Acid-Base Systems & pH Buffers

(Mathematical Background of Simple Closed-Form Expressions)

www.aqion.de/file/acid-base-systems.pdf

Harald Kalka

– revised: Jan 19, 2019 –
## Acid Base Systems

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### Acid Base Systems

#### Physico-Chemical Quantities

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<th>Definition</th>
</tr>
</thead>
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<tr>
<td>$a_j$</td>
<td>ionization fractions, $a_j = [j]/C_T$</td>
</tr>
<tr>
<td>Alk</td>
<td>total alkalinity, mol/L</td>
</tr>
<tr>
<td>ANC</td>
<td>acid-neutralizing capacity, mol/L</td>
</tr>
<tr>
<td>BNC</td>
<td>base-neutralizing capacity, mol/L</td>
</tr>
<tr>
<td>$\beta$</td>
<td>buffer intensity (normalized), $\beta = \frac{dn}{d\text{pH}}$</td>
</tr>
<tr>
<td>$\beta_C$</td>
<td>buffer intensity, $\beta_C = \frac{dC_B}{d\text{pH}} = C_T \beta$</td>
</tr>
<tr>
<td>$C_A$</td>
<td>concentration of (strong) monoprotic acid $C_A = [HX]_T$, mol/L</td>
</tr>
<tr>
<td>$C_B$</td>
<td>concentration of (strong) monoacidic base $C_B = [BOH]_T$, mol/L</td>
</tr>
<tr>
<td>$C_T$</td>
<td>total concentration of $N$-protic acid: $C_T = [HNA]_T$, mol/L</td>
</tr>
<tr>
<td>$\delta_{ij}$</td>
<td>KRONECKER delta, $\delta_{ij} = 1$ for $i=j$, and $\delta_{ij} = 0$ for $i \neq j$</td>
</tr>
<tr>
<td>$\text{EP}_n$</td>
<td>equivalence point (for integer and half-integer $n$)</td>
</tr>
<tr>
<td>$I$</td>
<td>ionic strength, mol/L</td>
</tr>
<tr>
<td>$\gamma_j$</td>
<td>activity correction for species $j$</td>
</tr>
<tr>
<td>$\Delta G^0$</td>
<td>GIBBS energy change, J/mol</td>
</tr>
<tr>
<td>$j$</td>
<td>index denoting the aqueous species $j$, $j = 0, 1, \ldots N$</td>
</tr>
<tr>
<td>$[j]$</td>
<td>molar concentration of aqueous species $j$: $[j] = [HNA]^j$</td>
</tr>
<tr>
<td>${{j}}$</td>
<td>activity of aqueous species $j$: ${{j}} = {HNA}^j$</td>
</tr>
<tr>
<td>$K_a$</td>
<td>acidic constant (general abbreviation), mol/L</td>
</tr>
<tr>
<td>$cK_a$</td>
<td>conditional acidic constant (non-thermodynamic quantity), mol/L</td>
</tr>
<tr>
<td>$K_{j}$</td>
<td>acidity constant of dissociation step $j$, mol/L</td>
</tr>
<tr>
<td>$k_j$</td>
<td>cumulative acidity constant, e.g. $k_j = K_1 K_2 \ldots K_j$, (mol/L)$^j$</td>
</tr>
<tr>
<td>$K_w$</td>
<td>equilibrium constant of autoprotonolysis (self-ionization of H$_2$O) (mol/L)$^2$</td>
</tr>
<tr>
<td>$n$</td>
<td>equivalent fraction of titration, $n = (C_B - C_A)/C_T$</td>
</tr>
<tr>
<td>$N$</td>
<td>number of protons (H$^+$) of the $N$-protic acid H$_N$A</td>
</tr>
<tr>
<td>$\text{pH}$</td>
<td>$\equiv -\lg{H^+} \approx -\lg[H^+] = -\lg x$</td>
</tr>
<tr>
<td>$\text{pH}_j$</td>
<td>$\equiv \frac{1}{2}(pK_j + pK_{j+1})$ as pH of equivalence point $\text{EP}_j$</td>
</tr>
<tr>
<td>$pK_j$</td>
<td>$\equiv -\lg K_j$</td>
</tr>
<tr>
<td>$pK_{j'}$</td>
<td>$\equiv -\lg K_{j'}$</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature in Kelvin, K</td>
</tr>
<tr>
<td>$R$</td>
<td>gas constant ($R = 8.314$ J mol$^{-1}$K$^{-1}$)</td>
</tr>
<tr>
<td>$x$</td>
<td>abbreviation for ${H^+}$, i.e. activity of H$^+$, mol/L</td>
</tr>
<tr>
<td>$Y_L$</td>
<td>$L^{th}$ moment constructed from $a_j$: $Y_L = \sum_{j}^{i} a_j$</td>
</tr>
<tr>
<td>$w(x)$</td>
<td>‘pure water balance’: $w \equiv [\text{OH}^-] - [\text{H}^+] = K_w/x - x$</td>
</tr>
<tr>
<td>$z_j$</td>
<td>charge of species $j$</td>
</tr>
<tr>
<td>$Z$</td>
<td>charge of highest protonated acid species</td>
</tr>
</tbody>
</table>

#### Units and Conversions:

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L$</td>
<td>liter ($1$ $L = 1$ dm$^3 = 10^{-3}$ m$^3$)</td>
</tr>
<tr>
<td>$M$</td>
<td>molarity ($1$ $M = 1$ mol/L)</td>
</tr>
<tr>
<td>$mM$</td>
<td>$1$ mM $= 10^{-3}$ mol/L</td>
</tr>
<tr>
<td>$\lg x$</td>
<td>decadic logarithm ($= \log_{10} x$) conversion: $\lg x = (\ln x)/(\ln 10)$</td>
</tr>
<tr>
<td>$\ln x$</td>
<td>natural logarithm ($= \log_e x$), conversion: $\ln x = (\ln 10)(\lg x)$</td>
</tr>
<tr>
<td>$\ln 10$</td>
<td>$= 2.303$</td>
</tr>
</tbody>
</table>

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Definitions & Abbreviations

**Acid Species.** The $N+1$ aqueous species of the polyprotic acid $H_N A$ are abbreviated by:

\[(0.1) \quad [j] = [H_{N-j} A^{Z-j}] \quad \text{for} \quad j = 0, 1, 2, \ldots, N\]

where the integer $j$ also labels the electrical charge of species $j$:

\[(0.2) \quad z_j = Z - j \quad \text{with} \quad \begin{cases} Z = 0 & \text{for common acids} \\ Z \geq 1 & \text{for zwitterionic acids (amino acids)} \end{cases}\]

**Total Concentration.** The sum of all species yields the total concentration of the acid:

\[(0.3) \quad C_T = [H_N A]_T = \sum_{j=0}^{N} [j] \quad \text{(mass balance)}\]

**Ionization Fractions.** Ionization fractions are ratios of the acid-species concentrations to the total amount of acid:

\[(0.4) \quad a_j = \frac{[j]}{C_T} \quad \text{for} \quad j = 0, 1, 2, \ldots, N\]

**Activities vs Concentrations.** In chemical thermodynamics one has to distinguish between molar concentrations and activities (cf. Appendix A):

- concentrations will be denoted by square brackets $[j]$
- activities will be denoted by curly brackets $\{j\}$

**x and pH.** The activity of $H^+$ will be abbreviated by $x$:

\[(0.5) \quad x \equiv \{H^+\} = 10^{pH} \iff pH = -\log x\]

**H$_2$O.** The autoprotolysis (self-ionization of water) is defined by

\[(0.6) \quad H_2O = H^+ + OH^- \quad \text{with} \quad K_w = \{H^+\}\{OH^-\}\]

and $K_w = 1.0 \cdot 10^{-14}$ at 25 °C. Using $x = \{H^+\}$, we get$^1$

\[(0.7) \quad [OH^-] \approx \{OH^-\} = \frac{K_w}{x}\]

In this context we introduce the quantity

\[(0.8) \quad w \equiv [OH^-] - [H^+] \approx \frac{K_w}{x} - x\]

For pure water, i.e. in the absence of any acid and base, we have $w = 0$.

---

$^1$ This approximation is justified for acid waters (and even for all waters with $pH < 12$) because the amount of $OH^-$ is too small to make a difference between activity and concentration.
INTRODUCTION

The lecture is focused on the mathematical description of acid-base reactions in water. This is not new; the theory has been known for more than 100 years. Three main concepts were successively developed during this period:

- In 1884, ARRHENIUS provided the first modern, molecular-based definition: an acid is a substance that releases $H^+$ in water; a base is a substance that releases $OH^-$. In this way, he predicted the dissociation into ions even before charged elementary particles were accepted and established (in the late 1890s). $H^+$ ions are just protons.

- In 1923, BRØNSTED and LOWRY extended the concept with the idea that an acid-base reaction involves a proton transfer from a proton donor (the acid) to a proton acceptor (the base). The solvent no longer has to be water, as the new concept also applies to liquid ammonia, alcohol, benzene, and other non-aqueous solutions.

- About 15 years later, G.N. LEWIS went one step further and stretched the “proton-transfer” concept of conventional acids and bases to the much broader concept of “electron-pair transfer”. The latter can also be used for ligand-metal ion coordination reactions and substitution reactions in organic chemistry.

Collapsing the ideas into one table yields:

<table>
<thead>
<tr>
<th></th>
<th>acid</th>
<th>base</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arrhenius (1884)</td>
<td>contains $H^+$</td>
<td>contains $OH^-$</td>
</tr>
<tr>
<td>Brønsted-Lowry (1923)</td>
<td>proton (H$^+$) donor</td>
<td>proton (H$^+$) acceptor</td>
</tr>
<tr>
<td>Lewis (1938)</td>
<td>e$^-$ pair acceptor</td>
<td>e$^-$ pair donor</td>
</tr>
</tbody>
</table>

The relationship between all three concepts can be visualized as a Venn diagram where the most general LEWIS concept encompasses both BRØNSTED-LOWRY theory and ARRHENIUS theory.

The proton-transfer mechanism makes acid-base reactions very fast, so that chemical equilibrium is always established in the shortest time. This allows the application of a pure thermodynamic description (while slow reactions, such as redox processes, require more sophisticated kinetic approaches). The framework was established long ago in form of the Law of mass action (by GULDBERG and WAAGE in 1864), where the equilibrium...
state is characterized by one single quantity – the equilibrium constant $K$. In modern chemistry this is derived from Gibbs energy (originally established in 1873).

If one speaks of acids or bases, one inevitably speaks of the pH value. This fundamental quantity, which appears in all formulas, is a measure of the $\text{H}^+$ concentration. It is therefore not surprising that we prefer the proton-transfer concept of BRØNSTED and LOWRY in the present lecture.

**Structure of the Lecture**

The lecture consists of four parts: Chapters 1 to 4. Chapter 1 begins with the description of polyprotic acids $\text{H}_N\text{A}$ with *any* number of protons $N$. Usually $N$ is a small number – 1, 2 or 3 for monoprotic, diprotic and triprotic acids – so why all the effort for higher $N$? The answer is threefold. First, there are indeed acids with up to 6 protons (see EDTA in § 4.1.4 on page 97). Second, new and deeper insight is obtained by treating $N$ as a *variable* integer (see e.g. classification of equivalence points in § 2.3). Third, the approach can easily be applied to other chemical equilibria such as redox reactions, hydrolysis, or metal-ligand complexation (where $N$ is usually high). The goal of Chapter 1 is to bundle a set of $N+3$ nonlinear equations into a single analytical formula.

In Chapter 2, the two-component acid system ($\text{H}_N\text{A}+\text{H}_2\text{O}$) of Chapter 1 is extended by a strong base to a three-component *acid-base system*. It opens the door to the description of acid-base *titrations*. Chapter 3 then introduces buffer capacities and buffer intensities. In Chapter 4, the mathematical description is applied beyond the realm of common acids to zwitterions and to surface complexation.

**Final Note.** The presented mathematical framework of *analytical* formulas widens our understanding of the acid-base system. However, it will and can never replace *numerical* models like PHREEQC, AQION or other software, which are able to handle real-world problems (including activity corrections, an arbitrary number of species and phases, aqueous complex formation, etc.).
1 POLYPROTIC ACIDS

1.1 What is an Acid?

1.1.1 Proton Transfer

An acid HA is a proton donor; it releases H\(^+\) ions (or H\(_3\)O\(^+\)) when dissolved in water:

\[
\begin{align*}
(1.1) & \quad HA = H^+ + A^- \\
(1.2) & \quad HA + H_2O = H_3O^+ + A^- 
\end{align*}
\]

In the following, we prefer the shorthand notation of Eq. (1.1). However keep in mind that H\(^+\) ions do not exist in a free state; they are extremely reactive and form hydronium ions H\(_3\)O\(^+\).

The definition of acids as proton donors is fully in line with ARRHENIUS’ notion that acids are substances that contain and release H\(^+\) ions. In the case of bases, however, both concepts differ:

- ARRHENIUS base: contains OH\(^-\) (e.g. NaOH, KOH, NH\(_4\)OH, ...)
- BRØNSTED-LOWRY base: H\(^+\) acceptor (e.g. OH\(^-\), Cl\(^-\), NH\(_3\), ...)

This allows all ARRHENIUS bases\(^2\) to be combined into a single H\(^+\) acceptor equation:

\[
(1.3) \quad OH^- + H^+ = H_2O
\]

Now something new comes into play (that the ARRHENIUS concept does not have): conjugated acid-base pairs. Adding Eq. (1.3) to Eq. (1.1) yields:

\[
\begin{align*}
(1.4) & \quad HA + OH^- = H_2O + A^- \\
(1.5) & \quad \text{acid + base} = \text{conjugate acid} + \text{conjugate base} \\
& \quad \quad \quad \text{(of base OH\(^-\))} \quad \text{(of acid HA)}
\end{align*}
\]

In this overall reaction, H\(^+\) ions do not appear (because they are transferred between conjugate acid-base pairs). H\(^+\) ions only appear in “half reactions”, such as in Eq. (1.1) or Eq. (1.3):

\[
(1.6) \quad \text{acid} = H^+ + \text{conjugate base} \\
\quad \quad \quad \text{(proton donor)} \quad \text{(proton acceptor)}
\]

Eq. (1.6) is a general concept that also applies to polyprotic acids, namely for each individual dissociation step (as shown in Eqs. (1.17) to (1.19) on page 13).

\(^2\) An ARRHENIUS base can be abbreviated, say, by BOH where the cation B\(^+\) stands for Na\(^+\), K\(^+\), NH\(_4\)\(^+\) etc.
**Autoprotolysis.** One very special case of Eq. (1.4) is the self-dissociation of water:

\[
H_2O + H_2O = H_3O^+ + OH^- 
\]

Here, water acts as an acid and a base at the same time. Such substances are named ampholytes.

### 1.1.2 Acidity Constants

The equilibrium constant of reaction (1.1) is called the *acidity constant*. There are two types of acidity constants:

\[
K_a = \frac{\{H^+\}\{A^-\}}{\{HA\}} \quad \text{(based on activities)} 
\]

\[
K_a^c = \frac{\{H^+\}\{A^-\}}{[HA]} \quad \text{(based on concentrations)} 
\]

Both equations are special types of the *law of mass action*. The value of \(K_a\) signifies the strength of the acid (strong acids: \(K_a\) large; weak acids: \(K_a\) small).

**Activities.** Activities are ‘effective concentrations’ which can be calculated by semi-empirical activity corrections \(\gamma_j\) (cf. Appendix A):

\[
{\{j\}} = \gamma_j [j] 
\]

The activity correction depends on the ionic strength \(I\). In dilute systems (low-concentrated waters) the ionic strength is very small (\(I \approx 0\)) and \(\gamma_j \approx 1\), so that activities and concentrations are almost the same.

**Note:** The mathematical derivations in this lecture rely on concentrations, except for \(H^+\), where we use the activity. Thus, the obtained results are valid either in dilute systems or by using the *conditional* acidity constant \(K_a^c\). We consider it as an assumption that applies to the whole text (and skip the small-letter superscript c on \(K_a\)). This remark about activities/concentrations is so important that we will return to it throughout the text.

**\(\lg K\).** In practice, it is often convenient to use the (base-10) logarithm of Eq. (1.9):

\[
\lg K_a = \lg \{H^+\} + \lg [A^-] - \lg [HA] 
\]

The negative decadic logarithm of the acidity constant is then abbreviated by \(pK_a\):

\[
pK_a = -\lg K_a 
\]

which parallels the definition of pH as \(pH = -\log [H^+]\). In this notation, Eq. (1.11) converts to

\[
pK_a = pH - \lg [A^-] + \lg [HA] 
\]

---

3 More precisely, it is a mixed-type conditional constant because we use the activity for \(H^+\) and concentrations for all other components (within the mass-action law).
This can also be written as the so-called HENDERSON-HASSELBACH equation:

\[
\text{pH} = \text{pK}_a + \log \frac{[A^-]}{[HA]} = \text{pK}_a + \log \frac{\text{proton acceptor}}{\text{proton donor}}
\]  

(1.14)

Here, the term \( \log \frac{[A^-]}{[HA]} \) vanishes for equal concentrations. In other words, the \( \text{pK}_a \) value is just the pH at which the amount of both species is equal, i.e. at which 50% of the species HA is dissociated into species A\(^-\). Therefore, it’s no surprise that the \( \text{pK}_a \) value is also called the ‘semi equivalence point’ – more about this topic in §1.4.2, Eq. (1.76).

The \( \text{pK}_a \) value allows a classification into strong and weak acids: the smaller the \( \text{pK}_a \), the stronger the acid – quite the opposite to a \( K_a \)-based ranking (see Eq. (1.20)).

**GIBBS Energy.** There is a fundamental link between the equilibrium constant \( K \) and the (change of) GIBBS energy:

\[
\Delta G^0 = -RT \ln K
\]

(1.15)

where \( R = 8.314 \text{ J mol}^{-1}\text{K}^{-1} \) is the gas constant and \( T \) the temperature in Kelvin. This equation can be rearranged to \( \log K \):

\[
\log K = \frac{-\Delta G^0}{\ln 10 \cdot RT} = \frac{-\Delta G^0}{2.303 \cdot RT} \quad \text{or} \quad \text{pK} = \frac{\Delta G^0}{2.303 \cdot RT}
\]

(1.16)

An example for the relationship between several \( \text{pK} \) values (of a triprotic acid) and \( \Delta G^0 \) is given in Fig. 1.6 on page 22.

### 1.1.3 Mono-, Di-, and Triprotic Acids

Acids can donate one, two, or more protons \( H^+ \). Typical examples are:

<table>
<thead>
<tr>
<th>Monoprotic acid (HA)</th>
<th>Diprotic acid (H(_2)A)</th>
<th>Triprotic acid (H(_3)A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>( H_2)CO(_3)</td>
<td>( H_3)PO(_4)</td>
</tr>
<tr>
<td>HNO(_3)</td>
<td>( H_2)SO(_4)</td>
<td>( H_3)AsO(_4)</td>
</tr>
<tr>
<td>HI</td>
<td>( H_2)CrO(_4)</td>
<td>( H_3)BO(_3)</td>
</tr>
<tr>
<td>HF</td>
<td>( H_2)SeO(_4)</td>
<td>citric acid</td>
</tr>
<tr>
<td>formic acid</td>
<td>oxalic acid</td>
<td></td>
</tr>
<tr>
<td>acetic acid</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A *monoprotic* acid is characterized by a single acidity constant \( K_1 (= K_a) \), a *diprotic* acid by two acidity constants \( (K_1, K_2) \), and a *triprotic* acid by three acidity constants \( (K_1, K_2, \text{ and } K_3) \):

\[
\begin{align*}
\text{1st dissociation step:} & \quad \text{H}_3\text{A} = \text{H}^+ + \text{H}_2\text{A}^- & K_1 \\
\text{2nd dissociation step:} & \quad \text{H}_2\text{A}^- = \text{H}^+ + \text{HA}^{2^-} & K_2 \\
\text{3rd dissociation step:} & \quad \text{HA}^{2^-} = \text{H}^+ + \text{A}^{3^-} & K_3
\end{align*}
\]

(1.17)  (1.18)  (1.19)
**Ranking.** Protons are released sequentially one after the other, with the first proton being the fastest and most easily lost, then the second, and then the third (which is the most strongly bound). This yields the following ranking of acidity constants of a polyprotic acid:

\[
K_1 > K_2 > K_3 \quad \text{or} \quad pK_1 < pK_2 < pK_3
\]

For example, phosphoric acid has \(pK_1 = 2.15\), \(pK_2 = 7.21\), and \(pK_3 = 12.35\). Other examples for acidity constants are listed in Tab. 1.1.

**Tab. 1.1 Examples for \(pK = -\lg K\) for four common acids**

<table>
<thead>
<tr>
<th>Acid</th>
<th>Formula</th>
<th>Type</th>
<th>(pK_1)</th>
<th>(pK_2)</th>
<th>(pK_3)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetic acid</td>
<td>CH₃COOH</td>
<td>HA</td>
<td>4.76</td>
<td></td>
<td></td>
<td>[M91]</td>
</tr>
<tr>
<td>(composite) carbonic acid⁵</td>
<td>H₂CO₃</td>
<td>H₂A</td>
<td>6.35</td>
<td>10.33</td>
<td></td>
<td>[W91]</td>
</tr>
<tr>
<td>phosphoric acid</td>
<td>H₃PO₄</td>
<td>H₃A</td>
<td>2.15</td>
<td>7.21</td>
<td>12.35</td>
<td>[M91]</td>
</tr>
<tr>
<td>citric acid</td>
<td>C₆H₈O₇</td>
<td>H₃A</td>
<td>3.13</td>
<td>4.76</td>
<td>6.4</td>
<td>[M91]</td>
</tr>
</tbody>
</table>

In addition to “common acids”, there are also zwitterionic acids (amino acids). The latter are described in § 4.1.

### 1.1.4 Strong Acids vs Weak Acids

Strong acids dissociate completely in water, while weak acids do not dissociate completely. In other words, the stronger the acid, the higher is the \(H^+\) concentration at equilibrium. A classification based on \(pK_a\) values (acidic strength) seems natural.

**Monoprotic Acids.** Let us consider a monoprotic acid with the total amount \(C_T = [HA]_T\) (which is de facto the acid’s initial concentration before it dissolves). In the equilibrium state, the total concentration splits into its undissociated and dissociated parts:

\[
C_T = [HA] + [A^-]
\]

Strong and weak acids then differ as follows (greatly simplified):

<table>
<thead>
<tr>
<th></th>
<th><strong>Strong Acid</strong></th>
<th><strong>Weak acid</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>acidity constant</td>
<td>(K_a &gt; 1)</td>
<td>(K_a \leq 1)</td>
</tr>
<tr>
<td>(pK_a = -\lg K_a)</td>
<td>(pK_a &lt; 0)</td>
<td>(pK_a &gt; 0)</td>
</tr>
<tr>
<td>([H^+] = 10^{-pH})</td>
<td>([H^+] \approx C_T)</td>
<td>([H^+] \ll C_T)</td>
</tr>
<tr>
<td>undissociated acid</td>
<td>([HA] \approx 0)</td>
<td>([HA] \approx C_T)</td>
</tr>
<tr>
<td>dissociated acid</td>
<td>([A^-] \approx C_T)</td>
<td>([A^-] \ll C_T)</td>
</tr>
</tbody>
</table>

---

⁴ In organic acids, the second and third acidity constants can be similar.

⁵ The composite carbonic acid is the sum of the unionized species \(CO_2(aq)\) and the pure acid: \(H_2CO_3^+ = CO_2(aq) + H_2CO_3\). To simplify the notation we omit the asterisk (*) on \(H_2CO_3\) throughout the paper.
In literature, there is no clear distinction between what we call a strong acid and what we call a weak acid. More refined classification schemes distinguish between very strong acids, strong acids, weak acids, and very weak acids. The easiest way is a subdivision into two groups:

- strong acids: acids with $pK_a < 0$
- weak acids: acids with $pK_a > 0$

**Polyprotic Acids.** The idea remains valid even for $N$-protic acids, $H_NA$. The acidity constant $K_a$ should be replaced by the first dissociation constant $K_1$. The mathematical description is quite simple:

\[
(1.22) \quad \text{undissociated fraction: } a_0 = \frac{[H_NA]}{C_T} \approx \frac{1}{1 + K_1/x} \quad \text{with } x = 10^{pH}
\]

Fig. 1.1 displays the pH dependence of the undissociated fraction $a_0$ for common acids, based on Eq. (1.22). The small circles mark the corresponding $pK_1$ values. As expected, strong acids are completely dissociated in real-world applications ($pH > 0$).

---

**Fig. 1.1** Undissociated fraction of some common acids. Strong acids are completely dissociated in the whole pH range beginning at $pH \approx 0$.

---

6 The exact formula for the ionization fraction $a_0$ is given in Eq. (1.62).
1.1.5 Weak Acids vs Dilute Acids

A weak acid and a dilute acid are two different things, like apples and oranges. The first relies on the acidity constants $K_a$ (which is a thermodynamic property of the acid that no one can change), while the second relies on the amount $C_T$ of a given acid:

- weak acid $\leftrightarrow$ strong acid $\iff$ small $K_a$ $\leftrightarrow$ large $K_a$
- dilute acid $\leftrightarrow$ concentrated acid $\iff$ small $C_T$ $\leftrightarrow$ large $C_T$

You cannot make a weak acid strong, but you can change the degree of dilution (or concentration) as you like. Tab. 1.2 summarizes the principal differences between the degree of strength and the degree of dilution. For polyprotic acids replace $K_a$ by $K_1$.

Tab. 1.2 Comparison between degree of strength and degree of dilution

<table>
<thead>
<tr>
<th></th>
<th>Degree of Strength</th>
<th>Degree of Dilution</th>
</tr>
</thead>
<tbody>
<tr>
<td>determined by</td>
<td>acidity constant $K_a$</td>
<td>amount of acid $C_T$</td>
</tr>
<tr>
<td>relationships</td>
<td>weak acid $\leftrightarrow$ strong acid $\iff$ small $K_a$ $\leftrightarrow$ large $K_a$ (positive $pK_a$ $\leftrightarrow$ negative $pK_a$)</td>
<td>dilute acid $\leftrightarrow$ concentrated acid $\iff$ small $C_T$ $\leftrightarrow$ large $C_T$</td>
</tr>
<tr>
<td>compares</td>
<td>two different acids</td>
<td>dilution of the same acid</td>
</tr>
<tr>
<td>describes</td>
<td>release of $H^+$</td>
<td>dilution of $H^+$</td>
</tr>
<tr>
<td>type</td>
<td>fundamental property</td>
<td>control parameter</td>
</tr>
<tr>
<td></td>
<td>(cannot be changed)</td>
<td>(can be changed)</td>
</tr>
</tbody>
</table>

Instead of $K$, the classification can also be based on $pK$, as indicated by the schema in Fig. 1.2. (Note: For polyprotic acids pK refers to the first dissociation step, i.e. to $pK_1$.)

Fig. 1.2 Relationship between weak/strong and dilute/concentrated acids
1.2 Basic Set of Equations

1.2.1 Special Case: Diprotic Acid

Before we tackle the most general case let’s start simple and consider the example of diprotic acids.

