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 $C_{HB}^{\ominus}$ and a given pK_a^{HB} value:
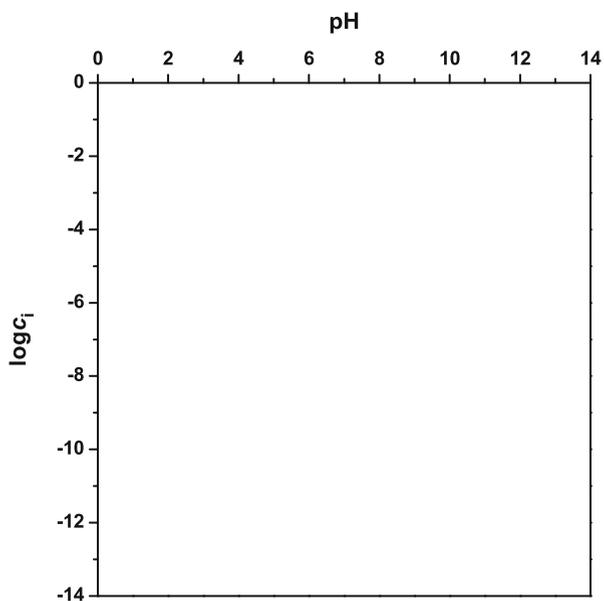

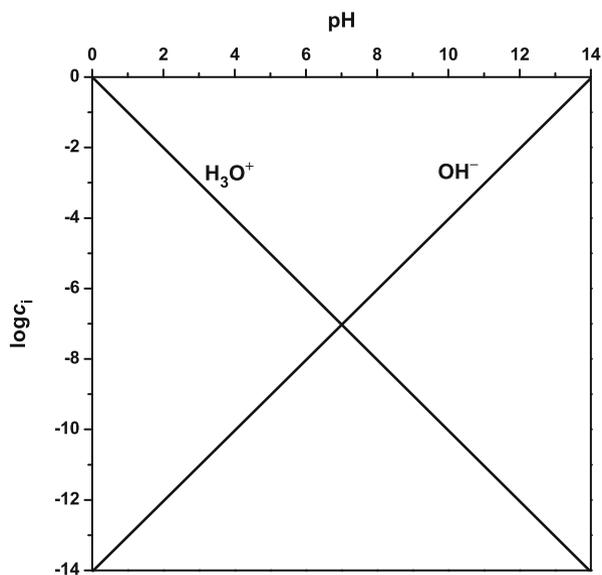**Fig. 10** The coordination system of the pH-logc_i diagram

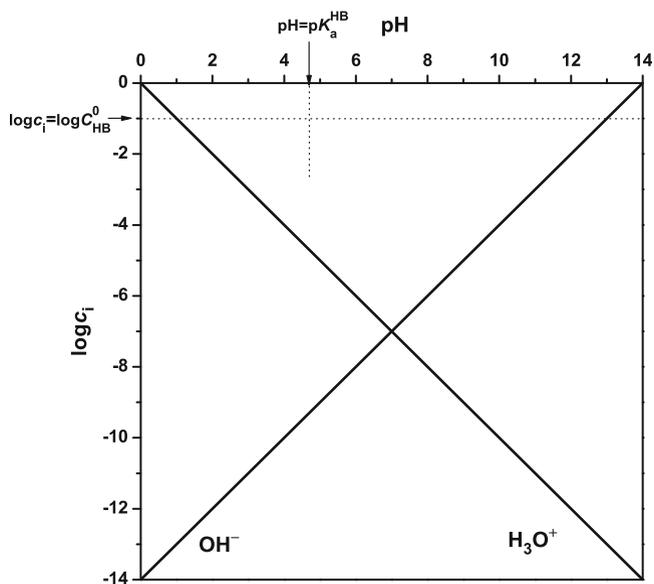**Fig. 11** Plotting the H_3O^+ and OH^- lines of the water system

