Short Lecture 2017

Acid-Base Systems & pH Buffers

(Mathematical Background of Simple Closed-Form Expressions)

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## Physico-Chemical Quantities

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<th>Description</th>
<th>SI Unit</th>
</tr>
</thead>
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<tr>
<td>(a_j)</td>
<td>ionization fractions, (a_j = [j]/C_T)</td>
<td>–</td>
</tr>
<tr>
<td>Alk</td>
<td>total alkalinity</td>
<td>mol/L</td>
</tr>
<tr>
<td>ANC</td>
<td>acid-neutralizing capacity</td>
<td>mol/L</td>
</tr>
<tr>
<td>BNC</td>
<td>base-neutralizing capacity</td>
<td>mol/L</td>
</tr>
<tr>
<td>(\beta)</td>
<td>buffer intensity (normalized), (\beta = dC_B/d\text{pH} = C_T\beta)</td>
<td>–</td>
</tr>
<tr>
<td>(\beta_C)</td>
<td>buffer intensity, (\beta_C = \frac{dC_B}{d\text{pH}} = C_T\beta)</td>
<td>mol/L</td>
</tr>
<tr>
<td>(C_A)</td>
<td>concentration of <strong>strong</strong> monoprotic acid (C_A = [HX]_T)</td>
<td>mol/L</td>
</tr>
<tr>
<td>(C_B)</td>
<td>concentration of <strong>strong</strong> monoacidic base (C_B = [BOH]_T)</td>
<td>mol/L</td>
</tr>
<tr>
<td>(C_T)</td>
<td>total concentration of (N)-protic acid: (C_T = [H_NA]_T)</td>
<td>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>
<td>–</td>
</tr>
<tr>
<td>(E_{P_n})</td>
<td>equivalence point (for integer and half-integer (n))</td>
<td>–</td>
</tr>
<tr>
<td>(I)</td>
<td>ionic strength</td>
<td>mol/L</td>
</tr>
<tr>
<td>(\gamma_j)</td>
<td>activity correction for species (j)</td>
<td>–</td>
</tr>
<tr>
<td>(\Delta G^0)</td>
<td>GIBBS energy change</td>
<td>J/mol</td>
</tr>
<tr>
<td>(\hat{j})</td>
<td>index denoting the aqueous species (j), (j = 0, 1, \ldots N)</td>
<td>–</td>
</tr>
<tr>
<td>([j])</td>
<td>molar concentration of aqueous species (j): ([j] = [H_{N_j}A^j])</td>
<td>mol/L</td>
</tr>
<tr>
<td>([i])</td>
<td>activity of aqueous species (j): ([i] = {H_{N_j}A^j})</td>
<td>mol/L</td>
</tr>
<tr>
<td>(K_a)</td>
<td>acidic constant (general abbreviation)</td>
<td>mol/L</td>
</tr>
<tr>
<td>(\tilde{K}_a)</td>
<td>conditional acidic constant (non-thermodynamic quantity)</td>
<td>mol/L</td>
</tr>
<tr>
<td>(K_j)</td>
<td>acidity constant of dissociation step (j)</td>
<td>mol/L</td>
</tr>
<tr>
<td>(k_i)</td>
<td>cumulative acidity constant, e.g. (k_i = K_1K_2...K_j)</td>
<td>(mol/L)(^i)</td>
</tr>
<tr>
<td>(K_w)</td>
<td>equilibrium constant of autoprotolysis (self-ionization of (H_2O))</td>
<td>(mol/L)(^2)</td>
</tr>
<tr>
<td>(n)</td>
<td>equivalent fraction of titration, (n = (C_B - C_A)/C_T)</td>
<td>–</td>
</tr>
<tr>
<td>(N)</td>
<td>number of protons ((\text{H}^+)) of the (N)-protic acid (H_NA)</td>
<td>–</td>
</tr>
<tr>
<td>(\text{pH})</td>
<td>(-\lg {\text{H}^+} = -\lg x)</td>
<td>–</td>
</tr>
<tr>
<td>(\text{pH}_j)</td>
<td>(\frac{1}{2}(pK_j + pK_{j+1})) as pH of equivalence point (E_{P_j})</td>
<td>–</td>
</tr>
<tr>
<td>(pK_j)</td>
<td>(-\lg k_j)</td>
<td>–</td>
</tr>
<tr>
<td>(pK_j')</td>
<td>(-\lg k_j')</td>
<td>–</td>
</tr>
<tr>
<td>(T)</td>
<td>temperature in Kelvin</td>
<td>K</td>
</tr>
<tr>
<td>(\text{R})</td>
<td>gas constant ((\text{R} = 8.314\ \text{J} \text{mol}^{-1}\text{K}^{-1}))</td>
<td>J mol(^{-1}\text{K}^{-1})</td>
</tr>
<tr>
<td>(x)</td>
<td>activity of (\text{H}^+), i.e. (x = [\text{H}^+])</td>
<td>mol/L</td>
</tr>
<tr>
<td>(Y_L)</td>
<td>(L^{th}) moment constructed from (a_j): (Y_L = \sum_j j^L a_j)</td>
<td>–</td>
</tr>
<tr>
<td>(w(x))</td>
<td>‘pure water balance’: (w \equiv [\text{OH}^-] - [\text{H}^+] = K_w/x - x)</td>
<td>mol/L</td>
</tr>
<tr>
<td>(z_j)</td>
<td>charge of species (j)</td>
<td>–</td>
</tr>
<tr>
<td>(Z)</td>
<td>charge of highest protonated acid species</td>
<td>–</td>
</tr>
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### Units and Conversions:

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<thead>
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<th>Symbol</th>
<th>Description</th>
<th>Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>(L)</td>
<td>liter ((1 \text{L} = 1 \text{dm}^3 = 10^{-3} \text{m}^3))</td>
<td>–</td>
</tr>
<tr>
<td>(M)</td>
<td>molarity ((1 \text{M} = 1 \text{mol/L}))</td>
<td>–</td>
</tr>
<tr>
<td>(\text{mM})</td>
<td>(1 \text{mM} = 10^{-3} \text{mol/L})</td>
<td>–</td>
</tr>
<tr>
<td>(\lg x)</td>
<td>decadic logarithm ((= \log_{10} x))</td>
<td>(\text{conversion: } \lg x = (\ln x)/(\ln 10))</td>
</tr>
<tr>
<td>(\ln x)</td>
<td>natural logarithm ((= \log_e x))</td>
<td>(\text{conversion: } \ln x = (\ln 10)(\lg x))</td>
</tr>
<tr>
<td>(\ln 10)</td>
<td>(= 2.303)</td>
<td>–</td>
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Definitions & Abbreviations

Acid Species. The polyprotic acid $H_NA$ has $N+1$ aqueous species, abbreviated by:

\begin{equation}
[j] = [H_{N-j}A^{Z-j}] \quad \text{for} \quad j = 0, 1, 2, \ldots N
\end{equation}

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

\begin{equation}
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{equation}

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

\begin{equation}
C_T = [H_NA]_T = \sum_{j=0}^{N} [j] \quad \text{(mass balance)}
\end{equation}

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

\begin{equation}
a_j = \frac{[j]}{C_T} \quad \text{for} \quad j = 0, 1, 2, \ldots N
\end{equation}

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 $x$:

\begin{equation}
x = \{H^+\} = 10^{-\text{pH}} \quad \Leftrightarrow \quad \text{pH} = -\log x
\end{equation}

$H_2O$. The self-ionization of water (autoprotolysis) is defined by

\begin{equation}
H_2O = H^+ + OH^- \quad \text{with} \quad K_w = \{H^+\}\{OH^-\}
\end{equation}

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

\begin{equation}
[OH^-] \approx \{OH^-\} = K_w/x
\end{equation}

In this context we introduce the quantity

\begin{equation}
w \equiv [OH^-] - [H^+] \approx \frac{K_w}{x} - x
\end{equation}

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

---

\(^1\) This approximation is justified for acidic 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.

Three acid-base concepts:

<table>
<thead>
<tr>
<th></th>
<th>acid</th>
<th>base</th>
</tr>
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<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.

![Fig. 0.1 Relationship between acid-base concepts](image)

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 $H^+$ 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 $H_NA$ 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 $N=6$ 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 a high number). 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 ($H_NA+H_2O$) 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 H₃O⁺) when dissolved in water:

(1.1) \[ HA = H^+ + A^- \]
(1.2) \[ HA + H_2O = H_3O^+ + A^- \]

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 H₃O⁺.

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, NH₃OH, ...)
BRØNSTED-LOWRY base: H⁺ acceptor (e.g. OH⁻, Cl⁻, NH₃, ...)

This allows all ARRHENIUS bases² to be combined into a single H⁺ acceptor equation:

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

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:

(1.4) \[ HA + OH^- = H_2O + A^- \]
(1.5) \[ \text{acid} + \text{base} = \text{conjugate acid} + \text{conjugate base} \]
\[ \text{(of base OH⁻)} \quad \text{(of acid HA)} \]

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

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⁺, NH₄⁺ etc.
**Acid Base Systems**

*Autoprotolysis.* One very special case of Eq. (1.4) is the self-dissociation of water:

(1.7) \[ \text{H}_2\text{O} + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{OH}^- \]

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 *acidity constant.* There are two types of acidity constants:

(1.8) acidity constant:

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

(based on activities)

(1.9) *conditional* acidity constant:

\[ \varepsilon K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \]  

(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):

(1.10) activity (effective concentration):

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

The activity corrections increase with the ionic strength \( I \) of the solution. In *ideal or near-ideal* solutions (i.e. diluted systems) we have \( I \approx 0 \) 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 \( \text{H}^+ \), where we use the activity. Thus, the obtained results are valid either in dilute systems or by using the *conditional* acidity constant \( \varepsilon K_a \). We consider it as an assumption that applies to the whole text (and skip the small-letter superscript \( c \) on \( \varepsilon K_a \)).

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

(1.11) \[ \lg K_a = \lg \{\text{H}^+\} + \lg \{\text{A}^-\} - \lg \{\text{HA}\} \]

The negative decadic logarithm of the acidity constant is then abbreviated by

(1.12) \[ pK_a = -\lg K_a \]

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

(1.13) \[ pK_a = \text{pH} - \lg \{\text{A}^-\} + \lg \{\text{HA}\} \]

This can also be written as the so-called **HENDERSON-HASSELBACH equation:**

---

3 More precisely, it is a *mixed-type* conditional constant because we use the activity for \( \text{H}^+ \) and concentrations for all other components (within the mass-action law).
(1.14) \[ \text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]}{[\text{HA}]} = \text{pK}_a + \log \frac{[\text{proton acceptor}]}{[\text{proton donor}]} \]

Here, the term \( \log [\text{A}^-]/[\text{HA}] \) vanishes for equal concentrations. In other words, the \( \text{pK}_a \) value is just the \( \text{pH} \) at which the amount of both species is equal, i.e. at which 50% of the species \( \text{HA} \) is dissociated into species \( \text{A}^- \). Therefore, it’s no surprise that the \( \text{pK}_a \) value is also called the ‘semi-equivalence point’ – more on 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 \( \text{K}_a \) based ranking (cf. Eq. (1.20) below).

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

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

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

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

An example for the relationship between several 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 \( \text{H}^+ \). 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 \( K_1 \) (= \( \text{K}_a \)), a *diprotic* acid by two acidity constants (\( K_1 \), \( K_2 \)), and a *triprotic* acid by three acidity constants (\( K_1 \), \( K_2 \), and \( K_3 \)):

(1.17) \[ 1^{\text{st}} \text{dissociation step:} \quad \text{H}_3\text{A} = \text{H}^+ + \text{H}_2\text{A}^- \quad \text{K}_1 \]

(1.18) \[ 2^{\text{nd}} \text{dissociation step:} \quad \text{H}_2\text{A}^- = \text{H}^+ + \text{HA}^2^- \quad \text{K}_2 \]

(1.19) \[ 3^{\text{rd}} \text{dissociation step:} \quad \text{HA}^2^- = \text{H}^+ + \text{A}^3^- \quad \text{K}_3 \]
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**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:

(1.20) \( K_1 > K_2 > K_3 \) or \( pK_1 < pK_2 < pK_3 \)

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 \( pK = -\log K \) of 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 \( C_T \equiv [HA]_T \) (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:

(1.21) \( C_T = [HA] + [A^-] \)

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

<table>
<thead>
<tr>
<th></th>
<th>strong acid</th>
<th>weak acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>acidity constant</td>
<td>( K_a \gg 1 )</td>
<td>( K_a \leq 1 )</td>
</tr>
<tr>
<td>( pK_a = -\log 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-cut 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:

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

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).

---

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

A weak acid and a dilute acid are two different things. 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 $\Leftrightarrow$ small $K_a$ $\leftrightarrow$ large $K_a$
- dilute acid $\leftrightarrow$ concentrated acid $\Leftrightarrow$ 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 small $K_a$ $\leftrightarrow$ large $K_a$ (positive $pK_a$ $\leftrightarrow$ negative $pK_a$)</td>
<td>diluted acid $\leftrightarrow$ concentrated acid 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 (cannot be changed)</td>
<td>control parameter (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 turn to the most general case let us start with the simple case of diprotic acids.

When a diprotic acid H₂A is added to pure water, the equilibrium state is characterized by five dissolved species: H⁺, OH⁻, H₂A, HA⁻, and A²⁻ (see Fig. 1.3). Thus, five equations are required for its mathematical description:

\[
\begin{align*}
K_w &= \{H^+\} \{OH^-\} \quad & \text{(self-ionization of H₂O)} \\
K_1 &= \{H^+\} \{HA^-\} / \{H₂A\} \quad & \text{(1st diss. step)} \\
K_2 &= \{H^+\} \{A^-²\} / \{HA^-\} \quad & \text{(2nd diss. step)} \\
C_T &= [H₂A] + [HA^-] + [A^-²] \quad & \text{(mass balance)} \\
0 &= [HA^-] + 2[A^-²] + [OH^-] - [H^+] \quad & \text{(charge balance)}
\end{align*}
\]

The first three equations are mass-action laws (of type (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.
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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 $[H_2A]$.\(^7\)

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 “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\(_2\)O' and the subsystem 'acid' are coupled by the charge-balance equation](image)

### 1.2.2 General Case: Polyprotic Acids ($H_NA$)

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

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

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

1. (1.28) $K_w = \{H^+\} \{OH^-\}$ (self-ionization $H_2O$)
2. (1.29) $K_1 = \{H^+\} \{H_{N-1}A^-\} / \{H_NA\}$ (1\(^{st}\) diss. step)
3. (1.30) $K_2 = \{H^+\} \{H_{N-2}A^{-2}\} / \{H_{N-1}A^-\}$ (2\(^{nd}\) diss. step)
4. \ldots
5. (1.31) $K_N = \{H^+\} \{A^{-N}\} / \{HA^{-\text{1}-(N-1)}\}$ (N\(^{th}\) diss. step)
6. (1.32) $C_T = [H_NA] + [H_{N-1}A^-] + \ldots + [A^{-N}]$ (mass balance)
7. (1.33) $0 = [H_{N-1}A^-] + 2[H_{N-2}A^{-2}] + \ldots + N[A^{-N}] + [\text{OH}^-] - [H^+]$ (charge bal.)

