Acid-Base Systems & pH Buffers

(Mathematical Background of Simple Closed-Form Expressions)

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# Physico-Chemical Quantities

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a_j )</td>
<td>ionization fractions, ( a_j = [j]/C_T )</td>
</tr>
<tr>
<td>( \text{Alk} )</td>
<td>total alkalinity</td>
</tr>
<tr>
<td>( \text{ANC} )</td>
<td>acid-neutralizing capacity</td>
</tr>
<tr>
<td>( \text{BNC} )</td>
<td>base-neutralizing capacity</td>
</tr>
<tr>
<td>( \beta )</td>
<td>buffer intensity, ( \beta = dn(pH,C_T)/d \text{pH} )</td>
</tr>
<tr>
<td>( \beta_C )</td>
<td>buffer intensity, ( \beta_C = n \beta )</td>
</tr>
<tr>
<td>( C_A )</td>
<td>concentration of (strong) monoprotic acid, ( C_A = [HX] )</td>
</tr>
<tr>
<td>( C_B )</td>
<td>concentration of (strong) monoacidic base, ( C_B = [BOH] )</td>
</tr>
<tr>
<td>( C_T )</td>
<td>total concentration of ( N )-protic acid, ( C_T = [HNA]_T )</td>
</tr>
<tr>
<td>( \delta_{ij} )</td>
<td>KROENECKER delta, ( \delta_{ij} = 1 ) for ( i=j ), and ( \delta_{ij} = 0 ) for ( i \neq j )</td>
</tr>
<tr>
<td>( \text{EP}_j )</td>
<td>equivalence point (belonging to species ( j ))</td>
</tr>
<tr>
<td>( \text{EP}_n )</td>
<td>equivalence point (belonging to integer and half-integer ( n ))</td>
</tr>
<tr>
<td>( I )</td>
<td>ionic strength</td>
</tr>
<tr>
<td>( \gamma_j )</td>
<td>activity correction for species ( j )</td>
</tr>
<tr>
<td>( \Delta G^0 )</td>
<td>GIBBS free energy (change)</td>
</tr>
<tr>
<td>( j )</td>
<td>index denoting the aqueous species ( j ), ( j = 0, 1, \ldots N )</td>
</tr>
<tr>
<td>( [j] )</td>
<td>molar concentration of aqueous species ( j ), ( [j] = [HNA^{-j}] )</td>
</tr>
<tr>
<td>( {j} )</td>
<td>activity of aqueous species ( j ), ( {j} = {HNA^{-j}} )</td>
</tr>
<tr>
<td>( K_a )</td>
<td>acidic constant (general abbreviation)</td>
</tr>
<tr>
<td>( K_a^c )</td>
<td>conditional acidic constant (non-thermodynamic quantity)</td>
</tr>
<tr>
<td>( K_j )</td>
<td>(composed) acidity constant, e.g. ( K_j = K_1K_2\ldots K_j )</td>
</tr>
<tr>
<td>( K_{w} )</td>
<td>constant for autoprotolysis (self-ionization of ( \text{H}_2\text{O} ))</td>
</tr>
<tr>
<td>( n )</td>
<td>equivalent fraction of titration, ( n = (C_B - C_A)/C_T )</td>
</tr>
<tr>
<td>( N )</td>
<td>number of protons (( \text{H}^+ )) in an ( N )-protic acid</td>
</tr>
<tr>
<td>( \text{pH} )</td>
<td>( -\lg {\text{H}^+} = -\lg [\text{H}^+] = -\lg x )</td>
</tr>
<tr>
<td>( \text{pH}_j )</td>
<td>( \frac{1}{2}(pK_j + pK_{j+1}) ) as ( \text{pH} ) of equivalence point ( \text{EP}_j )</td>
</tr>
<tr>
<td>( pK_j )</td>
<td>( -\lg K_j )</td>
</tr>
<tr>
<td>( pK_{j-1} )</td>
<td>( -\lg K_{j-1} )</td>
</tr>
<tr>
<td>( T )</td>
<td>temperature</td>
</tr>
<tr>
<td>( R )</td>
<td>gas constant (( R = 8.314 \text{ J mol}^{-1}\text{K}^{-1} ))</td>
</tr>
<tr>
<td>( x )</td>
<td>abbreviation for ([\text{H}^+])</td>
</tr>
<tr>
<td>( Y_k )</td>
<td>“( k )th moments” constructed from ( a_i ), ( Y_k = \Sigma_j j^k a_j )</td>
</tr>
<tr>
<td>( w )</td>
<td>“alkalinity of pure water”, ( w = K_w/x - x )</td>
</tr>
<tr>
<td>( z_j )</td>
<td>valence of ion ( j ) (electrical charge)</td>
</tr>
</tbody>
</table>

