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

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

Protolysis equilibria:

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

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

Laws of mass action:

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

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

Amount balance:

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

The following functions need to be derived:

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

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

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

H. Kahlert and F. Scholz, *Acid-Base Diagrams*,
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A1.1 $\log c_{H_2B} = f(pH)$

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):

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

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

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

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

Rearrangement gives:

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

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

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

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

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

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

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

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

2. $\log c_{H_2B^-} = f(pH)$ (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 $\dfrac{K_{a1}}{c_{H_3O^+}} = \dfrac{10^{-pK_{a1}}}{10^{-pH}} = 10^{pH - pK_{a1}}$, $\dfrac{K_{a1} K_{a2}}{c^2_{H_3O^+}} = \dfrac{10^{-pK_{a1} - pK_{a2}}}{10^{-2pH}} = 10^{2pH - pK_{a1} - pK_{a2}}$ and $\dfrac{K_{a1} K_{a2} K_{a3}}{c^3_{H_3O^+}} = \dfrac{10^{-pK_{a1} - pK_{a2} - pK_{a3}}}{10^{-3pH}} = 10^{3pH - pK_{a1} - pK_{a2} - pK_{a3}}$ follows

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

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

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

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

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

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:

$$C^{\circ}_{H_3B} = \frac{c^3_{H_3O^+} c_{B^{3-}}}{K_{a1}K_{a2}K_{a3}} + \frac{c^2_{H_3O^+} c_{B^{3-}}}{K_{a2}K_{a3}} + \frac{c_{H_3O^+} c_{B^{3-}}}{K_{a3}} + c_{B^{3-}}$$
$$= c_{B^{3-}} \left(1 + \frac{c^3_{H_3O^+}}{K_{a1}K_{a2}K_{a3}} + \frac{c^2_{H_3O^+}}{K_{a2}K_{a3}} + \frac{c_{H_3O^+}}{K_{a3}}\right) \quad (A.56)$$

$$c_{B^{3-}} = \frac{C^{\circ}_{H_3B}}{\left(1 + \frac{c^3_{H_3O^+}}{K_{a1}K_{a2}K_{a3}} + \frac{c^2_{H_3O^+}}{K_{a2}K_{a3}} + \frac{c_{H_3O^+}}{K_{a3}}\right)} \quad (A.57)$$

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

$$\log c_{B^{3-}} = \log C^{\circ}_{H_3B} - \log\left(1 + 10^{-pH+pK_{a3}} + 10^{-2pH+pK_{a2}+pK_{a3}} + 10^{-3pH+pK_{a1}+pK_{a2}+pK_{a3}}\right) \quad (A.58)$$

A3. Derivation of the Functions $\log c_i = f(pH)$ for Tetrabasic Acids

Protolysis equilibria:

$$H_4B + H_2O \rightleftarrows H_3B^{\cdot -} + H_3O^+ \quad (A.59)$$

$$H_3B^- + H_2O \rightleftarrows H_2B^{2-} + H_3O^+ \quad (A.60)$$

$$H_2B^{2-} + H_2O \rightleftarrows HB^{3-} + H_3O^+ \quad (A.61)$$

$$HB^{3-} + H_2O \rightleftarrows B^{4-} + H_3O^+ \quad (A.62)$$

Laws of mass action:

$$K_{S1} = \frac{c_{H_3B^-} c_{H_3O^+}}{c_{H_4B}} \quad (A.63)$$

$$K_{S2} = \frac{c_{H_2B^{2-}} c_{H_3O^+}}{c_{H_3B^-}} \tag{A.64}$$

$$K_{S3} = \frac{c_{HB^{3-}} c_{H_3O^+}}{c_{H_2B^{2-}}} \tag{A.65}$$

$$K_{S4} = \frac{c_{B^{4-}} c_{H_3O^+}}{c_{HB^{3-}}} \tag{A.66}$$

Amount balance:

$$C^{\circ}_{H_4B} = c_{H_4B} + c_{H_3B^-} + c_{H_2B^{2-}} + c_{HB^{3-}} + c_{B^{4-}} \tag{A.67}$$

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:

$$C^\circ_{H_4B} = c_{H_4B} + \frac{K_{a1}c_{H_4B}}{c_{H_3O^+}} + \frac{K_{a1}K_{a2}c_{H_4B}}{c^2_{H_3O^+}} + \frac{K_{a1}K_{a2}K_{a3}c_{H_4B}}{c^3_{H_3O^+}} + \frac{K_{a1}K_{a2}K_{a3}K_{a4}c_{H_4B}}{c^4_{H_3O^+}}$$
$$C^\circ_{H_4B} = c_{H_4B}\left(1 + \frac{K_{a1}}{c_{H_3O^+}} + \frac{K_{a1}K_{a2}}{c^2_{H_3O^+}} + \frac{K_{a1}K_{a2}K_{a3}}{c^3_{H_3O^+}} + \frac{K_{a1}K_{a2}K_{a3}K_{a4}}{c^4_{H_3O^+}}\right) \tag{A.77}$$

$$c_{H_4B} = \frac{C^\circ_{H_4B}}{\left(1 + \frac{K_{a1}}{c_{H_3O^+}} + \frac{K_{a1}K_{a2}}{c^2_{H_3O^+}} + \frac{K_{a1}K_{a2}K_{a3}}{c^3_{H_3O^+}} + \frac{K_{a1}K_{a2}K_{a3}K_{a4}}{c^4_{H_3O^+}}\right)} \tag{A.78}$$