\(^7\)The dissolved but undissociated neutral species is sometimes also abbreviated as $H_2A^0$. 
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 closed-form expressions (i.e. analytical formulas), we have to replace all activities by 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:

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

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 1-component *subsystem* ‘acid’. It exhibits the main (mathematical) features of the acid in its clearest form.
1.3 The Subsystem “Acid”

This paragraph focuses on the subsystem “acid” defined by the subset of \( N+1 \) equations (1.36) to (1.39). In other words, we ignore the charge-balance equation (1.40) and the self-ionization of water in Eq. (1.35).

1.3.1 Notation

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

\[
C_T \equiv [\text{H}_N\text{A}]_T = TOT \text{ H}_N\text{A}
\]

This acid is characterized by \( N+1 \) species:

- 1 undissociated species: \( \text{H}_N\text{A}(\text{aq}) \) (electro-neutral)
- \( N \) dissociated species: \( \text{H}_N\text{A}^{-1}, \ldots, \text{HA}^{-(N-1)}, \text{A}^{-N} \) (anionic)

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

\[
[j] \equiv [\text{H}_{N-j}\text{A}^j]
\]

for \( j = 0, 1, 2, \ldots, N \)

The symbol \( j \) is an integer, also indicating the negative charge of the individual species (which is equal to the number of \( \text{H}^+ \) released):

\[
z_j = 0 - j
\]

Thus, the species \([0]\) stands for the uncharged, undisassociated compound \( \text{H}_N\text{A}(\text{aq}) \).

In each successive dissociation step, \( j \) is enhanced by 1 (due to the release of 1 proton):

\[
j^{th} \text{ dissociation step:} \quad [j-1] \rightarrow [j]
\]

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

\[
\begin{aligned}
\text{acid:} & \quad [j-1] \\
\text{conjugate base:} & \quad [j]
\end{aligned}
\]

of \( j^{th} \) dissociation step

The sum of all species yields the total concentration \( C_T \):

\[
C_T = \sum_{j=0}^{N} [j] = [0] + [1] + \ldots + [N]
\]

---

\(^8\) This quantity should not be confused with the total amount of acid, \([\text{H}_N\text{A}]_T\).
Ionization Fractions. Instead of using the $N+1$ acid species $[j]$, it is more convenient to work with ionization fractions (as the ratio of the acid-species concentration to the total amount of acid):

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

1.3.2 Stepwise and Cumulative Dissociation

As we know from §1.1.3, a monoprotic acid is characterized by one 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: $H_3A = H^+ + H_2A^-$ $K_1$
2nd dissociation step: $H_2A^- = H^+ + HA^2^-$ $K_2$
3rd dissociation step: $HA^2^- = H^+ + A^3$ $K_3$

The three reactions 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 step-by-step release of a single $H^+$ in each dissociation step (it’s the way nature works); the second relates each dissociated species to the undissociated acid by a ‘many-proton’ or cumulative release. The latter is a mathematical trick to simplify further calculations.

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

$$K_1 = \{H^+\} [H_{N+1}A^-] / [H_NA]$$
$$K_2 = \{H^+\} [H_{N+2}A^2^-] / [H_{N+1}A^-]$$
$$\vdots$$
$$K_N = \{H^+\} [A^{N-1}] / [HA^{(N-1)}]$$

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

$$k_j = \begin{cases} 1 & \text{for } j = 0 \\ K_1K_2\cdots K_j & \text{for } j > 0 \text{ and } j \leq N \end{cases}$$

For $j$ values outside this range (i.e. either for negative $j$ or for $j > N$), we set $k_j = 0$. 

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In logarithmic form, using the common definition for $p k_j = \log k_j$, Eq. (1.49) becomes:

$$(1.50) \quad pk_j = \begin{cases} 
0 & \text{for } j = 0 \\
\log k_0 + \log k_1 + \cdots + \log k_j & \text{for } j > 0 \text{ and } j \leq N
\end{cases}$$

This simple additive relationship is illustrated in Fig. 1.6 for the triprotic acid, where the $pk_j$ and $pK_j$ values are plotted along a GIBBS-energy axis.

In contrast to the $pk_j$ values, which are arranged on an energy scale (like in Fig. 1.6), the $pK_j$ values can be arranged on a pH scale – see Fig. 1.7 on page 29.

[Note. The cumulative acidity constant $k_j$ should not be confused with the cumulative equilibrium constant for complex formation denoted by $\beta_j$ (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 compact form:

<table>
<thead>
<tr>
<th>reaction formula</th>
<th>law of mass action</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H_{N(j-1)}A^{(j-1)} = H^+ + H_{Nj}A^j )</td>
<td>( K_j = \frac{x \cdot [j]}{[j-1]} )</td>
</tr>
<tr>
<td>( H_NA = jH^+ + H_{Nj}A^j )</td>
<td>( k_j = \frac{x^j \cdot [j]}{[0]} = K_jK_{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 \Rightarrow \quad x = K_j \\
\frac{[j+1]}{[j]} = \frac{K_j K_{j+1}}{x} \quad \Rightarrow \quad x = (K_jK_{j+1})^{1/2} \\
\frac{[j]}{[0]} = \frac{k_j}{x} = \frac{K_1 K_2 \cdots K_j}{x} \\

Thus, once we know the concentration of a single species, say \([j]\), we are able to calculate all other concentrations, i.e. the equilibrium distribution of all species 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):

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

Using Eq. (1.52), the entire subset of the \( N+1 \) equations (1.36) to (1.39) collapses to:

\[
\begin{align*}
(1.58) \quad [j] &= \left( \frac{k_j}{x^j} \right) [0] \quad (N \text{ dissociation equations, } j = 1 \text{ to } N) \\
(1.59) \quad C_T &= \sum_{j=0}^{N} [j] = [0] \sum_{j=0}^{N} \frac{k_j}{x^j} \quad \text{(mass balance)}
\end{align*}
\]

As long as we consider the subsystem ‘acid’ alone, \( C_T \) itself is irrelevant.\(^9\) Dividing both equations by \( C_T \), we get with \( a_j = [j]/C_T \):

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

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

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

If \( a_0 \) is known, all other ionization fractions \( a_j \) can be calculated using Eq. (1.60). The set of ionization fractions – i.e. the normalized acid-species distribution – contains all information about the subsystem ‘acid’. The elegant and fascinating features of the ionization fractions will be discussed and presented in § 1.5.

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

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

---

\(^9\) \( C_T \) becomes relevant only if, in addition to \( H_NA \), other components or are present such like \( H_2O \) and/or other acids and bases.
**Inverse Task.** The inverse task is to calculate x or pH starting from a given a₀ (or any other aᵢ). Unfortunately, the inverse task does not hold a simple equation in store for us. On the contrary, it leads to a polynomial of high degree, namely of degree N (as derived in Appendix B.2.1):

\[
0 = \text{const} \cdot x^{N-j} + \sum_{i=j}^{N} k_i x^{N-i}
\]

with \(\text{const} = -\left(\frac{1-a_j}{a_j}\right) k_j\)

If we move from the subsystem ‘acid’ to the overall system ‘acid + H₂O’, the degree of the polynomial increases to \(N+2\), as it will be shown in Eq. (1.136) below.

**Example.** For a diprotic acid H₂A, Eq. (1.64) represents a quadratic equation (which can be solved quite easily). Let’s assume we know the value of a₀ and want to calculate the corresponding x. The steps are as follows (note that \(k₀ = 1\)):

\[
0 = -\left(\frac{1-a₀}{a₀}\right)x^2 + K_1 x + K_1 K_2
\]

\[
0 = x^2 - \alpha K_1 x - \alpha K_1 K_2
\]

with \(\alpha = \frac{a₀}{1-a₀}\)

The positive root of this quadratic equation is

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

Usually, \(K_2/K₁ ≪ 1\) applies, whereby the second term in the square root disappears. Then, for \(a₀ = \frac{1}{2}\) (i.e. \(\alpha = 1\)) we obtain the simple and nice result: \(x = K₁\).
1.4 Equivalence Points of Subsystem “Acid”

1.4.1 Definition of $EP_n$

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

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

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

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

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 species to its conjugate base. Thereby, two types of equivalence points emerge:

(1.68) $EP_j$: $[j-1] = [j+1]$

(1.69) semi-EP$_j$: $[j-1] = [j]$

The definition of $EP_j$ even applies for $j=0$ and $j=N$, if we extend our notation and identify $[-1]$ by $[H^+]$ and $[N+1]$ by $[OH^-]$. It yields:

(1.70) $EP_0$: $[H^+] = [1]$ (for $j = 0$)

(1.71) $EP_j$: $[j-1] = [j+1]$ (for $j = 1, 2, \ldots N-1$)

(1.72) $EP_N$: $[N-1] = [OH^-]$ (for $j = N$)

and

(1.73) semi-EP$_j$: $[j-1] = [j]$ (for $j = 1, 2, \ldots N$)

On the pH scale, each EP is the midpoint between two adjacent semi-EPs (as will be shown later in § 1.4.2). The acid $H_nA$ 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 $EP_n$, where $n$ runs over all integer and half-integer values.\(^\text{10}\)

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

According to Eqs. (1.70) to (1.73), $EP_n$ is defined by

\[ EP_n \iff \begin{cases} [n-1] = [n+1] & \text{for } n = 0, 1, 2, \ldots, N \ (EP_{j=n}) \\ [n-\frac{1}{2}] = [n+\frac{1}{2}] & \text{for } n = \frac{1}{2}, \frac{3}{2}, \ldots, N-\frac{1}{2} \ (\text{semi-EP}_{j=n+\frac{1}{2}}) \end{cases} \]

\(^\text{10}\) The choice of the small latter $n$ as the subscript on $EP_n$ is not accidental. The deep relationship between $EP_n$ and the variable $n = C_B/C_T$, 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 a specific pH value: $EP_n \iff pH_n$ (or $EP_n \iff x_n$). This correspondence can be easily established. But before we start, it is useful to make a distinction between so-called ‘external’ and ‘internal’ EPs, which separate the two outermost equivalence points $EP_0$ and $EP_N$ from the rest:

- *external* equivalence points: $EP_0$ and $EP_N$ (only two)
- *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 obtain (valid for $0 < j < N$):

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

It yields the following sequence:

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

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:\footnote{The index $j$ is always an integer; the index $n$ is both integer and half-integer.}

\[
\begin{align*}
\text{(1.83) } pH_n &= \begin{cases} \\
\frac{1}{2}(pK_n + pK_{n+1}) & \text{for } n = 1, 2, \ldots, N-1 \quad (EP_{j=n}) \\
pK_{n+\frac{1}{2}} & \text{for } n = \frac{1}{2}, \frac{3}{2}, \ldots, N-\frac{1}{2} \quad (\text{semi-EP}_{j=n+\frac{1}{2}})
\end{cases}
\end{align*}
\]

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$_n$A</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>
Tab. 1.4 lists the *internal* equivalence points of four common acids. *Internal* EPs are completely determined by the acid’s pK values (no other information is necessary). In this respect, they differ from *external* EPs which depend on the amount of acid, C_T.

**External EPs.** There are only two *external* equivalence points (EP₀ and EP_N). The formulas which refer to H⁺ or OH⁻ via Eqs. (1.70) or (1.72) are a bit trickier than for the internal EPs. From Eqs. (1.58) to (1.60) follows:

\[
\begin{align*}
(1.84) \quad & \text{EP₀: } [H^+] = [1] \quad \Rightarrow \quad x = C_T a_1 \quad \Rightarrow \quad C_T = \frac{x^2}{K_1} \cdot \frac{1}{a_0(x)} \\
(1.85) \quad & \text{EP_N: } [N-1] = [OH^-] \quad \Rightarrow \quad C_T a_{N-1} = \frac{K_w}{x} \quad \Rightarrow \quad C_T = \frac{K_w}{x^2} \cdot \frac{1}{a_N(x)}
\end{align*}
\]

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 *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-degree polynomial.]

The only thing we can offer are values for the asymptotic case. As shown later in Eqs. (1.104) and (1.105), we have a₀ = 1 for x → ∞ and a_N = 1 for x → 0. The last two equations then yield:

\[
\begin{align*}
(1.86) \quad & \text{EP₀: } \text{approaching } pH \to 0 \quad (\text{or } x \to \infty) \quad \text{when } C_T \to \infty \\
(1.87) \quad & \text{EP_N: } \text{approaching } pH \to 14 \quad (\text{or } x \to 0) \quad \text{when } C_T \to \infty
\end{align*}
\]

### 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 *internal* equivalent points in the form of Eq. (1.83):

- EP with integer n \((EP_1, EP_2, ..., EP_{N-1})\) at pH_n
- semi-EP with half-integer n \((EP_{1/2}, EP_{3/2}, ..., EP_{N-1/2})\) at pK_{n+1/2}

In addition, there are two *external*, non-constant equivalence points located at both ends of the pH scale when C_T→∞:

- EP₀: pH → 0
- EP_N: pH → 14

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

\[(1.88) \quad \text{pH}_0, \text{pH}_{1/2}, \text{pH}_1, \text{pH}_{3/2}, ..., \text{pH}_N\]

An example of such a sequence is shown schematically in Fig. 1.7 for the triprotic acid H₃PO₄.

---

12 For simplicity we set here \(x \approx [H^+]\), which deviates from our definition of x in Eq. (0.5).
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**Fig. 1.7** Equivalence points of a triprotic acid $H_3A$ arranged on the pH scale

**pH-C$_T$ Plots.** Fig. 1.8 shows all equivalence points of the carbonic acid (upper diagram) and the phosphoric acid (lower diagram) in the pH-C$_T$ diagram. The *internal* equivalence points (in red color) are independent of C$_T$ and therefore straight lines, 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 C$_T$ = f(pH). The curves are approximations valid for the subsystem ‘acid’ (i.e. without coupling to the subsystem ‘pure H$_2$O’).