### Units and Conversions:

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

\( \text{conversion: } \text{lg} x = (\text{lg} x)/(\text{ln} 10) \)

\( \text{conversion: } \text{ln} x = (\text{ln} 10)(\text{lg} x) \)

\( \text{ln} 10 = 2.303 \)
Acids & Buffer Systems

Definitions & Abbreviations

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

$$ [j] = [H_{N-j}A^j] \quad \text{for } j = 0, 1, 2, ... N $$

Here, $j$ also labels the electrical charge of species $j$.

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

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

**Ionization Fractions.** We introduce the ionization fractions as ratios of the acid species to the total amount of acid:

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

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

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

**x and pH.** The molar concentration of $H^+$ will be abbreviated by $x$. Its relation with the pH value is then given by:

$$ x \equiv [H^+] = 10^{-\text{pH}} \quad \Leftrightarrow \quad \text{pH} = -\lg x $$

Note: This is an approximation since pH is based on the activity of $H^+$: $\text{pH} = -\lg \{H^+\}$.

**H$_2$O.** The autoprotolysis (self-ionization of water) is defined by$^1$

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

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

$$ [OH^-] = K_w/x $$

In this context we also introduce the quantity

$$ w \equiv [OH^-] - [H^+] = \frac{K_w}{x} - x $$

For pure water – defined by $x = K_w^{1/2}$, or $\text{pH} = 7 - w$ vanishes exactly: $w = 0.$

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$^1$ To be more precise, $K_w$ is defined for activities: $K_w = \{H^+\}\{OH^-\}$. 

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1 POLYPROTIC ACIDS

1.1 Introduction

1.1.1 Proton Transfer

An acid HA is a proton donor; it produces H⁺ ions (or H₃O⁺) when dissolved in water:

\[
\begin{align*}
(1.1) \quad & \text{HA} = \text{H}^+ + \text{A}^- \\
(1.2) \quad & \text{HA} + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{A}^-
\end{align*}
\]

In the following we prefer the short notation of Eq. (1.1), but keep in mind that H⁺ ions do not exist in a free state; they are extremely reactive and form hydronium ions H₃O⁺.

In contrast, a base BOH (such like NaOH, KOH, or NH₄OH) is a proton acceptor:

\[
(1.3) \quad \text{BOH} + \text{H}^+ = \text{H}_2\text{O} + \text{B}^+ \quad \text{(or OH}^- + \text{H}^+ = \text{H}_2\text{O})
\]

where B⁺ = Na⁺, K⁺, or NH₄⁺.

According to Brønsted, protons are transferred between conjugate acid-base pairs, which becomes evident when Eq. (1.1) is added to Eq. (1.3):

\[
\begin{align*}
(1.4) \quad & \text{HA} + \text{BOH} = \text{H}_2\text{O} + \text{A}^- + \text{B}^+ \\
(1.5) \quad & \text{acid} + \text{base} = \text{conjugate acid} + \text{conjugate base} \\
& \quad \quad \quad \quad \quad \quad \quad \quad \quad \text{(of base BOH)} \quad \text{(of acid HA)}
\end{align*}
\]

[Note: The cation B⁺ itself acts like a spectator (which can be cancelled on both sides of the chemical reaction formula). In fact, B⁺ will not play any active role in the further treatment.]

The relation between conjugate acid-base pairs is simple:

\[
(1.6) \quad \text{conjugate acid} = \text{H}^+ + \text{conjugate base} \\
\quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \qua
1.1.2 Acidity Constants

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

\[
\begin{align*}
\text{(1.8) acidity constant:} & \quad K_a = \frac{[H^+][A^-]}{[HA]} \quad \text{(based on activities)} \\
\text{(1.9) conditional acidity constant:} & \quad K_a^c = \frac{[H^+][A^-]}{[HA]} \quad \text{(based on concentrations)}
\end{align*}
\]

Both equations are special types of the law of mass action. The value of $K_a$ resembles the strength of the acid (large numbers are strong acids, small numbers are weak acids).