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 $\text{pH} < \text{p}K_a$ and Eq. (34) for $\text{pH} > \text{p}K_a$. Example: acetic acid with $C_{HB}^{\ominus} = 0.1$ mol L^{-1} and $\text{p}K_a = 4.75$
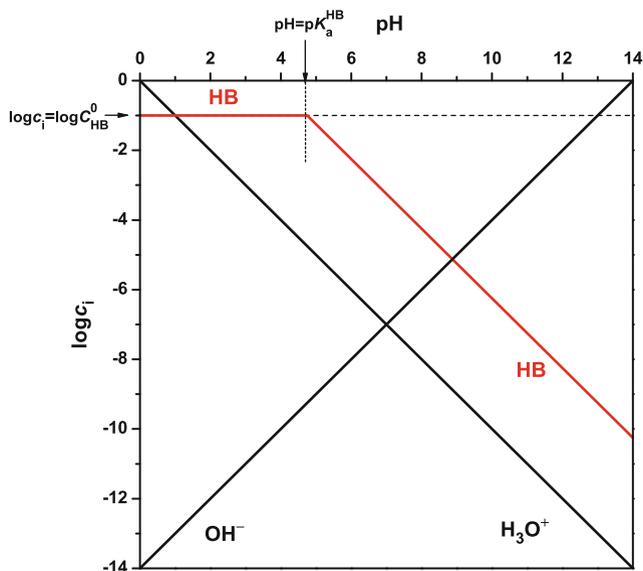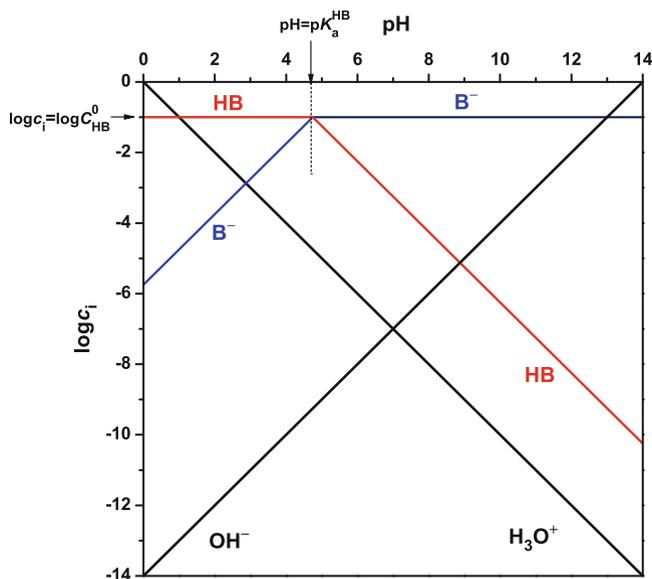

Fig. 14 Plotting the two asymptotes of B^- with Eq. (35) for $\text{pH} < \text{p}K_a$ and Eq. (36) for $\text{pH} > \text{p}K_a$. Example: acetic acid with $C_{HB}^{\ominus} = 0.1$ mol L^{-1} and $\text{p}K_a = 4.75$

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:

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

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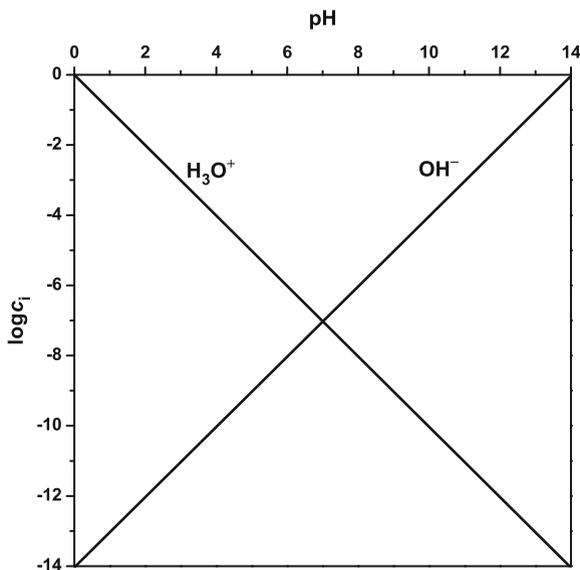
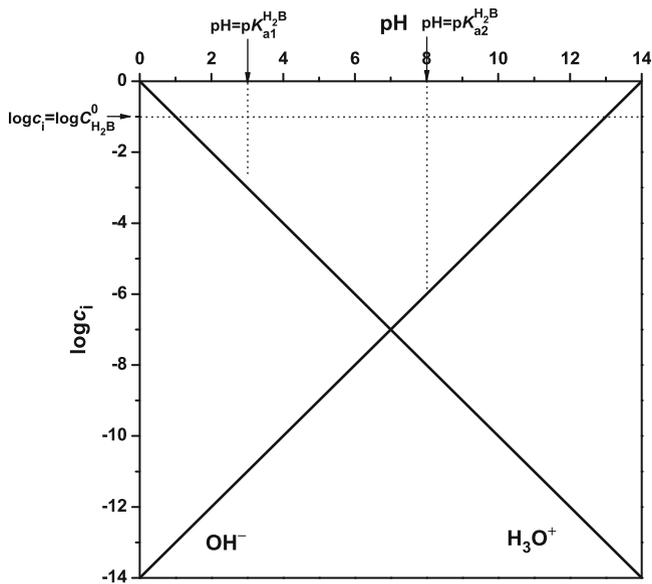**Fig. 15** Plotting the coordination system with the H_3O^+ and OH^- lines of water