The representation as *dashed* curves (instead of solid lines) in Fig. 1.8 reminds us that these are approximations, valid for the isolated subsystem ‘acid’ (i.e. without coupling to the subsystem ‘H$_2$O’). The general case is discussed later in §2.3, where we learn that all *internal* EPs represent the large-C$_T$ limit of the combined ‘$H_3A + H_2O$’ system.
1.5 Ionization Fractions: Degree of Dissociation

1.5.1 Definition of $a_j$

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

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

(1.89)

They form the mathematical skeleton of the subsystem ‘acid’ with its typical dependence on $x$ (or $\text{pH}$):\(^{13}\)

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

(1.90)

Combining the left and right equations yields:

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

(1.91)

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):

$$k_0 = 1, \quad k_1 = K_1, \quad k_2 = K_1K_2, \quad \ldots \quad k_N = K_1K_2\ldots K_N$$

(1.92)

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 obtained by multiplication with $C_T$:

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

(1.93)

To make the $\text{pH}$ dependence of $a_j$ more transparent, Eq. (1.91) can be written as

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

(1.94)

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

---

\(^{13}\) 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 curves and shapes of the ionization-fractions 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:

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

The ionization fractions are bound between 0 and 1:

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

They never become negative or greater than 1. [Strictly speaking: The functions will come very close to the values 0 and 1, but they never really reach them.]
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**Eps.** The equivalence points introduced in Eqs. (1.76) and (1.77) can also be defined by equating two ionization fractions:

\[(1.97) \quad \text{semi-EP}_j: \quad [j-1] = [j] \quad \Leftrightarrow \quad a_{j-1} = a_j \quad \Rightarrow \quad x = K_j\]

\[(1.98) \quad \text{EP}_j: \quad [j-1] = [j+1] \quad \Leftrightarrow \quad a_{j-1} = a_{j+1} \quad \Rightarrow \quad x = (K_j K_{j+1})^\frac{1}{2}\]

This applies only for the **internal** equivalence points:

<table>
<thead>
<tr>
<th>(1.99)</th>
<th>condition</th>
<th>range</th>
<th>pH</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>semi-EP(_j)</td>
<td>(a_{j-1} = a_j)</td>
<td>(j = 1, 2, ..., N)</td>
<td>(pK_j)</td>
<td>(j - \frac{1}{2})</td>
</tr>
<tr>
<td>(\text{EP}_j)</td>
<td>(a_{j-1} = a_{j+1})</td>
<td>(j = 1, 2, ..., N-1)</td>
<td>(pH_j \equiv \frac{1}{2} (pK_j + pK_{j+1}))</td>
<td>(j)</td>
</tr>
</tbody>
</table>

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)):

\[(1.101) \quad \text{semi-EP}_j \quad a_i = a_{j-1} \approx \frac{1}{2} \quad \text{all other } a_i \approx 0\]

\[(1.102) \quad \text{EP}_j \quad a_i = 1 - 2a_{j-1} \approx 1 \quad \text{all other } a_i \approx 0\]

### 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 acids subdivide the entire pH domain into distinct intervals, as shown in the left diagrams of Fig. 1.10. In this way, a polyprotic acid \(H_NA\) with its \(N\) \(pK_j\) values generates \(N+1\) intervals:

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

The \(j\)-th interval is the subdomain where the ionization fraction \(a_j\) exercises its full dominance – see right diagrams of Fig. 1.10. As indicated by the colors, there are two types of curves: S-shaped curves in the \(0^{\text{th}}\) and the \(N^{\text{th}}\) interval at the opposite ends of the pH scale (red color) and bell-shaped curves inside 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 are glued together (at minus and/or plus infinity).\(^{14}\)

\[\text{Fig. 1.10} \quad \text{Each ionization fraction } a_j \text{ has its own domain in the pH interval between two adjacent pK values.} \text{ (HA – acetic acid, } H_2A \text{ – carbonic acid, } H_3A \text{ – phosphoric acid)}\]

**Asymptotic Behavior.** At the opposite ends of the pH scale the two ionization fractions \(a_0\) and \(a_N\) attain the maximum value \(1:\)

\[\text{(1.104) strongly acidic: } \text{pH} \to 0 \text{ (or } x \to \infty): \quad a_0 = 1, \quad \text{all other } a_j = 0\]

\[\text{(1.105) strongly alkaline: } \text{pH} \to 14 \text{ (or } x \to 0): \quad a_N = 1, \quad \text{all other } a_j = 0\]

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

\(^{14}\) 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\text{N}A

<table>
<thead>
<tr>
<th>Ionization Fraction</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 ))</td>
<td>( pK_j &lt; pH &lt; pK_{j+1} )</td>
</tr>
<tr>
<td>Maximum at pH</td>
<td>( -\infty ) (for ( a_0 ))</td>
<td>( \frac{1}{2} (pK_j + pK_{j+1}) )</td>
</tr>
<tr>
<td>Asymptotic Behavior</td>
<td>( a_0 = 1, a_N = 0 )</td>
<td>( a_j = 0 )</td>
</tr>
<tr>
<td>( a_0 = 0, a_N = 1 )</td>
<td>( a_j = 0 )</td>
<td></td>
</tr>
</tbody>
</table>

### 1.5.4 Two Types of Approximations

The 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:

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

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 \( i^{\text{th}} \) 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

\[
\lg a_2 \approx (2-i) \cdot pH + (pK_i - pK_2)
\]
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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:

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

This approach relies 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\textsuperscript{15} 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.

\textsuperscript{15} 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).
Fig. 1.12 Hägg’s diagram: ionization fractions for phosphoric acid. Solid lines – exact description based on Eq. (1.90); dashed lines – approximations in Eqs. (1.107) to (1.109).

**Summary.** The two approaches are complementary, as demonstrated in Fig. 1.13 (for phosphoric 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, but if we look more closely, we see deviations in the log-plots for values below 10^{-4} (dashed curves in the top-right diagram).

Fig. 1.13 Ionization fractions for phosphoric acid in the two approximations (dashed lines). Solid lines – exact description based on Eq. (1.90).
1.6 Moments $Y_L$ – Sums over $a_j$

1.6.1 Definition

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

$$(1.110)\quad Y_L = \sum_{j=0}^{N} j^L a_j$$

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

$$(1.111)\quad Y_0 = a_0 + a_1 + \ldots + a_N = 1 \quad \text{for} \quad L = 0$$

For all other positive integers we have:

$$(1.112)\quad Y_L = a_1 + 2^L a_2 + 3^L a_3 + \ldots + N^L a_N \quad \text{for} \quad L \geq 1$$

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).

![Diagram](moments\_Y\_L.png)

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 (with 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.
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**Fig. 1.15** Construction of $Y_1$ (blue curve in bottom diagram) from summation over weighted ionization fraction $a_j$. (Example: phosphoric acid as a triprotic acid)

**pH Dependence.** The moments, just like the ionization fractions, are solely functions of $x$ (or $pH = -\lg x$); the only other ingredients are the (cumulative) equilibrium constants of the acid. From Eq. (1.91) we obtain:

\begin{equation}
Y_i(x) = \frac{\sum_{j=0}^{N} j \cdot k_j / x^j}{\sum_{j=0}^{N} k_j / x^j} = \frac{\sum_{j=0}^{N} j \cdot k_j x^{N-j}}{\sum_{j=0}^{N} k_j x^{N-j}}
\end{equation}

Converting $x$ to $pH$ yields:

\begin{equation}
Y_i(pH) = \frac{\sum_{j=0}^{N} j \cdot k_j 10^{j \cdot pH}}{\sum_{j=0}^{N} k_j 10^{j \cdot pH}}
\end{equation}

---

16 To obtain the last equation you should multiply both nominator and denominator by $x^N$. 

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Moments $Y_L$ (for $L = 1$ to 4)

![Graph of 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 the case of monoprotic acids (top-left diagram) all $Y_L$ are equal; the four curves lie on top of each other.

### 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):

\[
\begin{align*}
(1.115) & \quad \text{semi-EP}_j & pK_j & a_j = a_{j-1} \approx \frac{1}{2} & Y_L = \frac{1}{2} \left\{ (j-1)^L + j^L \right\} \\
(1.116) & \quad \text{EP}_j & pH_j = \frac{1}{2} (pK_j + pK_{j+1}) & a_j = 1 - 2a_{j-1} \approx 1 & Y_L = j^L
\end{align*}
\]

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:

\[
\begin{array}{|c|c|}
\hline
Y_L \text{ at semi-EP}_j & Y_L \text{ at EP}_j \\
\hline
(1.117) & Y_L(pK_j) = \frac{1}{2} & Y_L(pH_j) = 1 \\
(1.118) & Y_L(pK_2) = \frac{1}{2} (1 + 2^L) & Y_L(pH_2) = 2^L \\
(1.119) & Y_L(pK_3) = \frac{1}{2} (2^L + 3^L) & Y_L(pH_3) = 3^L \\
(1.120) & Y_L(pK_4) = j - \frac{1}{2} & Y_L(pH_4) = j \\
(1.121) & Y_L(pK_i) = (j - 1) j + \frac{1}{2} & Y_L(pH_i) = j^2 \\
\hline
\end{array}
\]
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):

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

In fact, it establishes the link between \( EP_n \) and \( pH_n \) defined in Eq. (1.83). A graphical representation is provided by the dots in Fig. 1.17.

**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 \( Y_1 \) we get the asymptotic values 0 and 3 at the opposite ends of the pH scale, as shown Fig. 1.17. These values correspond to the two external EPs (EP\(_0\) and EP\(_3\)). Thus, Eq. (1.122) seems to be applicable to external EPs defined by \( n = 0 \) and \( N \).
1.7 The Coupled System “H₂O + HₙA”

1.7.1 Basic Set of Equations

The stage is now set to solve the coupled system ‘H₂O+HₙA’. The basic set of N+3 equations, given in Eqs. (1.35) to (1.40), becomes (after replacing the acid species [j] by the ionization fractions \( a_i = [j]/C_T \)):

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

**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)):

\[
(1.131) \quad w = [OH^-] - [H^+] = \frac{K_w}{x} - x
\]

**HₙA.** The subsystem ‘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:

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

**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](image)
1.7.2 Closed-Form Expressions

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

- given pH ⇒ calculate Cᵰ
- given Cᵰ ⇒ calculate pH

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

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

\[
(1.133) \quad \text{amount of acid: } Cᵰ(x) = -\frac{w}{Yᵰ} \quad \text{with } Yᵰ = \sum_{j=0}^{N} j \cdot a_j(x)
\]

\[
(1.134) \quad \text{speciation: } [j] = Cᵰ(x) a_j(x) = \left( -\frac{w}{Yᵰ} \right)^a_j \quad \text{for } j = 0, 1, ... N
\]

Eq. (1.133) represents an *explicit* function:

\[
(1.135) \quad Cᵰ = f(\text{pH})
\]

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.]

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

\[
(1.136) \quad 0 = \sum_{j=0}^{N} \left( x^2 - jCᵰx - Kᵰ \right) k_j x^{N-j}
\]

Compared to the polynomial for the subsystem ‘acid’ 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 the special case \( n=0 \).
Fig. 1.19 Functional relationship between pH and the amount of acid $C_T$. The top diagram is based on Eq. (1.133); bottom diagram: same as top diagram, only axes interchanged.

**Example $N = 1$.** The monoprotic acid represents the simplest case, where the sum in Eq. (1.136) runs over two terms only, $j = 0$ 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) 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).

In the case of *strong acids*, all polynomials simplify; their degree reduces by one unit. This will be shown in § 2.2.5.
2 ACID-BASE SYSTEM

2.1 Introduction

2.1.1 Definitions

Chapter 1 provided the algebraic description of the two-component system $H_NA + H_2O$ (polyprotic acid in water). Starting from the set of equations (1.28) to (1.33) we arrived at an 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:

\begin{align}
\text{(2.1) strong monoacidic base:} & \quad BOH &= B^+ + OH^- \\
\text{(2.2) strong monoprotic acid:} & \quad HX &= H^+ + X^-
\end{align}

Here the ARRHENIUS base BOH stands for NaOH or KOH (i.e. $B^+ = Na^+$ or $K^+$) while 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:

\begin{align}
\text{(2.3) alkalimetric titration:} & \quad H_NA + BOH \quad \Rightarrow \quad \text{pH increases} \\
\text{(2.4) acidimetric titration:} & \quad H_NA + HX \quad \Rightarrow \quad \text{pH decreases}
\end{align}

$C_B$ and $C_A$ should denote the amounts of strong base and strong acid. They can be related to the total amount of $H_NA$ by

\begin{align}
\text{(2.5) } n_B &= \frac{C_B}{C_T} \quad \text{and} \quad n_A = \frac{C_A}{C_T}
\end{align}

Since the strong base and strong acid act in opposing directions (both cancel each other out), we combine the two equations into one

\begin{align}
\text{(2.6) equivalent fraction:} & \quad n = \frac{C_B - C_A}{C_T}
\end{align}

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 $C_T = 10$ 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 $f$. 

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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.

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 only difference between the top and bottom diagram in Fig. 2.2 is that the x- and y-axis are interchanged. The curves are calculated using Eq. (2.32) on page 50.
2.1.2 Special Case: Diprotic Acid

Given is a diprotic acid $H_2A$ with the amount $C_T$ to which a monoacidic strong base BOH (with $B^+ = \text{Na}^+ \text{ or K}^+$) is added:

\[
H_2A + n \text{BOH} = B_nH_{2-n}A + n \text{H}_2\text{O}
\]  

(2.7)

Here $n$ acts as a stoichiometric coefficient that embodies the ratio of the added strong base to the 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.

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

\[
C_B \equiv [\text{BOH}]_T = [B^+]\quad \text{(strong base)}
\]  

(2.8)

The special case of $n = 0, 1$ or 2 is particularly interesting. When these three integers are inserted into the reaction formula (2.7), the entity $B_nH_{2-n}A$ becomes a pure acid, an ampholyte and a (conjugate) base:

\[
\begin{align*}
(2.9) \quad n &= 0: \quad \text{pure H}_2\text{A solution (acid)} \quad \Leftrightarrow \quad \text{H}_2\text{A} \quad \text{EP} \\
(2.10) \quad n &= 1: \quad \text{pure BHA solution (ampholyte)} \quad \Leftrightarrow \quad \text{HA}^- \quad \text{EP} \\
(2.11) \quad n &= 2: \quad \text{pure B}_2\text{A solution (base)} \quad \Leftrightarrow \quad \text{A}^{2-} \quad \text{EP}
\end{align*}
\]

In fact, $n=0, 1, 2$ define the three equivalence points (EP$_0$, EP$_1$, EP$_2$) 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$_2$CO$_3$, NaHCO$_3$ and Na$_2$CO$_3$.]
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**Charge Balance.** The principle of *electro-neutrality* requires that a solution must contain equal numbers of anions and cations:

\[(2.12)\quad [\text{H}^+] + [\text{B}^+] = [\text{HA}^-] + 2[\text{A}^{2-}] + [\text{OH}^-] \]

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

\[(2.13)\quad C_B = [\text{HA}^-] + 2[\text{A}^{2-}] + [\text{OH}^-] - [\text{H}^+] \]

**Base Equations.** The set of algebraic 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:

\[(2.14)\quad K_w = \{\text{H}^+\} \{\text{OH}^-\} \quad \text{(self-ionization of H}_2\text{O)}\]

\[(2.15)\quad K_1 = \{\text{H}^+\} \{\text{HA}^-\} / \{\text{H}_2\text{A}\} \quad \text{(1st diss. step)}\]

\[(2.16)\quad K_2 = \{\text{H}^+\} \{\text{A}^{2-}\} / \{\text{HA}^-\} \quad \text{(2nd diss. step)}\]

\[(2.17)\quad C_T = [\text{H}_2\text{A}] + [\text{HA}^-] + [\text{A}^{2-}] \quad \text{(mass balance)}\]

\[(2.18)\quad C_B = [\text{HA}^-] + 2[\text{A}^{2-}] + [\text{OH}^-] - [\text{H}^+] \quad \text{(charge balance)}\]

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 this set of equations; the other four equations in this set are completely unrelated to \(C_B\). 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 which is explained in Appendix C. For the diprotic-acid case the proton balance yields:

\[(2.19)\quad 0 = [\text{H}^+] + n[H_2\text{A}] + (n-1)[\text{HA}^-] + (n-2)[\text{A}^{2-}] - [\text{OH}^-] \]

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 $H_2O$
- weak $N$-protic acid $H_NA$
- strong monoacidic base $BOH$

The ‘undisturbed system’ of Chapter 1 is characterized by $N+4$ species (variables):

- $H^+$, $OH^-$, $H_NA$, $H_{N-1}A^-$, ..., $A^{-N}$, $B^+$

Instead of $[B^+]$ we use the parameter $n = C_B/C_T$. The description of acid-base titration is then built on a set of $N+3$ nonlinear equations:

\[
\begin{align*}
(2.20) \quad K_N &= \{H^+\} \{OH^-\} \quad \text{(self-ionization $H_2O$)} \\
(2.21) \quad K_1 &= \{H^+\} \{H_{N-1}A^-\} / \{H_NA\} \quad \text{(1\textsuperscript{st} diss. step)} \\
(2.22) \quad K_2 &= \{H^+\} \{H_{N-2}A^-\} / \{H_{N-1}A^-\} \quad \text{(2\textsuperscript{nd} diss. step)} \\
& \quad \ldots \\
(2.23) \quad K_N &= \{H^+\} \{A^{-N}\} / \{HA^{(N-1)}\} \quad \text{(N\textsuperscript{th} diss. step)} \\
(2.24) \quad C_T &= [H_NA] + [H_{N-1}A^-] + \ldots + [A^{-N}] \quad \text{(mass balance)} \\
(2.25) \quad C_B &= [H_{N-1}A^-] + [H_{N-2}A^-] + \ldots + N[A^{-N}] + [OH^-] - [H^+] \quad \text{(charge balance)}
\end{align*}
\]

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 original set of equations (1.28) to (1.33) is just the charge-balance equation in the last line.

