frac{c_{HB}c_{OH^-}}{c_{B^-}}} \tag{60}$$

$$\boldsymbol{K_w = c_{H_3O^+}c_{OH^-}} \tag{9}$$

$$\boldsymbol{C^{\circ}_{B^-} = c_{HB} + c_{B^-}} \tag{61}$$

$$\boldsymbol{c_{H_3O^+} = c_{OH^-} - c_{HB}} \tag{62}$$

Equation (62) follows from reaction equation (15), as one HB is formed per OH^- on account of losing one B^- anion (see the box below Eq. (49)). The system of Eqs. (60), (9), (61), and (62) results in a cubic equation with respect to c_{OH^-}:

$$0 = c^3_{OH^-} + K_b c^2_{OH^-} - \left(K_b C^{\circ}_{B^-} + K_w\right) c_{OH^-} - K_b K_w \tag{63}$$

In the following section, it will be shown that pH-logc_i diagrams make it possible to find the approximate pH of various solutions in the diagram, as well as to find out what approximations are permitted in deriving simplified equations for pH calculations, to avoid the necessity to solving Eqs. (59) or (63), or even more complex equations.

For the derivation of simplified equations, it is necessary to consider what summand can be ignored in Eqs. (18), (49), (61) or (62): whether a summand can be neglected (taken as zero) depends only on the precision of the desired calculations. Normally, neglecting a summand is permitted when it contributes less than 1 % to the sum. This means that the smaller summand can be neglected when it is two orders of magnitude smaller than the other on the logc_i-scale of the pH-logc_i diagram.

(continued)

When in this book equations of the form $x \approx y$ are used to derive simplified equations, it would be strictly considered necessary to write in all the follow-up equations the symbol "≈". However, since the thus-derived equations are always denoted as simplified equations (approximations), this is not done, and the equality symbol (=) is used. This is in agreement with common practice.

4.1 Monobasic Acids and Their Corresponding Bases

4.1.1 Very Strong Acids and Their Corresponding Very Weak Bases

In the following derivations, the symbols HB and B^- are used throughout, even when specific examples are displayed in the figures. Solutions of HB are called acid solutions, and solutions of B^- are called base solutions, although the latter are in fact salt solutions (e.g., Na^+ B^-). Later it will be shown that there also exist cation acids that are part of salts, for example, $NH_4^+Cl^-$ and amino acid hydrochlorides (Sect. 4.2.1.2).

4.1.1.1 Very Strong Acids in High Concentration

Very strong acids possess pK_a values smaller than zero. Figure 32 shows the example of the very strong acid HCl (p$K_a = -7$) in rather high concentration (e.g., $\log C^{\circ}_{HCl} = -1$).

Of course, Eq. (49) must hold:

$$c_{H_3O^+} = c_{OH^-} + c_{B^-} \tag{49}$$

This excludes the fact that the real pH is situated on the right side of the crossing point P_1 in Fig. 32, as there the sum of $c_{OH^-} + c_{B^-}$ is always larger than $c_{H_3O^+}$. The real pH must be situated slightly left to $P_{1,}$ as the following reason shows. The overall H_3O^+ concentration is the sum of what was formed in reaction equation (1) and reaction equation (2). The concentration of OH^- which has to be considered in Eq. (49) can at most be 10^{-13} mol L^{-1} (see the crossing point P_3). Since 10^{-13} mol L^{-1} is negligible compared with 10^{-1} mol L^{-1} (the H_3O^+ concentration formed in the reaction of HCl with water), the crossing point P_1 gives accurately the pH of the solution, and it holds that

$$c_{H_3O^+} \approx c_{B^-} \tag{64}$$

Hence, the pH of the solution can be found on the pH scale at the crossing point of the H_3O^+ and the Cl^- lines, because the concentration of HCl is negligible in the pH range 0–14. Hence, it is possible to neglect c_{HB} relative to c_{B^-} in Eq. (18):

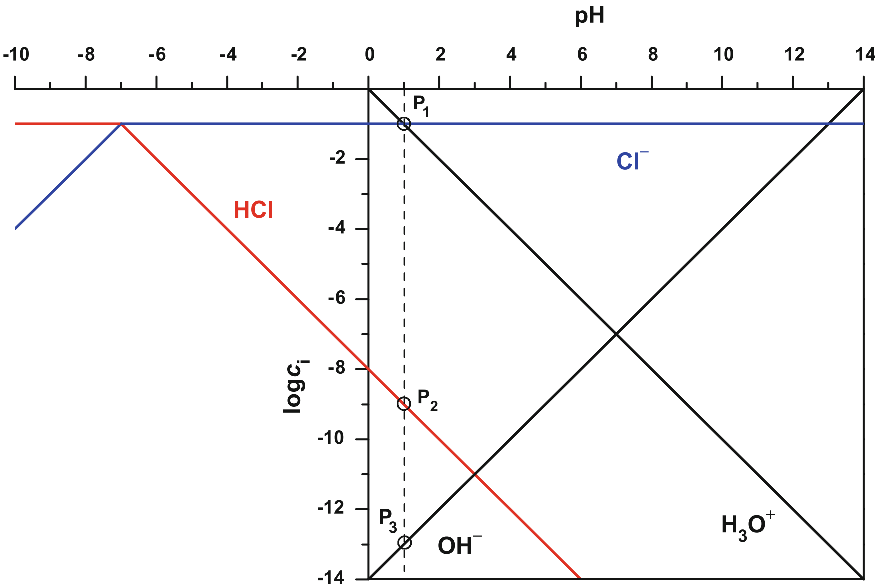


Fig. 32 pH-logc_i diagram of hydrochloric acid (p$K_a = -7$) at 0.1 mol L^{-1} concentration. The range for pH < 0 is only shown for didactic reasons. Normally this is not done

$$C^{\circ}_{HB} = c_{HB} + c_{B^-} \tag{18}$$

From this follows the relationship:

$$c_{B^-} \approx C^{\circ}_{HB} \tag{65}$$

Taking Eqs. (64) and (65), the following approximation can be derived:
Simplified equation for a very strong acid in high concentration:

$$\boldsymbol{c_{H_3O^+} \approx C^{\circ}_{HB}} \tag{66}$$

4.1.1.2 Very Strong Acid in Low Concentration

A hydrochloric acid solution of an overall concentration of 10^{-6} mol L^{-1} is presented in Fig. 33:

Since Eq. (49) holds here also, the real pH must be situated on the pH scale left of P_1. Furthermore, it holds that the concentration of HCl is negligible compared to that of the chloride ions. Hence, Eq. (18) can be simplified as follows:

$$c_{B^-} \approx C^{\circ}_{HB} \tag{65}$$

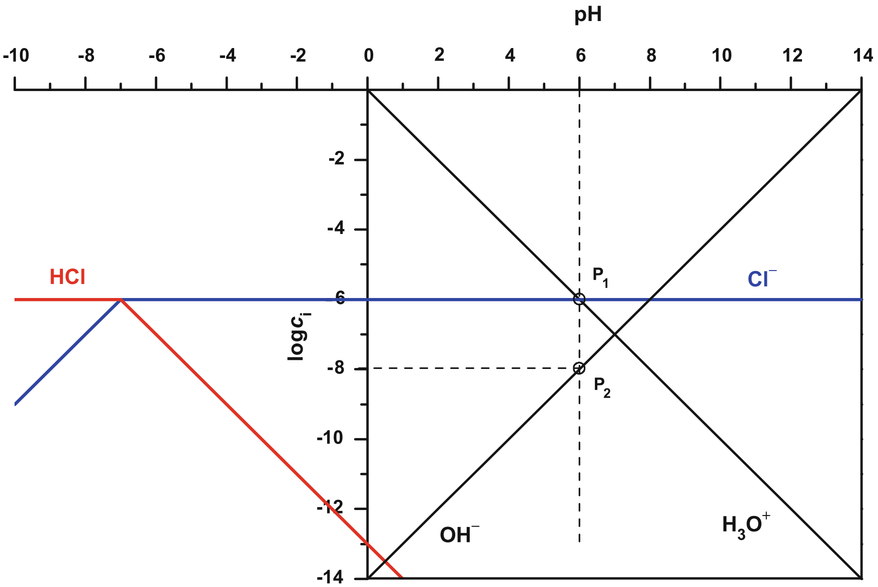


Fig. 33 pH-logc_i diagram of hydrochloric acid (pK_a = −7) at 10^{-6} mol L^{-1} concentration. The range for pH < 0 is only shown for didactic reasons. Normally this is not done

However, the equilibrium concentration of OH^- from the autoprotolysis of water is no longer negligible in the charge balance (Eq. (49)), and the pH of the solution will be slightly left to the crossing point P_1. Some rearrangement of the equations makes it possible to derive a simplified equation for this case:

$$c_{OH^-} = \frac{K_w}{c_{H_3O^+}} \ (11) \xrightarrow{\text{inserting (11) in (49)}} c_{H_3O^+} = \frac{K_w}{c_{H_3O^+}} + c_{B^-} \ (50)$$

$$c_{B^-} \approx C^{\bigcirc}_{HB} \ (65) \xrightarrow{\text{inserting (65) in (50)}} c_{H_3O^+} = \frac{K_w}{c_{H_3O^+}} + C^{\bigcirc}_{HB} \ (67)$$

$$\downarrow$$

$$c^2_{H_3O^+} = K_w + C^{\bigcirc}_{HB} c_{H_3O^+} \ (68)$$

$$\downarrow$$

$$0 = c^2_{H_3O^+} - C^{\bigcirc}_{HB} c_{H_3O^+} - K_w \ (69)$$

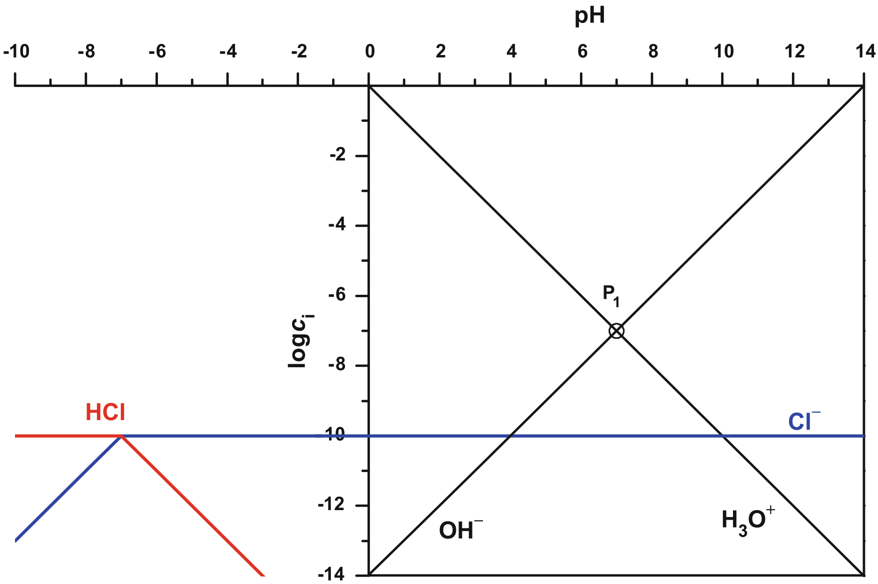


Fig. 34 pH-logc_i diagram of a hydrochloric acid (p$K_a = -7$) at 10^{-10} mol L^{-1} concentration. The range for pH < 0 is only shown for didactic reasons. Normally this is not done

This quadratic equation can be solved and yields:

Simplified equation for a very strong acid in low concentration:

$$\boldsymbol{c_{\mathrm{H_3O^+}} = \frac{C^{\circ}_{\mathrm{HB}}}{2} \pm \sqrt{\frac{\left(C^{\circ}_{\mathrm{HB}}\right)^2}{4} + K_\mathrm{w}}} \tag{70}$$

(The mathematical solution $c_{\mathrm{H_3O^+}} = \frac{C^{\circ}_{\mathrm{HB}}}{2} - \sqrt{\frac{\left(C^{\circ}_{\mathrm{HB}}\right)^2}{4} + K_\mathrm{w}}$ does not correspond to a real concentration, and therefore the equation is usually given without the minus sign.)

For very low overall concentrations, e.g., 10^{-10} mol L^{-1} (cf. Fig. 34) the diagram shows that the simplification equation (65) is still valid; however, in the equation of the charge balance, the concentration of OH^- from the autoprotolysis of water is much larger than the equilibrium concentration of the Cl^- ions. From this follows:

Simplified equation for a very strong acid in very low concentration:

$$\boldsymbol{c_{\mathrm{H_3O^+}} \approx c_{\mathrm{OH^-}} = \sqrt{K_\mathrm{w}}} \tag{71}$$

Of course, the real pH should be – no matter how little – left to the pH-coordinate of the neutrality point (P_1 in Fig. 34), as an acid solution can never have a neutral or basic pH.

4.1.1.3 Very Weak Bases

As an example, a solution of sodium chloride is chosen: the chloride anion is the very weak base corresponding to the very strong acid HCl. The aqua-complex of sodium ions is a very weak acid in terms of the Brønsted acid–base definition, and hence it does not affect the pH of the solution (see Sect. 4.1.4).

In case of a NaCl solution, the Eqs. (61) and (62), i.e., the amount balance and the charge balance, have to be fulfilled:

$$C^{\circ}_{\mathrm{B}^-} = c_{\mathrm{HB}} + c_{\mathrm{B}^-} \tag{61}$$

$$c_{\mathrm{H_3O^+}} = c_{\mathrm{OH}^-} - c_{\mathrm{HB}} \tag{62}$$

Equation (62) indicates that the real pH of the NaCl solution has to be – no matter how little – right to the point P_1 in Fig. 34. However, according to Figs. 32, 33, and 34 the degree of protonation of the chloride ions is in the entire pH range from 0 to 14, and for whatever overall concentrations of chloride, always negligible, and hence it follows as a very good approximation that:

$$c_{\mathrm{B}^-} \approx C^{\circ}_{\mathrm{B}^-} \tag{72}$$

Thus it holds for all NaCl solutions the pH is practically 7 (provided carbon dioxide is absent):

Simplified equation for a very weak base in any concentration:

$$\boldsymbol{c_{\mathrm{H_3O^+}} \approx c_{\mathrm{OH}^-} = \sqrt{K_{\mathrm{w}}}} \tag{71}$$

▶ The frequently given reasoning is that a NaCl solution is neutral because it is the salt of a very strong acid, and a very strong base is rather formal and does not allow a detailed understanding. A better reasoning is as follows: a NaCl solution is neutral because the chloride ion is a very weak base and the sodium-aqua ion is a very weak acid.

4.1.2 Strong Acids and Their Corresponding Weak Bases

4.1.2.1 Strong Acids in High Concentration

Formic acid has a pK_a value of 3.75 and thus it belongs to the strong acids. Figure 35 shows the pH-logc_i diagram for the overall concentration 10^{-1} mol L^{-1}.

As always, the charge balance must hold:

$$c_{\mathrm{H_3O^+}} = c_{\mathrm{OH}^-} + c_{\mathrm{B}^-} \tag{49}$$

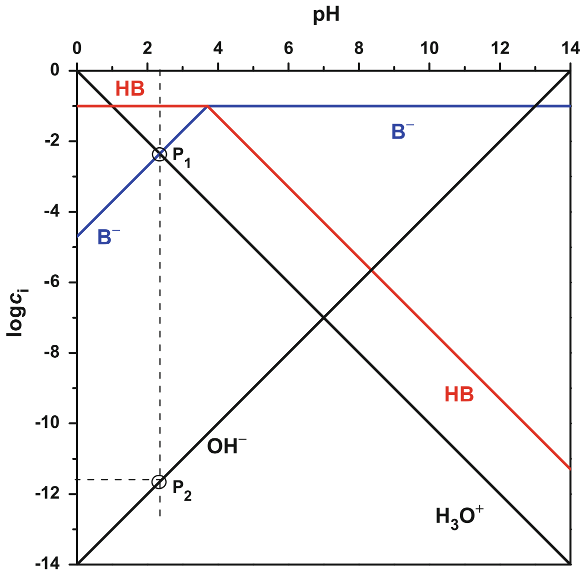


Fig. 35 pH-logc_i diagram for formic acid (pK_a = 3.75) at $C^{\circ}_{HB} = 10^{-1}$ mol L^{-1}

This means that the real pH will be somewhat left of the pH-coordinate of P_1, as to the right of this, the sum $c_{OH^-} + c_{B^-}$ is always larger than $c_{H_3O^+}$ (in other words, in addition to the H_3O^+ concentration produced by the protolysis of HB, there is also some H_3O^+ from the autoprotolysis of water). The diagram shows that the concentration of OH^- is at the point P_1, and also, to the left to it, much smaller than the concentration of B^- (cf. point P_2). Hence it is a good approximation to write:

$$c_{H_3O^+} \approx c_{B^-} \tag{64}$$

This means that the pH-coordinate of the crossing point of the H_3O^+ and B^- lines gives in very good approximation the pH of the solution.

A simplified equation can be easily derived when the amount balance (Eq. (18)) is taken in to account:

$$c_{H_3O^+} \approx c_{B^-} \ (64) \xrightarrow{\text{inserting (64) in (5)}} K_a = \frac{c_{B^-} c_{H_3O^+}}{c_{HB}} = \frac{c^2_{H_3O^+}}{c_{HB}} \ (73) \longrightarrow c_{HB} = \frac{c^2_{H_3O^+}}{K_a} \ (74)$$

$$c_{HB} = \frac{c^2_{H_3O^+}}{K_a} \ (74) \xrightarrow{\text{inserting (74) and (64) in (18)}} C^{\circ}_{HB} = \frac{c^2_{H_3O^+}}{K_a} + c_{H_3O^+} \ (75)$$

$$\downarrow$$

$$0 = c^2_{H_3O^+} + K_a c_{H_3O^+} - K_a C^{\circ}_{HB} \ (76)$$

Solving this equation leads to:

Simplified equation for a strong acid in high concentration:

$$\boldsymbol{c_{\mathrm{H_3O^+}} = -\frac{K_a}{2} \pm \sqrt{\frac{K_a^2}{4} + K_a C_{\mathrm{HB}}^{\circ}}} \tag{77}$$

(The mathematical solution $c_{\mathrm{H_3O^+}} = -\frac{K_a}{2} - \sqrt{\frac{K_a^2}{4} + K_a C_{\mathrm{HB}}^{\circ}}$ does not correspond to a real concentration, and therefore the equation is usually given without the minus sign.)

4.1.2.2 Strong Acids in Low Concentration

The considerations made in Sect. 4.1.2.1 are equally valid for such low concentrations that (i) the lines of HB are situated left of the H_3O^+ line, and (ii) the concentration of B^- is still much larger than that of OH^- at P_1 and left of that point (cf. Fig. 36). Also in this case, the pH is approximately given by the pH-coordinate of the crossing point of the B^- and H_3O^+ lines, and it can be calculated with the simplified equation (77).

In cases of such low concentrations that the approximation $c_{\mathrm{H_3O^+}} \approx c_{\mathrm{B^-}}$ (64) does not hold anymore (see Fig. 37) the cubic equation (59) has to be used. The equation $c_{\mathrm{H_3O^+}} \approx c_{\mathrm{OH^-}} = \sqrt{K_w}$ (Eq. (71)) is only valid for extremely low concentrations, as such solutions are practically neutral (see Fig. 38).

Fig. 36 pH-logc_i diagram of formic acid (pK_a = 3.75) at C_{HB}° = 10^{-4} mol L^{-1}

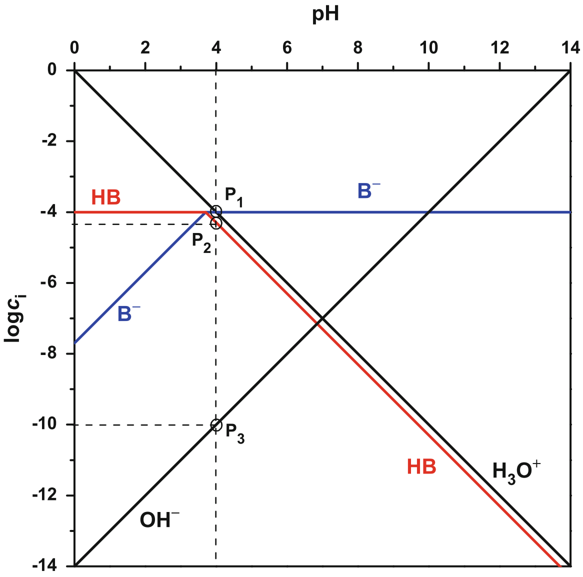


Fig. 37 pH-logc_i diagram of formic acid (pK_a = 3.75) at $C^{\circ}_{HB} = 10^{-6}$ mol L^{-1}

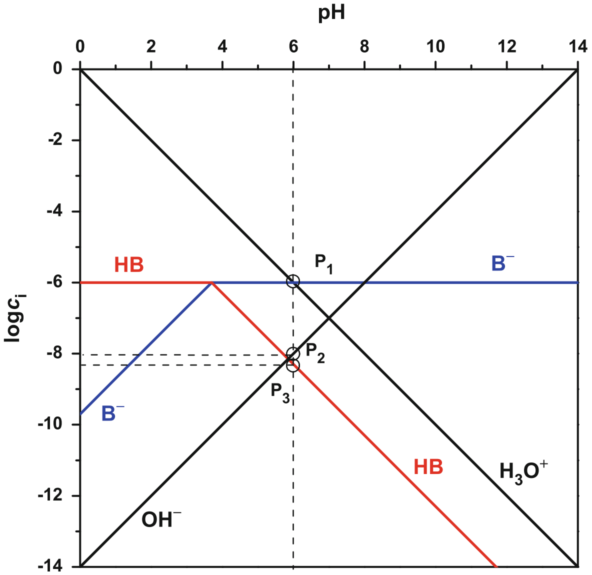
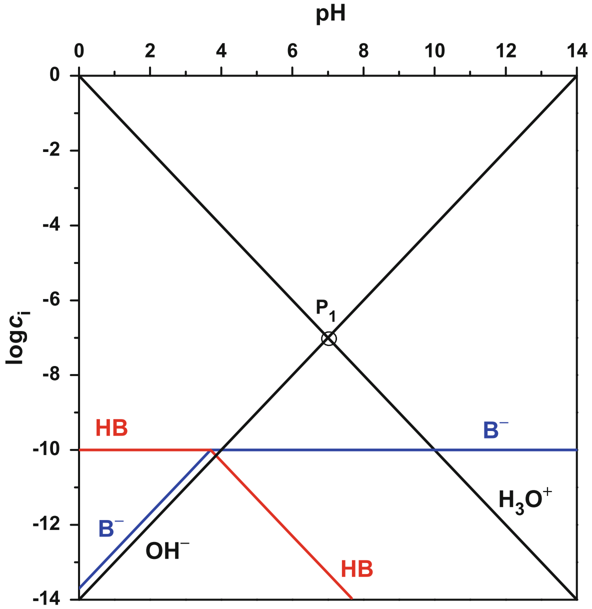


Fig. 38 pH-logc_i diagram of formic acid (pK_a = 3.75) at $C^{\circ}_{HB} = 10^{-10}$ mol L^{-1}



4.1.2.3 Weak Bases in High Concentration

Figure 39 depicts the situation of a solution of sodium formate at a concentration of 0.1 mol L^{-1}: the aqua-complex of sodium is a very weak Brønsted acid, and therefore only the protonation of formate ions can affect the pH.

The charge balance gives for this base solution:

$$c_{H_3O^+} = c_{OH^-} - c_{HB} \tag{62}$$

This equation indicates that the pH must be higher than the pH of point P$_1$ in Fig. 39, as otherwise the sum of $c_{H_3O^+} + c_{HB}$ would be larger than c_{OH^-}. It also holds that the equilibrium concentration of HB is much larger than the equilibrium concentration of H$_3$O$^+$, and thus Eq. (62) can be simplified and gives:

$$c_{HB} \approx c_{OH^-} \tag{78}$$

The pH of that sodium formate solution can be taken from the diagram as the pH-coordinate of the crossing point of the OH$^-$ and HB lines (point P$_1$ in Fig. 39).

For the derivation of a simplified equation, the equilibrium concentrations HB and B$^-$ have to be compared at the points P$_1$ and P$_3$: c_{HB} is 2 × 10^{-6} mol L^{-1} at P$_1$, and thus it is negligible compared to $c_{B^-} \approx 0.1$ mol L^{-1}. This makes it possible to simplify the amount balance in Eq. (61) to give:

$$c_{B^-} \approx C^{\circ}_{B^-} \tag{72}$$

The following rearrangements yield the desired simplified equation:

$$c_{B^-} \approx C^{\circ}_{B^-}\ (72) \xrightarrow{\text{inserting (72) in (60)}} K_b = \frac{c_{HB}c_{OH^-}}{C^{\circ}_{B^-}}\ (79)$$

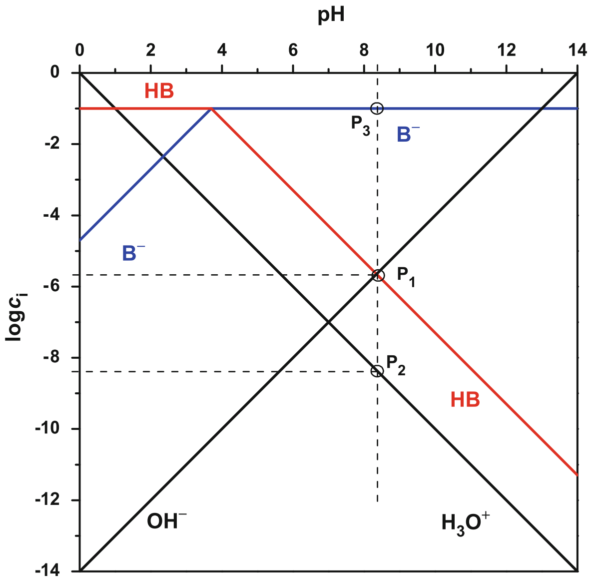
$$c_{HB} \approx c_{OH^-}\ (78) \xrightarrow{\text{inserting (78) in (79)}} K_b = \frac{c^2_{OH^-}}{C^{\circ}_{B^-}}\ (80) \longrightarrow c^2_{OH^-} = K_b C^{\circ}_{B^-}\ (81)$$

$$c_{OH^-} = \frac{K_w}{c_{H_3O^+}}\ (11) \xrightarrow{\text{inserting (11) in (81)}} \frac{K_w}{c_{H_3O^+}} = \sqrt{K_b C^{\circ}_{B^-}}\ (82) \longrightarrow c_{H_3O^+} = \frac{K_w}{\sqrt{K_b C^{\circ}_{B^-}}}\ (83)$$

Simplified equation for a weak base in high concentration:

$$\boldsymbol{c_{H_3O^+} = \frac{K_w}{\sqrt{K_b C^{\circ}_{B^-}}}} \tag{84}$$

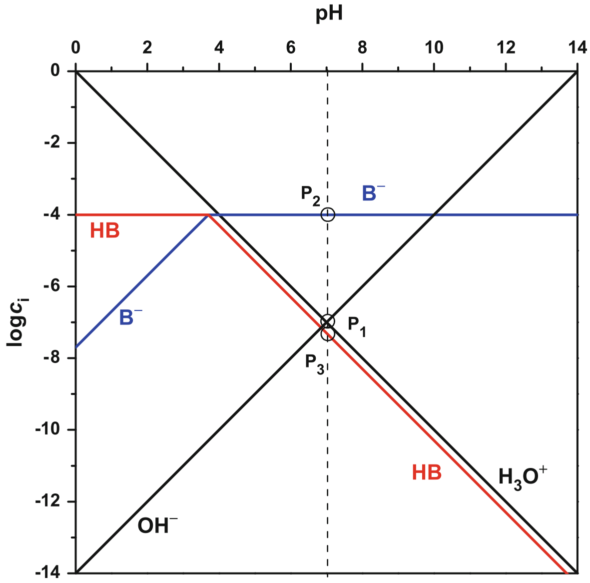
Fig. 39 pH-logc_i diagram of sodium formate solution at $C^{\circ}_{HB} = 10^{-1}$ mol L^{-1} (Formic acid: pK_a = 3.75)



4.1.2.4 Weak Bases in Low Concentration

When the concentration of the base is so low that the simplification equation (78) does not hold, i.e., when the line of HB is situated to the left of the H_3O^+ line (cf. Fig. 40), the pH of the solution must still be basic. The relationship equation (72) is still a good simplification, and the desired simplified equation follows as given here.

Fig. 40 pH-logc_i diagram of sodium formate solution at $C^{\circ}_{HB} = 10^{-4}$ mol L^{-1} (Formic acid: pK_a = 3.75)



$$c_{B^-} \approx C^{\circ}_{B^-} \; (72) \xrightarrow{\text{inserting (72) in (60)}} K_b = \frac{c_{HB}\, c_{OH^-}}{C^{\circ}_{B^-}} \; (79) \longrightarrow c_{HB} = \frac{C^{\circ}_{B^-} K_b}{c_{OH^-}} \; (85)$$

$$c_{HB} = \frac{C^{\circ}_{B^-} K_b}{c_{OH^-}} \; (85) \xrightarrow{\text{inserting (85) in (62)}} c_{H_3O^+} + \frac{K_b C^{\circ}_{B^-}}{c_{OH^-}} = c_{OH^-} \; (86)$$

$$c_{OH^-} = \frac{K_w}{c_{H_3O^+}} \; (11) \xrightarrow{\text{inserting (11) in (86)}} c_{H_3O^+} + \frac{K_b C^{\circ}_{B^-} c_{H_3O^+}}{K_w} = \frac{K_w}{c_{H_3O^+}} \; (87)$$

$$\downarrow$$

$$c^2_{H_3O^+} + c^2_{H_3O^+} \frac{K_b C^{\circ}_{B^-}}{K_w} = K_w \; (88)$$

$$\downarrow$$

$$c^2_{H_3O^+} \left(\frac{K_w + K_b C^{\circ}_{B^-}}{K_w} \right) = K_w \; (89)$$

Simplified equation for a weak base in low concentration:

$$\boldsymbol{c_{H_3O^+} = \sqrt{\frac{K_w^2}{K_w + K_b C^{\circ}_{B^-}}}} \qquad (90)$$

For very low concentrations of the base, Eq. (71) can be used.

4.1.3 Weak Acids and Their Corresponding Strong Bases

NH_4^+/NH_3 is a good example for a weak acid with a corresponding strong base. At first, an ammonium chloride solution is considered. In Sect. 4.1.1.3 it was discussed that chloride ions are not significantly protonated in the pH range of 0–14, i.e., the concentration of HCl is negligible in this range. Hence, only the ammonium ions (pK_a = 9.25) will affect the pH.

4.1.3.1 Weak Acids in High Concentration

Figure 41 depicts the pH-logc_i diagram of an ammonium chloride solution at $C^{\circ}_{HB} = 10^{-1}$ mol L^{-1}.

The charge balance

$$c_{H_3O^+} = c_{OH^-} + c_{B^-} \tag{49}$$

shows that the pH is somewhat left of the pH-coordinate of P_1 in Fig. 41, because on the right side of P_1 the sum $c_{OH^-} + c_{B^-}$ is always larger than $c_{H_3O^+}$. The equilibrium concentration of H_3O^+ is caused by the protolysis of HB and also by the autoprotolysis of water. However, the concentration of OH^- is at point P_1 1.3×10^{-9} mol L^{-1} (see point P_2). This is a negligible concentration compared to that of B^- (8×10^{-6} mol L^{-1}), and hence one can write

$$c_{H_3O^+} \approx c_{B^-} \tag{64}$$

This means that the pH-coordinate of the crossing point of the H_3O^+ and B^- lines gives the pH of the solution with a very satisfying precision. For deriving a simplified equation, the amount balance equation (18) of a weak acid has to be considered:

$$C^{\circ}_{HB} = c_{HB} + c_{B^-} \tag{18}$$

On the left side of P_1, it is a well-based simplification to neglect the equilibrium concentration of B^- relative to that of HB:

$$c_{HB} \approx C^{\circ}_{HB} \tag{91}$$

The simplified equation follows after some rearrangements:

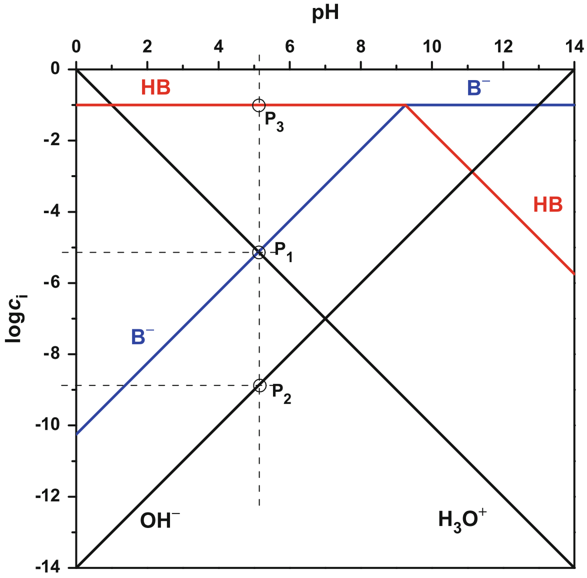
$$c_{H_3O^+} \approx c_{B^-} \ (64) \xrightarrow{\text{inserting (64) in (5)}} K_a = \frac{c_{B^-} c_{H_3O^+}}{c_{HB}} = \frac{c^2_{H_3O^+}}{c_{HB}} \ (73)$$

$$c_{HB} \approx C^{\circ}_{HB} \ (91) \xrightarrow{\text{inserting (91) in (73)}} K_a = \frac{c^2_{H_3O^+}}{C^{\circ}_{HB}} \ (92) \longrightarrow c_{H_3O^+} = \sqrt{K_a C^{\circ}_{HB}} \ (93)$$

Simplified equation for a weak acid in high concentration:

$$\boldsymbol{c_{H_3O^+} = \sqrt{K_a C^{\circ}_{HB}}} \tag{93}$$

Fig. 41 pH-logc_i diagram of an ammonium chloride solution at $C^{\circ}_{HB} = 10^{-1}$ mol L^{-1} (ammonium: $pK_a = 9.25$)

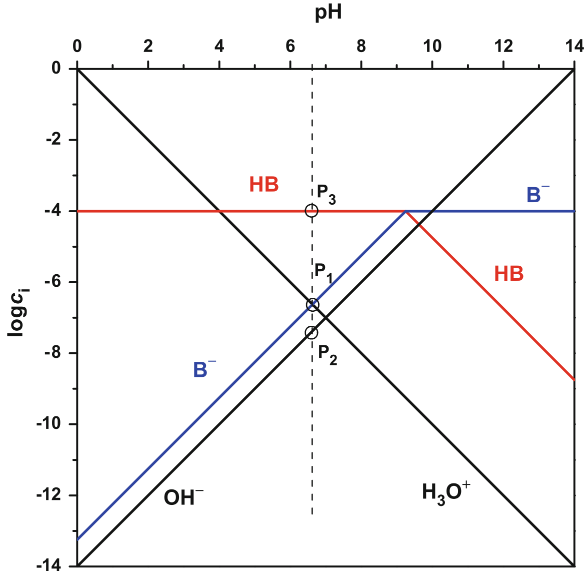


4.1.3.2 Weak Acids in Low Concentration

Figure 42 depicts the situation of an ammonium chloride solution at a concentration of 10^{-4} mol L^{-1}.

The charge balance (Eq. (49)) demands again that the pH must be slightly below the pH-coordinate of point P_1 in Fig. 42. However, here it is not possible to neglect the concentration of OH^- relative to that of B^-, i.e., the simplified relationship equation (64) is no longer allowed. In the amount balance equation (18), it is still appropriate to neglect the concentration of B^- with respect to that of HB,

Fig. 42 pH-logc_i diagram of an ammonium chloride solution at $C^{\circ}_{HB} = 10^{-4}$ mol L^{-1} (ammonium: $pK_a = 9.25$)



since – left of P_1 – the equilibrium concentration of B^- is always much smaller than the concentration of HB. Hence it is appropriate to write Eq. (91):

$$c_{HB} \approx C^{\circ}_{HB} \tag{91}$$

Rearrangements give a useful simplified equation:

$$\begin{tikzcd}
c_{HB} \approx C^{\circ}_{HB}\ (91) \arrow[r, "\text{inserting (91) in (5)}"] & K_a = \dfrac{c_{B^-}c_{H_3O^+}}{C^{\circ}_{HB}}\ (94) \arrow[r] & c_{B^-} = \dfrac{K_a C^{\circ}_{HB}}{c_{H_3O^+}}\ (95) \\
c_{OH^-} = \dfrac{K_w}{c_{H_3O^+}}\ (11) \arrow[r, "\text{inserting (11) and (95) in (49)}"] & c_{H_3O^+} = \dfrac{K_w}{c_{H_3O^+}} + \dfrac{K_a C^{\circ}_{HB}}{c_{H_3O^+}}\ (96) \arrow[d] & \\
 & c^2_{H_3O^+} = K_w + K_a C^{\circ}_{HB}\ (97) &
\end{tikzcd}$$

Simplified equation for a weak acid in low concentration:

$$\boldsymbol{c_{H_3O^+} = \sqrt{K_w + K_a C^{\circ}_{HB}}} \tag{98}$$

In the case of very low concentrations, Eq. (71) can be used.