Fig. 1.3 Addition of a diprotic acid to water results in an equilibrium state with several species

When a diprotic acid $\text{H}_2\text{A}$ is added to pure water, the equilibrium state is characterized by *five* dissolved species: $\text{H}^+$, $\text{OH}^-$, $\text{H}_2\text{A}$, $\text{HA}^-$, and $\text{A}^{2-}$ (see Fig. 1.3). Thus, *five* equations are required for a thorough mathematical description:

\[
\begin{align*}
(1.23) & \quad K_w = \{\text{H}^+\} \{\text{OH}^-\} & \text{(self-ionization of H}_2\text{O)} \\
(1.24) & \quad K_1 = \{\text{H}^+\} \{\text{HA}^-\} / \{\text{H}_2\text{A}\} & \text{(1}\text{st} \text{ diss. step)} \\
(1.25) & \quad K_2 = \{\text{H}^+\} \{\text{A}^{2-}\} / \{\text{HA}^-\} & \text{(2}\text{nd} \text{ diss. step)} \\
(1.26) & \quad C_T = [\text{H}_2\text{A}] + [\text{HA}^-] + [\text{A}^{2-}] & \text{(mass balance)} \\
(1.27) & \quad 0 = [\text{HA}^-] + 2[\text{A}^{2-}] + [\text{OH}^-] - [\text{H}^+] & \text{(charge balance)}
\end{align*}
\]

The first three equations are *mass-action* laws (of the type of Eq. (1.8)); the two last equations represent the *mass balance* and the *charge balance*. While the mass-action laws are based on *activities* (denoted by braces), the mass-balance and charge-balance equations rely on molar *concentrations* (denoted by square brackets) – see Fig. 1.4.
Acid Base Systems

Short Lecture

Note: The total concentration of a diprotic acid is abbreviated by $C_T = [H_2A]_T$. This quantity should not be confused with the neutral dissolved acid species $H_2A(aq)$ and its molar concentration $[H_2A]$.

As summarized in Fig. 1.5, the mathematical description of the diprotic acid system relies on two components (or subsystems) plus a coupling term:

- component $H_2O$ (subsystem “pure water”) described by Eq. (1.23)
- component $H_2A$ (subsystem “pure acid”) described by Eqs. (1.24) to (1.26)
- coupling of both subsystems described by Eq. (1.27)

In fact, the two subsystems are linked together by the charge-balance equation.

![Fig. 1.5 Diprotic acid system: The subsystem 'pure $H_2O$' and the subsystem 'acid' are coupled by the charge-balance equation.]

$K_w = [H^+] [OH^-]$

diprotic acid

$K_1 = [H^+] [HA] / [H_2A]$

$K_2 = [H^+] [A^{-2}] / [HA]$

$C_T = [H_2A] + [HA] + [A^{-2}]$

$0 = [H^+] - [OH^-] - [HA] - 2[A^{-2}]$

charge balance

1.2.2 General Case: Polyprotic Acids ($H_NA$)

Given is an $N$-protic acid $H_NA$. It is characterized by

$N+3$ species (variables): $H^+, OH^-, H_NA, H_{N-1}A^-, ..., A^{-N}$

$N+1$ acid species

Hence, a complete mathematical description is provided by a set of $N+3$ equations:

$$\begin{align}
(1.28) & \quad K_w = [H^+] [OH^-] \quad \text{(self-ionization $H_2O$)} \\
(1.29) & \quad K_1 = [H^+] [H_{N-1}A^-] / [H_NA] \quad \text{(1$^{st}$ diss. step)} \\
(1.30) & \quad K_2 = [H^+] [H_{N-2}A^{-2}] / [H_{N-1}A^-] \quad \text{(2$^{nd}$ diss. step)} \\
& \quad \vdots \\
(1.31) & \quad K_N = [H^+] [A^{-N}] / [HA^{(N-1)}] \quad \text{($N^{th}$ diss. step)} \\
(1.32) & \quad C_T = [H_NA] + [H_{N-1}A^-] + ... + [A^{-N}] \quad \text{(mass balance)} \\
(1.33) & \quad 0 = [H_{N-1}A^-] + 2[H_{N-2}A^{-2}] + ... + N[A^{-N}] + [OH^-] - [H^+] \quad \text{(charge bal.)}
\end{align}$$

$^7$ The undissolved (electro-neutral) species is sometimes abbreviated by $H_2A^0$. 

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The mathematical structure is similar to that of diprotic acids in § 1.2.1. All mass-action laws, i.e. the first \(N+1\) equations, are based on activities, \(\{j\}\), while the mass balance and charge balance, i.e. the last two equations, rely on molar concentrations, \([j]\).

This set of equations represents an exact description of the \(N\)-protic acid; however, due to the presence of activities in the mass-action formulas (requiring activity models as a prerequisite), this set of equations can only be solved numerically (by computer).

Thus, in order to deduce simple closed-form expressions (i.e. analytical formulas), we must therefore replace all activities with molar concentrations (except for \(H^+\)):

\[(1.34) \quad \{j\} \rightarrow [j] \quad \text{(requirement for closed-form expressions)}\]

This approximation is valid either in very dilute systems or by using conditional equilibrium constants \(^cK\) as introduced in Eq. (1.9). In the following we assume that this has been done (without explicitly specifying it by \(^cK\) in the notation). Thus we have:

\[(1.35) \quad K_w = \{H^+\} \cdot [OH^-] \quad \text{(self-ionization of H}_2\text{O)}\]
\[(1.36) \quad K_1 = \{H^+\} \cdot [H_{N-1}A^+] / [HA^-] \quad \text{(1\textsuperscript{st} diss. step)}\]
\[(1.37) \quad K_2 = \{H^+\} \cdot [H_{N-2}A^{2-}] / [H_{N-1}A^-] \quad \text{(2\textsuperscript{nd} diss. step)}\]
\[
\vdots
\]
\[(1.38) \quad K_N = \{H^+\} \cdot [A^{-N}] / [HA^{-(N-1)}] \quad \text{(N\textsuperscript{th} diss. step)}\]
\[(1.39) \quad C_T = [H_N A^+] + [H_{N-1}A^+] + \ldots + [A^{-N}] \quad \text{(mass balance)}\]
\[(1.40) \quad 0 = [H_{N-1}A^-] + 2[H_{N-2}A^{-2}] + \ldots + N[A^{-N}] + [OH^-] - [H^+] \quad \text{(charge bal.)}\]

This set of equations is the basis for all subsequent investigations. As a warm-up, the next paragraph starts with the subset of Eqs. (1.36) to (1.39) that defines the subsystem “pure acid”. It exhibits the main (mathematical) features of the acid in its clearest form.
1.3 The Subsystem “Pure Acid”

This paragraph focuses on the subsystem “pure acid” described by the subset of $N+1$ equations (1.36) to (1.39). In other words, the self-ionization of water, determined by Eq. (1.35), and the charge-balance equation (1.40) will be ignored.

1.3.1 Notation

Given is an $N$-protic acid with a total amount (molar concentration)

(1.41) \[ C_T \equiv [H_NA]_T = TOT\ H_NA \]

This acid is characterized by $N+1$ species:

\begin{itemize}
  \item 1 undissociated species: $H_NA(aq)$ (electro-neutral)
  \item $N$ dissociated species: $H_{N-1}A^-,$ ..., $HA^{-(N-1)},$ $A^-N$ (anionic)
\end{itemize}

To keep the notation simple, we abbreviate the molar concentrations of the dissolved species by

(1.42) \[ [j] \equiv [H_{Nj}A^{-j}] \quad \text{for} \quad j = 0, 1, 2, ... N \]

The symbol $j$ is an integer that also indicates the negative charge of the species (which is equal to the number of released protons):

(1.43) \[ z_j = 0 - j \]

Thus, species $[0]$ stands for the electro-neutral, undissociated species $H_NA(aq)$.

\[ \text{In each dissociation step, } j \text{ is enhanced by 1 (i.e. by releasing one proton):} \]

(1.44) \[ j^{th} \text{ dissociation step: } [j-1] \rightarrow [j] \]

where, according to the Eq. (1.6), the conjugate acid-base pair is composed of:

(1.45) acid:
(1.46) conjugate base:

\[ \left\{ \begin{array}{c}
[j-1] \\
[j]
\end{array} \right\} \text{ of } j^{th} \text{ dissociation step} \]

The molar concentrations of all species add up to the total concentration $C_T$:

(1.47) \[ C_T = \sum_{j=0}^{N} [j] = [0] + [1] + ... + [N] \]

---

8 This quantity should not be confused with the total amount of acid, $[H_NA]_T$. 
Ionization Fractions. Instead of using the $N+1$ acid species $[j]$, it is more convenient to work with ionization fractions (as ratios of the acid-species concentration to the total amount of acid):

$$a_j = \frac{[j]}{C_T} \quad \text{for } j = 0, 1, 2, ... N$$

1.3.2 Stepwise and Cumulative Dissociation

As already discussed in §1.1.3, a monoprotic acid is characterized by one single acidity constant $K_1 (= K_a)$, a diprotic acid by two acidity constants ($K_1$, $K_2$), and a triprotic acid by three acidity constants ($K_1$, $K_2$, $K_3$):

1st dissociation step: $H_3A = H^+ + H_2A^-$

2nd dissociation step: $H_2A^- = H^+ + HA_2^-$

3rd dissociation step: $HA_2^- = H^+ + A_3^-$

The three reaction steps of a triprotic acid can also be written as:

$$H_3A = H^+ + H_2A^- \quad k_1 = K_1$$

$$H_3A = 2H^+ + HA_2^- \quad k_2 = K_1K_2$$

$$H_3A = 3H^+ + A_3^- \quad k_3 = K_1K_2K_3$$

So we have two types of representation: The first representation describes the stepwise release of one single $H^+$ in each dissociation step (it’s the way nature works); the second relates each dissociated species directly to the undissociated acid by a ‘multi-proton’ or cumulative release. The latter is a mathematical trick to simplify some of our further calculations.

The transition to the second representation (in Tab. 1.3) requires a new set of mass-action laws based on cumulative acidity constants $k_1$, $k_2$, to $k_N$:

$$K_1 = \{H^+\} [H_{N-1}A^N] / [H_NA]$$

$$K_2 = \{H^+\} [H_{N-2}A^{N-2}] / [H_{N-1}A]$$

$$\ldots$$

$$K_N = \{H^+\} [A^{N-1}] / [HA^{(N-1)}]$$

which are products of $K_1$, $K_2$ etc.:

$$k_j = \begin{cases} 
1 & \text{for } j = 0 \\
K_jK_{j-1} \ldots K_1 & \text{for } j > 0 \text{ and } j \leq N
\end{cases}$$

In addition, $k_j = 0$ for $j$ values outside this range, i.e. for negative $j$ and for $j > N$. 

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Tab. 1.3 Acid species and their cumulative acidity constants (in the new representation)

<table>
<thead>
<tr>
<th>j</th>
<th>species</th>
<th>equilibrium reaction</th>
<th>cumulative acidity constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>[0] ≡ [HₐA]</td>
<td>HₐA = HₐA</td>
<td>k₀ = {HₐA}/[HₐA]</td>
</tr>
<tr>
<td>1</td>
<td>[1] ≡ [Hₐ₋₁A⁻]</td>
<td>HₐA = H⁺ + H₋₁A⁻</td>
<td>k₁ = {H⁺}[H₋₁A⁻]/[HₐA]</td>
</tr>
<tr>
<td>2</td>
<td>[2] ≡ [H₋₂₋₂A⁻²]</td>
<td>HₐA = 2H⁺ + H₋₂₋₂A⁻²</td>
<td>k₂ = {H⁺}²[H₋₂₋₂A⁻²]/[HₐA]</td>
</tr>
<tr>
<td>N</td>
<td>[N] ≡ [A⁻ᴺ]</td>
<td>HₐA = NH⁺ + A⁻ᴺ</td>
<td>kₙ = {H⁺}ᴺ[A⁻²]/[HₐA]</td>
</tr>
</tbody>
</table>

In logarithmic scale, using the common definition for pkₗ ≡ –lg kₗ, Eq. (1.49) becomes:

(1.50) \[ pk_j = \begin{cases} 0 & \text{for } j = 0 \\ pK_i + pK_2 + \cdots + pK_j & \text{for } j > 0 \text{ and } j \leq N \end{cases} \]

This simple additive relationship is illustrated in Fig. 1.6 for the triprotic acid, where the pkₗ and pKₗ values are plotted on a Gibbs-free energy axis (ΔG°).

Fig. 1.6 Relations between pk and pK values on a Gibbs-free energy axis (ΔG°) for a triprotic acid

In contrast to pkₗ values, which can be sequenced along an energy scale, like in Fig. 1.6, pKₗ values are sequenced on a pH scale – see Fig. 1.7 on page 29.

Note. The cumulative acidity constant kₗ should not be confused with the cumulative equilibrium constant for complex formation denoted by βₗ (stability constants). Acidity constants are dissociation constants, while complex-formation constants are association constants.
1.3.3 Generalized HENDERSON-HASSELBACH Equations

The two representations (i.e. the stepwise and the cumulative dissociation introduced in § 1.3.2) can be brought into a more compact form:

<table>
<thead>
<tr>
<th>Reaction Formula</th>
<th>Law of Mass Action</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_{(j-1)}A^{-j} = H^+ + H_{j-1}A^{-j}$</td>
<td>$K_j = \frac{x \cdot [j]}{[j-1]}$</td>
</tr>
<tr>
<td>$H_NA = J H^+ + H_{N-1}A^{-1}$</td>
<td>$K_j = \frac{x^j \cdot [j]}{[0]} = K_j K_{j-1} \cdots K_1$</td>
</tr>
</tbody>
</table>

Eq. (1.51) represents the $j^{th}$ dissociation step characterized by $K_j$ (where $j$ runs from 1 to $N$). In contrast, Eq. (1.52) is a representation for $N+1$ reactions (where $j$ runs from 0 to $N$), including the trivial case $H_NA = H_NA$ with $k_0 = 1$.

Eqs. (1.51) and (1.52) provide the pH (or $x$) dependence for concentration ratios:

$$\frac{[j]}{[j-1]} = \frac{K_j}{x} \quad \text{[j]} = [j-1] \quad x = K_j$$

$$\frac{[j+1]}{[j-1]} = \frac{K_j K_{j+1}}{x} \quad \text{[j+1]} = [j-1] \quad x = (K_j K_{j+1})^{1/2}$$

$$\frac{[j]}{[0]} = \frac{k_j}{x} = \frac{K_1 K_2 \cdots K_j}{x}$$

Thus, by knowing the concentration of one single species, say $[j]$, we are able to calculate all other concentrations, i.e. the complete equilibrium distribution for a given pH (or $x$). Under specific conditions (indicated by the blue arrows) the first two equations simplify and define two types of equivalence points, which will be discussed in § 1.4.

In logarithmic form, the first two equations are generalizations of the HENDERSON-HASSELBACH formula introduced in Eq. (1.14):

$$\text{pH} = pK_j + \lg \frac{[j]}{[j-1]} \quad \text{[j]} = [j-1] \quad \text{pH} = pK_j$$

$$\text{pH} = \frac{1}{2} \left( pK_j + pK_{j+1} \right) + \lg \frac{[j+1]}{[j-1]} \quad \text{[j+1]} = [j-1] \quad \text{pH} = \frac{pK_j + pK_{j+1}}{2}$$
1.3.4 Closed-Form Expressions

Using Eq. (1.52), the subset of $N+1$ equations (1.36) to (1.39) simplifies to:

(1.58) \[ [j] = \left( \frac{k_j}{x^j} \right) [0] \quad (N \text{ dissociation equations, } j = 1 \text{ to } N) \]

(1.59) \[ C_T = \sum_{j=1}^{N} [j] = [0] \sum_{j=0}^{N} \frac{k_j}{x^j} \quad (\text{mass balance}) \]

In the pure-acid case, $C_T$ itself is irrelevant\(^9\). Dividing both equations by $C_T$, and we get with $a_j = [j]/C_T$:

(1.60) \[ a_j = \left( \frac{k_j}{x^j} \right) a_0 \]

(1.61) \[ 1 = \sum_{j=0}^{N} a_j = a_0 \sum_{j=0}^{N} \frac{k_j}{x^j} = a_0 \left( 1 + \frac{k_1}{x} + \frac{k_2}{x^2} + \ldots + \frac{k_N}{x^N} \right) \]

The last equation provides a formula for $a_0$ as a function of $x$ (or pH):

(1.62) \[ a_0 = \left( 1 + \frac{k_1}{x} + \frac{k_2}{x^2} + \ldots + \frac{k_N}{x^N} \right)^{-1} = \left( 1 + \frac{K_1}{x} + \frac{K_1K_2}{x^2} + \ldots + \frac{K_1K_2\ldots K_N}{x^N} \right)^{-1} \]

Knowing $a_0$, all other ionization fractions $a_j$ can be calculated by Eq. (1.60). The set of ionization fractions – i.e. the \textit{normalized} acid-species distribution – contain all the information about the ‘pure acid’ subsystem. More about ionization fractions will be presented in § 1.5.

\textbf{Summary.} Given $x = 10^{pH}$, the species distribution of the ‘pure acid’ subsystem is completely determined by the set of $N+1$ ionization fractions (for $j = 0, 1, \ldots, N$):

\[ a_j = \left( \frac{k_j}{x^j} \right) a_0 \quad \text{with} \quad a_0 = \left( 1 + \frac{k_1}{x} + \frac{k_2}{x^2} + \ldots + \frac{k_N}{x^N} \right)^{-1} \]

---

\(^9\) $C_T$ becomes relevant only when, in addition to $H_2A$, other components or subsystems are present (like $H_2O$ and/or other acids and bases).
Inverse Task. The inverse task is to calculate x or pH from a given $a_0$ (or any other $a_j$). This leads to a polynomial of order $N$ in $x$ (as derived in Appendix B.2.1):

\[
0 = \text{const} \cdot x^{N-j} + \sum_{i=j}^{N} k_i x^{N-i} \quad \text{with} \quad \text{const} = -\left(\frac{1-a_j}{a_j}\right) k_j
\]

Example. For a diprotic acid $H_2A$, Eq. (1.64) reduces to a quadratic equation (which can be solved quite easily). Let’s assume we know the value of $a_0$ and want to calculate the corresponding $x$. The steps are as follows (note that $k_0 = 1$):

\[
0 = -\frac{1-a_0}{a_0} x^2 + K_i x + K_i K_2
\]

\[
0 = x^2 - \alpha K_i x - \alpha K_i K_2 \quad \text{with} \quad \alpha = \frac{a_0}{1-a_0}
\]

The positive root of this quadratic equation is

\[
x = \frac{\alpha K_i}{2} \left(1 + \sqrt{1 + \frac{4 \frac{K_2}{\alpha K_1}}{}}\right)
\]

Usually, $K_2/K_1 \ll 1$ and the second term in the square root can be neglected. Then, for $a_0 = \frac{1}{2}$ (i.e. $\alpha = 1$) we get the simple result $x = K_1$. 
1.4 Equivalence Points of Subsystem “Pure Acid”

1.4.1 Definition of $\text{EP}_n$

An equivalence point (EP) is a *special equilibrium state* at which chemically equivalent quantities of acids and bases have been mixed:

\[(1.66) \quad \text{equivalence point:} \quad [\text{acid}] = [\text{base}]\]

This concept also applies to any *conjugate* acid-base pair:

\[(1.67) \quad \text{equivalence point:} \quad [\text{acid}] = [\text{conjugate base}]\]

Thus, a polyprotic acid gives rise to a whole series of EPs, because – as we have seen in Eqs. (1.44) to (1.46) – each dissociation step (by releasing one proton) relates an acid to its conjugate base. Thereby, two types of equivalence points should be distinguished:

\[(1.68) \quad \text{EP}_j: \quad [j-1] = [j+1]\]
\[(1.69) \quad \text{semi-EP}_j: \quad [j-1] = [j]\]

The definition of $\text{EP}_j$ remains valid for $j=0$ and $j=N$, if we extend our notation and identify $[-1]$ by $[\text{H}^+]$ and $[N+1]$ by $[\text{OH}]$. It yields:

\[(1.70) \quad \text{EP}_0: \quad [\text{H}^+] = [1] \quad (\text{for } j = 0)\]
\[(1.71) \quad \text{EP}_j: \quad [j-1] = [j+1] \quad (\text{for } j = 1, 2, \ldots, N-1)\]
\[(1.72) \quad \text{EP}_N: \quad [N-1] = [\text{OH}] \quad (\text{for } j = N)\]

and

\[(1.73) \quad \text{semi-EP}_j: \quad [j-1] = [j] \quad (\text{for } j = 1, 2, \ldots, N)\]

Each EP is the midpoint between two adjacent semi-EPs (as will be shown in § 1.4.2). An acid $\text{H}_n\text{A}$ has $N+1$ EPs (the same number as the number of acid species) plus $N$ semi-EPs. In total, there are $2N+1$ equivalence points, called $\text{EP}_n$, where $n$ runs over all integer and half-integer values.\(^{10}\)

\[(1.74) \quad n = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \ldots, N-\frac{1}{2}, N\]

According to Eqs. (1.70) to (1.73), $\text{EP}_n$ is defined by

\[(1.75) \quad \text{EP}_n \Leftrightarrow \begin{cases} [n-1] = [n+1] & \text{for } n = 0, 1, 2, \ldots, N \quad (\text{EP}_n) \\ [n-\frac{1}{2}] = [n+\frac{1}{2}] & \text{for } n = \frac{1}{2}, \frac{3}{2}, \ldots, N-\frac{1}{2} \quad (\text{semi EP}_{\frac{n+1}{2}}) \end{cases}\]

\(^{10}\) The choice of the small latter $n$ as the index in $\text{EP}_n$ is not accidental. The deep relationship between $\text{EP}_n$ and the variable $n = \frac{C_B}{C_T}$, where $C_B$ is the amount of strong base, will be discussed in Chapter 2.
1.4.2 Correspondence between $EP_n$ and $pH_n$

An equivalence point is a special equilibrium state that is characterized by one specific pH value: $EP_n \leftrightarrow pH_n$ (or $EP_n \leftrightarrow x_n$). The correspondence can be easily established. Before we start, however, it’s useful to make a distinction between so-called ‘external’ and ‘internal’ EPs that separate the two outermost equivalence points $EP_0$ and $EP_N$ from the rest:

- **external** equivalence points $EP_0$ and $EP_N$
- **internal** equivalence points all other $EP_n$ (for $\frac{1}{2} \leq n \leq N-\frac{1}{2}$)

**Internal EPs.** The internal equivalence points deliver particularly simple formulas. From Eqs. (1.53) and (1.54), or Eqs. (1.56) and (1.57), we directly get (valid for $0 < j < N$):

\[
\begin{align*}
1.76 & \quad \text{semi-EP } j; \quad [j-1] = [j] \quad \Rightarrow \quad pH = pK_j \quad \Leftrightarrow \quad x = K_j \\
1.77 & \quad \text{EP } j; \quad [j-1] = [j+1] \quad \Rightarrow \quad pH = \frac{1}{2} (pK_j + pK_{j+1}) \quad \Leftrightarrow \quad x = (K_jK_{j+1})^{1/2}
\end{align*}
\]

It yields the following sequence:

\[
\begin{align*}
1.78 & \quad n = \frac{1}{2}: \quad EP_{1/2} \leftrightarrow pH_{1/2} = pK_1 \\
1.79 & \quad n = 1: \quad EP_1 \leftrightarrow pH_1 = \frac{1}{2} (pK_1 + pK_2) \\
1.80 & \quad n = 3/2: \quad EP_{3/2} \leftrightarrow pH_{3/2} = pK_2 \\
1.81 & \quad n = 2: \quad EP_2 \leftrightarrow pH_2 = \frac{1}{2} (pK_2 + pK_3) \\
1.82 & \quad n = N-\frac{1}{2}: \quad EP_{N-\frac{1}{2}} \leftrightarrow pH_{N-\frac{1}{2}} = pK_N
\end{align*}
\]

Here, the close relationship between equivalence points and pK values becomes evident. Each acid’s pK value represents exactly one semi-EP (characterized by half-integer n). On the other hand, EP_n with integer n are the midpoints between two adjacent semi-EPs. It can be summarized as follows: \(^\text{11}\)

\[
\begin{align*}
pH_n \equiv \begin{cases} 
\frac{1}{2} (pK_n + pK_{n+1}) & \text{for } n = 1, 2, \ldots, N-1 \quad (EP_{p-n}) \\
pK_{n+\frac{1}{2}} & \text{for } n = \frac{1}{2}, \frac{3}{2}, \ldots, N-\frac{1}{2} \quad \text{(semi EP \_p-n+\frac{1}{2})}
\end{cases}
\end{align*}
\]

**Tab. 1.4** Internal equivalence points of four acids (based on pK values in Tab. 1.1 on page 14)

<table>
<thead>
<tr>
<th>$N$</th>
<th>Acid $H_nA$</th>
<th>$pH_{1/2}$</th>
<th>$pH_1$</th>
<th>$pH_{3/2}$</th>
<th>$pH_2$</th>
<th>$pH_{5/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>acetic acid</td>
<td>4.76</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>(composite) carbonic acid</td>
<td>6.35</td>
<td>8.34</td>
<td>10.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>phosphoric acid</td>
<td>2.15</td>
<td>4.68</td>
<td>7.21</td>
<td>9.78</td>
<td>12.35</td>
</tr>
<tr>
<td>3</td>
<td>citric acid</td>
<td>3.13</td>
<td>3.94</td>
<td>4.76</td>
<td>5.58</td>
<td>6.4</td>
</tr>
</tbody>
</table>

\(^{11}\) The index $j$ is always an integer; the index $n$ is both integer and half-integer.
Tab. 1.4 lists the \textit{internal} equivalence points of four common acids. \textit{Internal} EPs are completely determined by the acid’s pK values (no other information is necessary). In this respect, they differ from \textit{external} EPs which depend on the amount of acid, $C_T$.

\textbf{External EPs.} There are only two \textit{external} equivalence points ($EP_0$ and $EP_N$). The formulas (which are related to $H^+$ or $OH^-$ via Eqs. (1.70) and (1.72)) are a bit trickier than for the internal EPs. From Eqs. (1.58) to (1.60) follows:\textsuperscript{12}

\begin{align*}
(1.84) \quad EP_0: \quad [H^+] = [1] & \Rightarrow x = C_T a_1 \quad \Rightarrow C_T = \frac{x^2}{K_1} \cdot \frac{1}{a_0(x)} \\
(1.85) \quad EP_N: \quad [N-1] = [OH^-] & \Rightarrow C_T a_{N-1} = \frac{K_w}{x} \quad \Rightarrow C_T = \frac{K_w K_N}{x^2} \cdot \frac{1}{a_N(x)}
\end{align*}

Here, the pH values (or $x$) depend on the total amount of acid, $C_T$. Unfortunately, the equations on the right-hand side can only be offered as \textit{implicit} functions of $x$: $C_T = C_T(x)$. [The inverse relationship, i.e. $x = x(C_T)$, would require root-solving of a high-order polynomial.]