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:

$$\log c_{H_4B} = \log C^\circ_{H_4B} - \log\left(1 + 10^{pH-pK_{a1}} + 10^{2pH-pK_{a1}-pK_{a2}} + 10^{3pH-pK_{a1}-pK_{a2}-pK_{a3}} + 10^{4pH-pK_{a1}-pK_{a2}-pK_{a3}-pK_{a4}}\right) \tag{A.79}$$

A3.2 $\log c_{H_3B^-} = f(pH)$

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

Rearranging Eqs. (A.63), (A.64), (A.65), and (A.66) gives:

$$c_{H_4B} = \frac{c^2_{H_3O^+}c_{H_2B^{2-}}}{K_{a1}K_{a2}} \tag{A.87}$$

$$c_{H_3B^-} = \frac{c_{H_3O^+}c_{H_2B^{2-}}}{K_{a2}} \tag{A.88}$$

$$c_{HB^{3-}} = \frac{K_{a3}c_{H_2B^{2-}}}{c_{H_3O^+}} \tag{A.89}$$

$$c_{B^{4-}} = \frac{K_{a3}K_{a4}c_{H_2B^{2-}}}{c^2_{H_3O^+}} \tag{A.90}$$

and insertion in Eq. (A.67) gives:

$$C^{\circ}_{H_4B} = c_{H_2B^{2-}} + \frac{c_{H_3O^+}c_{H_2B^{2-}}}{K_{a2}} + \frac{c^2_{H_3O^+}c_{H_2B^{2-}}}{K_{a1}K_{a2}} + \frac{K_{a3}c_{H_2B^{2-}}}{c_{H_3O^+}} + \frac{K_{a3}K_{a4}c_{H_2B^{2-}}}{c^2_{H_3O^+}}$$

$$C^{\circ}_{H_4B} = c_{H_2B^{2-}}\left(1 + \frac{c_{H_3O^+}}{K_{a2}} + \frac{c^2_{H_3O^+}}{K_{a1}K_{a2}} + \frac{K_{a3}}{c_{H_3O^+}} + \frac{K_{a3}K_{a4}}{c^2_{H_3O^+}}\right) \tag{A.91}$$

$$c_{H_2B^{2-}} = \frac{C^{\circ}_{H_4B}}{\left(1 + \frac{c_{H_3O^+}}{K_{a2}} + \frac{c^2_{H_3O^+}}{K_{a1}K_{a2}} + \frac{K_{a3}}{c_{H_3O^+}} + \frac{K_{a3}K_{a4}}{c^2_{H_3O^+}}\right)} \tag{A.92}$$

With $\frac{c^2_{H_3O^+}}{K_{a1}K_{a2}} = \frac{10^{-2pH}}{10^{-pK_{a1}-pK_{a2}}} = 10^{-2pH+pK_{a1}+pK_{a2}}$, $\frac{c_{H_3O^+}}{K_{a2}} = \frac{10^{-pH}}{10^{-pK_{a2}}} = 10^{-pH+pK_{a2}}$, $\frac{K_{a3}}{c_{H_3O^+}} = \frac{10^{-pK_{a3}}}{10^{-pH}} = 10^{pH-pK_{a3}}$, and $\frac{K_{a3}K_{a4}}{c^2_{H_3O^+}} = \frac{10^{-pK_{a3}-pK_{a4}}}{10^{-2pH}} = 10^{2pH-pK_{a3}-pK_{a4}}$ follows:

$$\begin{aligned}\log c_{H_2B^{2-}} = {} & \log C^{\circ}_{H_4B} - \log(1 + 10^{-2pH+pK_{a1}+pK_{a2}} + 10^{-pH+pK_{a2}} \\ & + 10^{pH-pK_{a3}} + 10^{2pH-pK_{a3}-pK_{a4}})\end{aligned} \tag{A.93}$$