4.1.3.3 Strong Bases in High Concentration

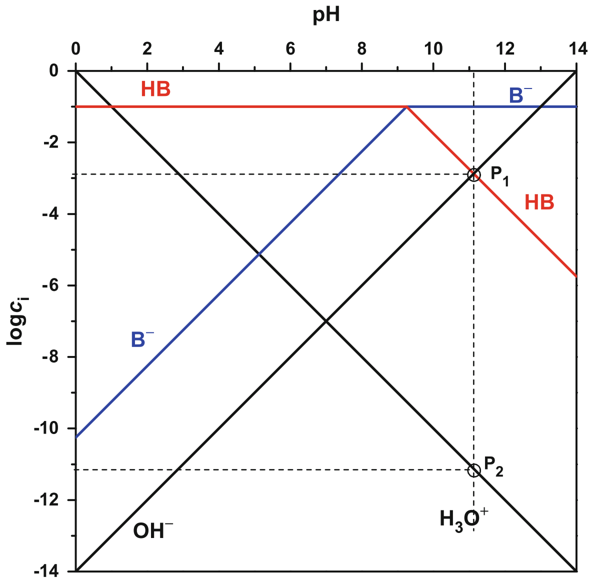
Figure 43 shows the diagram of an ammonia solution with an overall concentration of $C^{\circ}_{ammonia} = 10^{-1}$ mol L^{-1}. The diagram is of course identical with that shown in Fig. 41, but the information which needs to be extracted is now different: For the solution of a base, the charge balance is given by Eq. (62):

$$c_{H_3O^+} = c_{OH^-} - c_{HB} \tag{62}$$

From this follows that the pH of the solution must be somewhat higher than the pH-coordinate given by P_1 in Fig. 43. Otherwise, the sum $c_{H_3O^+} + c_{HB}$ would exceed the concentration of c_{OH^-}. The diagram shows that the concentration of H_3O^+ is equal or less than 6.8×10^{-12} mol L^{-1} (cf. P_2), i.e., it is negligible with respect to the concentration of HB at the point P_1. Hence, the Eq. (62) can be simplified to yield the relationship equation (78):

$$c_{HB} \approx c_{OH^-} \tag{78}$$

Fig. 43 pH-logc_i diagram of an ammonia solution, $C^{\circ}_{\text{ammonia}} = 10^{-1}$ mol L^{-1} (Ammonium: pK_a = 9.25)



From this follows that the pH-coordinate of the crossing point of the OH^- and HB lines gives a very good estimate of the real pH of the solution. A simplified equation can be derived as follows:

$$c_{HB} \approx c_{OH^-} \ (78) \xrightarrow{\text{Inserting (78) in (60)}} K_b = \frac{c_{HB}c_{OH^-}}{c_{B^-}} = \frac{c^2_{OH^-}}{c_{B^-}} \ (99) \longrightarrow c_{B^-} = \frac{c^2_{OH^-}}{K_b} \ (100)$$

$$c_{B^-} = \frac{c^2_{OH^-}}{K_b} \ (100) \xrightarrow{\text{Inserting (78) and (100) in (61)}} C^{\circ}_{B^-} = c_{OH^-} + \frac{c^2_{OH^-}}{K_b} \ (101)$$

$$\swarrow$$

$$0 = c^2_{OH^-} + K_b c_{OH^-} - K_b C^{\circ}_{B^-} \ (102)$$

$$c_{OH^-} = \frac{K_w}{c_{H_3O^+}} \ (11) \xrightarrow{\text{Inserting (11) in (102)}} 0 = \frac{K_w^2}{c^2_{H_3O^+}} + K_b \frac{K_w}{c_{H_3O^+}} - K_b C^{\circ}_{B^-} \ (103)$$

$$\downarrow$$

$$0 = c^2_{H_3O^+} - \frac{K_w}{C^{\circ}_{B^-}} c_{H_3O^+} - \frac{K_w^2}{K_b C^{\circ}_{B^-}} \ (104)$$

Simplified equation for a strong base in high concentration:

$$c_{\mathrm{H_3O^+}} = \frac{K_\mathrm{w}}{2C^{\circ}_{\mathrm{B^-}}} \pm \sqrt{\frac{K^2_\mathrm{w}}{4\left(C^{\circ}_{\mathrm{B^-}}\right)^2} + \frac{K^2_\mathrm{w}}{K_\mathrm{b}C^{\circ}_{\mathrm{B^-}}}} \qquad (105)$$

(The mathematical solution $c_{\mathrm{H_3O^+}} = \frac{K_\mathrm{w}}{2C^{\circ}_{\mathrm{B^-}}} - \sqrt{\frac{K^2_\mathrm{w}}{4\left(C^{\circ}_{\mathrm{B^-}}\right)^2} + \frac{K^2_\mathrm{w}}{K_\mathrm{b}C^{\circ}_{\mathrm{B^-}}}}$ does not correspond to a real concentration, and therefore the equation is usually given without the minus sign.)

In cases where the concentration of the base is so small that the relationship equation (78) does not hold anymore, the cubic equation (63) has to be solved. For very small concentrations, Eq. (71) can be used.

4.1.4 Very Weak Acids and Their Corresponding Very Strong Bases

4.1.4.1 Very Weak Acids

Ethanol has a pK_a value of 16, and thus it is a very weak acid. Figure 44 shows the pH-logc_i diagram of an aqueous solution of 10^{-1} mol L^{-1} ethanol. From the diagram, it is obvious that the concentration of B^- (ethanolate ions) is very small in the entire pH range from 0 to 14, i.e., ethanol reacts only in a negligible amount as an acid. The charge balance gives:

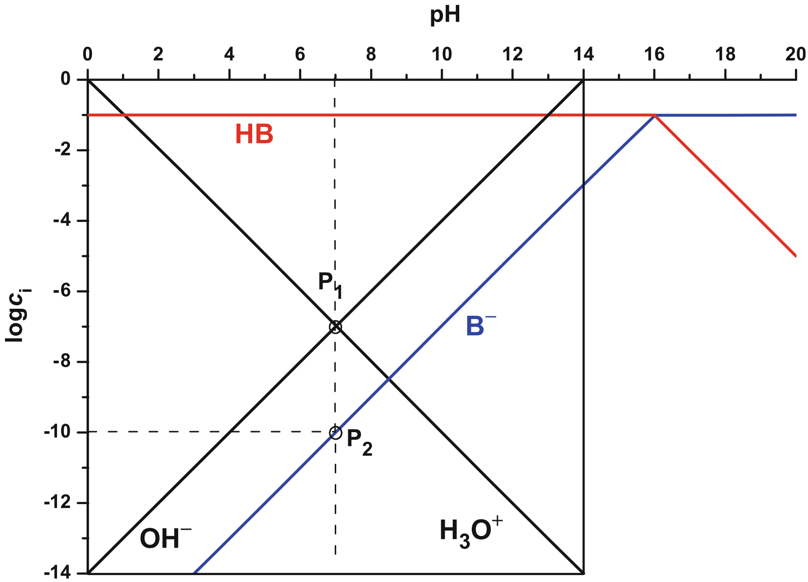


Fig. 44 pH-logc_i diagram of an aqueous solution of 10^{-1} mol L^{-1} ethanol (pK_a − 16). The range of pH > 14 is shown for didactic reasons only. Normally it is not shown

$$c_{H_3O^+} = c_{OH^-} + c_{B^-} \tag{49}$$

and thus the pH can only be lower than the pH-coordinate of point P_1 in Fig. 44, i.e., left of the neutrality point of water. There, however, the concentration of ethanolate (B^-) is so small that the relationship equation (71) holds:

Simplified equation for a very weak acid in (almost) any concentration:

$$\boldsymbol{c_{H_3O^+} \approx c_{OH^-} = \sqrt{K_w}} \tag{71}$$

4.1.4.2 Very Strong Bases in High Concentration

As discussed in Chap. 2, in water the strength of those bases which are stronger than OH^- ions are leveled off. As an example, ethanolate ions react with water to yield ethanol and OH^- ions. If one would try to prepare an aqueous solution of 10^{-1} mol L^{-1} of sodium ethanolate (cf. Fig. 45), the following charge balance must hold:

$$c_{H_3O^+} = c_{OH^-} - c_{HB} \tag{62}$$

This means that the pH of the solution must be situated slightly to the right of the pH-coordinate of P_1 in Fig. 45, since on the left side of P_1 the sum $c_{H_3O^+} + c_{HB}$ is always larger than the concentration OH^- (in other words, the overall concentration of OH^- results from the protolysis of $B^-$and autoprotolysis of water). The concentration of H_3O^+ at P_1 is about 10^{-13} mol L^{-1}, and so it can be neglected in the charge balance, and the pH is given by the pH-coordinate of the crossing point of the OH^- and ethanol (HB) lines:

$$c_{OH^-} \approx c_{HB} \tag{78}$$

The diagram also reveals that the equilibrium concentration of ethanolate ions can be neglected in relation to the ethanol concentration, so that the amount balance can be approximated by the relationship:

$$c_{HB} \approx C^{\circ}_{B^-} \tag{106}$$

This makes it possible to derive a simplified equation by using the Eqs. (78), (106), and (11):

Simplified equation for a very strong base in high concentration:

$$\boldsymbol{c_{OH^-} = C^{\circ}_{B^-} = \frac{K_w}{c_{H_3O^+}}} \tag{107}$$

$$\boldsymbol{c_{H_3O^+} = \frac{K_w}{C^{\circ}_{B^-}}} \tag{108}$$

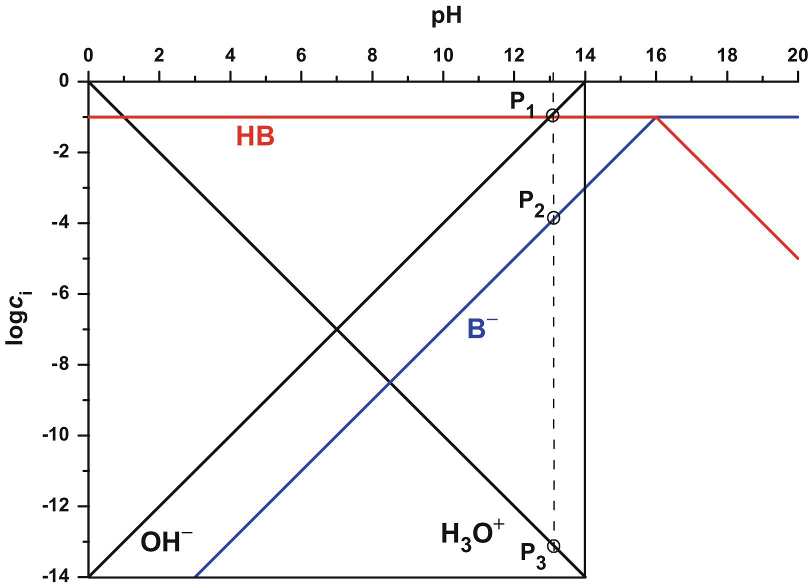


Fig. 45 pH-logc_i diagram of an aqueous solution prepared by dissolving 10^{-1} mol of sodium ethanolate in water so that 1 l of solution results. The range pH > 14 is shown for didactic reasons only. Normally it is not shown

4.1.4.3 Very Strong Bases in Low Concentration

Figure 46 shows the pH-logc_i diagram of a solution resulting from dissolution of 10^{-6} mol sodium ethanolate in 1 L of water. The charge balance is as follows:

$$c_{H_3O^+} = c_{OH^-} - c_{HB} \tag{62}$$

In this case also, the pH must be situated on the right side of the pH-coordinate of P_1 in Fig. 46, as on the left side the sum $c_{H_3O^+} + c_{HB}$ is always larger than the concentration of OH^- (in other words, the overall concentration of OH^- results from the protolysis of B^- and autoprotolysis of water). Here it is no longer permitted to use the simplified equation (78). The equilibrium concentration of H_3O^+ is not negligible in comparison to the ethanol concentration. However, the concentration of ethanolate ions can still be ignored in comparison to the ethanol concentration, so that the amount balance can be written as follows:

$$c_{HB} \approx C^{O}_{B^-} \tag{106}$$

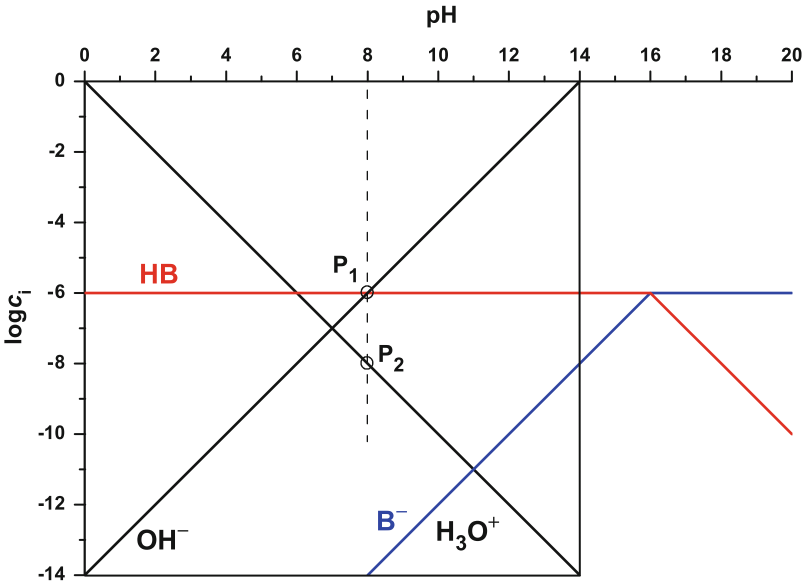


Fig. 46 pH-logc_i diagram of an aqueous solution prepared by dissolving 10^{-6} mol of sodium ethanolate in water so that 1 l of solution results. The range pH > 14 is shown for didactic reasons only. Normally it is not shown

Using Eq. (11) follows:

$$c_{\mathrm{OH^-}} = \frac{K_{\mathrm{w}}}{c_{\mathrm{H_3O^+}}}\ (11) \xrightarrow{\text{inserting (11) and (106) in (62)}} c_{\mathrm{H_3O^+}} + C^{\circ}_{\mathrm{B^-}} = \frac{K_{\mathrm{w}}}{c_{\mathrm{H_3O^+}}}\ (109)$$

$$\downarrow$$

$$0 = c^2_{\mathrm{H_3O^+}} + C^{\circ}_{\mathrm{B^-}} c_{\mathrm{H_3O^+}} - K_{\mathrm{w}}\ (110)$$

Solving the quadratic equation yields:
Simplified equation for a strong base in low concentration:

$$\boldsymbol{c_{\mathrm{H_3O^+}} = -\frac{C^{\circ}_{\mathrm{B^-}}}{2} \pm \sqrt{\frac{\left(C^{\circ}_{\mathrm{B^-}}\right)^2}{4} + K_{\mathrm{w}}}} \tag{111}$$

(The mathematical solution $c_{\mathrm{H_3O^+}} = -\frac{C^{\circ}_{\mathrm{B^-}}}{2} - \sqrt{\frac{\left(C^{\circ}_{\mathrm{B^-}}\right)^2}{4} + K_{\mathrm{w}}}$ does not describe a real concentration, and therefore the minus sign before the square root is usually not written.)

For solutions of very low concentrations, Eq. (71) can be used as a very good simplified equation.

4.1.5 Ranges of Validity of the Simplified Equations for Monobasic Acids

The simplified equations (66), (70), (77), (93), and (98) have been derived for some special cases; however, they are valid for larger ranges of $\log C^{\text{O}}_{\text{HB}}$ and pK_a. To display the ranges of validity, diagrams with the coordinates $\log C^{\text{O}}_{\text{HB}}$ and pK_a are very useful [1–6, 7]. For the determination of validity ranges, a maximum error needs to be defined: that maximum error is the maximum allowable deviation between the results using (a) the cubic equation (59) and (b) the respective simplified equation. Figure 47 shows the ranges of validity of the simplified equations (66), (70), (77), (93), and (98) with respect to $\log C^{\text{O}}_{\text{HB}}$ and pK_a when the maximum allowable error is 0.02 pH units. Should one accept larger errors, the validity ranges will expand, while for smaller errors they will shrink. This figure demonstrates that there is only a very small area in which no simplified equation can be used, and the cubic equation (59) has to be solved.

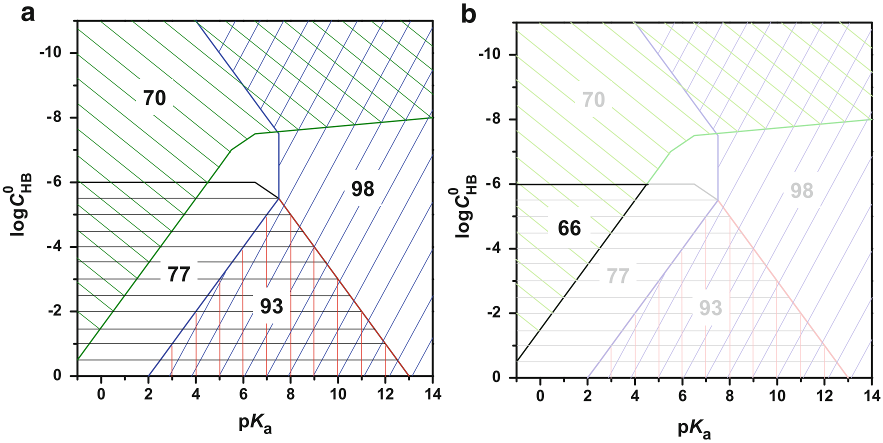


Fig. 47 (**a**) Validity ranges of the simplified equations (70), (77), (93), and (98). (**b**) Validity range of the simplified equation (66). For the calculation of the borderlines (validity ranges), a maximum allowable error of 0.02 pH units has been fixed

4.2 Dibasic Acids, Ampholytes, and Diacidic Bases

4.2.1 Dibasic Acids

When a dibasic acid H_2B is dissolved in water, the following equilibria have to be considered for the derivation of simplified equations for pH calculations:

$$H_2B + H_2O \rightleftarrows HB^- + H_3O^+ \tag{37}$$

$$HB^- + H_2O \rightleftarrows B^{2-} + H_3O^+ \tag{38}$$

$$H_2O + H_2O \rightleftarrows OH^- + H_3O^+ \tag{2}$$

The five variables $c_{H_2B}, c_{HB^-}, c_{B^{2-}}, c_{H_3O^+}$ and c_{OH^-} require the formulation of five independent equations. These are the equations of the laws of mass action of the protolysis equilibria (equations of the acidity constants of the acids H_2B, HB^-, and the ion product of water) and the amount and charge balances. Hence one needs the already introduced Eqs. (39) and (40) for the acidity constants, Eq. (9) for the ion product of water, Eq. (41) for the amount balance and Eq. (112) for the charge balance:

$$\boldsymbol{K_{a1} = \frac{c_{HB^-} c_{H_3O^+}}{c_{H_2B}}} \tag{39}$$

$$\boldsymbol{K_{a2} = \frac{c_{B^{2-}} c_{H_3O^+}}{c_{HB^-}}} \tag{40}$$

$$\boldsymbol{K_w = c_{H_3O^+} c_{OH^-}} \tag{9}$$

$$\boldsymbol{C^{\circ}_{H_2B} = c_{H_2B} + c_{HB^-} + c_{B^{2-}}} \tag{41}$$

$$\boldsymbol{c_{H_3O^+} = c_{OH^-} + c_{HB^-} + 2c_{B^{2-}}} \tag{112}$$

This system of equations leads to an equation of the degree 4, which is not derived here. Instead, a number of practically important cases will be treated here.

4.2.1.1 Dibasic Acids with One Very Strong and One Strong Protolysis Reaction: p$K_{a1} \ll 0$, p$K_{a2} > 0$

High Concentration

An important example for such acid is sulfuric acid having the following acidity constants: p$K_{a1} = -3$ and p$K_{a2} = 1.99$. Figure 48 shows the pH-logc_i diagram for a concentration of 10^{-1} mol L^{-1} of sulfuric acid.

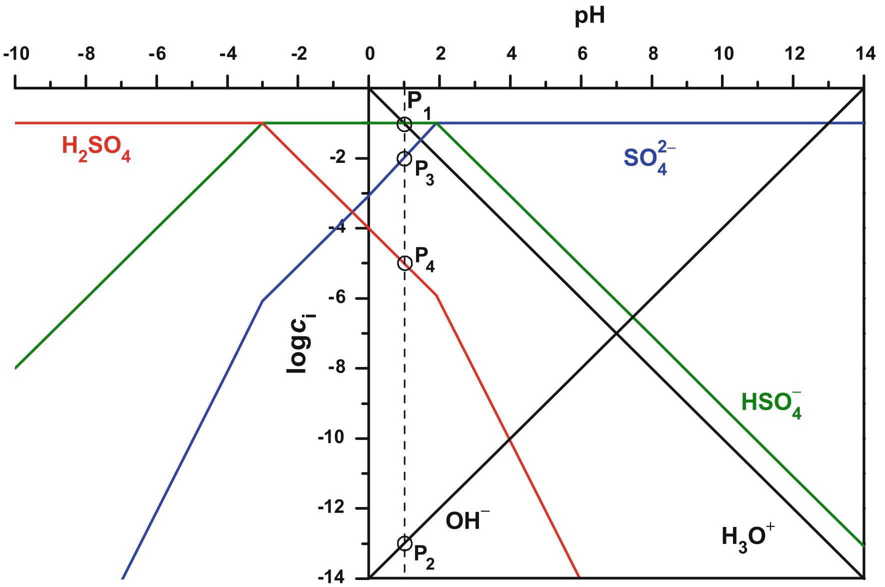


Fig. 48 pH-logc_i diagram of a solution containing 0.1 mol L^{-1} of sulfuric acid. The range pH < 0 is shown for didactic reasons only. Normally it is not shown

The charge balance gives in the case of a dibasic acid:

$$c_{H_3O^+} = c_{OH^-} + c_{HB^-} + 2c_{B^{2-}} \tag{112}$$

From Fig. 48, one can deduce that the pH must be left of the pH-coordinate of P_1, as on the right side the sum $c_{OH^-} + c_{HB^-} + 2c_{B^{2-}}$ is always larger than the equilibrium concentration of H_3O^+ (in other words, the H_3O^+ results from the protolysis of H_2B and HB, and also from the autoprotolysis of water). The pH is mainly given by the reaction equation (37), and the other two reactions have only a smaller contribution to the overall H_3O^+ concentration. To the left of the pH-coordinate of P_1, the equilibrium concentration of OH^- ions (cf. P_2) is so small that it can be neglected in the charge balance, and one can write:

$$c_{H_3O^+} = c_{HB^-} + 2c_{B^{2-}} \tag{113}$$

In the case of the amount balance, the equilibrium concentration of H_2B can be neglected in relation to the equilibrium concentrations of HB^- and B^{2-} (cf. P_4), and so it holds as a good approximation:

$$C^{\circ}_{H_2B} = c_{HB^-} + c_{B^{2-}} \tag{114}$$

For deriving a simplified equation, the following rearrangements have to be made:

$$c_{H_3O^+} = c_{HB^-} + 2c_{B^{2-}} \;(113) \longrightarrow c_{HB^-} = c_{H_3O^+} - 2c_{B^{2-}} \;(115) \xrightarrow{\text{inserting (115) in (114)}}$$

$$C^{\circ}_{H_2B} = c_{H_3O^+} - c_{B^{2-}} \;(116) \longrightarrow c_{B^{2-}} = c_{H_3O^+} - C^{\circ}_{H_2B} \;(117) \xrightarrow{\text{inserting (117) in (115)}}$$

$$c_{HB^-} = 2C^{\circ}_{H_2B} - c_{H_3O^+} \;(118) \xrightarrow{\text{inserting (117) and (118) in (40)}} K_{a2} = \frac{c^2_{H_3O^+} - C^{\circ}_{H_2B} c_{H_3O^+}}{2C^{\circ}_{H_2B} - c_{H_3O^+}} \;(119)$$

$$\downarrow$$

$$2K_{a2}C^{\circ}_{H_2B} - K_{a2}c_{H_3O^+} = c^2_{H_3O^+} - C^{\circ}_{H_2B}c_{H_3O^+} \;(120)$$

$$\downarrow$$

$$0 = c^2_{H_3O^+} + \left(K_{a2} - C^{\circ}_{H_2B}\right)c_{H_3O^+} - 2K_{a2}C^{\circ}_{H_2B} \;(121)$$

Using the formula for solving quadratic equations allows deriving the following simplified equation:

Simplified equation for a dibasic acid with p$K_{a1} \ll 0$ and p$K_{a2} > 0$ in high concentration:

$$\boldsymbol{c_{H_3O^+} = -\frac{\left(K_{a2} - C^{\circ}_{H_2B}\right)}{2} \pm \sqrt{\frac{\left(K_{a2} - C^{\circ}_{H_2B}\right)^2}{4} + 2K_{a2}C^{\circ}_{H_2B}}} \tag{122}$$

(The mathematical solution $c_{H_3O^+} = -\frac{\left(K_{a2} - C^{\circ}_{H_2B}\right)}{2} - \sqrt{\frac{\left(K_{a2} - C^{\circ}_{H_2B}\right)^2}{4} + 2K_{a2}C^{\circ}_{H_2B}}$ does not describe a real concentration and therefore the minus sign before the square root is usually not written.)

Low Concentration

Figure 49 shows the pH-logc_i diagram of sulfuric acid at a concentration of 10^{-5} mol L^{-1}. From the diagram one can conclude that the charge balance

$$c_{H_3O^+} = c_{OH^-} + c_{HB^-} + 2c_{B^{2-}} \tag{112}$$

can be simplified, as the pH will be slightly left of the pH-coordinate of P_1. There, the concentrations of OH$^-$ and HB$^-$ are negligible compared to that of B^{2-}:

$$c_{H_3O^+} \approx 2c_{B^{2-}} \tag{123}$$

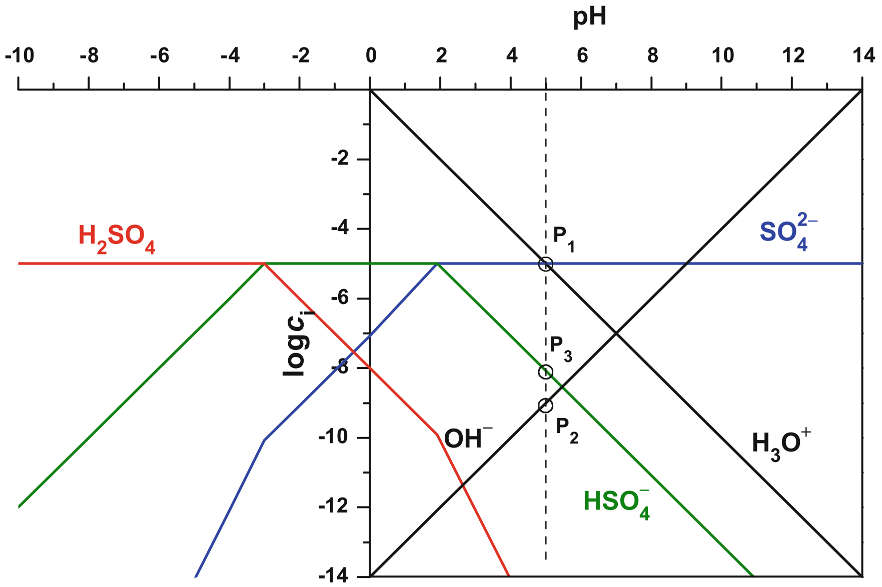


Fig. 49 pH-logc_i diagram of sulfuric acid at 10^{-5} mol L^{-1}. The range pH < 0 is shown for didactic reasons only. Normally it is not shown

A closer look at the amount balance

$$C^{\circ}_{H_2B} = c_{H_2B} + c_{HB^-} + c_{B^{2-}} \tag{41}$$

reveals that –left of P_1– the concentrations of HB^- (see P_3) and H_2B are very small in comparison to that of B^{2-} and so one can write:

$$c_{B^{2-}} \approx C^{\circ}_{H_2B} \tag{124}$$

Combining Eqs. (123) and (124) gives the following simplified equation:

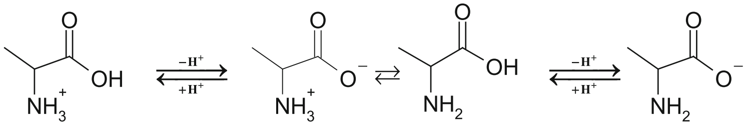
Simplified equation for a dibasic acid with $pK_{a1} \ll 0$ and $pK_{a2} > 0$ in low concentration:

$$\mathbf{c_{H_3O^+} = 2C^{\circ}_{H_2B}} \tag{125}$$

4.2.1.2 Dibasic Acid with a Large Difference in pK_a Values: $pK_{a1} > 0$, $pK_{a2} > 0$, $pK_{a1} \ll pK_{a2}$

High Concentration

Many **amino acids** are dibasic acids with pK_a values between 0 and 14. The K_a values usually differ by a factor of 10^5. A good example is alanine, which can exist in aqueous solutions in the following forms:



$$H_2Al^+ \underset{+H^+}{\overset{-H^+}{\rightleftarrows}} HAl^{+/-} \rightleftarrows HAl \underset{+H^+}{\overset{-H^+}{\rightleftarrows}} Al^-$$

The species H_2Al^+, $HAl^{+/-}$, and Al^- correspond to the forms H_2B, HB^- and B^{2-} of "ordinary" dibasic acids of the formula H_2B. Certainly, there is also an equilibrium of "intramolecular" proton transfer, i.e., a tautomeric equilibrium: $HAl \rightleftarrows HAl^{+/-}$. However, its equilibrium constant is so large that the concentration of HAl is very small. In ethanol–water mixtures as solvent, the respective equilibrium constants of glycine, L-alanine, L-valine, L-leucine, L-phenylalanine, L-isoleucine, L-methionine, and L-serine are all between 10^3 and 10^5 [8].

Figure 50 depicts the pH-logc_i diagram of an alanine hydrochloride ($H_2Al^+Cl^-$) solution of 0.1 mol L^{-1} ($pK_{a1} = 2.3$, $pK_{a2} = 9.9$).

The charge balance of a dibasic acid is:

$$c_{H_3O^+} = c_{OH^-} + c_{HB^-} + 2c_{B^{2-}} \tag{112}$$

According to Fig. 50, the pH of this solution must be found slightly left to the pH-coordinate of P_1 because on the right the sum $c_{OH^-} + c_{HB^-} + 2c_{B^{2-}}$ is always larger than the equilibrium concentration of H_3O^+ (in other words, the H_3O^+ concentration results from the protolysis of H_2B, the protolysis of HB, and the autoprotolysis of water). However, on the left side of P_1, the equilibrium concentrations of OH^- (see P_3) and B^{2-} are negligible, so that the charge balance can be simplified as follows:

$$c_{H_3O^+} \approx c_{HB^-} \tag{126}$$

Hence, the pH-coordinate of P_1 gives in a very good approximation the pH of the solution. The amount balance is:

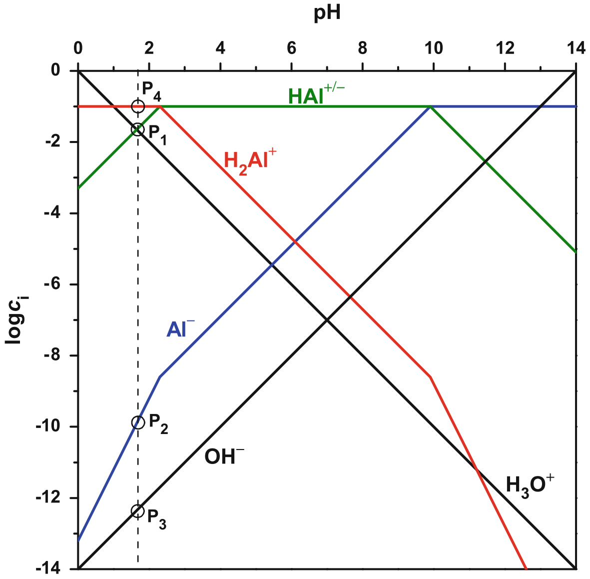
$$C^{\circ}_{H_2B} = c_{H_2B} + c_{HB^-} + c_{B^{2-}} \tag{41}$$

According to the diagram, the equilibrium concentration of B^{2-} is negligible in comparison to the concentrations of H_2B and HB^- (cf. the points P_1, P_2, and P_4 in Fig. 50), and so one can simplify this balance as follows:

$$C^{\circ}_{H_2B} \approx c_{H_2B} + c_{HB^-} \tag{127}$$

The following rearrangements show how a simplified equation can be derived:

Fig. 50 pH-logc_i diagram of an alanine hydrochloride ($H_2Al^+Cl^-$) solution of 0.1 mol L^{-1} (pK_{a1} = 2.3, pK_{a2} = 9.9)



$$c_{H_3O^+} \approx c_{HB^-} \quad (126) \xrightarrow{\text{inserting (126) in (39)}} K_{a1} = \frac{c_{HB^-} c_{H_3O^+}}{c_{H_2B}} = \frac{c^2_{H_3O^+}}{c_{H_2B}} \quad (128)$$

$$c_{H_2B} = \frac{c^2_{H_3O^+}}{K_{a1}} \quad (129) \xrightarrow{\text{inserting (126) and (129) in (127)}} C^{\circ}_{H_2B} = \frac{c^2_{H_3O^+}}{K_{a1}} + c_{H_3O^+} \quad (130)$$

$$\downarrow$$

$$0 = c^2_{H_3O^+} + K_{a1} c_{H_3O^+} - K_{a1} C^{\circ}_{H_2B} \quad (131)$$

This quadratic equation can be solved in the usual way, and one obtains the following simplified equation for the concentration of hydronium ions:

Simplified equation for a dibasic acid with large differences between the pK_a values (pK_{a1}, pK_{a2} > 0, pK_{a1} ≪ pK_{a2}) in high concentration:

$$\boldsymbol{c_{H_3O^+} = -\frac{K_{a1}}{2} \pm \sqrt{\frac{K^2_{a1}}{4} + K_{a1} C^{\circ}_{H_2B}}} \qquad (132)$$

(The mathematical solution $c_{H_3O^+} = -\frac{K_{a1}}{2} - \sqrt{\frac{K^2_{a1}}{4} + K_{a1} C^{\circ}_{H_2B}}$ does not describe a real concentration, and therefore the minus sign before the square root is usually not written.)

This formula shows that such acid appears as a strong monobasic acid, and only the first protolysis step determines the pH.

Low Concentration

Figure 51 shows the pH-logc_i diagram of an alanine hydrochloride ($H_2Al^+Cl^-$) solution at 10^{-4} mol L^{-1}. Even at this low concentration, the acid appears as a strong monobasic acid, and the second protolysis step can be neglected, i.e., the equilibrium concentration of B^{2-} is very small compared to those of HB^-, H_2B and H_3O^+. Thus, the pH can be approximately read as the pH-coordinate of P_1, completely as in the case of a strong monobasic acid, and the pH can be approximately calculated with Eq. (132).

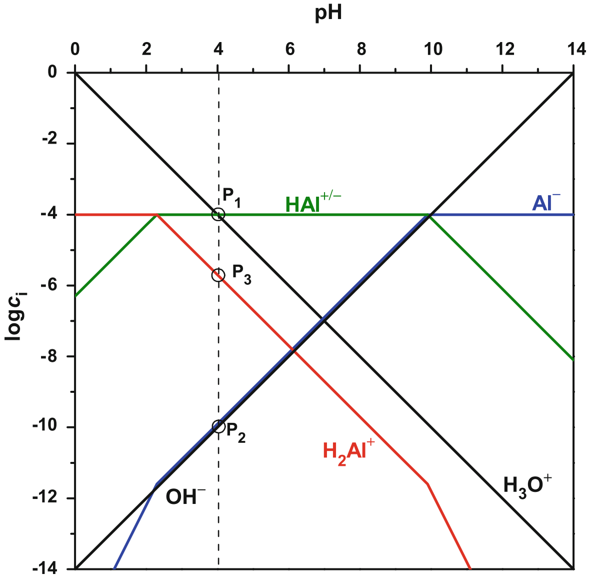


Fig. 51 pH-logc_i diagram of an alanine hydrochloride ($H_2Al^+Cl^-$) solution of 10^{-4} mol L^{-1} ($pK_{a1} = 2.3$, $pK_{a2} = 9.9$)

4.2.2 Simplified Equation for Ampholytes

An ampholyte reacts in solution both as acid and as base. The following protolysis equilibria are established in water:

$$HB^- + H_2O \rightleftarrows B^{2-} + H_3O^+ \tag{133}$$

$$HB^- + H_2O \rightleftarrows H_2B + OH^- \tag{134}$$

$$H_2O + H_2O \rightleftarrows OH^- + H_3O^+ \tag{2}$$

For the calculation of the five variables c_{H_2B}, c_{HB^-}, $c_{B^{2-}}$, $c_{H_3O^+}$ and c_{OH^-}, it is necessary to write down five independent equations. These are the equations of the law of mass action of the protolysis equilibria and the charge and mass balances:

$$\boldsymbol{K_{a2} = \frac{c_{B^{2-}} c_{H_3O^+}}{c_{HB^-}}} \tag{40}$$

$$\boldsymbol{K_{b2} = \frac{c_{H_2B} c_{OH^-}}{c_{HB^-}}} \tag{135}$$

$$\boldsymbol{K_w = c_{H_3O^+} c_{OH^-}} \tag{9}$$

$$\boldsymbol{C^{\circ}_{HB^-} = c_{H_2B} + c_{HB^-} + c_{B^{2-}}} \tag{136}$$

$$\boldsymbol{c_{H_3O^+} = c_{OH^-} + c_{B^{2-}} - c_{H_2B}} \tag{137}$$

▶ Equation 137 is based on the following consideration: The reaction Eqs. (133), (134), and (2) produce cations, here only H_3O^+, and the anions B^{2-} and OH^-, and anions are neutralized by the formation of H_2B. By consuming the anions HB^-, reaction equation (134) forms as many uncharged molecules H_2B as it has consumed HB^-. From this follows:

$$c_{H_3O^+} = c_{OH^-} + c_{B^{2-}} - c_{H_2B} \tag{137}$$

For an uncharged ampholyte HB the following equilibria have to be formulated:

$$HB + H_2O \rightleftarrows B^- + H_3O^+ \tag{133*}$$

$$HB + H_2O \rightleftarrows H_2B^+ + OH^- \tag{134*}$$

$$H_2O + H_2O \rightleftarrows OH^- + H_3O^+ \tag{2}$$

Then the charge balance gives:

$$c_{H_2B^+} + c_{H_3O^+} = c_{OH^-} + c_{B^-} \tag{137*}$$

4.2.2.1 An Ampholyte That Is Strongly Acidic and Weakly Basic

A good example is here sodium hydrogen sulfate $NaHSO_4$. Figure 52 gives the pH-logc_i diagram of a solution containing 10^{-1} mol L^{-1} $NaHSO_4$. The following pK values need to be considered: $pK_{a2} = 1.99$ for the reaction $HSO_4^- + H_2O \rightleftarrows SO_4^{2-} + H_3O^+$, and $pK_{b2} = 17$ for the reaction $HSO_4^- + H_2O \rightleftarrows H_2SO_4 + OH^-$.