Fig. 16 Marking the coordinates, here for the example of an acid with $\log c_i = \log C_{H_2B}^O = -1$, $pH = pK_{a1} = 3$ and $pH = pK_{a2} = 8$

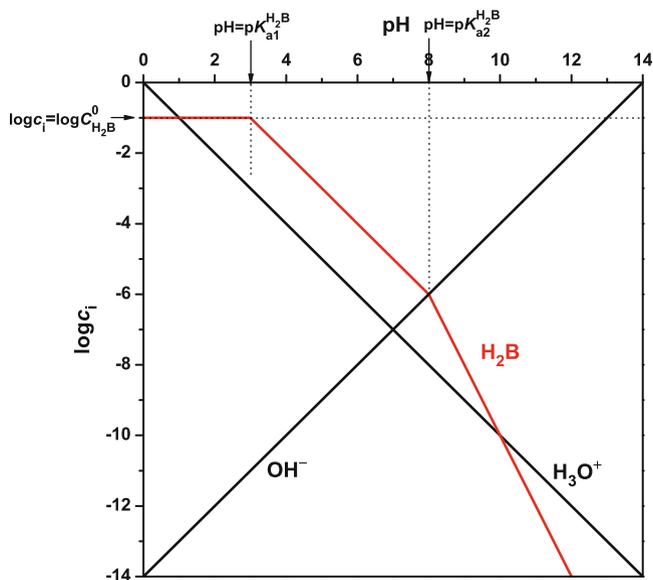**Fig. 17** Plotting the three lines of H_2B in the ranges $pH < pK_{a1}$, $pK_{a1} < pH < pK_{a2}$ and $pH > pK_{a2}$. Example: acid with $\log C_{H_2B}^O = -1$, $pK_{a1} = 3$ and $pK_{a2} = 8$

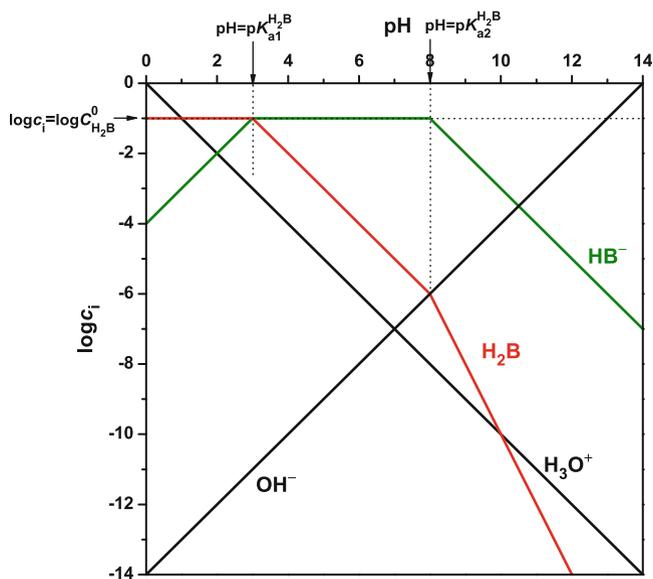**Fig. 18** Plotting the three lines of HB^- in the ranges $pH < pK_{a1}$, $pK_{a1} < pH < pK_{a2}$ and $pH > pK_{a2}$. Example: acid with $\log C_{H_2B}^O = -1$, $pK_{a1} = 3$ and $pK_{a2} = 8$
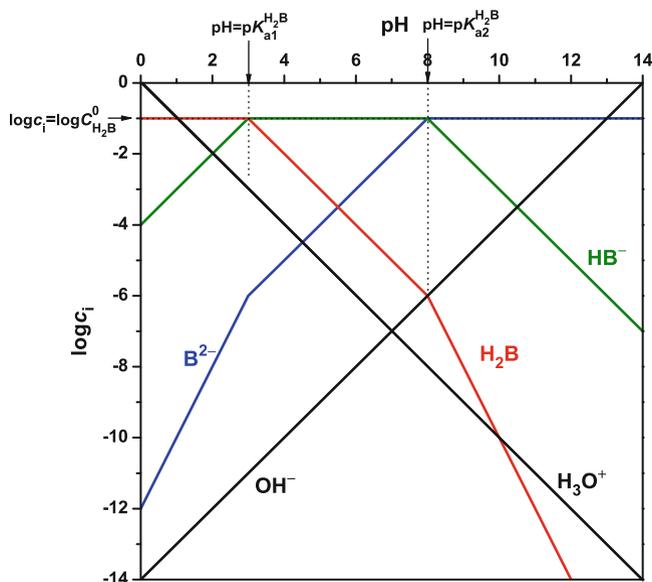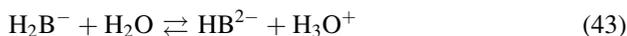
Fig. 19 Plotting the three lines of B^{2-} in the ranges $pH < pK_{a1}$, $pK_{a1} < pH < pK_{a2}$ and $pH > pK_{a2}$. Example: acid with $\log C^{\ominus}_{H_2B} = -1$, $pK_{a1} = 3$ and $pK_{a2} = 8$