A3.4 $\log c_{HB^{3-}} = f(pH)$

Rearranging Eqs. (A.63), (A.64), (A.65), and (A.66) gives:

$$c_{H_4B} = \frac{c^3_{H_3O^+}c_{HB^{3-}}}{K_{a1}K_{a2}K_{a3}} \tag{A.94}$$

$$c_{H_3B^-} = \frac{c^2_{H_3O^+}c_{HB^{3-}}}{K_{a2}K_{a3}} \tag{A.95}$$

$$c_{H_2B^{2-}} = \frac{c_{H_3O^+}c_{HB^{3-}}}{K_{a3}} \tag{A.96}$$

$$c_{B^{4-}} = \frac{K_{a4} c_{HB^{3-}}}{c_{H_3O^+}} \tag{A.97}$$

and insertion in Eq. (A.67) gives:

$$C^{\circ}_{H_4B} = c_{HB^{3-}} + \frac{c_{H_3O^+} c_{HB^{3-}}}{K_{a3}} + \frac{c^2_{H_3O^+} c_{HB^{3-}}}{K_{a2}K_{a3}} + \frac{c^3_{H_3O^+} c_{HB^{3-}}}{K_{a1}K_{a2}K_{a3}} + \frac{K_{a4} c_{HB^{3-}}}{c_{H_3O^+}}$$

$$C^{\circ}_{H_4B} = c_{HB^{3-}} \left(1 + \frac{c_{H_3O^+}}{K_{a3}} + \frac{c^2_{H_3O^+}}{K_{a2}K_{a3}} + \frac{c^3_{H_3O^+}}{K_{a1}K_{a2}K_{a3}} + \frac{K_{a4}}{c_{H_3O^+}}\right) \tag{A.98}$$

$$C^{\circ}_{H_4B} = c_{HB^{3-}} \left(1 + \frac{c_{H_3O^+}}{K_{a3}} + \frac{c^2_{H_3O^+}}{K_{a2}K_{a3}} + \frac{c^3_{H_3O^+}}{K_{a1}K_{a2}K_{a3}} + \frac{K_{a4}}{c_{H_3O^+}}\right) \tag{A.99}$$

With $\frac{c^3_{H_3O^+}}{K_{a1}K_{a2}K_{a3}} = \frac{10^{-3pH}}{10^{-pK_{a1}-pK_{a2}-pK_{a3}}} = 10^{-3pH+pK_{a1}+pK_{a2}+pK_{a3}}$, $\frac{c^2_{H_3O^+}}{K_{a2}K_{a3}} = \frac{10^{-2pH}}{10^{-pK_{a2}-pK_{a3}}}$ $= 10^{-2pH+pK_{a2}+pK_{a3}}$, $\frac{c_{H_3O^+}}{K_{a3}} = \frac{10^{-pH}}{10^{-pK_{a3}}} = 10^{-pH+pK_{a3}}$ and $\frac{K_{a4}}{c_{H_3O^+}} = \frac{10^{-pK_{a4}}}{10^{-pH}} = 10^{pH-pK_{a4}}$ follows:

$$\log c_{HB^{3-}} = \log C^{\circ}_{H_4B} - \log(1 + 10^{-3pH+pK_{a1}+pK_{a2}+pK_{a3}} + 10^{-2pH+pK_{a2}+pK_{a3}} + 10^{-pH+pK_{a3}} + 10^{pH-pK_{a4}}) \tag{A.100}$$

A3.5 $\log c_{B^{4-}} = f(pH)$

Rearranging Eqs. (A.63), (A.64), (A.65), and (A.66) gives:

$$c_{H_4B} = \frac{c^4_{H_3O^+} c_{B^{4-}}}{K_{a1}K_{a2}K_{a3}K_{a4}} \tag{A.101}$$

$$c_{H_3B^-} = \frac{c^3_{H_3O^+} c_{B^{4-}}}{K_{a2}K_{a3}K_{a4}} \tag{A.102}$$

$$c_{H_2B^{2-}} = \frac{c^2_{H_3O^+} c_{B^{4-}}}{K_{a3}K_{a4}} \tag{A.103}$$

$$c_{HB^{3-}} = \frac{c_{H_3O^+} c_{B^{4-}}}{K_{a4}} \tag{A.104}$$

and insertion in Eq. (A.67) gives:

$$C^{\circ}_{H_4B} = \frac{c^4_{H_3O^+} c_{B^{4-}}}{K_{a1}K_{a2}K_{a3}K_{a4}} + \frac{c^3_{H_3O^+} c_{B^{4-}}}{K_{a2}K_{a3}K_{a4}} + \frac{c^2_{H_3O^+} c_{B^{4-}}}{K_{a3}K_{a4}} + \frac{c_{H_3O^+} c_{B^{4-}}}{K_{a4}} + c_{B^{4-}}$$

$$C^{\circ}_{H_4B} = c_{B^{4-}} \left(1 + \frac{c^4_{H_3O^+}}{K_{a1}K_{a2}K_{a3}K_{a4}} + \frac{c^3_{H_3O^+}}{K_{a2}K_{a3}K_{a4}} + \frac{c^2_{H_3O^+}}{K_{a3}K_{a4}} + \frac{c_{H_3O^+}}{K_{a4}} \right) \tag{A.105}$$

$$c_{B^{4-}} = \frac{C^{\circ}_{H_4B}}{\left(1 + \frac{c^4_{H_3O^+}}{K_{a1}K_{a2}K_{a3}K_{a4}} + \frac{c^3_{H_3O^+}}{K_{a2}K_{a3}K_{a4}} + \frac{c^2_{H_3O^+}}{K_{a3}K_{a4}} + \frac{c_{H_3O^+}}{K_{a4}} \right)} \tag{A.106}$$

