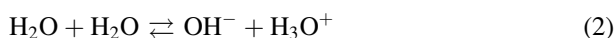
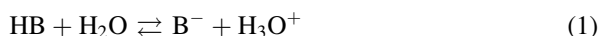


Figure 2 shows the coordination system as used for the construction of pH-log*c<sub>i</sub>* diagrams of aqueous solutions.

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



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

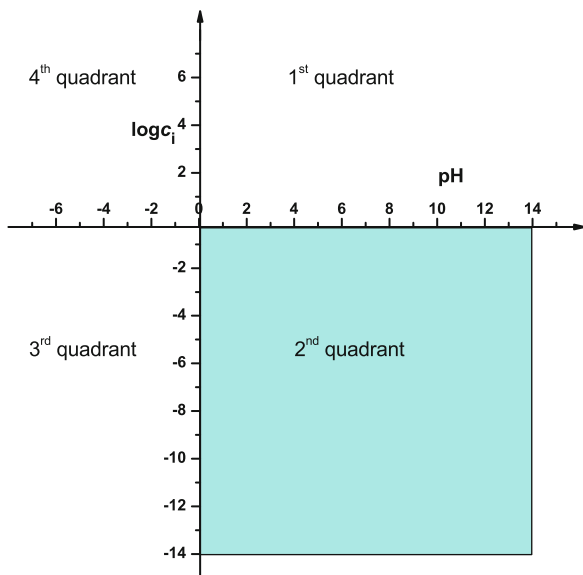
$$K_a = \frac{a_{\text{B}^-}^c a_{\text{H}_3\text{O}^+}^c}{a_{\text{HB}}^c} \quad (3)$$

This equilibrium constant is called *acidity constant*. It has no unit. The quantities  $a_i^c$  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<sup>-1</sup> by the relationship:

$$a_i^c = c_i \gamma_i \times \frac{1}{c^*} \quad (4)$$

The activity coefficients  $\gamma_i$  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<sup>-1</sup>. That quantity leads to unit-free activities. In fact, Eq. (3) also contains the activity of water; however, the *molar ratio activity* is  $a_{\text{H}_2\text{O}}^{\text{mb}} = 1$ , 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:

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



$$K_a = \frac{c_{B^-} c_{H_3O^+}}{c_{HB}} \quad (5)$$

The so defined acidity constant has a unit, here mol L<sup>-1</sup>, 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-log*c<sub>i</sub>* diagrams are generally not applicable to activities. At concentrations higher than 10<sup>-3</sup> mol L<sup>-1</sup>, 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-log*c<sub>i</sub>* 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<sup>-</sup>, H<sub>2</sub>O, H<sub>3</sub>O<sup>+</sup> and OH<sup>-</sup>. In this book, the solvated proton will be always written as H<sub>3</sub>O<sup>+</sup>, although more complex hydrates such as H<sub>5</sub>O<sub>2</sub><sup>+</sup>, H<sub>7</sub>O<sub>3</sub><sup>+</sup> and H<sub>9</sub>O<sub>4</sub><sup>+</sup> 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<sub>3</sub>O<sup>+</sup> determines the pH of a solution:

$$\text{pH} = -\log a_{H_3O^+}^c = -\log \left( c_{H_3O^+} \gamma_{H_3O^+} \times \frac{1}{c^*} \right) \quad (6)$$

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*<sup>+</sup>; 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)