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).
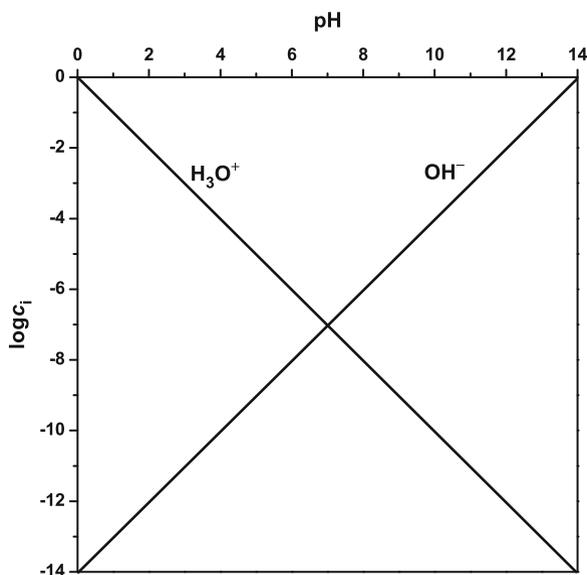
Fig. 20 Plotting the coordination system with the H_3O^+ and OH^- lines of water
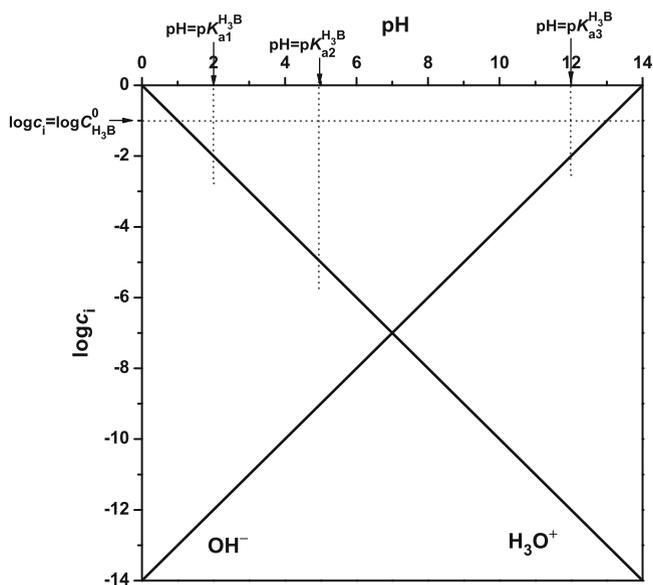
Fig. 21 Marking the coordinates, here for an acid with $\log c_i = \log C_{H_3B}^\ominus = -1$, $pH = pK_{a1} = 2$, $pH = pK_{a2} = 5$ and $pH = pK_{a3} = 12$