With $\frac{c^4_{H_3O^+}}{K_{a1}K_{a2}K_{a3}K_{a4}} = \frac{10^{-4pH}}{10^{-pK_{a1}-pK_{a2}-pK_{a3}-pK_{a4}}} = 10^{-4pH+pK_{a1}+pK_{a2}+pK_{a3}+pK_{a4}}$, $\frac{c^3_{H_3O^+}}{K_{a2}K_{a3}K_{a4}} = \frac{10^{-3pH}}{10^{-pK_{a2}-pK_{a3}-pK_{a4}}} = 10^{-3pH+pK_{a2}+pK_{a3}+pK_{a4}}$, $\frac{c^2_{H_3O^+}}{K_{a3}K_{a4}} = \frac{10^{-2pH}}{10^{-pK_{a3}-pK_{a4}}} = 10^{-2pH+pK_{a3}+pK_{a4}}$ and $\frac{c_{H_3O^+}}{K_{a4}} = \frac{10^{-pH}}{10^{-pK_{a4}}} = 10^{-pH+pK_{a4}}$ follows:

$$\log c_{B^{4-}} = \log C^{\circ}_{H_4B} - \log \left(1 + 10^{-4pH+pK_{a1}+pK_{a2}+pK_{a3}+pK_{a4}} + 10^{-3pH+pK_{a2}+pK_{a3}+pK_{a4}} + 10^{-2pH+pK_{a3}+pK_{a4}} + 10^{-pH+pK_{a4}} \right) \tag{A.107}$$

A4. Functions of the Asymptotes

A4.1 Dibasic acid H_2B

H_2B:	$\log c_{H_2B} = \log C^{\circ}_{H_2B} - \log(1 + 10^{pH-pK_{a1}} + 10^{2pH-pK_{a1}-pK_{a2}})$	
$pH < pK_{a1}$	$1 \gg 10^{pH-pK_{a1}} + 10^{2pH-pK_{a1}-pK_{a2}}$	$\log c_{H_2B} = \log C^{\circ}_{H_2B}$
$pK_{a1} < pH < pK_{a2}$	$10^{pH-pK_{a1}} \gg 1 + 10^{2pH-pK_{a1}-pK_{a2}}$	$\log c_{H_2B} = \log C^{\circ}_{H_2B} - \log\left(10^{pH-pK_{a1}}\right)$ $\log c_{H_2B} = -pH + \log C^{\circ}_{H_2B} + pK_{a1}$
$pK_{a2} < pH$	$10^{2pH-pK_{a1}-pK_{a2}} \gg 1 + 10^{pH-pK_{a1}}$	$\log c_{H_2B} = \log C^{\circ}_{H_2B} - \log\left(10^{2pH-pK_{a1}-pK_{a2}}\right)$ $\log c_{H_2B} = -2pH + \log C^{\circ}_{H_2B} + pK_{a1} + pK_{a2}$
HB^-:	$\log c_{HB^-} = \log C^{\circ}_{H_2B} - \log(1 + 10^{-pH+pK_{a1}} + 10^{pH-pK_{a2}})$	
$pH < pK_{a1}$	$10^{-pH+pK_{a1}} \gg 1 + 10^{pH-pK_{a2}}$	$\log c_{HB^-} = \log C^{\circ}_{H_2B} - \log\left(10^{-pH+pK_{a1}}\right)$ $\log c_{HB^-} = pH + \log C^{\circ}_{H_2B} - pK_{a1}$
$pK_{a1} < pH < pK_{a2}$	$1 \gg 10^{-pH+pK_{a1}} + 10^{pH-pK_{a2}}$	$\log c_{HB^-} = \log C^{\circ}_{H_2B}$
$pK_{a2} < pH$	$10^{pH-pK_{a2}} \gg 1 + 10^{-pH+pK_{a1}}$	$\log c_{HB^-} = \log C^{\circ}_{H_2B} - \log\left(10^{pH-pK_{a2}}\right)$ $\log c_{HB^-} = -pH + \log C^{\circ}_{H_2B} + pK_{a2}$
B^{2-}:	$\log c_{B^{2-}} = \log C^{\circ}_{H_2B} - \log(1 + 10^{-2pH+pK_{a1}+pK_{a2}} + 10^{-pH+pK_{a2}})$	
$pH < pK_{a1}$	$10^{-2pH+pK_{a1}+pK_{a2}} \gg 1 + 10^{-pH+pK_{a2}}$	$\log c_{B^{2-}} = \log C^{\circ}_{H_2B} - \log\left(10^{-2pH+pK_{a1}+pK_{a2}}\right)$ $\log c_{B^{2-}} = 2pH + \log C^{\circ}_{H_2B} - pK_{a1} - pK_{a2}$
$pK_{a1} < pH < pK_{a2}$	$10^{-pH+pK_{a2}} \gg 1 + 10^{-2pH+pK_{a1}+pK_{a2}}$	$\log c_{B^{2-}} = \log C^{\circ}_{H_2B} - \log\left(10^{-pH+pK_{a2}}\right)$ $\log c_{B^{2-}} = pH + \log C^{\circ}_{H_2B} - pK_{a2}$
$pK_{a2} < pH$	$1 \gg 10^{-2pH+pK_{a1}+pK_{a2}} + 10^{-pH+pK_{a2}}$	$\log c_{B^{2-}} = \log C^{\circ}_{H_2B}$