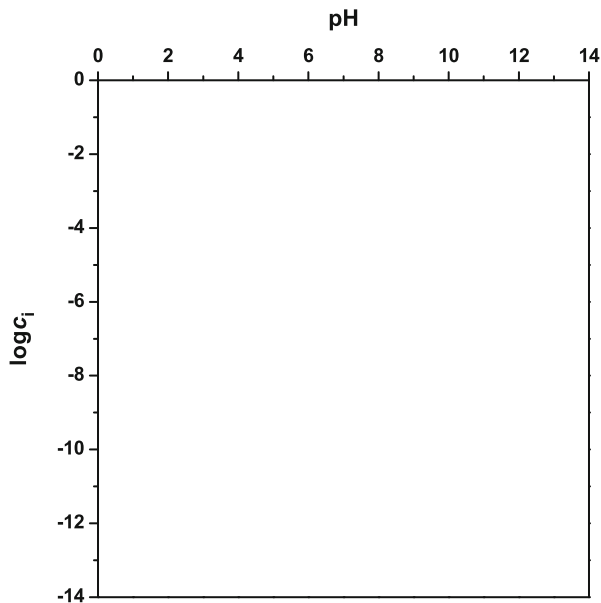


In line with the suggestions of the International Union of Pure and Applied Chemistry, pH is not written in italics, although it is a symbol of a physical quantity [2]. For a long time, it was believed that Sørensen had chosen “p” as a symbol for “power” (“Potenz” in German); however, a recent historical study has revealed that he used it simply as a symbol for a variable [3], standing for the  $H^+$  concentration  $C_p$  or  $10^{-p}$ . In modern style this is:  $c_{H_3O^+} = 10^{-pH}$ ! Nowadays, the definition  $pX = -\log c_X$  is generally used in chemistry for a species X, and also for various equilibrium constants, e.g.,  $pK_a = -\log K_a$  (see further down; here,  $K$  has to be written in italics). The equilibria (1) and (2) connect the activities (concentrations) of all species ( $HB$ ,  $B^-$ ,  $H_2O$ ,  $H_3O^+$ , 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  $1 \text{ mol L}^{-1}$  and  $1.0 \times 10^{-14} \text{ mol L}^{-1}$  are of any importance in real solutions (of course, there may be special cases with concentrations above  $1 \text{ mol L}^{-1}$ , but then the deviations of the activity coefficient from 1.0 will be very remarkable, and special calculations are necessary). Hence, on the  $\log c_i$  axis, the range from 0 to  $-14$  will be plotted in the diagrams. This  $\log c_i$  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  $\log c_{H_3O^+}$  and pH, as well as that between  $\log c_{OH^-}$  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:

$$pH = -\log c_{H_3O^+} \quad (7)$$

**Fig. 4** This is the quadratic diagram with the range of pH and log $c_i$  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

$$K_w = a_{\text{H}_3\text{O}^+}^c a_{\text{OH}^-}^c \quad (8)$$

and it can be approximately described by concentrations as follows:

$$K_w = c_{\text{H}_3\text{O}^+} c_{\text{OH}^-} \quad (9)$$

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

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

$$K_w = c_{\text{H}_3\text{O}^+} c_{\text{OH}^-} = 10^{-14} \text{ mol}^2 \text{ L}^{-2} \quad (10)$$

$$c_{\text{OH}^-} = \frac{K_w}{c_{\text{H}_3\text{O}^+}} \quad (11)$$

$$\log c_{\text{OH}^-} = \log K_w - \log c_{\text{H}_3\text{O}^+} \quad (12)$$

$$-\log c_{\text{OH}^-} = -\log K_w - (-\log c_{\text{H}_3\text{O}^+}) \quad (13)$$

$$\text{pOH} = \text{p}K_w - \text{pH} \quad (14)$$

Equation (14) also describes a straight line in the pH-log $c_i$  diagram. This is the so-called  $\text{OH}^-$  line (cf. Fig. 6).

**Fig. 5** The pH-log $c_i$  diagram with the  $\text{H}_3\text{O}^+$  line of water

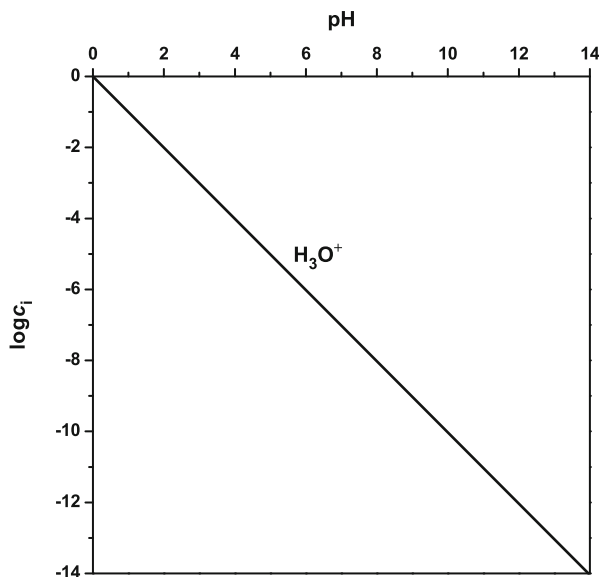
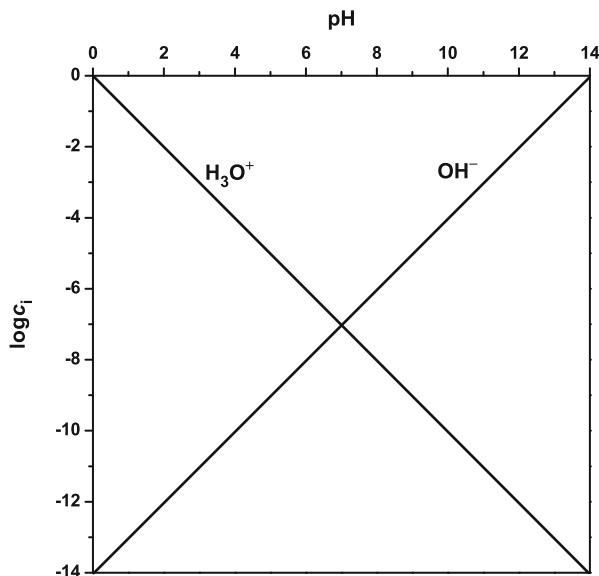