**Activities.** Activities are ‘effective concentrations’ which require semi-empirical activity corrections $\gamma_j$ (cf. Appendix A):

\[
\begin{align*}
\text{(1.10) activity (effective concentration):} & \quad \{j\} = \gamma_j [j] \\
\end{align*}
\]

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

**lg K.** In practice, it is often convenient to use the (base-10) logarithmic form of Eq. (1.8):

\[
\begin{align*}
\text{(1.11) } \quad \lg K_a = \lg \{H^+\} + \lg \{A^-\} - \lg \{HA\}
\end{align*}
\]

The negative decadic logarithm of the acidity constant is abbreviated by $pK_a$:

\[
\begin{align*}
\text{(1.12) } \quad pK_a = -\lg K_a
\end{align*}
\]

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

\[
\begin{align*}
\text{(1.13) } \quad pK_a = \text{pH} - \lg \{A^-\} + \lg \{HA\}
\end{align*}
\]

This can also be written as

\[
\begin{align*}
\text{(1.14) } \quad \text{pH} = pK_a + \lg \frac{[A^-]}{[HA]} = pK_a + \log \frac{\text{proton acceptor}}{\text{proton donor}}
\end{align*}
\]

The $pK_a$ value allows a classification into strong and weak acids: The smaller the $pK_a$ the stronger the acid – quite the opposite to a $K_a$-based ranking. In addition, $pK_a$ values define the semi-equivalence points as it will be shown in § 1.4.2, Eq. (1.72).

Note 1: In dilute systems or by using conditional acidity constant $^cK_a$, the activities $\{..\}$ in the above formulas should be replaced by concentrations $[..]$. 

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Note 2: In Eq. (1.14), the term \( \log \left( \frac{[A^-]}{[HA]} \right) \) or \( \log \left[ \frac{[A^-]}{[HA]} \right] \) vanishes for equal activities or concentrations. In other words, the pK_a value is just the pH at which the amount of both species is equal, i.e. at which 50% of species HA is dissociated into species A^-.

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

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

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

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

An example for the relationship between pK values and \( \Delta G^0 \) is shown in Fig. 1.4 on page 15.

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

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

<table>
<thead>
<tr>
<th>Monoprotic acid (HA)</th>
<th>Diprotic acid (H_2A)</th>
<th>Triprotic acid (H_3A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>H_2CO_3</td>
<td>H_3PO_4</td>
</tr>
<tr>
<td>HNO_3</td>
<td>H_2SO_4</td>
<td>H_3AsO_4</td>
</tr>
<tr>
<td>HI</td>
<td>H_2CrO_4</td>
<td>H_3BO_3</td>
</tr>
<tr>
<td>HF</td>
<td>H_2SeO_4</td>
<td>citric acid</td>
</tr>
<tr>
<td>formic acid</td>
<td>oxalic acid</td>
<td></td>
</tr>
<tr>
<td>acetic acid</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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

\[
\begin{align*}
\text{1st dissociation step:} & \quad H_3A^- = H^+ + H_2A^- & K_1 \\
\text{2nd dissociation step:} & \quad H_2A^- = H^+ + HA^2 & K_2 \\
\text{3rd dissociation step:} & \quad HA^2 = H^+ + A^-^3 & K_3
\end{align*}
\]

**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 most strongly bound). This yields the following ranking of acidity constants of a polyprotic acid:

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

\[2\] In organic acids, the second and third acidity constant may be similar.
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 $pK = -\log K$ for four common acids

<table>
<thead>
<tr>
<th>Acid</th>
<th>Formula</th>
<th>Type</th>
<th>$pK_1$</th>
<th>$pK_2$</th>
<th>$pK_3$</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetic acid</td>
<td>CH$_3$COOH</td>
<td>HA</td>
<td>4.76</td>
<td></td>
<td></td>
<td>[M91]</td>
</tr>
<tr>
<td>(composite) carbonic</td>
<td>H$_2$CO$_3$</td>
<td>H2A</td>
<td>6.35</td>
<td>10.33</td>
<td></td>
<td>[W91]</td>
</tr>
<tr>
<td>phosphoric acid</td>
<td>H$_3$PO$_4$</td>
<td>H$_3$A</td>
<td>2.15</td>
<td>7.21</td>
<td>12.35</td>
<td>[M91]</td>
</tr>
<tr>
<td>citric acid</td>
<td>C$_6$H$_8$O$_7$</td>
<td>H$_3$A</td>
<td>3.13</td>
<td>4.76</td>
<td>6.4</td>
<td>[M91]</td>
</tr>
</tbody>
</table>

### 1.2 Basic Set of Equations

#### 1.2.1 Special Case: Diprotic Acid

Before we tackle the general case let’s consider the example of diprotic acids.