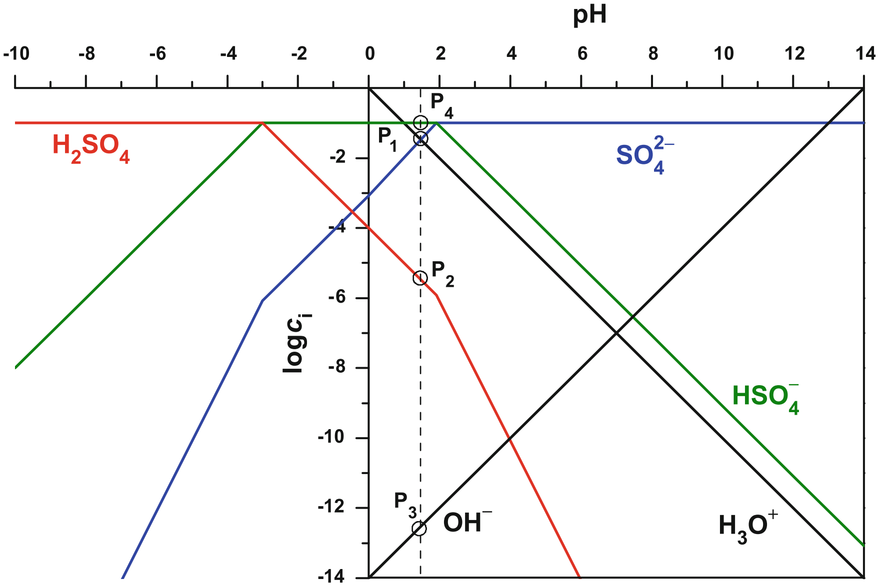


Fig. 52 pH-logc_i diagram of a $NaHSO_4$ solution at 10^{-1} mol L^{-1} ($pK_{a2} = 1.99$ and $pK_{b2} = 17$). The range pH < 0 is shown for didactic reasons only. Normally it is not shown

The charge balance is as follows:

$$c_{H_3O^+} = c_{OH^-} + c_{B^{2-}} - c_{H_2B} \tag{137}$$

Comparing the concentrations of H_2B and H_3O^+ in the entire pH range from 0 to 14 reveals that the concentration of H_2B is always much smaller than that of H_3O^+, and thus one can simplify the charge balance:

$$c_{H_3O^+} = c_{OH^-} + c_{B^{2-}} \tag{138}$$

This means that pH of the solution can be read slightly left of the pH-coordinate of P_1 in Fig. 52, as right of this the sum of the concentrations of OH^- and B^{2-} are always larger than that of H_3O^+ (in other words, the H_3O^+ concentration results from the protolysis of H_2B, that of HB, and the autoprotolysis of water). However, one can also see from the diagram that left of P_1 in Fig. 52 the equilibrium concentration of OH^- is very small (see P_3) in comparison to that of B^{2-}, and the charge balance can be further simplified to give:

$$c_{H_3O^+} \approx c_{B^{2-}} \tag{139}$$

and the pH of the solution can be approximately read as the pH-coordinate of P_1.

For deriving a simplified equation, one needs to compare the concentrations of H_2B, HB^-, and B^{2-} (see P_1, P_2 and P_4). The equilibrium concentration of H_2B is much smaller than those of HB^- and B^{2-}, and hence the amount balance can be simplified as follows:

$$C^{\circ}_{\mathrm{HB^-}} = c_{\mathrm{HB^-}} + c_{\mathrm{B^{2-}}} \tag{140}$$

The following rearrangements lead to a quadratic equation which can be easily solved:

$$\begin{tikzcd}
c_{\mathrm{H_3O^+}} \approx c_{\mathrm{B^{2-}}} \ (139) \arrow[r, "\text{inserting (139) in (140)}"] & C^{\circ}_{\mathrm{HB^-}} = c_{\mathrm{HB^-}} + c_{\mathrm{H_3O^+}} \ (141) \arrow[dl] \\
c_{\mathrm{HB^-}} = C^{\circ}_{\mathrm{HB^-}} - c_{\mathrm{H_3O^+}} \ (142) \arrow[r, "\text{inserting (139) and (142) in (40)}"] & K_{\mathrm{a2}} = \dfrac{c^2_{\mathrm{H_3O^+}}}{C^{\circ}_{\mathrm{HB^-}} - c_{\mathrm{H_3O^+}}} \ (143) \arrow[d] \\
 & K_{\mathrm{a2}} C^{\circ}_{\mathrm{H_2B}} - K_{\mathrm{a2}} c_{\mathrm{H_3O^+}} = c^2_{\mathrm{H_3O^+}} \ (144) \arrow[d] \\
 & 0 = c^2_{\mathrm{H_3O^+}} + K_{\mathrm{a2}} c_{\mathrm{H_3O^+}} - K_{\mathrm{a2}} C^{\circ}_{\mathrm{HB^-}} \ (145)
\end{tikzcd}$$

Solving this quadratic equation makes it possible to calculate the equilibrium concentration of the hydronium ions:

Simplified equation for ampholytes which are strongly acidic and weakly basic:

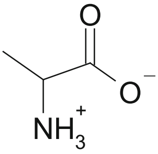
$$\boldsymbol{c_{\mathrm{H_3O^+}} = -\frac{K_{\mathrm{a2}}}{2} \pm \sqrt{\frac{K^2_{\mathrm{a2}}}{4} + K_{\mathrm{a2}} C^{\circ}_{\mathrm{HB^-}}}} \tag{146}$$

(The mathematical solution $c_{\mathrm{H_3O^+}} = -\frac{K_{\mathrm{a2}}}{2} - \sqrt{\frac{K^2_{\mathrm{a2}}}{4} + K_{\mathrm{a2}} C^{\circ}_{\mathrm{HB^-}}}$ does not describe a real concentration, and therefore the minus sign before the square root is usually not written.)

This shows that an ampholyte which is strongly acidic and weakly basic can be treated like a strong monobasic acid. The acidity character dominates over the basic character. This is also true at low concentrations.

4.2.2.2 An Ampholyte that is Weakly Acidic and Weakly Basic; pH Values of Amino Acid Solutions

As explained in Sect. 4.2.1.2, amino acids have a carboxyl group and an amine group, and the carboxyl group is a stronger acid than the protonated amino group, i.e., the carboxyl group protonates the amino group. Thus the nonionic form undergoes a rearrangement as follows HAl $\rightleftarrows$ $HAl^{+/-}$ (this is a tautomeric equilibrium) and a zwitterion is formed:



(zwitterion of alanine).

The term zwitterion is derived from the German word “Zwitter” for hybrid and hermaphrodite. Figure 53 shows the pH-logc_i diagram of solution containing 10^{-1} mol L^{-1} alanine ($pK_{a1} = 2.3, pK_{a2} = 9.9$). In contrast to Figs. 50 and 51, here a solution of HAl is considered, not a solution of alanine hydrochloride ($H_2Al^+Cl^-$)!

The charge balance gives:

$$c_{H_3O^+} = c_{OH^-} + c_{B^{2-}} - c_{H_2B} \tag{137}$$

As a first approximation, one can assume that $HAl^{+/-}$ will react to equal concentrations of the corresponding acid H_2Al^+ and the corresponding base Al^-, i.e., that the pH-coordinate of P_1 gives the pH of the solution. Although there the concentration $c_{H_3O^+}$ is not really two orders of magnitude smaller than c_{H_2B}, the concentration c_{OH^-} is even more than two orders of magnitude smaller than $c_{B^{2-}}$: thus one can simplify Eq. (137) to give: $c_{H_2B} \approx c_{B^{2-}}$. This means that the pH of the solution can be read as the pH-coordinate of P_1. The accuracy of that approximation certainly depends on the two pK_a values.

For the derivation of a simplified equation, one needs to consider the amount balance of an ampholyte solution (Eq. (136)):

$$C^{\circ}_{HB^-} = c_{H_2B} + c_{HB^-} + c_{B^{2-}} \tag{136}$$

The diagram (Fig. 53) shows that the concentrations of H_2B and B^{2-} in P_1 are negligibly small in comparison to that of HB^-, so that balance can be simplified as follows:

$$C^{\circ}_{HB^-} \approx c_{HB^-} \tag{147}$$

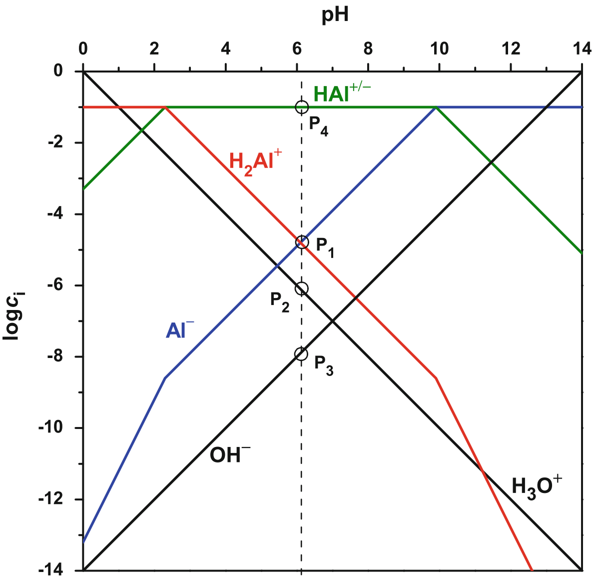


Fig. 53 pH-logc_i diagram of a solution containing 10^{-1} mol L^{-1} alanine ($pK_{a1} = 2.3$, $pK_{a2} = 9.9$) (H_2Al^+ corresponds to H_2B, $HAl^{+/-}$ corresponds to HB^-, and Al^- corresponds to B^{2-} of the dibasic acids H_2B)

The following rearrangements lead to a quadratic equation:

$$C^{\circ}_{HB^-} \approx c_{HB^-} \quad (147) \xrightarrow{\text{inserting (147) in (40)}} K_{a2} = \frac{c_{B^{2-}} c_{H_3O^+}}{C^{\circ}_{HB^-}} \quad (148) \longrightarrow c_{B^{2-}} = \frac{K_{a2} C^{\circ}_{HB^-}}{c_{H_3O^+}} \quad (149)$$

$$K_{b2} = \frac{K_w}{K_{a1}} = \frac{c_{H_2B} c_{OH^-}}{c_{HB^-}} \quad (135) \xrightarrow{\text{inserting (147) in (135)}} \frac{K_w}{K_{a1}} = \frac{c_{H_2B} c_{OH^-}}{C^{\circ}_{HB^-}} \quad (150)$$

$$c_{OH^-} = \frac{K_w}{c_{H_3O^+}} \quad (11) \xrightarrow{\text{inserting (11) in (150)}} c_{H_2B} = \frac{K_w C^{\circ}_{HB^-}}{K_{a1} c_{OH^-}} = \frac{c_{H_3O^+} C^{\circ}_{HB^-}}{K_{a1}} \quad (151)$$

$$\xrightarrow{\text{inserting (11), (149) and (151) in (137)}} \frac{c_{H_3O^+} C^{\circ}_{HB^-}}{K_{a1}} + c_{H_3O^+} = \frac{K_w}{c_{H_3O^+}} + \frac{K_{a2} C^{\circ}_{HB^-}}{c_{H_3O^+}} \quad (152)$$

$$\downarrow$$

$$c^2_{H_3O^+} \left(\frac{C^{\circ}_{HB^-}}{K_{a1}} + 1 \right) = K_w + K_{a2} C^{\circ}_{HB^-} \quad (153)$$

$$\downarrow$$

$$c^2_{H_3O^+} = \frac{K_{a1} K_w + K_{a1} K_{a2} C^{\circ}_{HB^-}}{C^{\circ}_{HB^-} + K_{a1}} \quad (154)$$

The quadratic equation can be solved to yield:

Simplified equation for an ampholyte which is weakly acidic and weakly basic:

$$\boldsymbol{c_{H_3O^+} = \sqrt{\frac{K_{a1}K_w + K_{a1}K_{a2}C^{\circ}_{HB^-}}{C^{\circ}_{HB^-} + K_{a1}}}} \tag{155}$$

For the case that $K_{a1}K_w \ll K_{a1}K_{a2}C^{\circ}_{HB^-}$ and $C^{\circ}_{HB^-} \gg K_{a1}$, Eq. (155) can be further simplified to give:

$$c_{H_3O^+} = \sqrt{K_{a1}K_{a2}} \tag{156}$$

This equation is based on the assumption that $c_{H_2B} \approx c_{B^{2-}}$, whereas Eq. (155) is based on the exact balance $c_{H_3O^+} = c_{OH^-} + c_{B^{2-}} - c_{H_2B}$.

Equation 156 is a good simplified equation for the amino acid alanine at a concentration of 10^{-1} mol L^{-1}: Eq. (155) gives pH = 6.01, and Eq. (156) gives pH = 6.10, i.e., the difference is smaller than 2 %.

4.2.3 Diacidic Bases

In a solution of a diacidic base, the following equilibria are established:

$$B^{2-} + H_2O \rightleftarrows HB^- + OH^- \tag{157}$$

$$HB^- + H_2O \rightleftarrows H_2B + OH^- \tag{134}$$

$$H_2O + H_2O \rightleftarrows OH^- + H_3O^+ \tag{2}$$

The determination of the five variables c_{H_2B}, c_{HB^-}, $c_{B^{2-}}$, $c_{H_3O^+}$, and c_{OH^-} requires five independent equations. These are the equations of the law of mass actions of all protolysis reactions and the equations for charge and amount balances:

$$\boldsymbol{K_{b1} = \frac{c_{HB^-}c_{OH^-}}{c_{B^{2-}}}} \tag{158}$$

$$\boldsymbol{K_{b2} = \frac{c_{H_2B}c_{OH^-}}{c_{HB^-}}} \tag{135}$$

$$\boldsymbol{K_w = c_{H_3O^+}c_{OH^-}} \tag{9}$$

$$\boldsymbol{C^{\circ}_{B^{2-}} = c_{H_2B} + c_{HB^-} + c_{B^{2-}}} \tag{159}$$

$$\boldsymbol{c_{OH^-} = c_{H_3O^+} + c_{HB^-} + 2c_{H_2B}} \tag{160}$$

4.2.3.1 Diacidic Base with a Strong and a Weak Protolysis Reaction

A good example for such base is the sulfide ion ($\mathrm{p}K_{\mathrm{b1}} = 0.1$ and $\mathrm{p}K_{\mathrm{b2}} = 7.0$). First, a high concentration is considered: Fig. 54 depicts the pH-logc_{i} diagram of a solution containing 0.1 mol L^{-1} $\mathrm{Na_2S}$.

The charge balance gives:

$$c_{\mathrm{OH^-}} = c_{\mathrm{H_3O^+}} + c_{\mathrm{HB^-}} + 2c_{\mathrm{H_2B}} \tag{160}$$

From the diagram follows that the pH should be read slightly to the right of the pH-coordinate of $\mathrm{P_1}$, as on the left side of $\mathrm{P_1}$ the sum of $\mathrm{HB^-}$, $\mathrm{H_3O^+}$, and $\mathrm{H_2B}$ is always larger than the concentration of $\mathrm{OH^-}$ ions. The diagram further tells that in this range the concentrations of $\mathrm{H_3O^+}$ and $\mathrm{H_2B}$ are much smaller than the concentration of $\mathrm{HB^-}$, so that it is a good approximation to write:

$$c_{\mathrm{OH^-}} \approx c_{\mathrm{HB^-}} \tag{161}$$

and the pH-coordinate of $\mathrm{P_1}$ indeed gives the pH of the solution in a very good approximation. The amount balance is:

$$C^{\circ}_{\mathrm{B^{2-}}} = c_{\mathrm{H_2B}} + c_{\mathrm{HB^-}} + c_{\mathrm{B^{2-}}} \tag{159}$$

Since the concentrations of $\mathrm{HB^-}$ and $\mathrm{B^{2-}}$ are much larger than that of $\mathrm{H_2B}$ (see $\mathrm{P_1}$, $\mathrm{P_3}$, and $\mathrm{P_3}$ in Fig. 54) the amount balance simplifies as follows:

$$C^{\circ}_{\mathrm{B^{2-}}} \approx c_{\mathrm{HB^-}} + c_{\mathrm{B^{2-}}} \tag{162}$$

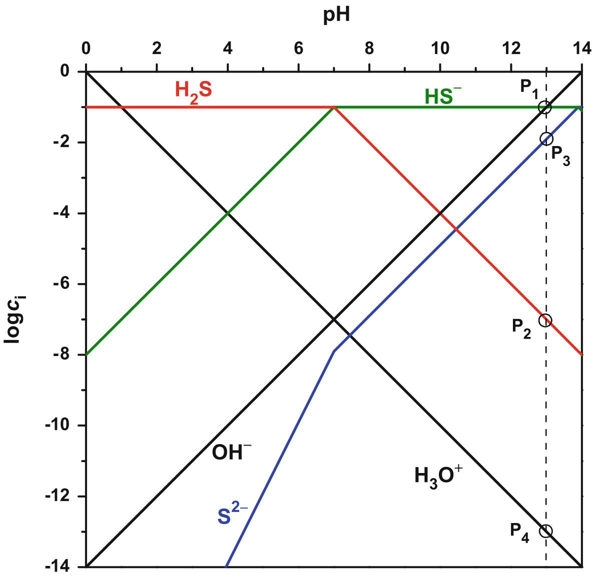


Fig. 54 pH-logc_i diagram of a solution containing 0.1 mol L^{-1} Na_2S

The following rearrangements make it possible to derive a quadratic equation:

$$c_{OH^-} \approx c_{HB^-} \ (161) \xrightarrow{\text{inserting (161) in (162)}} C^{\circ}_{B^{2-}} = c_{OH^-} + c_{B^{2-}} \ (163) \longrightarrow c_{B^{2-}} = C^{\circ}_{B^{2-}} - c_{OH^-} \ (164)$$

$$K_{b1} = \frac{c_{HB^-} c_{OH^-}}{c_{B^{2-}}} \ (158) \xrightarrow{\text{inserting (161) and (164) in (158)}} K_{b1} = \frac{c^2_{OH^-}}{C^{\circ}_{B^{2-}} - c_{OH^-}} \ (165)$$

$$c_{OH^-} = \frac{K_w}{c_{H_3O^+}} \ (11) \xrightarrow{\text{inserting (11) in (165)}} K_{b1} = \frac{K^2_w}{c^2_{H_3O^+}\left(C^{\circ}_{B^{2-}} - \dfrac{K_w}{c_{H_3O^+}}\right)} = \frac{K^2_w}{c^2_{H_3O^+} C^{\circ}_{B^{2-}} - K_w c_{H_3O^+}} \ (166)$$

$$\downarrow$$

$$0 = K_{b1} c^2_{H_3O^+} C^{\circ}_{B^{2-}} - K_{b1} K_w c_{H_3O^+} - K^2_w \ (167)$$

$$\downarrow$$

$$0 = c^2_{H_3O^+} - \frac{K_w}{C^{\circ}_{B^{2-}}} c_{H_3O^+} - \frac{K^2_w}{K_{b1} C^{\circ}_{B^{2-}}} \ (168)$$

The quadratic equation can be solved with respect to the concentration of H_3O^+ ions:

Simplified equation for a diacidic base with a strong and a weak protolysis reaction, and in high concentration:

$$\boldsymbol{c_{\mathrm{H_3O^+}} = \frac{K_{\mathrm{w}}}{2C^{\circ}_{\mathrm{B^{2-}}}} \pm \sqrt{\frac{K_{\mathrm{w}}^2}{4\left(C^{\circ}_{\mathrm{B^{2-}}}\right)^2} + \frac{K_{\mathrm{w}}^2}{K_{\mathrm{b1}}C^{\circ}_{\mathrm{B^{2-}}}}}} \tag{169}$$

(The mathematical solution $c_{\mathrm{H_3O^+}} = \frac{K_{\mathrm{w}}}{2C^{\circ}_{\mathrm{B^{2-}}}} - \sqrt{\frac{K_{\mathrm{w}}^2}{4\left(C^{\circ}_{\mathrm{B^{2-}}}\right)^2} + \frac{K_{\mathrm{w}}^2}{K_{\mathrm{b1}}C^{\circ}_{\mathrm{B^{2-}}}}}$ does not describe a real concentration, and therefore the minus sign before the square root is usually not written.)

In this case, the second protolysis reaction can be disregarded. The base behaves like a monoacidic base (see Eq. (105) in Sect. 4.1.3.3). For low concentrations of a diacidic base, a cubic equation has to be solved (see Eq. (63)).

4.2.3.2 Diacidic Base with Two Weak Protolysis Reactions

As an example for such base, the oxalate ion can be considered: $\mathrm{p}K_{\mathrm{b1}} = 9.73$ and $\mathrm{p}K_{\mathrm{b2}} = 12.73$. Figure 55 shows the pH-logc_{i} diagram of a solution containing 0.1 mol L^{-1} of sodium oxalate.

Considering the charge balance is

$$c_{\mathrm{OH^-}} = c_{\mathrm{H_3O^+}} + c_{\mathrm{HB^-}} + 2c_{\mathrm{H_2B}} \tag{160}$$

one can see that the pH of the solution should be slightly right of the pH-coordinate of $\mathrm{P_1}$, since left of this point the sum of the concentrations of $\mathrm{HB^-}$, $\mathrm{H_3O^+}$, and $\mathrm{H_2B}$ are always larger than that of the $\mathrm{OH^-}$ ions. Further, in this range, the concentrations of $\mathrm{H_3O^+}$ and $\mathrm{H_2B}$ are much smaller than that of $\mathrm{HB^-}$ (see $\mathrm{P_1}$, $\mathrm{P_2}$, and $\mathrm{P_3}$), so that the simplified charge balance

$$c_{\mathrm{OH^-}} \approx c_{\mathrm{HB^-}} \tag{161}$$

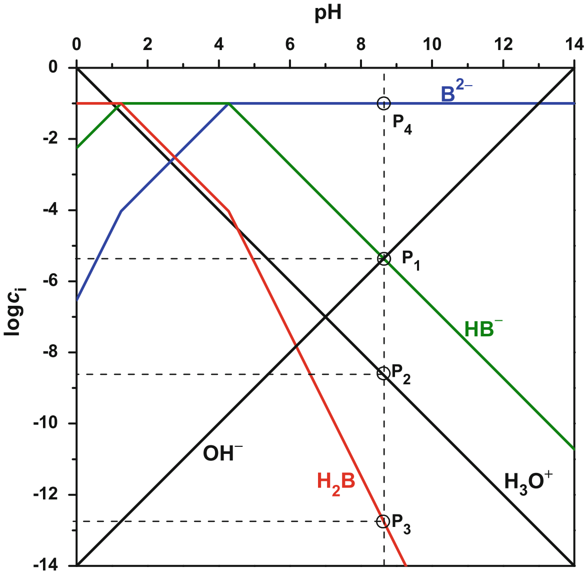
follows. Hence, the pH-coordinate of $\mathrm{P_1}$ gives the pH of the solution to a very good approximation. The amount balance

$$C^{\circ}_{\mathrm{B^{2-}}} = c_{\mathrm{H_2B}} + c_{\mathrm{HB^-}} + c_{\mathrm{B^{2-}}} \tag{159}$$

can also be simplified in $\mathrm{P_1}$ because the concentration of $\mathrm{B^{2-}}$ is much larger than those of $\mathrm{HB^-}$ and $\mathrm{H_2B}$:

$$C^{\circ}_{\mathrm{B^{2-}}} \approx c_{\mathrm{B^{2-}}} \tag{170}$$

Fig. 55 pH-logc_i diagram of a solution containing 0.1 mol L^{-1} of sodium oxalate (oxalate: $pK_{b1} = 9.73$ and $pK_{b2} = 12.73$)



The next rearrangements give a quadratic equation:

$$K_{b1} = \frac{c_{HB^-} c_{OH^-}}{c_{B^{2-}}} \ (158) \xrightarrow{\text{inserting (161) and (170) in (158)}} K_{b1} = \frac{c^2_{OH^-}}{C^{\circ}_{B^{2-}}} \ (171)$$

$$c_{OH^-} = \frac{K_w}{c_{H_3O^+}} \ (11) \xrightarrow{\text{inserting (11) in (171)}} K_{b1} = \frac{K_w^2}{c^2_{H_3O^+} C^{\circ}_{B^{2-}}} \ (172) \longrightarrow c^2_{H_3O^+} = \frac{K_w^2}{K_{b1} C^{\circ}_{B^{2-}}} \ (173)$$

Simplified equation for a diacidic base with two weak protolysis reactions and in a high concentration:

$$c_{H_3O^+} = \frac{K_w}{\sqrt{K_{b1} C^{\circ}_{B^{2-}}}} \tag{174}$$

This shows that this base can be treated like a weak monoacidic base because the second protolysis reaction can be disregarded (see Eq. (84) in Sect. 4.1.2.3).

4.3 Salt Solutions with Protolyzing Anions and Cations

As mentioned in the previous chapters, for the pH of a salt solution it is important whether the anion or the cation or both ions are undergoing protolysis reactions. If both ions exist in aqueous solutions as hydrated ions which do not undergo protolysis to any significant extent, the solution will be neutral, as in the case of sodium chloride NaCl (see Sect. 4.1.1.3).

When the hydrated cation does not react with water, but the anion does, the solutions are alkaline (the anions are bases which are protonated by water yielding OH^- ions). The pH-logc_i diagrams of such cases have been described in the previous chapters.

When only the hydrated cation reacts with water, the solution will be acidic. Such solutions can be treated like those of all other Brønsted acids.

Salts with protolysing anions and cations may give acidic, neutral, or basic solutions, or they may even completely decompose. The pH of such solutions can be rather easily found with the help of pH-logc_i diagrams. As first examples of such salts, we shall consider those having a monobasic acid and a monoacidic base, e.g., ammonium formate, ammonium acetate, and ammonium cyanide. Ammonium ion is a weak acid $pK_a^1 = 9.25$. The following Table 2 gives the pK_a values of the acids corresponding to the bases (the anions of the salt).

Table 2 pK_a^2-values of the acids corresponding to the anions

Anion	Corresponding acid	pK_a^2
Formate	Formic acid	3.75
Acetate	Acetic acid	4.75
Cyanide	Hydrogen cyanide	9.21

The pH-logc_i diagrams can be constructed in the usual way. The anions and cations exist in equal overall concentrations. Dissolving 0.1 mol of these salts in water so that one liter of solution results, the overall concentration of the pairs ammonium/ammonia and anion/corresponding acid is also 0.1 mol L^{-1}. In the Figs. 56, 57, and 58, the respective diagrams are shown for solutions containing 0.1 mol L^{-1} of the ammonium salts.

In the aqueous solution, the following equilibria are established:

$$A^1 + H_2O \rightleftarrows B^1 + H_3O^+ \tag{175}$$

$$B^2 + H_3O^+ \rightleftarrows A^2 + H_2O \tag{176}$$

i.e., water acts as a proton-transferring agent for the following net reaction:

$$A^1 + B^2 \rightleftarrows B^1 + A^2 \tag{177}$$

From this follows that the equilibrium concentrations of B^1 and A^2 should be equal. This condition is met in the crossing point of the acid line of the acid corresponding to the anion and the base line of the cation, i.e., in P_1 in Figs. 56, 57, and 58. The pH-coordinate of this point is the pH of the solutions. This graphical way of finding the pH is equivalent to the calculations derived for ampholytes which are weakly acidic and weakly basic (see Sect. 4.2.2.2):

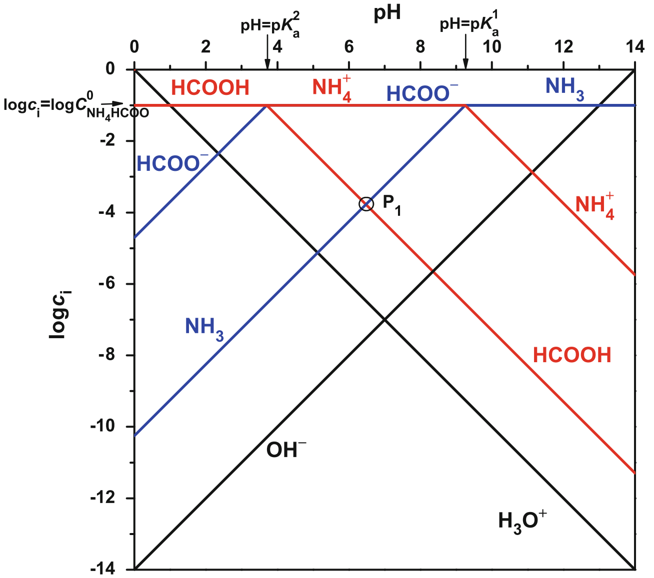


Fig. 56 pH-logc_i diagram of a solution containing 0.1 mol L^{-1} ammonium formate

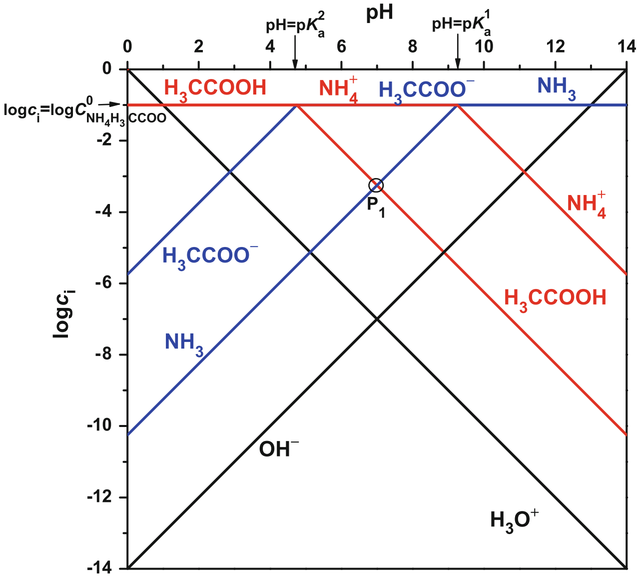


Fig. 57 pH-logc_i diagram of a solution containing 0.1 mol L^{-1} ammonium acetate

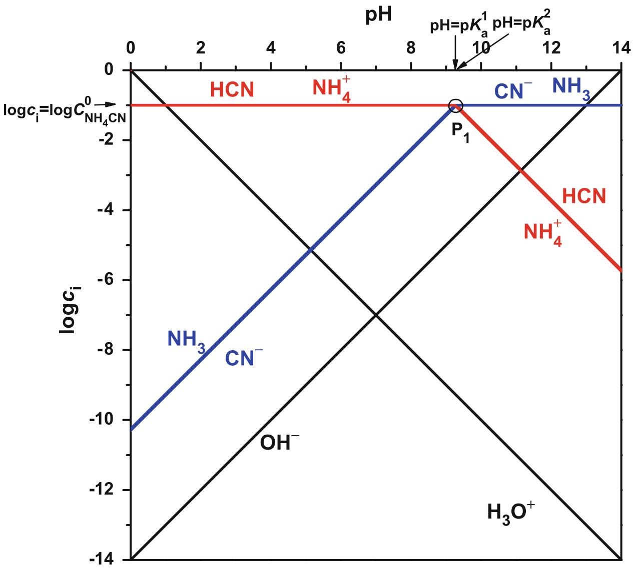


Fig. 58 pH-logc_i diagram of a solution containing 0.1 mol L^{-1} ammonium cyanide

$$c_{H_3O^+} = \sqrt{K_a^1 K_a^2} \tag{156}$$

In the case that the anions and cations have different charges, as, for example, in the case of ammonium oxalate, the approach is similar: The only difference to be taken into consideration is the different overall concentration of anions and cations. Figure 59 depicts the pH-logc_i diagram of a solution containing 0.1 mol L^{-1} $(NH_4)_2C_2O_4$. The total concentration of oxalate species is then 0.1 mol L^{-1}, however, the total concentration of ammonia/ammonium is 0.2 mol L^{-1}. The following proton transfer reactions take place in the solution:

$$NH_4^+ + H_2O \rightleftarrows NH_3 + H_3O^+ \tag{178}$$

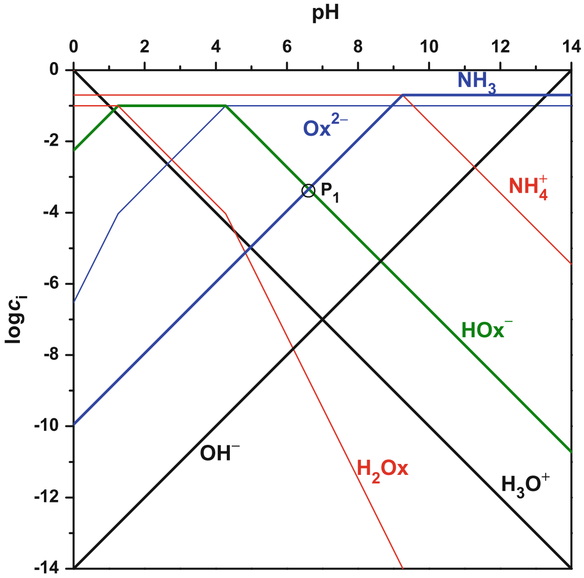
$$C_2O_4^{2-} + H_3O^+ \rightleftarrows HC_2O_4^- + H_2O \tag{179}$$

The net equilibrium is:

$$NH_4^+ + C_2O_4^{2-} \rightleftarrows NH_3 + HC_2O_4^- \tag{180}$$

The pH of the solution can be read as the pH-coordinate of P_1 in Fig. 59, as that is the crossing point of the lines of NH_3 and $HC_2O_4^-$, i.e., the point where their concentrations are equal. Please note that the pH *cannot* be calculated using Eq. (156)!

Fig. 59 pH-logc_i diagram of a solution containing 0.1 mol L^{-1} ammonium oxalate



4.4 Examples

4.4.1 The pH-logc_i Diagram of Water

It is also possible to construct a pH-logc_i diagram for water. With the density of water at 20 °C (0.998203 g cm^{-3}) and its molar mass (18.0153 g mol^{-1}) one can calculate the concentration of pure water: 55.408 mol L^{-1} ($\log C^{\circ}_{H_2O} = 1.74$). Water is an ampholyte:

$$H_2O + H_2O \rightleftarrows OH^- + H_3O^+ \tag{2}$$

As mentioned at the very beginning, it is impossible to give the pK_a value of H_3O^+ and the pK_b value of OH^- on a strictly thermodynamic basis [9]. However, using the concentration of water in pure water ($\log C^{\circ}_{H_2O} = 1.74$), one can construct the diagram shown in Fig. 60. From this diagram, one can read the *apparent* pK_a values of H_3O^+ (-1.74) and H_2O (15.74). However, both values are based on the surely wrong assumption that the activity of water in water is equal to its molar concentration! Therefore, one should regard Fig. 60 simply as a *formal presentation*, just to show that there is also a function of H_2O, corresponding to the lines of H_3O^+ and OH^-.

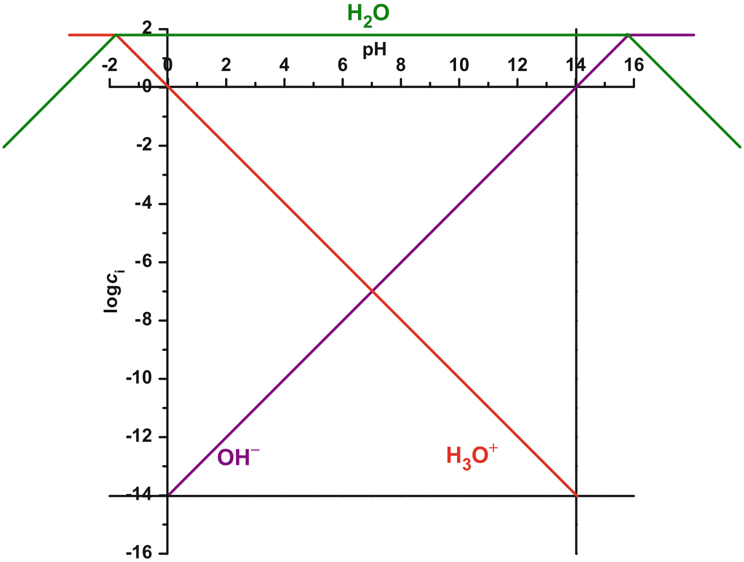


Fig. 60 pH-logc_i diagram of water with $\log C^\circ_{\mathrm{H_2O}} = 1.74$ and the two not entirely correct values $\mathrm{p}K_\mathrm{a}(\mathrm{H_3O^+}) = -1.74$ and $\mathrm{p}K_\mathrm{a}(\mathrm{H_2O}) = 15.74$

4.4.2 Acetic Acid/Acetate

Figure 61 shows the pH-logc_i diagram of the corresponding acid–base pair acetic acid/acetate ions.

In this diagram, one can read the pH values of the following solutions:

P$_1$: aqueous solution containing 0.1 mol L^{-1} of sodium acetate: $c_{\mathrm{HAc}} \approx c_{\mathrm{OH^-}}$, pH = 8.86.

P$_2$: aqueous solution of 0.1 mol L^{-1} acetic acid: $c_{\mathrm{H_3O^+}} \approx c_{\mathrm{Ac^-}}$, pH = 2.88.

P$_3$: acetic acid/acetate buffer with maximum buffer capacity (see Chap. 2): 0.05 mol L^{-1} acetic acid + 0.05 mol L^{-1} sodium acetate; pH = pK_S = 4.75.

P$_4$: acetic acid/acetate buffer with lower buffer capacity: 0.1 mol L^{-1} acetic acid, 0.01 mol L^{-1} sodium acetate; pH = 3.75.

P$_5$: acetic acid/acetate buffer with lower buffer capacity: 0.01 mol L^{-1} acetic acid, 0.1 mol L^{-1} sodium acetate; pH = 5.75.