Figure 6 displays only the components  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$ . These species are part of the two acid–base systems  $\text{H}_3\text{O}^+/\text{H}_2\text{O}$  and  $\text{H}_2\text{O}/\text{OH}^-$ .  $\text{H}_3\text{O}^+$  is the strongest acid which can exist in water, and  $\text{OH}^-$  is the strongest base in water. In the case of all acids HB which are stronger than  $\text{H}_3\text{O}^+$  in water, the equilibrium (1) is so much shifted to the right side that one can claim a complete conversion to  $\text{H}_3\text{O}^+$  and  $\text{B}^-$ , 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  $\text{OH}^-$  in water will be almost “completely” converted to HB and  $\text{OH}^-$  according to the reaction

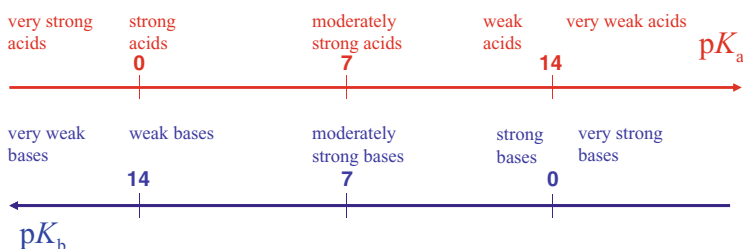


This leads to the effect that all acids which are much stronger than  $\text{H}_3\text{O}^+$  appear to be of the same strength of acidity, i.e., concentration of  $\text{H}_3\text{O}^+$  (provided they have equal analytical concentrations of HB). All bases which are much stronger than  $\text{OH}^-$  will appear also to be of the same strength, i.e., exhibiting the same concentrations of  $\text{OH}^-$  (at equal analytical concentrations of  $\text{B}^-$ ). 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-log $c_i$  diagram with the  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  lines of water



It certainly makes sense to designate acids which are stronger than  $\text{H}_3\text{O}^+$  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  $\text{p}K_a$  value of  $\text{H}_3\text{O}^+$  in water on a strict thermodynamic basis [4]. Similarly, no  $\text{p}K_b$  value can be defined for  $\text{OH}^-$ . Nevertheless it is reasonable to assume that the  $\text{p}K_a$  of  $\text{H}_3\text{O}^+$  is near to 0 (more precisely, slightly below zero) and the  $\text{p}K_a$  of  $\text{H}_2\text{O}$  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  $\text{p}K_a$  values according to Eq. (3) is based on the transfer of a proton from  $\text{HB}$  to  $\text{H}_2\text{O}$ , it is the basicity of  $\text{H}_2\text{O}$  that determines the strength of an acid in water. Hence, all  $\text{p}K_a$  values defined by Eq. (3) are valid for water only, and in other solvents different  $\text{p}K_a$  values have to be used [5]. Table 1 gives a number of  $\text{p}K_a$  values of acids in water.