![Fig. 1.1](image.png)

When a diprotic acid $H_2A$ is added to pure water the equilibrium system is characterized by five dissolved species: $H^+$, $OH^-$, $H_2A$, $HA^-$, and $A^{2-}$ (see Fig. 1.1). Thus, five equations are required for a rigor mathematical description:

(1.21)  $K_w = \{H^+\} \{OH^-\}$  \quad (self-ionization of H$_2$O)

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

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

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

(1.25)  $0 = [H^+] - [OH^-] - [HA^-] - 2[A^{2-}]$  \quad (charge balance)

The first three equations are *mass-action* laws (of the type of Eq. (1.8)); the last two equations represent the *mass balance* and the *charge balance*. While the mass-action laws are based on activities (denoted by curly braces), the mass-balance and charge-
balance equations rely on molar concentrations (denoted by square brackets) – see Fig. 1.2.

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

\[
\begin{align*}
K_w & = \{H^+\}\{OH^-\} \\
K_1 & = \{H^+\}\{HA^-\} / \{H_2A\} \\
K_2 & = \{H^+\}\{A^{2-}\} / \{HA^-\}
\end{align*}
\]

Based on activities \{\ldots\}  

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

Mass balance  

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

Charge balance

As shown in Fig. 1.3, the mathematical description of the diprotic acid system relies on two subsystems plus a coupling term between them:

- subsystem “pure water” described by Eq. (1.21)
- subsystem “pure acid” described by Eqs. (1.22) to (1.24)
- coupling of both subsystems described by Eq. (1.25)

In fact, the subsystems are combined by the charge-balance equation.
1.2.2 **General Case: Polyprotic Acids (H\textsubscript{N}A)**

Given is an \( N \)-protic acid \( H\textsubscript{N}A \), which is characterized by

\[
\begin{align*}
N+3 \text{ species (variables)}: & \quad H^+, OH^-, H\textsubscript{N}A, H_{N-1}A^-, \ldots, A^N \\\nN+1 \text{ species} & \quad \phantom{N+3 \text{ species (variables):}}
\end{align*}
\]

Thus, a complete description is provided by a set of \( N+3 \) equations:

\[
\begin{align*}
\text{(1.26)} & \quad K_w = [H^+] \cdot [OH^-] \quad \text{(self-ionization H}_2\text{O)} \\
\text{(1.27)} & \quad K_1 = [H^+] \cdot [H\textsubscript{N-1}A^-] / [H\textsubscript{N}A] \quad \text{(1}^{\text{st}} \text{ diss. step)} \\
\text{(1.28)} & \quad K_2 = [H^+] \cdot [H\textsubscript{N-2}A^{2-}] / [H\textsubscript{N-1}A^-] \quad \text{(2}^{\text{nd}} \text{ diss. step)} \\
\text{(1.29)} & \quad K_N = [H^+] \cdot [A^N] / [HA^{(N-1)}] \quad \text{(N}^{\text{th}} \text{ diss. step)} \\
\text{(1.30)} & \quad C_T = [H\textsubscript{N}A] + [H\textsubscript{N-1}A^-] + \ldots + [A^N] \quad \text{(mass balance)} \\
\text{(1.31)} & \quad 0 = [H^+] - [OH^-] - [H\textsubscript{N-1}A^-] - 2[H\textsubscript{N-2}A^{2-}] - \ldots - N[A^N] \quad \text{(charge bal.)}
\end{align*}
\]

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

The above set of equations represents an exact description of the \( N \)-protic acid. Due to the appearance of activities, \( \{j\} \), in the mass-action formulas (which, in addition, require activity models), however, this set of equations can only be solved numerically (by computer programs).