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

Two assumptions are necessary to derive closed-form expressions (one-line formulas) from the set of equations (2.20) to (2.25):

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

**Assumption 2:** the strong base $BOH$ dissolves completely, without forming aqueous species $B_nH_{2-n}A(aq)^{20}$

---

\[^{20}\] such like $NaCO_3^-$ or $NaHCO_3(aq)$ – which really exist, but only in small concentrations
The first assumption is fulfilled either in dilute systems or by switching to conditional equilibrium constants $^\text{c}K$ introduced in Eq. (1.9). If the two assumptions are fulfilled, we speak of ‘ideal conditions’ (counterexamples for ‘real conditions’ will be given in § 2.4.4).

### 2.2.2 Closed-Form Expressions

The procedure for solving the set of algebraic equations (2.20) to (2.25) is the same as that we used in previous paragraphs (cf. in § 1.7.1):

- replace activities by concentrations: $^{21}$ $\{..\} \Rightarrow [..]$ in Eqs. (2.20) to (2.23)
- replace acid species $[j]$ by ionization fractions $a_j$ – in Eqs. (2.21) to (2.25)
- replace $\{\text{H}^+\}$ by $x$ and $[\text{OH}^-]$ by $K_w/x – x$, and use $w(x)$ defined in Eq. (1.131)
- use the compact notation $Y_1$ for summation over $a_j$

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

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

This set of equations upgrades Eqs. (1.125) to (1.130) from an acid system to an acid-base system with the parameter $n$ 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. (2.26) to (2.30) – is encapsulated in the definition of $Y_1$ and $w$:

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

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).

---

$^{21}$ except for $\text{H}^+$, 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).

Fig. 2.4 illustrates how the three components ‘pure H$_2$O’, ‘$N$-protic acid’, and ‘strong base’ are coupled via one single equation: the charge-balance equation.

### 2.2.3 Polynomials for $x = 10^{-pH}$

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 degree $N+2$ in $x$ (i.e., $N+2$ is the highest power of $x$):

$$0 = \sum_{j=0}^{N} \left\{ x^2 + (n-j)C_T x - K_w \right\} k_j x^{N-j} \tag{2.35}$$

For $n=0$ it falls back to Eq. (1.136) on page 42. Theoretically, this equation can be used to calculate $x$, but in practice it’s a difficult task, even for a cubic equation. For higher-order polynomials, numerical root-finding methods should be used.

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

$$0 = x^3 + \{ K_1 + nC_T \} x^2 + \{ (n-1)C_T K_1 - K_w \} x - K_1 K_w \tag{2.36}$$

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:

$$0 = x^3 + \{ K_1 + C_B \} x^2 + \{ (C_B - C_T) K_1 - K_w \} x - K_1 K_w \tag{2.37}$$
Example $N=2$. For diprotic acids, the polynomial in Eq. (2.35) becomes a quartic equation, i.e. a polynomial of degree 4 in $x (=10^{-\text{pH}})$:

$$(2.38) \quad 0 = x^4 + \{K_1 + nC_T\} x^3 + \{K_1K_2 + (n-1)C_T K_1 - K_w\} x^2 + K_1 \{(n-2)C_T K_2 - K_w\} x - K_1K_2K_w$$

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:

$$(2.39) \quad 0 = x^4 + \{K_1 + C_B\} x^3 + \{K_1K_2 + (C_B - C_T) K_1 - K_w\} x^2 + K_1 \{(C_B - 2C_T) K_2 - K_w\} x - K_1K_2K_w$$

If you set $K_2=0$, you arrive at Eqs. (2.36) and (2.37). As will be shown later in § 2.2.5, in the case of strong acids all polynomials simplify (their degree decreases 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.

At the lowest level there are the $N$ acidity constants $K_1$ to $K_N$ (as 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 fractions $a_j$ (which embody the law of mass action in each dissociation step). Then, the ionization fractions are summed up to form the moment $Y_1$ as 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 clear in Chapter 3 when they are used as building blocks of other key quantities:

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

### 2.2.5 Strong Acids are Simpler

The mathematical description of *strong polyprotic 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).\(^{22}\) Because the amount of the undissociated species is zero, \([0] = 0\) or \( a_0 = 0 \), it is 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 \( N+3 \) 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 constant of strong acids is often not known precisely enough.

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

\[
(2.40) \quad \text{strong acid: } \frac{x}{K_1} \to 0 \quad \text{for all practice-relevant } x \quad (\text{i.e. } x \leq 1)
\]

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:

<table>
<thead>
<tr>
<th>general case</th>
<th>strong acids</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K_1, K_2, \ldots K_N )</td>
<td>( \infty, K_2, \ldots K_N )</td>
</tr>
</tbody>
</table>

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

\[
(2.41) \quad k_1 = K_1 \Rightarrow k_1 = 1
\]

\[
(2.42) \quad k_2 = K_1K_2 \Rightarrow k_2 = K_2
\]

\[
(2.43) \quad k_3 = K_1K_2K_3 \Rightarrow k_3 = K_2K_3
\]

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**
  \[
  a_0 = \left(1 + \frac{K_1}{x} + \frac{K_2}{x^2} + \cdots \right)^{-1} \quad \Rightarrow \quad a_0 = 0
  \]
  \[
  a_1 = \left(\frac{x}{K_1} + 1 + \frac{K_2}{x} + \cdots \right)^{-1} \quad \Rightarrow \quad a_1 = \left(1 + \frac{K_2}{x} + \frac{K_1K_2}{x^2} + \cdots \right)^{-1}
  \]
  \[
  a_j = \left(\frac{k_j}{x^j}\right) a_0 \quad \Rightarrow \quad a_j = \left(\frac{k_j}{x^{1+j}}\right) a_1 \quad \text{for } j > 1
  \]

(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 have derived for the acid-base system is Eq. (2.32). As an one-liner, it summarizes all the information contained in the \( N+3 \) equations (2.26) to (2.31), and it interconnects three components: \( H_2O \), \( HMA \), and the strong base (as sketched in Fig. 2.4). This one-liner is just the **charge-balance equation**.
Acid Base Systems

Let’s inspect and derive the charge-balance equation from another point of view. For this purpose we introduce the following quantities of the $N$-protic acid:

(2.50) total charge of acid: \[ Z_T = \sum_{j=0}^{N} z_j[j] \]

(2.51) average charge of acid: \[ z_a = \frac{Z_T}{C_T} = \sum_{j=0}^{N} z_j a_j \]

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

(2.52) \[ z_j = Z - j \]

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

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 to this seemingly obvious rule are the zwitterionic acids (e.g. amino acids discussed in § 4.1).

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

(2.53) \[ z_a = \sum_{j=0}^{N} (Z - j) a_j = Z \sum_{j=0}^{N} a_j - \sum_{j=0}^{N} ja_j = Z - Y_1 \]

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, $\text{H}_2\text{O}$, $\text{H}_N\text{A}$) and set it to zero:

(2.54) \[ 0 = [\text{B}^+] + [\text{H}^+] - [\text{OH}^-] + \text{total charge of acid} \]

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

(2.55) \[ 0 = n - \frac{w}{C_T} + z_a = n - \frac{w}{C_T} + (Z - Y_1) \]

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

(2.56) \[ n = \left( Y_1(x) - Z \right) + \frac{w(x)}{C_T} \]

with $Z \geq 1$ for zwitterions

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) contains all the information about the acid-base system. Plotting the equivalent fraction as a function of pH, i.e. \( n = n(pH) \), provides titration curves:

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

This formula for \( n \) consists of two parts: \( Y_1(x) \) as the contribution from the subsystem ‘acid’ and \( w(x) \) as the contribution from the subsystem ‘\( \text{H}_2\text{O} \)’. As indicated by the arrow, the latter term vanishes for high enough \( C_T \) values (i.e. for high-concentrated acids). What remains is the simple 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.

Fig. 2.7 compares the titration curves in the ‘high-\( C_T \) limit’ (top diagram; same as top diagram in Fig. 2.6) with the general/normal case, \( n = Y_1 + w/C_T \), for different values of \( C_T \) (bottom diagram). Here too, the dark blue curve represents \( Y_1 \) as the ‘high-\( C_T \) limit’, i.e. \( C_T = \infty \).
HA, H₂A, H₃A. Titration curves of four common acids for different values of Cₜ (including the high-Cₜ case n(pH) = Y₁ as a dark blue curve) are displayed in Fig. 2.8.

Fig. 2.7 Titration curves of carbonic acid for different Cₜ values. Top diagram: the ‘pure-acid’ case: n(pH) = Y₁(pH) = a₁ + 2a₂; bottom diagram: the ‘pure-acid’ case (Cₜ = ∞) together with four finite Cₜ values.

Fig. 2.8 Titration curves of four common acids for different values of Cₜ (including the ‘pure-acid case’ n(pH) = Y₁)
2.3 Equivalence Points: General Approach

2.3.1 Definitions

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

\[
\text{EP}_j: \quad [j-1] = [j+1] \iff \text{EP}_n: \quad [n-1] = [n+1] \quad \text{for integer } n = j
\]

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

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

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

**General Approach.** The general approach is not based on the equality of two acid species, but on the equality of chemical compounds:

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

The latter is the same as

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

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

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

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

\[
n = Y_1(\text{pH}) + \frac{w(\text{pH})}{C_T} \quad \text{for } n = 0, \frac{1}{2}, 1, \frac{3}{2}, \ldots, N
\]

Plotting it as a function of pH yields the blue titration curve in Fig. 2.9 (for \(H_2CO_3\) with \(C_T = 100\) mM). The small circles at integer and half-integer values of \(n\) mark the \(\text{EP}_n\)-\(\text{pH}_n\) assignment. Since \(H_2CO_3\) is a 2-protic acid there are \(2 \times 2 + 1 = 5\) equivalence points in total.

\[^{23}\text{Here, the notation is extended to implement the external EPs by setting } [-1] = [H^+] \text{ and } [N+1] = [OH^-].\]
Acid Base Systems

**Short Lecture**

![Fig. 2.9 Titration curve of diprotic acid H$_2$CO$_3$ based on Eq. (2.64) with EPs and semi-EPs located at integer and half-integer values of n](image)

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

Eq. (2.64) can be rearranged into the form

$$C_T = \frac{w(pH)}{n - Y_1(pH)}$$  \hspace{1cm} (2.66)

Now it is 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 acids. The dashed curves and lines are approximations corresponding to the high-C$_T$ limit as displayed in Fig. 1.8 on page 29.

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

- **subsystem ‘acid’**: \( C_T \to \infty \)
- **subsystem ‘H$_2$O’**: \( C_T \to 0 \)

---

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 coupled. 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).

![Diagram](image)

\[\text{Fig. 2.10 } \text{pH dependence of EPs and semi-EPs plotted as } C_T = f(\text{pH}) \text{ for four acids}\]

The subsystem ‘$H_2O$’ overtakes the rule when $C_T$ drops below $10^{-7}$ M, which is just the amount of $H^+$ and $OH^-$ in pure water.

The two extremes (i.e. the two isolated subsystems) can be deduced from Eq. (2.66) by setting either the nominator or the denominator to zero:

\[
C_T = \frac{w}{n-Y_i} \iff \begin{cases} 
  w = 0 & \implies C_T = 0 \\
  n-Y_i = 0 & \implies C_T \to \infty
\end{cases}
\]

(2.67)

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 $H_2O$’ is at the position where the nominator in Eq. (2.66) or Eq. (2.67) becomes zero (which is exactly at pH = 7):

\[
C_T = 0
\]

(2.68)
2.3.3 Summary: Systematics & Classification

First. Equivalence points are special equilibrium states in which the equivalent fraction $n = C_B/C_T$ becomes an integer or half-integer value. An $N$-protic acid has a total of $2N+1$ equivalence points:

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

The ‘trivial’ case $EP_0$ refers to the base-free system with $pH_0$ as the pH value of the acid with amount $C_T$ dissolved in water. [It corresponds to the \textit{isoionic point} in § 4.1.6].]

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

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

$EP_n$ (integer $n$) \quad \Leftrightarrow \quad \text{minimum buffer intensity} \ \beta$
semi-$EP_n$ (half-integer $n$) \quad \Leftrightarrow \quad \text{maximum buffer intensity} \ \beta
Fourth. In the limiting case of highly concentrated acids (C_T → ∞), the general relationship simplifies to:

\[(2.71) \quad Y_1(pH) - n = 0\]

This equation asserts the direct link between pH_n and the acidity constants: \(^{25}\)

\[
\begin{align*}
\text{pH}_n &= \frac{1}{2} (pK_n + pK_{n+1}) \quad \text{for integer } n \quad (\text{EP}_n) \\
\text{pH}_n &= pK_{n+1/2} \quad \text{for half-integer } n \quad (\text{semi-EP}_n)
\end{align*}
\]

These simple and beautiful relationships are applicable for \(C_T > 10^{-3} \text{ M}\), but fail in very dilute acids when the influence of the 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. This definition is an approximation that applies strictly only to the high-C_T case. (Nonetheless, in carbonate systems, for example, 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

Tab. 2.1 compares the two approaches to equivalence points. The left column summarizes the alternative definition based on the equality of species concentrations (as introduced in § 1.4 for the simplified ‘pure acid’ case). This is in sharp contrast to the general approach (right column in Tab. 2.1) where real chemical compounds are set equal.

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.