The only things we can offer are values for the asymptotic case. As shown in Eqs. (1.104) and (1.105), we have $a_0 = 1$ for $x \to \infty$ and $a_N = 1$ for $x \to 0$. The last two equations on the far right then yield:

\begin{align*}
(1.86) \quad EP_0: \quad \text{approaching pH} \to 0 \quad \text{(or} \ x \ \text{to} \ \infty) \quad \text{when} \ C_T \to \infty \\
(1.87) \quad EP_N: \quad \text{approaching pH} \to 14 \quad \text{(or} \ x \ \text{to} \ 0) \quad \text{when} \ C_T \to \infty
\end{align*}

\subsection{1.4.3 Summary and Examples}

The same acidity constants (or pK values) that characterize the $N$-protic acid represent the pH values of the so-called \textit{internal} equivalent points in the form of Eq. (1.83):

- $EP$ with integer $n$ \quad (EP\textsubscript{1}, EP\textsubscript{2}, ..., EP\textsubscript{N-1}) \quad \text{at pH}_n$
- semi-$EP$ with half-integer $n$ \quad (EP\textsubscript{1/2}, EP\textsubscript{3/2}, ..., EP\textsubscript{N-1/2}) \quad \text{at pH}_{n+1/2}$

In addition, there are two \textit{external}, non-constant equivalence points located at both ends of the pH scale when $C_T \to \infty$:

- $EP_0$: \quad pH $\to$ 0
- $EP_N$: \quad pH $\to$ 14

The EPs (external and internal) are arranged on the pH scale in the sequence of increasing $n$, in the way as in Eq. (1.74):

\begin{equation}
(1.88) \quad \text{pH}_0, \ \text{pH}_{1/2}, \ \text{pH}_1, \ \text{pH}_{3/2}, \ ... \ , \ \text{pH}_N
\end{equation}

An example of such a sequence is shown schematically in Fig. 1.7 for the triprotic acid H$_3$PO$_4$.

\textsuperscript{12} For simplicity we set here $x \approx [H^+]$, which deviates from our definition of $x$ in Eq. (0.5).
Acid Base Systems

Fig. 1.7 Classification of equivalence points of the subsystem ‘pure acid’ (example: triprotic acid H₃PO₄)

**pH-Cₜ Plots.** Fig. 1.8 shows all equivalence points of carbonic acid (upper diagram) and phosphoric acid (lower diagram) in the pH-Cₜ diagram. The *internal* equivalence points (red lines) are independent of Cₜ while the two *external* EPs (blue and green curves) are not.

![Fig. 1.8 pH dependence of EPs and semi-EPs for two acids plotted as Cₜ = f(pH). These curves are approximations valid for the isolated subsystem ‘pure acid’ (i.e. without coupling to the subsystem ‘pure H₂O’).](image)

The representation as *dashed* curves (instead of solid lines) in Fig. 1.8 reminds us that these are approximations, valid for the isolated subsystem ‘pure acid’ (i.e. without coupling to the subsystem ‘H₂O’). The general case will be discussed in § 2.3. There, we will learn that all *internal* EPs represent the large-Cₜ limit of the combined ‘HₙA + H₂O’ system.
1.5 Ionization Fractions: Degree of Dissociation

1.5.1 Definition of \( a_j \)

The \( N \)-protic acid \( H_NA \) comprises \( N+1 \) acid species denoted by \([j]\), where \( j \) runs from 0 to \( N \). Instead of the molar concentrations \([j]\) (that add up to the total amount \( C_T \)), it is convenient to use normalized, *unitless* ionization fractions \( a_0, a_1 \) to \( a_N \):

(1.89) \[ a_j = \frac{[j]}{C_T} \quad \text{for } j = 0, 1, 2, ... N \]

They form the mathematical skeleton of the subsystem ‘pure acid’ with their typical dependence on \( x \) (or \( \text{pH} = –\lg x \)):

\[
(1.90) \quad a_j = \left( \frac{k_j}{x^j} \right) a_0 \quad \text{with} \quad a_0 = \left( 1 + \sum_{k=1}^N \frac{k_k}{x^k} \right)^{-1}
\]

Combining the left and right equations yields:

(1.91) \[ a_j = \left( \frac{k_j}{x^j} \right) a_0 = \frac{k_j / x^j}{\sum_{j=0}^N k_j / x^j} \quad \text{for } j = 0, 1, 2, ... N \]

The ionization fractions are solely functions of \( x \) (or \( \text{pH} = –\lg x \)); the only other ingredients are the *cumulative* equilibrium constants, introduced in Eq. (1.49):

(1.92) \[ k_0 = 1, \quad k_1 = K_1, \quad k_2 = K_1 K_2, \quad ... \quad k_N = K_1 K_2 ... K_N \]

Due to its definition in Eq. (1.89), the ionization fractions are independent of the total concentration \( C_T \), which is useful in graphical representations, as shown in Fig. 1.9. On the other hand, once we know \( a_j \), the molar concentration of the acid species is immediately obtained by multiplication with \( C_T \):

(1.93) \[ [j] = C_T a_j(x) \quad \text{for } j = 0, 1, \ldots, N \]

To clearly exhibit the \( \text{pH} \) dependence of \( a_j \), Eq. (1.91) can also be written as

(1.94) \[ a_j(\text{pH}) = a_0 \cdot k_j 10^{j \cdot \text{pH}} = \frac{k_j 10^{j \cdot \text{pH}}}{\sum_{j=0}^N k_j 10^{j \cdot \text{pH}}} \]

The ionization fractions are the building blocks of all relevant quantities, which we will derive in the next chapters.

\[\text{It was derived in §1.3.4, Eq. (1.63).}\]
1.5.2 **BJERRUM Plots and Special Features of $a_j$**

**BJERRUM plots** (as dissociation diagrams) are a convenient way to visualize the pH dependence of the ionization fractions $a_j$. This is demonstrated in Fig. 1.9 for four acids (based on pK values taken from Tab. 1.1).

![BJERRUM Plots](image)

**Fig. 1.9** BJERRUM plots of ionization fractions for four acids (blue circles denote semi-EPs)

**Universality.** Ionization fractions have the nice feature that they are *independent* of the acid’s total amount $C_T$. Regardless of the assumed $C_T$ (either constant or pH-dependent), the ionization-fractions curves remain the same – see examples in § 2.4.5 (H$_2$A as titrant vs H$_2$A as analyte) and § 2.4.6 (open vs. closed CO$_2$ system).

**Mass Balance.** For any chosen value of $x$ (or pH) the sum of all ionization fractions adds up to 1:

$$1 = a_0 + a_1 + ... + a_N = \sum_{j=0}^{N} a_j(x) \quad \text{for any } x \text{ (or pH)}$$

The ionization fractions are bound between 0 and 1:

$$0 < a_j < 1 \quad \text{for all } j$$

They do not become negative or greater than 1. Strictly speaking, the functions will come very close to the boundaries, but will never actually reach the values 0 and 1.
**Acid Base Systems**

**Short Lecture**

**EPs.** The equivalence points, introduced in Eqs. (1.76) and (1.77) can also be defined by equating \( a_j \)'s:

\[
\begin{align*}
(1.97) & \quad \text{semi-EP}_j: \quad [j-1] = [j] \iff a_{j-1} = a_j \implies x = K_j \\
(1.98) & \quad \text{EP}_j: \quad [j-1] = [j+1] \iff a_{j-1} = a_{j+1} \implies x = (K_j K_{j+1})^j
\end{align*}
\]

This applies only for the *internal* equivalence points:

\[
\begin{array}{|c|c|c|c|c|}
\hline
\text{condition} & \text{range} & \text{pH} & n \\
\hline
\text{semi-EP}_j & a_{j-1} = a_j & j = 1, 2, \ldots, N & pK_j & j - \frac{1}{2} \\
\hline
\text{EP}_j & a_{j-1} = a_{j+1} & j = 1, 2, \ldots, N-1 & pK_j = \frac{1}{2} (pK_j + pK_{j+1}) & j \\
\hline
\end{array}
\]

The equivalence points are easily recognizable in the diagrams of Fig. 1.9. The semi-EPs are located at the intersection of two adjacent ionization fractions, \( a_{j-1} \) and \( a_j \) (marked as blue circles); the EPs for integer \( n \) are at intersections of ionization fractions \( a_{j-1} \) and \( a_{j+1} \) (marked as yellow circles). Notice that the latter are located at the *maximum* of \( a_j \) (whose mathematical verification is given in Eq. (B.34) of Appendix B.3.2).

The actual values at the points of intersection are (cf. Eq. (B.36)):

\[
\begin{align*}
(1.101) & \quad \text{semi-EP}_j \quad a_j = a_{j-1} \approx \frac{1}{2} \quad \text{all other } a_i \approx 0 \\
(1.102) & \quad \text{EP}_j \quad a_j = 1 - 2a_{j-1} \approx 1 \quad \text{all other } a_i \approx 0
\end{align*}
\]

### 1.5.3 Two Types of \( a_j \): S-shaped vs. Bell-shaped

The distinction between *external* and *internal* equivalence points (as introduced in § 1.4.2) has its deep cause in the fact that there are two types of ionization fractions \( a_j \). Let’s take a step back and start our considerations from the equilibrium constants (in the form of \( pK_j \) values).

The one, two or \( N \) \( pK_j \) values of a mono-, di- or \( N \)-protic acid subdivide the entire pH domain into distinct intervals, as shown in the left diagrams of Fig. 1.10. Principally, a polyprotic acid \( H_{N'A} \) with its \( N \) \( pK \) values generates \( N+1 \) intervals:

\[
\begin{align*}
\text{0th interval} & \quad \text{for } pH < pK_1 \\
\text{1st interval} & \quad \text{between } pK_1 \text{ and } pK_2 \\
& \vdots \\
\text{i-th interval} & \quad \text{between } pK_i \text{ and } pK_{i+1} \\
& \vdots \\
\text{N-th interval} & \quad \text{for } pH > pK_N
\end{align*}
\]

The \( j \)-th interval is the domain where the ionization fraction \( a_j \) exercises its full dominion; see right diagrams of Fig. 1.10. As indicated by the colors, there are two types of curves: S-shaped curves in the 0\(^{th}\) and the \( N \)\(^{th}\) interval at the opposite ends of the pH scale (red color) and bell-shaped curves in all other intervals (blue color). The latter reach their maxima exactly in the middle of the interval. In contrast, the S-shaped
curves appear as the two halves of a bell-shaped curve when the opposite ends of the two S-shaped curves are glued together (at minus and/or plus infinity).

Asymptotic Behavior. At the opposite ends of the pH scale there are only the ionization fractions $a_0$ or $a_N$ (which attain the maximum value 1):

\begin{align*}
(1.104) \text{ strongly acidic: } & \quad \text{pH} \to 0 \quad (\text{or } x \to \infty): \quad a_0 = 1 \quad \text{all other } a_j = 0 \\
(1.105) \text{ strongly alkaline: } & \quad \text{pH} \to 14 \quad (\text{or } x \to 0): \quad a_N = 1 \quad \text{all other } a_j = 0
\end{align*}

Note: In principle, the pH scale does not end at 0 or 14, but can be extended beyond these boundaries (for a mathematician even to $-\infty$ and $+\infty$).

\footnote{For a mathematician this isn't even as crazy as it seems (when acting on the complex Riemann sphere, for example).}
Summary. Tab. 1.5 compares the two types of ionization fractions with each other.

Tab. 1.5 The two types of ionization fractions of an \( N \)-protic acid \( H_nA \)

<table>
<thead>
<tr>
<th></th>
<th>Type 1 (S-shaped)</th>
<th>Type 2 (bell-shaped)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ionization fraction</td>
<td>( a_0 ) and ( a_N )</td>
<td>( a_j ) for ( j \neq 0 ) and ( N ) (does not exist for monoprotic acids)</td>
</tr>
<tr>
<td>domain (pH interval)</td>
<td>( pH &lt; pK_1 ) (for ( a_0 )) \n( pH &gt; pK_N ) (for ( a_N ))</td>
<td>( pK_i &lt; pH &lt; pK_{i+1} )</td>
</tr>
<tr>
<td>maximum at pH</td>
<td>( -\infty ) (for ( a_0 )) \n( +\infty ) (for ( a_N ))</td>
<td>( \frac{1}{2} (pK_i + pK_{i+1}) )</td>
</tr>
<tr>
<td>asymptotic behavior:</td>
<td>strong acidic (( pH \to 0 )) \nstrong alkaline (( pH \to 14 ))</td>
<td>( a_0 = 1, \ a_N = 0 ) \n( a_0 = 0, \ a_N = 1 ) \n( a_j = 0 ) \n( a_j = 0 )</td>
</tr>
<tr>
<td>associated equivalence points</td>
<td>two external EP: \n( EP_0 ) and ( EP_N )</td>
<td>( N-1 ) internal EP: \n( EP_1, \ EP_2, \ldots \ EP_N-1 )</td>
</tr>
</tbody>
</table>

1.5.4 Two Types of Approximations

The general formula for the ionization fractions in Eq. (1.90) can be approximated in two radically different ways:

- **Approach 1**: “piecewise log-scale approximation” for \( \lg a_j \)
- **Approach 2**: “midpoint approximation” for \( a_j \)

**Approach 1.** The first approach is an approximation for the logarithm of \( a_j \) (i.e., for \( \lg a_j \) instead of \( a_j \) itself). It’s exactly the approach that is used in textbooks as a graphical method for solving the algebraic equations of equilibrium systems (in double-logarithmic diagrams).

The approximate formula for \( \lg a_j \) represents a sequence of linear function in pH:

\[
(1.106) \quad \lg a_j \approx (j-i) \cdot pH + (pk_i - pk_j) \quad \text{for the } i^{th} \text{ interval}
\]

where \( pk_i = pK_1 + pK_2 + \ldots + pK_i \) and \( pk_0 = 0 \). (For the derivation we refer to Appendix B.1.1.) Note: In the special case of \( j = i \) we get \( \lg a_j = 0 \), that is \( a_j = 1 \).

Fig. 1.11 shows the approximation for phosphoric acid (as a triprotic acid). There are three pK values that subdivide the pH domain into four intervals. In each \( i^{th} \) interval, \( \lg a_j \) represents a straight line with integer-valued slope \( (j-i) \) and offset \( (pk_i - pk_j) \). For example, for \( a_2 \) (green dashed curve) we have

\[
a_2 \approx (2-i) \cdot pH + (pk_i - pk_2)
\]
with the following segments (straight lines) in the $i^{th}$ intervals:

\[
\begin{align*}
  i = 0: \quad & (2 - 0) \text{pH} + (0 - pK_2) = 2 \text{pH} - (pK_1 + pK_2) = 2 \text{pH} - 9.35 \\
  i = 1: \quad & (2 - 1) \text{pH} + (pK_1 - pK_2) = \text{pH} - pK_2 = \text{pH} - 7.21 \\
  i = 2: \quad & (2 - 2) \text{pH} + (pK_2 - pK_2) = 0 = 0 \\
  i = 3: \quad & (2 - 3) \text{pH} + (pK_3 - pK_2) = - \text{pH} + pK_3 = - \text{pH} + 12.35
\end{align*}
\]

**Approach 2.** The second approach for $a_j$ is based on the fact that the curves in Fig. 1.9 look so elementary that one wonders whether these cannot be described by a much simpler formula—and this is indeed so. You can replace the exact formulas in Eq. (1.90) by simpler ones:

\[
\begin{align*}
  a_0 \approx & \left(1 + \frac{K_1}{x}\right)^{-1} \\
  a_j \approx & \left(\frac{x}{K_j} + 1 + \frac{K_{j+1}}{x}\right)^{-1} \quad \text{for } j = 1 \text{ to } N-1 \\
  a_N \approx & \left(\frac{x}{K_N} + 1\right)^{-1}
\end{align*}
\]

This approach is based on no more than two (adjacent) pK values; all other pK values are ignored. In fact, for diprotic acids it just coincides with the exact formula,\footnote{Of course, it also provides an exact solution for monoprotic acids $N = 1$, where $a_0$ and $a_1$ are described by Eq. (1.107) and Eq. (1.109).} but for $N$-protic acids with $N > 2$ it deviates slightly. The small deviations from the exact description can only be recognized in logarithmic plots of $a_j$—as shown for phosphoric acid ($N = 3$) in Fig. 1.12.
Summary. The two approaches are complementary, as demonstrated in Fig. 1.13 (for phosphoric acid as a triprotic acid). **Approach 1** offers a very nice approximation in logarithmic plots, but fails to reproduce the S-shaped and bell-shaped curves in pH-$a_j$ diagrams (dashed curves in bottom-left diagram). Conversely, **Approach 2** reproduces the $a_j$ curves perfectly. However, if we take a closer look, we recognize deviations in the log-plots for values below $10^{-4}$ (dashed curves in the top-right diagram).
1.6 Moments $Y_L$ – Sums over $a_j$

1.6.1 Definition

If we sum up (weighted) ionization fractions $a_j$ we get so-called moments. The $L^{th}$ moment is defined by:

$$ Y_L = \sum_{j=0}^{N} j^L a_j $$

For $L = 0$ it represents the mass conservation (because $0^0 = 1$):

$$ Y_0 = a_0 + a_1 + \ldots + a_N = 1 \quad \text{for } L = 0 $$

For all other positive integers we have:

$$ Y_L = a_1 + 2^L a_2 + 3^L a_3 + \ldots + N^L a_N \quad \text{for } L \geq 1 $$

As indicated in Fig. 1.14, those moments are the building blocks of a whole series of relevant quantities: $Y_0$ represents the mass balance; $Y_1$ will turn out to be the key quantity in the description of acid-base titration curves in Chapter 2; $Y_2$ and $Y_3$ will enter the buffer intensity and its derivative in Chapter 3 (cf. Eqs. (3.42) to (3.44) on page 84).

Fig. 1.14 Moments $Y_L$ as building blocks for other quantities defined in Eqs. (3.42) to (3.44) on page 84

The moments $Y_L$ are positive functions, living in the range $0 < Y_L \leq N^L$ (here the equal sign applies only for $Y_0$, all other $Y_L$ never reach the upper limit of $N^L$).

Examples. Fig. 1.15 illustrates how the ‘titration curve’ $Y_1$ emerges from the set of ionization fractions $a_j$ (for phosphoric acid as a triprotic acid).

Fig. 1.16 displays the pH dependency of $Y_1$ to $Y_4$ for four acids (based on pK values taken from Tab. 1.1). Notice that for monoprotic acids (top-left diagram) all moments are equal; i.e. the four $Y_L$-curves cover each other.
**pH Dependence.** The moments, just like the ionization fractions, are solely functions of \(x\) (or \(\text{pH} = -\log x\)); the only other ingredients are the (cumulative) equilibrium constants of the acid. From Eq. (1.91) we obtain: \(^{16}\)

\[
(1.113) \quad Y_j(x) = \frac{\sum_{j=0}^{N} j \cdot k_j / x^j}{x / x} = \frac{\sum_{j=0}^{N} j \cdot k_j x^{N-j}}{\sum_{j=0}^{N} k_j x^{N-j}}
\]

Converting \(x\) to \(\text{pH}\) yields:

\[
(1.114) \quad Y_j(\text{pH}) = \frac{\sum_{j=0}^{N} j \cdot k_j 10^{j \cdot \text{pH}}}{\sum_{j=0}^{N} k_j 10^{j \cdot \text{pH}}}
\]

---

\(^{16}\) To obtain the last equation you should multiply both nominator and denominator by \(x^N\).
Moments $Y_L$ (for $L = 1$ to $4$)

![Graphs showing pH dependence of $Y_1$ to $Y_4$ for four acids.](image)

**Fig. 1.16** pH dependence of $Y_1$ to $Y_4$ for four acids [In case of mono-protic acids (top-left diagram) all $Y_L$ are equal.]

### 1.6.2 Moments and EP’s

**Internal EPs.** For the two types of equivalence points, the following simple relationships are obtained (see Eqs. (B.27) and (B.28) in Appendix B.3.1):

1. **semi-EP$_j$:**
   
   \[
   Y_L(pK_j) = \frac{1}{2} \quad \text{and} \quad Y_L(pH_j) = \frac{1}{2} \quad (j = 1, 2, \ldots, N-1) \]

2. **EP$_j$:**
   
   \[
   Y_L(pK_j) = \frac{1}{2} \left( pK_j + pK_{j+1} \right) \quad \text{and} \quad Y_L(pH_j) = \frac{1}{2} \left( \frac{1}{2} (1 + 2L) \right) \]

This is valid only for the so-called *internal* equivalence points ($j = 1$ to $N-1$), and for $L \geq 1$. From these expressions the following special values are obtained for $Y_L$:

<table>
<thead>
<tr>
<th>$L$ at semi-EP$_j$</th>
<th>$L$ at EP$_j$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Y_L(pK_j) = \frac{1}{2}$</td>
<td>$Y_L(pH_j) = 1$</td>
</tr>
<tr>
<td>$Y_L(pK_j) = \frac{1}{2} (1 + 2^L)$</td>
<td>$Y_L(pH_j) = 2^L$</td>
</tr>
<tr>
<td>$Y_L(pK_j) = \frac{1}{2} (2^L + 3^L)$</td>
<td>$Y_L(pH_j) = 3^L$</td>
</tr>
<tr>
<td>$Y_L(pK_j) = j - \frac{1}{2}$</td>
<td>$Y_L(pH_j) = j$</td>
</tr>
<tr>
<td>$Y_L(pK_j) = (j - 1) j - \frac{1}{2}$</td>
<td>$Y_L(pH_j) = j^2$</td>
</tr>
</tbody>
</table>
Acid Base Systems

The two relations in Eq. (1.120) can be combined into the remarkable formula valid for all *internal* EPs and semi-EPs to a very good approximation (though not exactly):

\[(1.122)\quad Y_1(pH_n) - n = 0 \quad \text{for } n = \frac{1}{2}, 1, \ldots, N - \frac{1}{2}\]

In fact, it establishes the link between EP<sub>n</sub> with integer or half-integer <i>n</i> and pH<sub>n</sub> defined in Eq. (1.83). A graphical representation is provided by the dots in Fig. 1.17.

![Graph showing pH vs. Y<sub>1</sub>(pH)](image)

**Asymptotic Behavior.** The asymptotic behavior results from Eqs. (1.104) and (1.105):

\[(1.123)\quad Y_L(pH \to 0) = 0 \quad \text{or} \quad Y_L(x \to \infty) = 0\]

\[(1.124)\quad Y_L(pH \to 14) = N^L \quad \text{or} \quad Y_L(x \to 0) = N^L\]

In particular, for Y<sub>1</sub> we get the asymptotic values 0 and 3 at opposite ends of the pH scale, as shown Fig. 1.17. These values correspond to the two *external* EPs (EP<sub>0</sub> and EP<sub>3</sub>). Thus, Eq. (1.122) seems to be applicable to external EPs defined by <i>n</i> = 0 and N.
1.7 The Coupled System “H₂O + HₙA”

1.7.1 Basic Set of Equations

The stage is now set for a mathematical closed-form solution of the coupled system ‘H₂O + HₙA’. The basic set of N+1 equations, formerly given in Eqs. (1.35) to (1.40), becomes (after replacing the acid species [j] by the ionization fractions 𝑎_𝑗 = [j]/C_T):

(1.125)  \[ K_w = x(x+w) \]  (subsystem ‘H₂O’)
(1.126)  \[ k_1 = x(a_1/a_0) \quad \text{or} \quad a_1 = (k_1/x) a_0 \]
(1.127)  \[ k_2 = x(a_2/a_0) \quad \text{or} \quad a_2 = (k_2/x^2) a_0 \]
...  
(1.128)  \[ k_N = x(a_N/a_0) \quad \text{or} \quad a_N = (k_N/x^N) a_0 \]
(1.129)  \[ 1 = a_0 + a_1 + a_2 + ... + a_N \]
(1.130)  \[ 0 = (a_1 + 2a_2 + ... + N a_N) + w/C_T = Y_1 + w/C_T \]  (charge balance)

H₂O. The subsystem ‘pure H₂O’ with its two components H⁺ and OH⁻ is expressed by \( x = \{H^+\} \) and \( w(x) \). The latter includes the self-ionization of water \( K_w \) (cf. Eq. (0.8)):

(1.131)  \[ w \equiv [\text{OH}^-] - [\text{H}^+] \approx \frac{K_w}{x} - x \]

HₙA. The subsystem ‘pure acid’ (HₙA) with its N+1 species [j] comprises N+1 equations, i.e. Eqs. (1.126) to (1.129). As shown in § 1.3, it is described by the set of N+1 ionization fractions:

(1.132)  \[ a_j(x) = \left( \frac{k_j}{x} \right) a_0 \quad \text{with} \quad a_0(x) = \left( 1 + \frac{k_1}{x} + \frac{k_2}{x^2} + ... + \frac{k_N}{x^N} \right)^{-1} \]

HₙA + H₂O. Both subsystems are linked together by the charge-balance equation (1.130). The schema in Fig. 1.18 (for an N-protic acid HₙA) is a generalization of Fig. 1.5 (for a diprotic acid H₂A).

**Fig. 1.18** Polyprotic acid system: The subsystem ‘pure H₂O’ and the subsystem ‘acid’ are coupled via the charge-balance equation

<table>
<thead>
<tr>
<th>pure H₂O</th>
<th>N-protic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K_w = x(x+w) )</td>
<td>( a_1 = (k_1/x) a_0 )</td>
</tr>
<tr>
<td>( a_2 = (k_2/x^2) a_0 )</td>
<td>...</td>
</tr>
<tr>
<td>( a_N = (k_N/x^N) a_0 )</td>
<td>( 1 = a_0 + a_1 + a_2 + ... + a_N )</td>
</tr>
<tr>
<td>( 0 = w/C_T + Y_1 )</td>
<td>charge balance</td>
</tr>
</tbody>
</table>

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1.7.2 Closed-Form Expressions

The system ‘H₂O + H₃A’ is controlled by two ‘master variables’: pH and the amount of acid Cₜ, but only one of them can be freely selected. Hence, two tasks emerge:

- given pH ⇒ calculate Cₜ
- given Cₜ ⇒ calculate pH

\[ \text{pH} \Rightarrow C_{\text{H}_2O} \]

For a given pH (or \( x = 10^{-\text{pH}} \)), the composition of the equilibrium system is obtained as follows:

\[ \text{given: } \text{pH} \text{ (or } x = 10^{-\text{pH}}) \]

\[ C_T(x) = -\frac{w}{Y_1} \]

with \( Y_1 = \sum_{j=0}^{N} j \cdot a_j(x) \)

Eq. (1.133) represents an explicit function:

\[ C_T = f(\text{pH}) \]

This dependence is displayed in the upper diagram of Fig. 1.19. [Note: exactly the same functions represent the pH dependence of the equivalence points EP₀ plotted as blue curves in the diagrams of Fig. 2.10 on page 60.]

\[ \text{CT} \Rightarrow \text{pH} \]

The inverse task, to calculate the pH (or \( x \)) for a given \( C_T \), is intricate, because an explicit function, such as \( \text{pH} = f(C_T) \), does not exist for \( N > 1 \). The only thing we can offer is an ‘implicit function’ in the form of a polynomial of order \( N+2 \):

\[ 0 = \sum_{j=0}^{N} \left\{ x^2 - jC_Tx - K_w \right\} k_j x^{N-j} \]

Compared to the polynomial for the pure-acid subsystem in Eq. (1.64), this polynomial is two degrees higher (\( N+2 \) rather than \( N \)), which makes the solution more difficult. [Note: Principally, there is no algebraic expression for solving polynomials with a degree higher than 4, no matter how hard we try. Thus, numerical root-finding methods should be applied.]

---

17 The curves in the bottom diagram of Fig. 1.19 were plotted by a trick: Take the upper diagram and interchange the axes.

18 The derivation is presented in Appendix B.2.2 – see Eq. (B.19) for \( n=0 \).
Fig. 1.19 Functional relationship between pH and the amount of acid $C_T$. The upper diagram is based on Eq. (1.133); lower diagram: same as upper diagram, only axes interchanged.