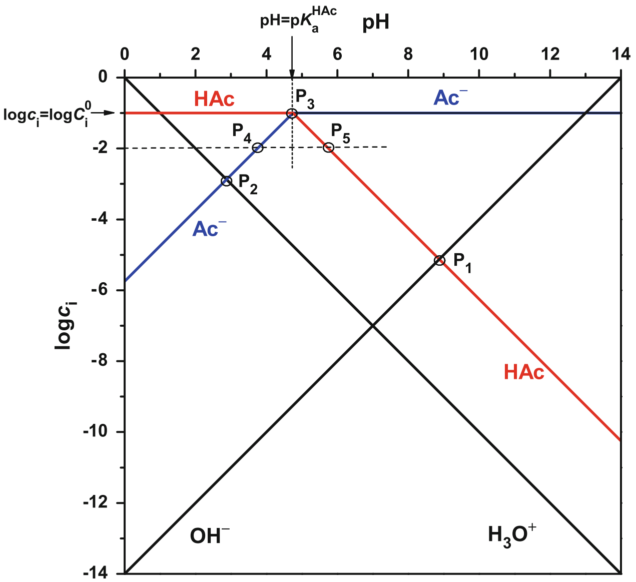


Fig. 61 pH-logc_i diagram of the corresponding acid–base pair acetic acid/acetate ions $\log C_i^{\circ} = -1.00$, $pK_a = 4.75$

4.4.3 Hydrogen Sulfide

In classical chemical separations, hydrogen sulfide is frequently used to separate and identify metal ions. Metal sulfides also play an important role in the environment. With the help of the pH-logc_i diagram of hydrogen sulfide, one can easily find what sulfide species are present in a solution, and what metal sulfides can be precipitated under certain pH conditions. At 20 °C, a saturated solution of this gas in water contains 0.197 mol L^{-1} H_2S following establishment of the equilibrium:

$$H_2S_{(gas)} \rightleftarrows H_2S_{(dissolved)} \tag{181}$$

Figure 62 shows the pH-logc_i diagram of hydrogen sulfide for this overall concentration (log $C_{H_2S}^{\circ} = -0.71$) and the acidity constants $pK_{a1} = 7.00$ and $pK_{a2} = 13.9$.

The diagram makes it possible to determine the following pH data:

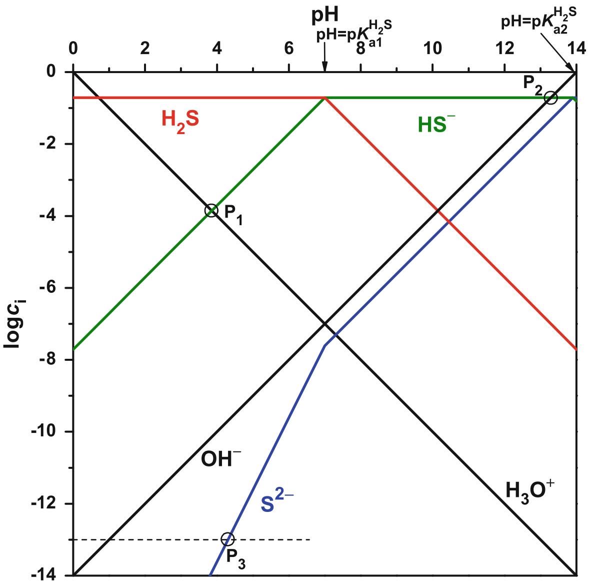
P$_1$: saturated aqueous solution of hydrogen sulfide: $c_{H_3O^+} \approx c_{HS^-}$, pH = 3.87.

P$_2$: aqueous solution containing 0.197 mol L^{-1} Na_2S: $c_{OH^-} \approx c_{HS^-}$, pH = 13.3.

To tell at what pH the precipitation of a certain metal sulfide will take place, the following approach can be chosen. Assuming a manganese solution containing 10^{-2} mol L^{-1} Mn^{2+} ions, one needs to find the solubility product of MnS in a reference book. The solubility product K_s is 10^{-15} mol^2 L^{-2} (at 20 °C):

$$K_s = c_{Mn^{2+}} c_{S^{2-}} \tag{182}$$

Fig. 62 pH-logc_i diagram of hydrogen sulfide ($\log C^{\ominus}_{\mathrm{H_2S}} = -0.71$ and $\mathrm{p}K_{\mathrm{a1}} = 7.00$, $\mathrm{p}K_{\mathrm{a2}} = 13.9$)



Manganese sulfide will precipitate when its solubility product is exceeded, i.e., when the S^{2-} concentration becomes larger than 10^{-13} mol L^{-1} (for the given Mn^{2+} concentration of 10^{-2} mol L^{-1}). According to the pH-logc_i diagram (Fig. 62) this is the case at P_3, i.e., the precipitation will take place for pH values above 4.3. At lower pH values, the sulfide ion concentration is insufficient to produce a precipitate.

4.4.4 Phosphoric Acid

Phosphoric acid is a tribasic acid (see Fig. 63).

The diagram allows reading the following pH values:

P_1: aqueous solution of 0.1 mol L^{-1} H_3PO_4: $c_{\mathrm{H_3O^+}} \approx c_{\mathrm{H_2PO_4^-}}$, pH = 1.58.

P_2: aqueous solution containing equimolar concentrations (0.05 mol L^{-1}) of H_3PO_4 and NaH_2PO_4: pH = pK_{a1} = 2.15.

P_3: aqueous solution containing 0.1 mol L^{-1} NaH_2PO_4: $c_{\mathrm{H_3PO_4}} \approx c_{\mathrm{HPO_4^{2-}}}$, pH = 4.68.

P_4: aqueous solution containing 0.1 mol L^{-1} NaH_2PO_4 and 0.01 mol L^{-1} Na_2HPO_4 (NaH_2PO_4 and Na_2HPO_4 in the ratio of 10:1): pH = 6.2.

P_5: aqueous solution containing equimolar concentrations (0.05 mol L^{-1}) of NaH_2PO_4 and Na_2HPO_4: pH = pK_{a2} = 7.2.

P_6: aqueous solution containing NaH_2PO_4 and Na_2HPO_4 in the ratio 1:10 (0.01 mol L^{-1} NaH_2PO_4, 0.1 mol L^{-1} Na_2HPO_4): pH = 8.2.

P_7: aqueous solution containing 0.1 mol L^{-1} Na_2HPO_4: $c_{\mathrm{H_2PO_4^-}} \approx c_{\mathrm{PO_4^{3-}}}$, pH =9.77.

P_8: aqueous solution containing equimolar concentrations (0.05 mol L^{-1}) of Na_2HPO_4 and Na_3PO_4: pH = pK_{a3} = 12.35.

P_9: aqueous solution containing 0.1 mol L^{-1} Na_3PO_4: $c_{\mathrm{OH^-}} \approx c_{\mathrm{HPO_4^{2-}}}$, pH = 12.67.

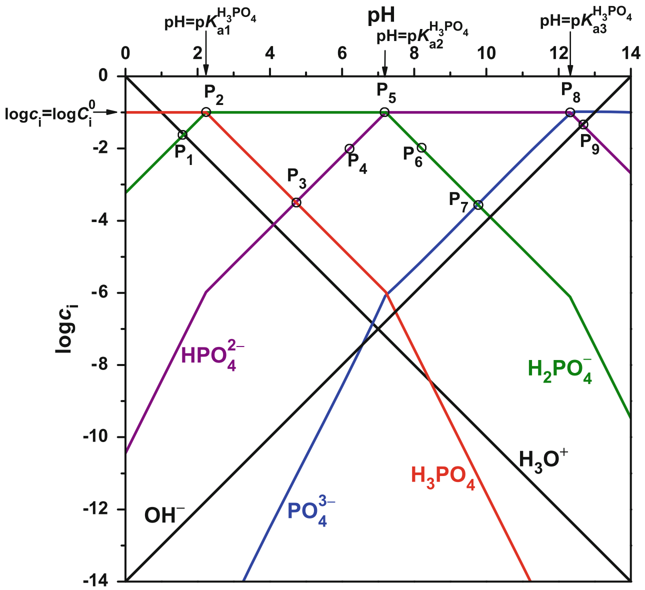
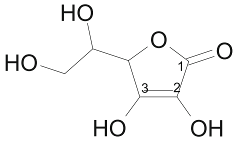


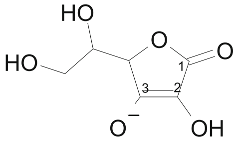
Fig. 63 pH-logc_i diagram of phosphoric acid ($\log C_i^O = -1.00$ and p$K_{a1} = 2.15$, p$K_{a2} = 7.2$ and p$K_{a3} = 12.35$)

4.4.5 Ascorbic Acid

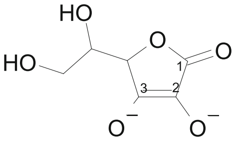
In aqueous solutions ascorbic acid can be present in the following forms:



Ascorbic acid, H$_2$A



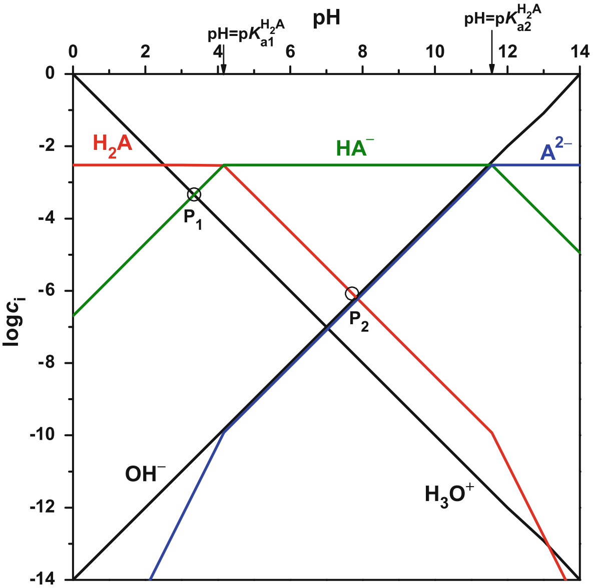
Hydrogenascorbate, HA$^-$



Ascorbate A^{2-}

For simplicity, only one mesomeric formula is given for HA$^-$ and A^{2-}, although the different resonance structures contribute much to the stability of the bases, and thus also explain the rather high acidity of the OH groups (which are normally less acidic). Hydrogen ascorbate is frequently called simply ascorbate, which is strictly speaking wrong, but this custom results from the fact that ascorbate A^{2-} does not play any role in real, especially biochemically relevant, solutions. In food products, ascorbic acid, i.e., vitamin C, is present especially in fruits and vegetables. Citrus fruits in particular, such as oranges and lemons, contain large amounts after harvesting. Since ascorbic acid is easily oxidized, it is frequently used as an antioxidant to preserve food products. As the structural formula shows, ascorbic acid has four hydroxyl groups; however, only those at the C-2 and C-3 atoms can be deprotonated in water. The pK_a values are p$K_{a1} = 4.17$ and p$K_{a2} = 11.57$. Ascorbic acid is often added to fruit juices and beverages. Thus, there are apple juices which

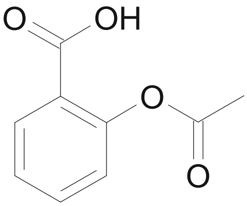
Fig. 64 pH-logc_i diagram of ascorbic acid ($\log C_i^{\circ} = -2.52$, $pK_{a1} = 4.17$, $pK_{a2} = 11.57$)



contain – according to the producers – 55 mg vitamin C in 100 mL juice. This is a concentration of 3×10^{-3} mol L^{-1} ($\log C_i^{\circ} = -2.52$). Figure 64 shows the respective pH-logc_i diagram.

The pH-coordinate of P_1 gives the pH of an aqueous solution of vitamin C of that example: $c_{H_3O^+} \approx c_{HA^-}$, pH = 3.33. Since fruit juices also contain other acids with similar pK_a values, their pH is usually in the range of 3 to 4. A solution of sodium hydrogen ascorbate would have at the same concentration a pH of 7.7 (see P_2 in Fig. 64, $c_{H_2A} \approx c_{A^{2-}}$). For parenteral delivery of vitamin C (injections, infusions), hydrogen ascorbate is used to make the solution pH compatible with blood.

4.4.6 Acetylsalicylic Acid



Acetylsalicylic acid (ASA, Aspirin®) is a common analgetic, anti-inflammatory, and antipyretic drug. Because of its acidity (pK_a = 3.49) it can also cause some irritations which can prompt side reaction such as heartburn and vomiting when orally administered. Moreover, when regularly taken, it may lead to mucosal irritation and bleeding in the gastrointestinal tract, and also may lead to gastric

Fig. 65 pH-logc_i diagram of an ASA solution ($\log C_i^{\circ} = -1.73$, $pK_a = 3.48$)

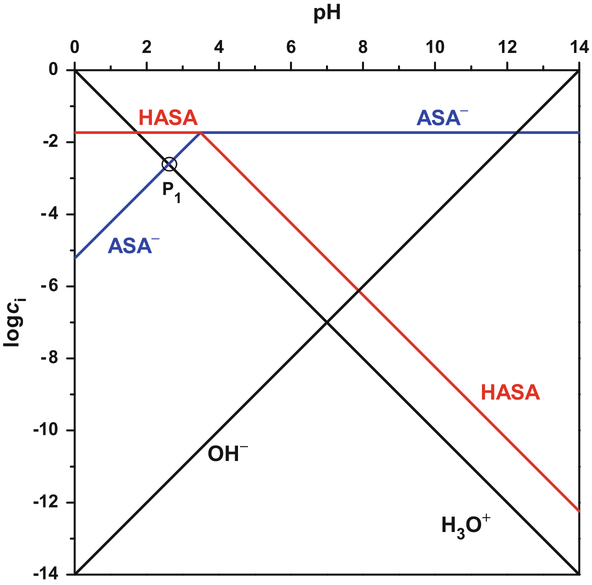
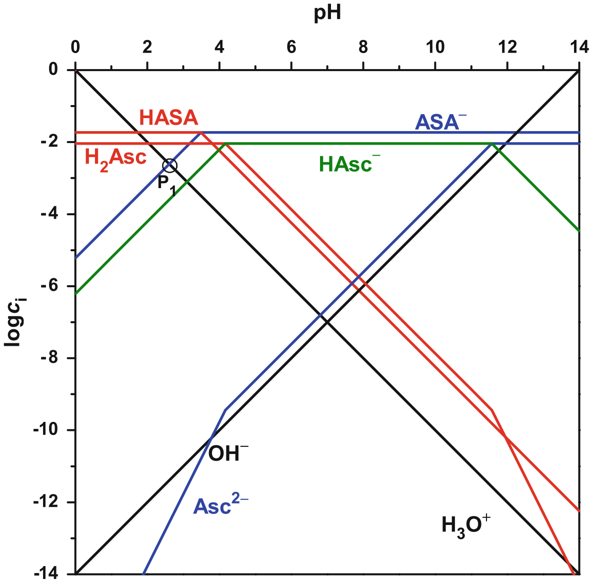


Fig. 66 pH-logc_i diagram for a solution containing 400 mg ASA and 240 mg vitamin C in 150 mL water



ulcers. Typical dosage forms are tablets and effervescent tablets. One tablet may contain 500 mg ASA. This tablet dissolved in 150 mL of water will give an overall concentration of 0.018 mol L^{-1}. Figure 65 depicts the pH-logc_i diagram of this solution ($\log C_i^{\circ} = -1.73$).

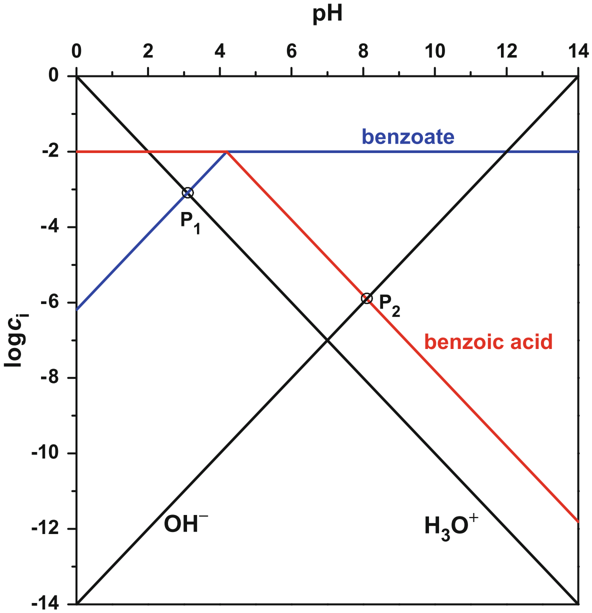
P_1 ($c_{H_3O^+} \approx c_{ASA^-}$) allows reading the pH which is 2.63. In effervescent tablets ASA is usually mixed with ascorbic acid, sodium dihydrogencitrate and citric acid, as well as with sodium hydrogen carbonate and disodium carbonate. If a tablet containing only 400 mg ASA and 240 mg vitamin C is dissolved in 150 mL water (this corresponds to 0.0148 mol L^{-1} ASA and 0.009 mol L^{-1} vitamin C) one can describe the solution with the help of the pH-logc_i diagram shown in Fig. 66.

The pH at P_1 is 2.63. Because of the slightly less acidic ascorbic acid, some additional H_3O^+ is produced and the pH will be below 2.63. In commercial effervescent tablets, the above-mentioned added buffer systems keep the pH much higher, as the acids will be partially neutralized by the carbonates.

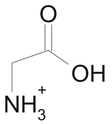
4.4.7 Benzoic Acid

In the food industry, benzoic acid (E 210 according to European codification), sodium benzoate (E 211), potassium benozoate (E 212), and calcium benzoate (E 213) are used as preservatives in ketchup, sausages, mustard, sauces, margarine, fish salads, and pickled foods. Benzoic acid is a moderately strong acid with $pK_a = 4.19$. However, the acid is only sparingly soluble in water (2.9 g l^{-1}, i.e., 0.024 mol L^{-1} at 25 °C). Fig. 67 shows the pH-logc_i diagram of benzoic acid for an overall concentration of 0.01 mol L^{-1}. The pH of a solution containing 10^{-2} mol L^{-1} benzoic acid can be read at P_1 ($c_{H_3O^+} \approx c_{benzoate^-}$): it is 3.10. The pH of a solution containing 10^{-2} mol L^{-1} sodium benzoate can be read at P_2 ($c_{OH^-} \approx c_{benzoic\ acid}$): it is 8.1.

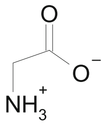
Fig. 67 pH-logc_i diagram of benzoic acid at an overall concentration of 0.01 mol L^{-1}



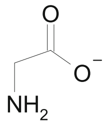
4.4.8 Glycine



H_2G^+



$HG^{+/-}$



G^-

Glycine is the most simple α-amino acid. It is an essential amino acid and a constituent of most proteins. It cannot be synthesized by the human organism. In aqueous solution, it exists mainly in the zwitterionic form $HG^{+/-}$ because the carboxylate group is so acidic (pK_{a1} (H_2G^+) $= 2.4$) that it protonates the amino group (pK_{a2} ($HG^{+/-}$) $= 9.8$). In glycine hydrochloride, it is in the cationic form (H_2G^+), i.e., both the amino group and the carboxylate group are protonated (Fig. 68).

The diagram makes it possible to read the following pH values:

P_1: aqueous solution containing 0.1 mol L^{-1} glycine hydrochloride: $c_{H_3O^+} \approx c_{HG^{+/-}}$, pH $= 1.71$.

P_2: aqueous solution containing 0.1 mol L^{-1} glycine: $c_{H_2G^+} \approx c_{G^-}$, pH $= 6.1$.

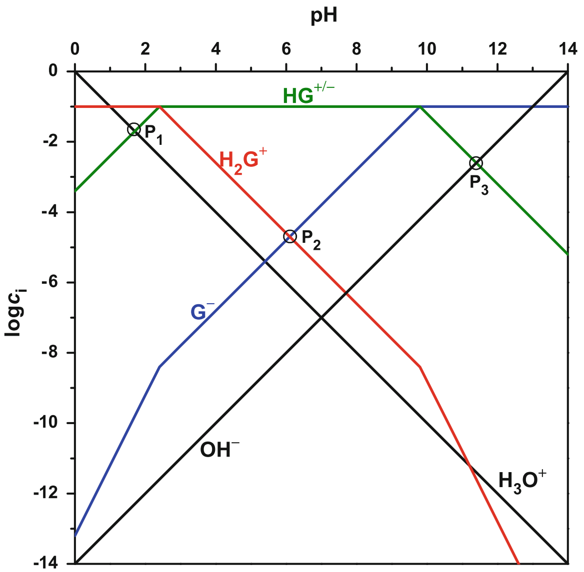
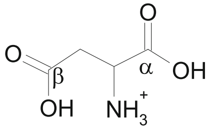


Fig. 68 pH-logc_i diagram of glycine at an overall concentration of 0.1 mol L^{-1}

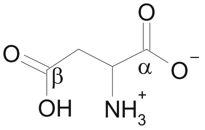
P_3: aqueous solution containing 0.1 mol L^{-1} sodium glycinate: $c_{OH^-} \approx c_{HG^{+/-}}$, pH = 11.41.

Comment: P_2 is called the *isoelectric point*; the amino acid exists there mainly in the zwitterionic form, and only in very small and equal concentrations of the cationic and anionic forms. In an electric field, amino acids do not move at that pH, which is important in electrophoresis for isoelectric focussing.

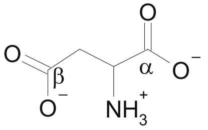
4.4.9 Aspartic Acid



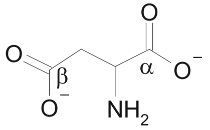
H_3A^+



$H_2A^{+/-}$



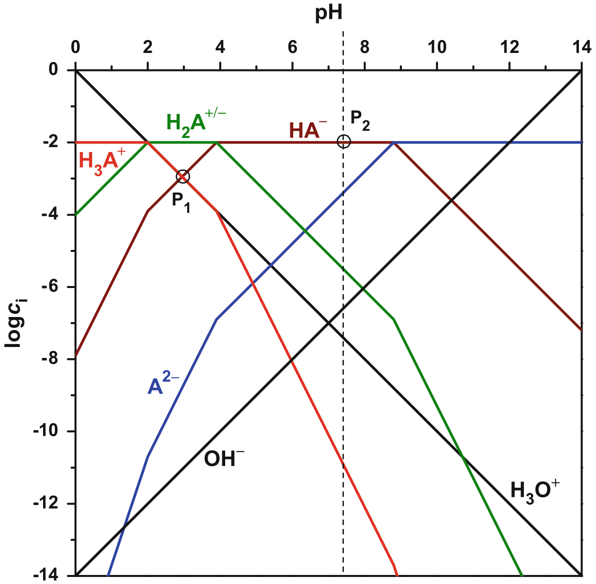
HA^- (hydrogenaspartate)



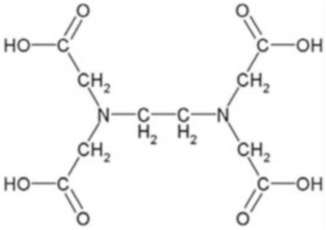
A^{2-}

Frequently, hydrogen aspartate is called aspartate because the real aspartate (A^{2-}) does not exist in significant concentrations under physiological conditions. Aspartic acid has two carboxyl groups. The carboxyl group at the α-C atom ($pK_{a1} = 2.0$) is more acidic than that at the β-C atom ($pK_{a2} = 3.9$). pK_{a3}, i.e., the pK_a value of the ammonium group is 8.8. Figure 69 shows the pH-logc_i diagram of aspartic acid at an overall concentration of 0.01 mol L^{-1}. The isoelectric point (P_1: $c_{H_3A^+} \approx c_{HA^-}$) is at pH = 2.95. Under physiological conditions (pH = 7.4), hydrogen aspartate is the dominating species (P_2 in Fig. 69).

Fig. 69 pH-logc_i diagram of aspartic acid at an overall concentration of 0.01 mol L^{-1}



4.4.10 Ethylenediaminetetraacetic Acid (EDTA)



Ethylenediaminetetraacetic acid (H_4Y) plays an important role as a complex-forming reagent because it forms chelate complexes. For the metal complex formation of the ligand, i.e., the anion base Y^{4-}, the protonation equilibria of the ligand are very important. The acid H_4Y is a tetrabasic acid. Instead of the sparingly soluble acid H_4Y, the disodium or the trisodium salts are normally used in complexometric titrations. In a pH-logc_i diagram, one can easily read the pH values of these solutions: given an overall concentration of EDTA of 0.02 mol L^{-1} ($\log C_\mathrm{i}^{\circ} = -1.70$), which is a common concentration for complexometric titrations, Fig. 70 depicts the pH-logc_i diagram.

The diagram makes it possible to read the following pH values:

P$_1$: aqueous solution of 0.02 mol L^{-1} EDTE (H_4Y): $c_{H_3O^+} \approx c_{H_3Y^-}$, pH = 1.89.

P$_2$: aqueous solution of 0.02 mol L^{-1} Na EDTE (NaH_3Y): $c_{H_4Y} \approx c_{H_2Y^{2-}}$, pH = 2.41.

P$_3$: aqueous solution of 0.02 mol L^{-1} Na$_2$ EDTE (Na_2H_2Y): $c_{H_3Y^-} \approx c_{HY^{3-}}$, pH = 4.50.

P$_4$: aqueous solution of 0.02 mol L^{-1} Na$_3$ EDTE (Na_3HY): $c_{H_2Y^{2-}} \approx c_{Y^{4-}}$, pH = 8.29.

P$_5$: aqueous solution of 0.02 mol L^{-1} Na$_4$ EDTE (Na_4Y): $c_{OH^-} \approx c_{HY^{3-}}$, pH = 11.34.

The pH-logc_i diagram is very useful to find the pH at which a solution should be buffered for a successful complexometric titration. This can be demonstrated as follows: given a solution containing 10^{-1} mol L^{-1} Ca^{2+} ions ($C^{\circ}_{Ca^{2+}}$). The question is: at what pH this titration can be performed with an error not exceeding 1 %?

$1\ \%$ of 10^{-1} mol L^{-1} $\hat{=}$ 10^{-3} mol L^{-1}

This is the maximum concentration of calcium $c^{\mathrm{eqp}}_{Ca^{2+}}$ which may be left uncomplexated at the equivalence point. Since complex formation proceeds in a 1:1 ratio, this is also the overall concentration of EDTA which may stay in the solution at the equivalence point. Figure 71 shows the pH-logc_i diagram of EDTA for $\log C_\mathrm{i}^{\circ} = -3$.

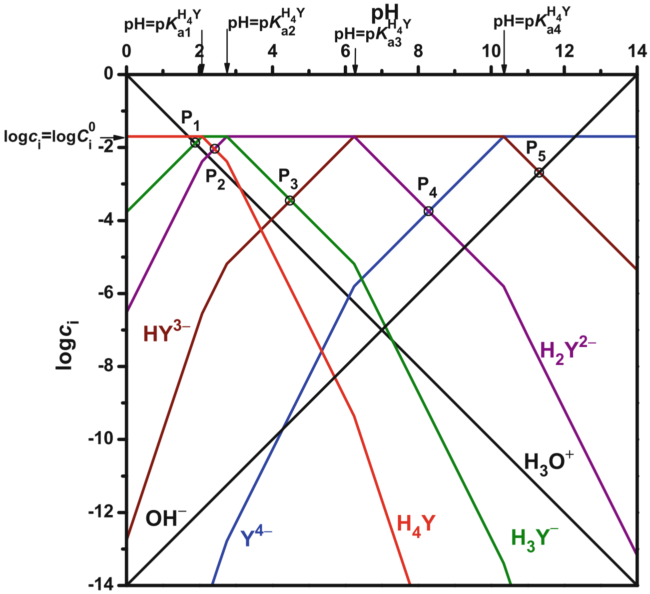


Fig. 70 pH-logc_i of an EDTA solution ($\log C_i^{\circ} = -1.70$, p$K_{a1} = 2.07$, p$K_{a2} = 2.75$, p$K_{a3} = 6.24$, p$K_{a4} = 10.34$)

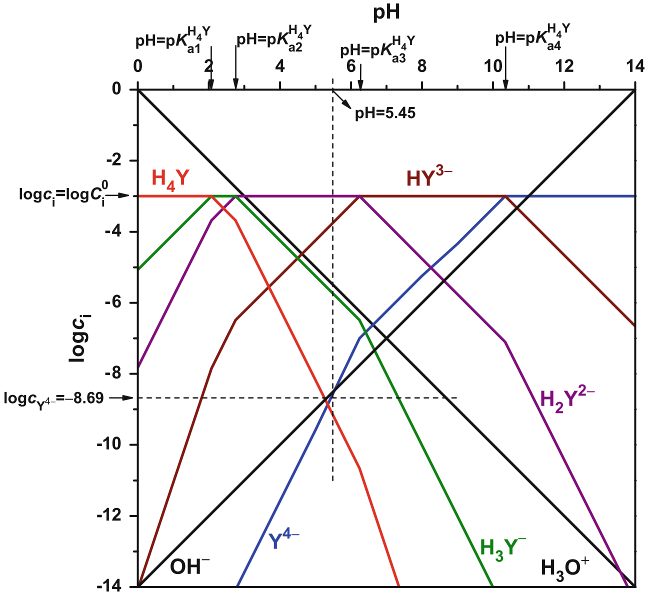


Fig. 71 pH-logc_i diagram of EDTA ($\log C_i^{\circ} = -3$, p$K_{a1} = 2.07$, p$K_{a2} = 2.75$, p$K_{a3} = 6.24$, p$K_{a4} = 10.34$)

From the stability constant of the Ca^{2+}-EDTA complex ($K_{stab} = 10^{10.69}\ \text{mol L}^{-1}$) one can calculate the allowable equilibrium concentration of the free ligand Y^{4-}. For this, only the protonations of the ligand have to be taken into account, and possible side reactions of calcium ions may be disregarded. For the equilibrium concentration of the Ca^{2+}-EDTA complex $c_{CaY^{2-}}$ one can use the starting concentration of calcium ions $C^{\circ}_{Ca^{2+}}$ as a good approximation, since the error should be smaller than 1 %:

$$K_{stab} = \frac{c_{CaY^{2-}}}{c^{eqp}_{Ca^{2+}} c_{Y^{4-}}} \tag{183}$$

$$c_{Y^{4-}} = \frac{c_{CaY^{2-}}}{K_{stab} c^{eqp}_{Ca^{2+}}} \approx \frac{C^{\circ}_{Ca^{2+}}}{K_{stab} c^{eqp}_{Ca^{2+}}} = \frac{10^{-1}}{10^{10.69}\, 10^{-3}}\,\text{mol L}^{-1} = 10^{-8.69}\text{mol L}^{-1} \tag{184}$$

This equilibrium concentration of Y^{4-} is in the solution at pH = 5.45 (cf. Fig. 71). This means that the pH should be kept at least at 5.45 (or higher), when the error should be kept equal to or smaller than 1 %.

Literature

1. Narasaki H (1979) Talanta 26:605–607
2. Narasaki H (1980) Talanta 27:187–191
3. Narasaki H (1980) Talanta 27:193–199
4. Narasaki H (1980) Talanta 27:409–415
5. Henrion G, Schmidt R, Marquardt D (1980) Z Chem 20:433–436
6. Narasaki H (1987) Fresenius Z Anal Chem 328:633–638
7. Bliefert C (1978) pH-Wert-Berechnungen. Verlag Chemie, Weinheim
8. Doğan A, Kılıç E (2007) Anal Biochem 365:7–13
9. Henrion G, Scholz F, Schmidt W, Zettler M (1982) Z Phys Chem (Leipzig) 263:634–636

The Use of pH-logc_i Diagrams for the Construction of Titration Diagrams

5

Diagrams displaying acid–base titrations show the pH on the *y*-axis as a function of the advancement of the titration. The advancement of titration can be given by the added volume of titrator. However, using the volume of added titrator on the *x*-axis, each titration would need a differently scaled *x*-axis. To avoid this, one likes to use a normation, which is possible by calculating a so-called "degree of titration" τ (lower case Greek letter "tau"). The degree of titration can be defined as follows:

$$\tau = \frac{\text{added amount of titrator [in mol]}}{\text{amount of titrator [in mol] which is necessary to reach the equivalence point}}.$$

▶ Different definitions are given in the literature. However, since they are more difficult to grasp, the above definition is given here.

The degree of titration can assume values between zero and infinity. It is unity (1.00) at the equivalence point, that is, for an almost 100 % conversion of the titrated species, and exactly an addition of 100 % of the titrator with respect to the titrated species. To easily understand titration diagrams, it makes sense to plot them in the range of $\tau = 0$ to $\tau = 2$. The condition $\tau = 2$ means a 100 % *overtitration*, which means that 200 % of the titrator has been added with respect to the amount of species to be titrated. One should understand here that the titration reaction takes place only up to $\tau = 1$, and after $\tau = 1$ the amount of reacting species tends to zero (although it is not zero because the equilibrium is still shifted). For small equilibrium constants of the titration reaction, the amount of species that are converted after $\tau = 1$ may of course be more significant. Such titration reactions are certainly less useful for analytical purposes.

It is important to understand that the degree of titration is a normation giving the advancement of titration.

H. Kahlert and F. Scholz, *Acid-Base Diagrams*,
DOI 10.1007/978-3-642-37902-4_5,

▶ Comment: the lambda value measured with the help of lambda probes in cars is nothing but a degree of titration, here the degree of oxidation of the petrol by the oxygen of the air. The burning of petrol can be considered a redox titration!

When mixtures of acids or polybasic acids are titrated, there is the problem of how to define the "amount of titrator [in mol] which is necessary to reach the equivalence point": there is no common rule for this, but it makes sense to take here the **overall amount of protons that can be titrated**. This would mean that in the case of phosphoric acid, the first proton is titrated at $\tau = 1/3$ (yielding a solution mainly containing $H_2PO_4^-$), the second proton is titrated at $\tau = 2/3$ (yielding a solution mainly containing HPO_4^{2-}), and the third proton is titrated at $\tau = 3/3 = 1$ (yielding a solution mainly containing PO_4^{3-}). Of course one may define τ *also* in such way that it is 1 for the titration of the first, 2 for the titration of the second, and 3 for the titration of the third proton. In that case, one should plot the diagram in the range $0 \leq \tau \leq 4$ so as to reach a final concentration of NaOH that is equivalent to the starting concentration of phosphoric acid. Titrations of bases can be treated in an analogous way, as it will be shown in some examples.

Of course, titration curves can be also completely (and exactly) calculated, and software packages are available for this (e.g., at http://www2.iq.usp.br/docente/gutz/Curtipot_.html). However, such calculations are beyond the scope of this book, which is focused on demonstrating how titration diagrams can be constructed in such a way that the most important features are displayed.

For constructing titration diagrams from pH-logc_i diagrams, the latter have to be turned by 90° to the right, then the mirror image (with respect to the horizontal line at pH = 7) has to be produced (cf. Fig. 72a, b, c). The resulting pH-logc_i diagram allows the parallel arrangement of the titration diagram (see Fig. 72d).

For the construction of titration diagrams, the dilution which occurs during titration can be disregarded, as normally the volume of added titrator is smaller than the volume of titrand, and dilution affects the curves only marginally.

In constructing titration diagrams, the following idea is very helpful: *a titration is a synthesis*, i.e., by titrating hydrochloric acid with sodium hydroxide, one has synthesized a pure sodium chloride solution when $\tau = 1.0$ ($c_{Na^+} = c_{Cl^-} = \frac{1}{1} C^{\circ}_{\text{hydrochloric acid}}$) is reached. At $\tau = 0.5$, one has performed only 50 % of the synthesis, and the solution contains equal concentrations of sodium chloride and hydrochloric acid. At $\tau = 1.5$, the hydrochloric acid has been completely (100 %) converted to sodium chloride, and the solution contains an excess of 50 % of sodium hydroxide. At $\tau = 2.0$, that excess amounts to 100 %.

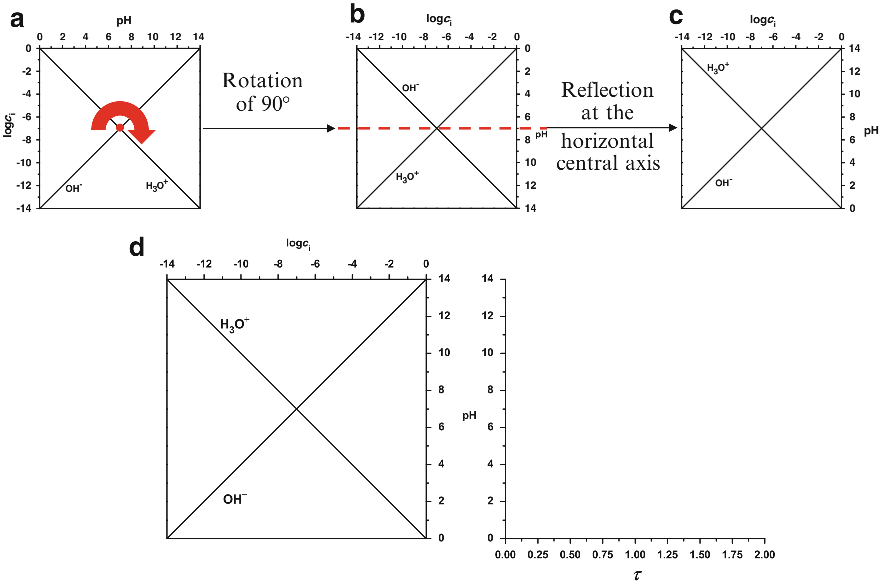


Fig. 72 (**a**) pH-logc_i diagram. (**b**) pH-logc_i following a turning by 90° to the right side (*around the center*). (**c**) pH-logc_i diagram resulting in (**b**) and mirrored at the middle axis (pH = 7). (**d**) pH-logc_i diagram together with the titration diagram, so that both pH scales are parallel aligned

5.1 Titration of Hydrochloric Acid of Various Concentrations with Sodium Hydroxide Solution

Figure 73 shows the titration diagram of hydrochloric acid ($\log C^{\circ}_{\text{hydrochloric acid}} = -1$) with sodium hydroxide solution.

The following pH values can be taken from the pH-logc_i diagram to construct the titration diagram (always disregarding the dilution):

P₁: $\tau = 0.0$; starting point of the titration (i.e., condition before titration), $C^{\circ}_{\text{hydrochloric acid}} = c_{\text{Cl}^-} = c_{\text{H}_3\text{O}^+}$, pH = 1.

P₂: $\tau = 0.9$; the concentration of hydrochloric acid is 10 % of the starting concentration, i.e., 0.01 mol L^{-1}, pH = 2.

P₃: $\tau = 0.99$; the concentration of hydrochloric acid is 1 % of the starting concentration, i.e., 0.001 mol L^{-1}, pH = 3.

P₄: $\tau = 1.0$; the added amount of sodium hydroxide exactly equals the amount of hydrochloric acid at the start of the titration, i.e., there is only sodium chloride dissolved in the solution ($c_{\text{Na}^+} = c_{\text{Cl}^-} = \frac{1}{1} C^{\circ}_{\text{hydrochloric acid}}$). The solution is neutral, i.e., pH = 7.