**Table 1** pK<sub>a</sub> values of acids in water. Most data are from Ref. [10]

Acid–base pair	pK <sub>a</sub> values [ionic strength] <sup>a</sup> (25 °C)
HClO <sub>4</sub> /ClO <sub>4</sub> <sup>−</sup>	ca. −10
HI/I <sup>−</sup>	ca. −10
HBr/Br <sup>−</sup>	ca. −9
HCl/Cl <sup>−</sup>	ca. −7
H <sub>2</sub> SO <sub>4</sub> /HSO <sub>4</sub> <sup>−</sup>	−3 [0]
HNO <sub>3</sub> /NO <sub>3</sub> <sup>−</sup>	−1.34 [0]
C <sub>2</sub> O <sub>4</sub> H <sub>2</sub> /C <sub>2</sub> O <sub>4</sub> H <sup>−</sup> (oxalic acid/hydrogenoxalate)	1.271
HSO <sub>4</sub> <sup>−</sup> /SO <sub>4</sub> <sup>2−</sup>	1.99 [0], 1.55 [0.1]
H <sub>3</sub> PO <sub>4</sub> /H <sub>2</sub> PO <sub>4</sub> <sup>−</sup>	2.148 [0], 2.0 [0.1]
[Fe(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup> /[Fe(H <sub>2</sub> O) <sub>5</sub> OH] <sup>2+</sup>	2.19 [0], 2.83 [0.1]
HF/F <sup>−</sup>	3.17 [0], 2.92 [01], 2.96 [1.0]
HCOOH/HCOO <sup>−</sup> (formic acid/formate)	3.752
C <sub>2</sub> O <sub>4</sub> H <sup>−</sup> /C <sub>2</sub> O <sub>4</sub> <sup>2−</sup> (hydrogenoxalate/oxalate)	4.266
H <sub>3</sub> CCOOH/H <sub>3</sub> CCOO <sup>−</sup> (acetic acid/acetate)	4.756
[Al(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup> /[Al(H <sub>2</sub> O) <sub>5</sub> OH] <sup>2+</sup>	4.99 [0], 5.69 [0.1]
H <sub>2</sub> CO <sub>3</sub> /HCO <sub>3</sub> <sup>−</sup>	6.35 [0], 6.16 [0.1], 6.02 [1.0]
H <sub>2</sub> S/HS <sup>−</sup>	7.02 [0], 6.83 [0.1], 6.61 [1.0]
H <sub>2</sub> PO <sub>4</sub> <sup>−</sup> /HPO <sub>4</sub> <sup>2−</sup>	7.199[0], 6.72 [0.1], 6.46 [1.0]
NH <sub>4</sub> <sup>+</sup> /NH <sub>3</sub>	9.244 [0], 9.29 [0.1], 9.40 [1.0]
HCN/CN <sup>−</sup>	9.21 [0], 9.01 [0.1], 8.95 [1.0]
[Fe(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup> /[Fe(H <sub>2</sub> O) <sub>5</sub> OH] <sup>+</sup>	9.5 [0]

(continued)

**Table 1** (continued)

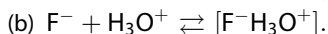
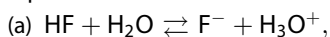
Acid–base pair	p <i>K</i> <sub>a</sub> values [ionic strength] <sup>a</sup> (25 °C)
HCO <sub>3</sub> <sup>−</sup> /CO <sub>3</sub> <sup>2−</sup>	10.33 [0], 10.0 [0.1], 9.57 [1.0]
HPO <sub>4</sub> <sup>2−</sup> /PO <sub>4</sub> <sup>3−</sup>	12.35 [0], 11.74 [0.1], 10.79 [3.0]
HS <sup>−</sup> /S <sup>2−</sup>	13.9 [0], 13.8 [1.0] <sup>b</sup>
NH <sub>3</sub> /NH <sub>2</sub> <sup>−</sup>	ca. 23

<sup>a</sup>The ionic strength can affect the p*K*<sub>a</sub> values. Normally those data are tabulated which are extrapolated for an ionic strength of zero

<sup>b</sup>For the second protolysis stage of hydrogen sulfide, even p*K*<sub>a</sub> values of 16 and 18 are given in the literature

- A closer look at the data in Table 1 shows that the p*K*<sub>a</sub> values of very strong acids (p*K*<sub>a</sub> below 0) and very weak acids (p*K*<sub>a</sub> larger than 14) are not given with the high precision of acids with p*K*<sub>a</sub> 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<sup>−</sup> are extremely small, and a precise experimental determination is difficult. Thus, these p*K*<sub>a</sub> 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 p*K*<sub>a</sub> value of HF is surprisingly large (−4 would probably be a better understandable value). This can be easily explained with the following equilibria:



The species [F<sup>−</sup>H<sub>3</sub>O<sup>+</sup>] is a very stable ion pair having no net charge. The p*K*<sub>a</sub> value is calculated according to  $K_a = \frac{a_{\text{F}^-} a_{\text{H}_3\text{O}^+}}{a_{\text{HF}}}$  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<sup>−</sup>H<sub>3</sub>O<sup>+</sup>], and thus a too large p*K*<sub>a</sub> 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 p*K*<sub>a</sub> 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

$$\log c_{\text{HB}} = f(\text{pH}) \quad (16)$$

and

$$\log c_{\text{B}^-} = f(\text{pH}) \quad (17)$$

in the pH-log $c_i$  diagram (Fig. 6), it is necessary to derive appropriate equations. This requires the law of mass action (5)  $K_a = \frac{c_{\text{B}^-} c_{\text{H}_3\text{O}^+}}{c_{\text{HB}}}$ , and an equation connecting the quantities  $c_{\text{HB}}$  and  $c_{\text{B}^-}$ . According to the reaction (1),  $\text{HB} + \text{H}_2\text{O} \rightleftharpoons \text{B}^- + \text{H}_3\text{O}^+$ , the acid can be present in solution either as HB or as  $\text{B}^-$ . Using concentrations in the unit  $\text{mol L}^{-1}$ , i.e., number of particles (amount in mol) per volume, the following equation must hold for the overall concentration  $C_{\text{HB}}^\circ$ :

$$C_{\text{HB}}^\circ = c_{\text{HB}} + c_{\text{B}^-} \quad (18)$$

Relations of that kind will be called here “amount balances.” The *overall* concentration  $C_{\text{HB}}^\circ$  has to be carefully distinguished from *equilibrium* concentrations, such as  $c_{\text{HB}}$  and  $c_{\text{B}^-}$ : 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  $\text{mol L}^{-1}$ . When using mass concentrations, e.g., in  $\text{g L}^{-1}$ , Eq. (18) would be wrong, as HB has a larger mass than  $\text{B}^-$ .

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

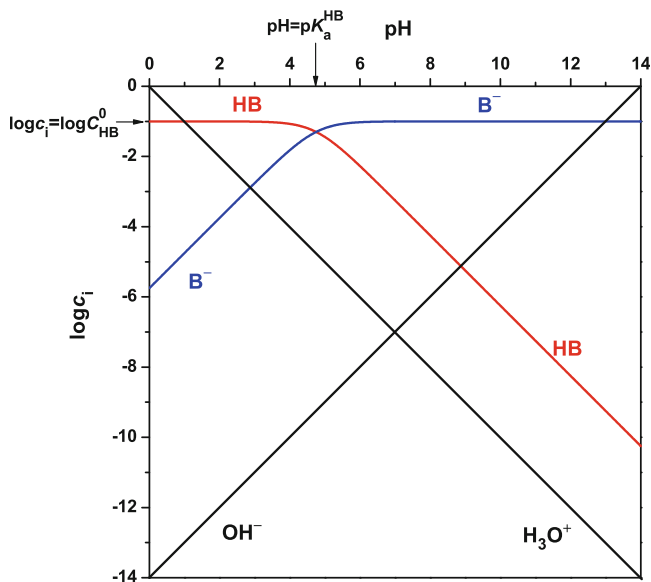
$$K_a = \frac{c_{B^-} c_{H_3O^+}}{c_{HB}} \quad (5)$$