(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^-:	$\log c_{H_2B^-} = \log C^{\circ}_{H_3B} - \log(1 + 10^{-pH+pK_{a1}} + 10^{pH-pK_{a2}} + 10^{2pH-pK_{a2}-pK_{a3}})$	
$pH < pK_{a1}$	$10^{-pH+pK_{a1}} \gg 1 + 10^{pH-pK_{a2}} + 10^{2pH-pK_{a2}-pK_{a3}}$	$\log c_{H_2B^-} = \log C^{\circ}_{H_3B} - \log(10^{-pH+pK_{a1}})$ $\log c_{H_2B^-} = pH + \log C^{\circ}_{H_3B} - pK_{a1}$
$pK_{a1} < pH < pK_{a2}$	$1 \gg 10^{-pH+pK_{a1}} + 10^{pH-pK_{a2}} + 10^{2pH-pK_{a2}-pK_{a3}}$	$\log c_{H_2B^-} = \log C^{\circ}_{H_3B}$
$pK_{a2} < pH < pK_{a3}$	$10^{pH-pK_{a2}} \gg 1 + 10^{-pH+pK_{a1}} + 10^{2pH-pK_{a2}-pK_{a3}}$	$\log c_{H_2B^-} = \log C^{\circ}_{H_3B} - \log(10^{pH-pK_a})$ $\log c_{H_2B^-} = -pH + \log C^{\circ}_{H_3B} + pK_{a2}$
$pK_{a3} < pH$	$10^{2pH-pK_{a2}-pK_{a3}} \gg 1 + 10^{-pH+pK_{a1}} + 10^{pH-pK_{a2}}$	$\log c_{H_2B^-} = \log C^{\circ}_{H_3B} - \log(10^{2pH-pK_{a2}-pK_{a3}})$ $\log c_{H_2B^-} = -2pH + \log C^{\circ}_{H_3B} + pK_{a2} + pK_{a3}$

HB^{2-}:	$\log c_{HB^{2-}} = \log C^{\circ}_{H_3B} - \log\left(1 + 10^{-2pH+pK_{a1}+pK_{a2}} + 10^{-pH+pK_{a2}} + 10^{pH-pK_{a3}}\right)$	
$pH < pK_{a1}$	$10^{-2pH+pK_{a1}+pK_{a2}} \gg 1 + 10^{-pH+pK_{a2}} + 10^{pH-pK_{a3}}$	$\log c_{HB^{2-}} = \log C^{\circ}_{H_3B} - \log\left(10^{-2pH+pK_{a1}+pK_{a2}}\right)$ $\log c_{HB^{2-}} = 2pH + \log C^{\circ}_{H_3B} - pK_{a1} - pK_{a2}$
$pK_{a1} < pH < pK_{a2}$	$10^{-pH+pK_{a2}} \gg 1 + 10^{-2pH+pK_{a1}+pK_{a2}} + 10^{pH-pK_{a3}}$	$\log c_{HB^{2-}} = \log C^{\circ}_{H_3B} - \log\left(10^{-pH+pK_{a2}}\right)$ $\log c_{HB^{2-}} = pH + \log C^{\circ}_{H_3B} - pK_{a2}$
$pK_{a2} < pH < pK_{a3}$	$1 \gg 10^{-2pH+pK_{a1}+pK_{a2}} + 10^{-pH+pK_{a2}} + 10^{pH-pK_{a3}}$	$\log c_{HB^{2-}} = \log C^{\circ}_{H_3B}$
$pK_{a3} < pH$	$10^{pH-pK_{a3}} \gg 1 + 10^{-2pH+pK_{a1}+pK_{a2}} + 10^{-pH+pK_{a2}}$	$\log c_{HB^{2-}} = \log C^{\circ}_{H_3B} - \log\left(10^{pH-pK_{a3}}\right)$ $\log c_{HB^{2-}} = -pH + \log C^{\circ}_{H_3B} + pK_{a3}$
B^{3-}:	$\log c_{B^{3-}} = \log C^{\circ}_{H_3B} - \log\left(1 + 10^{-pH+pK_{a3}} + 10^{-2pH+pK_{a2}+pK_{a3}} + 10^{-3pH+pK_{a1}+pK_{a2}+pK_{a3}}\right)$	
$pH < pK_{a1}$	$10^{-3pH+pK_{a1}+pK_{a2}+pK_{a3}} \gg 1 + 10^{-pH+pK_{a3}} + 10^{-2pH+pK_{a2}+pK_{a3}}$	$\log c_{B^{3-}} = \log C^{\circ}_{H_3B} - \log\left(10^{-3pH+pK_{a1}+pK_{a2}+pK_{a3}}\right)$ $\log c_{B^{3-}} = 3pH + \log C^{\circ}_{H_3B} - pK_{a1} - pK_{a2} - pK_{a3}$
$pK_{a1} < pH < pK_{a2}$	$10^{-2pH+pK_{a2}+pK_{a3}} \gg 1 + 10^{-pH+pK_{a3}} + 10^{-3pH+pK_{a1}+pK_{a2}+pK_{a3}}$	$\log c_{B^{3-}} = \log C^{\circ}_{H_3B} - \log\left(10^{-2pH+pK_{a2}+pK_{a3}}\right)$ $\log c_{B^{3-}} = 2pH + \log C^{\circ}_{H_3B} - pK_{a2} - pK_{a3}$
$pK_{a2} < pH < pK_{a3}$	$10^{-pH+pK_{a3}} \gg 1 + 10^{-2pH+pK_{a2}+pK_{a3}} + 10^{-3pH+pK_{a1}+pK_{a2}+pK_{a3}}$	$\log c_{B^{3-}} = \log C^{\circ}_{H_3B} - \log\left(10^{-pH+pK_{a3}}\right)$ $\log c_{B^{3-}} = pH + \log C^{\circ}_{H_3B} - pK_{a3}$
$pK_{a3} < pH$	$1 \gg 10^{-pH+pK_{a3}} + 10^{-2pH+pK_{a2}+pK_{a3}} + 10^{-3pH+pK_{a1}+pK_{a2}+pK_{a3}}$	$\log c_{B^{3-}} = \log C^{\circ}_{H_3B}$