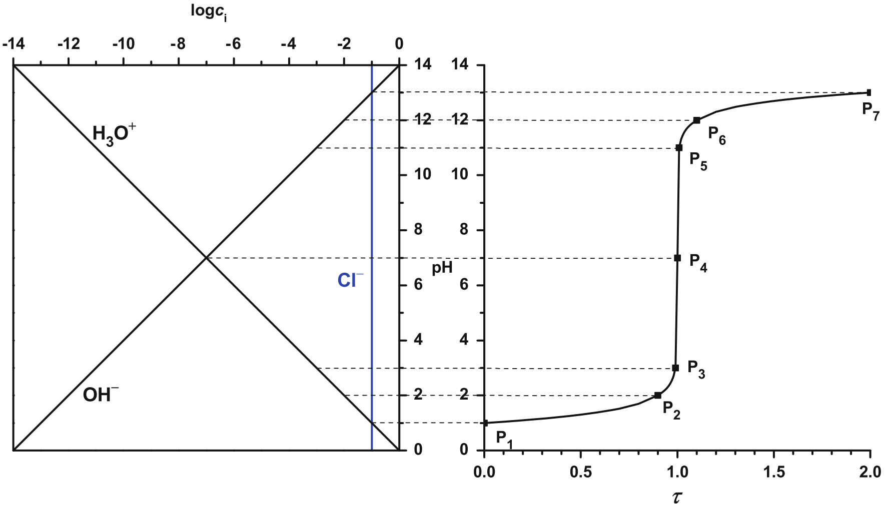


Fig. 73 Titration diagram of hydrochloric acid ($\log C^{\circ}_{\text{hydrochloric acid}} = -1$) with sodium hydroxide solution

P$_5$: $\tau = 1.01$; this is a solution of sodium chloride with additional sodium hydroxide: $c_{\text{OH}^-} = \frac{1}{100} C^{\circ}_{\text{hydrochloricacid}} = 0.001\ \text{molL}^{-1}$ (the concentration of sodium ions is not relevant for the titration; however, it can be given as follows: $c_{\text{Na}^+} = \left(\frac{1}{1} + \frac{1}{100}\right) C^{\circ}_{\text{hydrochloricacid}} = 0.101\ \text{molL}^{-1}$), pH = 11.

P$_6$: $\tau = 1.1$; this is a solution of sodium chloride with additional sodium hydroxide: $c_{\text{OH}^-} = \frac{1}{10} C^{\circ}_{\text{hydrochloric acid}} = 0.01\ \text{mol L}^{-1}$ ($c_{\text{Na}^+} = \left(\frac{1}{1} + \frac{1}{10}\right) C^{\circ}_{\text{hydrochloric acid}} = 0.11$ mol L^{-1}), pH = 12.

P$_7$: $\tau = 2.0$; this is a solution of sodium chloride with additional sodium hydroxide: $c_{\text{OH}^-} = \frac{1}{1} C^{\circ}_{\text{hydrochloric acid}} = 0.1\ \text{molL}^{-1}$ ($c_{\text{Na}^+} = \left(\frac{1}{1} + \frac{1}{1}\right) C^{\circ}_{\text{hydrochloric acid}} = 0.2$ mol L^{-1}), pH = 13.

Figure 74 displays a number of titration curves for different starting concentrations of hydrochloric acid. The important conclusions from this figure are: (i) the pH at the equivalence point is unaffected by the starting concentration, i.e., always 7.0, (ii) the pH jump around the equivalence point, defined as ΔpH between $\tau = 0.99$ and $\tau = 1.01$, decreases with decreasing initial concentration of hydrochloric acid. This means that $\frac{\text{dpH}}{\text{d}\tau}$ decreases with decreasing initial concentration (this feature is not noticeable in the diagram because of the used scales). Decreasing $\frac{\text{dpH}}{\text{d}\tau}$ leads to increasing random errors, which will be explained further down when errors are explained.

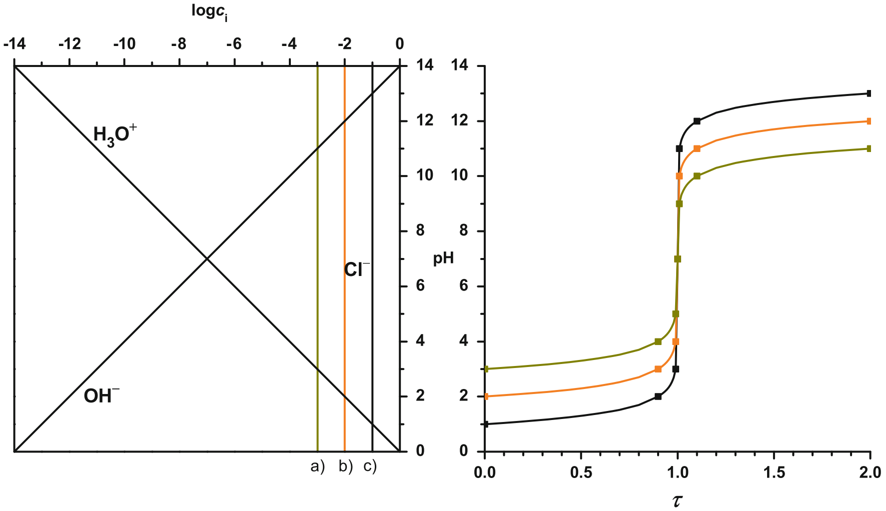


Fig. 74 Titration diagram of hydrochloric acid solutions of different concentrations with sodium hydroxide solution. (**a**) $\log C^{\circ}_{\text{hydrochloric acid}} = -3$. (**b**) $\log C^{\circ}_{\text{hydrochloric acid}} = -2$. (**c**) $\log C^{\circ}_{\text{hydrochloric acid}} = -1$

5.2 Titration of Sodium Hydroxide Solution with Hydrochloric Acid

The following pH values can be taken from the pH-logc_i diagram to construct the titration diagram (always disregarding the dilution) (Fig. 75):

P$_1$: $\tau = 0.0$; starting point of the titration (i.e., condition before titration), $C^{\circ}_{\text{NaOH}} = c_{\text{Na}^+} = c_{\text{OH}^-}$, pH = 13.

P$_2$: $\tau = 0.9$; the concentration of sodium hydroxide is 10 % of the starting concentration, i.e., 0.01 mol L^{-1}, pH = 12.

P$_3$: $\tau = 0.99$; the concentration of sodium hydroxide is 1 % of the starting concentration, i.e., 0.001 mol L^{-1}, pH = 11.

P$_4$: $\tau = 1.0$; the added amount of hydrochloric acid exactly equals the amount of sodium hydroxide at the start of the titration, i.e., there is only sodium chloride dissolved in the solution ($c_{\text{Na}^+} = c_{\text{Cl}^-} = \frac{1}{1} C^{\circ}_{\text{NaOH}}$). The solution is neutral, i.e., pH = 7.

P$_5$: $\tau = 1.01$; this is a solution of sodium chloride with additional hydrochloric acid: $c_{\text{H}_3\text{O}^+} = \frac{1}{100} C^{\circ}_{\text{NaOH}} = 0.001 \text{ mol L}^{-1}$ (the concentration of chloride ions is not relevant for the titration; however, it can be given as follows: $c_{\text{Cl}^-} = \left(\frac{1}{1} + \frac{1}{100}\right) C^{\circ}_{\text{NaOH}} = 0.101 \text{ mol L}^{-1}$), pH = 3.

P$_6$: $\tau = 1.1$; this is a solution of sodium chloride with additional hydrochloric acid: $c_{\text{H}_3\text{O}^+} = \frac{1}{10} C^{\circ}_{\text{NaOH}} = 0.01 \text{ mol L}^{-1}$ ($c_{\text{Cl}^-} = \left(\frac{1}{1} + \frac{1}{10}\right) C^{\circ}_{\text{NaOH}} = 0.11 \text{ mol L}^{-1}$), pH = 2.

P$_7$: $\tau = 2.0$; this is a solution of sodium chloride with additional hydrochloric acid: $c_{\text{H}_3\text{O}^+} = \frac{1}{1} C^{\circ}_{\text{NaOH}} = 0.1 \text{ mol L}^{-1}$ ($c_{\text{Cl}^-} = \left(\frac{1}{1} + \frac{1}{1}\right) C^{\circ}_{\text{NaOH}} = 0.2 \text{ mol L}^{-1}$), pH = 1.

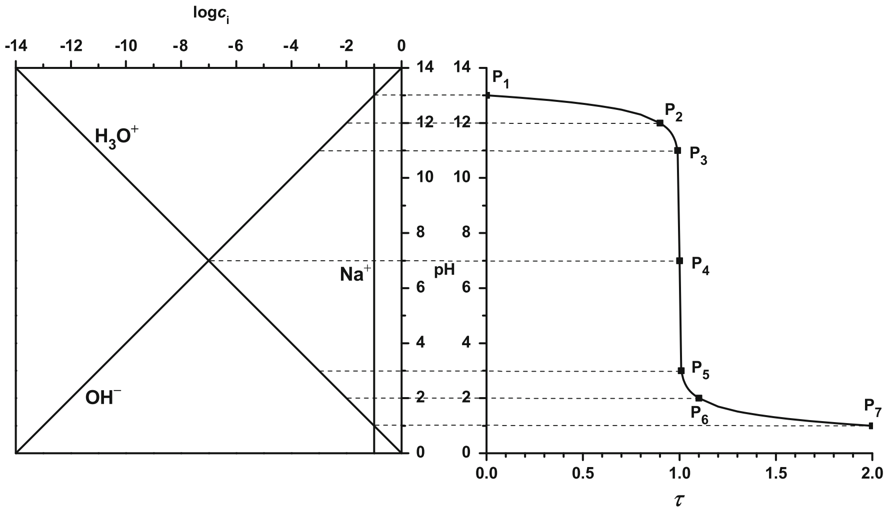


Fig. 75 Titration diagram of sodium hydroxide with hydrochloric acid ($\log C^{\circ}_{\mathrm{NaOH}} = -1$)

5.3 Titration of Different Concentrations of Acetic Acid with Sodium Hydroxide

The following pH values can be taken from the pH-logc_i diagram to construct the titration diagram (always disregarding the dilution) (Fig. 76):

P$_1$: $\tau = 0.0$; starting point of the titration (i.e., condition before titration), $c_{\mathrm{H_3O^+}} \approx c_{\mathrm{Ac^-}}$ (see Sect. 4.1.3.1, Eq. (93)), pH = 2.88.

P$_2$: $\tau = 0.5$; acetic acid and acetate are present at equal concentrations. This is the so-called buffer point: $c_{\mathrm{HAc}} = c_{\mathrm{Ac^-}}$, pH = p$K_a$ = 4.75.

P$_3$: $\tau = 1.0$; the added amount of sodium hydroxide exactly equals the amount of acetic acid at the start of the titration, i.e., there is only sodium acetate dissolved in the solution: $c_{\mathrm{HAc}} \approx c_{\mathrm{OH^-}}$ (see Sect. 4.1.2.3, Eq. (84)), pH = 8.875. The solution is basic at the equivalence point!

P$_4$: $\tau = 1.01$; this is a solution of sodium acetate with additional sodium hydroxide. From the presence of NaOH, the additional concentration of OH$^-$ ions is: $c_{\mathrm{OH^-}} = \frac{1}{100} C^{\circ}_{\mathrm{aceticacid}} = 0.001\ \mathrm{mol\ L^{-1}}$. The OH$^-$ concentration formed by protonation of acetate ions is smaller than 10^{-7} mol L^{-1}, and hence it can be disregarded: the pH is 11.

P$_5$: $\tau = 1.1$; this is a solution of sodium acetate with additional sodium hydroxide. From the presence of NaOH the additional concentration of OH$^-$ ions is: $c_{\mathrm{OH^-}} = \frac{1}{10} C^{\circ}_{\mathrm{aceticacid}} = 0.01\ \mathrm{mol\ L^{-1}}$. The OH$^-$ concentration formed by protonation of acetate ions is smaller than 10^{-8} mol L^{-1}, and hence it can be disregarded: the pH is 12.

P$_6$: $\tau = 2.0$; this is a solution of sodium acetate with additional sodium hydroxide: $c_{\mathrm{OH^-}} = \frac{1}{1} C^{\circ}_{\mathrm{aceticacid}} = 0.1\ \mathrm{mol\ L^{-1}}$, pH = 13.

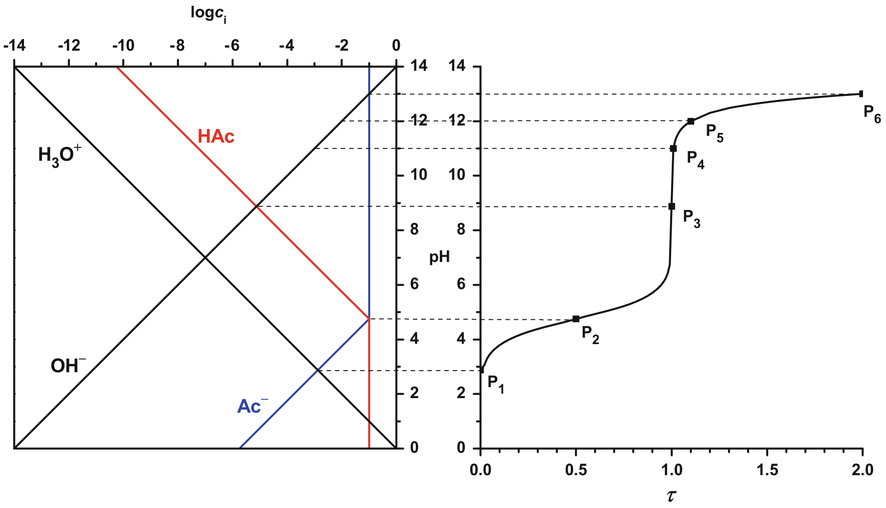


Fig. 76 Titration diagram of acetic acid ($\log C^{\circ}_{\text{acetic acid}} = -1$; $pK_a = 4.75$) with sodium hydroxide

Figure 77 shows the titration diagrams of acetic acid of different concentrations.
P_1: Equivalence point for acetic acid with $\log C^{\circ}_{\text{acetic acid}} = -3$, pH = 7.875.

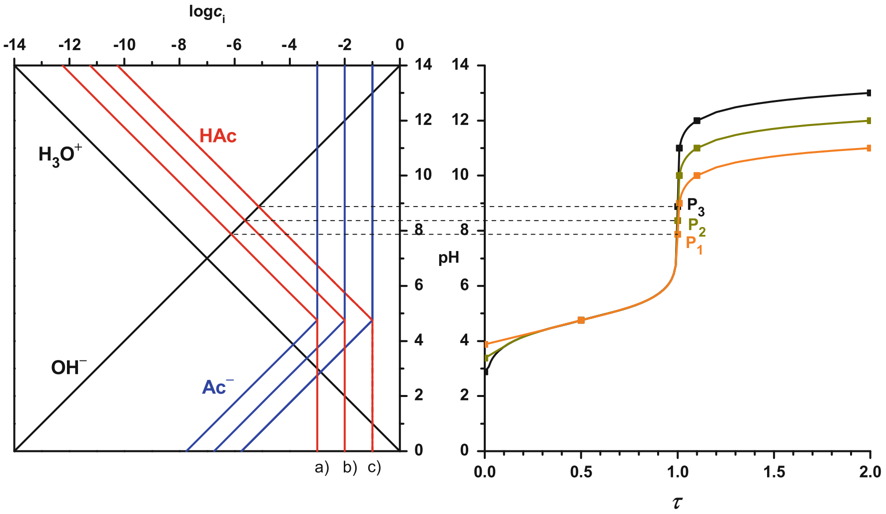


Fig. 77 Titration diagrams of acetic acid of different concentrations ($pK_a = 4.75$) with sodium hydroxide. (**a**) $\log C^{\circ}_{\text{acetic acid}} = -3$. (**b**) $\log C^{\circ}_{\text{acetic acid}} = -2$. (**c**) $\log C^{\circ}_{\text{acetic acid}} = -1$

P_2: Equivalence point for acetic acid with $\log C^{\circ}_{\text{acetic acid}} = -2$, pH $= 8.375$.
P_3: Equivalence point for acetic acid with $\log C^{\circ}_{\text{acetic acid}} = -1$, pH $= 8.875$.

The important conclusions from this figure are: (i) the pH at the equivalence point decreases with decreasing concentration, (ii) the pH jump around the equivalence point, defined as ΔpH between $\tau = 0.99$ and $\tau = 1.01$, decreases with decreasing concentration. The latter also means that the slope $\frac{\mathrm{dpH}}{\mathrm{d}\tau}$ decreases with concentration, and thus the random error will increase, since the random error is always related to a constant ΔpH typical for a certain indication method (see further down the discussion of random errors of titrations).

5.4 Titration of Moderately Strong Acids Having Different pK_a Values with Sodium Hydroxide

Figures 78, 79, and 80 show titration diagrams of three moderately strong acids with different pK_a values. In each diagram, only for one case are the distinct points of titration labeled. They are derived from the pH-logc_i diagrams as in the case of acetic acid (see Sect. 5.3).

The most important conclusions from these figures are: (i) the pH at the buffer point increases with increasing pK_a values, (ii) the pH at the equivalence points increases with increasing pK_a values, and (iii) the pH jump around the equivalence point, defined as ΔpH between $\tau = 0.99$ and $\tau = 1.01$, decreases with increasing pK_a values. The latter means that the slope $\frac{\mathrm{dpH}}{\mathrm{d}\tau}$ decreases also with increasing pK_a values, which leads to increasing random errors, as any indication always relates to a specific constant ΔpH (see further down the discussion of random errors of titrations).

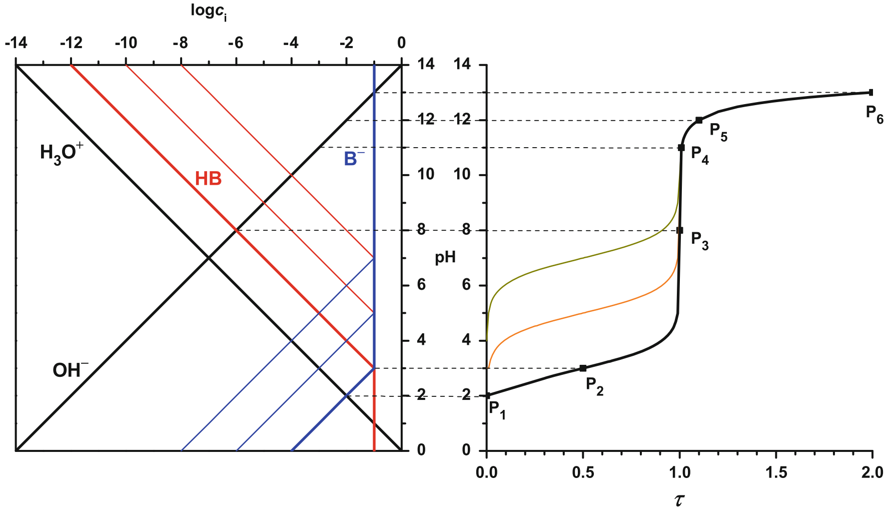


Fig. 78 Titration diagrams of three acids ($\log C^{\circ}_{\text{acid}} = -1$) with p$K_a = 3$ (*black line*), p$K_a = 5$ (*orange line*), and p$K_a = 7$ (*olive line*) with sodium hydroxide solution. The distinctive points are given only for p$K_a = 3$

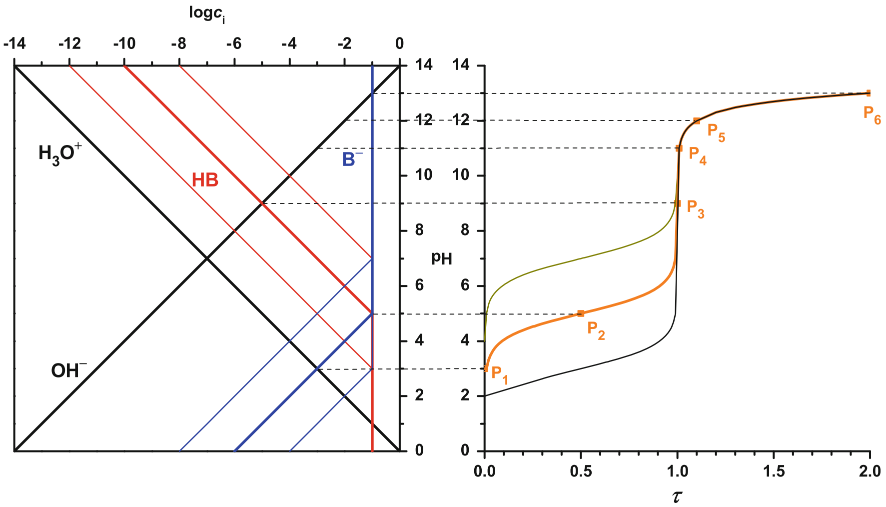


Fig. 79 Titration diagrams of three acids ($\log C^{\circ}_{\text{acid}} = -1$) with p$K_a$ = 3 (*black line*); pK_a = 5 (*orange line*) and pK_a = 7 (*olive line*) with sodium hydroxide solution. The distinctive points are given only for pK_a = 5

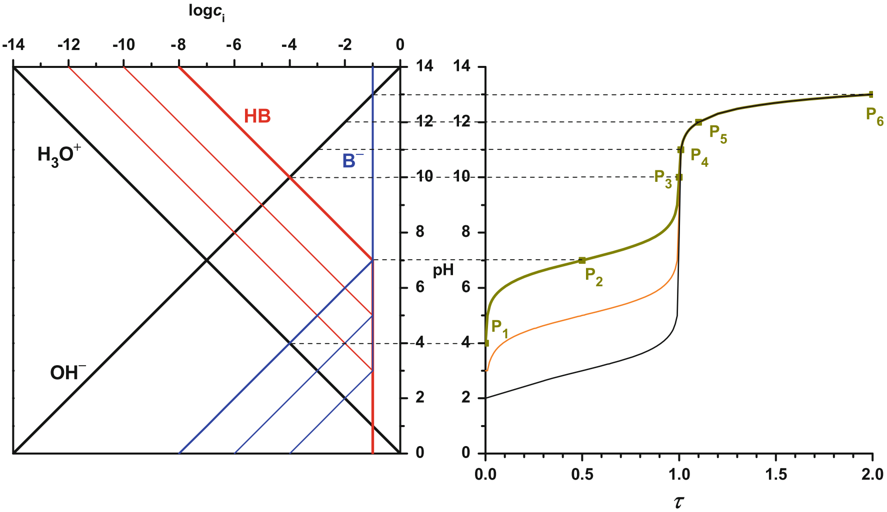


Fig. 80 Titration diagrams of three acids ($\log C^{\circ}_{\text{acid}} = -1$) with p$K_a$ = 3 (*black line*); pK_a = 5 (*orange line*) and pK_a = 7 (*olive line*) with sodium hydroxide solution. The distinctive points are given only for pK_a = 7

5.5 Titration of Sulfuric Acid

In Sect. 4.2.1.1, it was explained how the pH of sulfuric acid solutions has to be calculated. For constructing the titration diagram, a number of the simplifications used there can be applied again (see Fig. 81).

The following pH values can be taken from the pH-logc_i diagram to construct the titration diagram (always disregarding the dilution):

P₁: $\tau = 0.0$; starting point of titration: it is a good simplification to write $c_{H_3O^+} = c_{HSO_4^-}$, and this gives pH = 1. This means disregarding the protolysis of HSO_4^-, which should not (!) be done in calculating the pH (see Sect. 4.2.1.1), as a calculation with Eq. (122) gives pH = 0.96.

P₂: $\tau = 0.5$; the added amount of sodium hydroxide is such that a solution containing 0.1 mol L^{-1} sodium hydrogen sulfate results (see Sect. 4.2.2.1), i.e., it holds that $c_{H_3O^+} \approx c_{B^{2-}}$ (Eq. (139)): pH = 1.54.

P₃: $\tau = 0.75$; the solution contains equal concentrations of sulfate and hydrogen sulfate, i.e., it is hydrogen sulfate/sulfate buffer: $c_{HSO_4^-} = c_{SO_4^{2-}}$ pH = pK_{a2} = 1.99.

P₄: $\tau = 1.0$; the added amount of sodium hydroxide exactly equals the amount of titratable protons, it is twice the amount of sulfuric acid. It is a solution of sodium sulfate. Protolysis leads to $c_{HSO_4^-} = c_{OH^-}$: pH = 7.49.

P₅: $\tau = 1.005$; this is a solution of sodium sulfate with additional sodium hydroxide: $c_{OH^-} = \frac{1}{100} C^{\circ}_{\text{sulfuric acid}} = 0.001$ mol L^{-1}: pH = 11. The pH effect due to the protonation of SO_4^{2-} can be disregarded.

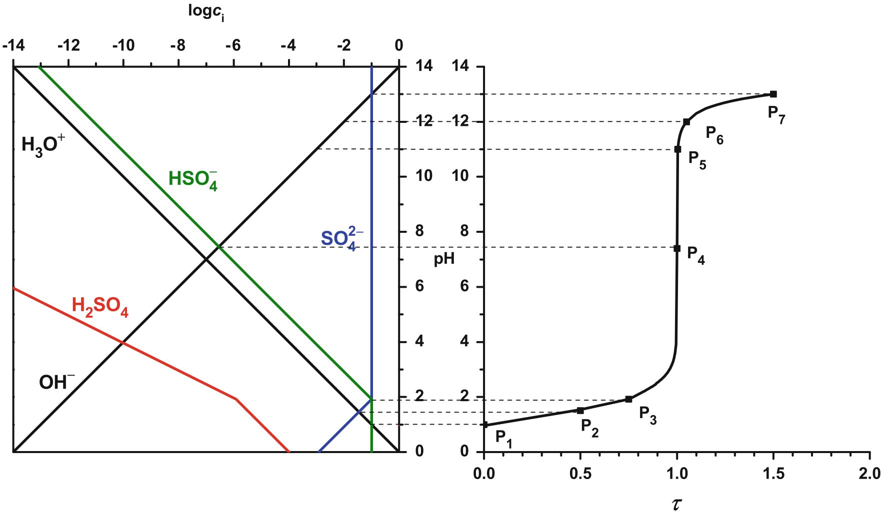


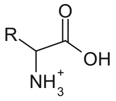
Fig. 81 Titration diagram of sulfuric acid (log $C^{\circ}_{\text{sulfuric acid}} = -1$), p$K_{a1} = -3$, p$K_{a2} = 1.99$ with sodium hydroxide

P_6: $\tau = 1.05$; this is a solution of sodium sulfate with additional sodium hydroxide: $c_{\mathrm{OH^-}} = \frac{1}{10} C^{\mathrm{O}}_{\text{sulfuric acid}} = 0.01\ \mathrm{mol\ L^{-1}}$, pH = 12. The pH effect due to the protonation of $\mathrm{SO_4^{2-}}$ can be disregarded.

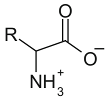
P_7: $\tau = 1.5$; this is a solution of sodium sulfate with additional sodium hydroxide: $c_{\mathrm{OH^-}} = \frac{1}{1} C^{\mathrm{O}}_{\text{sulfuric acid}} = 0.1\ \mathrm{mol\ L^{-1}}$, pH = 13. The pH effect due to the protonation of $\mathrm{SO_4^{2-}}$ can be disregarded.

5.6 Titration of Dibasic Amino Acids

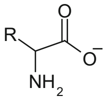
Amino acids are commercially available as so-called hydrochlorides, i.e., in the form of the salts $\mathrm{H_2AS^+Cl^-}$ (see Sects. 4.2.1.2 and 4.4.8). This is the reason that the titration of $\mathrm{H_2AS^+}$ will be discussed here (see Fig. 82). In the pH-logc_i diagram, the following three forms of the amino acid have been coded as follows:



$\mathrm{H_2AS^+}$



$\mathrm{HAS^{+/-}}$



$\mathrm{AS^-}$

The following pH values can be taken from the pH-logc_i diagram to construct the titration diagram (always disregarding the dilution):

P_1: $\tau = 0.0$; starting point of titration: $c_{\mathrm{H_3O^+}} \approx c_{\mathrm{HAS^{+/-}}}$.

P_2: $\tau = 0.25$; one half of the initial amount of $\mathrm{H_2AS^+}$ has been converted to $\mathrm{HAS^{+/-}}$, i.e., the solution contains a buffer: $c_{\mathrm{H_2AS^+}} \approx c_{\mathrm{HAS^{+/-}}}$ and pH = pK_{a1}.

P_3: $\tau = 0.5$; the added amount of sodium hydroxide exactly equals the initial amount of the hydrochloride. Hence the amino acid is present in its zwitterionic form $\mathrm{HAS^{+/-}}$: $c_{\mathrm{H_2AS^+}} \approx c_{\mathrm{AS^-}}$ and Eq. (156) $c_{\mathrm{H_3O^+}} = \sqrt{K_{\mathrm{a1}} K_{\mathrm{a2}}}$ is valid so that pH $= \frac{\mathrm{p}K_{\mathrm{a1}} + \mathrm{p}K_{\mathrm{a2}}}{2}$.

P_4: $\tau = 0.75$; one half of $\mathrm{HAS^{+/-}}$ has been converted to $\mathrm{AS^-}$, i.e., another buffer results: $c_{\mathrm{HAS^{+/-}}} = c_{\mathrm{AS^-}}$ and pH = pK_{a2}.

P_5: $\tau = 1.0$; the added amount of sodium hydroxide exactly equals the amount of titratable protons of the dibasic amino acid. This is a solution of $\mathrm{Na^+AS^-}$. Protonation of $\mathrm{AS^-}$ gives: $c_{\mathrm{OH^-}} \approx c_{\mathrm{HAS^{+/-}}}$.

P_6: $\tau = 1.5$; this is a solution of $\mathrm{Na^+AS^-}$ containing additional sodium hydroxide: $c_{\mathrm{OH^-}} = \frac{1}{1} C^{\mathrm{O}}_{\text{alanine}} = 0.1\ \mathrm{mol\ L^{-1}}$. The pH effect due to the protonation of $\mathrm{AS^-}$ can be disregarded.

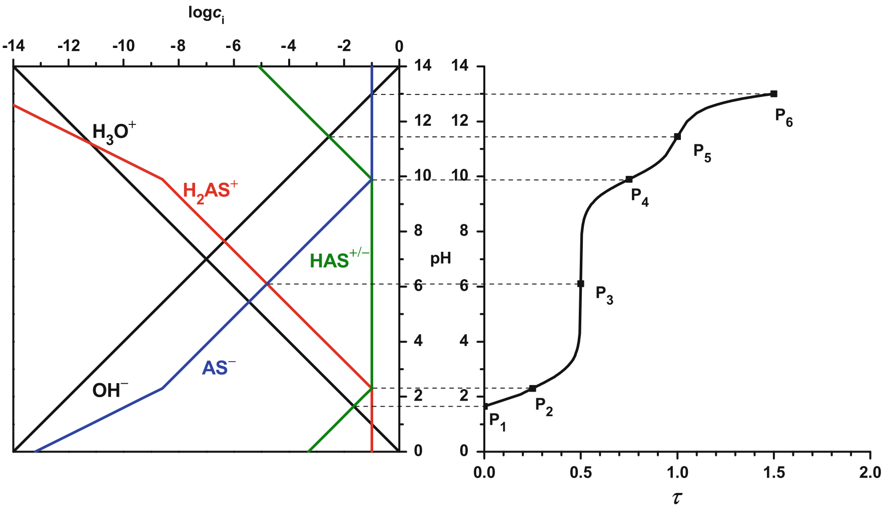


Fig. 82 Titration diagram of alanine ($\log C^{\circ}_{\text{alanine}} = -1$, $pK_{a1} = 2.3$, $pK_{a2} = 9.9$) with sodium hydroxide

5.7 Comparison of the Titrations of an Acid and its Corresponding Base: (a) Ammonium Ions with Sodium Hydroxide, (b) Ammonia with Hydrochloric Acid

This example is aimed at illustrating that titration curves may be significantly different for the case that an acid is titrated and the case where the corresponding base is titrated. Fig. 83 displays the titration curves for ammonium ions with sodium hydroxide and ammonia with hydrochloric acid.

The titration curves are constructed as follows:

(a) Titration of ammonium ions with NaOH:

P_1: $\tau = 0.0$; starting point of titration: $c_{H_3O^+} \approx c_{NH_3}$

P_2: $\tau = 0.5$; ammonium ions and ammonia are present at equal concentrations. This is the buffer point of the ammonium/ammonia buffer: $c_{NH_4^+} = c_{NH_3}$, $pH = pK_a^{NH_4^+} = 9.25$.

P_3: $\tau = 1.0$; the added amount of sodium hydroxide exactly equals the initial amount of ammonia. The solution contains ammonia and sodium chloride: $c_{NH_4^+} \approx c_{OH^-}$.

P_4: $\tau = 1.1$; this is a solution containing ammonia, sodium chloride and an additional concentration of sodium hydroxide. The OH^- concentration due to NaOH is: $c_{OH^-} = \frac{1}{10} C^{\circ}_{\text{ammonium}} = 0.01\ \text{molL}^{-1}$. The OH^- concentration due to protonation of ammonia is less than 10^{-4} mol L^{-1} and can be disregarded. Hence the pH is 12.

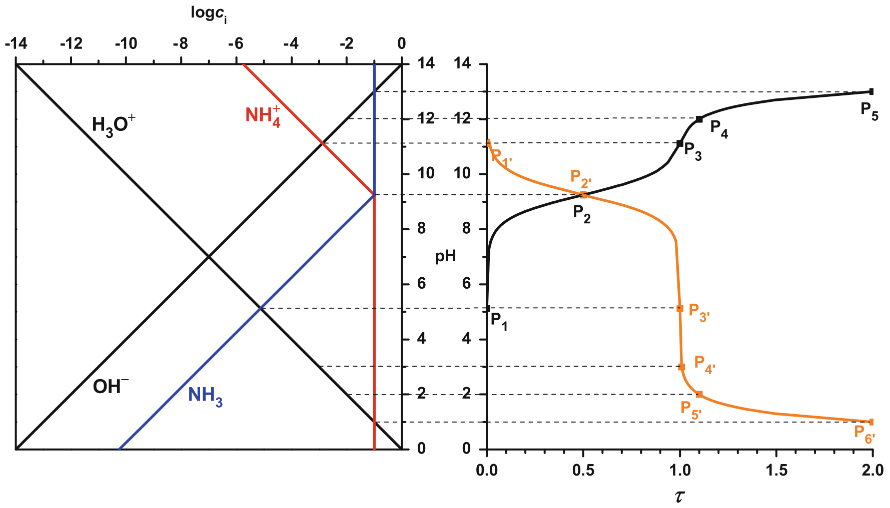


Fig. 83 Titration diagram of ammonia with hydrochloric acid (*orange line*) and ammonium ions (e.g., ammonium chloride) with sodium hydroxide (*black line*) ($\log C^{\circ} = -1$, $\mathrm{p}K_a^{NH_4^+} = 9.25$)

P$_5$: $\tau = 2.0$; this is a solution containing ammonia, sodium chloride and an additional concentration of sodium hydroxide. The OH$^-$ concentration due to NaOH is: $c_{OH^-} = \frac{1}{1} C^{\circ}_{\text{ammonium}} = 0.1 \text{ mol L}^{-1}$, pH = 13. The OH$^-$ concentration due to protonation of ammonia can be disregarded.

(b) Titration of ammonia with hydrochloric acid:

P$_{1'}$: $\tau = 0.0$; starting point of titration: $c_{NH_4^+} \approx c_{OH^-}$

P$_{2'}$: $\tau = 0.5$; ammonium ions and ammonia are present at equal concentrations. This is the buffer point of the ammonium/ammonia buffer: $c_{NH_4^+} = c_{NH_3}$, $\mathrm{pH} = \mathrm{p}K_a^{NH_4^+} = 9.25$.

P$_{3'}$: $\tau = 1.0$; the added amount of hydrochloric acid exactly equals the initial amount of ammonia. This is a solution of ammonium chloride: $c_{H_3O^+} \approx c_{NH_3}$

P$_{4'}$: $\tau = 1.01$; this is a solution of ammonium chloride with an addition of hydrochloric acid. The H_3O^+ concentration due to the presence of hydrochloric acid is: $c_{H_3O^+} = \frac{1}{100} C^{\circ}_{\text{ammonia}} = 0.001 \text{ mol L}^{-1}$. The H_3O^+ due to protolysis of ammonium ions is less than 10^{-7} mol L^{-1}, and it can be disregarded. The pH is 3.

P$_{5'}$: $\tau = 1.1$; this is a solution of ammonium chloride with an addition of hydrochloric acid. The H_3O^+ concentration due to the presence of hydrochloric acid is: $c_{H_3O^+} = \frac{1}{10} C^{\circ}_{\text{ammonia}} = 0.01 \text{ mol L}^{-1}$. The H_3O^+ due to protolysis of ammonium ions is less than 10^{-8} mol L^{-1}, and it can be disregarded. The pH is 2.

$P_{6'}$: $\tau = 2.0$; this is a solution of ammonium chloride with an addition of hydrochloric acid. The H_3O^+ concentration due to the presence of hydrochloric acid is: $c_{H_3O^+} = \frac{1}{1} C^{\circ}_{\text{ammonia}} = 0.1$ mol L^{-1}. The H_3O^+ due to protolysis of ammonium ions can be disregarded. The pH is 1.

Comparing the two titration curves one can recognize that the steepness of the titration curve at the equivalence point is much larger in case of the titration of ammonia with hydrochloric acid, than for the case of titration of ammonium ions with sodium hydroxide. This means that the random errors will be much smaller when ammonia is titrated with hydrochloric acid, and this titration is strongly to be preferred.

Titration Errors

6

There are two types of titration errors: *systematic* and *random* errors. Systematic errors can be easily estimated with the help of pH-logc_i diagrams. The diagrams are especially helpful for choosing the best color indicators. The diagrams are also useful to find, in the case of alternative titrations, the one with the smallest random error (see Sect. 5.7). The following estimation of systematic titration errors is confined to cases where the autoprotolysis of water can be ignored, because a comprehensive and detailed treatment including autoprotolysis would be completely beyond the scope of this book and only of importance in rather exotic cases of very dilute solutions.