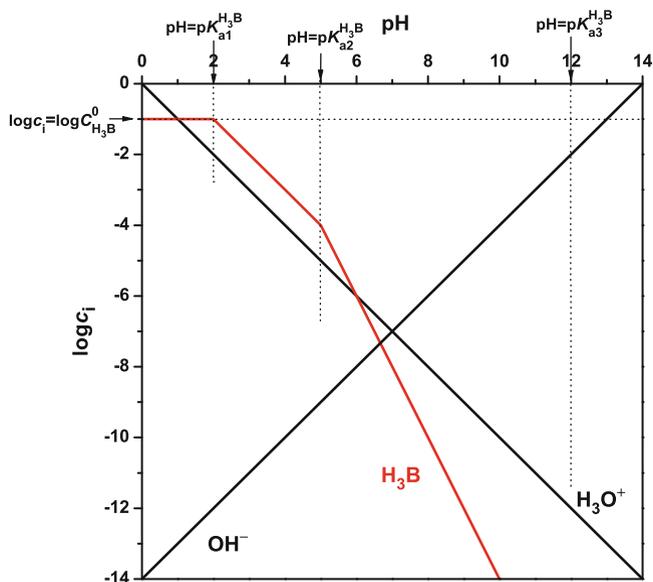**Fig. 22** Plotting the three lines of H_3B in the ranges $pH < pK_{a1}$, $pK_{a1} < pH < pK_{a2}$ and $pK_{a2} < pH < pK_{a3}$. The line of H_3B for $pH > pK_{a3}$ is situated outside the range of the diagram. Example: $\log C_{H_3B}^{O} = -1$, $pK_{a1} = 2$, $pK_{a2} = 5$ and $pK_{a3} = 12$
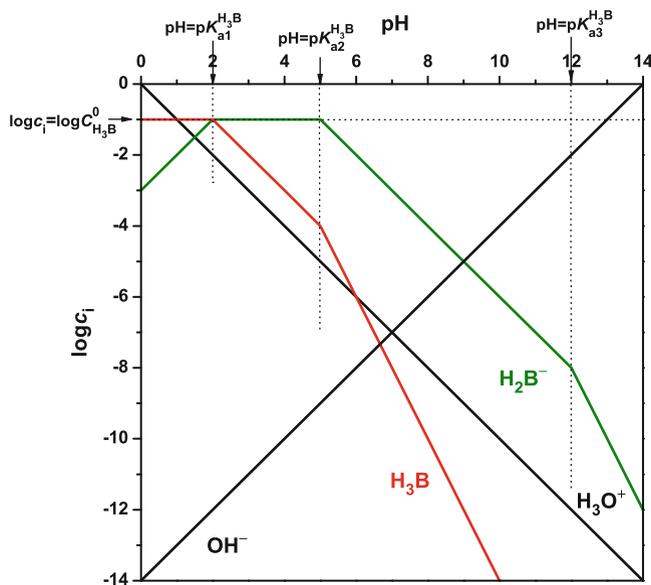

Fig. 23 Plotting the lines of H_2B^- in the ranges $pH < pK_{a1}, pK_{a1} < pH < pK_{a2}, pK_{a2} < pH < pK_{a3}$ and $pH > pK_{a3}$. Example: $\log C_{H_3B}^{O} = -1$, $pK_{a1} = 2$, $pK_{a2} = 5$ and $pK_{a3} = 12$
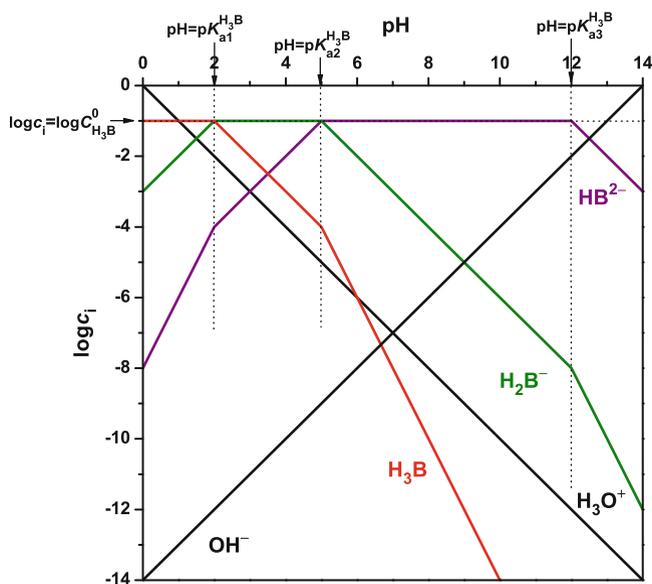
Fig. 24 Plotting the lines of HB^{2-} in the ranges $pH < pK_{a1}, pK_{a1} < pH < pK_{a2}, pK_{a2} < pH < pK_{a3}$ and $pH > pK_{a3}$. Example: $\log C^{\ominus}_{H_3B} = -1$, $pK_{a1} = 2$, $pK_{a2} = 5$ and $pK_{a3} = 12$
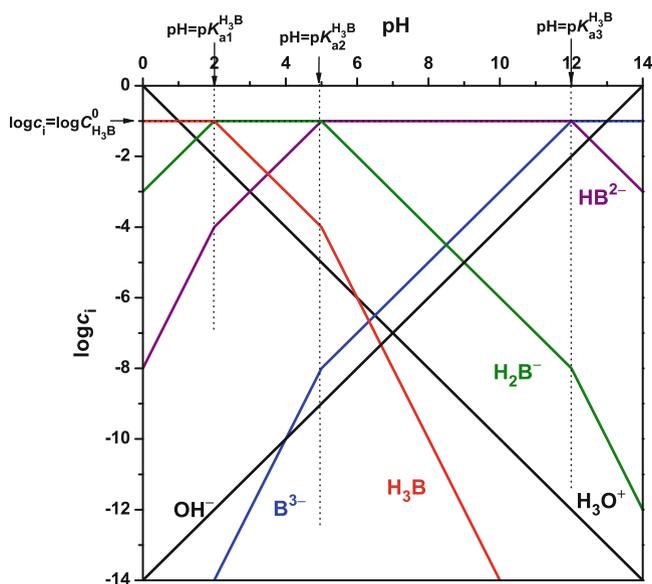