In order to deduce ‘simple’ closed-form expressions (i.e., analytical formulas) we have to replace all activities by molar concentrations:

\[
\text{(1.32)} \quad \{j\} \to [j] \quad \text{(requirement for closed-form expressions)}
\]

This approximation is valid either in very dilute systems or by switching to conditional equilibrium constants \( K^e \) as introduced in Eq. (1.9). In the following we assume that this has been done (without explicitly mark them by \( K^e \) in the notation). Thus we have:

\[
\begin{align*}
\text{(1.33)} & \quad K_w = [H^+] \cdot [OH^-] \quad \text{(self-ionization H}_2\text{O)} \\
\text{(1.34)} & \quad K_1 = [H^+] \cdot [H\textsubscript{N-1}A^-] / [H\textsubscript{N}A] \quad \text{(1}^{\text{st}} \text{ diss. step)} \\
\text{(1.35)} & \quad K_2 = [H^+] \cdot [H\textsubscript{N-2}A^{2-}] / [H\textsubscript{N-1}A^-] \quad \text{(2}^{\text{nd}} \text{ diss. step)} \\
\text{(1.36)} & \quad K_N = [H^+] \cdot [A^N] / [HA^{(N-1)}] \quad \text{(N}^{\text{th}} \text{ diss. step)} \\
\text{(1.37)} & \quad C_T = [H\textsubscript{N}A] + [H\textsubscript{N-1}A^-] + \ldots + [A^N] \quad \text{(mass balance)} \\
\text{(1.38)} & \quad 0 = [H^+] - [OH^-] - [H\textsubscript{N-1}A^-] - 2[H\textsubscript{N-2}A^{2-}] - \ldots - N[A^N] \quad \text{(charge bal.)}
\end{align*}
\]

This set of equations is the starting-point of all subsequent investigations.
1.3 The Subsystem “Pure Acid”

This paragraph focuses on the subsystem ‘pure acid’ described by the subset of $N+1$ equations (1.34) to (1.37). In other words, the self-ionization of water, determined by Eq. (1.33), and the charge-balance equation (1.38) will be ignored.

1.3.1 Notation

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

(1.39) \[ C_T \equiv [H_NA]_T = \text{TOT} \ H_NA \]

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

- 1 undissolved species: $H_NA(aq)$
- $N$ dissolved species: $H_{N-1}A^{-1}, \ldots, HA^{(N-1)}, A^{-N}$

It is convenient to abbreviate the molar concentrations of the dissolved species by

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

In this notation, the symbol $j$ also indicates the negative charge of the ion (which is equal to the number of released protons). Thus, $[0]$ stands for the electro-neutral species, $H_NA(aq)$, as the undissolved acid.\(^3\) Then, in each dissociation step (by releasing one proton) $j$ is enhanced by 1:

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

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

(1.42) \[ \text{conjugate acid:} \quad [j-1] \]
(1.43) \[ \text{conjugate base:} \quad [j] \quad \{ \text{of } j^\text{th} \text{ dissociation step} \} \]

According to mass balance, the molar concentrations of all species add up to $C_T$:

(1.44) \[ C_T = \sum_{j=0}^{N} [j] \]

**Ionization Fractions.** Instead of using the $N+1$ acid species $[j]$ itself it is often convenient to work with ionization fractions as ratios of the acid species concentration to the total amount of acid:

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

---

3 This quantity should not be confused with the total amount of acid, $[H_NA]_T$. 

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1.3.2 Two Kinds of Representation

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

<table>
<thead>
<tr>
<th>Dissociation Step</th>
<th>Equilibrium Reaction</th>
<th>$k_j$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st</td>
<td>$H_3A = H^+ + H_2A^-$</td>
<td>$k_1 = K_1$</td>
</tr>
<tr>
<td>2nd</td>
<td>$H_2A^- = H^+ + HA^{-2}$</td>
<td>$k_2 = K_1K_2$</td>
</tr>
<tr>
<td>3rd</td>
<td>$HA^{-2} = H^+ + A^{-3}$</td>
<td>$k_3 = K_1K_2K_3$</td>
</tr>
</tbody>
</table>

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

$H_3A = H^+ + H_2A^-$  \( k_1 = K_1 \)
$H_3A = 2H^+ + HA^{-2}$ \( k_2 = K_1K_2 \)
$H_3A = 3H^+ + A^{-3}$ \( k_3 = K_1K_2K_3 \)

These are two kinds of representation: The first as the standard representation describes the successive release of one single $H^+$ in each dissociation step (it’s the way how nature works); the second relates each dissolved species directly to the undissolved acid by a ‘multi-proton’ release. The latter is a mathematical trick to simplify some of our further calculations.