6.1 Systematic Titration Errors

The reason for systematic titration errors is that the equivalence point is indicated too early or too late. This happens when the transition point of the indicator does not exactly match the pH of the equivalence point of the titration (systematic errors caused by wrongly calibrated pipettes or burettes will not be discussed here). The transition point of an indicator gives the experimental endpoint of the titration. Because the term endpoint can also be applied in the sense of "theoretical endpoint = equivalence point" we shall use here the term "transition point" to be clear. The same can happen in case of instrumental methods of indication when these methods do not identify the equivalence point correctly, but systematically deviate from it. Color indicators are themselves acid–base systems HI/I^- ($HI + H_2O \rightleftarrows I^- + H_3O^+$), the p$K_a$ value of which is usually denoted as the pK_I value, and it normally falls in the range of 2–12. There are bichromic and monochromic indicators. For example, a bichromic indicator may be red as an acid and blue as a base, and a monochromic may be colorless as an acid and violet as a base. In the case of bichromic indicators, the color changes when $c_{HI} = c_{I^-}$, that is at the buffer point of the indicator. Of course, the color change does not abruptly occur there, but it is smeared out in an interval (the so-called transition interval of an indicator), roughly in the

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Table 3 pK_I values and transition intervals of some common acid–base indicators

Indicator	pK_I	Transition interval	Color of the acid	Color of the base
Methyl orange	4.0	3.1–4.4	Red	Yellow–orange
Methyl red	5.8	4.2–6.3	Red	Yellow
Bromthymol blue	7.1	6.0–7.6	Yellow	Blue
Neutral red	7.0	6.8–8.0	Red	Yellow
Phenolphthalein	8.4	8.2–10.0	Colorless	Pink (fuchsia)
Thymolphthalein	10.0	9.3–10.6	Colorless	Blue

range $\frac{1}{10} \leq \frac{c_{HI}}{c_{I^-}} \leq \frac{10}{1}$, in which a mixed color results. According to the buffer equation (see Chap. 2) this is equal to the pH range: $\Delta(\text{pH}) = \text{p}K_I \pm 1$. In Table 3, p$K_I$ values and transition ranges of some indicators are given. In case of monochromic indicators one can detect the colored form already when it presents only 10 % of the overall indicator concentration (which additionally depends on the overall concentration). This leads to the phenomenon that the transition point of monochromic indicators appears to be systematically shifted from the pK_I value toward the colorless side.

6.1.1 Systematic Titration Errors in Titrations of Acids with pK_a Values Between 0 and 14 with Very Strong Bases (e.g., NaOH)

pH-logc_i diagrams are very well suited to estimate systematic titration errors. At the equivalence point (eqp) of a titration, the amount of titrator added to the sample solution exactly equals the given amount of titrand (compound to be titrated). When the amount n°_{HB} of an acid with a pK_a value between 0 and 14 is titrated up to the equivalence point, the amount of added OH$^-$ is $\left(n^{\circ}_{OH^-}\right)_{eqp} = n^{\circ}_{HB}$. When NaOH is used, this is equal to $\left(n^{\circ}_{Na^+}\right)_{eqp}$. If one were to evaporate the solution at the equivalence point, pure NaB would be obtained. Hence, the solution has at the equivalence point exactly the pH of a NaB solution of the respective concentration (see Sects. 4.1.2.3 and 4.1.3.3): when the autoprotolysis of water is disregarded, the pH is given by the condition $c_{HB} \approx c_{OH^-}$ (P$_3$ in Fig. 76). In a real titration, the indicator will indicate the transition point (tp), which may deviate from the equivalence point. The absolute titration error F'_{abs}, expressed as an amount in mol, is the difference between the amount of added titrator (OH$^-$ ions) until reaching the transition point $\left(n^{\circ}_{OH^-}\right)_{tp}$ and the amount of acid to be titrated n°_{HB}:

$$F'_{abs} = \left(n^{\circ}_{OH^-}\right)_{tp} - n^{\circ}_{HB} \tag{185}$$

The amount of OH^- ions added until the transition point $\left(n^{\circ}_{OH^-}\right)_{tp}$ has been used to form B^-; however, not completely, as there is still present an amount $(n_{OH^-})_{tp}$, which is understandable when looking at the reaction Eq. (15). Hence the following relation holds:

$$\left(n^{\circ}_{OH^-}\right)_{tp} = (n_{B^-})_{tp} + (n_{OH^-})_{tp} \tag{186}$$

$(n_{B^-})_{tp}$ is the amount of B^- at the equivalence point. For n°_{HB} one can write:

$$n^{\circ}_{HB} = (n_{HB})_{tp} + (n_{B^-})_{tp} \tag{187}$$

and it follows that

$$F'_{abs} = \left[(n_{B^-})_{tp} + (n_{OH^-})_{tp}\right] - \left[(n_{HB})_{tp} + (n_{B^-})_{tp}\right] = (n_{OH^-})_{tp} - (n_{HB})_{tp} \tag{188}$$

Disregarding the dilution which always accompanies a titration, one can calculate the absolute error and give it in the unit (mol L^{-1}) as follows:

$$F_{abs}[\text{mol L}^{-1}] = \frac{F'_{abs}}{1\text{ L}} = \frac{(n_{OH^-})_{tp} - (n_{HB})_{tp}}{1\text{ L}} = (c_{OH^-})_{tp} - (c_{HB})_{tp} \tag{189}$$

Relating the absolute error to the starting concentration of the acid C°_{HB} yields the dimensionless relative error:

$$F_{rel} = \frac{F_{abs}}{C^{\circ}_{HB}} \tag{190}$$

Figure 84 shows the example of a titration of acetic acid with sodium hydroxide to illustrate how the titration error can be derived from a pH-logc_i diagram.

The concentrations $(c_{OH^-})_{tp}$ can be read at the logc_i axis at P_{1a} (methyl red), P_{2a} (neutral red) and P_{3a} (phenolphthalein). Similarly, the concentrations $(c_{HB})_{tp}$ can be read at P_{1b} (methyl red), P_{2b} (neutral red) and P_{3b} (phenolphthalein). Table 4 gives these data, and also the systematic errors as calculated according to Eqs. (189) and (190).

A negative systematic error means that the turning point is systematically showing up before the equivalence point, and a positive systematic error means that the turning point shows up after the equivalence point.

When the equivalence point is near to pH = 7, the autoprotolysis of water has to be considered, and the equations are more complicated [1–3]. However, when the equivalence point is very near to pH = 7, the titration can be treated as that of a very strong acid (see Sect. 6.1.3).

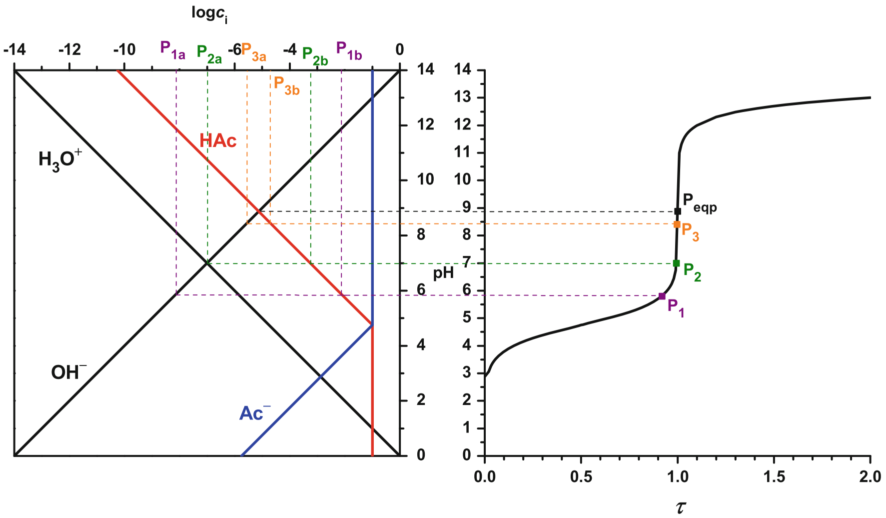

Fig. 84 Reading of the relevant concentration data from the pH-logc_i diagram for estimation of the systematic titration errors in case of the titration of acetic acid ($C^{\circ}_{\text{acetic acid}} = 0.1$ mol L^{-1}) with sodium hydroxide. $\mathrm{P_{eqp}}$: equivalence point, $\mathrm{P_1}$ to $\mathrm{P_3}$ are transition points of the indicators methyl red, neutral red, and phenolphthalein

Table 4 Systematic errors in case of the titration of acetic acid ($C^{\circ}_{\text{acetic acid}} = 0.1$ mol L^{-1}) with sodium hydroxide when using different indicators. The concentration data are taken from Fig. 84

Indicator	pK_I	$(c_{\mathrm{OH^-}})_\mathrm{tp}$ (mol L^{-1})	$(c_\mathrm{HB})_\mathrm{tp}$ (mol L^{-1})	F_abs (mol L^{-1})	F_rel	F_rel (%)
Methyl red	5.8	7.2×10^{-9}	7.4×10^{-3}	-7.4×10^{-3}	-7.4×10^{-2}	-7.4
Neutral red	7.0	1.0×10^{-7}	5.6×10^{-4}	-5.6×10^{-4}	-5.6×10^{-3}	-0.56
Phenolphthalein	8.4	2.8×10^{-6}	2.0×10^{-5}	-1.72×10^{-5}	-1.72×10^{-4}	-0.0172 (≈ -0.02)

6.1.2 Systematic Titration Errors of Titrations of Bases with pK_b Values Between 0 and 14 with a Very Strong Acid (e.g., Hydrochloric Acid)

This is completely analogous to the case of acids. When $n^{\circ}_{\mathrm{B^-}}$ denotes the amount (mol) of base to be titrated, and $\left(n^{\circ}_{\mathrm{H_3O^+}}\right)_\mathrm{tp}$ is the amount of acid added until the transition point of the indicator, the absolute error is:

$$F'_\mathrm{abs} = \left(n^{\circ}_{\mathrm{H_3O^+}}\right)_\mathrm{tp} - n^{\circ}_{\mathrm{B^-}} \tag{191}$$

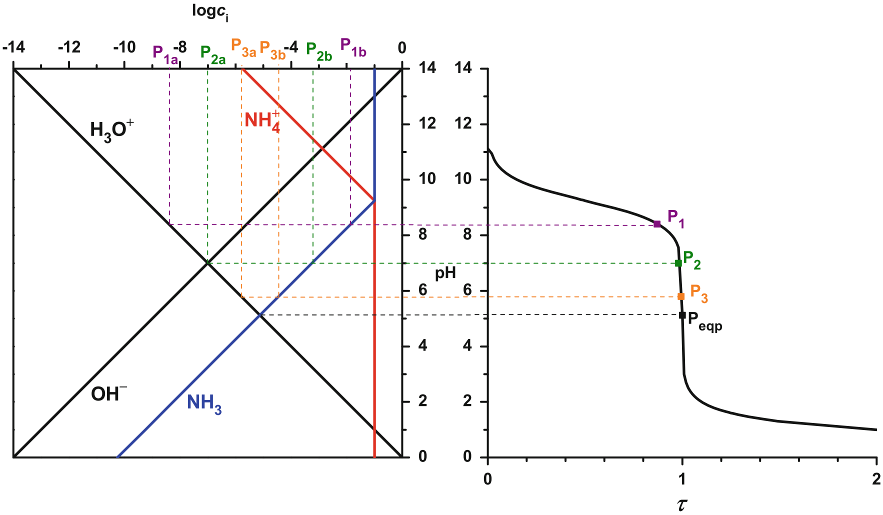

Fig. 85 Reading of the relevant concentration data from the pH-logc_i diagram for estimation of the systematic titration errors in case of the titration of ammonia ($C^{\circ}_{\text{ammonia}} = 0.1$ mol L^{-1}) with hydrochloric acid using different color indicators: P_{eqp}: equivalence point, P_1 to P_3 are the transition points of the indicators phenolphthalein, neutral red, and methyl red

The absolute error in the unit (mol L^{-1}) follows as:

$$F_{\text{abs}}[\text{mol L}^{-1}] = \frac{F'_{\text{abs}}}{1\ \text{L}} = \frac{\left(n^{\circ}_{\text{H}_3\text{O}^+}\right)_{\text{tp}} - n^{\circ}_{\text{B}^-}}{1\ \text{L}} = \frac{\left(n_{\text{H}_3\text{O}^+}\right)_{\text{tp}} - \left(n_{\text{B}^-}\right)_{\text{tp}}}{1\ \text{L}}$$
$$= \left(c_{\text{H}_3\text{O}^+}\right)_{\text{tp}} - \left(c_{\text{B}^-}\right)_{\text{tp}} \qquad (192)$$

The relative error is then:

$$F_{\text{rel}} = \frac{F_{\text{abs}}}{C^{\circ}_{\text{B}^-}} \qquad (193)$$

Figure 85 illustrates how the relevant data can be read from a pH-logc_i diagram using the example of a titration of ammonia with hydrochloric acid.

The concentrations $\left(c_{\text{H}_3\text{O}^+}\right)_{\text{tp}}$ can be read at the logc_i axis at P_{1a} (phenolphthalein), P_{2a} (neutral red) and P_{3a} (methyl red). Similarly, the concentrations $\left(c_{\text{B}^-}\right)_{\text{tp}}$ can be read at P_{1b} (phenolphthalein), P_{2b} (neutral red) and P_{3b} (methyl red). The data and the calculated systematic errors (using Eqs. (192) and (193)) are given in Table 5.

When the equivalence point is near to pH = 7, the autoprotolysis of water has to be considered, and the equations are more complicated [1–3]. However, when the equivalence point is very near to pH = 7, the titration can be treated as that of a very strong base (see Sect. 6.1.3).

Table 5 Systematic errors in case of the titration of ammonia ($C^{\circ}_{\text{ammonia}} = 0.1$ mol L^{-1}) with hydrochloric acid when using different indicators. The concentration data are taken from Fig. 85

Indicator	pK_I	$\left(c_{H_3O^+}\right)_{tp}$ (mol L^{-1})	$\left(c_{B^-}\right)_{tp}$ (mol L^{-1})	F_{abs} (mol L^{-1})	F_{rel}	F_{rel} (%)
Phenolphthalein	8.4	4.2×10^{-9}	1.4×10^{-2}	-1.4×10^{-2}	-1.4×10^{-1}	−14.0
Neutral red	7.0	1.0×10^{-7}	6.0×10^{-4}	-6.0×10^{-4}	-6.0×10^{-3}	−0.60
Methyl red	5.8	1.6×10^{-6}	3.5×10^{-5}	-3.34×10^{-5}	-3.34×10^{-4}	−0.0334 (≈ −0.03)

6.1.3 Systematic Titration Errors of Titrations of Very Strong Acids with Very Strong Bases and Vice Versa

Examples for such titrations are the titration of hydrochloric acid with sodium hydroxide and vice versa. The systematic absolute error in (mol) is here:

$$F'_{abs} = \left(n^{\circ}_{OH^-}\right)_{tp} - n^{\circ}_{H_3O^+} \tag{194}$$

$n^{\circ}_{H_3O^+}$ is the amount (mol) of very strong acid HB to be titrated, $\left(n^{\circ}_{OH^-}\right)_{tp}$ is the amount (mol) of base (OH$^-$) added until the transition point of the indicator. At the transition point, the amounts $\left(n_{OH^-}\right)_{tp}$ and $\left(n_{H_3O^+}\right)_{tp}$ are present in the solution. The systematic absolute error in the unit (mol L^{-1}) is then:

$$F_{abs}[\text{mol L}^{-1}] = \frac{F'_{abs}}{1\text{ L}} = \frac{\left(n^{\circ}_{OH^-}\right)_{tp} - n^{\circ}_{H_3O^+}}{1\text{ L}} = \frac{\left(n_{OH^-}\right)_{tp} - \left(n_{H_3O^+}\right)_{tp}}{1\text{ L}}$$
$$= \left(c_{OH^-}\right)_{tp} - \left(c_{H_3O^+}\right)_{tp} \tag{195}$$

Figure 86 illustrates how the relevant concentration data can be read from the pH-logc_i diagram.

The concentration $\left(c_{OH^-}\right)_{tp}$ can be read on the logc_i axis at P_{1a} (methyl orange), P_{2a} (methyl red), P_{3a} (phenolphthalein) and P_{4a} (thymolphthalein). Similarly, the concentration $\left(c_{H_3O^+}\right)_{tp}$ at P_{1b} (methyl orange), P_{2b} (methyl red), P_{3b} (phenolphthalein) and P_{4b} (thymolphthalein) can be read at the transition points of the indicators. Table 6 gives the relevant concentrations, and the systematic errors calculated according to Eqs. (194) and (195).

When a very strong base is titrated with a very strong acid, the following equations are valid:

$$F'_{abs} = \left(n^{\circ}_{H_3O^+}\right)_{tp} - n^{\circ}_{OH^-} \tag{196}$$

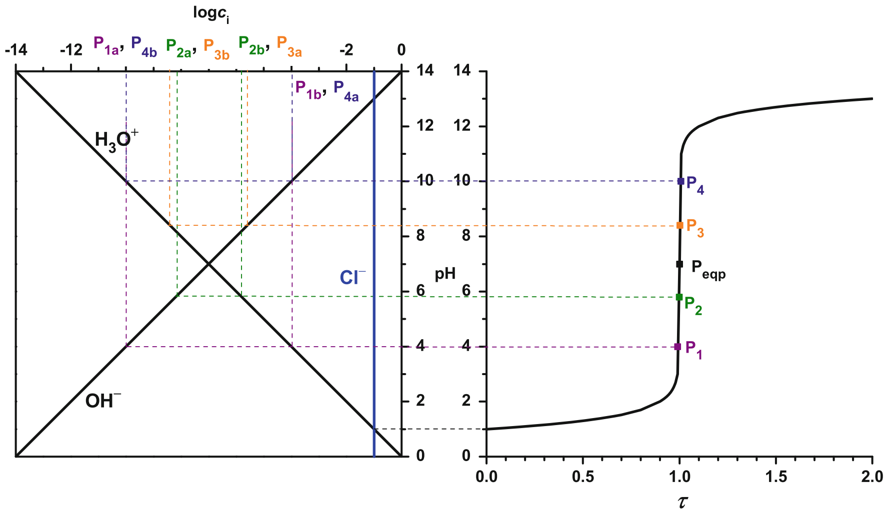

Fig. 86 Reading of the relevant concentration data from the pH-logc_i diagram for estimation of the systematic titration errors in case of the titration of hydrochloric acid ($C^{\circ}_{\text{hydrochloric acid}} = 0.1$ mol L^{-1}) with sodium hydroxide. P$_{eqp}$: equivalence point, P$_1$ to P$_4$ are the transition points of the color indicators methyl orange, methyl red, phenolphthalein, and thymolphthalein

Table 6 Systematic errors in case of the titration of hydrochloric acid ($C^{\circ}_{\text{hydrochloric acid}} = 0.1$ mol L^{-1}) with sodium hydroxide when using different indicators. The concentration data are taken from Fig. 86

Indicator	pK_I	$(c_{OH^-})_{tp}$ (mol L^{-1})	$(c_{H_3O^+})_{tp}$ (mol L^{-1})	F_{abs} (mol L^{-1})	F_{rel}	F_{rel} (%)
Methyl orange	4.0	10^{-10}	10^{-4}	-10^{-4}	-10^{-3}	-0.1
Methyl red	5.8	6.25×10^{-9}	1.6×10^{-6}	-1.6×10^{-6}	-1.6×10^{-5}	-1.6×10^{-3}
Phenolphthalein	8.4	2.5×10^{-6}	4.0×10^{-9}	2.5×10^{-6}	2.5×10^{-5}	2.5×10^{-3}
Thymolphthalein	10.0	10^{-4}	10^{-10}	10^{-4}	10^{-3}	0.1

$n^{\circ}_{OH^-}$ is the amount of base B$^-$ to be titrated. As it is a very strong base, this is equal to the amount $n^{\circ}_{OH^-}$ present in the solution: the systematic absolute error is:

$$F_{abs}[\text{mol L}^{-1}] = \frac{F'_{abs}}{1\text{ L}} = \frac{\left(n^{\circ}_{H_3O^+}\right)_{tp} - n^{\circ}_{OH^-}}{1\text{ L}} = \frac{\left(n_{H_3O^+}\right)_{tp} - \left(n_{OH^-}\right)_{tp}}{1\text{ L}}$$
$$= \left(c_{H_3O^+}\right)_{tp} - \left(c_{OH^-}\right)_{tp} \tag{197}$$

6.2 Random Titration Errors

Random titration errors have the origin in the fact that color indicators always have a transition *range around the transition point*. Also, instrumental methods of indication always "react" within a certain range of pH, never instantaneously at a certain pH point! Within that range, a randomized reading is made to determine the endpoint of titration. This means that in repeated titration this endpoints will be scattered within the transition range following the laws of statistic distribution (mostly indeed according to the Gaussian distribution). When the titration curve is very steep around the transition point (which hopefully will coincide with the equivalence point, so that no systematic error will arise) this will lead to a small range of τ values corresponding to a certain pH range. A small variation of τ values corresponds then also to a small range of volume readings at the indicated endpoints, i.e., a small standard deviation of results, i.e., a small random error. Figure 87 shows schematically how the steepness in the transition range effects the scattering of τ values and thus volume readings at the endpoints. .

Figure 88 illustrates the fact that in case of the titration of ammonia with hydrochloric acid, the random error will be much smaller (see $\Delta\tau_2$) than in case of the titration of ammonium ions with sodium hydroxide (see $\Delta\tau_1$). Since τ is

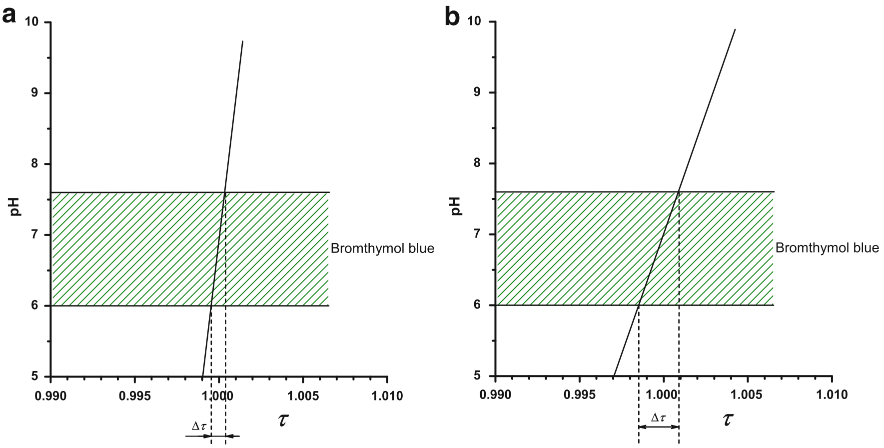

Fig. 87 $\Delta\tau$ range corresponding to a fixed pH range of the transition of an indicator (here bromthymol blue; transition range from pH 6.0 to 7.7): (**a**) for the case of a titration curve which is very steep in that pH range, and (**b**) for a titration curve which is less steep in that range

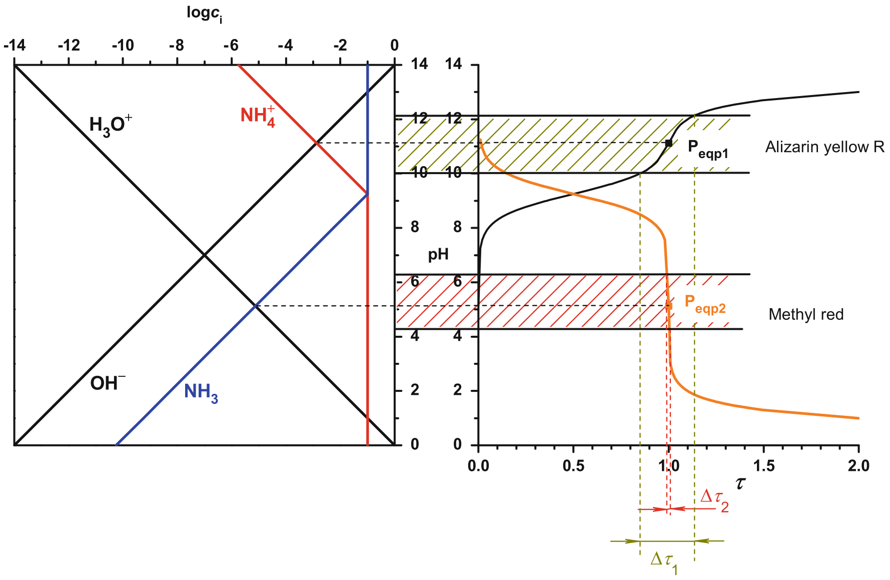

Fig. 88 pH-logc_i diagram and diagram of the titrations of ammonia with hydrochloric acid (*orange line* with equivalence point P_{eqp2}) and of ammonium ions with sodium hydroxide (*black line* with equivalence point P_{eqp1}). The *shadowed ranges* indicate the transition ranges of the indicators alizarin yellow R and methyl red

directly proportional to the volumes of titrator, a large $\Delta\tau$ means a large range $\Delta v_{\text{titrator}}$, i.e., a wide range in which the results will be scattered randomly.

Literature

1. Buttler JN (1998) Ionic equilibrium. Solubility and pH calculations. Wiley, New York
2. Seel F (1976) Grundlagen der Analytischen Chemie, 6th edn. Verlag Chemie, Weinheim
3. Blumenthal G (1993) Grundlagen der quantitativen chemischen Analyse. In: Kolditz L (ed) Anorganikum, 13th edn. Barth, Leipzig

Appendix A: Derivation of the Exact Functions and the Equations of the Asymptotes for Multibasic Acids

A1. Derivation of the Functions $\log c_\mathrm{i} = f(\mathrm{pH})$ for Dibasic Acids

Protolysis equilibria:

$$\mathrm{H_2B + H_2O \rightleftarrows HB^- + H_3O^+} \tag{A.1}$$

$$\mathrm{HB^- + H_2O \rightleftarrows B^- + H_3O^+} \tag{A.2}$$

Laws of mass action:

$$K_\mathrm{a1} = \frac{c_\mathrm{HB^-}\, c_\mathrm{H_3O^+}}{c_\mathrm{H_2B}} \tag{A.3}$$

$$K_\mathrm{a2} = \frac{c_\mathrm{B^{2-}}\, c_\mathrm{H_3O^+}}{c_\mathrm{HB^-}} \tag{A.4}$$

Amount balance:

$$C^{\circ}_\mathrm{H_2B} = c_\mathrm{H_2B} + c_\mathrm{HB^-} + c_\mathrm{B^{2-}} \tag{A.5}$$

The following functions need to be derived:

1. $\log c_\mathrm{H_2B} = f(\mathrm{pH})$ (A.6)

2. $\log c_\mathrm{HB^-} = f(\mathrm{pH})$ (A.7)

3. $\log c_\mathrm{B^{2-}} = f(\mathrm{pH})$ (A.8)

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A1.1 $\log c_{H_2B} = f(\text{pH})$

Equations need to be found for the concentrations c_{HB^-} and $c_{B^{2-}}$ which have as unknown concentrations only c_{H_2B} and $c_{H_3O^+}$. This can be done by rearranging Eqs. (A.3) and (A.4):

$$c_{HB^-} = \frac{K_{a1} c_{H_2B}}{c_{H_3O^+}} \tag{A.9}$$

$$c_{B^{2-}} = \frac{K_{a1} K_{a2} c_{H_2B}}{c^2_{H_3O^+}} \tag{A.10}$$

and insertion in Eq. (A.5) gives:

$$C^{\circ}_{H_2B} = c_{H_2B} + \frac{K_{a1} c_{H_2B}}{c_{H_3O^+}} + \frac{K_{a1} K_{a2} c_{H_2B}}{c^2_{H_3O^+}} = c_{H_2B}\left(1 + \frac{K_{a1}}{c_{H_3O^+}} + \frac{K_{a1} K_{a2}}{c^2_{H_3O^+}}\right) \tag{A.11}$$

Rearrangement gives:

$$c_{H_2B} = \frac{C^{\circ}_{H_2B}}{\left(1 + \frac{K_{a1}}{c_{H_3O^+}} + \frac{K_{a1} K_{a2}}{c^2_{H_3O^+}}\right)} \tag{A.12}$$

With $\frac{K_{a1}}{c_{H_3O^+}} = \frac{10^{-\text{p}K_{a1}}}{10^{-\text{pH}}} = 10^{\text{pH}-\text{p}K_{a1}}$ and $\frac{K_{a1} K_{a2}}{c^2_{H_3O^+}} = \frac{10^{-\text{p}K_{a1}-\text{p}K_{a2}}}{10^{-2\text{pH}}} = 10^{2\text{pH}-\text{p}K_{a1}-\text{p}K_{a2}}$ follows:

$$\log c_{H_2B} = \log C^{\circ}_{H_2B} - \log\left(1 + 10^{\text{pH}-\text{p}K_{a1}} + 10^{2\text{pH}-\text{p}K_{a1}-\text{p}K_{a2}}\right) \tag{A.13}$$

A1.2 $\log c_{HB^-} = f(\text{pH})$

Equations need to be found for the concentrations c_{H_2B} and $c_{B^{2-}}$ which have as unknown concentrations only c_{HB^-} and $c_{H_3O^+}$. This can be done by rearranging Eqs. (A.3) and (A.4):

$$c_{H_2B} = \frac{c_{HB^-} c_{H_3O^+}}{K_{a1}} \tag{A.14}$$

$$c_{B^{2-}} = \frac{K_{a2} c_{HB^-}}{c_{H_3O^+}} \tag{A.15}$$

and insertion in Eq. (A.5) gives:

$$C^{\circ}_{H_2B} = \frac{c_{HB^-} c_{H_3O^+}}{K_{a1}} + c_{HB^-} + \frac{K_{a2} c_{HB^-}}{c_{H_3O^+}} = c_{HB^-} \left(1 + \frac{c_{H_3O^+}}{K_{a1}} + \frac{K_{a2}}{c_{H_3O^+}}\right) \tag{A.16}$$

Rearrangement gives:

$$c_{HB^-} = \frac{C^{\circ}_{H_2B}}{\left(1 + \frac{c_{H_3O^+}}{K_{a1}} + \frac{K_{a2}}{c_{H_3O^+}}\right)} \tag{A.17}$$

With $\frac{c_{H_3O^+}}{K_{a1}} = \frac{10^{-\mathrm{pH}}}{10^{-\mathrm{p}K_{a1}}} = 10^{-\mathrm{pH}+\mathrm{p}K_{a1}}$ and $\frac{K_{a2}}{c_{H_3O^+}} = \frac{10^{-\mathrm{p}K_{a2}}}{10^{-\mathrm{pH}}} = 10^{\mathrm{pH}-\mathrm{p}K_{a2}}$ follows:

$$\log c_{HB^-} = \log C^{\circ}_{H_2B} - \log\left(1 + 10^{-\mathrm{pH}+\mathrm{p}K_{a1}} + 10^{\mathrm{pH}-\mathrm{p}K_{a2}}\right) \tag{A.18}$$

A1.3 $\log c_{B^{2-}} = f(\mathrm{pH})$

Equations need to be found for the concentrations c_{H_2B} and c_{HB^-}, which have as unknown concentrations only $c_{B^{2-}}$ and $c_{H_3O^+}$. This can be done by rearranging Eqs. (A.3) and (A.4):

$$c_{HB^-} = \frac{c_{H_3O^+} c_{B^{2-}}}{K_{a2}} \tag{A.19}$$

$$c_{H_2B} = \frac{c^2_{H_3O^+} c_{B^{2-}}}{K_{a1} K_{a2}} \tag{A.20}$$

and insertion in Eq. (A.5) gives:

$$C^{\circ}_{H_2B} = \frac{c^2_{H_3O^+} c_{B^{2-}}}{K_{a1} K_{a2}} + \frac{c_{H_3O^+} c_{B^{2-}}}{K_{a2}} + c_{B^{2-}} = c_{B^{2-}} \left(1 + \frac{c^2_{H_3O^+}}{K_{a1} K_{a2}} + \frac{c_{H_3O^+}}{K_{a2}}\right) \tag{A.21}$$

Rearrangement gives:

$$c_{B^{2-}} = \frac{C^{\circ}_{H_2B}}{\left(1 + \frac{c^2_{H_3O^+}}{K_{a1} K_{a2}} + \frac{c_{H_3O^+}}{K_{a2}}\right)} \tag{A.22}$$

With $\frac{c_{H_3O^+}}{K_{a2}} = \frac{10^{-pH}}{10^{-pK_{a2}}} = 10^{pK_{a2}-pH}$ and $\frac{c^2_{H_3O^+}}{K_{a1}K_{a2}} = \frac{10^{-2pH}}{10^{-pK_{a1}-pK_{a2}}} = 10^{-2pH+pK_{a1}+pK_{a2}}$ follows:

$$\log c_{B^{2-}} = \log C^{\circ}_{H_2B} - \log\left(1 + 10^{-2pH+pK_{a1}+pK_{a2}} + 10^{-pH+pK_{a2}}\right) \tag{A.23}$$

A2. Derivation of the Functions $\log c_i = f(\mathrm{pH})$ for a Tribasic Acid

Protolysis equilibria:

$$H_3B + H_2O \rightleftarrows H_2B^- + H_3O^+ \tag{A.24}$$

$$H_2B^- + H_2O \rightleftarrows HB^{2-} + H_3O^+ \tag{A.25}$$

$$HB^{2-} + H_2O \rightleftarrows B^{3-} + H_3O^+ \tag{A.26}$$

Laws of mass action:

$$K_{a1} = \frac{c_{H_2B^-}c_{H_3O^+}}{c_{H_3B}} \tag{A.27}$$

$$K_{a2} = \frac{c_{HB^{2-}}c_{H_3O^+}}{c_{H_2B^-}} \tag{A.28}$$

$$K_{a3} = \frac{c_{B^{3-}}c_{H_3O^+}}{c_{HB^{2-}}} \tag{A.29}$$

Amount balance:

$$C^{\circ}_{H_3B} = c_{H_3B} + c_{H_2B^-} + c_{HB^{2-}} + c_{B^{3-}} \tag{A.30}$$

The following functions need to be derived:

1. $\log c_{H_3B} = f(\mathrm{pH})$ (A.31)

2. $\log c_{H_2B^-} = f(\mathrm{pH})$ (A.32)

3. $\log c_{HB^{2-}} = f(\mathrm{pH})$ (A.33)

4. $\log c_{B^{3-}} = f(\mathrm{pH})$ (A.34)

A2.1 $\log c_{H_3B} = f(\mathrm{pH})$

For the concentrations $c_{H_2B^-}$, $c_{HB^{2-}}$ and $c_{B^{3-}}$ one can derive equations by rearranging Eqs. (A.27), (A.28) and (A.29):

$$c_{H_2B^-} = \frac{K_{a1} c_{H_3B}}{c_{H_3O^+}} \tag{A.35}$$

$$c_{HB^{2-}} = \frac{K_{a1} K_{a2} c_{H_3B}}{c^2_{H_3O^+}} \tag{A.36}$$

$$c_{B^{3-}} = \frac{K_{a1} K_{a2} K_{a3} c_{H_3B}}{c^3_{H_3O^+}} \tag{A.37}$$

and insertion in Eq. (A.30) gives:

$$\begin{aligned} C^{\circ}_{H_3B} &= c_{H_3B} + \frac{K_{a1} c_{H_3B}}{c_{H_3O^+}} + \frac{K_{a1} K_{a2} c_{H_3B}}{c^2_{H_3O^+}} + \frac{K_{a1} K_{a2} K_{a3} c_{H_3B}}{c^3_{H_3O^+}} \\ &= c_{H_3B}\left(1 + \frac{K_{a1}}{c_{H_3O^+}} + \frac{K_{a1} K_{a2}}{c^2_{H_3O^+}} + \frac{K_{a1} K_{a2} K_{a3}}{c^3_{H_3O^+}}\right) \end{aligned} \tag{A.38}$$

$$c_{H_3B} = \frac{C^{\circ}_{H_3B}}{\left(1 + \frac{K_{a1}}{c_{H_3O^+}} + \frac{K_{a1} K_{a2}}{c^2_{H_3O^+}} + \frac{K_{a1} K_{a2} K_{a3}}{c^3_{H_3O^+}}\right)} \tag{A.39}$$

With $\dfrac{K_{a1}}{c_{H_3O^+}} = \dfrac{10^{-\mathrm{p}K_{a1}}}{10^{-\mathrm{pH}}} = 10^{\mathrm{pH}-\mathrm{p}K_{a1}}$, $\dfrac{K_{a1} K_{a2}}{c^2_{H_3O^+}} = \dfrac{10^{-\mathrm{p}K_{a1}-\mathrm{p}K_{a2}}}{10^{-2\mathrm{pH}}} = 10^{2\mathrm{pH}-\mathrm{p}K_{a1}-\mathrm{p}K_{a2}}$ and $\dfrac{K_{a1} K_{a2} K_{a3}}{c^3_{H_3O^+}} = \dfrac{10^{-\mathrm{p}K_{a1}-\mathrm{p}K_{a2}-\mathrm{p}K_{a3}}}{10^{-3\mathrm{pH}}} = 10^{3\mathrm{pH}-\mathrm{p}K_{a1}-\mathrm{p}K_{a2}-\mathrm{p}K_{a3}}$ follows

$$\log c_{H_3B} = \log C^{\circ}_{H_3B} - \log\left(1 + 10^{\mathrm{pH}-\mathrm{p}K_{a1}} + 10^{2\mathrm{pH}-\mathrm{p}K_{a1}-\mathrm{p}K_{a2}} + 10^{3\mathrm{pH}-\mathrm{p}K_{a1}-\mathrm{p}K_{a2}-\mathrm{p}K_{a3}}\right) \tag{A.40}$$

A2.2 $\log c_{H_2B^-} = f(\mathrm{pH})$

Rearranging Eq. (A.27), (A.28), and (A.29) gives:

$$c_{H_3B} = \frac{c_{H_3O^+} c_{H_2B^-}}{K_{a1}} \tag{A.41}$$

$$c_{HB^{2-}} = \frac{K_{a2} c_{H_2B^-}}{c_{H_3O^+}} \tag{A.42}$$

$$c_{B^{3-}} = \frac{K_{a2} K_{a3} c_{H_2B^-}}{c^2_{H_3O^+}} \tag{A.43}$$

and insertion in Eq. (A.30) gives:

$$\begin{aligned} C^{\circ}_{H_3B} &= \frac{c_{H_3O^+} c_{H_2B^-}}{K_{a1}} + c_{H_2B^-} + \frac{K_{a2} c_{H_2B^-}}{c_{H_3O^+}} + \frac{K_{a2} K_{a3} c_{H_2B^-}}{c^2_{H_3O^+}} \\ &= c_{H_2B^-} \left(1 + \frac{c_{H_3O^+}}{K_{a1}} + \frac{K_{a2}}{c_{H_3O^+}} + \frac{K_{a2} K_{a3}}{c^2_{H_3O^+}} \right) \end{aligned} \tag{A.44}$$

$$c_{H_2B^-} = \frac{C^{\circ}_{H_3B}}{\left(1 + \frac{c_{H_3O^+}}{K_{a1}} + \frac{K_{a2}}{c_{H_3O^+}} + \frac{K_{a2} K_{a3}}{c^2_{H_3O^+}} \right)} \tag{A.45}$$