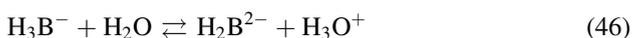**Fig. 25** Plotting the lines of B^{3-} in the ranges $pK_{a1} < pH < pK_{a2}$, $pK_{a2} < pH < pK_{a3}$ and $pH > pK_{a3}$. The line for $pH < pK_{a1}$ is situated outside the range of the coordination system. Example: $\log C^{\ominus}_{H_3B} = -1$, $pK_{a1} = 2$, $pK_{a2} = 5$ and $pK_{a3} = 12$

3.4   Tetrabasic Acids

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

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

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

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

$$HB^{3-} + H_2O \rightleftarrows B^{4-} + H_3O^+ \tag{48}$$
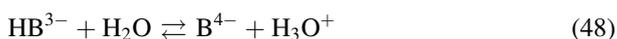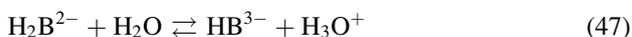
The mathematical equations of the functions are given in the Appendix. The plotting of all species in the diagram can be made with the help of the line equations given in the Appendix. Following the procedures for the mono- to tribasic acids, this is stepwise made in Figs. 26, 27, 28, 29, 30, and 31.

The line of H_4B has the slope -2 in the range $pK_{a2} < pH < pK_{a3}$ (H_2B^{2-} is dominating). The slope is -3 in the range $pK_{a3} < pH < pK_{a4}$ (HB^{3-} is dominating). Sometimes, also in the example shown in Fig. 27, the concentrations of B^{4-} are so small in the range $pH > pK_{a4}$ 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 $pK_{a3} < pH < pK_{a4}$ (HB^{3-} is dominating). For $pH > pK_{a4}$ (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 $pH < pK_{a1}$ where H_4B is dominating. For $pH > pK_{a4}$, the slope is -2 (B^{4-} is dominating).