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

Acid HB	Base B <sup>-</sup>
$\log c_{HB} = f(\text{pH}) \quad (16)$	$\log c_{B^-} = f(\text{pH}) \quad (17)$
$K_a = \frac{(C_{HB}^{\circ} - c_{HB}) c_{H_3O^+}}{c_{HB}} \quad (19)$	$K_a = \frac{c_{B^-} c_{H_3O^+}}{C_{HB}^{\circ} - c_{B^-}} \quad (25)$
$K_a c_{HB} = C_{HB}^{\circ} c_{H_3O^+} - c_{HB} c_{H_3O^+} \quad (20)$	$K_a C_{HB}^{\circ} - K_a c_{B^-} = c_{B^-} c_{H_3O^+} \quad (26)$
$K_a c_{HB} + c_{HB} c_{H_3O^+} = C_{HB}^{\circ} c_{H_3O^+} \quad (21)$	$K_a C_{HB}^{\circ} = c_{B^-} c_{H_3O^+} + K_a c_{B^-} \quad (27)$
$c_{HB} = \frac{C_{HB}^{\circ} c_{H_3O^+}}{c_{H_3O^+} + K_a} \quad (22)$	$c_{B^-} = \frac{K_a C_{HB}^{\circ}}{c_{H_3O^+} + K_a} \quad (28)$
$c_{HB} = \frac{C_{HB}^{\circ}}{1 + \frac{K_a}{c_{H_3O^+}}} \quad (23)$	$c_{B^-} = \frac{C_{HB}^{\circ}}{1 + \frac{c_{H_3O^+}}{K_a}} \quad (29)$
with $\frac{K_a}{c_{H_3O^+}} = \frac{10^{-pK_a}}{10^{-\text{pH}}} = 10^{\text{pH} - pK_a} \quad (24)$	with $\frac{c_{H_3O^+}}{K_a} = \frac{10^{-\text{pH}}}{10^{-pK_a}} = 10^{-\text{pH} + pK_a} \quad (30)$
follows	follows
$\log c_{HB} = \log C_{HB}^{\circ} - \log(1 + 10^{\text{pH} - pK_a}) \quad (31)$	$\log c_{B^-} = \log C_{HB}^{\circ} - \log(1 + 10^{-\text{pH} + pK_a}) \quad (32)$

Equations (31) and (32) describe curves in the pH-log<sub>i</sub> 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<sup>-</sup> 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  $\text{pH} = pK_a$  do the hyperbola



**Fig. 8** The pH-log<sub>i</sub> diagram with the lines of H<sub>3</sub>O<sup>+</sup>, OH<sup>-</sup>, HB and B<sup>-</sup> for acetic acid with  $C_{\text{HB}}^{\circ} = 0.1 \text{ mol L}^{-1}$  and  $\text{p}K_{\text{a}} = 4.75$

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  $(1 + 10^{\text{pH}-\text{p}K_{\text{a}}})$  will dominate in the two pH ranges, below and above  $\text{p}K_{\text{a}}$ :

$$\log c_{\text{HB}} = \log C_{\text{HB}}^{\circ} - \log(1 + 10^{\text{pH}-\text{p}K_{\text{a}}}) \quad (31)$$

$\text{p}K_{\text{a}}$	
$\text{pH} < \text{p}K_{\text{a}}$	
Here holds the relation:	
$1 \gg 10^{\text{pH}-\text{p}K_{\text{a}}}$	
and it follows that	
$\log c_{\text{HB}} = \log C_{\text{HB}}^{\circ} \quad (33)$	
$\text{pH} > \text{p}K_{\text{a}}$	
Here holds the relation:	
$1 \ll 10^{\text{pH}-\text{p}K_{\text{a}}}$	
and it follows that	
	$\log c_{\text{HB}} = -\text{pH} + \log C_{\text{HB}}^{\circ} + \text{p}K_{\text{a}} \quad (34)$

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

$$\log c_{B^-} = \log C_{HB}^{\circ} - \log(1 + 10^{-\text{pH}+\text{p}K_a}) \quad (32)$$

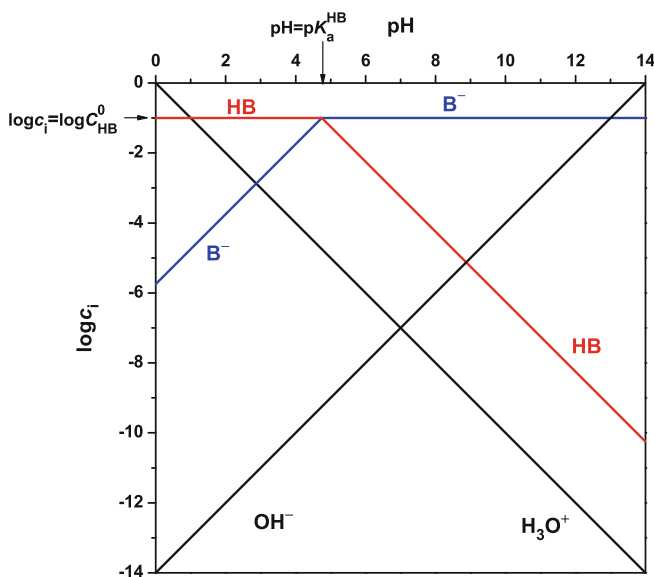
pK <sub>a</sub>	
pH < pK <sub>a</sub>	pH > pK <sub>a</sub>
Here holds the relation:	Here holds the relation:
$1 \ll 10^{-\text{pH}+\text{p}K_a}$	$1 \gg 10^{-\text{pH}+\text{p}K_a}$
and it follows that	and it follows that
$\log c_{B^-} = \text{pH} + \log C_{HB}^{\circ} - \text{p}K_a \quad (35)$	$\log c_{B^-} = \log C_{HB}^{\circ} \quad (36)$