**Example N=1.** The monoprotic acid represents the simplest case, where the sum in Eq. (1.136) runs only over two terms, $j = 0$ and 1. With $k_0 = 1$ and $k_1 = K_1$ we get a cubic equation:

$$0 = x^3 + K_1 x^2 - (C_T K_1 + K_w) x - K_1 K_w$$

(1.137)

**Example N=2.** For a diprotic acid, we get from Eq. (1.136), and with $k_0 = 1$, $k_1 = K_1$ and $k_2 = K_1 K_2$, a quartic equation:

$$0 = x^4 + K_1 x^3 + (K_1 K_2 - C_T K_1 - K_w) x^2 - K_1 (2C_T K_2 + K_w) x - K_1 K_2 K_w$$

(1.138)

This equation can be found in textbooks, e.g. [SM96]. If you set $K_2 = 0$, you arrive at Eq. (1.137).

As it will be shown in § 2.2.5, in the case of *strong acids*, all polynomials simplify. Their degree of order reduces by one unit.
2 ACID-BASE SYSTEM

2.1 Introduction

2.1.1 Definitions

Chapter 1 was devoted to the mathematical description of the two-component system $H_NA + H_2O$ (polyprotic acid and water). Starting from the set of equations (1.28) to (1.33), we arrived at a simple analytical formula in Eq. (1.133) which predicts the amount of $C_T$ for a given pH and vice versa.

A new degree of freedom comes into play when a strong base or strong acid is added to this ‘undisturbed’ system: the 2-component system becomes a 3-component system. Here, ‘strong’ means complete dissociation in water:

(2.1) strong monoacidic base: $BOH = B^+ + OH^-$
(2.2) strong monoprotic acid: $HX = H^+ + X^-$

Here, the Arrhenius base $BOH$ stands for NaOH or KOH (i.e. $B^+ = Na^+$ or $K^+$) and $HX$ represents HCl, HI, or HBr (i.e. $X^- = Cl^-, I^-, or Br^-$).

The addition of a strong base or a strong acid (to the weak acid $H_NA$) is known as:

(2.3) alkalimetric titration: $H_NA + BOH \Rightarrow pH$ increases
(2.4) acidimetric titration: $H_NA + HX \Rightarrow pH$ decreases

The amounts of strong base and strong acid added are denoted by $C_B$ and $C_A$, respectively. It can be related to the total amount of $H_NA$ by the ratios:

(2.5) $n_B = \frac{C_B}{C_T}$ and $n_A = \frac{C_A}{C_T}$

Since the strong base and strong acid operate in opposing directions (both canceling each other out), we combine both equations into one:

(2.6) equivalent fraction: $n = \frac{C_B - C_A}{C_T}$

where either $C_B$ or $C_A$ is zero. In this way, the equivalent fraction of the titrant, $n$, is positive for the alkalimetric titration and negative for the acidimetric titration.\(^{19}\) Clearly, $n = 0$ represents the ‘undisturbed’ system.

**Example.** Fig. 2.1 provides the acid-base titration of the carbonate system with $C_T = 10 \text{ mM } H_2CO_3$. The pure $H_2CO_3$ system is characterized by pH = 4.17 (at $n = 0$). Larger pH values are obtained through the addition of NaOH ($n$ is positive); lower pH values...

\(^{19}\) In Sigg and Morgan [SM96], the equivalent fractions $n$ is abbreviated by $f$. 
through the addition of HCl (n is negative). The small circles at the three integer values $n = 0, 1, \text{ and } 2$ indicate equivalence points.

Fig. 2.1 Titration curve $n(pH)$ of the carbonate system (10 mM $\text{H}_2\text{CO}_3$)

The same titration curve as in Fig. 2.1 (valid for $C_T = 10 \text{ mM}$) is shown in Fig. 2.2 together with two additional curves for $C_T = 1 \text{ mM}$ and $100 \text{ mM}$. The two diagrams in Fig. 2.2 differ only by the choice of x-axis (where the x- and y-axis are interchanged).

Fig. 2.2 Titration curves of the carbonate system (for 1, 10, and 100 mM $\text{H}_2\text{CO}_3$). Upper diagram: $n = n(pH)$, lower diagram: $pH = pH(n)$. 
2.1.2 Special Case: Diprotic Acid

Let’s consider a diprotic acid $H_2A$ with the amount $C_T$ to which a monoacidic strong base $BOH$ (with $B^+ = Na^+$ or $K^+$) is added:

\[
H_2A + n BOH = B_nH_{2-n}A + n H_2O
\]

Here, $n$ acts as a stoichiometric coefficient that embodies the ratio of the added amount of a strong base, $C_B$, to the total amount of the diprotic acid: $n = C_B/C_T$ as introduced in Eqs. (2.5) and (2.6).

The entity $B_nH_{2-n}A$ in reaction formula (2.7) does not survive in water; it dissociates into several aqueous species – as indicated in Fig. 2.3.

![Fig. 2.3 Alkalimetric titration of a diprotic acid with a strong base](image)

The variation of $n$ (or $C_B$) in reaction formula (2.7) through the addition of a strong base is called *alkalimetric* titration. Because a strong base dissociates completely, we have:

\[
C_B \equiv [BOH]_T = [B^+]
\]

The special case of $n = 0, 1,$ and $2$ is particularly interesting. Inserting these three integer values into reaction formula (2.7) we obtain for $B_nH_{2-n}A$ a pure acid, an ampholyte, and a (conjugate) base:

\[
\begin{align*}
(2.9) & \quad n = 0: \quad \text{pure } H_2A \text{ solution (acid)} & & \Leftrightarrow & & H_2A \quad \text{EP} \\
(2.10) & \quad n = 1: \quad \text{pure } BHA \text{ solution (ampholyte)} & & \Leftrightarrow & & HA^- \quad \text{EP} \\
(2.11) & \quad n = 2: \quad \text{pure } B_2A \text{ solution (base)} & & \Leftrightarrow & & A^- \quad \text{EP}
\end{align*}
\]

In fact, $n = 0, 1,$ and $2$ define the three equivalence points (EP0, EP1, EP2) of a diprotic acid – introduced in § 1.4 and discussed in § 2.4.2. [Example: For $H_2CO_3$ and the strong base NaOH we obtain pure solutions of $H_2CO_3$, $NaHCO_3$ and $Na_2CO_3$.]

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Acid Base Systems

Short Lecture

**Charge Balance.** The principle of *electro-neutrality* requires that a solution must contain equal numbers of anions and cations:

\[
[H^+] + [B^+] = [HA^-] + 2[A^{2-}] + [OH^-]
\]

Replacing \([B^+]\) by \(C_B\), as stated in Eq. (2.8), we get

\[
C_B = [HA^-] + 2[A^{2-}] + [OH^-] - [H^+]
\]

**Base Equations.** The set of mathematical equations to describe the alkalimetric titration of a diprotic acid by a strong base is a generalization of Eqs. (1.23) to (1.27) introduced in § 1.2.1:

\[
K_w = \{H^+\} \{OH^-\} \quad \text{(self-ionization of H}_2\text{O)}
\]

\[
K_1 = \{H^+\} \{HA^-\} / \{H_2A\} \quad \text{(1st diss. step)}
\]

\[
K_2 = \{H^+\} \{A^{2-}\} / \{HA^-\} \quad \text{(2nd diss. step)}
\]

\[
C_T = [H_2A] + [HA^-] + [A^{2-}] \quad \text{(mass balance)}
\]

\[
C_B = [HA^-] + 2[A^{2-}] + [OH^-] - [H^+] \quad \text{(charge balance)}
\]

It differs from the original set of equations by the last equation only, which is the charge balance taken from Eq. (2.13). In fact, the last equation is the sole equation into which the ‘strong base’ creeps into the set of equations; the other four equations in this set are fully independent of \(C_B\). In other words, for \(C_B = 0\), the set reduces to the description of the *base-free* diprotic-acid system.

**Proton Balance.** In textbooks, Eq. (2.18) is sometimes introduced through the concept of ‘proton balance’ – a special topic explained in Appendix C. For the diprotic acid, for example, proton balance yields:

\[
0 = [H^+] + n[H_2A] + (n-1)[HA^-] + (n-2)[A^{2-}] - [OH^-]
\]

Using \(n = C_B/C_T\) and \(C_T = [H_2A] + [HA^-] + [A^{2-}]\), this formula converts to Eq. (2.18).
2.2 Basic Set of Equations

2.2.1 The Three-Component System

The acid-base system is made up of three components:

- pure water H₂O
- weak N-protic acid HₙA
- strong monoacidic base BOH

The acid-base system is characterized by \( N + 4 \) species (variables):

\[
\begin{align*}
    \text{H}^+ & , \text{OH}^- , \text{H}_n\text{A} , \text{H}_{n-1}\text{A}^- , \ldots \text{A}^{-N} , \text{B}^+ \\
\end{align*}
\]

Instead of \([B^+]\) we use the variable \( n = \frac{C_B}{C_T} \). The exact description of the acid-base titration relies on a set of \( N + 3 \) nonlinear equations:

\[
\begin{align*}
    (2.20) \quad K_w & = [\text{H}^+] [\text{OH}^-] & (\text{self-ionization} \ H_2O) \\
    (2.21) \quad K_1 & = [\text{H}^+] \left[ \frac{[\text{H}_{n-1}\text{A}^-]}{[\text{H}_n\text{A}]} \right] & (1^{\text{st}} \text{ diss. step}) \\
    (2.22) \quad K_2 & = [\text{H}^+] \left[ \frac{[\text{H}_{n-2}\text{A}^{-2}]}{[\text{H}_{n-1}\text{A}^-]} \right] & (2^{\text{nd}} \text{ diss. step}) \\
    \vdots & & \text{acid: } N+1 \text{ equations} \\
    (2.23) \quad K_N & = [\text{H}^+] \left[ \frac{[\text{A}^{-N}]}{[\text{HA}^{-N-1}]} \right] & (N^{th} \text{ diss. step}) \\
    (2.24) \quad C_T & = [\text{H}_n\text{A}] + [\text{H}_{n-1}\text{A}^-] + \ldots + [\text{A}^{-N}] & (\text{mass balance}) \\
    (2.25) \quad C_B & = [\text{H}_{n-1}\text{A}^-] + [\text{H}_{n-2}\text{A}^{-2}] + \ldots + N[A^{-N}] + [\text{OH}^-] - [\text{H}^+] & (\text{charge balance}) \\
\end{align*}
\]

This set of equations is an extension of the diprotic-acid case in Eqs. (2.14) to (2.18) from \( N = 2 \) to any arbitrary \( N \). This is also an extension of the ‘undisturbed \( H_nA \) system’ defined by the set of \( N + 3 \) equations (1.28) to (1.33). The latter is re-established when \( C_B \) is zero (in the last equation).

In fact, the only difference to the set of equations (1.28) to (1.33) is just the last line, i.e. the charge balance equation.

Since we have \( N + 4 \) variables, but only \( N + 3 \) equations, the description has one degree of freedom: We can vary \( n \) to change the pH (for any fixed value of \( C_T \)).

Two assumptions are necessary to derive closed-form expressions, i.e. a one-line formula, from the set of equations (2.20) to (2.25) in the next paragraph:

\textbf{Assumption 1:} activities should be replaced by concentrations: \{..\} \Rightarrow [..]

\textbf{Assumption 2:} the strong base BOH dissolves completely, without forming aqueous species \( B_nH_{2-n}A(aq) \)

\( ^{20} \) such like NaCO₃ or NaHCO₃(aq) – which really exist, but only in small concentrations
The first assumption is fulfilled either in dilute systems or by switching to conditional equilibrium constants $cK$, introduced in Eq. (1.9). If the two assumptions are valid, we speak of ‘ideal conditions’ (examples for ‘real conditions’ will be given in § 2.4.4).

### 2.2.2 Closed-Form Expressions

The procedure to solve the set of mathematical equations (2.20) to (2.25) is the same one we used in the previous paragraphs (cf. in § 1.7.1):

- replace activities by concentrations: $\{..\} \Rightarrow [..]$ in Eqs. (2.20) to (2.23)
- replace acid species $[j]$ by ionization fractions $a_j$ – in Eqs. (2.21) to (2.25)
- replace $\{H^+\}$ by $x$ and $[OH^-]$ by $K_w/x - x$, and use $w(x)$ defined in Eq. (1.131)
- use the compact notation $Y_1$ for sums over $a_j$

In this way, we obtain a more handy form of the set of $N+3$ equations:

\[
\begin{align*}
(2.26) \quad K_w &= x (x + w) \quad \text{(self-ionization)} \\
(2.27) \quad k_1 &= x (a_1/a_0) \quad \text{or} \quad a_1 = (k_1/x) a_0 \\
(2.28) \quad k_2 &= x (a_2/a_0) \quad \text{or} \quad a_2 = (k_2/x^2) a_0 \\
&\vdots \\
(2.29) \quad k_N &= x (a_N/a_0) \quad \text{or} \quad a_N = (k_N/x^N) a_0 \\
(2.30) \quad 1 &= a_0 + a_1 + a_2 + \ldots + a_N \\
(2.31) \quad n &= Y_1 + w/C_T \quad \text{(charge balance)}
\end{align*}
\]

This set of equations upgrades Eqs. (1.125) to (1.130) from an acid system to an acid-base system with $n$ as the new ingredient.

The essence of the whole set of equations is contained in the closed-form expression (taken from the last line):

\[
(2.32) \quad n = Y_1(x) + \frac{w(x)}{C_T}
\]

The information contained in all other equations – i.e. Eqs. (2.22) to (2.26) – is encapsulated in the definition of $Y_1$ and $w$:

\[
\begin{align*}
(2.33) \quad Y_1 &= \sum_{j=0}^{N} j \cdot a_j = a_1 + 2a_2 + \ldots + Na_N \\
(2.34) \quad w &= [OH^-] - [H^+] \approx \frac{K_w}{x} - x
\end{align*}
\]

Each of the three terms in Eq. (2.32) represents one of the three components (subsystems): $n$ – the strong base, $w/C_T$ – the water, and $Y_1$ – the acid (see also Fig. 2.4).

\[\text{---}
\]

\[\text{21 except for H}, \text{ where the definition in Eq. (0.5) is used}\]
**Summary.** Either the closed-form expression in Eq. (2.32) or the polynomial in Eq. (2.35) are self-sufficient ways to describe the acid-base titration completely. Both are different encodings of one and the same thing, namely the set of \(N+3\) equations (2.26) to (2.31).

![Equations of the acid-base titration](image)

**Fig. 2.4** Equations of the acid-base titration. The three components 'acid', 'H₂O', and 'strong base' are coupled via the charge-balance equation.

**2.2.3 Polynomials for \(x = 10^{\text{pH}}\)**

Eq. (2.32) can be solved for \(x\) (or pH). This is done in Appendix B.2.2, with the final result in Eq. (B.19), which is a polynomial of order \(N+2\) in \(x\) (i.e., \(N+2\) is the highest power of \(x\)):

\[
0 = \sum_{j=0}^{N-j} \left\{ x^2 + (n-j)C_T x - K_w \right\} k_j x^{N-j}
\]

(2.35)

For \(n=0\) it falls back to Eq. (1.136) on page 42. Theoretically, one can use this equation to calculate \(x\); practically, however, it’s a difficult task, even for a cubic equation. For higher-order polynomials, *numerical* root-finding methods should be applied.

**Example \(N=1\).** The monoprotic acid represents the simplest case, where the sum in Eq. (2.35) runs only over two terms, \(j = 0\) and 1. With \(k_0 = 1\) and \(k_1 = K_1\) we get a *cubic equation*:

\[
0 = x^3 + \{ K_1 + nC_T \} x^2 + \{ (n-1)C_T K_1 - K_w \} x - K_1 K_w
\]

(2.36)

which generalizes the cubic equation (1.137) for \(n \neq 0\). It predicts \(x\) (or pH) for any given pair of \(C_T\) and \(n\). Alternatively, replacing \(n\) by \(C_B = nC_T\) yields:

\[
0 = x^3 + \{ K_1 + C_B \} x^2 + \{ (C_B - C_T) K_1 - K_w \} x - K_1 K_w
\]

(2.37)
**Example N=2.** For diprotic acids, the polynomial in Eq. (2.35) becomes a *quartic equation*, i.e. a polynomial of 4th order in \(x = 10^{-pH}\):

\[
0 = x^4 + \{K_1 + nC_T\} x^3 + \{K_1K_2 + (n-1)C_TK_1 - K_w\} x^2 + K_1 \{(n-2)C_TK_2 - K_w\} x - K_1K_2K_w
\]

which generalizes the quartic equation (1.138) for \(n \neq 0\). It predicts \(x\) (or \(pH\)) for any given pair of \(C_T\) and \(n\). Alternatively, replacing \(n\) by \(C_B = nC_T\) yields:

\[
0 = x^4 + \{K_1 + C_B\} x^3 + \{K_1K_2 + (C_B - C_T) K_1 - K_w\} x^2 + K_1 \{(C_B - 2C_T) K_2 - K_w\} x - K_1K_2K_w
\]

If you set \(K_2=0\), you arrive at Eqs. (2.36) and (2.37). As it will be shown in § 2.2.5, in the case of strong acids, all polynomials simplify (their degree of order reduces by one unit).

### 2.2.4 Lego Set of Building Blocks

The analytical solution in Eq. (2.32) can be constructed Lego-like from building blocks of increasing complexity (acidity constants \(K_j\), ionization fractions \(a_j\), moments \(Y_L\)). The hierarchy is sketched in Fig. 2.5.

**Fig. 2.5** The analytical solution in Eq. (2.32) is constructed from acidity constants and ionization fractions

At the lowest level there are the \(N\) acidity constants \(K_1\) to \(K_N\) (as the irreducible essence of acid \(H_NA\)), which – after multiplication – form *cumulative* equilibrium constants \(k_1\) to \(k_N\). These constants, in combination with the variable \(x = [H^+]\), enter the ionization

\[
a_0 = \left(1 + \frac{k_1}{x} + \frac{k_2}{x^2} + \cdots + \frac{k_N}{x^N}\right)^{-1}
\]
fractions (which embody the law of mass action of each dissociation step). Then, the ionization fractions are summed up to form the moment \( Y_1 \), the central part of the final equation. The only other ingredient is the quantity \( w(x) = \frac{K_w}{x - x} \) expressing the self-ionization of water.

There is more to say about our ‘Lego set’. The usefulness of the other moments \( Y_L \) (i.e. for \( L \geq 2 \)) becomes obvious in Chapter 3, when they are used as building blocks of several relevant quantities:

- \( Y_0 \Rightarrow \) mass balance \((Y_0 = 1)\)
- \( Y_1 \Rightarrow \) enters buffer capacity (titration function) \( \text{in Eq. (2.32)} \)
- \( Y_2 \Rightarrow \) enters buffer intensity \( \beta \) \( \text{in Eq. (3.43)} \)
- \( Y_3 \Rightarrow \) enters 1st derivative of \( \beta \) \( \text{in Eq. (3.44)} \)

### 2.2.5 Strong Acids are Simpler

The mathematical description of *strong acids* is simpler than that of weak acids, since strong acids never occur in the *undissociated* state at \( \text{pH} \geq 0 \) (at least one \( \text{H}^+ \) is always released).\(^{22}\) Knowing that the amount of the undissociated species is zero, \( [0] = 0 \) or \( a_0 = 0 \), it’s not necessary to explicitly calculate the first dissociation step. In other words, we can remove Eq. (2.21) or Eq. (2.27) from our set of \( N+3 \) nonlinear equations and completely forego the first dissociation constant \( K_1 \) (keeping in mind that \( K_1 \) is a large number – as discussed in § 1.1.4). That is good news, because the first dissociation constants of strong acids are often not known precisely enough.

To simplify our analytical formulas, we use the fact that \( K_1 \) is very large. But instead of handling \( K_1 \rightarrow \infty \), it’s easier to use the inverted case:

\[
\text{(2.40) \quad strong acid:} \quad \frac{x}{K_1} \rightarrow 0 \quad \text{for all practice-relevant } x \quad (\text{i.e. } x < 10)
\]

Thus, we divide our analytical formulas by \( K_1 \) and then set all terms containing \( x/K_1 \) to zero (this is demonstrated, for example, in Appendix B.1.2 for the ionization fractions). In this way, \( K_1 \) disappears from all equations:

The cumulative acidity constants \( k_j \) in Eq. (1.92) are also redefined:

\[
\begin{align*}
(2.41) & \quad k_1 = K_1 & \Rightarrow & \quad k_1 = 1 \\
(2.42) & \quad k_2 = K_1 K_2 & \Rightarrow & \quad k_2 = K_2 \\
(2.43) & \quad k_3 = K_1 K_2 K_3 & \Rightarrow & \quad k_3 = K_2 K_3
\end{align*}
\]

and so on.

\(^{22}\) as shown in Fig. 1.1 on page 15
Ionization Fractions. The ionization fractions $a_j$, originally defined in Eq. (1.90), simplify as follows:

- **General Case**
  
  \[ a_0 = \left( 1 + \frac{K_1}{x} + \frac{K_2 K_3}{x^2} + \ldots \right)^{-1} \]
  
  \[ a_0 = 0 \]

- **Strong Acids**
  
  \[ a_1 = \left( \frac{x}{K_1} + 1 + \frac{K_2}{x} + \ldots \right)^{-1} \]
  
  \[ a_1 = \left( 1 + \frac{K_2}{x} + \frac{K_3}{x^2} + \ldots \right)^{-1} \]

\[ a_j = \left( \frac{k_j}{x^j} \right) a_0 \]

\[ a_j = \left( \frac{k_j}{x^{j-1}} \right) a_1 \] for $j > 1$

(For the derivation see Appendix B.1.2.)

**Polynomials.** For strong acids, the polynomial in Eq. (2.35) becomes one degree less in $x$ (Note: the summation now starts with $j = 1$):

\[ 0 = \sum_{j=1}^{N} \left\{ x^2 + (n - j) C_T x - K_w \right\} k_j x^{N-j} \]

**Example $N = 1$.** For a strong monoprotic acid, the sum in Eq. (2.47) runs only over one single term, $j = 1$. With $k_1 = 1$, we get a quadratic equation:

\[ 0 = x^2 + (n-1) C_T x - K_w \]

This simple equation does not contain any acidity constant.

**Example $N = 2$.** For a strong diprotic acid, the polynomial in Eq. (2.47) becomes a cubic equation:

\[ 0 = x^3 + \{ (n-1) C_T + K_2 \} x^2 + \{ (n-2) C_T K_2 - K_w \} x - K_2 K_w \]

This equation can also be derived from Eq. (2.38) by applying the condition $x/K_1 = 0$ from Eq. (2.40).

### 2.2.6 Charge-Balance Equation (in Extended Form)

The central formula we derived for the acid-base system is Eq. (2.32). As a one-liner, it summarizes all the information contained in the $N+3$ equations (2.26) to (2.31), and it interconnects three components: $H_2O$, $HN_A$, and the strong base (as sketched in Fig. 2.4). This one-liner is just the charge-balance equation.
Let’s inspect and derive the charge-balance equation from another viewpoint. For this purpose we introduce the following quantities of the $N$-protic acid:

\begin{align*}
\text{(2.50)} & \quad \text{total charge of acid:} \quad Z_T = \sum_{j=0}^{N} z_j[j] \\
\text{(2.51)} & \quad \text{average charge of acid:} \quad z_a = \frac{Z_T}{C_T} = \sum_{j=0}^{N} z_j a_j
\end{align*}

where $z_j$ symbolizes the charge of the individual acid species $j$.

\begin{align*}
\text{(2.52)} & \quad z_j = Z - j \quad \text{with} \quad \begin{cases} 
Z = 0 & \text{for common acids} \\
Z \geq 1 & \text{for zwitterionic acids (amino acids)}
\end{cases}
\end{align*}

You may wonder why the parameter $Z$ was introduced here. Usually this parameter is equal to zero and can be skipped throughout. The only exception from this seemingly obvious rule are the so-called zwitterionic acids (e.g. amino acids discussed in § 4.1).

Inserting Eq. (2.52) into Eq. (2.51) yields for the average charge:

\begin{align*}
\text{(2.53)} & \quad z_a = \sum_{j=0}^{N} (Z - j) a_j = Z \sum_{j=0}^{N} a_j - \sum_{j=0}^{N} j a_j = Z - Y_1
\end{align*}

On the right-hand-side, the mass-conservation formula in Eq. (1.95) and the definition of $Y_1$ were applied.

**Charge Balance.** The net charge of the solution should be zero. Thus, we have to add all ions of the 3-component system (strong base, $H_2O$, $H_NA$) and set it to zero:

\begin{align*}
\text{(2.54)} & \quad 0 = [B^+] + [H^+] - [OH^-] + \text{total charge of acid}
\end{align*}

As we already know, $[B^+]$ is equal to $C_B = nC_T$, and $[H^+] - [OH^-]$ can be expressed by $w$ according to Eq. (2.34). Then, after division of Eq. (2.54) by $C_T$ we get:

\begin{align*}
\text{(2.55)} & \quad 0 = n - \frac{w}{C_T} + z_a = n - \frac{w}{C_T} + (Z - Y_1)
\end{align*}

This is a generalization of our central formula in Eq. (2.32), because it now applies to both common acids ($Z = 0$) and zwitterionic acids ($Z \geq 1$):

\begin{align*}
\text{(2.56)} & \quad n = \left( Y_1(x) - Z \right) + \frac{w(x)}{C_T} \quad \text{with } Z \geq 1 \text{ for zwitterions}
\end{align*}

The case $Z \geq 1$ will be considered later in § 4.1.
2.2.7 Titration Curves

The closed-form expression in Eq. (2.32) – or its generalized form in Eq. (2.56) – contains the whole information about the acid-base system. Plotting the equivalent fraction as a function of pH, \( n = n(pH) \), just yields titration curves:

\[
(2.57) \quad n = Y_1(pH) + \frac{w(pH)}{C_T} \quad \frac{C_T \rightarrow \infty}{\text{CT} \rightarrow \infty} \quad n = Y_1(pH)
\]

The right-hand-side of the first equation consists of two parts: \( Y_1(x) \) as the contribution from the subsystem ‘pure acid’ and \( w(x) \) as the contribution from ‘pure water’. As indicated by the arrow, the latter term vanishes for \( C_T \) values if they are high enough (i.e. for high-concentrated acids). What remains is the reduced formula \( n = Y_1 \).

Example. The upper diagram in Fig. 2.6 shows the titration curve of carbonic acid in the high-\( C_T \) limit, where \( n(pH) = Y_1 = a_1 + 2a_2 \). The corresponding ionization fractions \( a_j \) – as the building blocks of \( Y_1 \) – are displayed in the bottom diagram.
The normal case, \( n = Y_1 + w/C_T \), is shown in Fig. 2.7. It compares titration curves of carbonic acid for different \( C_T \) values (including the case \( C_T = \infty \) from the upper diagram in dark blue).

**Fig. 2.7** Titration curves of carbonic acid for different \( C_T \) values. Upper diagram: the 'pure-acid' case: \( n(pH) = Y_1(pH) = a_1 + a_2 \); lower diagram: the 'pure-acid' case \( (C_T = \infty) \) together with four finite \( C_T \) values.

**HA, H_2A, H_3A.** Titration curves of four common acids for different values of \( C_T \) (including the pure-acid case \( n(pH) = Y_1 \) as a dark blue curve) are displayed in Fig. 2.8.