With $\frac{c_{H_3O^+}}{K_{a1}} = \frac{10^{-\mathrm{pH}}}{10^{-\mathrm{p}K_{a1}}} = 10^{-\mathrm{pH}+\mathrm{p}K_{a1}}$, $\frac{K_{a2}}{c_{H_3O^+}} = \frac{10^{-\mathrm{p}K_{a2}}}{10^{-\mathrm{pH}}} = 10^{\mathrm{pH}-\mathrm{p}K_{a2}}$ and $\frac{K_{a2} K_{a3}}{c^2_{H_3O^+}} = \frac{10^{-\mathrm{p}K_{a2}-\mathrm{p}K_{a3}}}{10^{-2\mathrm{pH}}} = 10^{2\mathrm{pH}-\mathrm{p}K_{a2}-\mathrm{p}K_{a3}}$ follows:

$$\log c_{H_2B^-} = \log C^{\circ}_{H_3B} - \log\left(1 + 10^{-\mathrm{pH}+\mathrm{p}K_{a1}} + 10^{\mathrm{pH}-\mathrm{p}K_{a2}} + 10^{2\mathrm{pH}-\mathrm{p}K_{a2}-\mathrm{p}K_{a3}}\right) \tag{A.46}$$

A2.3 $\log c_{HB^{2-}} = f(\mathrm{pH})$

Rearranging Eqs. (A.27), (A.28), and (A.29) gives:

$$c_{H_3B} = \frac{c^2_{H_3O^+} c_{HB^{2-}}}{K_{a1} K_{a2}} \tag{A.47}$$

$$c_{\mathrm{H_2B^-}} = \frac{c_{\mathrm{H_3O^+}} c_{\mathrm{HB^{2-}}}}{K_{\mathrm{a2}}} \tag{A.48}$$

$$c_{\mathrm{B^{3-}}} = \frac{K_{\mathrm{a3}} c_{\mathrm{HB^{2-}}}}{c_{\mathrm{H_3O^+}}} \tag{A.49}$$

and insertion in Eq. (A.30) gives:

$$\begin{aligned} C^{\circ}_{\mathrm{H_3B}} &= \frac{c^2_{\mathrm{H_3O^+}} c_{\mathrm{HB^{2-}}}}{K_{\mathrm{a1}}K_{\mathrm{a2}}} + \frac{c_{\mathrm{H_3O^+}} c_{\mathrm{HB^{2-}}}}{K_{\mathrm{a2}}} + c_{\mathrm{HB^{2-}}} + \frac{K_{\mathrm{a3}} c_{\mathrm{HB^{2-}}}}{c_{\mathrm{H_3O^+}}} \\ &= c_{\mathrm{HB^{2-}}} \left(1 + \frac{c^2_{\mathrm{H_3O^+}}}{K_{\mathrm{a1}}K_{\mathrm{a2}}} + \frac{c_{\mathrm{H_3O^+}}}{K_{\mathrm{a2}}} + \frac{K_{\mathrm{a3}}}{c_{\mathrm{H_3O^+}}} \right) \end{aligned} \tag{A.50}$$

$$c_{\mathrm{HB^{2-}}} = \frac{C^{\circ}_{\mathrm{H_3B}}}{\left(1 + \frac{c^2_{\mathrm{H_3O^+}}}{K_{\mathrm{a1}}K_{\mathrm{a2}}} + \frac{c_{\mathrm{H_3O^+}}}{K_{\mathrm{a2}}} + \frac{K_{\mathrm{a3}}}{c_{\mathrm{H_3O^+}}} \right)} \tag{A.51}$$

With $\frac{c_{\mathrm{H_3O^+}}}{K_{\mathrm{a2}}} = \frac{10^{-\mathrm{pH}}}{10^{-\mathrm{p}K_{\mathrm{a2}}}} = 10^{-\mathrm{pH}+\mathrm{p}K_{\mathrm{a2}}}$, $\frac{c^2_{\mathrm{H_3O^+}}}{K_{\mathrm{a1}}K_{\mathrm{a2}}} = \frac{10^{-2\mathrm{pH}}}{10^{-\mathrm{p}K_{\mathrm{a1}}-\mathrm{p}K_{\mathrm{a2}}}} = 10^{-2\mathrm{pH}+\mathrm{p}K_{\mathrm{a1}}+\mathrm{p}K_{\mathrm{a2}}}$ and $\frac{K_{\mathrm{a3}}}{c_{\mathrm{H_3O^+}}} = \frac{10^{-\mathrm{p}K_{\mathrm{a3}}}}{10^{-\mathrm{pH}}} = 10^{\mathrm{pH}-\mathrm{p}K_{\mathrm{a3}}}$ follows:

$$\log c_{\mathrm{HB^{2-}}} = \log C^{\circ}_{\mathrm{H_3B}} - \log\left(1 + 10^{-2\mathrm{pH}+\mathrm{p}K_{\mathrm{a1}}+\mathrm{p}K_{\mathrm{a2}}} + 10^{-\mathrm{pH}+\mathrm{p}K_{\mathrm{a2}}} + 10^{\mathrm{pH}-\mathrm{p}K_{\mathrm{a3}}}\right) \tag{A.52}$$

A2.4 log $c_{\mathrm{B^{3-}}} = f(\mathrm{pH})$

Rearranging Eqs. (A.27), (A.28), and (A.29) gives:

$$c_{\mathrm{HB^{2-}}} = \frac{c_{\mathrm{H_3O^+}} c_{\mathrm{B^{3-}}}}{K_{\mathrm{a3}}} \tag{A.53}$$

$$c_{\mathrm{H_2B^-}} = \frac{c^2_{\mathrm{H_3O^+}} c_{\mathrm{B^{3-}}}}{K_{\mathrm{a2}}K_{\mathrm{a3}}} \tag{A.54}$$

$$c_{\mathrm{H_3B}} = \frac{c^3_{\mathrm{H_3O^+}} c_{\mathrm{B^{3-}}}}{K_{\mathrm{a1}}K_{\mathrm{a2}}K_{\mathrm{a3}}} \tag{A.55}$$

and insertion in Eq. (A.30) gives:

$$
\begin{aligned}
C^{\circ}_{\mathrm{H_3B}} &= \frac{c^3_{\mathrm{H_3O^+}} c_{\mathrm{B^{3-}}}}{K_{\mathrm{a1}} K_{\mathrm{a2}} K_{\mathrm{a3}}} + \frac{c^2_{\mathrm{H_3O^+}} c_{\mathrm{B^{3-}}}}{K_{\mathrm{a2}} K_{\mathrm{a3}}} + \frac{c_{\mathrm{H_3O^+}} c_{\mathrm{B^{3-}}}}{K_{\mathrm{a3}}} + c_{\mathrm{B^{3-}}} \\
&= c_{\mathrm{B^{3-}}} \left(1 + \frac{c^3_{\mathrm{H_3O^+}}}{K_{\mathrm{a1}} K_{\mathrm{a2}} K_{\mathrm{a3}}} + \frac{c^2_{\mathrm{H_3O^+}}}{K_{\mathrm{a2}} K_{\mathrm{a3}}} + \frac{c_{\mathrm{H_3O^+}}}{K_{\mathrm{a3}}} \right)
\end{aligned}
\tag{A.56}
$$

$$
c_{\mathrm{B^{3-}}} = \frac{C^{\circ}_{\mathrm{H_3B}}}{\left(1 + \frac{c^3_{\mathrm{H_3O^+}}}{K_{\mathrm{a1}} K_{\mathrm{a2}} K_{\mathrm{a3}}} + \frac{c^2_{\mathrm{H_3O^+}}}{K_{\mathrm{a2}} K_{\mathrm{a3}}} + \frac{c_{\mathrm{H_3O^+}}}{K_{\mathrm{a3}}} \right)} \tag{A.57}
$$

With $\frac{c_{\mathrm{H_3O^+}}}{K_{\mathrm{a3}}} = \frac{10^{-\mathrm{pH}}}{10^{-\mathrm{p}K_{\mathrm{a3}}}} = 10^{-\mathrm{pH}+\mathrm{p}K_{\mathrm{a3}}}$, $\frac{c^2_{\mathrm{H_3O^+}}}{K_{\mathrm{a2}} K_{\mathrm{a3}}} = \frac{10^{-2\mathrm{pH}}}{10^{-\mathrm{p}K_{\mathrm{a2}}-\mathrm{p}K_{\mathrm{a3}}}} = 10^{-2\mathrm{pH}+\mathrm{p}K_{\mathrm{a2}}+\mathrm{p}K_{\mathrm{a3}}}$ and $\frac{c^3_{\mathrm{H_3O^+}}}{K_{\mathrm{a1}} K_{\mathrm{a2}} K_{\mathrm{a3}}} = \frac{10^{-3\mathrm{pH}}}{10^{-\mathrm{p}K_{\mathrm{a1}}-\mathrm{p}K_{\mathrm{a2}}-\mathrm{p}K_{\mathrm{a3}}}} = 10^{-3\mathrm{pH}+\mathrm{p}K_{\mathrm{a1}}+\mathrm{p}K_{\mathrm{a2}}+\mathrm{p}K_{\mathrm{a3}}}$ follows:

$$
\begin{aligned}
\log c_{\mathrm{B^{3-}}} &= \log C^{\circ}_{\mathrm{H_3B}} \\
&\quad - \log\left(1 + 10^{-\mathrm{pH}+\mathrm{p}K_{\mathrm{a3}}} + 10^{-2\mathrm{pH}+\mathrm{p}K_{\mathrm{a2}}+\mathrm{p}K_{\mathrm{a3}}} + 10^{-3\mathrm{pH}+\mathrm{p}K_{\mathrm{a1}}+\mathrm{p}K_{\mathrm{a2}}+\mathrm{p}K_{\mathrm{a3}}}\right)
\end{aligned}
\tag{A.58}
$$

A3. Derivation of the Functions log $c_i = f(\mathrm{pH})$ for Tetrabasic Acids

Protolysis equilibria:

$$\mathrm{H_4B + H_2O \rightleftarrows H_3B^{\cdot -} + H_3O^+} \tag{A.59}$$

$$\mathrm{H_3B^- + H_2O \rightleftarrows H_2B^{2-} + H_3O^+} \tag{A.60}$$

$$\mathrm{H_2B^{2-} + H_2O \rightleftarrows HB^{3-} + H_3O^+} \tag{A.61}$$

$$\mathrm{HB^{3-} + H_2O \rightleftarrows B^{4-} + H_3O^+} \tag{A.62}$$

Laws of mass action:

$$K_{\mathrm{S1}} = \frac{c_{\mathrm{H_3B^-}} c_{\mathrm{H_3O^+}}}{c_{\mathrm{H_4B}}} \tag{A.63}$$

$$K_{S2} = \frac{c_{H_2B^{2-}}\, c_{H_3O^+}}{c_{H_3B^-}} \tag{A.64}$$

$$K_{S3} = \frac{c_{HB^{3-}}\, c_{H_3O^+}}{c_{H_2B^{2-}}} \tag{A.65}$$

$$K_{S4} = \frac{c_{B^{4-}}\, c_{H_3O^+}}{c_{HB^{3-}}} \tag{A.66}$$

Amount balance:

$$C^{\bigcirc}_{H_4B} = c_{H_4B} + c_{H_3B^-} + c_{H_2B^{2-}} + c_{HB^{3-}} + c_{B^{4-}} \tag{A.67}$$

The following functions need to be derived:

1. $\log c_{H_4B} = f(\mathrm{pH})$ (A.68)

2. $\log c_{H_3B^-} = f(\mathrm{pH})$ (A.69)

3. $\log c_{H_2B^{2-}} = f(\mathrm{pH})$ (A.70)

4. $\log c_{HB^{3-}} = f(\mathrm{pH})$ (A.71)

5. $\log c_{B^{4-}} = f(\mathrm{pH})$ (A.72)

A3.1 $\log c_{H_4B} = f(\mathrm{pH})$

Rearranging Eqs. (A.63), (A.64), (A.65), and (A.66) gives:

$$c_{H_3B^-} = \frac{K_{a1} c_{H_4B}}{c_{H_3O^+}} \tag{A.73}$$

$$c_{H_2B^{2-}} = \frac{K_{a1} K_{a2} c_{H_4B}}{c^2_{H_3O^+}} \tag{A.74}$$

$$c_{HB^{3-}} = \frac{K_{a1} K_{a2} K_{a3} c_{H_4B}}{c^3_{H_3O^+}} \tag{A.75}$$

$$c_{B^{4-}} = \frac{K_{a1}K_{a2}K_{a3}K_{a4}c_{H_4B}}{c^4_{H_3O^+}} \tag{A.76}$$

and insertion in Eq. (A.67) gives:

$$\begin{aligned} C^{\circ}_{H_4B} &= c_{H_4B} + \frac{K_{a1}c_{H_4B}}{c_{H_3O^+}} + \frac{K_{a1}K_{a2}c_{H_4B}}{c^2_{H_3O^+}} + \frac{K_{a1}K_{a2}K_{a3}c_{H_4B}}{c^3_{H_3O^+}} + \frac{K_{a1}K_{a2}K_{a3}K_{a4}c_{H_4B}}{c^4_{H_3O^+}} \\ C^{\circ}_{H_4B} &= c_{H_4B}\left(1 + \frac{K_{a1}}{c_{H_3O^+}} + \frac{K_{a1}K_{a2}}{c^2_{H_3O^+}} + \frac{K_{a1}K_{a2}K_{a3}}{c^3_{H_3O^+}} + \frac{K_{a1}K_{a2}K_{a3}K_{a4}}{c^4_{H_3O^+}}\right) \end{aligned} \tag{A.77}$$

$$c_{H_4B} = \frac{C^{\circ}_{H_4B}}{\left(1 + \frac{K_{a1}}{c_{H_3O^+}} + \frac{K_{a1}K_{a2}}{c^2_{H_3O^+}} + \frac{K_{a1}K_{a2}K_{a3}}{c^3_{H_3O^+}} + \frac{K_{a1}K_{a2}K_{a3}K_{a4}}{c^4_{H_3O^+}}\right)} \tag{A.78}$$

With $\frac{K_{a1}}{c_{H_3O^+}} = \frac{10^{-pK_{a1}}}{10^{-pH}} = 10^{pH-pK_{a1}}$, $\frac{K_{a1}K_{a2}}{c^2_{H_3O^+}} = \frac{10^{-pK_{a1}-pK_{a2}}}{10^{-2pH}} = 10^{2pH-pK_{a1}-pK_{a2}}$, $\frac{K_{a1}K_{a2}K_{a3}}{c^3_{H_3O^+}} = \frac{10^{-pK_{a1}-pK_{a2}-pK_{a3}}}{10^{-3pH}} = 10^{3pH-pK_{a1}-pK_{a2}-pK_{a3}}$ and $\frac{K_{a1}K_{a2}K_{a3}K_{a4}}{c^4_{H_3O^+}} = \frac{10^{-pK_{a1}-pK_{a2}-pK_{a3}-pK_{a4}}}{10^{-4pH}} = 10^{4pH-pK_{a1}-pK_{a2}-pK_{a3}-pK_{a4}}$ follows:

$$\begin{aligned} \log c_{H_4B} = &\log C^{\circ}_{H_4B} - \log\left(1 + 10^{pH-pK_{a1}} + 10^{2pH-pK_{a1}-pK_{a2}}\right. \\ &\left. + 10^{3pH-pK_{a1}-pK_{a2}-pK_{a3}} + 10^{4pH-pK_{a1}-pK_{a2}-pK_{a3}-pK_{a4}}\right) \end{aligned} \tag{A.79}$$

A3.2 $\log c_{H_3B^-} = f(\mathrm{pH})$

Rearranging Eqs. (A.63), (A.64), (A.65), and (A.66) gives:

$$c_{H_4B} = \frac{c_{H_3O^+}c_{H_3B^-}}{K_{a1}} \tag{A.80}$$

$$c_{H_2B^{2-}} = \frac{K_{a2}c_{H_3B^-}}{c_{H_3O^+}} \tag{A.81}$$

$$c_{HB^{3-}} = \frac{K_{a2}K_{a3}c_{H_3B^-}}{c^2_{H_3O^+}} \tag{A.82}$$

$$c_{B^{4-}} = \frac{K_{a2}K_{a3}K_{a4}c_{H_3B^-}}{c^3_{H_3O^+}} \tag{A.83}$$

and insertion in Eq. (A.67) gives:

$$C^{\circ}_{H_4B} = c_{H_3B^-} + \frac{c_{H_3O^+}c_{H_3B^-}}{K_{a1}} + \frac{K_{a2}c_{H_3B^-}}{c_{H_3O^+}} + \frac{K_{a2}K_{a3}c_{H_3B^-}}{c^2_{H_3O^+}} + \frac{K_{a2}K_{a3}K_{a4}c_{H_3B^-}}{c^3_{H_3O^+}}$$

$$C^{\circ}_{H_4B} = c_{H_3B^-}\left(1 + \frac{c_{H_3O^+}}{K_{a1}} + \frac{K_{a2}}{c_{H_3O^+}} + \frac{K_{a2}K_{a3}}{c^2_{H_3O^+}} + \frac{K_{a2}K_{a3}K_{a4}}{c^3_{H_3O^+}}\right) \tag{A.84}$$

$$c_{H_3B^-} = \frac{C^{\circ}_{H_4B}}{\left(1 + \frac{c_{H_3O^+}}{K_{a1}} + \frac{K_{a2}}{c_{H_3O^+}} + \frac{K_{a2}K_{a3}}{c^2_{H_3O^+}} + \frac{K_{a2}K_{a3}K_{a4}}{c^3_{H_3O^+}}\right)} \tag{A.85}$$

With $\frac{c_{H_3O^+}}{K_{a1}} = \frac{10^{-pH}}{10^{-pK_{a1}}} = 10^{-pH+pK_{a1}}$, $\frac{K_{a2}}{c_{H_3O^+}} = \frac{10^{-pK_{a2}}}{10^{-pH}} = 10^{pH-pK_{a2}}$, $\frac{K_{a2}K_{a3}}{c^2_{H_3O^+}} = \frac{10^{-pK_{a2}-pK_{a3}}}{10^{-2pH}} = 10^{2pH-pK_{a2}-pK_{a3}}$ and $\frac{K_{a2}K_{a3}K_{a4}}{c^3_{H_3O^+}} = \frac{10^{-pK_{a2}-pK_{a3}-pK_{a4}}}{10^{-3pH}}$ $= 10^{3pH-pK_{a2}-pK_{a3}-pK_{a4}}$ follows

$$\log c_{H_3B^-} = \log C^{\circ}_{H_4B} - \log\left(1 + 10^{-pH+pK_{a1}} + 10^{pH-pK_{a2}} + 10^{2pH-pK_{a2}-pK_{a3}} + 10^{3pH-pK_{a2}-pK_{a3}-pK_{a4}}\right) \tag{A.86}$$

A3.3 $\log c_{H_2B^{2-}} = f(\mathrm{pH})$

Rearranging Eqs. (A.63), (A.64), (A.65), and (A.66) gives:

$$c_{H_4B} = \frac{c^2_{H_3O^+}c_{H_2B^{2-}}}{K_{a1}K_{a2}} \tag{A.87}$$

$$c_{H_3B^-} = \frac{c_{H_3O^+}c_{H_2B^{2-}}}{K_{a2}} \tag{A.88}$$

$$c_{HB^{3-}} = \frac{K_{a3}c_{H_2B^{2-}}}{c_{H_3O^+}} \tag{A.89}$$

$$c_{\mathrm{B^{4-}}} = \frac{K_{\mathrm{a3}} K_{\mathrm{a4}} c_{\mathrm{H_2B^{2-}}}}{c^2_{\mathrm{H_3O^+}}} \tag{A.90}$$

and insertion in Eq. (A.67) gives:

$$C^{\circ}_{\mathrm{H_4B}} = c_{\mathrm{H_2B^{2-}}} + \frac{c_{\mathrm{H_3O^+}} c_{\mathrm{H_2B^{2-}}}}{K_{\mathrm{a2}}} + \frac{c^2_{\mathrm{H_3O^+}} c_{\mathrm{H_2B^{2-}}}}{K_{\mathrm{a1}} K_{\mathrm{a2}}} + \frac{K_{\mathrm{a3}} c_{\mathrm{H_2B^{2-}}}}{c_{\mathrm{H_3O^+}}} + \frac{K_{\mathrm{a3}} K_{\mathrm{a4}} c_{\mathrm{H_2B^{2-}}}}{c^2_{\mathrm{H_3O^+}}}$$

$$C^{\circ}_{\mathrm{H_4B}} = c_{\mathrm{H_2B^{2-}}} \left(1 + \frac{c_{\mathrm{H_3O^+}}}{K_{\mathrm{a2}}} + \frac{c^2_{\mathrm{H_3O^+}}}{K_{\mathrm{a1}} K_{\mathrm{a2}}} + \frac{K_{\mathrm{a3}}}{c_{\mathrm{H_3O^+}}} + \frac{K_{\mathrm{a3}} K_{\mathrm{a4}}}{c^2_{\mathrm{H_3O^+}}} \right) \tag{A.91}$$

$$c_{\mathrm{H_2B^{2-}}} = \frac{C^{\circ}_{\mathrm{H_4B}}}{\left(1 + \frac{c_{\mathrm{H_3O^+}}}{K_{\mathrm{a2}}} + \frac{c^2_{\mathrm{H_3O^+}}}{K_{\mathrm{a1}} K_{\mathrm{a2}}} + \frac{K_{\mathrm{a3}}}{c_{\mathrm{H_3O^+}}} + \frac{K_{\mathrm{a3}} K_{\mathrm{a4}}}{c^2_{\mathrm{H_3O^+}}} \right)} \tag{A.92}$$

With $\frac{c^2_{\mathrm{H_3O^+}}}{K_{\mathrm{a1}} K_{\mathrm{a2}}} = \frac{10^{-2\mathrm{pH}}}{10^{-\mathrm{p}K_{\mathrm{a1}} - \mathrm{p}K_{\mathrm{a2}}}} = 10^{-2\mathrm{pH} + \mathrm{p}K_{\mathrm{a1}} + \mathrm{p}K_{\mathrm{a2}}}$, $\frac{c_{\mathrm{H_3O^+}}}{K_{\mathrm{a2}}} = \frac{10^{-\mathrm{pH}}}{10^{-\mathrm{p}K_{\mathrm{a2}}}} = 10^{-\mathrm{pH} + \mathrm{p}K_{\mathrm{a2}}}$, $\frac{K_{\mathrm{a3}}}{c_{\mathrm{H_3O^+}}} = \frac{10^{-\mathrm{p}K_{\mathrm{a3}}}}{10^{-\mathrm{pH}}} = 10^{\mathrm{pH} - \mathrm{p}K_{\mathrm{a3}}}$, and $\frac{K_{\mathrm{a3}} K_{\mathrm{a4}}}{c^2_{\mathrm{H_3O^+}}} = \frac{10^{-\mathrm{p}K_{\mathrm{a3}} - \mathrm{p}K_{\mathrm{a4}}}}{10^{-2\mathrm{pH}}} = 10^{2\mathrm{pH} - \mathrm{p}K_{\mathrm{a3}} - \mathrm{p}K_{\mathrm{a4}}}$ follows:

$$\begin{aligned} \log c_{\mathrm{H_2B^{2-}}} &= \log C^{\circ}_{\mathrm{H_4B}} - \log(1 + 10^{-2\mathrm{pH} + \mathrm{p}K_{\mathrm{a1}} + \mathrm{p}K_{\mathrm{a2}}} + 10^{-\mathrm{pH} + \mathrm{p}K_{\mathrm{a2}}} \\ &\quad + 10^{\mathrm{pH} - \mathrm{p}K_{\mathrm{a3}}} + 10^{2\mathrm{pH} - \mathrm{p}K_{\mathrm{a3}} - \mathrm{p}K_{\mathrm{a4}}}) \end{aligned} \tag{A.93}$$

A3.4 $\log c_{\mathrm{HB^{3-}}} = f(\mathrm{pH})$

Rearranging Eqs. (A.63), (A.64), (A.65), and (A.66) gives:

$$c_{\mathrm{H_4B}} = \frac{c^3_{\mathrm{H_3O^+}} c_{\mathrm{HB^{3-}}}}{K_{\mathrm{a1}} K_{\mathrm{a2}} K_{\mathrm{a3}}} \tag{A.94}$$

$$c_{\mathrm{H_3B^-}} = \frac{c^2_{\mathrm{H_3O^+}} c_{\mathrm{HB^{3-}}}}{K_{\mathrm{a2}} K_{\mathrm{a3}}} \tag{A.95}$$

$$c_{\mathrm{H_2B^{2-}}} = \frac{c_{\mathrm{H_3O^+}} c_{\mathrm{HB^{3-}}}}{K_{\mathrm{a3}}} \tag{A.96}$$

$$c_{\mathrm{B}^{4-}} = \frac{K_{\mathrm{a}4} c_{\mathrm{HB}^{3-}}}{c_{\mathrm{H_3O}^+}} \tag{A.97}$$

and insertion in Eq. (A.67) gives:

$$\begin{aligned} C^{\circ}_{\mathrm{H_4B}} &= c_{\mathrm{HB}^{3-}} + \frac{c_{\mathrm{H_3O}^+} c_{\mathrm{HB}^{3-}}}{K_{\mathrm{a}3}} + \frac{c^2_{\mathrm{H_3O}^+} c_{\mathrm{HB}^{3-}}}{K_{\mathrm{a}2} K_{\mathrm{a}3}} + \frac{c^3_{\mathrm{H_3O}^+} c_{\mathrm{HB}^{3-}}}{K_{\mathrm{a}1} K_{\mathrm{a}2} K_{\mathrm{a}3}} + \frac{K_{\mathrm{a}4} c_{\mathrm{HB}^{3-}}}{c_{\mathrm{H_3O}^+}} \\ C^{\circ}_{\mathrm{H_4B}} &= c_{\mathrm{HB}^{3-}} \left(1 + \frac{c_{\mathrm{H_3O}^+}}{K_{\mathrm{a}3}} + \frac{c^2_{\mathrm{H_3O}^+}}{K_{\mathrm{a}2} K_{\mathrm{a}3}} + \frac{c^3_{\mathrm{H_3O}^+}}{K_{\mathrm{a}1} K_{\mathrm{a}2} K_{\mathrm{a}3}} + \frac{K_{\mathrm{a}4}}{c_{\mathrm{H_3O}^+}} \right) \end{aligned} \tag{A.98}$$

$$C^{\circ}_{\mathrm{H_4B}} = c_{\mathrm{HB}^{3-}} \left(1 + \frac{c_{\mathrm{H_3O}^+}}{K_{\mathrm{a}3}} + \frac{c^2_{\mathrm{H_3O}^+}}{K_{\mathrm{a}2} K_{\mathrm{a}3}} + \frac{c^3_{\mathrm{H_3O}^+}}{K_{\mathrm{a}1} K_{\mathrm{a}2} K_{\mathrm{a}3}} + \frac{K_{\mathrm{a}4}}{c_{\mathrm{H_3O}^+}} \right) \tag{A.99}$$

With $\frac{c^3_{\mathrm{H_3O}^+}}{K_{\mathrm{a}1} K_{\mathrm{a}2} K_{\mathrm{a}3}} = \frac{10^{-3\mathrm{pH}}}{10^{-\mathrm{p}K_{\mathrm{a}1} - \mathrm{p}K_{\mathrm{a}2} - \mathrm{p}K_{\mathrm{a}3}}} = 10^{-3\mathrm{pH} + \mathrm{p}K_{\mathrm{a}1} + \mathrm{p}K_{\mathrm{a}2} + \mathrm{p}K_{\mathrm{a}3}}$, $\frac{c^2_{\mathrm{H_3O}^+}}{K_{\mathrm{a}2} K_{\mathrm{a}3}} = \frac{10^{-2\mathrm{pH}}}{10^{-\mathrm{p}K_{\mathrm{a}2} - \mathrm{p}K_{\mathrm{a}3}}} = 10^{-2\mathrm{pH} + \mathrm{p}K_{\mathrm{a}2} + \mathrm{p}K_{\mathrm{a}3}}$, $\frac{c_{\mathrm{H_3O}^+}}{K_{\mathrm{a}3}} = \frac{10^{-\mathrm{pH}}}{10^{-\mathrm{p}K_{\mathrm{a}3}}} = 10^{-\mathrm{pH} + \mathrm{p}K_{\mathrm{a}3}}$ and $\frac{K_{\mathrm{a}4}}{c_{\mathrm{H_3O}^+}} = \frac{10^{-\mathrm{p}K_{\mathrm{a}4}}}{10^{-\mathrm{pH}}} = 10^{\mathrm{pH} - \mathrm{p}K_{\mathrm{a}4}}$ follows:

$$\begin{aligned} \log c_{\mathrm{HB}^{3-}} = \log C^{\circ}_{\mathrm{H_4B}} - \log(1 &+ 10^{-3\mathrm{pH} + \mathrm{p}K_{\mathrm{a}1} + \mathrm{p}K_{\mathrm{a}2} + \mathrm{p}K_{\mathrm{a}3}} + 10^{-2\mathrm{pH} + \mathrm{p}K_{\mathrm{a}2} + \mathrm{p}K_{\mathrm{a}3}} \\ &+ 10^{-\mathrm{pH} + \mathrm{p}K_{\mathrm{a}3}} + 10^{\mathrm{pH} - \mathrm{p}K_{\mathrm{a}4}}) \end{aligned} \tag{A.100}$$

A3.5 $\log c_{B^{4-}} = f(pH)$

Rearranging Eqs. (A.63), (A.64), (A.65), and (A.66) gives:

$$c_{\mathrm{H_4B}} = \frac{c^4_{\mathrm{H_3O}^+} c_{\mathrm{B}^{4-}}}{K_{\mathrm{a}1} K_{\mathrm{a}2} K_{\mathrm{a}3} K_{\mathrm{a}4}} \tag{A.101}$$

$$c_{\mathrm{H_3B}^-} = \frac{c^3_{\mathrm{H_3O}^+} c_{\mathrm{B}^{4-}}}{K_{\mathrm{a}2} K_{\mathrm{a}3} K_{\mathrm{a}4}} \tag{A.102}$$

$$c_{\mathrm{H_2B}^{2-}} = \frac{c^2_{\mathrm{H_3O}^+} c_{\mathrm{B}^{4-}}}{K_{\mathrm{a}3} K_{\mathrm{a}4}} \tag{A.103}$$

$$c_{\mathrm{HB}^{3-}} = \frac{c_{\mathrm{H_3O}^+} c_{\mathrm{B}^{4-}}}{K_{\mathrm{a}4}} \tag{A.104}$$

and insertion in Eq. (A.67) gives:

$$C^{\circ}_{\mathrm{H_4B}} = \frac{c^4_{\mathrm{H_3O^+}} c_{\mathrm{B^{4-}}}}{K_{\mathrm{a1}}K_{\mathrm{a2}}K_{\mathrm{a3}}K_{\mathrm{a4}}} + \frac{c^3_{\mathrm{H_3O^+}} c_{\mathrm{B^{4-}}}}{K_{\mathrm{a2}}K_{\mathrm{a3}}K_{\mathrm{a4}}} + \frac{c^2_{\mathrm{H_3O^+}} c_{\mathrm{B^{4-}}}}{K_{\mathrm{a3}}K_{\mathrm{a4}}} + \frac{c_{\mathrm{H_3O^+}} c_{\mathrm{B^{4-}}}}{K_{\mathrm{a4}}} + c_{\mathrm{B^{4-}}}$$

$$C^{\circ}_{\mathrm{H_4B}} = c_{\mathrm{B^{4-}}}\left(1 + \frac{c^4_{\mathrm{H_3O^+}}}{K_{\mathrm{a1}}K_{\mathrm{a2}}K_{\mathrm{a3}}K_{\mathrm{a4}}} + \frac{c^3_{\mathrm{H_3O^+}}}{K_{\mathrm{a2}}K_{\mathrm{a3}}K_{\mathrm{a4}}} + \frac{c^2_{\mathrm{H_3O^+}}}{K_{\mathrm{a3}}K_{\mathrm{a4}}} + \frac{c_{\mathrm{H_3O^+}}}{K_{\mathrm{a4}}}\right) \tag{A.105}$$

$$c_{\mathrm{B^{4-}}} = \frac{C^{\circ}_{\mathrm{H_4B}}}{\left(1 + \frac{c^4_{\mathrm{H_3O^+}}}{K_{\mathrm{a1}}K_{\mathrm{a2}}K_{\mathrm{a3}}K_{\mathrm{a4}}} + \frac{c^3_{\mathrm{H_3O^+}}}{K_{\mathrm{a2}}K_{\mathrm{a3}}K_{\mathrm{a4}}} + \frac{c^2_{\mathrm{H_3O^+}}}{K_{\mathrm{a3}}K_{\mathrm{a4}}} + \frac{c_{\mathrm{H_3O^+}}}{K_{\mathrm{a4}}}\right)} \tag{A.106}$$

With $\frac{c^4_{\mathrm{H_3O^+}}}{K_{\mathrm{a1}}K_{\mathrm{a2}}K_{\mathrm{a3}}K_{\mathrm{a4}}} = \frac{10^{-4\mathrm{pH}}}{10^{-\mathrm{p}K_{\mathrm{a1}}-\mathrm{p}K_{\mathrm{a2}}-\mathrm{p}K_{\mathrm{a3}}-\mathrm{p}K_{\mathrm{a4}}}} = 10^{-4\mathrm{pH}+\mathrm{p}K_{\mathrm{a1}}+\mathrm{p}K_{\mathrm{a2}}+\mathrm{p}K_{\mathrm{a3}}+\mathrm{p}K_{\mathrm{a4}}}$, $\frac{c^3_{\mathrm{H_3O^+}}}{K_{\mathrm{a2}}K_{\mathrm{a3}}K_{\mathrm{a4}}} = \frac{10^{-3\mathrm{pH}}}{10^{-\mathrm{p}K_{\mathrm{a2}}-\mathrm{p}K_{\mathrm{a3}}-\mathrm{p}K_{\mathrm{a4}}}} = 10^{-3\mathrm{pH}+\mathrm{p}K_{\mathrm{a2}}+\mathrm{p}K_{\mathrm{a3}}+\mathrm{p}K_{\mathrm{a4}}}$, $\frac{c^2_{\mathrm{H_3O^+}}}{K_{\mathrm{a3}}K_{\mathrm{a4}}} = \frac{10^{-2\mathrm{pH}}}{10^{-\mathrm{p}K_{\mathrm{a3}}-\mathrm{p}K_{\mathrm{a4}}}} = 10^{-2\mathrm{pH}+\mathrm{p}K_{\mathrm{a3}}+\mathrm{p}K_{\mathrm{a4}}}$ and $\frac{c_{\mathrm{H_3O^+}}}{K_{\mathrm{a4}}} = \frac{10^{-\mathrm{pH}}}{10^{-\mathrm{p}K_{\mathrm{a4}}}} = 10^{-\mathrm{pH}+\mathrm{p}K_{\mathrm{a4}}}$ follows:

$$\log c_{\mathrm{B^{4-}}} = \log C^{\circ}_{\mathrm{H_4B}} - \log\Big(1 + 10^{-4\mathrm{pH}+\mathrm{p}K_{\mathrm{a1}}+\mathrm{p}K_{\mathrm{a2}}+\mathrm{p}K_{\mathrm{a3}}+\mathrm{p}K_{\mathrm{a4}}} + 10^{-3\mathrm{pH}+\mathrm{p}K_{\mathrm{a2}}+\mathrm{p}K_{\mathrm{a3}}+\mathrm{p}K_{\mathrm{a4}}} + 10^{-2\mathrm{pH}+\mathrm{p}K_{\mathrm{a3}}+\mathrm{p}K_{\mathrm{a4}}} + 10^{-\mathrm{pH}+\mathrm{p}K_{\mathrm{a4}}}\Big) \tag{A.107}$$

A4. Functions of the Asymptotes

A4.1 Dibasic acid H_2B		
H_2B:	$\log c_{H_2B} = \log C^{\circ}_{H_2B} - \log(1 + 10^{pH-pK_{a1}} + 10^{2pH-pK_{a1}-pK_{a2}})$	
$pH < pK_{a1}$	$1 \gg 10^{pH-pK_{a1}} + 10^{2pH-pK_{a1}-pK_{a2}}$	$\log c_{H_2B} = \log C^{\circ}_{H_2B}$
$pK_{a1} < pH < pK_{a2}$	$10^{pH-pK_{a1}} \gg 1 + 10^{2pH-pK_{a1}-pK_{a2}}$	$\log c_{H_2B} = \log C^{\circ}_{H_2B} - \log(10^{pH-pK_{a1}})$ $\log c_{H_2B} = -pH + \log C^{\circ}_{H_2B} + pK_{a1}$
$pK_{a2} < pH$	$10^{2pH-pK_{a1}-pK_{a2}} \gg 1 + 10^{pH-pK_{a1}}$	$\log c_{H_2B} = \log C^{\circ}_{H_2B} - \log(10^{2pH-pK_{a1}-pK_{a2}})$ $\log c_{H_2B} = -2pH + \log C^{\circ}_{H_2B} + pK_{a1} + pK_{a2}$
HB^-:	$\log c_{HB^-} = \log C^{\circ}_{H_2B} - \log(1 + 10^{-pH+pK_{a1}} + 10^{pH-pK_{a2}})$	
$pH < pK_{a1}$	$10^{-pH+pK_{a1}} \gg 1 + 10^{pH-pK_{a2}}$	$\log c_{HB^-} = \log C^{\circ}_{H_2B} - \log(10^{-pH+pK_{a1}})$ $\log c_{HB^-} = pH + \log C^{\circ}_{H_2B} - pK_{a1}$
$pK_{a1} < pH < pK_{a2}$	$1 \gg 10^{-pH+pK_{a1}} + 10^{pH-pK_{a2}}$	$\log c_{HB^-} = \log C^{\circ}_{H_2B}$
$pK_{a2} < pH$	$10^{pH-pK_{a2}} \gg 1 + 10^{-pH+pK_{a1}}$	$\log c_{HB^-} = \log C^{\circ}_{H_2B} - \log(10^{pH-pK_{a2}})$ $\log c_{HB^-} = -pH + \log C^{\circ}_{H_2B} + pK_{a2}$
B^{2-}:	$\log c_{B^{2-}} = \log C^{\circ}_{H_2B} - \log(1 + 10^{-2pH+pK_{a1}+pK_{a2}} + 10^{-pH+pK_{a2}})$	
$pH < pK_{a1}$	$10^{-2pH+pK_{a1}+pK_{a2}} \gg 1 + 10^{-pH+pK_{a2}}$	$\log c_{B^{2-}} = \log C^{\circ}_{H_2B} - \log(10^{-2pH+pK_{a1}+pK_{a2}})$ $\log c_{B^{2-}} = 2pH + \log C^{\circ}_{H_2B} - pK_{a1} - pK_{a2}$
$pK_{a1} < pH < pK_{a2}$	$10^{-pH+pK_{a2}} \gg 1 + 10^{-2pH+pK_{a1}+pK_{a2}}$	$\log c_{B^{2-}} = \log C^{\circ}_{H_2B} - \log(10^{-pH+pK_{a2}})$ $\log c_{B^{2-}} = pH + \log C^{\circ}_{H_2B} - pK_{a2}$
$pK_{a2} < pH$	$1 \gg 10^{-2pH+pK_{a1}+pK_{a2}} + 10^{-pH+pK_{a2}}$	$\log c_{B^{2-}} = \log C^{\circ}_{H_2B}$