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

The line of B^{4-} has a slope of $+4$ for $pH < pK_{a1}$ 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 $pK_{a1} < pH < pK_{a2}$, i.e., the range where H_3B^- dominates, the slope is $+3$, and for $pK_{a2} < pH < pK_{a3}$ the slope is $+2$ (H_2B^{2-} is dominating).
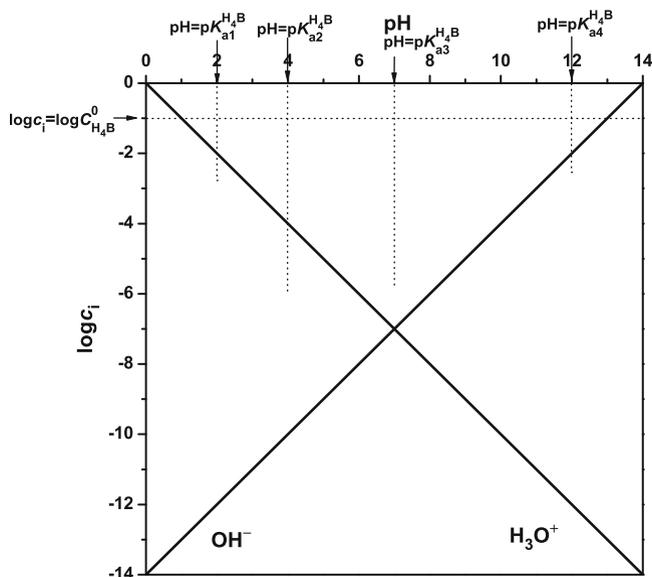
Fig. 26 Plotting the coordination system with the H_3O^+ and OH^- lines of water, and marking the coordinates, here for an example of an acid with $\log c_i = \log C^O_{H_4B} = -1$, $pH = pK_{a1} = 2$, $pH = pK_{a2} = 4$, $pH = pK_{a3} = 7$ and $pH = pK_{a4} = 12$
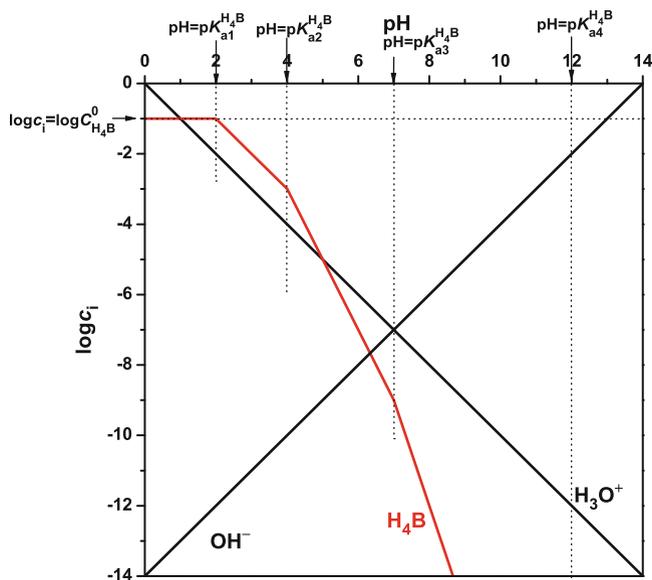
Fig. 27 Plotting the lines of H_4B for $pH < pK_{a1}$, $pK_{a1} < pH < pK_{a2}$, $pK_{a2} < pH < pK_{a3}$ and $pK_{a3} < pH < pK_{a4}$. The line of H_4B for $pH > pK_{a4}$ is situated outside the plotted range. Example: acid with $\log C^O_{H_4B} = -1$, $pK_{a1} = 2$, $pK_{a2} = 4$, $pK_{a3} = 7$ and $pK_{a4} = 12$
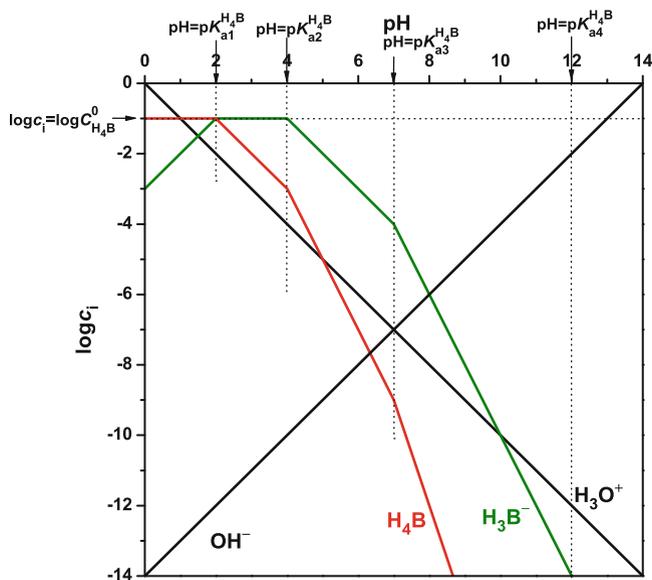