**Fig. 2.8** Titration curves of four common acids for different values of \( C_T \) (including the 'pure-acid limit' \( n(pH) = Y_1 \))
2.3 Equivalence Points: General Approach

2.3.1 Definitions

In § 1.4, equivalence points were introduced by equating two adjacent acid species \([j]\):\(^{23}\)

\[
(2.58) \quad \text{EP}_j: \quad [j-1] = [j+1] \quad \Leftrightarrow \quad \text{EP}_n: \quad [n-1] = [n+1] \quad \text{for integer } n = j
\]

\[
(2.59) \quad \text{semi-EP}_j: \quad [j-1] = [j] \quad \Leftrightarrow \quad \text{EP}_n: \quad [n-\frac{1}{2}] = [n+\frac{1}{2}] \quad \text{for half-integer } n = j-\frac{1}{2}
\]

It leads to simple formulas for the corresponding pH values (cf. § 1.4.2), where the so-called internal EPs are directly related to the acidity constants \(K_j\):

\[
(2.60) \quad \text{EP}_n \Leftrightarrow \text{pH}_n = \begin{cases} \frac{1}{2} (pK_n + pK_{n+1}) & \text{for } n = 1, 2, \ldots, N-1 \\ pK_{n+\frac{1}{2}} & \text{for } n = \frac{1}{2}, \frac{3}{2}, \ldots, N-\frac{1}{2} \end{cases} \quad (\text{EP})
\]

\[
(2.60) \quad \text{semi-EP}_n \Leftrightarrow \text{pH}_n = \begin{cases} \frac{1}{2} (pK_n + pK_{n+1}) & \text{for } n = 1, 2, \ldots, N-1 \\ pK_{n+\frac{1}{2}} & \text{for } n = \frac{1}{2}, \frac{3}{2}, \ldots, N-\frac{1}{2} \end{cases} \quad (\text{semi EP})
\]

**General Approach.** The general approach does not rely on the equivalence of two acid species, but on the equivalence of the chemical compounds:

\[
(2.61) \quad \text{EP: } [N\text{-protic acid}]_T = [\text{strong base}]_T
\]

which is the same as

\[
(2.62) \quad \text{EP: } C_T = C_B \quad \text{or} \quad n = \frac{C_B}{C_T} = 1
\]

This, in fact, defines the equivalence point \(\text{EP}_1\). The extension to all other EPs and semi-EPs (for integer and half-integer \(n\)) is easy:

\[
(2.63) \quad \text{EP}_n: \quad n = \frac{C_B}{C_T} \quad \text{for } n = 0, \frac{1}{2}, 1, \frac{3}{2}, \ldots, N
\]

The mathematical relationship between the \(\text{EP}_n\) and the corresponding pH\(_n\) values is provided by the equivalence-fraction formula in Eq. (2.32):

\[
(2.64) \quad n = Y_i(pH) + \frac{w(pH)}{C_T} \quad \text{for } n = 0, \frac{1}{2}, 1, \frac{3}{2}, \ldots, N
\]

Plotting it as a function of pH yields the blue titration curve in Fig. 2.9 (for \(\text{H}_2\text{CO}_3\) with \(C_T = 100 \text{ mM}\)). The small circles at integer and half-integer values of \(n\) mark the \(\text{EP}_n\)-pH\(_n\) assignment. Since \(\text{H}_2\text{CO}_3\) is a 2-protic acid there are \(2 \times 2 + 1 = 5\) equivalence points in total.

\(^{23}\) Here, the notation is extended to implement the external EPs by setting \([-1] = [\text{H}^+]\) and \([N+1] = [\text{OH}^-]\).
Fig. 2.9 Titration curve of diprotic acid $\text{H}_2\text{CO}_3$ based on Eq. (2.64) with EPs and semi-EPs located at integer and half-integer values of $n$

$C_T \rightarrow \infty$. When $C_T$ increases steadily, the second term in Eq. (2.64) approaches zero, and we get the simple relationship:

\begin{equation}
(2.65) \quad \text{EP}_n \; \text{for} \; C_T \rightarrow \infty \quad \Leftrightarrow \quad 0 = n - Y_1(\text{pH}_n) \quad \text{('pure acid' case)}
\end{equation}

In fact, according to Eq. (1.122), it offers the intimate relationship between the pH of an internal equivalence point and the acidity constants, as stated in Eq. (2.60). In other words, the pure-acid case from §1.4 is immanent in Eq. (2.64) and comes to light when the coupling term w/C$_T$ disappears.

### 2.3.2 EP$_n$ as Curves in pH-C$_T$ Diagrams

Eq. (2.64) can be rearranged into the form

\begin{equation}
(2.66) \quad C_T = \frac{w(\text{pH})}{n - Y_1(\text{pH})}
\end{equation}

Now, it’s easy to plot all EP$_n$ as distinct curves into a pH-C$_T$ diagram (one curve for one integer or half-inter value of $n$). This is done in Fig. 2.10 for four common acids. The dashed curves are approximations corresponding to the ‘pure-acid’ case as displayed in Fig. 1.8 on page 29.

Let’s explain the general behavior of the EP$_n$ curves in pH-C$_T$ diagrams using phosphoric acid (as a triprotic acid). This example is illustrated in Fig. 2.11 and consists of two diagrams. In the upper diagram, we have the two uncoupled components or subsystems located at opposite ends of the C$_T$ scale:

- subsystem ‘pure acid’: $C_T \rightarrow \infty$
- subsystem ‘pure H$_2$O’: $C_T \rightarrow 0$

---

24 Eq. (2.65) is more general than Eq. (2.60). Both equations are equivalent for $N \leq 2$, but deviate for higher $N$ (albeit the deviation is very, very small).
The bottom diagram shows the situation in which both subsystems are linked to each other. Starting at pH 7, the curves fan out when $C_T$ increases until they fit the ‘pure-acid’ values at the top of the chart. The whole behavior is determined by Eq. (2.66).

In mathematical jargon, the corresponding pH values of the ‘pure acid’ system (listed in Tab. 1.4) are the poles (or singularities) of Eq. (2.66) or Eq. (2.67). On the other hand, the single EP of ‘pure H$_2$O’ is at the position where the nominator in Eq. (2.66) or Eq. (2.67) becomes zero (which is exactly at pH = 7):

\[ \text{EP of ‘pure H}_2\text{O’} \iff 0 = w(x) \iff C_T = 0 \]
2.3.3 Summary: Systematics & Classification

First. Equivalence points are special equilibrium states in which the equivalent fraction \( n = \frac{C_B}{C_T} \) becomes an integer or half-integer value. An \( N \)-protic acid has in total \( 2N + 1 \) equivalence points:

\[
(2.69) \quad \text{EP}_n \quad \frac{C_B}{C_T} = n \quad \text{for} \quad n = 0, 1, \ldots, N
\]
\[
(2.70) \quad \text{semi-EP}_n \quad \frac{C_B}{C_T} = n \quad \text{for} \quad n = \frac{1}{2}, \frac{3}{2}, \ldots, N - \frac{1}{2}
\]

The ‘trivial’ case \( \text{EP}_0 \) refers to the base-free system with \( \text{pH}_0 \) as the pH value of the acid with the amount \( C_T \) dissolved in water. [It corresponds to the isoionic point in § 4.1.6.]

Second. Each \( \text{EP}_n \) is characterized by a specific pH value, which we call \( \text{pH}_n \). The mathematical relationship \( \text{EP}_n \Leftrightarrow \text{pH}_n \) is given by \( n = Y_1(\text{pH}) + w(\text{pH})/C_T \), i.e. Eq. (2.64), where \( Y_1 \) describes the acid and \( w \) the water.

Third. The equivalent fraction \( n = Y_1(\text{pH}) + w(\text{pH})/C_T \) (titration curve) represents the buffer capacity, as it will be shown in Chapter 3. Its first pH-derivative is the buffer intensity \( \beta = dn/d\text{pH} \). The EPs are the extreme points of \( \beta \):

\[
\text{EP}_n \quad \text{(integer n)} \quad \Leftrightarrow \quad \text{minimum buffer intensity } \beta
\]
\[
\text{semi-EP}_n \quad \text{(half-integer n)} \quad \Leftrightarrow \quad \text{maximum buffer intensity } \beta
\]
Fourth. In the limiting case of highly concentrated acids \((C_T \to \infty)\), the general relationship simplifies to:

\[
Y_1(pH) - n = 0
\]

This equation asserts the direct link between \(pH_n\) and the acidity constants:

\[
pH_n = \frac{1}{2} (pK_n + pK_{n+1}) \quad \text{for integer } n \quad \text{(EP}_n\text{)}
\]

\[
pH_n = pK_{n+1/2} \quad \text{for half-integer } n \quad \text{(semi-EP}_n\text{)}
\]

These simple and nice relationships are applicable for \(C_T > 10^{-3} \text{M}\), but fail for very dilute acids when the influence of water becomes dominant. Then, the general formula in Eq. (2.64) must be used instead of Eq. (2.71).

Fifth. An alternative definition of EPs is based on the equality of species concentrations, as done in Eqs. (2.58) and (2.59), and originally established in §1.4 for the pure-acid case. (Example: In carbonate systems EP\(_1\) is often introduced as the equilibrium state for which \([\text{CO}_2] = [\text{CO}_3^{-2}]\) applies.)

Tab. 2.1 Comparison of two approaches to equivalence points

<table>
<thead>
<tr>
<th>“Pure Acid” Case</th>
<th>General Approach</th>
</tr>
</thead>
<tbody>
<tr>
<td>based on acid species</td>
<td>based on total amount of compounds</td>
</tr>
<tr>
<td>(\text{EP}_n: \quad [n-1] = [n+1])</td>
<td>(\text{EP}_n: \quad [H_nA]_T = n [\text{strong base}]_T)</td>
</tr>
<tr>
<td>semi-EP(_n): ([n-\frac{1}{2}] = [n+\frac{1}{2}])</td>
<td>(C_T)</td>
</tr>
</tbody>
</table>

\[
pH_n = \frac{1}{2} (pK_n + pK_{n+1}) \iff \text{EP}_n
\]

\[
pH_n = pK_{n+1/2} \iff \text{semi-EP}_n
\]

\[
C_T \to \infty
\]

\[
n - Y_i = 0
\]

Sixth. The concept can be extended to zwitterionic acids in §4.1.5, where Eq. (2.64) will become Eq. (4.7). This provides a new perspective on Tab. 2.1: The simplified approach in the left column is related to isoelectric points (i.e. points that only exist for zwitterions, but not for common acids), while the right-column approach refers to isoionic points – see §4.1.6.

---

It’s strictly valid for diprotic acids only, but remains a very good approximation for polyprotic acids with \(N \geq 3\).
2.4 Carbonic Acid System (N=2)

2.4.1 Plots and Relationships between pH, C_T, and n

The actual equilibrium state of a diprotic acid H_2A (i.e. the concentrations of the 3 aqueous species [j]: H_2A, HA^−, and A^{2−}) is completely controlled by two parameters chosen from the triple (C_T, n, pH) or (C_T, C_B, pH), where C_B = nC_T, which is also known as alkalinity: Alk = C_B (see Eq. (3.28)). Once we know two of them, the third is automatically determined:

\[
\text{pH (C}_T, n) = -\lg x_n \quad \text{with } x_n \text{ as positive root of Eq. (2.38)}; \quad [j] = C_T a_j
\]

\[
\text{pH (C}_T, \text{ Alk}) = -\lg x_n \quad \text{with } x_n \text{ as positive root of Eq. (2.39)}; \quad [j] = C_T a_j
\]

\[
n (C_T, \text{ pH}) = a_1 + 2a_2 + w/C_T \quad [j] = C_T a_j
\]

\[
\text{Alk (C}_T, \text{ pH}) = C_T (a_1 + 2a_2) + w \quad [j] = C_T a_j
\]

\[
C_T (n, \text{ pH}) = w/(n - a_1 - 2a_2) \quad [j] = [w/(n - a_1 - 2a_2)] a_j
\]

\[
C_T (\text{ Alk, pH}) = (\text{Alk} - w)/(a_1 + 2a_2) \quad [j] = [(\text{Alk} - w)/(a_1 + 2a_2)] a_j
\]

Fig. 2.12 Relationships between pH, C_T, and n for the carbonic acid system (at 25 °C)
It’s quite useful to exhibit the non-linearity of all these equations graphically. The diagrams in Fig. 2.12 display all possible combinations of one dependent and two independent variables (taken from the triplet $C_T$, $n$, and pH) for the carbonate system.

All diagrams are redrawn in Fig. 2.13 for the case when the normalized amount of the added strong base, $n = C_B/C_T$, is replaced by the total alkalinity ($\text{Alk} = nC_T$).

**Fig. 2.13** Relationships between pH, $C_T$, and Alk for the carbonic acid system (at 25 °C)
### 2.4.2 Three Equivalence Points

The carbonate system is the vehicle that controls the pH in most natural waters. Due to the existence of three major carbonate species (CO$_2$, HCO$_3^-$, CO$_3^{2-}$), textbooks usually focus on three equivalence points:

- **EP$_0$** (also known as EP of CO$_2$): \[ [H^+] = [HCO_3^-] \]
- **EP$_1$** (also known as EP of HCO$_3^-$): \[ [H_2CO_3] = [CO_3^{2-}] \]
- **EP$_2$** (also known as EP of CO$_3^{2-}$): \[ [HCO_3^-] = [OH^-] \]

The identification of EPs as points of equal *species* concentrations, as done here on the right-hand side, is an approximation, though a very good one. In BJERRUM plots, these are points of intersections of two concentration curves. Fig. 2.14 maps those intersections from the two lower diagrams (one for $C_T = 10^{-3}$ M and one for $10^{-4}$ M) upwards into the pH-$C_T$ diagram where they constitute the small circles on the EP curves.

**Fig. 2.14** Equivalence points of the carbonate system. Map of intersection points from BJERRUM plots (bottom and middle diagrams) upwards into the pH-$C_T$ diagram (top).
Here, we observe a different behavior for the *external* equivalence points (EP₀ and EP₂) and for the *internal* equivalence point EP₁.

**EP₀ and EP₂.** The two external EPs are $C_T$-dependent:

<table>
<thead>
<tr>
<th></th>
<th>$C_T = 10^{-4} M$</th>
<th>$C_T = 10^{-3} M$</th>
</tr>
</thead>
<tbody>
<tr>
<td>EP₀ at pH</td>
<td>5.18</td>
<td>4.68</td>
</tr>
<tr>
<td>EP₂ at pH</td>
<td>9.86</td>
<td>10.56</td>
</tr>
</tbody>
</table>

**EP₁.** The EP₁, in contrast, does not depend on $C_T$. The intersection points of the CO₂ and CO₃²⁻ curves in the two lower diagrams are both at the same fixed pH value of $\frac{1}{2}(pK_1 + pK_2) = 8.34$, which belongs to the high-$C_T$ limit of the red curve in the upper diagram. Thus, the simple relationship $[CO_2] = [CO_3^{2-}]$ does not work for a small $C_T$; that is, it fails for very dilute acids.

### 2.4.3 Example: Seawater

The closed-form expressions in Eqs. (2.32) and (2.64) are based on the assumption that activities could be replaced by concentrations, $\{j\} \to [j]$. This is valid either for dilute systems with zero ionic strength ($I = 0$), or for non-dilute systems when thermodynamic equilibrium constants are replaced by conditional constants, $K \to ^cK$.

Seawater has $I \approx 0.7 M$, which is almost at the upper limit of the validity range of common activity models (as discussed in Appendix A.2). Hence, in oceanography, chemists prefer conditional equilibrium constants $^cK$. There are several compilations for $^cK$ in literature; one example is given in Tab. 2.2.

<table>
<thead>
<tr>
<th>Tab. 2.2 Thermodynamic and conditional equilibrium constants for the carbonic acid system in pure water and seawater (at 25°C, 1 atm)</th>
<th>thermodynamic $K$ (pure water, $I = 0$)</th>
<th>conditional $^cK$ [Mi95] (seawater, $I = 0.7 M$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$pK_1$</td>
<td>6.35</td>
<td>6.00</td>
</tr>
<tr>
<td>$pK_2$</td>
<td>10.33</td>
<td>9.10</td>
</tr>
<tr>
<td>$pK_w$</td>
<td>14.0</td>
<td>13.9</td>
</tr>
</tbody>
</table>

Fig. 2.15 compares the results calculated by Eq. (2.64) for both the standard case (solid lines based on thermodynamic equilibrium constants $K$) and seawater (dashed lines based on conditional constants $^cK$). The solid curves in Fig. 2.15 are identical to the solid curves displayed in Fig. 2.14.
2.4.4 From Ideal to Real Conditions

All calculations so far were performed for the *ideal* case (i.e. no activity corrections, no complexation – cf. Assumptions 1 and 2 at the end of §2.2.1). Modern hydrochemistry programs do not adhere to those restrictions; they always perform activity corrections (cf. Appendix A). In this respect, they are able to predict the relationship between pH and a given $C_T$ more accurately.

Given is a carbonic acid system titrated with NaOH. Fig. 2.16 compares the results of the closed-form equation (2.64) (solid lines) with the numerical-model predictions (dots).²⁶

---

²⁶Such calculations can be done by free hydrochemistry software (PHREEQC, AQION, etc.).
As expected, deviations between the ideal and real case occur only at very high $C_T$ values. There are two reasons:

- With increasing $C_T$ the ionic strength $I$ increases; as a result, the activity corrections are amplified.\(^{27}\)
- Numerical models consider the formation of aquatic complexes such as $\text{NaHCO}_3^-$ and $\text{Na}_2\text{CO}_3(aq)$ (which are ignored in the present approach). These aquatic complexes become particularly relevant at high concentrations for $n = 1$ and 2.

[Note: Similar results are obtained when Na is replaced by K.]

### 2.4.5 Acid-Base Titration with $\text{H}_2\text{CO}_3$ as Titrant

During titration, the titrant is added to the analyte in order to achieve the equivalence point and determine the concentration of the analyte. Two cases (that are opposite to each other) will be considered:

**var A** 100 mM $\text{H}_2\text{CO}_3$ solution will be titrated by strong base/acid (NaOH and HCl)

**var B** 100 mM NaOH solution will be titrated by $\text{H}_2\text{CO}_3$

In **var A** $C_T$ is kept fixed and $C_B$ is varied, while in **var B** $C_B$ is kept fixed and $C_T$ is varied.

The aim is to calculate the species distribution $[j]$ of the carbonic acid as a function of pH. In both cases we start with the ionization fractions $a_j$ in Fig. 2.17 (based on Eq. (1.90)). They are exactly the same for **var A** and **var B**.

![Fig. 2.17 Ionization fractions $a_j$ of $\text{H}_2\text{CO}_3$](image)

From $a_j$ we get the species concentrations $[j]$ by multiplication with $C_T$:

\[
[2.78] \quad [j] = C_T \ a_j
\]

\(^{27}\) At very high values of $C_T$ between 1 and 10 M $\text{Na}_2\text{CO}_3$ (i.e. the most upper part of the green curve) we are outside the applicability range of common activation models.
The variants differ from each other only by the $C_T$ value:

(2.79)  \textbf{var A} \quad C_T = \text{const} \quad \text{with } C_T = 100 \text{ mM}

(2.80)  \textbf{var B} \quad C_T = (C_B - w)/Y_1 \quad \text{with } C_B = 100 \text{ mM}

The latter formula comes from the general relationship in Eq. (2.32), where $n = C_B/C_T$.

The results are displayed in Fig. 2.18 as Bjerrum plots: \textbf{var A} (left diagrams) and \textbf{var B} (right diagrams). The orange curve represents the total concentration $C_T$ as the sum of all three carbonic-acid species. The upper and lower diagrams differ by the concentration scale: y-axis is linear (upper) and logarithmic (lower).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Fig_2.18.png}
\caption{Species distribution of H$_2$CO$_3$ as a function of pH for \textbf{var A} (left) and \textbf{var B} (right). Upper diagrams: concentrations in linear scale; bottom diagrams in logarithmic scale.}
\end{figure}

Although both cases rely on exactly the same ionization fractions, the pH dependence of the species concentrations in \textbf{var A} and \textbf{var B} differs fundamentally. While the species in \textbf{var A} (upper left diagram) show the same behavior as the $a_i$ in Fig. 2.17, \textbf{var B} is completely out of line. [Note: In \textbf{var B}, pH values below 5 are not available in practice.]
2.4.6 Open vs. Closed CO₂ System

All considerations so far have been based on the assumption of a “closed CO₂ system”. Conversely, in an open system, the aqueous solution is in chemical equilibrium with the CO₂ of the atmosphere. Let’s compare both cases:

- **var A** titration of 100 mM H₂CO₃ solution “closed CO₂ system” (same as in § 2.4.5)
- **var C** titration of 100 mM H₂CO₃ solution “open CO₂ system”

Again, as in § 2.4.5, we start with the ionization fractions aᵢ based on Eq. (1.90); they are displayed in Fig. 2.17 (and are exactly the same for var A and var C). Again, as in § 2.4.5, the two variants differ only in the value or function of Cₜ. The latter should be specified for the open system.

The “open system” is described by

\[(\text{2.81})\quad \text{HENRY’s law: } \text{CO}_2(\text{aq}) \text{ is proportional to } \text{CO}_2(\text{g})\]

or, more particularly:

\[(\text{2.82})\quad [\text{H}_2\text{CO}_3(\text{aq})] = K_H \cdot P \quad \text{with } K_H = 10^{-1.47} \text{ M/atm} \quad (\text{at } 25 ^\circ \text{C})\]

and where P is the partial CO₂ pressure in atm. In our notation, Eq. (2.82) becomes:

\[(\text{2.83})\quad [0] = K_H \cdot P\]

From \([0] = C_T a_0\) – as a special case of Eq. (2.78) – we finally get:

\[(\text{2.84})\quad \text{open CO}_2\text{ system: } C_T = \frac{K_H \cdot P}{a_0}\]

The variants differ from each other only by the Cₜ value:

\[(\text{2.85})\quad \text{var A } \quad C_T = \text{const} \quad \text{with } C_T = 100 \text{ mM}\]
\[(\text{2.86})\quad \text{var C } \quad C_T = K_H P/a_0 \quad \text{at } P = 10^{-3.408} \text{ atm}^{28}\]

The results are displayed in Fig. 2.19: var A (left diagrams) and var C (right diagrams). The orange curve represents the total concentration Cₜ as the sum of all three carbonic-acid species. The upper and lower diagrams differ by the concentration scale: y-axis is linear (upper) and logarithmic (lower).

Although both cases rely on exactly the same ionization fractions, the pH dependence of the species concentrations in var A and var C differs fundamentally. While the species in var A (upper left diagram) show the same behavior as the aᵢ in Fig. 2.17, var C is completely out of line: The more alkaline the solution becomes the more CO₂ is sucked

---

\[^{28}\text{valid under normal atmospheric conditions (P = 0.00039 atm, 25 °C)}\]
from the atmosphere (which increases the $C_T$ exponentially). [Note: In var C, pH values above 11 are not available in practice.]

**Fig. 2.19** Species distribution of $\text{H}_2\text{CO}_3$ as a function of pH for var A (left) and var C (right). Upper diagrams: concentrations in linear scale; bottom diagrams in logarithmic scale.

**Resume.** The three variants (var A, var B, var C) in the last two paragraphs reveal the fundamental role of the ionization fractions $a_j$ (shown in Fig. 2.17), which remain the same irrespective of the chosen model (i.e. the functional dependence of $C_T$). This is because the ionization fractions rely only on the log K values (acidity constants) and nothing else.
2.5 Multicomponent Systems

2.5.1 Mixtures of Several Acids

It’s not difficult to extend the results of the acid-base system (with one single acid) to mixtures of several acids:

\[
\text{acid a + acid b + acid c + ... with amount } C_a, C_b, C_c, ...
\]

The total sum of all amounts will again be abbreviated by \( C_T \):

\[
(2.87) \quad C_T = C_a + C_b + C_c + ...
\]

The equivalent fraction, i.e. the titration curve, of the multi-acid system (including, as before, one strong base of amount \( C_B = nC_T \)) is described by the same formula as in Eq. (2.32):

\[
(2.88) \quad n = \tilde{Y}_1(x) + \frac{w(x)}{C_T}
\]

but now with the \textit{generalized} moment \( \tilde{Y}_1 \) as a superposition of moments of the individual acids \( \alpha \):

\[
(2.89) \quad \tilde{Y}_1 = n_a Y_1^{(a)} + n_b Y_1^{(b)} + n_c Y_1^{(c)} + ... \quad \text{with coefficients } \quad n_{\alpha} = \frac{C_{\alpha}}{C_T}
\]

The individual moments are constructed from the ionization fractions in the usual way (i.e. according to Eq. (1.110)):

\[
(2.90) \quad Y_L^{(\alpha)} = \sum_{j=1}^{N_{\alpha}} j^L a_j^{(\alpha)}
\]

where the ionization fractions \( a_j^{(\alpha)} \) are determined by the (cumulative) acidity constants of the individual acids \( k_j^{(\alpha)} \), according to Eq. (1.90).

\textbf{Example.} Let’s consider the superposition of two acids, phosphoric acid and carbonic acid with equal amounts: \( C_{\text{phos}} = C_{\text{carb}} = C_T/2 \). The first moment \( \tilde{Y}_1 \) of the two-acid-system is displayed as a blue curve in the upper diagram of Fig. 2.20. It’s simply the sum of \( Y_1^{(\text{phos})} \) and \( Y_1^{(\text{carb})} \). The degree of the two-acid-system is \( N = 3+2 = 5 \); thus, \( Y_1 \) approaches 5 when \( pH \to 14 \).

The bottom diagram of Fig. 2.20 displays the ionization fractions of the two acids. The blue curve in the upper diagram of Fig. 2.20 represents the ‘titration curve’ for the special case of high-concentrated acids (pure-acid limit).
2.5.2 $H_NA$ as a Superposition of $N$ Monoprotic Acids

From a mathematical point of view, the titration curve of an $N$-protic acid (defined by $K_1$, $K_2$ to $K_N$) can be generated by a superposition of (virtual) $N$ monoprotic acids having the acidity constants $K_1$, $K_2$ to $K_N$. This statement is not completely exact, but a very good approximation. The underlying mathematics will be demonstrated for a diprotic acid, $H_2A$.