(continued)

A4.3 Tetrabasic acids H_4B

H_4B:	$\log c_{H_4B} = \log C^{\circ}_{H_4B} - \log(1 + 10^{pH-pK_{a1}} + 10^{2pH-pK_{a1}-pK_{a2}} + 10^{3pH-pK_{a1}-pK_{a2}-pK_{a3}} + 10^{4pH-pK_{a1}-pK_{a2}-pK_{a3}-pK_{a4}})$	
$pH < pK_{a1}$	$1 \gg 10^{pH-pK_{a1}} + 10^{2pH-pK_{a1}-pK_{a2}} + 10^{3pH-pK_{a1}-pK_{a2}-pK_{a3}} + 10^{4pH-pK_{a1}-pK_{a2}-pK_{a3}-pK_{a4}}$	$\log c_{H_4B} = \log C^{\circ}_{H_4B}$
$pK_{a1} < pH < pK_{a2}$	$10^{pH-pK_{a1}} \gg 1 + 10^{2pH-pK_{a1}-pK_{a2}} + 10^{3pH-pK_{a1}-pK_{a2}-pK_{a3}} + 10^{4pH-pK_{a1}-pK_{a2}-pK_{a3}-pK_{a4}}$	$\log c_{H_4B} = \log C^{\circ}_{H_4B} - \log(10^{pH-pK_{a1}})$ $\log c_{H_4B} = -pH + \log C^{\circ}_{H_4B} + pK_{a1}$
$pK_{a2} < pH < pK_{a3}$	$10^{2pH-pK_{a1}-pK_{a2}} \gg 1 + 10^{pH-pK_{a1}} + 10^{3pH-pK_{a1}-pK_{a2}-pK_{a3}} + 10^{4pH-pK_{a1}-pK_{a2}-pK_{a3}-pK_{a4}}$	$\log c_{H_4B} = \log C^{\circ}_{H_4B} - \log(10^{2pH-pK_{a1}-pK_{a2}})$ $\log c_{H_4B} = -2pH + \log C^{\circ}_{H_4B} + pK_{a1} + pK_{a2}$
$pK_{a3} < pH < pK_{a4}$	$10^{3pH-pK_{a1}-pK_{a2}-pK_{a3}} \gg 1 + 10^{pH-pK_{a1}} + 10^{2pH-pK_{a1}-pK_{a2}} + 10^{4pH-pK_{a1}-pK_{a2}-pK_{a3}-pK_{a4}}$	$\log c_{H_4B} = \log C^{\circ}_{H_4B} - \log(10^{3pH-pK_{a1}-pK_{a2}-pK_{a3}})$ $\log c_{H_4B} = -3pH + \log C^{\circ}_{H_4B} + pK_{a1} + pK_{a2} + pK_{a3}$
$pK_{a4} < pH$	$10^{4pH-pK_{a1}-pK_{a2}-pK_{a3}-pK_{a4}} \gg 1 + 10^{pH-pK_{a1}} + 10^{2pH-pK_{a1}-pK_{a2}} + 10^{3pH-pK_{a1}-pK_{a2}-pK_{a3}}$	$\log c_{H_4B} = \log C^{\circ}_{H_4B} - \log(10^{4pH-pK_{a1}-pK_{a2}-pK_{a3}-pK_{a4}})$ $\log c_{H_4B} = -4pH + \log C^{\circ}_{H_4B} + pK_{a1} + pK_{a2} + pK_{a3} + pK_{a4}$
H_3B^-:	$\log c_{H_3B^-} = \log C^{\circ}_{H_4B} - \log(1 + 10^{-pH+pK_{a1}} + 10^{pH-pK_{a2}} + 10^{2pH-pK_{a2}-pK_{a3}} + 10^{3pH-pK_{a2}-pK_{a3}-pK_{a4}})$	
$pH < pK_{a1}$	$10^{-pH+pK_{a1}} \gg 1 + 10^{pH-pK_{a2}} + 10^{2pH-pK_{a2}-pK_{a3}} + 10^{3pH-pK_{a2}-pK_{a3}-pK_{a4}}$	$\log c_{H_3B^-} = \log C^{\circ}_{H_4B} - \log(10^{-pH+pK_{a1}})$ $\log c_{H_3B^-} = pH + \log C^{\circ}_{H_4B} - pK_{a1}$
$pK_{a1} < pH < pK_{a2}$	$1 \gg 10^{-pH+pK_{a1}} + 10^{pH-pK_{a2}} + 10^{2pH-pK_{a2}-pK_{a3}} + 10^{3pH-pK_{a2}-pK_{a3}-pK_{a4}}$	$\log c_{H_3B^-} = \log C^{\circ}_{H_4B}$