\(^{25}\) It is strictly valid for diprotic acids only, but remains a very good approximation for N-protic acids with \(N \geq 3\).
2.4 Carbonic Acid System \((N=2)\)

2.4.1 Relationships between \(pH\), \(C_T\), and Alkalinity

The actual equilibrium state of a diprotic acid \(H_2A\) (i.e. the concentrations of the three 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 \(C_B = nC_T = Alk\) (see Eq. (3.28)). Once we know two of them, the third is inevitably fixed:

\[
\begin{align*}
\text{(2.72)} & \quad \text{pH (}C_T, n\text{)} = -\log x_n \quad \text{with } x_n \text{ as positive root of Eq. (2.38);} \\
\text{(2.73)} & \quad \text{pH (}C_T, \text{Alk)} = -\log x_n \quad \text{with } x_n \text{ as positive root of Eq. (2.39);}
\end{align*}
\]

\[
\begin{align*}
\text{(2.74)} & \quad n (C_T, \text{pH)} = a_1 + 2a_2 + w/C_T & [j] = C_T a_j \\
\text{(2.75)} & \quad \text{Alk (}C_T, \text{pH)} = C_T (a_1 + 2a_2) + w & [j] = C_T a_j \\
\text{(2.76)} & \quad C_T (n, \text{pH)} = w/(n - a_1 - 2a_2) & [j] = [w/(n - a_1 - 2a_2)] a_j \\
\text{(2.77)} & \quad C_T (\text{Alk}, \text{pH)} = (\text{Alk} - w)/(a_1 + 2a_2) & [j] = [(\text{Alk} - w)/(a_1 + 2a_2)] a_j
\end{align*}
\]

Fig. 2.12 Relationships between \(pH\), \(C_T\), and \(n\) for the carbonic acid system (at 25 °C)
These nonlinear relationships are displayed for carbonic acid in Fig. 2.12 and Fig. 2.13. The diagrams show all possible combinations of 1 dependent and 2 independent variables taken from the triple $C_T$, pH, and $n$ ($Alk = nC_T$).

Note how the “simple transformation” of the variable $n$ into $Alk = nC_T$ dramatically changes the shape of the curves in Fig. 2.13 (compared to Fig. 2.12).
2.4.2 Three Equivalence Points

The carbonate system 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. Assignment of the EPs in the upper pH-$C_T$ diagram to the intersection points of species concentrations (two lower diagrams).
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 Cₜ-dependent:

<table>
<thead>
<tr>
<th></th>
<th>Cₜ = 10⁻⁴ M</th>
<th>Cₜ = 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 Cₜ. The intersection points of the CO₂ and CO₃⁻² curves in the two lower diagrams are both at the *same* fixed pH value of \(\frac{1}{2}(pK₁ + pK₂) = 8.34\), which belongs to the high-Cₜ limit of the red curve in the upper diagram. Only when we decrease Cₜ further below 10⁻⁴ M, i.e. for very dilute acids, the simple relationship [CO₂] = [CO₃⁻²] no longer works correctly.

### 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, \([j] \rightarrow [j]\). 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, \(K \rightarrow K^c\).

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 \(K^c\). There are several compilations for \(K^c\) in literature; one example is given in Tab. 2.2.

<table>
<thead>
<tr>
<th>Tab. 2.2</th>
<th>Thermodynamic and conditional equilibrium constants for H₂CO₃ in pure water and seawater (at 25 °C, 1 atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>thermodynamic K (pure water, I = 0)</td>
</tr>
<tr>
<td>pK₁</td>
<td>6.35</td>
</tr>
<tr>
<td>pK₂</td>
<td>10.33</td>
</tr>
<tr>
<td>pKₗw</td>
<td>14.0</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 \(K^c\)). The solid curves in Fig. 2.15 are identical to the solid curves displayed in the top diagram 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 $C_T$ for real systems more accurately.

Given is a carbonic acid system titrated with NaOH. Fig. 2.16 compares the results of the closed-form equation (2.66) (solid lines) with the numerical-model predictions (dots).\(^\text{26}\)

---

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

- With increasing \( C_T \) the ionic strength \( I \) increases; consequently, the activity corrections are larger.\(^{27}\)
- Numerical models consider the formation of aquatic complexes such as \( \text{NaHCO}_3^- \) and \( \text{Na}_2\text{CO}_3(\text{aq}) \), which are ignored in the present approach. The 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* to reach the target 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 is titrated by a strong base/acid (NaOH and HCl)

**var B** 100 mM NaOH solution is 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**.

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 two variants differ from each other only in the C_T value:

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

\[(2.80) \quad \text{var B} \quad C_T = \frac{(C_B - w)}{Y_1} \quad \text{with } C_B = 100 \text{ mM}\]

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

The obtained species distributions are displayed in Fig. 2.18: var A (left diagrams) and 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 only differ by the concentration scale: y-axis is linear (upper) and logarithmic (lower).

![Species distribution of H₂CO₃ as a function of pH for var A (left) and var B (right).](image)

Although both variants rely on exactly the same ionization fractions, the pH dependence of the species in var A and var B is fundamentally different. While the species distribution in var A (top left diagram) reflects the behavior of the ionization fractions in Fig. 2.17, var B is completely out of line. [Note: In var B, pH < 5 are not available in practice.]
2.4.6 Open vs. Closed CO₂ System

All considerations so far have assumed a “closed CO₂ system”. In contrast, an open system, the aqueous solution is in 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”

As in § 2.4.5 we start with the ionization fractions \( a_j \) displayed in Fig. 2.17 (based on Eq. (1.90)); they are the same for **var A** and **var C**. As in § 2.4.5 the two variants differ only in the value or function of \( C_T \). The latter should be specified for the open system.

The “open system” is described by

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

or more explicitly:

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

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

(2.83) \[ [0] = K_H \cdot P \]

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

(2.84) \[ C_T = \frac{K_H \cdot P}{a_0} \]

Thus the two variants only differ in the \( C_T \) value:

(2.85) **var A** \( C_T = \text{const} \) \( \text{with } C_T = 100 \text{ mM} \)

(2.86) **var C** \( C_T = K_H P/a_0 \) \( \text{at } P = 10^{-3.408} \text{ atm}^{28} \)

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

Although both cases rely on the same ionization fractions, the pH dependence of the species in **var A** and **var C** differs fundamentally. While the species in **var A** (upper left diagram) show the same behavior as the \( a_j \) in Fig. 2.17, **var C** is completely out of line: The more alkaline the solution becomes, the more CO₂ is sucked out of the atmosphere (which increases the \( C_T \) exponentially). [Note: In **var C**, pH > 11 are not available in practice.]

---

28 valid under normal atmospheric conditions (\( P = 0.00039 \text{ atm}, 25^\circ\text{C} \)
Fig. 2.19  Species distribution of H$_2$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) discussed in the last two paragraphs reveal the key role of the ionization fractions $a_i$ (shown in Fig. 2.17), which remain exactly the same regardless 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 acid) to mixtures of several acids:

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

The total sum of all acids is abbreviated by \( C_T \):

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

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):

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

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

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

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

\[ Y_1^{(a)} = \sum_{j=1}^{N_a} j^1 a_j^{(a)} \] (2.90)

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

**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 is 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 \textit{H}_{N}A \text{ as Superposition of \textit{N} Monoprotic Acids}

From a mathematical point of view, the titration curve of an \textit{N}-protic acid (defined by $K_1$, $K_2$ to $K_N$) can be generated by a superposition of (virtual) \textit{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 the 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 is sufficient to focus on $Y_1$:

\begin{equation}
Y_1 = a_1 + 2a_2 = (a_1 + a_2) + a_2
\end{equation}

From Eq. (1.90) we then get:

\begin{equation}
a_1 + a_2 = \left(\frac{K_1}{x} + \frac{K_1K_2}{x^2}\right) \left(1 + \frac{K_1}{x} + \frac{K_1K_2}{x^2}\right)^{-1} = \frac{K_1^{(a)}}{x} \left(1 + \frac{K_1^{(a)}}{x}\right)^{-1} \equiv a_1^{(a)}
\end{equation}

\begin{equation}
a_2 = \frac{K_2}{x} \left(\frac{x}{K_1} + 1\right)^{-1} = \frac{K_1^{(b)}}{x} \left(1 + \frac{K_1^{(b)}}{x}\right)^{-1} \equiv a_1^{(b)}
\end{equation}
Acid Base Systems

Here, we introduced new acidity constants $K_i^{(a)}$ and $K_i^{(b)}$ that are (almost) identical with the two acidity constants of $H_2A$:

\[(2.94) \quad K_i^{(a)} = K_i \left(1 + \frac{K_2}{x}\right) \quad \xrightarrow{K_3/x \ll 1, \ pH \to 0} \quad K_i^{(a)} \approx K_i\]

\[(2.95) \quad K_i^{(b)} = K_2 \left(1 + \frac{x}{K_1}\right) \quad \xrightarrow{x/K_1 \ll 1, \ pH \to 14} \quad K_i^{(b)} \approx K_2\]

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

\[(2.96) \quad Y_i = a_i + 2a_2 \quad \Leftleftrightarrow \quad Y_i = Y_i^{(a)} + Y_i^{(b)}\]

diprotic acid \quad \text{superposition of 2 monoprotic acids}

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

\[(2.97) \quad Y_i = a_i + 2a_2 + 3a_3 + \ldots \quad \Leftleftrightarrow \quad Y_i = Y_i^{(a)} + Y_i^{(b)} + Y_i^{(c)} + \ldots\]

$N$-protic acid \quad \text{superposition of $N$ monoprotic acids}

**Fig. 2.21** $Y_i$ of carbonic and phosphoric acids generated as superposition of two and three (virtual) monoprotic acids
Examples. Two examples are presented in Fig. 2.21 where $Y_1$ of carbonic acid ($H_2A$) and phosphoric acid ($H_3A$) are generated from two and three (virtual) monoprotic acids:

- **carbonic acid:**
  \[ Y_1 = a_i^{(a)} + a_i^{(b)} \]

- **phosphoric acid:**
  \[ Y_1 = a_i^{(a)} + a_i^{(b)} + a_i^{(c)} \]

The blue curves in the present diagram are de facto indistinguishable from the blue curves (showing $Y_1$) 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\textsubscript{A} (with amount C\textsubscript{T}) plus a strong base (with amount C\textsubscript{B}). The pH of this system is completely determined by two quantities: C\textsubscript{T} and C\textsubscript{B}, or alternatively, C\textsubscript{T} and n (= C\textsubscript{B}/C\textsubscript{T}). The main relationship is presented by Eq. (2.32) in § 2.2.2.

ANC. The acid-neutralizing capacity [ANC] is the amount of basicity of the acid-base system that can be titrated with a strong acid to a chosen equivalence point EP\textsubscript{j} (at pH\textsubscript{j}):

\begin{equation}
[\text{ANC}]_{\text{n=j}} = \text{basicity in initial state} - \text{basicity at EP\textsubscript{j}}
\end{equation}

\begin{equation}
[\text{ANC}]_{\text{n=j}} = C\textsubscript{B}(\text{pH}) - C\textsubscript{B}(\text{pH}\textsubscript{j})
\end{equation}

The small subscript \text{n} on the symbol [ANC]\textsubscript{n} remind us that the neutralizing capacity always refers to a chosen reference point, usually EP\textsubscript{n}. In the special case of n=0, which corresponds to the base-free system, i.e. C\textsubscript{B}(pH\textsubscript{0}) = 0, ANC becomes\textsuperscript{29}

\begin{equation}
[\text{ANC}]_{0} = C\textsubscript{B}(\text{pH})
\end{equation}

Eq. (3.2) can also be written as

\begin{equation}
\frac{[\text{ANC}]_{\text{n=j}}}{C\textsubscript{T}} = n(\text{pH}) - n(\text{pH}\textsubscript{j})
\end{equation}

\text{function of pH}

\text{fixed integer value (EP\textsubscript{j}): n(\text{pH}\textsubscript{j}) = j}

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

\begin{equation}
n(x) = Y\textsubscript{1}(x) + \frac{w(x)}{C\textsubscript{T}}
\end{equation}

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

\begin{equation}
\frac{[\text{ANC}]_{\text{n=j}}}{C\textsubscript{T}} = Y\textsubscript{1}(x) + \frac{w(x)}{C\textsubscript{T}} - j
\end{equation}

or

\begin{equation}
[\text{ANC}]_{\text{n=j}} = \{ Y\textsubscript{1}(x) - j \} C\textsubscript{T} + w(x)
\end{equation}

\textsuperscript{29}pH\textsubscript{0} is the pH value of acid H\textsubscript{A} with amount C\textsubscript{T}. In other words, pH\textsubscript{0} is the root of polynomial (1.136).
To give an example, the amount of strong acid (e.g. HCl) required to neutralize the system from startpoint $x = 10^{\text{pH}}$ towards a particular EP$_j$ (as the titration endpoint) is

\[(3.8) \quad [\text{ANC}]_0 = \{ Y_1(x) - 0 \} C_T + w(x) = \{ Y_1(x) C_T + w(x) \} - 0 \cdot C_T\]

\[(3.9) \quad [\text{ANC}]_1 = \{ Y_1(x) - 1 \} C_T + w(x) = \{ Y_1(x) C_T + w(x) \} - 1 \cdot C_T\]

\[(3.10) \quad [\text{ANC}]_2 = \{ Y_1(x) - 2 \} C_T + w(x) = \{ Y_1(x) C_T + w(x) \} - 2 \cdot C_T\]

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 $C_T$) 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 the exact opposite of ANC:

\[(3.11) \quad [\text{BNC}]_n = -[\text{ANC}]_n\]

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

\[(3.12) \quad [\text{BNC}]_{n=j} = \{ j - Y_1(x) \} C_T - w(x)\]

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 \( C_T = 10 \text{ mM} \). 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 \( n(pH) = 5/2 \))
- **point B** at \( pH = 2.3 \) (belongs to equivalent fraction \( n(pH) = -1/2 \))

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 **A** \( \text{pH} = 11.7 \Rightarrow \text{pH}_n \)
- alkalimetric titration with strong base from **B** \( \text{pH} = 2.3 \Rightarrow \text{pH}_n \)

ANC. The required amount of *strong acid* (indicated by green arrows) to attain EP₁, EP₂, and EP₃ is just the acid-neutralizing capacity given in Eqs. (3.8) to (3.10):

\[
\begin{align*}
(3.13) \quad [\text{ANC}]_0 &= \{ 5/2 - 0 \} \cdot C_T = 25 \text{ mM} \\
(3.14) \quad [\text{ANC}]_1 &= \{ 5/2 - 1 \} \cdot C_T = 15 \text{ mM} \\
(3.15) \quad [\text{ANC}]_2 &= \{ 5/2 - 2 \} \cdot C_T = 5 \text{ mM}
\end{align*}
\]
**Acid Base Systems**

**Short Lecture**

**BNC.** The required amount of *strong base* (indicated by red arrows) to attain $EP_1$, $EP_2$, and $EP_3$ is just the base-neutralizing capacity:

\[
\begin{align*}
[BNC]_0 &= - \left\{ -1/2 - 0 \right\} C_T = 5 \text{ mM} \\
[BNC]_1 &= - \left\{ -1/2 - 1 \right\} C_T = 15 \text{ mM} \\
[BNC]_2 &= - \left\{ -1/2 - 2 \right\} C_T = 25 \text{ mM}
\end{align*}
\]

The 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 $[ANC]$ is known as *alkalinity* and $[BNC]$ as *acidity*. Again, it is necessary to distinguish between different types of alkalinity and acidity, which depend on the reference point $EP_j$ chosen. The carbonic acid has three EPs, hence there are three types of alkalinity (cf. Fig. 3.3):