Since the general formula for the titration curve – according to Eq. (2.32) – is $n = Y_1 + w/C_T$, it’s sufficient to focus on $Y_1$:

(2.91) $Y_1 = a_1 + 2a_2 = (a_1 + a_2) + a_2$

From Eq. (1.90) we then get:

(2.92) $a_1 + a_2 = \left(\frac{K_1}{x} + \frac{K_2}{x^2}\right)\left(1 + \frac{K_1}{x} + \frac{K_2}{x^2}\right)^{-1} = \frac{K_1^{(a)}}{x} \left(1 + \frac{K_1^{(a)}}{x}\right)^{-1} \equiv a_1^{(a)}$

(2.93) $a_2 = \frac{K_2}{x} \left(1 + \frac{K_2}{x}\right)^{-1} = \frac{K_2^{(b)}}{x} \left(1 + \frac{K_2^{(b)}}{x}\right)^{-1} \equiv a_1^{(b)}$
Here, we introduced new acidity constants $K_1^{(a)}$ and $K_1^{(b)}$ that are (almost) identical with the two acidity constants of $H_2A$:

\[
K_1^{(a)} = K_1 \left[ 1 + \frac{K_2}{x} \right] \quad \frac{K_2/x \ll 1}{pH \to 0} \quad K_1^{(a)} \approx K_1
\]

\[
K_1^{(b)} = K_1 \left( 1 + \frac{x}{K_1} \right) \quad \frac{x/K_1 \ll 1}{pH \to 14} \quad K_1^{(b)} \approx K_2
\]

In fact, $a_1^{(a)}$ and $a_1^{(b)}$ are just the ionization fractions of the two monoprotic acids that define their first moments $Y_1^{(a)} = a_1^{(a)}$ and $Y_1^{(b)} = a_1^{(b)}$. This leads to the final conclusion:

\[
Y_1 = a_1 + 2a_2 \quad \Leftrightarrow \quad Y_1 = Y_1^{(a)} + Y_1^{(b)}
\]

diprotic acid superposition of 2 monoprotic acids

This superposition principle can be extended to any $N$-protic acid:

\[
Y_1 = a_1 + 2a_2 + 3a_3 + \ldots \quad \Leftrightarrow \quad Y_1 = Y_1^{(a)} + Y_1^{(b)} + Y_1^{(c)} + \ldots
\]

$N$-protic acid superposition of $N$ monoprotic acids

---

Fig. 2.21 $Y_1$ of carbonic and phosphoric acids generated as superposition of (virtual) monoprotic acids
Examples. Two examples are presented in Fig. 2.21 where Y₁ of carbonic acid (H₂A) and phosphoric acid (H₃A) are generated from two and three (virtual) monoprotic acids:

- Carbonic acid: \[ Y₁ = a_i^{(a)} + a_i^{(b)} \]
- Phosphoric acid: \[ Y₁ = a_i^{(a)} + a_i^{(b)} + a_i^{(c)} \]

The blue curves in the present diagram are de facto indistinguishable from the blue curves (showing Y₁) in Fig. 2.8.
3 Buffer Capacity & Intensity

3.1 Buffer Capacities

3.1.1 Acid- and Base-Neutralizing Capacities

The starting-point is the acid-base system of Chapter 2. It is composed of a weak acid $H_NA$ (with amount $C_T$) plus a strong base (with amount $C_B$). The pH of this system is entirely determined by two quantities: $C_T$ and $C_B$, or alternatively, $C_T$ and $n (=C_B/C_T)$. The relationship is established by Eq. (2.32) in §2.2.2.

**ANC.** The acid-neutralizing capacity $[\text{ANC}]$ is the amount of base within the acid-base system that can be titrated with a *strong acid* to a chosen equivalence point $EP_j$ (at pH$_j$):

$$[\text{ANC}]_{n=j} = \frac{\text{amount of base}}{\text{in initial state}} - \frac{\text{amount of base}}{\text{at EP}_i}$$

$$[\text{ANC}]_{n=j} = C_B(pH) - C_B(pH_j)$$

The small subscript $n$ on the symbol $[\text{ANC}]_n$ reminds us that the neutralizing capacity always refers to one chosen *reference point*, usually an $EP_n$. In the special case of $n=0$, which corresponds to the base-free system, i.e. $C_B(pH_0) = 0$, it simplifies to

$$[\text{ANC}]_0 = C_B(pH)$$

Eq. (3.2) can also be written as

$$\frac{[\text{ANC}]_{n=j}}{C_T} = n(pH) - n(pH_j)$$

It consists of two terms; the first term is the function $n(pH)$ given in Eq. (2.32):

$$n(x) = Y_1(x) + w(x)/C_T$$

The second term, $n(pH_j)$ – as the definition of integer equivalence points (cf. Eq. (2.64)) – is a fixed integer value: $n(pH_j) = j$, where $j = 0, 1, 2, ...$. Thus, Eq. (3.4) becomes

$$\frac{[\text{ANC}]_{n=j}}{C_T} = Y_1(x) + \frac{w(x)}{C_T} - j$$

or

$$[\text{ANC}]_{n=j} = \{ Y_1(x) - j \} C_T + w(x)$$

---

29 pH$_0$ is the pH value of acid $H_NA$ with amount $C_T$. In other words, pH$_0$ is the root of polynomial (1.136).
In other words, the amount of strong acid (e.g. HCl) required to neutralize the system from a start point $x = 10^{-pH}$ towards a particular EP (as the titration endpoint) is

\[
\begin{align*}
[\text{ANC}]_0 &= \{ Y_1(x) - 0 \} C_T + w(x) = \{ Y_1(x) C_T + w(x) \} - 0 \cdot C_T \\
[\text{ANC}]_1 &= \{ Y_1(x) - 1 \} C_T + w(x) = \{ Y_1(x) C_T + w(x) \} - 1 \cdot C_T \\
[\text{ANC}]_2 &= \{ Y_1(x) - 2 \} C_T + w(x) = \{ Y_1(x) C_T + w(x) \} - 2 \cdot C_T
\end{align*}
\]  

An example is shown in the top diagram of Fig. 3.1 for carbonic acid ($C_T = 10$ mM). The three EPs for $n=0,1,2$ are marked by small circles at pH$_0 = 4.2$, pH$_1 = 8.2$ and pH$_2 = 11.1$. The curves display the amount of strong acid (normalized by $C_T$) that is required to attain pH$_0$ (blue curve), pH$_1$ (green curve), and pH$_2$ (red curve). Of course, the highest amount (blue curve) is required to attain the lowest pH, namely pH$_0 = 4.2$. Negative ANC values indicate that the strong acid should be removed to attain the EP (which is the same as the addition of a strong base – see Eq. (3.11)).

**BNC.** The base-neutralizing capacity [BNC] is just the reverse of [ANC]:

\[
\text{[BNC]}_n = -[\text{ANC}]_n
\]

which parallels Eq. (3.7), but now with the opposite sign,

\[
\text{[BNC]}_{nj} = \{ j - Y_1(x) \} C_T - w(x)
\]

BNC curves are shown in the bottom diagram of Fig. 3.1 for carbonic acid ($C_T = 10$ mM).
### 3.1.2 Titration Example

Given is a carbonic-acid system with $C_T = 10$ mM. The titration curve – based on Eq. (3.5) – is displayed in Fig. 3.2. The three EPs for $n=0, 1, 2$ are marked by small yellow circles at pH$_0 = 4.2$, pH$_1 = 8.2$ and pH$_1 = 11.1$.

Let’s select two points on the titration curve as displayed in Fig. 3.2:

- point A at pH = 11.7 (belongs to equivalent fraction $n$(pH) = 2.5)
- point B at pH = 2.3 (belongs to equivalent fraction $n$(pH) = -0.5)

These two points (located on the opposite corners of the diagram) should be the starting points for the two types of titration:

- acidimetric titration with strong acid from pH = 12.7 $\Rightarrow$ pH$_n$
- alkalimetric titration with strong base from pH = 1.3 $\Rightarrow$ pH$_n$

![Titration curve for carbonic acid with $[\text{ANC}]$ and $[\text{BNC}]$ values](image)

**ANC.** The required amount of strong acid (indicated by green arrows) to attain EP$_1$, EP$_2$, and EP$_3$ is just the acid-neutralizing capacity given in Eqs. (3.8) to (3.10):

(3.13) $[\text{ANC}]_0 = \{ 2.5 - 0 \} C_T = 25$ mM

(3.14) $[\text{ANC}]_1 = \{ 2.5 - 1 \} C_T = 15$ mM

(3.15) $[\text{ANC}]_2 = \{ 2.5 - 2 \} C_T = 5$ mM
Acid Base Systems

BNC. The required amount of strong base (indicated by red arrows) to attain \( \text{EP}_1, \text{EP}_2, \) and \( \text{EP}_3 \) is just the base-neutralizing capacity:

\[
\begin{align*}
(3.16) \quad \text{[BNC]}_0 &= -\{ -0.5 - 0 \} \text{ C}_T = 5 \text{ mM} \\
(3.17) \quad \text{[BNC]}_1 &= -\{ -0.5 - 1 \} \text{ C}_T = 15 \text{ mM} \\
(3.18) \quad \text{[BNC]}_2 &= -\{ -0.5 - 2 \} \text{ C}_T = 25 \text{ mM}
\end{align*}
\]

Addition of a strong base is equivalent to the removal of a strong acid and vice versa.

### 3.1.3 Alkalinity and Acidity

In carbonate systems, \([\text{ANC}]\) is named alkalinity, while \([\text{BNC}]\) acidity. Here, too, a distinction must be made between different types of alkalinity and acidity, which depend on the chosen reference point \( \text{EP}_j \). The carbonic acid has three EPs, hence there are three types of alkalinity (cf. Fig. 3.3):

\[
\begin{align*}
(3.19) \quad \text{total alkalinity (M alkalinity):} \quad [\text{Alk}] &= [\text{ANC}]_{n=0} \\
(3.20) \quad \text{P alkalinity:} \quad [\text{P-Alk}] &= [\text{ANC}]_{n=1} \\
(3.21) \quad \text{caustic alkalinity:} \quad [\text{OH-Alk}] &= [\text{ANC}]_{n=2}
\end{align*}
\]

Correspondingly, there are three types of acidity:

\[
\begin{align*}
(3.22) \quad \text{mineral acidity:} \quad [\text{H-Acy}] &= [\text{BNC}]_{n=0} \\
(3.23) \quad \text{CO}_2 \text{ acidity:} \quad [\text{CO}_2\text{-Acy}] &= [\text{BNC}]_{n=1} \\
(3.24) \quad \text{acidity:} \quad [\text{Acy}] &= [\text{BNC}]_{n=2}
\end{align*}
\]

Alkalinity and acidity are complementary. In particular, from Eq. (3.11) we get:

\[
\begin{align*}
(3.25) \quad [\text{ANC}]_0 &= -[\text{BNC}]_0 \quad \Rightarrow \quad [\text{Alk}] &= -[\text{H-Acy}] \\
(3.26) \quad [\text{ANC}]_1 &= -[\text{BNC}]_1 \quad \Rightarrow \quad [\text{P-Alk}] &= -[\text{CO}_2\text{-Acy}] \\
(3.27) \quad [\text{ANC}]_2 &= -[\text{BNC}]_2 \quad \Rightarrow \quad [\text{OH-Alk}] &= -[\text{Acy}]
\end{align*}
\]

**Fig. 3.3** and **Fig. 3.2** display the same curve; the only difference between both diagrams is that the x- and y-axes are interchanged.

**Fig. 3.3** Titration curve \( n = n(pH) \) for carbonic acid \((C_T = 10 \text{ mM})\) with equivalence points and the corresponding types of alkalinity and acidity.
Of all three alkalinity types, the most important quantity is the total alkalinity; according to Eq. (3.28) it is given by

$$\text{[Alk]} = \text{[ANC]}_0 = C_B = n C_T$$

Plots of alkalinity were presented in Fig. 2.13 on page 64. In addition, from Eq. (3.7) one gets for the difference between M- and P-alkalinity the amount of $C_T$,

$$[\text{M-Alk}] - [\text{P-Alk}] = C_T (= \text{DIC})$$

which is equivalent to the ‘dissolved inorganic carbon’ DIC.

### 3.1.4 pH as Reference Point of ANC and BNC

In § 3.1.1, ANC and BNC has been defined with respect to an equivalence point $\text{EP}_n$. ANC and BNC can also be defined with respect to a particular pH value. This can be any chosen pH value. In practice, however, it is common to use the pH values of the carbonate-acid’s equivalence points $\text{EP}_0$ and $\text{EP}_1$ (shown as yellow dots in Fig. 3.3 and Fig. 3.2):

$$\begin{align*}
\text{EP}_0: & \quad \text{pH} \approx 4.3 \\
\text{EP}_1: & \quad \text{pH} \approx 8.2
\end{align*}$$

valid for carbonate acid with $C_T \approx 1 \ldots 10 \text{mM}$

The usefulness of both values lies in the fact that these are the pH values of common indicators: indicator methylorange (titration endpoint 4.2 to 4.5) and indicator phenolphthalein (titration endpoint 8.2 to 8.3).

The two EP’s are shown as yellow dots in Fig. 3.2 and Fig. 3.3. The corresponding pH values serve as titration end points in water analysis. The measured amount of strong acid or base to reach the endpoint is called:

$$\begin{align*}
\text{ANC to pH 4.3:} & \quad [\text{ANC}]_{\text{pH} 4.3} \quad (\approx [\text{Alk}]) \\
\text{ANC to pH 8.2:} & \quad [\text{ANC}]_{\text{pH} 8.2} \quad (\approx [\text{P-Alk}]) \\
\text{BNC to pH 4.3:} & \quad [\text{BNC}]_{\text{pH} 4.3} \quad (\approx [\text{Alk}]) \\
\text{BNC to pH 8.2:} & \quad [\text{BNC}]_{\text{pH} 8.2} \quad (\approx [\text{P-Alk}])
\end{align*}$$

The measured “ANC to pH 4.3” corresponds to the total alkalinity (or M-alkalinity) of the system; the measured “ANC to pH 8.2” to the P-alkalinity. Here, the abbreviation “M” refers to the indicator methylorange and “P” to phenolphthalein.
3.2 Buffer Intensity

3.2.1 Definitions

Given is the acid-neutralizing capacity (at EP₀) taken from Eq. (3.3):

\[ [\text{ANC}]_0 = C_T Y_1(x) + w(x) = C_B(x) \quad (\text{buffer capacity}) \]

Dividing it by \( C_T \) yields \( n(x) = \frac{[\text{ANC}]_0}{C_T} \) with

\[ n(x) = Y_1(x) + \frac{w(x)}{C_T} \quad (\text{‘normalized’ buffer capacity}) \]

The latter is just the formula for the ‘normalized’ titration curve of an \( N \)-protic acid (see Eq. (2.32)). To exhibit its pH dependence we replace \( x \) by \( 10^{-\text{pH}} \) and write:

\[ n(\text{pH}) = Y_1(\text{pH}) + \frac{w(\text{pH})}{C_T} \quad \text{with} \quad Y_1(\text{pH}) = \sum_{j=0}^{N} j \cdot a_j(\text{pH}) \]

The buffer intensity is the derivative of the buffer capacity with respect to pH. Depending on the expression for the buffer capacity (either its normalized form, \( n(\text{pH}) \), or as \( C_B \) as in Eq. (3.36)) we distinguish between two types of buffer intensities:

\[ \beta = \frac{\text{dn}}{\text{d}\text{pH}} \quad [\text{unitless}] \]

\[ \beta_C = \frac{\text{d}C_B}{\text{d}\text{pH}} = \beta C_T \quad [\text{mol/L}] \]

Both quantities differ by their physical unit: \( \beta \) is unitless, while \( \beta_C \) has units of concentration: mol/L or eq/L.

The acid-neutralizing capacity is re-established by integration of the buffer intensity over a definite pH interval (starting from an equivalence point EPₙ):

\[ [\text{ANC}]_n = \int_{\text{pH}_0}^{\text{pH}} \beta_C(\text{pH}) \, \text{d}\text{pH} \]

3.2.2 Optimal Buffer Range

Before we present formulas for the buffer intensity \( \beta \), some qualitative considerations are appropriate. A good pH buffer should mitigate pH changes when the system is attacked by a strong base or acid. That is, the change of pH, i.e. \( \Delta \text{pH} \), should be small for any changes \( \Delta n \) of \( n = C_B/C_T \). In other words, the slope of the titration curve, \( \Delta n/\Delta \text{pH} \), should be large for maximum buffering capability. The buffer intensity, \( \beta = \text{dn/dpH} \), itself is the measure of this slope.
Acid Base Systems

Short Lecture

To sum up: the steeper the slope of a titration curve – as sketched in Fig. 3.4 – the higher the buffer intensity $\beta = dn/dpH$, i.e. the higher the system’s resistance to pH changes (caused by a strong base). Thus, the pH where $\beta$ reaches its maximum represents the optimal buffer range (bounded by $pH_{max} \pm 1$) – see example in Fig. 3.5.

Fig. 3.4 The steeper the slope of a titration curve the higher is the system’s buffer intensity

Fig. 3.5 Optimal buffer range ($H_2CO_3$ system). Calculations based on Eqs. (3.42) to (3.44).

Since the titration curve (in blue color) is an ever-increasing function, its pH-derivative, i.e. the buffer intensity $\beta$, is always positive (green curve). This is in agreement with Le Châtelier’s principle: Every solution resists pH changes.

In the next paragraphs, two things will be done: First, we present closed-form equations for $\beta$ and $d\beta/dpH$. Second, we show that the maxima of the buffer intensity $pH_{max}$ are related to the semi-equivalence points at $pK_j$. 

Jan 19, 2019
3.2.3 Closed-Form Expressions

What is termed ‘buffer capacity’ in Eq. (3.38) is exactly our ‘titration-curve’ formula, \( n = n(pH) \), that was derived and used Chapter 2. All considerations about the buffer capacity remain valid when we expand our scope to zwitterionic acids, as it was done in § 2.2.6. In other words, we start out from the more general Eq. (2.56), which differs from Eq. (3.38) by a constant offset \( Z \) (that will vanish after pH-derivation).

The first pH-derivative of \( n(pH) \) yields the buffer intensity \( \beta(pH) \); it can be obtained with help of Eqs. (B.51) and (B.41). The next highest derivative yields \( d\beta/dpH \), which can be obtained using Eqs. (B.54) and (B.42). Thus, we get:

\[
\text{buffer capacity: } n(x) = \left( Y_1(x) - Z \right) + \frac{w(x)}{C_T} \\
\text{buffer intensity: } \beta(x) = \frac{dn}{dpH} = \ln 10 \left( Y_2 - Y_1^2 + \frac{w + 2x}{C_T} \right) \\
1\text{st derivative of } \beta: \frac{d\beta}{dpH} = \frac{d^2n}{dpH^2} = (\ln 10)^2 \left( Y_3 - 3Y_1Y_2 + 2Y_1^3 + \frac{w}{C_T} \right)
\]

These three functions are displayed in Fig. 3.5 and all subsequent diagrams (for common acids, i.e. \( Z = 0 \)). Since \( Y_2 \geq Y_1^2 \), the buffer intensity is a positive function which never drops below zero. The maxima and minima of the buffer intensity are identified by the zeros of its derivative, i.e. they are located at pH values where \( d\beta/dpH = 0 \).

**Pure-Acid Limit.** The titration curve and its derivatives simplify for large values of \( C_T \), where the last term in the equations above (containing \( C_T \) in the denominator) vanish. Hence, for \( C_T >> w \) we have:

\[
\text{titration curve: } n(x) = Y_1(x) - Z \\
\text{buffer intensity: } \beta(x) = \frac{dn}{dpH} = \ln 10 \left( Y_2 - Y_1^2 \right) \\
1\text{st derivative of } \beta: \frac{d\beta}{dpH} = \frac{d^2n}{dpH^2} = (\ln 10)^2 \left( Y_3 - 3Y_1Y_2 + 2Y_1^3 \right)
\]

The principal behavior of the buffer-intensity curves is determined by the *equivalence points* of the N-protic acid. The best way to demonstrate it is to investigate just the pure-acid limit (in the next paragraph).

\[\text{30 The maximum or minimum is where the slope (i.e. the derivative) of a function becomes zero.}\]
3.2.4 Minima and Maxima (Pure-Acid Limit)

This paragraph relies on the buffer intensity $\beta$ and its derivative $d\beta/dpH$, as given in Eqs. (3.46) and (3.47) for the pure-acid limit $C_T \gg w$ (where the contribution from ‘H$_2$O’ is negligible):

\begin{align*}
\beta(x) &= \ln 10 \left( Y_2 - Y_1^2 \right) \\
\frac{d\beta}{dpH} &= (\ln 10)^2 \left( Y_3 - 3Y_1Y_2 + 2Y_1^3 \right)
\end{align*}

These are smooth functions made of $Y_1$, $Y_2$, and $Y_3$ alone. The behavior of $Y_L$ is entirely determined by the set of acid’s equilibrium constants $K_j$, or alternatively, by the internal equivalence points $EP_n$ as given in Eqs. (1.115) and (1.116):

\begin{align*}
\text{(3.50)} & \quad \text{semi-EP} \quad \text{at } pK_j \quad Y_L = \frac{1}{2} \left\{ (j-1)^{\frac{1}{2}} + j^{\frac{1}{2}} \right\} \quad (n = j^{\frac{1}{2}}) \\
\text{(3.51)} & \quad \text{EP}_j \quad \text{at } pH = \frac{1}{2}(pK_j + pK_{j+1}) \quad Y_L = j^{\frac{1}{2}} \quad (n = j)
\end{align*}

Inserting it into Eq. (3.48) we get

\begin{align*}
\text{(3.52)} & \quad \frac{\beta(pK_j)}{\ln 10} = Y_2(pK_j) - Y_1^2(pK_j) = (j(j-1)^{\frac{1}{2}}) - (j(j-1)^{\frac{1}{2}}) = \frac{j}{4} \\
\text{(3.53)} & \quad \frac{\beta(pH_j)}{\ln 10} = Y_2(pH_j) - Y_1^2(pH_j) = j^2 - j^2 = 0
\end{align*}

Now, we prove that these equivalence points are extrema points of the buffer intensity. The maximum or minimum is known to be the point at which the slope (i.e. the derivative) of a function becomes zero. Hence, local maxima and minima of the buffer intensity $\beta(pH)$ occur at pH values where $d\beta/dpH = 0$. The derivative itself is given by Eq. (3.49) above, where we focus on $Y_3 - 3Y_1Y_2 + 2Y_1^3$.

For the semi-EP$_n$ with half-integer $n = j^{\frac{1}{2}}$, we get from Eq. (3.50):

\begin{align*}
\text{(3.54)} & \quad Y_3 - 3Y_1Y_2 + 2Y_1^3 = \frac{1}{2} \left\{ (j-1)^{\frac{3}{2}} + j^{\frac{3}{2}} \right\} - 3(j^{\frac{1}{2}})^2(j(j-1)^{\frac{1}{2}}) + 2(j^{\frac{1}{2}})^3 \\
& \quad = 0 \quad \text{at } pH = pK_j \quad \text{for } j = 1, 2, ..., N
\end{align*}

For EP$_n$ with integer $n = j$, we get from Eq. (3.51):

\begin{align*}
\text{(3.55)} & \quad Y_3 - 3Y_1Y_2 + 2Y_1^3 = j^3 - 3j^{\frac{3}{2}}j^{\frac{3}{2}} + 2j^3 \\
& \quad = 0 \quad \text{at } pH = pH_j \quad \text{for } j = 1, 2, ..., N-1
\end{align*}

Hence, the zeros of $d\beta/dpH$ occur exactly at the internal equivalence points $EP_n$ for both integer and half-integer $n$. To decide whether the zeros indicate a maximum or minimum, we need the next higher derivative $d^2\beta/dpH^2$ (or $d^3Y/dpH^3$, which is presented in Eq. (B.55).
In summary, we get the following assignment:\(^{31}\)

\[(3.56)\] semi-EP\(_j\) at pK\(_j\) \iff\ maximum of \(\beta\)  
\[(d^3 Y/dpH^3)|_{pK_j} < 0\]

\[(3.57)\] EP\(_j\) at pH\(_j\) \iff\ minimum of \(\beta\)  
\[(d^3 Y/dpH^3)|_{pH_j} > 0\]

The buffer intensity attains its maximum at semi-equivalence points located at pK\(_j\). The actual values of \(\beta\) at this extrema were already presented in Eqs. (3.52) and (3.53):

\[(3.58)\] maxima of \(\beta\) at semi-EP\(_n\) \quad \beta_{\text{max}} = \frac{\ln 10}{4} \approx 0.576 \quad \text{for half-integer } n

\[(3.59)\] minima of \(\beta\) at EP\(_n\) \quad \beta_{\text{min}} = 0 \quad \text{for } n = 1, 2, \ldots N-1

This behavior of the buffer intensity is illustrated in Fig. 3.6 for four common acids. The maxima of \(\beta\) (green curve) are indicated by the corresponding pK\(_j\) values, where the zeros of d\(\beta/dpH\) (red curve) are marked by small blue dots.

**Fig. 3.6** Maxima and minima of the buffer intensity \(\beta\) (green curves) are located at zeros of d\(\beta/dpH\) (red curves). Calculations for the pure-acid case, C\(_T\)/w \(\gg\) 1.

**Example.** The carbonate system, as shown in the bottom-left diagram of Fig. 3.6, has two semi-EPs. Hence, there are two maxima of the buffer intensity (green curve) located at pK\(_1\) = 6.35 and pK\(_2\) = 10.33, while the minimum of \(\beta\) is located at pH\(_1\) = \(\frac{1}{2}\) (pK\(_1\) + pK\(_2\)) = 8.34 (which is an integer-valued EP).

\(^{31}\) This is strictly valid for high enough C\(_T\) values.
3.2.5 Examples for the Normal Case (C_T is finite)

The preceding paragraph focused on the *pure-acid case* valid for $C_T \to \infty$. Now, the realistic case of *finite* $C_T$ values takes into account the effect of $H_2O$ through $w(x)$ in Eqs. (3.42) to (3.44). The results are displayed in diagrams, each containing three curves:

- $n(pH)$ buffer capacity Eq. (3.42) (blue curve)
- $\beta = dn/dpH$ buffer intensity Eq. (3.43) (green curve)
- $d\beta/dpH$ 1st derivative of $\beta$ Eq. (3.44) (red curve)

All three quantities are unitless. The small blue dots mark the zeros of $d\beta/dpH$; they correspond to minima and maxima of the buffer intensity.

**Example 1.** Given is the carbonic acid system with $C_T = 100$ mM, 10 mM, and 1 mM $H_2CO_3$; the results are shown in Fig. 3.7.

**Example 2.** Fig. 3.8 to Fig. 3.10 displays the results for four common acids with an amount of $C_T = 100$ mM, 10 mM, and 1 mM. These results should be compared with pure-acid case ($C_T \to \infty$) in Fig. 3.6.
Fig. 3.8 Titration curve (blue), buffer intensity (green), and $d\beta/dpH$ (red) for four common acids with $C_T = 100 \text{ mM}$

Fig. 3.9 Titration curve (blue), buffer intensity (green), and $d\beta/dpH$ (red) for four common acids with $C_T = 10 \text{ mM}$
Fig. 3.10  Titration curve (blue), buffer intensity (green), and $\frac{d\beta}{dpH}$ (red) for four common acids with $C_T = 1$ mM
4 BEYOND COMMON ACIDS

The framework introduced in the previous chapters can easily be extended to other phenomena beyond the realm of common acids: zwitterionic acids, surface complexation, hydrolysis of metals, etc. In § 4.1 we focus on zwitterionic acids (amino acids); in § 4.2 on surface complexation.

4.1 Zwitterions and Amino Acids

4.1.1 Definition

A zwitterion is a molecule with functional groups, of which at least one has a positive and one has a negative electrical charge. The net charge of the entire molecule is zero.