$pK_{a2} < pH < pK_{a3}$	$10^{pH-pK_{a2}} \gg 1 + 10^{-pH+pK_{a1}} + 10^{2pH-pK_{a2}-pK_{a3}} + 10^{3pH-pK_{a2}-pK_{a3}-pK_{a4}}$	$\log c_{H_3B^-} = \log C^{\circ}_{H_4B} - \log\left(+10^{pH-pK_{a2}}\right)$ $\log c_{H_3B^-} = -pH + \log C^{\circ}_{H_4B} + pK_{a2}$
$pK_{a3} < pH < pK_{a4}$	$10^{2pH-pK_{a2}-pK_{a3}} \gg 1 + 10^{-pH+pK_{a1}} + 10^{pH-pK_{a2}} + 10^{3pH-pK_{a2}-pK_{a3}-pK_{a4}}$	$\log c_{H_3B^-} = \log C^{\circ}_{H_4B} - \log\left(10^{2pH-pK_{a2}-pK_{a3}}\right)$ $\log c_{H_3B^-} = -2pH + \log C^{\circ}_{H_4B} + pK_{a2} + pK_{a3}$
$pK_{a4} < pH$	$10^{3pH-pK_{a2}-pK_{a3}-pK_{a4}} \gg 1 + 10^{-pH+pK_{a1}} + 10^{pH-pK_{a2}} + 10^{2pH-pK_{a2}-pK_{a3}}$	$\log c_{H_3B^-} = \log C^{\circ}_{H_4B} - \log\left(10^{3pH-pK_{a2}-pK_{a3}-pK_{a4}}\right)$ $\log c_{H_3B^-} = -3pH + \log C^{\circ}_{H_4B} + pK_{a2} + pK_{a3} + pK_{a4}$
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-}:	$\log c_{HB^{3-}} = \log C^{\circ}_{H_4B} - \log\left(1 + 10^{-3pH+pK_{a1}+pK_{a2}+pK_{a3}} + 10^{-2pH+pK_{a2}+pK_{a3}} + 10^{-pH+pK_{a3}} + 10^{pH-pK_{a4}}\right)$	
$pH < pK_{a1}$	$10^{-3pH+pK_{a1}+pK_{a2}+pK_{a3}} \gg 1 + 10^{-2pH+pK_{a2}+pK_{a3}} + 10^{-pH+pK_{a3}} + 10^{pH-pK_{a4}}$	$\log c_{HB^{3-}} = \log C^{\circ}_{H_4B} - \log\left(10^{-3pH+pK_{a1}+pK_{a2}+pK_{a3}}\right)$ $\log c_{HB^{3-}} = 3pH + \log C^{\circ}_{H_4B} - pK_{a1} - pK_{a2} - pK_{a3}$
$pK_{a1} < pH < pK_{a2}$	$10^{-2pH+pK_{a2}+pK_{a3}} \gg 1 + 10^{-3pH+pK_{a1}+pK_{a2}+pK_{a3}} + 10^{-pH+pK_{a3}} + 10^{pH-pK_{a4}}$	$\log c_{HB^{3-}} = \log C^{\circ}_{H_4B} - \log\left(10^{-2pH+pK_{a2}+pK_{a3}}\right)$ $\log c_{HB^{3-}} = 2pH + \log C^{\circ}_{H_4B} - pK_{a2} - pK_{a3}$
$pK_{a2} < pH < pK_{a3}$	$10^{-pH+pK_{a3}} \gg 1 + 10^{-3pH+pK_{a1}+pK_{a2}+pK_{a3}} + 10^{-2pH+pK_{a2}+pK_{a3}} + 10^{pH-pK_{a4}}$	$\log c_{HB^{3-}} = \log C^{\circ}_{H_4B} - \log\left(10^{-pH+pK_{a3}}\right)$ $\log c_{HB^{3-}} = pH + \log C^{\circ}_{H_4B} - pK_{a3}$
$pK_{a3} < pH < pK_{a4}$	$1 \gg 10^{-3pH+pK_{a1}+pK_{a2}+pK_{a3}} + 10^{-2pH+pK_{a2}+pK_{a3}} + 10^{-pH+pK_{a3}} + 10^{pH-pK_{a4}}$	$\log c_{HB^{3-}} = \log C^{\circ}_{H_4B}$
$pK_{a4} < pH$	$10^{pH-pK_{a4}} \gg 1 + 10^{-3pH+pK_{a1}+pK_{a2}+pK_{a3}} + 10^{-2pH+pK_{a2}+pK_{a3}} + 10^{-pH+pK_{a3}}$	$\log c_{HB^{3-}} = \log C^{\circ}_{H_4B} - \log\left(10^{pH-pK_{a4}}\right)$ $\log c_{HB^{3-}} = -pH + \log C^{\circ}_{H_4B} + pK_{a4}$
B^{4-}:	$\log c_{B^{4-}} = \log C^{\circ}_{H_4B} - \log\left(1 + 10^{-4pH+pK_{a1}+pK_{a2}+pK_{a3}+pK_{a4}} + 10^{-3pH+pK_{a2}+pK_{a3}+pK_{a4}} + 10^{-2pH+pK_{a3}+pK_{a4}} + 10^{-pH+pK_{a4}}\right)$	
$pH < pK_{a1}$	$10^{-4pH+pK_{a1}+pK_{a2}+pK_{a3}+pK_{a4}} \gg 1 + 10^{-3pH+pK_{a2}+pK_{a3}+pK_{a4}} + 10^{-2pH+pK_{a3}+pK_{a4}} + 10^{-pH+pK_{a4}}$	$\log c_{B^{4-}} = \log C^{\circ}_{H_4B} - \log\left(10^{-4pH+pK_{a1}+pK_{a2}+pK_{a3}+pK_{a4}}\right)$ $\log c_{B^{4-}} = 4pH + \log C^{\circ}_{H_4B} - pK_{a1} - pK_{a2} - pK_{a3} - pK_{a4}$
$pK_{a1} < pH < pK_{a2}$	$10^{-3pH+pK_{a2}+pK_{a3}+pK_{a4}} \gg 1 + 10^{-4pH+pK_{a1}+pK_{a2}+pK_{a3}+pK_{a4}} + 10^{-2pH+pK_{a3}+pK_{a4}} + 10^{-pH+pK_{a4}}$	$\log c_{B^{4-}} = \log C^{\circ}_{H_4B} - \log\left(10^{-3pH+pK_{a2}+pK_{a3}+pK_{a4}}\right)$ $\log c_{B^{4-}} = 3pH + \log C^{\circ}_{H_4B} - pK_{a2} - pK_{a3} - pK_{a4}$