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

Correspondingly, there are three types of acidity:

\[
\begin{align*}
\text{mineral acidity:} & \quad [H-\text{Acy}] = [BNC]_{n=0} \\
\text{CO}_2 \text{ acidity:} & \quad [CO_2-\text{Acy}] = [BNC]_{n=1} \\
\text{acidity:} & \quad [\text{Acy}] = [BNC]_{n=2}
\end{align*}
\]

Alkalinity and acidity are complementary. From Eq. (3.11) we get:

\[
\begin{align*}
[ANC]_0 &= - [BNC]_0 \quad \Rightarrow \quad [\text{Alk}] = - [H-\text{Acy}] \\
[ANC]_1 &= - [BNC]_1 \quad \Rightarrow \quad [P-\text{Alk}] = - [CO_2-\text{Acy}] \\
[ANC]_2 &= - [BNC]_2 \quad \Rightarrow \quad [OH-\text{Alk}] = - [\text{Acy}]
\end{align*}
\]

**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.
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Of all three types of alkalinity, *total alkalinity* is the most important; as introduced in Eq. (3.19), it is given by

\[(3.28) \quad [\text{Alk}] = [\text{ANC}]_0 = C_B = n C_T\]

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

\[(3.29) \quad [\text{M-alk}] - [\text{P-alk}] = [\text{ANC}]_0 - [\text{ANC}]_1 = C_T \quad (= \text{DIC})\]

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 have 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 (which can be any chosen $pH$ value). In practice, however, it is common to use the $pH$ values of the equivalence points $\text{EP}_0$ and $\text{EP}_1$ of the carbonate system:

\[(3.30) \quad \text{EP}_0: \quad \text{pH} \approx 4.3 \quad \text{valid for carbonic acid with } C_T \approx 1 \ldots 10 \text{ mM}\]
\[(3.31) \quad \text{EP}_1: \quad \text{pH} \approx 8.2\]

The usefulness of this choice is 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 EPs are shown as yellow dots in Fig. 3.2 and Fig. 3.3. The corresponding $pH$ values serve as titration end points in hydrochemistry. The measured amount of strong acid or base to reach the endpoint is called:

\[(3.32) \quad \text{ANC to pH 4.3: } [\text{ANC}]_{\text{pH 4.3}} \approx [\text{Alk}]\]
\[(3.33) \quad \text{ANC to pH 8.2: } [\text{ANC}]_{\text{pH 8.2}} \approx [\text{P-alk}]\]
\[(3.34) \quad \text{BNC to pH 4.3: } [\text{BNC}]_{\text{pH 4.3}} \approx [\text{Alk}]\]
\[(3.35) \quad \text{BNC to pH 8.2: } [\text{BNC}]_{\text{pH 8.2}} \approx [\text{P-alk}]\]

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 $E_{P0}$) taken from Eq. (3.3):

\[(3.36) \quad [\text{ANC}]_0 = C_T Y_1(x) + w(x) = C_B(x) \quad \text{(buffer capacity)}\]

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

\[(3.37) \quad n(x) = Y_1(x) + \frac{w(x)}{C_T} \quad \text{('normalized' buffer capacity)}\]

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 $10^{-pH}$ and write:

\[(3.38) \quad n(pH) = Y_1(pH) + \frac{w(pH)}{C_T} \quad \text{with} \quad Y_1(pH) = \sum_{j=0}^{N} j \cdot a_j(pH)\]

The buffer intensity is the pH-derivative of the buffer capacity. Depending on the expression for buffer capacity (either in its normalized form, $n(pH)$, or as $C_B$ as in Eq. (3.36)), we distinguish two types of buffer intensities:

\[(3.39) \quad \text{‘normalized’ buffer intensity:} \quad \beta = \frac{dn}{dpH} \quad \text{[unitless]}\]

\[(3.40) \quad \text{buffer intensity:} \quad \beta_C = \frac{dC_B}{dpH} = \beta C_T \quad \text{[mol/L]}\]

Both quantities differ in their physical unit: $\beta$ is unitless, while $\beta_C$ has concentration units: 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 $E_{Pn}$):

\[(3.41) \quad [\text{ANC}]_n = \int_{pH_0}^{pH} \beta_C(pH') dpH'\]

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. This means that the change of the pH value, i.e. $\Delta pH$, should be small for all changes $\Delta n$ of $n = C_B/C_T$. In other words, the slope of the titration curve, $\Delta n/\Delta pH$, should be large for maximum buffering capability. The buffer intensity, $\beta = dn/dpH$, is the measure of this slope.
To sum up: the steeper the slope of a titration curve – as sketched in Fig. 3.4 – the higher the buffer intensity $\beta = \frac{dn}{dpH}$, i.e. the higher the resistance of the system 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.

\[ p\beta = \text{max} \implies \text{optimal buffer range} \]

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 agrees with the principle of LE CHÂTELIER: 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 $pK_j$. 

---

Fig. 3.4 The steeper the slope of a titration curve, the higher is the resistance of the system to pH changes.

Fig. 3.5 Optimal buffer range ($H_2CO_3$ system). Calculations based on Eqs. (3.42) to (3.44).
3.2.3 Closed-Form Expressions

What is called ‘buffer capacity’ in Eq. (3.38) is exactly our formula for the ‘titration-curve’, \( n = n(pH) \), which was derived and used in Chapter 2. All considerations about the buffer capacity remain valid if we extend our scope to include zwitterionic acids, as it was done in § 2.2.6. For this purpose we start from the more general Eq. (2.56), which differs from Eq. (3.38) by a constant offset \( Z \) (which disappear anyway after pH-derivation).

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

\[
\begin{align*}
(3.42) & \quad \text{buffer capacity:} & n(x) &= \left( Y_1(x) - Z \right) + \frac{w(x)}{C_T} \\
(3.43) & \quad \text{buffer intensity:} & \beta(x) &= \frac{dn}{dpH} = \ln10 \left( Y_2 - Y_1^2 + \frac{w + 2x}{C_T} \right) \\
(3.44) & \quad 1^\text{st} \text{derivative of } \beta: & \frac{d\beta}{dpH} &= \frac{d^2n}{dpH^2} = \left( \ln10 \right)^2 \left( Y_3 - 3Y_1Y_2 + 2Y_1^3 + \frac{w}{C_T} \right)
\end{align*}
\]

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 \( d\beta/dpH = 0 \).

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

\[
\begin{align*}
(3.45) & \quad \text{titration curve:} & n(x) &= Y_1(x) - Z \\
(3.46) & \quad \text{buffer intensity:} & \beta(x) &= \frac{dn}{dpH} = \ln10 \left( Y_2 - Y_1^2 \right) \\
(3.47) & \quad 1^\text{st} \text{derivative of } \beta: & \frac{d\beta}{dpH} &= \frac{d^2n}{dpH^2} = \left( \ln10 \right)^2 \left( Y_3 - 3Y_1Y_2 + 2Y_1^3 \right)
\end{align*}
\]

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 high-\( C_T \) limit (in the next paragraph).

---

\(^{30}\) The maximum or minimum is where the slope (i.e. the derivative) of a function becomes zero.
### 3.2.4 Minima and Maxima (High-C<sub>T</sub> Limit)

This paragraph relies on the buffer intensity β and its derivative dβ/dpH, as given in Eqs. (3.46) and (3.47) for the high-C<sub>T</sub> limit (C<sub>T</sub> ≫ w), where the contribution from ‘H₂O’ is negligible:

\[
\beta(x) = \ln 10 \left( Y_1 - Y_1^2 \right)
\]

\[
\frac{d\beta}{dpH} = (\ln 10)^2 \left( Y_3 - 3Y_1Y_2 + 2Y_1^3 \right)
\]

These are smooth functions made of Y₁, Y₂, and Y₃ alone. The behavior of Y₉ is entirely determined by the set of acid’s equilibrium constants Kᵢ, or alternatively, by the *internal* equivalence points EP<sub>n</sub> as given in Eqs. (1.115) and (1.116):

\[
\begin{align*}
\text{(3.50)} & \quad \text{semi-EP}_n \quad \text{at } pK_j \quad \text{Y}_L = \frac{1}{2} \{ (j-1)^{\frac{1}{2}} + j^{\frac{1}{2}} \} \quad (n = j^{\frac{1}{2}}) \\
\text{(3.51)} & \quad \text{EP}_j \quad \text{at } pH_j = \frac{1}{2}(pK_j+pK_{j+1}) \quad \text{Y}_L = j^{\frac{1}{2}} \quad (n = j)
\end{align*}
\]

Inserting it into Eq. (3.48) we get

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

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 β(pH) occur at pH values where dβ/dpH = 0. The derivative itself is given by Eq. (3.49) above, where we focus on Y₃ – 3Y₁Y₂ + 2Y₁³.

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

\[
\text{(3.54)} \quad Y_3 - 3Y_1Y_2 + 2Y_1^3 = \frac{1}{2} \{ (j-1)^{3} + j^{3} \} - 3(j-\frac{1}{2})(j^{\frac{3}{2}}) + 2(j^{\frac{3}{2}})^{3} = 0 \quad \text{at } pH = pK_j \quad \text{for } j = 1, 2, ..., N
\]

For EP<sub>n</sub> with integer n = j, we get from Eq. (3.51):

\[
\text{(3.55)} \quad Y_3 - 3Y_1Y_2 + 2Y_1^3 = j^{3} - 3j j^{2} + 2 j^{3} = 0 \quad \text{at } pH = pH_j \quad \text{for } j = 1, 2, ..., N-1
\]

Hence, the zeros of dβ/dpH occur exactly at the *internal* equivalence points EP<sub>n</sub> for both integer and half-integer n. To decide whether the zeros indicate a maximum or minimum, we need the next higher derivative d²β/dpH² (or d³Y₁/dpH³), which is presented in Eq. (B.55) in Appendix B.4.
In summary, we get the following assignment:\textsuperscript{31}

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

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

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):

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

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

This behavior of the buffer intensity is illustrated in Fig. 3.6 for four 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 high-\(C_T\) 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).

\textsuperscript{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 case valid for $C_T \to \infty$. Now, the more realistic case of finite $C_T$ values considers 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 $d\beta/dpH$, which 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.

![Fig. 3.7 Titration curve $n(pH)$, buffer intensity $\beta$, and $d\beta/dpH$ for three $C_T$ values of the carbonate system](image)

**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 the curves for the case $C_T \to \infty$ in Fig. 3.6.
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Short Lecture

**Fig. 3.8** Titration curve (blue), buffer intensity (green), and $d\beta/dpH$ (red) for four common acids with $C_T = 100$ mM

**Fig. 3.9** Titration curve (blue), buffer intensity (green), and $d\beta/dpH$ (red) for four common acids with $C_T = 10$ mM
Fig. 3.10 Titration curve (blue), buffer intensity (green), and $d\beta/dpH$ (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) and 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):

$$\text{H}_2\text{N} - \text{C} - \text{COOH} \rightleftharpoons \text{H}_2\text{N}^+ - \text{C} - \text{COO}^-$$

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:

$$\text{H}^+ \frac{K_1}{pK_1} \text{H}_2\text{N}^+ - \text{C} - \text{COO}^-$$

This parallels the behavior of a diprotic acid:

$$\text{H}_2\text{A} \underset{pK_1}{\rightleftharpoons} \text{HA}^- \frac{K_2}{pK_2} \text{A}^{2-}$$

$^{32}$ R denotes the side chain (glycine: R = H, alanine: R = CH$_3$, and so on).
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When an amino acid dissolves in water, the zwitterion interacts with H₂O molecules – it acts both as an acid and a base. But unlike amphoteric compounds, which can only form either a cationic or an anionic species, a zwitterion has both ionic states simultaneously.

4.1.2 Zwitterions as Diprotic 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>species</th>
<th>diprotic acid</th>
<th>zwitterion (simplest amino acids)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st dissociation</td>
<td>H₂A = H⁺ + HA⁻</td>
<td>H₂A⁺ = H⁺ + HA⁻</td>
</tr>
<tr>
<td>2nd dissociation</td>
<td>HA⁻ = H⁺ + A²⁻</td>
<td>HA = H⁺ + A⁻</td>
</tr>
</tbody>
</table>

In both cases there are \( N=2 \) dissociation steps (controlled by two acidity constants \( K_1 \) and \( K_2 \)) 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 acid types.

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

\[
(4.4) \quad z_j = Z - j
\]

This yields:

<table>
<thead>
<tr>
<th>diprotic acid (Z=0)</th>
<th>zwitterion (Z=1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[0]: [H₂A] (neutral)</td>
<td>[H₂A⁺] (cation) (highest protonated)</td>
</tr>
<tr>
<td>[1]: [HA⁻] (anion)</td>
<td>[HA] (neutral)</td>
</tr>
<tr>
<td>[2]: [A²⁻] (anion)</td>
<td>[A⁻] (anion) (fully deprotonated)</td>
</tr>
</tbody>
</table>

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

\[
(4.5) \quad Z = z_0
\]

The last line in Tab. 4.1 represents the average charge of the acid (as defined in Eq. (2.51)).
**Basic Equations.** The description of common acids and zwitterionic acids is based on the *same* equations 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 offset $Z$, as the new feature, enters only the titration formula (i.e. buffer capacity) in Eq. (3.42); the buffer intensity $\beta$ and its pH-derivative are independent of $Z$ – see Eqs. (3.43) and (3.44).

### 4.1.3 Example: Glycine

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

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

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

- glycine: $\text{pK}_1 = 2.35$  
  $\text{pK}_2 = 9.78$  
- (carbonic acid: $\text{pK}_1 = 6.35$  
  $\text{pK}_2 = 11.33$)

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

**Titration Curves.** The titration curves $n = n(\text{pH})$ in Fig. 4.2 show what happens to the amino acid *glycine* when you change the pH by adding a strong acid (HCl) or a strong base (NaOH). These curves were calculated using Eq. (3.42).
The right diagram in Fig. 4.2 compares the analytical formula for $C_T = 100$ mM with numerical calculations using PHREEQC 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 $|n|$).

**Fig. 4.2** Titration curves $n = n(pH)$ for the amino acid glycine. Left: calculations based on Eq. (3.42) for four amounts of $C_T$. Right: comparison with numerical program PHREEQC and/or AQION (dots).

**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).
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This is done for two cases: infinitely high concentrated glycine (CT → ∞) and CT = 500 mM. The calculations are based on Eqs. (3.42) to (3.44). The small dots are the zeros of dβ/dpH, which indicate the extrema of the buffer intensity β 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 (bottom diagram), except that the x- and y-axis are swapped.

4.1.4 Zwitterions as N-protic Acids: H\textsubscript{N}A\textsuperscript{+Z}

In addition to the simplest 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 listed in Tab. 4.2 and Fig. 4.4. To recap: N is the number of H\textsuperscript{+} in the highest protonated species and Z is the positive charge of the highest protonated species.