Amino acids are the best-known examples of zwitterions. They contain an amine group (basic) and a carboxylic group (acidic). The -NH$_2$ group is the stronger base, and so it picks up H$^+$ from the -COOH group to leave a zwitterion (i.e. the amine group deprotonates the carboxylic acid):$^{32}$

$$\begin{align*}
\text{H}_2\text{N} - \text{C} - \text{COOH} & \quad \text{amino acid} \\
\text{H}_3\text{N} - \text{C} - \text{COO}^- & \quad \text{zwitterion}
\end{align*}$$

The (neutral) zwitterion is the usual form amino acids exist in solution. Depending on the pH, there are two other forms, an anion and a cation:

$$\begin{align*}
\text{H}_3\text{N} - \text{C} - \text{COOH} & \quad \text{cation (at low pH)} \\
\text{H}_2\text{N} - \text{C} - \text{COO}^- & \quad \text{zwitterion} \\
\text{H}_2\text{N} - \text{C} - \text{COO}^- & \quad \text{anion (at high pH)}
\end{align*}$$

This parallels the behavior of a diprotic acid:

$$\begin{align*}
\text{H}_2\text{A} & \quad \text{undissolved acid (at low pH)} \\
\text{H}_3\text{A}^- & \quad \text{fully deprotonated (at high pH)}
\end{align*}$$

$^{32}$ R denotes the side chain (glycine: R = H, alanine: R = CH$_3$, and so on).
Acid Base Systems

When an amino acid dissolves in water, the zwitterion interacts with H₂O molecules – acting as both an acid and a base. But, unlike simple amphoteric compounds that may only form either a cationic or an anionic species, a zwitterion has both ionic states simultaneously.

4.1.2 Zwitterions as Diprotonic Acids

The acid-base behavior of the simplest zwitterions (that contain one amine group and one carboxylic group) is similar to that of a diprotic acid – see Tab. 4.1.

Tab. 4.1 Diprotic acid vs simplest zwitterions

<table>
<thead>
<tr>
<th>1st dissociation</th>
<th>diprotic acid</th>
<th>zwitterion (simplest amino acids)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂A = H⁺ + HA</td>
<td>K₁</td>
<td>H₂A⁺ = H⁺ + HA</td>
</tr>
<tr>
<td>2nd dissociation</td>
<td>HA⁻ = H⁺ + A⁻</td>
<td>K₂</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>species</th>
<th>abbreviation [j]</th>
<th>ion. fractions a_j</th>
<th>charge z_j</th>
<th>average charge z_a</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂A</td>
<td>[0]</td>
<td>a₀</td>
<td>0</td>
<td>(0·[H₂A] − 1·[HA] − 2·[A⁻]) / C₇</td>
</tr>
<tr>
<td>HA⁻</td>
<td>[1]</td>
<td>a₁</td>
<td>-1</td>
<td>(1·[H₂A⁺] − 0·[HA] − 1·[A⁻]) / C₇</td>
</tr>
<tr>
<td>H₂A⁺</td>
<td>[0]</td>
<td>a₀</td>
<td>+1</td>
<td></td>
</tr>
<tr>
<td>HA</td>
<td>[1]</td>
<td>a₁</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

In both cases there are N=2 dissociation steps (controlled by two acidity constants K₁ and K₂) and three species: [0], [1], and [2], where [0] refers to the highest protonated species. The number of H⁺ in the highest protonated species is N=2 for both.

The only difference is that there is an offset by Z=1, where Z represents the positive charge of the highest protonated species (which equals the number of amine groups in the molecule). Obviously, common diprotic acids are characterized by Z=0. The offset determines the individual charge, i.e.

\[
\text{(4.4) charge of species } j: \quad z_j = Z - j
\]

This yields:

<table>
<thead>
<tr>
<th>diprotic acid (Z=0)</th>
<th>zwitterion (Z=1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[H₂A] (neutral)</td>
<td>[H₂A⁺] (cation)</td>
</tr>
<tr>
<td>[HA⁻] (anion)</td>
<td>[HA] (neutral)</td>
</tr>
<tr>
<td>[A⁻] (anion)</td>
<td>[A⁻] (anion)</td>
</tr>
</tbody>
</table>

(highest protonated) (fully deprotonated)

By the way, Eq. (4.4) confirms the statement that the offset Z equals the charge of the highest protonated acid-species:

\[
\text{(4.5) } Z = z₀
\]

The last line in Tab. 4.1 represents the average charge of the acid (as defined in Eq. (2.51)).
**Acid Base Systems**

**Basic Equations.** The description of common acids and zwitterionic acids is based on the *same* framework derived in the previous chapters (except the offset $Z$). That is, everything relies on exactly the same building blocks (ionization fractions $a_j$ and moments $Y_L$), as introduced in § 1.5. The only difference is the offset $Z$ that enters the titration formula (i.e. buffer capacity) in Eq. (3.42), but only this formula. The buffer intensity $\beta$ and its pH-derivative are independent of $Z$ – see Eqs. (3.43) and (3.44). Example calculations are presented in the subsequent sections.

**4.1.3 Example: Glycine**

The simplest amino acid is glycine ($\text{NH}_2\text{-CH}_2\text{-COOH}$), which we abbreviate by $\text{HGly}$, or shorter, by $\text{HA}$ with $A = \text{Gly}$. Its structural formula is shown in Eq. (4.1) with the shortest side chain $R = \text{H}$. The three species are:

$$\begin{align*}
[0] &= [\text{H}_2\text{A}^+] = [\text{H}_2\text{Gly}^+] : \text{NH}_3^+\text{-CH}_2\text{-COOH} \quad (\text{glycinium cation}) \\
[1] &= [\text{HA}] = [\text{HGly}] : \text{NH}_3^+\text{-CH}_2\text{-COO}^- \quad (\text{neutral zwitterion}) \\
[2] &= [\text{A}^-] = [\text{Gly}^-] : \text{NH}_2\text{-CH}_2\text{-COO}^- \quad (\text{glycinate anion})
\end{align*}$$

The two acidity constants (compared to carbonic acid) are:

|        | Glycine: $pK_1$ | $pK_1 = 2.35$ | Carbonic acid: $pK_1$ | $pK_1 = 6.35$ | $pK_2$ = 9.78 | $pK_2$ = 11.33 |

Fig. 4.1 displays the pH dependence of the three ionization fractions $a_j$ of glycine and carbonic acid. Both graphs are based on the same formulas given in Eq. (1.90).

**Fig. 4.1** Ionization fractions $a_j$ of two diprotic acids: glycine (upper) and carbonic acid (lower diagram)
Titration Curves. The titration curves $n = n(pH)$ in Fig. 4.2 show what happens to the amino acid glycine as you change the pH by adding either a strong acid (HCl) or base (NaOH) to the solution. These curves were calculated with Eq. (3.42).

The right diagram in Fig. 4.2 compares the analytical formula for $C_T = 100 \text{mM}$ with numerical calculations using PPhreeqc or Aqion. The numerical calculations are more accurate and more realistic due to the activity corrections for HCl and NaOH at high ionic strengths (i.e. at high values of $|n|$).
Buffer Capacity & Intensity. Fig. 4.3 displays the buffer capacity (blue titration curve) together with the corresponding buffer intensity \( \beta \) (green) and its derivative \( d\beta/dpH \) (red). This is done for two cases: infinitely high concentrated glycine \( (C_T \to \infty) \) and \( C_T = 500 \text{ mM} \). The calculations are based on Eqs. (3.42) to (3.44). The small dots are the zeros of \( d\beta/dpH \), which indicate the extrema of the buffer intensity \( \beta \) and mark the inflection points of the titration curves. The blue titration curve in Fig. 4.2 (left diagram) is the same as in Fig. 4.3 (lower diagram), except that the x- and y-axis are swapped.

4.1.4 Zwitterions as \( N \)-protic Acids: \( H_NA^{+Z} \)

In addition to the most simple zwitterions \( (N=2, Z=1) \) discussed in § 4.1.2, there are other compounds with higher values of \( N \) and/or \( Z \). Some examples are given in Tab. 4.2 and Fig. 4.4. To recap: \( N \) is the number of \( H^+ \) in the highest protonated species and \( Z \) is the positive charge of the highest protonated species.

<table>
<thead>
<tr>
<th>( N )</th>
<th>( Z )</th>
<th>( pK_1 )</th>
<th>( pK_2 )</th>
<th>( pK_3 )</th>
<th>( pK_4 )</th>
<th>( pK_5 )</th>
<th>( pK_6 )</th>
<th>( [j=0] )</th>
<th>( [j=Z] )</th>
<th>( [j=N] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>carbonic acid</td>
<td>2</td>
<td>0</td>
<td>6.35</td>
<td>11.33</td>
<td></td>
<td></td>
<td></td>
<td>( H_A^{-} )</td>
<td>( H_A^{-} )</td>
<td>( A^{-} )</td>
</tr>
<tr>
<td>glycine</td>
<td>2</td>
<td>1</td>
<td>2.35</td>
<td>9.778</td>
<td></td>
<td></td>
<td></td>
<td>( H_A^{+} )</td>
<td>( H_A^{-} )</td>
<td>( A^{-} )</td>
</tr>
<tr>
<td>glutamic acid</td>
<td>3</td>
<td>1</td>
<td>2.16</td>
<td>4.30</td>
<td>9.96</td>
<td></td>
<td></td>
<td>( H_A^{+} )</td>
<td>( H_A^{-} )</td>
<td>( A^{-} )</td>
</tr>
<tr>
<td>NTA</td>
<td>4</td>
<td>1</td>
<td>1.0</td>
<td>2.0</td>
<td>2.942</td>
<td>10.28</td>
<td></td>
<td>( H_A^{+} )</td>
<td>( H_A^{-} )</td>
<td>( A^{-} )</td>
</tr>
<tr>
<td>EDTA</td>
<td>6</td>
<td>2</td>
<td>0</td>
<td>1.5</td>
<td>2.16</td>
<td>3.119</td>
<td>6.281</td>
<td>10.94</td>
<td>( H_A^{-2} )</td>
<td>( H_A^{-2} )</td>
</tr>
</tbody>
</table>

Fig. 4.4 Structural formulas of four zwitterionic acids

Such zwitterionic acids have \( N+1 \) species:

\[
[j] = [H_{N-j}A^{Z-j}] \quad \text{with charge} \quad z_{j} = Z - j \quad \text{(for} \ j = 0 \ \text{to} \ N)
\]

Of all \( N+1 \) species, three species are particularly interesting:

<table>
<thead>
<tr>
<th>( j )</th>
<th>( [0] = [H_A^{+2}] )</th>
<th>( \text{common acid} )</th>
<th>( Z = 0 )</th>
<th>( \text{zwitterion} )</th>
<th>( 0 &lt; Z &lt; N )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( j = 0 )</td>
<td>( [0] = [H_A^{+2}] )</td>
<td>highest protonated</td>
<td>neutral ( [Z] = [0] )</td>
<td>cation</td>
<td></td>
</tr>
<tr>
<td>( j = Z )</td>
<td>( [Z] = [H_{N-z}A] )</td>
<td>undissociated acid</td>
<td>neutral ( [Z] = [0] )</td>
<td>neutral</td>
<td></td>
</tr>
<tr>
<td>( j = N )</td>
<td>( [N] = [A^{(N-z)}] )</td>
<td>fully deprotonated</td>
<td>anion</td>
<td>anion</td>
<td></td>
</tr>
</tbody>
</table>

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Fig. 4.5 Titration curves, buffer capacity $\beta$ and its derivative $d\beta/dpH$ for four zwitterionic acids (from Tab. 4.2). Calculations performed for the pure-acid case $C_T \to \infty$ (i.e. highly concentrated acids).

Fig. 4.6 Titration curves, buffer capacity $\beta$ and its derivative $d\beta/dpH$ for four zwitterionic acids (from Tab. 4.2). Calculations performed for $C_T = 500$ mM.
Fig. 4.5 and Fig. 4.6 show titration curves (blue) together with the corresponding buffer capacity $\beta$ (green) and its derivative $d\beta/dpH$ (red) for four zwitterionic acids taken from Tab. 4.2. This is done for two cases:

- infinitely high concentrated acids ($C_T \to \infty$) in Fig. 4.5
- $C_T = 500$ mM in Fig. 4.6

The calculations are based on Eqs. (3.42) to (3.44). The small dots are the zeros of $d\beta/dpH$, which indicate the extrema of the buffer capacity $\beta$ and mark inflection points of the titration curves.

**EDTA.** Ethylenediaminetetraacetic acid is especially interesting because, in this lecture, it represents the acid with the highest number of dissociation steps: $N=6$ (defined by the six acidity constants in Tab. 4.2).

There are $N+1 = 7$ acid species, where the highest protonated species is $H_6A^{2+}$ and the fully deprotonated species is $A^-$. Fig. 4.7 displays the pH dependence of EDTA’s seven ionization fractions $a_0$, $a_1$ to $a_6$ based on the formulas given in Eq. (1.90).

![Fig. 4.7 Ionization fractions $a_j$ of EDTA in linear scale (upper) and logarithmic scale (lower diagram)](image_url)

Titration curves based on Eq. (3.42) for three amounts of $C_T$ are displayed in Fig. 4.8. The red dots represent numerical calculations with PHREEQC or AQION.\(^{33}\) [Note: In contrast to Fig. 4.5 and Fig. 4.6, which also contain titration curves of EDTA, the x and y axes are interchanged in Fig. 4.8.]

\(^{33}\) In these calculations, complex-formation of EDTA are ignored.
Acid Base Systems

4.1.5 Equivalence Points

In § 2.3, the mathematical relationship between the EP\textsubscript{n} and the corresponding pH\textsubscript{n} values was established. This concept can be extended to zwitterions by taking into account the offset Z:

\[ EP\textsubscript{n} \iff n = \left( Y_{1}(pH) - Z \right) + \frac{w(pH)}{C_{T}} \quad \text{for } n = -Z, ..., -\frac{1}{2}, 0, \frac{1}{2}, ..., N-Z \]

For Z = 0, this relationship falls back to Eq. (2.64).
Acid Base Systems

Short Lecture

Fig. 4.9 shows the titration curve of glycine for $C_T = 500$ mM (same as in Fig. 4.3, lower diagram). The small circles at integer and half-integer values of $n$ mark just the $E_{pH}$ assignment. Since HGly acts as a 2-protic acid, there are $2 \times 2 + 1 = 5$ equivalence points in total.

The main difference to the diprotic acid $H_2CO_3$ (shown in Fig. 2.9 on page 59) is the occurrence of EPs with negative integer and half-integer values of $n$.

**pH-C$_T$ Diagrams.** Rearranging Eq. (4.7) we get

\[ C_T = \frac{w(pH)}{n + Z - Y_1(pH)} \]

as a generalization of Eq. (2.66) for $Z > 0$. This relationship is plotted in Fig. 4.10 – one curve for each integer and half-integer value of $n$. The dashed curves (straight lines) correspond to the subsystem ‘pure acid’. This diagram should be compared with the plots in Fig. 2.10 on page 60, done for common acids.

**4.1.6 Isoionic and Isoelectric Points**

The _isoionic_ point is the pH of the pure, neutral polyprotic acid (i.e. when the neutral zwitterion is dissolved in water). The _isoelectric_ point pI is the pH at which the average charge $z_a$ of the polyprotic acid is zero:

\[ \text{isoionic point: } \quad \text{pH}_0 = \text{pH of EP}_0 \]

\[ \text{isolectric point: } \quad \text{pI} = \text{pH at which } z_a(\text{pH}) = 0 \]

From Eq. (4.7) and from the definition of $z_a$ in Eq. (2.51), we get the analytical formulas to determine the two points (at least implicitly):

\[ \text{isoionic point: } \quad Z - Y_1(pH) = \frac{w(pH)}{C_T} \]

\[ \text{isolectric point: } \quad Z - Y_1(pH) = 0 \]

---

34 The net charge of the solution is always zero.
As $C_T$ increases, both points approach each other until they become identical for large enough values of $C_T$. This behavior is shown in Fig. 4.11.

The difference between the isoionic and isoelectric points (even if it is numerically very small) can be summarized as follows:

<table>
<thead>
<tr>
<th>isoionic point</th>
<th>isoelectric point (pl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH of pure acid</td>
<td>pH when net charge of all acid species is zero</td>
</tr>
<tr>
<td>depends on $C_T$ (approaches pl for $C_T \to \infty$)</td>
<td>independent of $C_T$</td>
</tr>
<tr>
<td>$Z - Y_1(pH) = w(pH)/C_T$</td>
<td>$Z - Y_1(pH) = 0$</td>
</tr>
<tr>
<td>exists for common acids and zwitterions</td>
<td>exists only for zwitterions</td>
</tr>
</tbody>
</table>

**Special Case.** For the special case of a diprotic acid (glycine) we have $Z = 1$, which after insertion into Eq. (4.12), leads to:

$$\text{isoelectric point: } 1 - Y_1 = 0 \quad \Leftrightarrow \quad \text{pI} = \frac{1}{2}(pK_1 + pK_2)$$

The right-hand-side equation follows from Eq. (1.122) and Eq. (1.116).

![Fig. 4.11 Isoelectric and isoionic points of glycine as a function of $C_T$. This diagram is an enlarged section of Fig. 4.10 (with focus on EPo).](image)
4.2 Surface Complexation

4.2.1 Definition

Surface complexation is described in many textbooks, e.g. [SM96]. We apply it here for the simplest case when COULOMB interactions are ignored. This is valid, for example, in the vicinity of pH$_{pzc}$, the point of zero charge.

Let’s consider a surface hydroxyl group ≡OH, where ≡ symbolizes the surface. Uptake and release of protons can be described by two dissociation steps:

\begin{align*}
(4.14) & \quad 1^{\text{st}} \text{ dissociation step:} & \equiv\text{OH}^{2+} & = H^+ + \equiv\text{OH} & K_1 \\
(4.15) & \quad 2^{\text{nd}} \text{ dissociation step:} & \equiv\text{OH} & = H^+ + \equiv\text{O}^- & K_2
\end{align*}

In the absence of COULOMB interactions, $K_1$ and $K_2$ are so-called intrinsic equilibrium constants. Some examples are given in Tab. 4.3.

As for the case of a zwitterionic acid $H_2A^+$, there are $N+1 = 3$ surface species:

\begin{align*}
[0] &= \equiv\text{SOH}^2+ & \text{cationic} \\
[1] &= \equiv\text{SOH} & \text{neutral} \\
[2] &= \equiv\text{SO}^- & \text{anionic}
\end{align*}

The sum of all species represents the total amount of surface sites $C_T$.

Tab. 4.3 Intrinsic pK values and point of zero charge for surface complexation on four (clay) minerals [data from www.hzdr.de/res3t]

<table>
<thead>
<tr>
<th></th>
<th>kaolinite</th>
<th>mica</th>
<th>goethite</th>
<th>gibbsite</th>
</tr>
</thead>
<tbody>
<tr>
<td>$pK_1$</td>
<td>2.52</td>
<td>6.01</td>
<td>7.13</td>
<td>7.53</td>
</tr>
<tr>
<td>$pK_2$</td>
<td>5.88</td>
<td>7.65</td>
<td>9.60</td>
<td>9.87</td>
</tr>
<tr>
<td>pH$_{pzc} = \frac{1}{2} (pK_1+pK_2)$</td>
<td>4.20</td>
<td>6.83</td>
<td>8.37</td>
<td>8.70</td>
</tr>
</tbody>
</table>

4.2.2 Example Calculations

The pH behavior of surface complexation relies on Eqs. (3.42) to (3.44) with $N=2$ and $Z=1$. The smallest ‘building blocks’ are the ionization fractions $a_0$, $a_1$ and $a_2$ as shown in Fig. 4.12; they represent the species distribution on kaolinite (in the absence of COULOMB interactions).

---

35 In PHREEQC the non-Coulomb option refers to “no_edl”.
The ‘average charge’ defined in Eq. (2.53) represents the surface charge:

\begin{equation}
(4.16) \quad z_a = 1 - Y_1(pH) = a_0 - a_2 = \frac{1}{C_T} \left( \left[ \equiv sH_2O^+ \right] - \left[ \equiv sO^- \right] \right)
\end{equation}

This quantity is shown in Fig. 4.13 for the four surface types defined in Tab. 4.3.

The pH at which the surface charge is zero \((z_a = 0)\) defines the PZC (point of zero charge):

\begin{equation}
(4.17) \quad pH_{\text{pzc}} = \frac{1}{2} \left( pK_1 + pK_2 \right)
\end{equation}

PZC is equivalent to the isoelectric point when there is no adsorption of other ions than \(H^+/OH^-\) (pristine surface).
Acid Base Systems

REFERENCES


ADDITIONAL LINKS

PowerPoint Presentations:

- Acid-Base Systems
  www.slideshare.net/aqion/acidbase-systems
- Equivalence Points (EP and semi-EP)
  www.slideshare.net/aqion/equivalence-points
- Aqueous Speciation
  www.slideshare.net/aqion/aqueous-speciation
- Open vs Closed CO₂ System
  www.slideshare.net/aqion/open-vs-closed-carbonate-system
- Diprotic Acids & Equivalence Points
  www.slideshare.net/aqion/diprotic-acids-and-equivalence-points
- Buffer Systems & Titration
  www.slideshare.net/aqion/buffer-systems-and-titration
- Composite Carbonic Acid (Kinetics)
  www.slideshare.net/aqion/composite-carbonic-acid-and-carbonate-kinetics
A ACTIVITY & IONIC STRENGTH

A.1 Activity and Ionic Strength

A.1.1 Activity vs Concentration

Ions in solution interact with each other and with H₂O molecules. In this way, ions behave chemically like they are less concentrated than they really are (or measured). This effective concentration, which is available for reactions, is called activity:

\[
\text{activity} = \text{effective concentration} \leq \text{real concentration}
\]  

Notation. To distinguish between concentration and activity the following nomenclature is used

- molar concentrations are denoted by square brackets \([\ldots]\)
- activities are denoted by curly brackets \(\{\ldots\}\)

Thus, given an aqueous species \(j\), its concentration is abbreviated by \([j]\) and its activity by \(\{j\}\).

Activity Coefficient. Once we know the concentration \([j]\) of the aqueous species \(j\), we convert it to the activity \(\{j\}\) using the activity coefficient \(\gamma_j\):

\[
\{j\} = \gamma_j [j] \quad \text{(activity} = \gamma_j \times \text{concentration)}
\]  

As will be shown in § A.2, there are several approaches to calculate \(\gamma_j\). In the limit of infinitely dilute systems, the activity coefficient becomes 1:

\[
\text{ideal solution:} \quad \gamma_i = 1 \quad \text{(infinitely diluted system)}
\]

that is, activity and concentration coincide:

\[
\text{ideal solution:} \quad \{i\} = [i]
\]

\(\gamma_i\) corrects for electrostatic shielding by other ions; hence, \(\gamma_i\) depends on the ionic strength (defined in Eq. (A.5)).

A.1.2 Ionic Strength

The ionic strength of a solution is a function of the concentration of all ions present in a solution:

\[
I = \frac{1}{2} \sum_j z_j^2 [j]
\]
Here, \([j]\) and \(z_j\) are the molar concentration and the charge of ion \(j\). The sum is taken of all ions in the solution. Due to the square of \(z_j\), multivalent ions contribute strongly to the ionic strength. [Note: In literature, the ionic strength, \(I\), is also abbreviated by the Greek symbol \(\mu\).]

For comparison: typical ionic strengths of natural waters are:

- surface water: \(I = 0.001 – 0.005\) M
- potable water / groundwater: \(I = 0.001 – 0.02\) M
- seawater: \(I = 0.7\) M

### A.2 Activity Models

The step from molar concentrations (analytical data) to activities (that enter law-of-mass-action calculations) requires the calculation of activity coefficients \(\gamma_j\). For this task, several approaches are available, where each activity model has its own range of validity defined by the ionic strength \(I\), as shown here:

(A.6) **DEBYE-HÜCKEL (DH)** \[\log \gamma_j = -A z_j^2 \sqrt{I} \quad \text{for } I < 10^{-2.3} \text{ M}\]

(A.7) **Extended DH** \[\log \gamma_j = -A z_j^2 \left( \frac{\sqrt{I}}{1 + B \alpha_j \sqrt{I}} \right) \quad \text{for } I < 0.1 \text{ M}\]

(A.8) **DAVIES** \[\log \gamma_j = -A z_j^2 \left( \frac{\sqrt{I}}{1 + \sqrt{I} - 0.3I} \right) \quad \text{for } I \leq 0.5 \text{ M}\]

(A.9) **TRUESDELL-JONES** \[\log \gamma_j = -A z_j^2 \left( \frac{\sqrt{I}}{1 + B \alpha_j^0 \sqrt{I} + b_j I} \right) \quad \text{for } I < 1 \text{ M}\]

Here, \(z_j\) is the valence of ion \(j\). All quantities carrying the subscript \(j\) are ion-specific parameters (\(\alpha_j\), \(\alpha_j^0\) and \(b_j\)). On the other hand, the parameters \(A\) and \(B\) depend on temperature \(T\) and the dielectric constant \(\varepsilon\):

(A.10) \[A = 1.82 \cdot 10^6 (\varepsilon T)^{3/2}\]

(A.11) \[B = 3.281 \text{ M}^{1/2} \text{ nm}^{-1}\]

For standard conditions (water at 25 °C) we get:

(A.12) \[A = 0.5085 \text{ M}^{1/2}\]

(A.13) \[B = 3.281 \text{ M}^{1/2} \text{ nm}^{-1}\]

Please note the length unit: 1 nm = \(10^{-9}\) m = 1 Ångström.
B MATHEMATICAL RELATIONSHIPS

B.1 Approximations for \(a_j\)

B.1.1 Piecewise Approximation for \(\lg a_j\)

We start with the definition of \(a_0\) in Eq. (1.90):

\[
(B.1) \quad a_0^{-1} = \left(1 + \frac{k_1}{x} + \frac{k_2}{x^2} + \ldots + \frac{k_N}{x^N}\right) = \left(1 + \frac{K_1}{x} + \frac{K_1K_2}{x^2} + \ldots + \frac{K_1K_2\ldots K_N}{x^N}\right)
\]

In each pH interval, as defined in Eq. (1.103), we can approximate \(a_0\) as follows (because \(K_1 > K_2 > \ldots > K_N\)):

- in the 0th interval (\(pH < pK_1\)) where \(x > K_1\) \(\Rightarrow\) \(a_0^{-1} \approx 1\)
- in the 1st interval (\(pK_1 < pH < pK_2\)) where \(K_1 < x < K_2\) \(\Rightarrow\) \(a_0^{-1} \approx k_1/x\)
- in the 2nd interval (\(pK_2 < pH < pK_3\)) where \(K_2 < x < K_3\) \(\Rightarrow\) \(a_0^{-1} \approx k_2/x^2\)
- \ldots
- in the Nth interval (\(pH > pK_N\)) where \(x < K_N\) \(\Rightarrow\) \(a_0^{-1} \approx k_N/x^N\)

Thus, we can approximate \(\lg a_0\) in the \(i^{th}\) interval by

\[
(B.2) \quad \lg a_0 \approx \lg \frac{x^i}{k_i} = i \lg x - \lg k_i = -i \cdot pH + pk_i
\]

where \(pk_i = pK_1 + pK_2 + \ldots + pK_i\) and \(pk_0 = 0\).

The generalization of this result to all other \(a_j\) is simple. Again, we refer to Eq. (1.90):

\[
(B.3) \quad a_j = \left(\frac{k_j}{x^j}\right) a_0 \quad \Rightarrow \quad \lg a_j = \lg a_0 + j \cdot pH - pk_j
\]

Inserting the approximation in Eq. (B.2) for \(\lg a_0\) yields

\[
(B.4) \quad \lg a_j \approx (j - i) \cdot pH + (pk_i - pk_j) \quad \text{for the } i^{th} \text{ interval}
\]

This is a linear function of the pH value with an integer-valued slope \((j - i)\) and offset \((pk_i - pk_j)\).