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-log<sub>i</sub> diagram.

Looking at Fig. 9 can prompt the following question: how is it possible that the concentration of B<sup>−</sup> so strongly varies in the range pH < pK<sub>a</sub> whereas that of HB is constant, if Eq. (18)  $C_{HB}^{\circ} = c_{HB} + c_{B^-}$  holds true? The answer is: (a) in the entire range pH < pK<sub>a</sub>, 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<sub>B<sup>−</sup></sub> is plotted, a straight line with the slope +1 follows, but — with the exception of the vicinity of pH = pK<sub>a</sub> — very small concentrations c<sub>B<sup>−</sup></sub> are involved, and thus it follows that  $\log c_{HB} \approx \log C_{HB}^{\circ}$  is a good approximation.

The philosophy of pH-log<sub>i</sub> 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-log $c_i$  diagram with the  $\text{H}_3\text{O}^+$  line, the  $\text{OH}^-$  line and the asymptotes of HB and  $\text{B}^-$  for acetic acid with  $C_{\text{HB}}^0 = 0.1 \text{ mol L}^{-1}$  and  $\text{p}K_a = 4.75$

- The crossing point of the HB and  $\text{B}^-$  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)  $K_a = \frac{c_{\text{B}^-} c_{\text{H}_3\text{O}^+}}{c_{\text{HB}}}$  gives  $\log K_a = \log c_{\text{H}_3\text{O}^+} + \log \frac{c_{\text{B}^-}}{c_{\text{HB}}}$ , i.e.,  $\log c_{\text{H}_3\text{O}^+} = \log K_a + \log \frac{c_{\text{HB}}}{c_{\text{B}^-}}$  or  $\text{pH} = \text{p}K_a - \lg \frac{c_{\text{HB}}}{c_{\text{B}^-}}$ . 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  $\frac{c_{\text{B}^-}}{c_{\text{HB}}} = 1$ , the buffer has a pH equal to the  $\text{p}K_a$  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*  $\beta = \frac{dn}{d(\text{pH})}$ . Here,  $\frac{dn}{d(\text{pH})}$  is the first derivative of the function  $n = f(\text{pH})$  in which  $n$  is the amount of added  $\text{H}_3\text{O}^+$  or  $\text{OH}^-$ . Thus, the buffer capacity is the reciprocal value of the slope of the dependence of the pH as function of added amounts of  $\text{H}_3\text{O}^+$  or  $\text{OH}^-$ . The buffer capacity decreases for  $\frac{c_{\text{B}^-}}{c_{\text{HB}}} < 1$  and  $1 < \frac{c_{\text{B}^-}}{c_{\text{HB}}}$ , and an acceptable buffer capacity can be realized only in the range  $0.1 \leq \frac{c_{\text{B}^-}}{c_{\text{HB}}} \leq 10$ , i.e., in the range  $(\text{p}K_a - 1) \leq \text{pH} \leq (\text{p}K_a + 1)$ . The pH of buffers depends not only on the ratio  $\frac{c_{\text{B}^-}}{c_{\text{HB}}}$ , but the buffer capacity depends also on the overall concentration of the acid and base forms  $C^0 = c_{\text{B}^-} + c_{\text{HB}}$ .

## 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, Štěcha L (1985) *Handbook of chemical equilibria in analytical chemistry*. E. Horwood Ltd., Chichester

Acid-Base Diagrams

Kahlert, H.; Scholz, F.

2013, X, 136 p. 104 illus., 78 illus. in color., Hardcover

ISBN: 978-3-642-37901-7