Tab. 4.2 Acidity constants for selected zwitterionic acids (equilibrium constants are taken from [M91])

<table>
<thead>
<tr>
<th></th>
<th>N</th>
<th>Z</th>
<th>pK\textsubscript{1}</th>
<th>pK\textsubscript{2}</th>
<th>pK\textsubscript{3}</th>
<th>pK\textsubscript{4}</th>
<th>pK\textsubscript{5}</th>
<th>pK\textsubscript{6}</th>
<th>[j=0]</th>
<th>[j=Z]</th>
<th>[j=N]</th>
</tr>
</thead>
<tbody>
<tr>
<td>carboxylic acid</td>
<td>2</td>
<td>0</td>
<td>17.96</td>
<td>10.50</td>
<td>4.86</td>
<td>3.42</td>
<td>2.37</td>
<td>1.25</td>
<td>H\textsubscript{2}A</td>
<td>H\textsubscript{2}A</td>
<td>A\textsuperscript{2}</td>
</tr>
<tr>
<td>glycine</td>
<td>2</td>
<td>1</td>
<td>17.96</td>
<td>10.50</td>
<td>4.86</td>
<td>3.42</td>
<td>2.37</td>
<td>1.25</td>
<td>H\textsubscript{2}A\textsuperscript{+}</td>
<td>HA</td>
<td>A\textsuperscript{2}</td>
</tr>
<tr>
<td>glutamic acid</td>
<td>3</td>
<td>1</td>
<td>17.96</td>
<td>10.50</td>
<td>4.86</td>
<td>3.42</td>
<td>2.37</td>
<td>1.25</td>
<td>H\textsubscript{2}A\textsuperscript{+}</td>
<td>H\textsubscript{2}A</td>
<td>A\textsuperscript{2}</td>
</tr>
<tr>
<td>NTA</td>
<td>4</td>
<td>1</td>
<td>17.96</td>
<td>10.50</td>
<td>4.86</td>
<td>3.42</td>
<td>2.37</td>
<td>1.25</td>
<td>H\textsubscript{2}A\textsuperscript{+}</td>
<td>H\textsubscript{2}A</td>
<td>A\textsuperscript{3}</td>
</tr>
<tr>
<td>EDTA</td>
<td>6</td>
<td>2</td>
<td>17.96</td>
<td>10.50</td>
<td>4.86</td>
<td>3.42</td>
<td>2.37</td>
<td>1.25</td>
<td>H\textsubscript{2}A\textsuperscript{+2}</td>
<td>H\textsubscript{2}A\textsuperscript{+}</td>
<td>A\textsuperscript{4}</td>
</tr>
</tbody>
</table>

Fig. 4.4 Structural formulas of four zwitterionic acids

The zwitterionic acids have N+1 species:

\[(4.6) \quad [j] = [H\textsubscript{Nj}A\textsuperscript{Z-j}] \quad \text{with charge} \quad z\textsubscript{j} = Z - j \quad \text{(for j = 0 to N)}\]

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

| j = 0 | [0] = [H\textsubscript{N}A\textsuperscript{Z}] | highest protonated | neutral \[Z] = [0] | cation |
| j = Z | [Z] = [H\textsubscript{N}Z\textsubscript{+}] | undissociated acid | neutral | |
| j = N | [N] = [A\textsuperscript{Z-N}] | fully deprotonated | anion | |
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 case $C_T \rightarrow \infty$ (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.
Acid Base Systems

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:

- highly concentrated acids ($C_T \rightarrow \infty$) 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 particularly interesting because it represents the acid with the highest number of dissociation steps in this lecture: $N = 6$ (defined by the six acidity constants in Tab. 4.2).

There are $N+1 = 7$ acid species, the highest protonated species being $H_6A^{+2}$ and the fully deprotonated species being $A^{-4}$. Fig. 4.7 displays the pH dependence of EDTA’s seven ionization fractions $a_0$ to $a_6$ based on the formulas given in Eq. (1.90).

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

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 EDTA titration curves, the x and y axes are swapped in Fig. 4.8.]

\[^{33}\] In these calculations complex-formation of EDTA is ignored.
4.1.5 Equivalence Points

In §2.3 the mathematical relationship between the $E_{P_n}$ and the corresponding $pH_n$ values was established. This concept can easily be extended to zwitterions by considering the offset $Z$:

$$E_{P_n} \Leftrightarrow n = \left( Y_1(pH) - Z \right) + \frac{w(pH)}{C_T} \quad \text{for } n = -Z, \ldots, -\frac{1}{2}, 0, \frac{1}{2}, \ldots, N-Z$$

For $Z = 0$, this relationship falls back to Eq. (2.64).

---

Fig. 4.9 Titration curve of glycine with EPs and semi-EPs located at integer and half-integer values of $n$
Fig. 4.9 shows the titration curve of glycine for $C_T = 500 \text{ mM}$ (same as in Fig. 4.3, bottom diagram). The small circles at integer and half-integer values of $n$ mark the EP$_n$-pH$_n$ 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 a generalization of Eq. (2.66) for $Z > 0$

$$C_T = \frac{w(pH)}{n + Z - Y_1(pH)} \quad \tag{4.8}$$

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 “acid”. This diagram should be compared with the plots in Fig. 2.10 on page 60, done for common acids.

![Fig. 4.10 pH dependence of EPs and semi-EPs plotted as $C_T = f(pH)$ for glycine](image)

### 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 *isolectric* point $pI$ is the pH at which the average charge $z_a$ of the polyprotic acid is zero:

$$z_a(pH) = 0 \quad \tag{4.10}$$

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):

$$z - Y_1(pH) = \frac{w(pH)}{C_T} \quad \tag{4.11}$$

$$z - Y_1(pH) = 0 \quad \tag{4.12}$$

$^{34}$ 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 (pI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH of pure acid</td>
<td>pH at which the net charge of all acid species is zero</td>
</tr>
<tr>
<td>depends on $C_T$ (approaches pI-value 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:

\[(4.13) \quad \text{isoelectric point:} \quad 1 - Y_1 = 0 \quad \Leftrightarrow \quad pI = \frac{1}{2}(pK_1 + pK_2)\]

The equation on the right side 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 $EP_0$).
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\(_{pzc}\), which is the point of zero charge.

Let’s consider a surface hydroxyl group \(\equiv\text{OH}\), where \(\equiv\) symbolizes the surface. The uptake and release of protons can be described by two dissociation steps:

\[
\begin{align*}
\text{1st dissociation step:} & \quad \equiv\text{OH}_2^+ = \text{H}^+ + \equiv\text{OH} & K_1 \\
\text{2nd dissociation step:} & \quad \equiv\text{OH} = \text{H}^+ + \equiv\text{O}^- & K_2
\end{align*}
\]

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 \(\text{H}_2\text{A}^+\), there are \(N+1=3\) surface species:

\[
\begin{align*}
[0] &= [\equiv\text{OH}_2^+] \quad \text{cationic} \\
[1] &= [\equiv\text{OH}] \quad \text{neutral} \\
[2] &= [\equiv\text{O}^-] \quad \text{anionic}
\end{align*}
\]

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).

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

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

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):

\[ \text{pH}_{\text{pzc}} = \frac{1}{2} (\text{pK}_1 + \text{pK}_2) \]  

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


ADDITIONAL LINKS

PowerPoint Presentations:

- Acid-Base Systems  www.slideshare.net/aqion/acidbase-systems
- 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 notation 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 can 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:

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

that is, activity and concentration coincide:

\[
\text{ideal solution: } \{j\} = [j]
\]

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

A.1.2 Ionic Strength

The ionic strength of a solution is determined by the concentrations of all ions present in the 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 particularly strongly to the ionic strength. [Note: In literature, the ionic strength is also abbreviated by the Greek symbol \(\mu\).]

For comparison: typical ionic strengths of natural waters are:

- surface water: \(I = 0.001\ M\) to \(0.005\ M\)
- potable water / groundwater: \(I = 0.001\ M\) to \(0.02\ M\)
- seawater: \(I = 0.7\ M\)

### A.2 Activity Models

The step from molar concentrations (measured data) to activities (which enter law-of-mass-action calculations) requires the knowledge 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)** \[\lg \gamma_j = -Az_j^2 \sqrt{I} \quad \text{for } I < 10^{-2.3} \, \text{M}\]

(A.7) Extended DH \[\lg \gamma_j = -Az_j^2 \left(\frac{\sqrt{I}}{1 + B\alpha_j \sqrt{I}}\right) \quad \text{for } I < 0.1 \, \text{M}\]

(A.8) **DAVIES** \[\lg \gamma_j = -Az_j^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}}\right) - 0.3 \cdot I \quad \text{for } I \leq 0.5 \, \text{M}\]

(A.9) **TRUESDELL-JONES** \[\lg \gamma_j = -Az_j^2 \left(\frac{\sqrt{I}}{1 + B\alpha_j^0 \sqrt{I} + b_j I}\right) \quad \text{for } I < 1 \, \text{M}\]

Here, \(z_j\) is the charge or 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 = 10 Ångström.
**B MATHEMATICAL RELATIONSHIPS**

**B.1 Approximations for \( a_j \)**

**B.1.1 Piecewise Approximation for \( \log a_j \)**

We start with the definition of \( a_0 \) in Eq. (1.90):

\[
(B.1) \quad a_0^{-1} = \left( 1 + \frac{k_1}{x} + \frac{k_2}{x^2} + \ldots + \frac{k_N}{x^N} \right) = \left( 1 + \frac{K_1}{x} + \frac{K_2}{x^2} + \ldots + \frac{K_N}{x^N} \right)
\]

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 \( K_2 < x < K_3 \) \( \Rightarrow \) \( a_0^{-1} \approx k_2/x^2 \)
- in the Nth interval (\( pH > pK_N \)) where \( x < K_N \) \( \Rightarrow \) \( a_0^{-1} \approx k_N/x^N \)

Thus, we can approximate \( \log a_0 \) in the \( i \)th interval by

\[
(B.2) \quad \log a_0 \approx \log \frac{x^i}{k_i} = i \log x - \log k_i = -i \cdot pH + pk_i
\]

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):

\[
(B.3) \quad a_j = \left( \frac{k_i}{x^i} \right) a_0 \quad \Rightarrow \quad \log a_j = \log a_0 + j \cdot pH - pk_j
\]

Inserting the approximation in Eq. (B.2) for \( \log a_0 \) yields

\[
(B.4) \quad \log a_j \approx (j-i) \cdot pH + (pk_i - pk_j) \quad \text{for the } i \text{th interval}
\]

This is a linear function of pH 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:

- $a_0 \approx (0 – i) \text{pH} + (pK_i – pK_0)$ (blue dashed curve)

  with the following segments in the $i^{th}$ intervals:

  \[
  \begin{align*}
  i = 0: & \quad (0 – 0) \text{pH} + (0 – 0) = 0 = 0 \\
  i = 1: & \quad (0 – 1) \text{pH} + (pK_1 – 0) = -\text{pH} + pK_1 = \text{pH} + 2.15 \\
  i = 2: & \quad (0 – 2) \text{pH} + (pK_2 – 0) = -2 \text{pH} + (pK_1 + pK_2) \\
  i = 3: & \quad (0 – 3) \text{pH} + (pK_3 – 0) = -3 \text{pH} + (pK_1 + pK_2 + pK_3) \\
  \end{align*}
  \]

- $a_1 \approx (1 – i) \text{pH} + (pK_i – pK_1)$ (brown dashed curve)

  with the following segments in the $i^{th}$ intervals:

  \[
  \begin{align*}
  i = 0: & \quad (1 – 0) \text{pH} + (0 – pK_1) = \text{pH} - pK_1 = \text{pH} - 2.15 \\
  i = 1: & \quad (1 – 1) \text{pH} + (pK_1 – pK_1) = 0 = 0 \\
  i = 2: & \quad (1 – 2) \text{pH} + (pK_2 – pK_1) = -\text{pH} + pK_2 = -\text{pH} + 7.21 \\
  i = 3: & \quad (1 – 3) \text{pH} + (pK_3 – pK_1) = -2 \text{pH} + (pK_2 + pK_3) \\
  \end{align*}
  \]

- $a_2 \approx (2 – i) \text{pH} + (pK_i – pK_2)$ (green dashed curve)

  with the following segments in the $i^{th}$ intervals:

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

- $a_3 \approx (3 – i) \text{pH} + (pK_i – pK_3)$ (orange dashed curve)

  with the following segments in the $i^{th}$ intervals:

  \[
  \begin{align*}
  i = 0: & \quad (3 – 0) \text{pH} + (0 – pK_3) = 3 \text{pH} - (pK_1 + pK_2 + pK_3) \\
  \hspace{2cm} & \hspace{2cm} = 3 \text{pH} - 21.7 \\
  i = 1: & \quad (3 – 1) \text{pH} + (pK_1 – pK_3) = 2 \text{pH} - (pK_2 + pK_3) = 2 \text{pH} - 19.55 \\
  i = 2: & \quad (3 – 2) \text{pH} + (pK_2 – pK_3) = \text{pH} - pK_3 = \text{pH} - 12.35 \\
  i = 3: & \quad (3 – 3) \text{pH} + (pK_3 – pK_3) = 0 = 0 \\
  \end{align*}
  \]
B.1.2 Strong Acids

The ionization fractions $a_j$ are defined in Eq. (1.90). They simplify for strong acids, where the condition $x/K_1 \to 0$ holds for all relevant $x$ (as discussed in Eq. (2.40)).

Let’s start with

$$a_0^{-1} = \left(1 + \frac{K_2}{x} + \frac{K_2 K_3}{x^2} + \cdots\right)$$

$$= \frac{K_1}{x} \left(\frac{x}{K_1} + 1 + \frac{K_2}{x} + \cdots\right)$$

$$= \frac{K_1}{x} \left(1 + \frac{K_2}{x} + \cdots\right)$$

(because $x/K_1 \approx 0$)

It yields

$$a_0 = \frac{x}{K_1} \left(1 + \frac{K_2}{x} + \cdots\right)^{-1} = 0$$

(because $x/K_1 \approx 0$)

According to the general formula $a_1 = (K_1/x) a_0$, the term in the brackets of Eq. (B.5) represents $a_1$:

$$a_1 = \left(1 + \frac{K_2}{x} + \cdots\right)^{-1}$$

and we successively get

$$a_0 = 0$$

$$a_1 = \left(1 + \frac{K_2}{x} + \frac{K_2 K_3}{x^2} + \cdots\right)^{-1} = \left(1 + \frac{k_2}{x} + \frac{k_3}{x^2} + \cdots + \frac{k_n}{x^{n-1}}\right)^{-1}$$

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

with “redefined” cumulative acidity constants $k_j$

$$k_0 = 0, \quad k_1 = 1, \quad k_2 = K_2, \ldots, \quad k_n = K_2 K_3 \ldots K_N$$

Note that $K_1$ disappeared from all equations.
B.2 Polynomials in x

B.2.1 The Subsystem H_NA

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 degree N in x.

For this purpose, let’s start with a_0 and transform it in the following way:

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

\[ \frac{x^N}{a_0} = x^N + k_1 x^{N-1} + \ldots + k_N = \sum_{j=0}^{N} k_j x^{N-j} \]

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 \( a_0 = (x/k_j) a_j \) 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 degree N:

\[ 0 = \text{const} \cdot x^{N-j} + \sum_{i=j}^{N} k_i x^{N-i} \quad \text{with} \quad \text{const} = -\left( \frac{1 - a_0}{a_j} \right) k_j \]

For j = 0 (and with k_0 = 1), this formula reduces to Eq. (B.14).