Fig. 28 Plotting the lines of H_3B^- for $pH < pK_{a1}$, $pK_{a1} < pH < pK_{a2}$, $pK_{a2} < pH < pK_{a3}$ and $pK_{a3} < pH < pK_{a4}$. Example: acid with $\log C_{H_4B}^O = -1$, $pK_{a1} = 2$, $pK_{a2} = 4$, $pK_{a3} = 7$ and $pK_{a4} = 12$
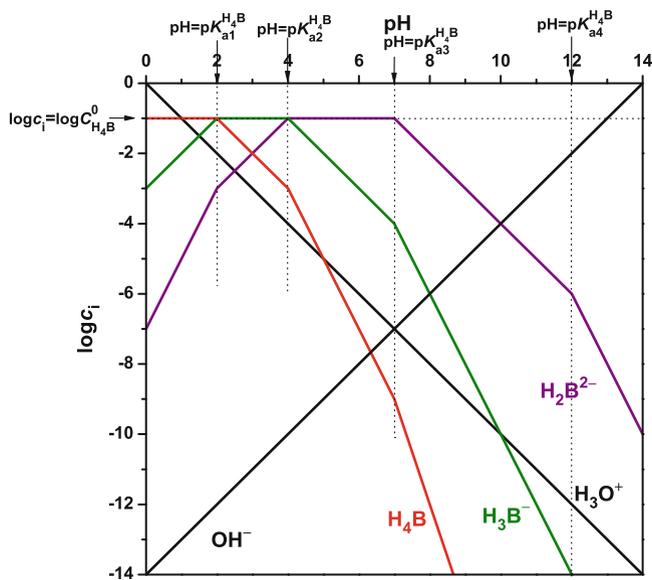
Fig. 29 Plotting the lines of H_2B^{2-} for $pH < pK_{a1}$, $pK_{a1} < pH < pK_{a2}$, $pK_{a2} < pH < pK_{a3}$, $pK_{a3} < pH < pK_{a4}$ and $pH > pK_{a4}$. Example: acid with $\log C_{H_4B}^O = -1$, $pK_{a1} = 2$, $pK_{a2} = 4$, $pK_{a3} = 7$ and $pK_{a4} = 12$
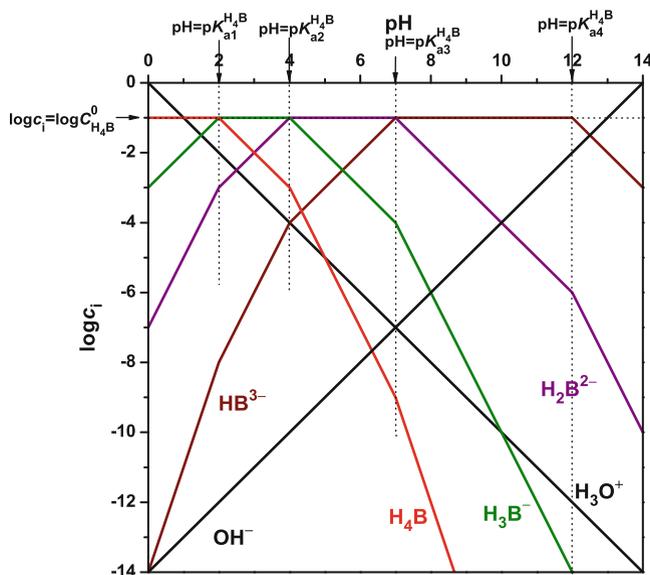
Fig. 30 Plotting the lines of HB^{3-} for pH < pK_{a1}, pK_{a1} < pH < pK_{a2}, pK_{a2} < pH < pK_{a3}, pK_{a3} < pH < pK_{a4} and pH > pK_{a4}. Example: acid with log $C^{\circ}_{H_4B}$ = −1, pK_{a1} = 2, pK_{a2} = 4, pK_{a3} = 7 and pK_{a4} = 12
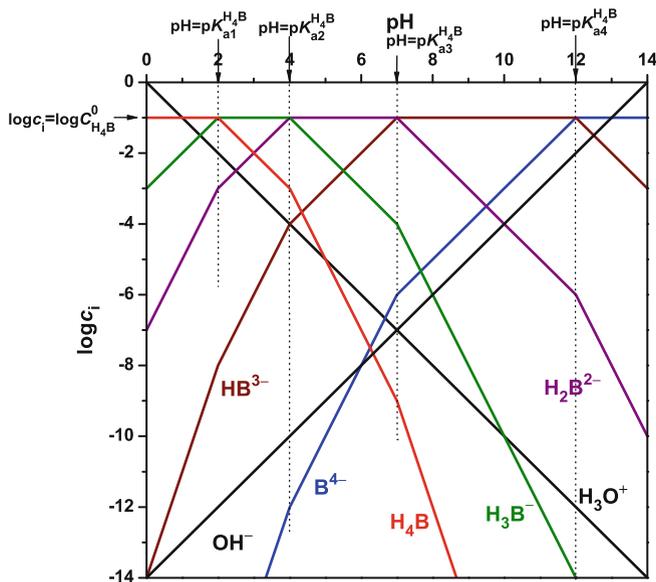
Fig. 31 Plotting the lines of B^{4-} for pK_{a1} < pH < pK_{a2}, pK_{a2} < pH < pK_{a3}, pK_{a3} < pH < pK_{a4} and pH > pK_{a4}. Example: acid with log $C^{\circ}_{H_4B}$ = −1, pK_{a1} = 2, pK_{a2} = 4, pK_{a3} = 7 and pK_{a4} = 12