$pK_{a2} < pH < pK_{a3}$	$10^{-2pH+pK_{a3}+pK_{a4}} \gg 1 + 10^{-4pH+pK_{a1}+pK_{a2}+pK_{a3}+pK_{a4}}$ $+ 10^{-3pH+pK_{a2}+pK_{a3}+pK_{a4}} + 10^{-pH+pK_{a4}}$	$\log c_{B^{4-}} = \log C^{\circ}_{H_4B} - \log\left(10^{-2pH+pK_{a3}+pK_{a4}}\right)$ $\log c_{B^{4-}} = 2pH + \log C^{\circ}_{H_4B} - pK_{a3} - pK_{a4}$
$pK_{a3} < pH < pK_{a4}$	$10^{-pH+pK_{a4}} \gg 1 + 10^{-4pH+pK_{a1}+pK_{a2}+pK_{a3}+pK_{a4}}$ $+ 10^{-3pH+pK_{a2}+pK_{a3}+pK_{a4}} + 10^{-2pH+pK_{a3}+pK_{a4}}$	$\log c_{B^{4-}} = \log C^{\circ}_{H_4B} - \log\left(10^{-pH+pK_{a4}}\right)$ $\log c_{B^{4-}} = pH + \log C^{\circ}_{H_4B} - pK_{a4}$
$pK_{a4} < pH$	$1 \gg 10^{-4pH+pK_{a1}+pK_{a2}+pK_{a3}+pK_{a4}} + 10^{-3pH+pK_{a2}+pK_{a3}+pK_{a4}}$ $+ 10^{-2pH+pK_{a3}+pK_{a4}} + 10^{-pH+pK_{a4}}$	$\log c_{B^{4-}} = \log C^{\circ}_{H_4B}$

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