B.2.2 The General Case: H_NA + H_2O + Strong Base

The titration of a polyprotic acid H_NA by a strong base is described by Eq. (2.32), which we now write as

\[ Y_1(x) = n - w(x)/C_T \quad \text{with} \quad n = \frac{C_B}{C_T} \]

For Y_1 on the left-hand side, we apply Eq. (1.113). That is,
**Acid Base Systems**

**Short Lecture**

\(Y_1(x) = \frac{\sum_{j=0}^{N} j \cdot k_j x^{N-j}}{\sum_{j=0}^{N} k_j x^{N-j}}\)

Inserting it into Eq. (B.17) and multiplying both sides by \(\sum k_j x^{N-j}\) yields:

\[
0 = \sum_{j=0}^{N} \left\{ j - n + \frac{w}{C_T} \right\} k_j x^{N-j}
\]

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

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

(both sides are multiplied by \(C_T\))

(both sides are multiplied by \(C_T\))

(Eq. (2.34) is used for \(w\))

After multiplication of both sides by \(-x\), we get a polynomial of degree \(N+2\) in \(x\):

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

To show that the polynomial is indeed of degree \(N+2\), you can rewrite Eq. (B.19) as

\[
0 = \sum_{j=0}^{N+2} f_j x^{N+2-j} \quad \text{with} \quad f_j = k_j + k_{j+1} (n + 1 - j) C_T - K_w k_{j+2}
\]

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 degree \(N\):

\[
0 = \sum_{j=0}^{N} (n-j) k_j x^{N-j}
\]

**Zwitterionic Acids.** The generalization to zwitterionic acids \(H_N A^{+Z}\) is simple. Replace the constant \(n\) by the constant \(n + Z\). That’s all. The generalized form of Eq. (B.19) is

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

We are still dealing with a polynomial of the same degree \(N+2\).
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 $a_j$:

\[(B.23) \quad Y_L = \sum_{j=0}^{N} j^L a_j = 0^L a_0 + 1^L a_1 + 2^L a_2 + ... + N^L a_N\]

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:

\[
\begin{align*}
n &= n \\
n Y_0 &= n \quad \text{(because $Y_0 = 1$)} \\
n Y_0 - Y_1 &= n - Y_1 \quad \text{($Y_1$ subtracted from both sides)} \\
n \sum j a_j - \sum j a_j &= n - Y_1 \quad \text{(using Eq. (B.23) on left-hand side)}
\end{align*}
\]

which finally yields the result:

\[(B.24) \quad \sum_{j=0}^{N} (n - j) a_j = n - Y_1 \quad \text{or} \quad \sum_{j=0}^{N} (n - j) [j] = (n - Y_1) C_T\]

**Equivalence Points.** The two types of equivalence points are characterized by (c.f. Eqs. (1.101) and (1.102)):

\[(B.25) \quad \text{semi-EP}_j: \quad \text{pH} = \text{pK}_j \quad \Rightarrow \quad a_j = a_{j-1} = \frac{1}{2}\]

\[(B.26) \quad \text{EP}_j: \quad \text{pH}_j = \frac{1}{2} (\text{pK}_j + \text{pK}_{j+1}) \quad \Rightarrow \quad a_j (\text{pH}_j) \approx 1\]

all other ionization fractions are almost zero. In this way, the whole sum in Eq. (B.23) is reduced to one or two terms:

\[(B.27) \quad Y_L (\text{pK}_j) = (j - 1)^L a_{j-1} + j^L a_j = \frac{1}{2} \{ (j - 1)^L + j^L \} \quad \text{for} \ L \geq 1\]

\[(B.28) \quad Y_L (\text{pH}_j) = j^L a_j \approx j^L \quad \text{for} \ L \geq 1\]

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:

\[(B.29) \quad \frac{d a_j}{d \text{pH}} = 0 \quad \Leftrightarrow \quad \text{extremum of} \ a_j\]

According to Eq. (B.48) on page 116, this is equivalent to the condition:
(B.30) \((j - Y_1) a_j = 0\) or \(j - Y_1 = 0\)

From Eq. (B.24) one gets

(B.31) \[\sum_{i=0}^{N} (j-i) a_i = 0\]

or, more explicitly,

(B.32) \[-j a_0 - (j-1) a_1 - ... - a_{j-1} + 0 + a_{j+1} + ... + (N-j) a_N = 0\]

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) maximum of \(a_j\) \(\iff\) \(a_{j-1} = a_{j+1}\) or \(\frac{a_{j+1}}{a_{j-1}} = 1\)

The pH at the maximum is obtained from Eq. (1.54):

(B.34) \[\frac{a_{j+1}}{a_{j-1}} = \frac{[j+1]}{[j-1]} = \frac{K_j K_{j+1}}{x^2} \implies x_{\text{max}} = (K_j K_{j+1})^{1/2}\]

According to Eq. (1.77), the ionization fraction \(a_j\) has its maximum at the equivalence point:

(B.35) maximum of \(a_j\) at \(\text{EP}_j\) with \(\text{pH} = \frac{1}{2} (pK_j + pK_{j+1})\)

From mass conservation, i.e. Eq. (1.95), one gets the value of \(a_j\) at the maximum as:

(B.36) \(a_j(x_{\text{max}}) = 1 - a_{j-1} - a_{j+1} = 1 - 2a_{j-1}\)

which, in most cases, is close to 1.

**B.4 Derivatives with Respect to pH**

**B.4.1 Basic Equations**

Given is

(B.37) \(x = \{H^+\} = 10^{-\text{pH}} = e^{-(\ln 10) \text{pH}}\)

The first and the \(k\)-th derivative of \(x\) with respect to pH are:

(B.38) \(\frac{dx}{d\text{pH}} = (-\ln 10) x\)

(B.39) \(\frac{d^k x}{d\text{pH}^k} = (-\ln 10)^k x\)
This result can be used to differentiate any given function $f(x)$ with respect to pH (by application of the chain rule):

\[(B.40) \quad \frac{df(x)}{dpH} = \frac{dx}{dpH} \frac{df(x)}{dx} = (-\ln 10) x \frac{df(x)}{dx}\]

**Example 1.** For $w(x) = K_w/x - x$, introduced in Eq. (0.8), we get:

\[(B.41) \quad \frac{dw(x)}{dpH} = \ln 10 (K_w/x + x) = \ln 10 (w + 2x)\]

\[(B.42) \quad \frac{d^2w(x)}{dpH^2} = (\ln 10)^2 (w + 2x - 2x) = (\ln 10)^2 w\]

All higher derivatives repeat this pattern:

\[(B.43) \quad \frac{d^k w(x)}{dpH^k} = (\ln 10)^k \begin{cases} w & \text{for } k \text{ even} \\ w + 2x & \text{for } k \text{ odd} \end{cases}\]

**Example 2.** Let’s consider the function, $g = 1/a_0$, that is

\[(B.44) \quad g(x) = 1 + \frac{k_1}{x} + \frac{k_2}{x^2} + \cdots + \frac{k_N}{x^N}\]

Its first derivative is then given by

\[(B.45) \quad \frac{dg(x)}{dpH} = \ln 10 \left( \frac{k_1}{x} + 2 \frac{k_2}{x^2} + \cdots + N \frac{k_N}{x^N} \right) = \frac{\ln 10}{a_0} \left( a_1 + 2a_2 + \cdots + Na_N \right)\]

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:

\[(B.46) \quad \frac{dg(x)}{dpH} = \frac{d}{dpH} \frac{1}{a_0} = \ln 10 \frac{Y_1}{a_0}\]
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)):

\[ \frac{d a_0(x)}{d \text{pH}} = \frac{d}{d \text{pH}} \frac{1}{g(x)} = \frac{1}{g^2} \frac{dg(x)}{d \text{pH}} = -a_0^2 (\ln 10) \frac{Y_1}{a_0} = (-\ln 10) Y_1 a_0 \]

In the same way, we get from a_j = (k_j/x_j) a_0 the general result for each ionization coefficient a_j:

\[ \frac{d a_j(x)}{d \text{pH}} = (-\ln 10) (Y_1 - j) a_j \]

**Moments.** Applying the above results to the sums over a_i yields

\[ \frac{d}{d \text{pH}} \sum_{j=0}^{N} a_j = (-\ln 10) \sum_{j=0}^{N} (Y_1 - j) a_j = (-\ln 10) (Y_1 - Y_1) = 0 \]

\[ \frac{d}{d \text{pH}} \sum_{j=0}^{N} j a_j = (-\ln 10) \sum_{j=0}^{N} j (Y_1 - j) a_j = (-\ln 10) (Y_1^2 - Y_2) \]

The first relation, which gives zero, is obvious because it represents the derivation of a constant, namely d l/d pH = 0. Eq (B.50) is just the first derivative of Y_1:

\[ \frac{d Y_1(x)}{d \text{pH}} = (-\ln 10) (Y_1^2 - Y_2) \]

In the same way, for all higher moments Y_L we get:

\[ \frac{d Y_L(x)}{d \text{pH}} = (-\ln 10) \sum_{j=0}^{N} j^L (Y_1 - j) a_j = (-\ln 10) (Y_1 Y_L - Y_{L+1}) \]
B.4.3 Higher Derivatives of $a_j$ and $Y_L$

The $2^{nd}$ derivative of $a_j$ is given by

$$\frac{d^2a_j(x)}{d\text{pH}^2} = (-\ln 10) \frac{d}{d\text{pH}} (Y_i - j) a_j$$

$$= (-\ln 10) \left\{ a_j \frac{dY_i}{d\text{pH}} + (Y_i - j) \frac{da_j}{d\text{pH}} \right\}$$

(use Eqs. (B.48) and (B.51))

$$= (-\ln 10)^2 \{ (Y_i^2 - Y_2) + (Y_1 - j)^2 \} a_j \tag{B.53}$$

The second derivative of $Y_1$ is given by

$$\frac{d^2Y_1}{d\text{pH}^2} = (-\ln 10) \frac{d}{d\text{pH}} (Y_1^2 - Y_2)$$

$$= (-\ln 10) \left\{ 2Y_1 \frac{dY_1}{d\text{pH}} - \frac{dY_2}{d\text{pH}} \right\}$$

$$= (-\ln 10)^2 \{ 2Y_1 (Y_2 - Y_1^2) - (Y_1Y_2 - Y_3) \}$$

$$= (-\ln 10)^2 \{ 2Y_1^3 - 3Y_1Y_2 + Y_3 \} \tag{B.54}$$

The third derivative of $Y_1$ is:

$$\frac{d^3Y_1}{d\text{pH}^3} = (-\ln 10)^2 \frac{d}{d\text{pH}} (2Y_1^3 - 3Y_1Y_2 + Y_3)$$

$$= (-\ln 10)^2 \left\{ 3(2Y_1^2 - Y_2) \frac{dY_1}{d\text{pH}} - 3Y_1 \frac{dY_2}{d\text{pH}} + \frac{dY_3}{d\text{pH}} \right\}$$

$$= (-\ln 10)^3 \{ 3(2Y_1^2 - Y_2)(Y_1^2 - Y_2) - Y_1 (3Y_1Y_2 - 4Y_3) - Y_4 \} \tag{B.55}$$
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):

\[
TOT_H = \text{excess protons} - \text{deficient protons}
\]  

**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):

\[
PRL_{\text{excess protons}} = \text{deficient protons}
\]

\[
\text{H}_2\text{O} [H^+] = [OH^-]
\]  

The proton balance of the subsystem ‘pure water’ is then expressed by:

\[
TOT_H|_w = [H^+] - [OH^-] = -w(x)
\]  

where w(x) was introduced in Eq. (1.131). In fact, for pure water we have \(TOT_H|_w = 0\). Because water is ever-present in a 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 \(n = 0, 1, \text{and } 2\):

\[
PRL \begin{array}{lll}
\text{excess protons} & \text{deficient protons} \\
\text{n} = 0: & \text{H}_2\text{A} & 0 & [\text{HA}^-] + 2 [\text{A}^2^-] \\
\text{n} = 1: & \text{HA}^- & [\text{H}_2\text{A}] & [\text{A}^2^-] \\
\text{n} = 2: & \text{A}^2^- & 2 [\text{H}_2\text{A}] + [\text{HA}^-] & 0
\end{array}
\]

\[
TOT_H|_0 = -[\text{HA}^-] - 2[\text{A}^2^-] \\
TOT_H|_1 = [\text{H}_2\text{A}] - [\text{A}^2^-] \\
TOT_H|_2 = 2 [\text{H}_2\text{A}] + [\text{HA}^-]
\]  

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⁻² 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⁻² is deficient by 1 proton (species enters the right-hand side).

In Eq. (C.6), A⁻² 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⁻² (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:

\[
\text{PRL} \quad TOT H = \text{excess protons} - \text{deficient protons}
\]

\[
(C.7) \quad H_{2-n} A^n \quad \left| TOTH \right|_n = n [H_2A] + (n-1) [HA] + (n-2) [A^{-2}] = 0
\]

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 \( n = 0 \):

\[
(C.8) \quad N = 1: \quad \left| TOTH \right|_0 = - [A^-]
\]

\[
(C.9) \quad N = 2: \quad \left| TOTH \right|_0 = - [HA^-] - 2[A^{-2}]
\]

\[
(C.10) \quad N = 3: \quad \left| TOTH \right|_0 = - [H_2A^-] - 2[HA^{-2}] - 3[A^{-3}]
\]

\( H_2A + H_2O \). 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 \( n = 0, 1, 2 \)):

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

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\(_n\).
C.2 General Case: N-Protic Acid

**Subsystem H\textsubscript{N}A.** It’s not difficult to generalize the results of the previous paragraph to an \(N\)-protic acid \(H\textsubscript{N}A\). It has \(N+1\) distinct PRL (i.e. for each species \(H\textsubscript{N-n}A\) one proton reference level, or the corresponding EP\(n\)):

\[
(C.12) \quad \text{PRL } H_{N-n}A^n; \quad TOT H|^{(acid)}_n = n[H_NA] + (n-1) [H_{N-1}A^-] + (n-2) [H_{N-2}A^{2-}] + ... + (n-N) [A^{-N}] = 0
\]

or in compact notation:

\[
(C.13) \quad \text{PRL } H_{N-n}A^n; \quad TOT H|^{(acid)}_n = \sum_{j=0}^{N} (n-j) [j] = 0
\]

According to Eq. (B.24) in the Appendix, the last equation can also be expressed by

\[
(C.14) \quad TOT H|^{(acid)}_n = (n - Y_1) C_T = 0
\]

**\(H\textsubscript{N}A + H_2O.** The proton balance of the whole system is then the sum of Eq. (C.3) and Eq. (C.14):

\[
(C.15) \quad TOT H|_n \equiv TOT H|_w + TOT H|^{(acid)}_n
\]

which is equivalent to

\[
(C.16) \quad TOT H|_n = -w + (n - Y_1) C_T = 0
\]

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:

\[
(C.17) \quad TOT H|_n = -w + (n - Y_1) C_T = 0 \quad \Rightarrow \quad w + Y_1 C_T = n C_T
\]

\(n = 0\)

\[
(C.18) \quad TOT H|_0 = -w - Y_1 C_T = 0 \quad \Rightarrow \quad w + Y_1 C_T = 0
\]

The last equation is equivalent to:

\[
(C.19) \quad \text{charge balance: } 0 = [H^+] - [OH^-] - [H_{N-1}A^-] - 2 [H_{N-2}A^{2-}] - ... - N[A^{-N}]
\]