(continued)

A4.2 Tribasic acids H_3B

H_3B:	$\log c_{H_3B} = \log C^{\circ}_{H_3B} - \log(1 + 10^{pH-pK_{a1}} + 10^{2pH-pK_{a1}-pK_{a2}} + 10^{3pH-pK_{a1}-pK_{a2}-pK_{a3}})$	
$pH < pK_{a1}$	$1 \gg 10^{pH-pK_{a1}} + 10^{2pH-pK_{a1}-pK_{a2}} + 10^{3pH-pK_{a1}-pK_{a2}-pK_{a3}}$	$\log c_{H_3B} = \log C^{\circ}_{H_3B}$
$pK_{a1} < pH < pK_{a2}$	$10^{pH-pK_{a1}} \gg 1 + 10^{2pH-pK_{a1}-pK_{a2}} + 10^{3pH-pK_{a1}-pK_{a2}-pK_{a3}}$	$\log c_{H_3B} = \log C^{\circ}_{H_3B} - \log(10^{pH-pK_{a1}})$ $\log c_{H_3B} = -pH + \log C^{\circ}_{H_3B} + pK_{a1}$
$pK_{a2} < pH < pK_{a3}$	$10^{2pH-pK_{a1}-pK_{a2}} \gg 1 + 10^{pH-pK_{a1}} + 10^{3pH-pK_{a1}-pK_{a2}-pK_{a3}}$	$\log c_{H_3B} = \log C^{\circ}_{H_3B} - \log(10^{2pH-pK_{a1}-pK_{a2}})$ $\log c_{H_3B} = -2pH + \log C^{\circ}_{H_3B} + pK_{a1} + pK_{a2}$
$pK_{a3} < pH$	$10^{3pH-pK_{a1}-pK_{a2}-pK_{a3}} \gg 1 + 10^{pH-pK_{a1}} + 10^{2pH-pK_{a1}-pK_{a2}}$	$\log c_{H_3B} = \log C^{\circ}_{H_3B} - \log\left(10^{3pH-(pK_{a1}+pK_{a2}+pK_{a3})}\right)$ $\log c_{H_3B} = -3pH + \log C^{\circ}_{H_3B} + pK_{a1} + pK_{a2} + pK_{a3}$
H_2B^-:	$\log c_{H_2B^-} = \log C^{\circ}_{H_3B} - \log(1 + 10^{-pH+pK_{a1}} + 10^{pH-pK_{a2}} + 10^{2pH-pK_{a2}-pK_{a3}})$	
$pH < pK_{a1}$	$10^{-pH+pK_{a1}} \gg 1 + 10^{pH-pK_{a2}} + 10^{2pH-pK_{a2}-pK_{a3}}$	$\log c_{H_2B^-} = \log C^{\circ}_{H_3B} - \log(10^{-pH+pK_{a1}})$ $\log c_{H_2B^-} = pH + \log C^{\circ}_{H_3B} - pK_{a1}$
$pK_{a1} < pH < pK_{a2}$	$1 \gg 10^{-pH+pK_{a1}} + 10^{pH-pK_{a2}} + 10^{2pH-pK_{a2}-pK_{a3}}$	$\log c_{H_2B^-} = \log C^{\circ}_{H_3B}$
$pK_{a2} < pH < pK_{a3}$	$10^{pH-pK_{a2}} \gg 1 + 10^{-pH+pK_{a1}} + 10^{2pH-pK_{a2}-pK_{a3}}$	$\log c_{H_2B^-} = \log C^{\circ}_{H_3B} - \log(10^{pH-pK_{a}})$ $\log c_{H_2B^-} = -pH + \log C^{\circ}_{H_3B} + pK_{a2}$
$pK_{a3} < pH$	$10^{2pH-pK_{a2}-pK_{a3}} \gg 1 + 10^{-pH+pK_{a1}} + 10^{pH-pK_{a2}}$	$\log c_{H_2B^-} = \log C^{\circ}_{H_3B} - \log(10^{2pH-pK_{a2}-pK_{a3}})$ $\log c_{H_2B^-} = -2pH + \log C^{\circ}_{H_3B} + pK_{a2} + pK_{a3}$

$\mathbf{HB^{2-}}$**:**	$\log c_{\mathrm{HB^{2-}}} = \log C^{\circ}_{\mathrm{H_3B}} - \log(1 + 10^{-2\mathrm{pH}+\mathrm{p}K_{\mathrm{a1}}+\mathrm{p}K_{\mathrm{a2}}} + 10^{-\mathrm{pH}+\mathrm{p}K_{\mathrm{a2}}} + 10^{\mathrm{pH}-\mathrm{p}K_{\mathrm{a3}}})$	
$\mathrm{pH} < \mathrm{p}K_{\mathrm{a1}}$	$10^{-2\mathrm{pH}+\mathrm{p}K_{\mathrm{a1}}+\mathrm{p}K_{\mathrm{a2}}} \gg 1 + 10^{-\mathrm{pH}+\mathrm{p}K_{\mathrm{a2}}} + 10^{\mathrm{pH}-\mathrm{p}K_{\mathrm{a3}}}$	$\log c_{\mathrm{HB^{2-}}} = \log C^{\circ}_{\mathrm{H_3B}} - \log\left(10^{-2\mathrm{pH}+\mathrm{p}K_{\mathrm{a1}}+\mathrm{p}K_{\mathrm{a2}}}\right)$ $\log c_{\mathrm{HB^{2-}}} = 2\mathrm{pH} + \log C^{\circ}_{\mathrm{H_3B}} - \mathrm{p}K_{\mathrm{a1}} - \mathrm{p}K_{\mathrm{a2}}$
$\mathrm{p}K_{\mathrm{a1}} < \mathrm{pH} < \mathrm{p}K_{\mathrm{a2}}$	$10^{-\mathrm{pH}+\mathrm{p}K_{\mathrm{a2}}} \gg 1 + 10^{-2\mathrm{pH}+\mathrm{p}K_{\mathrm{a1}}+\mathrm{p}K_{\mathrm{a2}}} + 10^{\mathrm{pH}-\mathrm{p}K_{\mathrm{a3}}}$	$\log c_{\mathrm{HB^{2-}}} = \log C^{\circ}_{\mathrm{H_3B}} - \log\left(10^{-\mathrm{pH}+\mathrm{p}K_{\mathrm{a2}}}\right)$ $\log c_{\mathrm{HB^{2-}}} = \mathrm{pH} + \log C^{\circ}_{\mathrm{H_3B}} - \mathrm{p}K_{\mathrm{a2}}$
$\mathrm{p}K_{\mathrm{a2}} < \mathrm{pH} < \mathrm{p}K_{\mathrm{a3}}$	$1 \gg 10^{-2\mathrm{pH}+\mathrm{p}K_{\mathrm{a1}}+\mathrm{p}K_{\mathrm{a2}}} + 10^{-\mathrm{pH}+\mathrm{p}K_{\mathrm{a2}}} + 10^{\mathrm{pH}-\mathrm{p}K_{\mathrm{a3}}}$	$\log c_{\mathrm{HB^{2-}}} = \log C^{\circ}_{\mathrm{H_3B}}$
$\mathrm{p}K_{\mathrm{a3}} < \mathrm{pH}$	$10^{\mathrm{pH}-\mathrm{p}K_{\mathrm{a3}}} \gg 1 + 10^{-2\mathrm{pH}+\mathrm{p}K_{\mathrm{a1}}+\mathrm{p}K_{\mathrm{a2}}} + 10^{-\mathrm{pH}+\mathrm{p}K_{\mathrm{a2}}}$	$\log c_{\mathrm{HB^{2-}}} = \log C^{\circ}_{\mathrm{H_3B}} - \log\left(10^{\mathrm{pH}-\mathrm{p}K_{\mathrm{a3}}}\right)$ $\log c_{\mathrm{HB^{2-}}} = -\mathrm{pH} + \log C^{\circ}_{\mathrm{H_3B}} + \mathrm{p}K_{\mathrm{a3}}$
$\mathbf{B^{3-}}$**:**	$\log c_{\mathrm{B^{3-}}} = \log C^{\circ}_{\mathrm{H_3B}} - \log\left(1 + 10^{-\mathrm{pH}+\mathrm{p}K_{\mathrm{a3}}} + 10^{-2\mathrm{pH}+\mathrm{p}K_{\mathrm{a2}}+\mathrm{p}K_{\mathrm{a3}}} + 10^{-3\mathrm{pH}+\mathrm{p}K_{\mathrm{a1}}+\mathrm{p}K_{\mathrm{a2}}+\mathrm{p}K_{\mathrm{a3}}}\right)$	
$\mathrm{pH} < \mathrm{p}K_{\mathrm{a1}}$	$10^{-3\mathrm{pH}+\mathrm{p}K_{\mathrm{a1}}+\mathrm{p}K_{\mathrm{a2}}+\mathrm{p}K_{\mathrm{a3}}} \gg 1 + 10^{-\mathrm{pH}+\mathrm{p}K_{\mathrm{a3}}} + 10^{-2\mathrm{pH}+\mathrm{p}K_{\mathrm{a2}}+\mathrm{p}K_{\mathrm{a3}}}$	$\log c_{\mathrm{B^{3-}}} = \log C^{\circ}_{\mathrm{H_3B}} - \log\left(10^{-3\mathrm{pH}+\mathrm{p}K_{\mathrm{a1}}+\mathrm{p}K_{\mathrm{a2}}+\mathrm{p}K_{\mathrm{a3}}}\right)$ $\log c_{\mathrm{B^{3-}}} = 3\mathrm{pH} + \log C^{\circ}_{\mathrm{H_3B}} - \mathrm{p}K_{\mathrm{a1}} - \mathrm{p}K_{\mathrm{a2}} - \mathrm{p}K_{\mathrm{a3}}$
$\mathrm{p}K_{\mathrm{a1}} < \mathrm{pH} < \mathrm{p}K_{\mathrm{a2}}$	$10^{-2\mathrm{pH}+\mathrm{p}K_{\mathrm{a2}}+\mathrm{p}K_{\mathrm{a3}}} \gg 1 + 10^{-\mathrm{pH}+\mathrm{p}K_{\mathrm{a3}}} + 10^{-3\mathrm{pH}+\mathrm{p}K_{\mathrm{a1}}+\mathrm{p}K_{\mathrm{a2}}+\mathrm{p}K_{\mathrm{a3}}}$	$\log c_{\mathrm{B^{3-}}} = \log C^{\circ}_{\mathrm{H_3B}} - \log\left(10^{-2\mathrm{pH}+\mathrm{p}K_{\mathrm{a2}}+\mathrm{p}K_{\mathrm{a3}}}\right)$ $\log c_{\mathrm{B^{3-}}} = 2\mathrm{pH} + \log C^{\circ}_{\mathrm{H_3B}} - \mathrm{p}K_{\mathrm{a2}} - \mathrm{p}K_{\mathrm{a3}}$
$\mathrm{p}K_{\mathrm{a2}} < \mathrm{pH} < \mathrm{p}K_{\mathrm{a3}}$	$10^{-\mathrm{pH}+\mathrm{p}K_{\mathrm{a3}}} \gg 1 + 10^{-2\mathrm{pH}+\mathrm{p}K_{\mathrm{a2}}+\mathrm{p}K_{\mathrm{a3}}} + 10^{-3\mathrm{pH}+\mathrm{p}K_{\mathrm{a1}}+\mathrm{p}K_{\mathrm{a2}}+\mathrm{p}K_{\mathrm{a3}}}$	$\log c_{\mathrm{B^{3-}}} = \log C^{\circ}_{\mathrm{H_3B}} - \log\left(10^{-\mathrm{pH}+\mathrm{p}K_{\mathrm{a3}}}\right)$ $\log c_{\mathrm{B^{3-}}} = \mathrm{pH} + \log C^{\circ}_{\mathrm{H_3B}} - \mathrm{p}K_{\mathrm{a3}}$
$\mathrm{p}K_{\mathrm{a3}} < \mathrm{pH}$	$1 \gg 10^{-\mathrm{pH}+\mathrm{p}K_{\mathrm{a3}}} + 10^{-2\mathrm{pH}+\mathrm{p}K_{\mathrm{a2}}+\mathrm{p}K_{\mathrm{a3}}} + 10^{-3\mathrm{pH}+\mathrm{p}K_{\mathrm{a1}}+\mathrm{p}K_{\mathrm{a2}}+\mathrm{p}K_{\mathrm{a3}}}$	$\log c_{\mathrm{B^{3-}}} = \log C^{\circ}_{\mathrm{H_3B}}$

(continued)

A4.3 Tetrabasic acids H_4B

H_4B:	$\log c_{\mathrm{H_4B}} = \log C^{\circ}_{\mathrm{H_4B}} - \log(1 + 10^{\mathrm{pH}-\mathrm{p}K_{a1}} + 10^{2\mathrm{pH}-\mathrm{p}K_{a1}-\mathrm{p}K_{a2}} + 10^{3\mathrm{pH}-\mathrm{p}K_{a1}-\mathrm{p}K_{a2}-\mathrm{p}K_{a3}} + 10^{4\mathrm{pH}-\mathrm{p}K_{a1}-\mathrm{p}K_{a2}-\mathrm{p}K_{a3}-\mathrm{p}K_{a4}})$	
$\mathrm{pH} < \mathrm{p}K_{a1}$	$1 \gg 10^{\mathrm{pH}-\mathrm{p}K_{a1}} + 10^{2\mathrm{pH}-\mathrm{p}K_{a1}-\mathrm{p}K_{a2}} + 10^{3\mathrm{pH}-\mathrm{p}K_{a1}-\mathrm{p}K_{a2}-\mathrm{p}K_{a3}}$ $+ 10^{4\mathrm{pH}-\mathrm{p}K_{a1}-\mathrm{p}K_{a2}-\mathrm{p}K_{a3}-\mathrm{p}K_{a4}}$	$\log c_{\mathrm{H_4B}} = \log C^{\circ}_{\mathrm{H_4B}}$
$\mathrm{p}K_{a1} < \mathrm{pH} < \mathrm{p}K_{a2}$	$10^{\mathrm{pH}-\mathrm{p}K_{a1}} \gg 1 + 10^{2\mathrm{pH}-\mathrm{p}K_{a1}-\mathrm{p}K_{a2}} + 10^{3\mathrm{pH}-\mathrm{p}K_{a1}-\mathrm{p}K_{a2}-\mathrm{p}K_{a3}}$ $+ 10^{4\mathrm{pH}-\mathrm{p}K_{a1}-\mathrm{p}K_{a2}-\mathrm{p}K_{a3}-\mathrm{p}K_{a4}}$	$\log c_{\mathrm{H_4B}} = \log C^{\circ}_{\mathrm{H_4B}} - \log\left(10^{\mathrm{pH}-\mathrm{p}K_{a1}}\right)$ $\log c_{\mathrm{H_4B}} = -\mathrm{pH} + \log C^{\circ}_{\mathrm{H_4B}} + \mathrm{p}K_{a1}$
$\mathrm{p}K_{a2} < \mathrm{pH} < \mathrm{p}K_{a3}$	$10^{2\mathrm{pH}-\mathrm{p}K_{a1}-\mathrm{p}K_{a2}} \gg 1 + 10^{\mathrm{pH}-\mathrm{p}K_{a1}} + 10^{3\mathrm{pH}-\mathrm{p}K_{a1}-\mathrm{p}K_{a2}-\mathrm{p}K_{a3}}$ $+ 10^{4\mathrm{pH}-\mathrm{p}K_{a1}-\mathrm{p}K_{a2}-\mathrm{p}K_{a3}-\mathrm{p}K_{a4}}$	$\log c_{\mathrm{H_4B}} = \log C^{\circ}_{\mathrm{H_4B}} - \log\left(10^{2\mathrm{pH}-\mathrm{p}K_{a1}-\mathrm{p}K_{a2}}\right)$ $\log c_{\mathrm{H_4B}} = -2\mathrm{pH} + \log C^{\circ}_{\mathrm{H_4B}} + \mathrm{p}K_{a1} + \mathrm{p}K_{a2}$
$\mathrm{p}K_{a3} < \mathrm{pH} < \mathrm{p}K_{a4}$	$10^{3\mathrm{pH}-\mathrm{p}K_{a1}-\mathrm{p}K_{a2}-\mathrm{p}K_{a3}} \gg 1 + 10^{\mathrm{pH}-\mathrm{p}K_{a1}} + 10^{2\mathrm{pH}-\mathrm{p}K_{a1}-\mathrm{p}K_{a2}}$ $+ 10^{4\mathrm{pH}-\mathrm{p}K_{a1}-\mathrm{p}K_{a2}-\mathrm{p}K_{a3}-\mathrm{p}K_{a4}}$	$\log c_{\mathrm{H_4B}} = \log C^{\circ}_{\mathrm{H_4B}} - \log\left(10^{3\mathrm{pH}-\mathrm{p}K_{a1}-\mathrm{p}K_{a2}-\mathrm{p}K_{a3}}\right)$ $\log c_{\mathrm{H_4B}} = -3\mathrm{pH} + \log C^{\circ}_{\mathrm{H_4B}} + \mathrm{p}K_{a1} + \mathrm{p}K_{a2} + \mathrm{p}K_{a3}$
$\mathrm{p}K_{a4} < \mathrm{pH}$	$10^{4\mathrm{pH}-\mathrm{p}K_{a1}-\mathrm{p}K_{a2}-\mathrm{p}K_{a3}-\mathrm{p}K_{a4}} \gg 1 + 10^{\mathrm{pH}-\mathrm{p}K_{a1}} + 10^{2\mathrm{pH}-\mathrm{p}K_{a1}-\mathrm{p}K_{a2}}$ $+ 10^{3\mathrm{pH}-\mathrm{p}K_{a1}-\mathrm{p}K_{a2}-\mathrm{p}K_{a3}}$	$\log c_{\mathrm{H_4B}} = \log C^{\circ}_{\mathrm{H_4B}} - \log\left(10^{4\mathrm{pH}-\mathrm{p}K_{a1}-\mathrm{p}K_{a2}-\mathrm{p}K_{a3}-\mathrm{p}K_{a4}}\right)$ $\log c_{\mathrm{H_4B}} = -4\mathrm{pH} + \log C^{\circ}_{\mathrm{H_4B}} + \mathrm{p}K_{a1} + \mathrm{p}K_{a2}$ $+ \mathrm{p}K_{a3} + \mathrm{p}K_{a4}$
H_3B^-:	$\log c_{\mathrm{H_3B^-}} = \log C^{\circ}_{\mathrm{H_4B}} - \log(1 + 10^{-\mathrm{pH}+\mathrm{p}K_{a1}} + 10^{\mathrm{pH}-\mathrm{p}K_{a2}} + 10^{2\mathrm{pH}-\mathrm{p}K_{a2}-\mathrm{p}K_{a3}} + 10^{3\mathrm{pH}-\mathrm{p}K_{a2}-\mathrm{p}K_{a3}-\mathrm{p}K_{a4}})$	
$\mathrm{pH} < \mathrm{p}K_{a1}$	$10^{-\mathrm{pH}+\mathrm{p}K_{a1}} \gg 1 + 10^{\mathrm{pH}-\mathrm{p}K_{a2}} + 10^{2\mathrm{pH}-\mathrm{p}K_{a2}-\mathrm{p}K_{a3}} + 10^{3\mathrm{pH}-\mathrm{p}K_{a2}-\mathrm{p}K_{a3}-\mathrm{p}K_{a4}}$	$\log c_{\mathrm{H_3B^-}} = \log C^{\circ}_{\mathrm{H_4B}} - \log\left(10^{-\mathrm{pH}+\mathrm{p}K_{a1}}\right)$ $\log c_{\mathrm{H_3B^-}} = \mathrm{pH} + \log C^{\circ}_{\mathrm{H_4B}} - \mathrm{p}K_{a1}$
$\mathrm{p}K_{a1} < \mathrm{pH} < \mathrm{p}K_{a2}$	$1 \gg 10^{-\mathrm{pH}+\mathrm{p}K_{a1}} + 10^{\mathrm{pH}-\mathrm{p}K_{a2}} + 10^{2\mathrm{pH}-\mathrm{p}K_{a2}-\mathrm{p}K_{a3}} + 10^{3\mathrm{pH}-\mathrm{p}K_{a2}-\mathrm{p}K_{a3}-\mathrm{p}K_{a4}}$	$\log c_{\mathrm{H_3B^-}} = \log C^{\circ}_{\mathrm{H_4B}}$

$pK_{a2} < pH < pK_{a3}$	$10^{pH-pK_{a2}} \gg 1 + 10^{-pH+pK_{a1}} + 10^{2pH-pK_{a2}-pK_{a3}} + 10^{3pH-pK_{a2}-pK_{a3}-pK_{a4}}$	$\log c_{H_3B^-} = \log C^{\circ}_{H_4B} - \log\left(+10^{pH-pK_{a2}}\right)$ $\log c_{H_3B^-} = -pH + \log C^{\circ}_{H_4B} + pK_{a2}$
$pK_{a3} < pH < pK_{a4}$	$10^{2pH-pK_{a2}-pK_{a3}} \gg 1 + 10^{-pH+pK_{a1}} + 10^{pH-pK_{a2}} + 10^{3pH-pK_{a2}-pK_{a3}-pK_{a4}}$	$\log c_{H_3B^-} = \log C^{\circ}_{H_4B} - \log\left(10^{2pH-pK_{a2}-pK_{a3}}\right)$ $\log c_{H_3B^-} = -2pH + \log C^{\circ}_{H_4B} + pK_{a2} + pK_{a3}$
$pK_{a4} < pH$	$10^{3pH-pK_{a2}-pK_{a3}-pK_{a4}} \gg 1 + 10^{-pH+pK_{a1}} + 10^{pH-pK_{a2}} + 10^{2pH-pK_{a2}-pK_{a3}}$	$\log c_{H_3B^-} = \log C^{\circ}_{H_4B} - \log\left(10^{3pH-pK_{a2}-pK_{a3}-pK_{a4}}\right)$ $\log c_{H_3B^-} = -3pH + \log C^{\circ}_{H_4B} + pK_{a2} + pK_{a3} + pK_{a4}$
$\mathbf{H_2B^{2-}}$**:**	$\log c_{H_2B^{2-}} = \log C^{\circ}_{H_4B} - \log\left(1 + 10^{-2pH+pK_{a1}-pK_{a2}} + 10^{-pH+pK_{a2}} + 10^{pH-pK_{a3}} + 10^{2pH-pK_{a3}-pK_{a4}}\right)$	
$pH < pK_{a1}$	$10^{-2pH+pK_{a1}+pK_{a2}} \gg 1 + 10^{-pH+pK_{a2}} + 10^{pH-pK_{a3}} + 10^{2pH-pK_{a3}-pK_{a4}}$	$\log c_{H_2B^{2-}} = \log C^{\circ}_{H_4B} - \log\left(10^{-2pH+pK_{a1}+pK_{a2}}\right)$ $\log c_{H_2B^{2-}} = 2pH + \log C^{\circ}_{H_4B} - pK_{a1} - pK_{a2}$
$pK_{a1} < pH < pK_{a2}$	$10^{-pH+pK_{a2}} \gg 1 + 10^{-2pH+pK_{a1}+pK_{a2}} + 10^{pH-pK_{a3}} + 10^{2pH-pK_{a3}-pK_{a4}}$	$\log c_{H_2B^{2-}} = \log C^{\circ}_{H_4B} - \log\left(10^{-pH+pK_{a2}}\right)$ $\log c_{H_2B^{2-}} = pH + \log C^{\circ}_{H_4B} - pK_{a2}$
$pK_{a2} < pH < pK_{a3}$	$1 \gg 10^{-2pH+pK_{a1}+pK_{a2}} + 10^{-pH+pK_{a2}} + 10^{pH-pK_{a3}} + 10^{2pH-pK_{a3}-pK_{a4}}$	$\log c_{H_2B^{2-}} = \log C^{\circ}_{H_4B}$
$pK_{a3} < pH < pK_{a4}$	$10^{pH-pK_{a3}} \gg 1 + 10^{-2pH+pK_{a1}+pK_{a2}} + 10^{-pH+pK_{a2}} + 10^{2pH-pK_{a3}-pK_{a4}}$	$\log c_{H_2B^{2-}} = \log C^{\circ}_{H_4B} - \log\left(10^{pH-pK_{a3}}\right)$ $\log c_{H_2B^{2-}} = -pH + \log C^{\circ}_{H_4B} + pK_{a3}$
$pK_{a4} < pH$	$10^{2pH-pK_{a3}-pK_{a4}} \gg 1 + 10^{-2pH+pK_{a1}+pK_{a2}} + 10^{-pH+pK_{a2}} + 10^{pH-pK_{a3}}$	$\log c_{H_2B^{2-}} = \log C^{\circ}_{H_4B} - \log\left(10^{2pH-pK_{a3}-pK_{a4}}\right)$ $\log c_{H_2B^{2-}} = -2pH + \log C^{\circ}_{H_4B} + pK_{a3} + pK_{a4}$

(continued)

HB^{3-}:	$\log c_{\mathrm{HB}^{3-}} = \log C^{\circ}_{\mathrm{H_4B}} - \log\left(1 + 10^{-3\mathrm{pH}+\mathrm{p}K_{a1}+\mathrm{p}K_{a2}+\mathrm{p}K_{a3}} + 10^{-2\mathrm{pH}+\mathrm{p}K_{a2}+\mathrm{p}K_{a3}} + 10^{-\mathrm{pH}+\mathrm{p}K_{a3}} + 10^{\mathrm{pH}-\mathrm{p}K_{a4}}\right)$	
$\mathrm{pH} < \mathrm{p}K_{a1}$	$10^{-3\mathrm{pH}+\mathrm{p}K_{a1}+\mathrm{p}K_{a2}+\mathrm{p}K_{a3}} \gg 1 + 10^{-2\mathrm{pH}+\mathrm{p}K_{a2}+\mathrm{p}K_{a3}} + 10^{-\mathrm{pH}+\mathrm{p}K_{a3}} + 10^{\mathrm{pH}-\mathrm{p}K_{a4}}$	$\log c_{\mathrm{HB}^{3-}} = \log C^{\circ}_{\mathrm{H_4B}} - \log\left(10^{-3\mathrm{pH}+\mathrm{p}K_{a1}+\mathrm{p}K_{a2}+\mathrm{p}K_{a3}}\right)$ $\log c_{\mathrm{HB}^{3-}} = 3\mathrm{pH} + \log C^{\circ}_{\mathrm{H_4B}} - \mathrm{p}K_{a1} - \mathrm{p}K_{a2} - \mathrm{p}K_{a3}$
$\mathrm{p}K_{a1} < \mathrm{pH} < \mathrm{p}K_{a2}$	$10^{-2\mathrm{pH}+\mathrm{p}K_{a2}+\mathrm{p}K_{a3}} \gg 1 + 10^{-3\mathrm{pH}+\mathrm{p}K_{a1}+\mathrm{p}K_{a2}+\mathrm{p}K_{a3}} + 10^{-\mathrm{pH}+\mathrm{p}K_{a3}} + 10^{\mathrm{pH}-\mathrm{p}K_{a4}}$	$\log c_{\mathrm{HB}^{3-}} = \log C^{\circ}_{\mathrm{H_4B}} - \log\left(10^{-2\mathrm{pH}+\mathrm{p}K_{a2}+\mathrm{p}K_{a3}}\right)$ $\log c_{\mathrm{HB}^{3-}} = 2\mathrm{pH} + \log C^{\circ}_{\mathrm{H_4B}} - \mathrm{p}K_{a2} - \mathrm{p}K_{a3}$
$\mathrm{p}K_{a2} < \mathrm{pH} < \mathrm{p}K_{a3}$	$10^{-\mathrm{pH}+\mathrm{p}K_{a3}} \gg 1 + 10^{-3\mathrm{pH}+\mathrm{p}K_{a1}+\mathrm{p}K_{a2}+\mathrm{p}K_{a3}} + 10^{-2\mathrm{pH}+\mathrm{p}K_{a2}+\mathrm{p}K_{a3}} + 10^{\mathrm{pH}-\mathrm{p}K_{a4}}$	$\log c_{\mathrm{HB}^{3-}} = \log C^{\circ}_{\mathrm{H_4B}} - \log\left(10^{-\mathrm{pH}+\mathrm{p}K_{a3}}\right)$ $\log c_{\mathrm{HB}^{3-}} = \mathrm{pH} + \log C^{\circ}_{\mathrm{H_4B}} - \mathrm{p}K_{a3}$
$\mathrm{p}K_{a3} < \mathrm{pH} < \mathrm{p}K_{a4}$	$1 \gg 10^{-3\mathrm{pH}+\mathrm{p}K_{a1}+\mathrm{p}K_{a2}+\mathrm{p}K_{a3}} + 10^{-2\mathrm{pH}+\mathrm{p}K_{a2}+\mathrm{p}K_{a3}} + 10^{-\mathrm{pH}+\mathrm{p}K_{a3}} + 10^{\mathrm{pH}-\mathrm{p}K_{a4}}$	$\log c_{\mathrm{HB}^{3-}} = \log C^{\circ}_{\mathrm{H_4B}}$
$\mathrm{p}K_{a4} < \mathrm{pH}$	$10^{\mathrm{pH}-\mathrm{p}K_{a4}} \gg 1 + 10^{-3\mathrm{pH}+\mathrm{p}K_{a1}+\mathrm{p}K_{a2}+\mathrm{p}K_{a3}} + 10^{-2\mathrm{pH}+\mathrm{p}K_{a2}+\mathrm{p}K_{a3}} + 10^{-\mathrm{pH}+\mathrm{p}K_{a3}}$	$\log c_{\mathrm{HB}^{3-}} = \log C^{\circ}_{\mathrm{H_4B}} - \log\left(10^{\mathrm{pH}-\mathrm{p}K_{a4}}\right)$ $\log c_{\mathrm{HB}^{3-}} = -\mathrm{pH} + \log C^{\circ}_{\mathrm{H_4B}} + \mathrm{p}K_{a4}$
B^{4-}:	$\log c_{\mathrm{B}^{4-}} = \log C^{\circ}_{\mathrm{H_4B}} - \log\left(1 + 10^{-4\mathrm{pH}+\mathrm{p}K_{a1}+\mathrm{p}K_{a2}+\mathrm{p}K_{a3}+\mathrm{p}K_{a4}} + 10^{-3\mathrm{pH}+\mathrm{p}K_{a2}+\mathrm{p}K_{a3}+\mathrm{p}K_{a4}} + 10^{-2\mathrm{pH}+\mathrm{p}K_{a3}+\mathrm{p}K_{a4}} + 10^{-\mathrm{pH}+\mathrm{p}K_{a4}}\right)$	
$\mathrm{pH} < \mathrm{p}K_{a1}$	$10^{-4\mathrm{pH}+\mathrm{p}K_{a1}+\mathrm{p}K_{a2}+\mathrm{p}K_{a3}+\mathrm{p}K_{a4}} \gg 1 + 10^{-3\mathrm{pH}+\mathrm{p}K_{a2}+\mathrm{p}K_{a3}+\mathrm{p}K_{a4}}$ $+ 10^{-2\mathrm{pH}+\mathrm{p}K_{a3}+\mathrm{p}K_{a4}} + 10^{-\mathrm{pH}+\mathrm{p}K_{a4}}$	$\log c_{\mathrm{B}^{4-}} = \log C^{\circ}_{\mathrm{H_4B}} - \log\left(10^{-4\mathrm{pH}+\mathrm{p}K_{a1}+\mathrm{p}K_{a2}+\mathrm{p}K_{a3}+\mathrm{p}K_{a4}}\right)$ $\log c_{\mathrm{B}^{4-}} = 4\mathrm{pH} + \log C^{\circ}_{\mathrm{H_4B}} - \mathrm{p}K_{a1} - \mathrm{p}K_{a2} - \mathrm{p}K_{a3} - \mathrm{p}K_{a4}$
$\mathrm{p}K_{a1} < \mathrm{pH} < \mathrm{p}K_{a2}$	$10^{-3\mathrm{pH}+\mathrm{p}K_{a2}+\mathrm{p}K_{a3}+\mathrm{p}K_{a4}} \gg 1 + 10^{-4\mathrm{pH}+\mathrm{p}K_{a1}+\mathrm{p}K_{a2}+\mathrm{p}K_{a3}+\mathrm{p}K_{a4}}$ $+ 10^{-2\mathrm{pH}+\mathrm{p}K_{a3}+\mathrm{p}K_{a4}} + 10^{-\mathrm{pH}+\mathrm{p}K_{a4}}$	$\log c_{\mathrm{B}^{4-}} = \log C^{\circ}_{\mathrm{H_4B}} - \log\left(10^{-3\mathrm{pH}+\mathrm{p}K_{a2}+\mathrm{p}K_{a3}+\mathrm{p}K_{a4}}\right)$ $\log c_{\mathrm{B}^{4-}} = 3\mathrm{pH} + \log C^{\circ}_{\mathrm{H_4B}} - \mathrm{p}K_{a2} - \mathrm{p}K_{a3} - \mathrm{p}K_{a4}$

$\mathrm{p}K_{\mathrm{a2}} < \mathrm{pH} < \mathrm{p}K_{\mathrm{a3}}$	$10^{-2\mathrm{pH}+\mathrm{p}K_{\mathrm{a3}}+\mathrm{p}K_{\mathrm{a4}}} \gg 1 + 10^{-4\mathrm{pH}+\mathrm{p}K_{\mathrm{a1}}+\mathrm{p}K_{\mathrm{a2}}+\mathrm{p}K_{\mathrm{a3}}+\mathrm{p}K_{\mathrm{a4}}}$ $+ 10^{-3\mathrm{pH}+\mathrm{p}K_{\mathrm{a2}}+\mathrm{p}K_{\mathrm{a3}}+\mathrm{p}K_{\mathrm{a4}}} + 10^{-\mathrm{pH}+\mathrm{p}K_{\mathrm{a4}}}$	$\log c_{\mathrm{B}^{4-}} = \log C^{\circ}_{\mathrm{H_4B}} - \log\left(10^{-2\mathrm{pH}+\mathrm{p}K_{\mathrm{a3}}+\mathrm{p}K_{\mathrm{a4}}}\right)$ $\log c_{\mathrm{B}^{4-}} = 2\mathrm{pH} + \log C^{\circ}_{\mathrm{H_4B}} - \mathrm{p}K_{\mathrm{a3}} - \mathrm{p}K_{\mathrm{a4}}$
$\mathrm{p}K_{\mathrm{a3}} < \mathrm{pH} < \mathrm{p}K_{\mathrm{a4}}$	$10^{-\mathrm{pH}+\mathrm{p}K_{\mathrm{a4}}} \gg 1 + 10^{-4\mathrm{pH}+\mathrm{p}K_{\mathrm{a1}}+\mathrm{p}K_{\mathrm{a2}}+\mathrm{p}K_{\mathrm{a3}}+\mathrm{p}K_{\mathrm{a4}}}$ $+ 10^{-3\mathrm{pH}+\mathrm{p}K_{\mathrm{a2}}+\mathrm{p}K_{\mathrm{a3}}+\mathrm{p}K_{\mathrm{a4}}} + 10^{-2\mathrm{pH}+\mathrm{p}K_{\mathrm{a3}}+\mathrm{p}K_{\mathrm{a4}}}$	$\log c_{\mathrm{B}^{4-}} = \log C^{\circ}_{\mathrm{H_4B}} - \log\left(10^{-\mathrm{pH}+\mathrm{p}K_{\mathrm{a4}}}\right)$ $\log c_{\mathrm{B}^{4-}} = \mathrm{pH} + \log C^{\circ}_{\mathrm{H_4B}} - \mathrm{p}K_{\mathrm{a4}}$
$\mathrm{p}K_{\mathrm{a4}} < \mathrm{pH}$	$1 \gg 10^{-4\mathrm{pH}+\mathrm{p}K_{\mathrm{a1}}+\mathrm{p}K_{\mathrm{a2}}+\mathrm{p}K_{\mathrm{a3}}+\mathrm{p}K_{\mathrm{a4}}} + 10^{-3\mathrm{pH}+\mathrm{p}K_{\mathrm{a2}}+\mathrm{p}K_{\mathrm{a3}}+\mathrm{p}K_{\mathrm{a4}}}$ $+ 10^{-2\mathrm{pH}+\mathrm{p}K_{\mathrm{a3}}+\mathrm{p}K_{\mathrm{a4}}} + 10^{-\mathrm{pH}+\mathrm{p}K_{\mathrm{a4}}}$	$\log c_{\mathrm{B}^{4-}} = \log C^{\circ}_{\mathrm{H_4B}}$

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