---

\(^{36}\) see also left diagrams in Fig. 1.10 on page 33
Example. Phosphoric acid is defined by $N=3$ equilibrium constants ($pK_1 = 2.15$, $pK_2 = 7.21$, $pK_3 = 12.35$). Equation (B.4) is plotted in Fig. 1.11 on page 35. Each $\lg a_i$ consists of four linear segments, with one segment in each interval. In particular, we have:

- $a_0 \approx (0 - i) \, pH + (pK_i - pK_0)$ (blue dashed curve)

  with the following segments in the $i$th intervals:

  - $i = 0$: $\, (0 - 0) \, pH + (0 - 0) = 0 = 0$
  - $i = 1$: $\, (0 - 1) \, pH + (pK_1 - 0) = - pH + pK_1 = pH + 2.15$
  - $i = 2$: $\, (0 - 2) \, pH + (pK_2 - 0) = - 2 \, pH + (pK_1 + pK_2) = - 2 \, pH + 9.35$
  - $i = 3$: $\, (0 - 3) \, pH + (pK_3 - 0) = - 3 \, pH + (pK_1 + pK_2 + pK_3) = - 3 \, pH + 21.7$

- $a_1 \approx (1 - i) \, pH + (pK_i - pK_1)$ (brown dashed curve)

  with the following segments in the $i$th intervals:

  - $i = 0$: $\, (1 - 0) \, pH + (0 - pK_1) = pH - pK_1 = pH - 2.15$
  - $i = 1$: $\, (1 - 1) \, pH + (pK_1 - pK_1) = 0 = 0$
  - $i = 2$: $\, (1 - 2) \, pH + (pK_2 - pK_1) = - pH + pK_2 = - pH + 7.21$
  - $i = 3$: $\, (1 - 3) \, pH + (pK_3 - pK_1) = - 2 \, pH + (pK_2 + pK_3) = - 2 \, pH + 19.55$

- $a_2 \approx (2 - i) \, pH + (pK_i - pK_2)$ (green dashed curve)

  with the following segments in the $i$th intervals:

  - $i = 0$: $\, (2 - 0) \, pH + (0 - pK_2) = 2 \, pH - (pK_1 + pK_2) = 2 \, pH - 9.35$
  - $i = 1$: $\, (2 - 1) \, pH + (pK_1 - pK_2) = pH - pK_2 = pH - 7.21$
  - $i = 2$: $\, (2 - 2) \, pH + (pK_2 - pK_2) = 0 = 0$
  - $i = 3$: $\, (2 - 3) \, pH + (pK_3 - pK_2) = - pH + pK_3 = - pH + 12.35$

- $a_3 \approx (3 - i) \, pH + (pK_i - pK_3)$ (orange dashed curve)

  with the following segments in the $i$th intervals:

  - $i = 0$: $\, (3 - 0) \, pH + (0 - pK_3) = 3 \, pH - (pK_1 + pK_2 + pK_3) = 3 \, pH - 21.7$
  - $i = 1$: $\, (3 - 1) \, pH + (pK_1 - pK_3) = 2 \, pH - (pK_2 + pK_3) = 2 \, pH - 19.55$
  - $i = 2$: $\, (3 - 2) \, pH + (pK_2 - pK_3) = pH - pK_3 = pH - 12.35$
  - $i = 3$: $\, (3 - 3) \, pH + (pK_3 - pK_3) = 0 = 0$
B.1.2 Strong Acids

The ionization fractions $a_j$ of the general case are defined in Eq. (1.90). They become simpler for strong acids, where the condition $x/K_1 \rightarrow 0$ holds for all relevant $x$ (as discussed in Eq. (2.40)).

Let’s start with

$$a_0^{-1} = \left( 1 + \frac{K_2}{x} + \frac{K_3 K_2}{x^2} + \ldots \right)$$

$$= \frac{K_1}{x} \left( \frac{x}{K_1} + 1 + \frac{K_2}{x} + \ldots \right)$$

$$= \frac{K_1}{x} \left( 1 + \frac{K_2}{x} + \ldots \right) \quad \text{(because } x/K_1 \approx 0)$$

It yields

$$a_0 = \frac{x}{K_1} \left( 1 + \frac{K_2}{x} + \ldots \right)^{-1} = 0 \quad \text{(because } x/K_1 \approx 0)$$

According to the general formula $a_1 = (K_i/x) a_0$, the term in the brackets of Eq. (B.5) represents $a_1$:

$$a_1 = \left( 1 + \frac{K_2}{x} + \ldots \right)^{-1}$$

and we successively get

$$a_0 = 0$$

$$a_1 = \left( 1 + \frac{K_2}{x} + \frac{K_3 K_2}{x^2} + \ldots \right)^{-1} = \left( 1 + \frac{k_2}{x} + \frac{k_3}{x^2} + \ldots + \frac{k_N}{x^{N-1}} \right)^{-1}$$

$$a_j = \left( \frac{k_j}{x^{j-1}} \right) a_i \quad \text{for } j > 1$$

with the “redefined” cumulative acidity constants $k_j$

$$k_0 = 0, \ k_1 = 1, \ k_2 = K_2, \ldots, \ k_N = K_2 K_3 \ldots K_N$$

Note that $K_1$ disappeared from all equations.
B.2 Polynomials in x

B.2.1 The Subsystem H\textsubscript{N}A

The ionization fractions \(a_j\) of an \(N\)-protic acid are functions of \(x\) (\(j = 1\) to \(N\)):

\[
 a_j(x) = \left(\frac{k_j}{x^j}\right) a_0 \quad \text{with} \quad a_0(x) = \left(1 + \frac{k_1}{x} + \frac{k_2}{x^2} + \ldots + \frac{k_N}{x^N}\right)^{-1}
\]

The task is to solve it for \(x\), that is, to find a formula that calculates \(x\) for a given value of \(a_j\). This will lead to a polynomial of order \(N\) in \(x\).

For this purpose, let’s start with \(a_0\) and transform it in the following way:

\[
 a_0^{-1} = \left(1 + \frac{k_1}{x} + \frac{k_2}{x^2} + \ldots\right) \cdot \frac{x^N}{a_0} = x^N + k_1 x^{N-1} + \ldots + k_N = \sum_{j=0}^{N} k_j x^{N-j}
\]

It yields a polynomial of order \(N\) in \(x\) (i.e. the highest power of \(x\) is \(N\)):

\[
 0 = \text{const} \cdot x^N + k_1 x^{N-1} + \ldots + k_N \quad \text{with} \quad \text{const} = -\left(\frac{1-a_0}{a_0}\right)
\]

The result can be generalized to any other \(a_j\). To do this, insert \(a_0 = (x^j/k_j) \cdot a_j\) into the left-hand side of Eq. (B.13):

\[
 \left(\frac{k_j}{a_j}\right) x^{N-j} = \sum_{i=0}^{N} k_i x^{N-i}
\]

Again, the obtained polynomial is of order \(N\):

\[
 0 = \text{const} \cdot x^{N-j} + \sum_{i=j}^{N} k_i x^{N-i} \quad \text{with} \quad \text{const} = -\left(\frac{1-a_j}{a_j}\right) k_j
\]

For \(j = 0\) (and with \(k_0 = 1\)), this formula reduces to Eq. (B.14).

B.2.2 The General Case: H\textsubscript{N}A + H\textsubscript{2}O + Strong Base

The titration of a polyprotic acid \(\text{H}_N\text{A}\) by a strong base is described by Eq. (2.32), which we now write as

\[
 Y_1(x) = n - w(x)/C_T \quad \text{with} \quad n = \frac{C_h}{C_T}
\]

For \(Y_1\) on the left-hand side, we apply Eq. (1.113). That is,
(B.18) \[ Y_j(x) = \frac{\sum_{j=0}^{N} j \cdot k_j x^{N-j}}{\sum_{j=0}^{N} k_j x^{N-j}} \]

Inserting it into Eq. (B.17) and multiplying both sides by \( \Sigma k_j x^{N-j} \) yields:

\[
\sum_{j=0}^{N} j \cdot k_j x^{N-j} = \left\{ n - \frac{W}{C_T} \right\} \sum_{j=0}^{N} k_j x^{N-j} \\
0 = \sum_{j=0}^{N} \left\{ j - n + \frac{W}{C_T} \right\} k_j x^{N-j} \\
= \sum_{j=0}^{N} \left\{ C_T (j-n) + w \right\} k_j x^{N-j} \quad \text{(both sides are multiplied by } C_T) \\
= \sum_{j=0}^{N} \left\{ C_T (j-n) - x + \frac{K_w}{x} \right\} k_j x^{N-j} \quad \text{(Eq. (2.34) is used for } w) 
\]

After multiplication of both sides by \(-x\), we get a polynomial of order \( N+2 \) in \( x \):

(B.19) \[ 0 = \sum_{j=0}^{N} \left( x^2 + (n-j) C_T x - K_w \right) k_j x^{N-j} \]

To show that the polynomial is indeed of order \( N+2 \), you can rewrite Eq. (B.19) as

(B.20) \[ 0 = \sum_{j=0}^{N+2} f_j x^{N+2-j} \quad \text{with } f_j = k_j + k_{j+1} (n+1-j) C_T - K_w k_{j+2} \]

The combined equilibrium constants \( k_j \) are defined in Eq. (1.49). The first and the last coefficients of this polynomial are: \( f_0 = 1 \) and \( f_{N+2} = -K_w K_1 K_2 \ldots K_N \). [Note: \( k_j \) is per definition zero for negative values of \( j \).]

**Special Case:** \( C_T \to \infty \). In the so-called “pure-acid case”, Eq. (B.19) simplifies to a polynomial of order \( N \):

(B.21) \[ 0 = \sum_{j=0}^{N} (n-j) k_j x^{N-j} \]

**Zwitterionic Acids.** The generalization to zwitterionic acids \( H_N A^{\pm Z} \) is simple. Replace the constant \( n \) by the constant \( n + Z \). That’s all. The generalized form of Eq. (B.19) is

(B.22) \[ 0 = \sum_{j=0}^{N} \left( x^2 + (n+Z-j) C_T x - K_w \right) k_j x^{N-j} \]

We are still dealing with a polynomial of the same order \( N+2 \).
B.3 Simple Relationships between $a_j$ and $Y_L$

B.3.1 Relationships for $Y_L$

The moments $Y_L$ are defined as finite sums over the ionization fractions $a_j$:

\[ Y_L = \sum_{j=0}^{N} j^L a_j = 0^L a_0 + 1^L a_1 + 2^L a_2 + \ldots + N^L a_N \]

with the special case $Y_0 = 1$ (mass balance) – see Eqs. (1.95) and (1.111).

One simple relationship between $a_j$ and $Y_1$ can be established in the following sequence of steps:

\[
\begin{align*}
n &= n \\
n Y_0 &= n \quad \text{(because $Y_0 = 1$)} \\
n Y_0 - Y_1 &= n - Y_1 \quad \text{($Y_1$ subtracted from both sides)} \\
n \sum a_j - \sum j a_j &= n - Y_1 \quad \text{(using Eq. (B.23) on left-hand side)}
\end{align*}
\]

which finally yields the result:

\[ \sum_{j=0}^{N} (n-j) a_j = n - Y_1 \quad \text{or} \quad \sum_{j=0}^{N} (n-j) [j] = (n - Y_1) C_T \]

**Equivalence Points.** The two types of equivalence points are characterized by (c.f. Eqs. (1.101) and (1.102)):

\[
\begin{align*}
\text{semi-EP}_j: & \quad pH = pK_j \quad \Rightarrow \quad a_j = a_{j-1} = \frac{1}{2} \\
\text{EP}_j: & \quad pH_j = \frac{1}{2} (pK_j + pK_{j+1}) \quad \Rightarrow \quad a_j (pH_j) \approx 1
\end{align*}
\]

all other ionization fractions are almost zero. In this way, the whole sum in Eq. (B.23) is reduced to one or two terms:

\[
\begin{align*}
Y_L (pK_j) &= (j-1)^L a_{j-1} + j^L a_j = \frac{1}{2} \{ (j-1)^L + j^L \} \quad \text{for } L \geq 1 \\
Y_L (pH_j) &= j^L a_j \approx j^L \quad \text{for } L \geq 1
\end{align*}
\]

B.3.2 Maximum of $a_j$

The maximum (extrema) of an ionization fraction $a_j$ is obtained under the condition that its first derivative should vanish:

\[ \frac{da_j}{d pH} = 0 \quad \Leftrightarrow \quad \text{extremum of } a_j \]

According to Eq. (B.48) on page 116, this is equivalent to the condition:

\[ (j - Y_1) a_j = 0 \quad \text{or} \quad j - Y_1 = 0 \]
From Eq. (B.24) one gets

\[(B.31) \quad \sum_{i=0}^{N} (j-i) a_i = 0\]

or, more explicitly,

\[(B.32) \quad -j a_0 - (j-1) a_1 - ... - a_{j-1} + 0 + a_{j+1} + ... + (N-j) a_N = 0\]

From the viewpoint of \(a_j\), only its two neighbors \(a_{j-1}\) and \(a_{j+1}\) are of relevance (all other are nearly zero). Thus, Eq. (B.31) collapses to \(-a_{j-1} + a_{j+1} = 0\), that is

\[(B.33) \quad \text{maximum of } a_j \iff a_{j-1} = a_{j+1} \quad \text{or} \quad \frac{a_{j+1}}{a_{j-1}} = 1\]

The pH at the maximum is obtained from Eq. (1.54):

\[(B.34) \quad \frac{a_{j+1}}{a_{j-1}} = \frac{[j+1]}{[j-1]} = \frac{K_j K_{j+1}}{x^2} \quad \Rightarrow \quad x_{\text{max}} = (K_j K_{j+1})^{1/2}\]

According to Eq. (1.77), the ionization fraction \(a_j\) has its maximum at the equivalence point:

\[(B.35) \quad \text{maximum of } a_j \quad \text{at EP}_j \quad \text{with} \quad \text{pH} = \frac{j}{2}(pK_j + pK_{j+1})\]

From mass conservation, i.e. Eq. (1.95), one gets the value of \(a_j\) at the maximum as:

\[(B.36) \quad a_j(x_{\text{max}}) = 1 - a_{j-1} - a_{j+1} = 1 - 2a_{j-1}\]

which, in most cases, is close to 1.

### B.4 Derivatives with Respect to pH

#### B.4.1 Basic Equations

Given is

\[(B.37) \quad x = \{H^+\} = 10^{-\text{pH}} = e^{-(\ln 10) \text{pH}}\]

The first and the \(k\)-th derivative of \(x\) with respect to \(\text{pH}\) are:

\[(B.38) \quad \frac{dx}{d\text{pH}} = (-\ln 10) x\]

\[(B.39) \quad \frac{d^k x}{d\text{pH}^k} = (-\ln 10)^k x\]
This result can be used to differentiate any given function, \( f(x) \), with respect to pH (by application of the chain rule):

\[
\frac{df(x)}{dpH} = \frac{dx}{dpH} \frac{df(x)}{dx} = (-\ln 10) x \frac{df(x)}{dx}
\]

\textit{Example 1.} For \( w(x) = K_w/x - x \), introduced in Eq. (0.8), we get:

\[
\frac{dw(x)}{dpH} = \ln 10 (K_w/x + x) = \ln 10 (w + 2x)
\]

\[
\frac{d^2w(x)}{dpH^2} = (\ln 10)^2 (w + 2x - 2x) = (\ln 10)^2 w
\]

All higher derivatives repeat this pattern:

\[
\frac{d^k w(x)}{dpH^k} = (\ln 10)^k \left\{ \begin{array}{ll} w & \text{for } k \text{ even} \\ w + 2x & \text{for } k \text{ odd} \end{array} \right.
\]

\textit{Example 2.} Let’s consider the function, \( g = 1/a_0 \), that is

\[
g(x) = 1 + \frac{k_1}{x} + \frac{k_2}{x^2} + \cdots + \frac{k_N}{x^N}
\]

Its first derivative is then given by

\[
\frac{dg(x)}{dpH} = \ln 10 \left( \frac{k_1}{x} + \frac{k_2}{x^2} + \cdots + N \frac{k_N}{x^N} \right) = \ln 10 \left( \frac{a_1 + 2a_1 + \cdots + Na_N}{a_0} \right)
\]

where on the right-hand side Eq. (1.60) was applied. Using the definition of \( Y_1 \) in Eq. (1.112), it yields the interesting result:

\[
\frac{dg(x)}{dpH} = \frac{d}{dpH} \frac{1}{a_0} = \ln 10 \frac{Y_1}{a_0}
\]
B.4.2 First Derivative of $a_j$ and $Y_L$

We start with the first derivative of $a_0$ by applying the results of the last example (particularly Eq. (B.46)):

\[
\frac{da_0(x)}{dpH} = \frac{d}{dpH} \frac{1}{g(x)} = -\frac{1}{g^2} \frac{dg(x)}{dpH} = -a_0^2 \frac{(ln10) Y_j}{a_0} = -(ln10) Y_j a_0
\]

In the same way, we get from $a_j = (k_j/x^j) a_0$ the general result for any ionization coefficient $a_j$:

\[
\frac{da_j(x)}{dH} = -ln10 \ (j - Y_j) a_j
\]

**Moments.** Applying the above results to the sums over $a_i$ yields

\[
\frac{d}{dpH} \sum_{j=0}^{N} a_j = \ln10 \ \sum_{j=0}^{N} (j - Y_j) a_j = \ln10 (Y_i - Y_j) = 0
\]

\[
\frac{d}{dpH} \sum_{j=0}^{N} j a_j = \ln10 \ \sum_{j=0}^{N} j (j - Y_j) a_j = \ln10 (Y_2 - Y_i^2)
\]

The first relation, which gives zero, is obvious because it represents the derivation of a constant, namely $d1/dpH = 0$. Eq (B.50) is nothing but the first derivative of $Y_1$:

\[
\frac{dY_1(x)}{dH} = \ln10 (Y_2 - Y_i^2)
\]

In the same way, for all higher moments $Y_L$ we get:

\[
\frac{dY_L(x)}{dH} = \ln10 \sum_{j=0}^{N} j^L (j - Y_j) a_j = \ln10 (Y_{L+1} - Y_i Y_L)
\]
B.4.3 Higher Derivatives of $a_j$ and $Y_l$

The 2\(^{nd}\) derivative of $a_j$ is given by

$$\frac{d^2 a_j(x)}{dpH^2} = -\ln 10 \frac{da_j(x)}{dpH} \frac{(j-Y_l)}{a_j}$$

$$= -\ln 10 \left[ a_j \frac{d}{dpH} (j-Y_l) + (j-Y_l) \frac{da_j}{dpH} \right] \quad \text{(now use Eq. (B.51))}$$

$$= -\ln 10 \left[ a_j \left\{ -\ln 10 (Y_2 - Y_1^2) \right\} + (j-Y_l) \left\{ -\ln 10 (j-Y_l) \right\} a_j \right]$$

$$= (\ln 10)^2 \left\{ (Y_2 - Y_1^2) + (j-Y_l)^2 \right\} a_j$$

(B.53) $$= (\ln 10)^2 \left\{ Y_2 - 2jY_l + j^2 \right\} a_j$$

The second derivative of $Y_1$ is given by

(B.54) $$\frac{d^2 Y_1}{dpH^2} = \ln 10 \frac{d}{dpH} (Y_2 - Y_1^2)$$

$$= (\ln 10)^2 \left( Y_3 - Y_1Y_2 - 2Y_1 (Y_2 - Y_1^2) \right)$$

$$= (\ln 10)^2 \left( Y_3 - 3Y_1Y_2 + 2Y_1^3 \right)$$

The third derivative of $Y_1$ is:

(B.55) $$\frac{d^3 Y_1}{dpH^3} = (\ln 10)^2 \frac{d}{dpH} (Y_3 - 3Y_1Y_2 + 2Y_1^3)$$

$$= (\ln 10)^3 \left\{ (Y_4-Y_1Y_3) - 3Y_2 (Y_2 - Y_1^2) - 3Y_1 (Y_3 - Y_1Y_2) + 6Y_1^2 (Y_2 - Y_1^2) \right\}$$

$$= (\ln 10)^3 \left\{ Y_4 - Y_1 (4Y_3 - 3Y_1Y_2) - 3(Y_2 - 2Y_1^2) (Y_2 - Y_1^2) \right\}$$
C PROTON BALANCE

C.1 Special Case: Diprotic Acid

The proton balance is often used in acid-base theory. It is a balance between the species that have *excess* protons versus those that are *deficient* in protons (*relative* to a defined proton reference level – PRL):

\[(C.1) \quad TOTH = \text{excess protons} - \text{deficient protons}\]

**Subsystem H₂O.** The simplest case is pure water with its three species H⁺, OH⁻, and H₂O. Choosing H₂O as the reference level, the species H⁺ is enriched in 1 proton (excess proton), while OH⁻ is depleted in 1 proton (deficient proton):

\[(C.2) \quad \text{PRL} \quad \text{excess protons} = \text{deficient protons} \]

\[
\begin{align*}
\text{H}_2\text{O} & \quad [\text{H}^+] = [\text{OH}^-]
\end{align*}
\]

The proton balance of the subsystem ‘pure water’ is then expressed by:

\[(C.3) \quad TOTH|_w = [\text{H}^+] - [\text{OH}^-] = -w(x)\]

where \(w(x)\) was introduced in Eq. (1.131). In fact, for pure water we have \(TOTH|_w = 0\).

Because water is ever-present in any acid-base system, H⁺ and OH⁻ are always a part of the proton balance – see Eqs. (C.15) and (C.16) below.

**Subsystem H₂A.** The diprotic acid H₂A has three distinct reference levels denoted by \(n = 0, 1,\) and 2:

\[
\begin{align*}
\text{PRL} & \quad \text{excess protons} & \quad \text{deficient protons} \\
(C.4) & \quad n = 0: \quad \text{H}_2\text{A} & \quad 0 & \quad [\text{HA}^-] + 2[A^-] & \quad TOTH|_0 = -[\text{HA}^-] - 2[A^-] \\
(C.5) & \quad n = 1: \quad \text{HA}^- & \quad [\text{H}_2\text{A}] & \quad [A^-] & \quad TOTH|_1 = [\text{H}_2\text{A}] - [A^-] \\
(C.6) & \quad n = 2: \quad A^- & \quad 2[\text{H}_2\text{A}] + [\text{HA}^-] & \quad 0 & \quad TOTH|_2 = 2[\text{H}_2\text{A}] + [\text{HA}^-]
\end{align*}
\]

How to write down these equations? In Eq. (C.4), H₂A is the reference level. There are no species that have more protons than H₂A, hence, there is nothing to add to the left-hand side. Conversely, HA⁻ is deficient by 1 proton and A⁻ by 2 protons; therefore, both species enter the right-hand side. (If a species has lost 2 protons relative to PRL, its concentration is multiplied by 2.)

In Eq. (C.5), HA⁻ is the reference level. From this perspective, H₂A has 1 excess proton (species enters the left-hand side), while A⁻ is deficient by 1 proton (species enters the right-hand side).

In Eq. (C.6), A⁻ is the reference level. Now, H₂A has 2 excess protons and HA⁻ has 1 excess proton (both species enter the left-hand side); but there are no species that have less protons than A⁻ (i.e. no carbonate species enters the right-hand side).
Taken together, the three PRL of the subsystem ‘diprotic acid’, denoted by $H_{2-n}A^n$ (for $n = 0, 1, 2$), yield the following proton balance equation:

\[
\text{PRL} \quad \text{TOT H} = \text{excess protons} - \text{deficient protons}
\]

(C.7)  \[ H_{2-n}A^n \quad \text{TOT H} |_n = n [H_2A] + (n-1) [HA] + (n-2) [A^{-2}] = 0 \]

This one-liner comprises all three equations (C.4) to (C.6). [Example: In the case of a carbonic acid system the three PRL correspond to $H_2CO_3$, $HCO_3^-$, and $CO_3^{2-}$.

Fig. C.1 tries to illustrate how the choice of the origin (yellow dots) of a coordinate system (x axis: species; y axis: number of excess/deficient protons) alters the proton balance equation.

For example, given a mono-, di-, and tri-protic acid we have for $n = 0$:

(C.8)  \[ N = 1: \quad \text{TOT H} |_0 = - [A^{-1}] \]

(C.9)  \[ N = 2: \quad \text{TOT H} |_0 = - [HA^{-1}] - 2[A^{-2}] \]

(C.10)  \[ N = 3: \quad \text{TOT H} |_0 = - [H_2A^{-1}] - 2[HA^{-2}] - 3[A^{-3}] \]

$H_2A + H_2O$. The combined system as the sum of subsystem ‘pure water’ and subsystem ‘diprotic acid’ obeys the proton balance for the three PRL at $H_{2-n}A^n$ (with $n = 0, 1, 2$):

\[
\text{TOT H} |_w + \text{TOT H} |_n = [H^+] - [OH^-] + n [H_2A] + (n-1) [HA] + (n-2) [A^{-2}] = 0
\]

(C.11)

The two species, $H^+$ and $OH^-$, that appear in this equation trace back to the $H_2O$-reference level in Eq. (C.2). They have a permanent place in any $H_2O$ containing system.

One fact is of relevance: The PRLs are usually chosen at equivalence points $EP_n$ (with integer n). There is a direct correspondence between PRL at $n$ and $EP_n$. 

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C.2 General Case: N-Protic Acid

Subsystem $H_NA$. It’s not difficult to generalize the results of the previous paragraph to an $N$-protic acid $H_NA$. It has $N+1$ distinct PRL (i.e. for each species $H_{N-n}A^n$ one proton reference level, or the corresponding EP$_n$):

(C.12) PRL $H_{N-n}A^n$: $TOT$ $H|_n^{(acid)} = n[H_NA] + (n-1)[H_{N-1}A] + (n-2)[H_{N-2}A^2] + ... + (n-N)[A^{-N}] = 0$

or in compact notation:

(C.13) PRL $H_{N-n}A^n$: $TOT$ $H|_n^{(acid)} = \sum_{j=0}^{N} (n-j)[j] = 0$

According to Eq. (B.24) in the Appendix, the last equation can also be expressed by

(C.14) $TOT$ $H|_n^{(acid)} = (n - Y_1)C_T = 0$

$H_NA + H_2O$. The proton balance of the whole system is then the sum of Eq. (C.3) and Eq. (C.14):

(C.15) $TOTH|_n = TOTH|_w + TOT$ $H|_n^{(acid)}$

which is equivalent to

(C.16) $TOTH|_n = -w + (n - Y_1)C_T = 0$

This proton-balance equation, in the form of $0 = [H^+] - [OH^-] + n C_T - Y_1 C_T$, is equivalent to Eq. (2.25) and Eq. (2.31) in § 2.2.

Charge Balance. The concept of proton balance is more general than the concept of charge balance (electro-neutrality). Only in the special case of $n=0$ both charge balance and proton balance coincide:

(C.17) *proton balance* $TOTH|_n = -w + (n - Y_1)C_T = 0$ $\Rightarrow$ $w + Y_1C_T = nC_T$

(C.18) *charge balance* $TOTH|_0 = -w - Y_1C_T = 0$ $\Rightarrow$ $w + Y_1C_T = 0$

The last equation is equivalent to:

(C.19) *charge balance* $0 = [H^+] - [OH^-] - [H_{N-1}A] - 2[H_{N-2}A^2] - ... - N[A^{-N}]$