The changeover to the second representation (in Tab. 1.2) requires a new set of mass-action laws and equilibrium constants $k_1, k_2$, to $k_N$:

\[
\begin{align*}
K_1 &= [H^+] [H_{N-1}A^-] /[H_NA] \\
K_2 &= [H^+] [H_{N-2}A^2^-] /[H_{N-1}A^-] \\
& \quad \vdots \\
K_N &= [H^+] [A^{-N}] /[HA^{-\text{(N-1)}}] \\
\end{align*}
\]

which are related to $K_1, K_2$ etc. by:

\[
k_j = \begin{cases} 
1 & \text{for } j = 0 \\
k_1k_2\ldots k_j & \text{for } j > 0 \text{ and } j \leq N 
\end{cases}
\]

(1.46)

Tab. 1.2 Acid species and their corresponding equilibrium constants (in the new representation)

<table>
<thead>
<tr>
<th>$j$</th>
<th>Species</th>
<th>Equilibrium Reaction</th>
<th>Equilibrium Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>[H$_N$A]</td>
<td>$H_NA = H_NA$</td>
<td>$k_0 = [H_NA]/[H_NA]$ = 1</td>
</tr>
<tr>
<td>1</td>
<td>[H$_{N-1}$A]</td>
<td>$H_NA = H^+ + H_{N-1}A^-$</td>
<td>$k_1 = [H^+] [H_{N-1}A^-] /[H_NA]$ = $K_1$</td>
</tr>
<tr>
<td>2</td>
<td>[H$_{N-2}$A$^2$]</td>
<td>$H_NA = 2H^+ + H_{N-2}A^2$</td>
<td>$k_2 = [H^+]^2 [H_{N-2}A^2^-] /[H_NA]$ = $K_2K_2$</td>
</tr>
<tr>
<td>$N$</td>
<td>[A$^{-N}$]</td>
<td>$H_NA = NH^+ + A^{-N}$</td>
<td>$k_N = [H^+]^N [A^{-N}] /[H_NA]$ = $K_1K_2\ldots K_N$</td>
</tr>
</tbody>
</table>
In logarithmic scale, using the common definition for $p_{k_j} \equiv -\lg k_j$, Eq. (1.46) becomes:

\[
(1.47) \quad p_{k_j} = \begin{cases} 
1 & \text{for } j = 0 \\
pK_1 + pK_j + \cdots + pK_j & \text{for } j > 0 \text{ and } j \leq N
\end{cases}
\]

This simple additive relationship is illustrated in Fig. 1.4 for a triprotic acid, where the $p_{k_j}$ and $pK_j$ values are plotted on a Gibb's-free energy axis ($\Delta G^0$).

In contrast to $p_{k_j}$ values, which can be sequenced along an energy scale, like in Fig. 1.4, $pK_j$ values are sequenced on a pH scale – see Fig. 1.5 on page 21, for example.

### 1.3.3 Basic Relationships

The two representations introduced in § 1.3.2 can be cast into the following compact form (where $[j]$ symbolizes the acid species and $x = [H^+]$):

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

Eq. (1.48) represents the $j^{\text{th}}$ dissociation step characterized by $K_j$ (where $j$ runs from 1 to $N$). In contrast, Eq. (1.49) is a representation for $N+1$ reactions (where $j$ runs from 0 to $N$), including the trivial case $H_NA = H_NA$ with $k_0 = 1$. 

---

Fig. 1.4 Relations between $p_k$ and $pK$ values on a Gibb's-free energy axis ($\Delta G^0$) for a triprotic acid
Just from Eqs. (1.48) and (1.49) we obtain the pH dependence for concentration ratios (which are also relevant for equivalence points – EP):

\[
\frac{[j]}{[j-1]} = \frac{K_j}{x} \quad \Rightarrow \text{semi-EP (in § 1.4)}
\]

\[
\frac{[j+1]}{[j-1]} = \frac{K_j K_{j+1}}{x} \quad \Rightarrow \text{EP (in § 1.4)}
\]

Thus, knowing the concentration of one single species, say \([j]\), we are able to calculate all other species’ concentrations, i.e. the complete equilibrium distribution for a given pH (or \(x\)).

### 1.3.4 Closed-Form Expressions

Using Eq. (1.49), the subset of \(N+1\) equations (1.34) to (1.37), that describes the subsystem ‘pure acid’, simplifies to

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

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

\(C_T\) itself is irrelevant\(^4\), so, both equations are divided by \(C_T\), and we get with \(a_j = [j]/C_T\):

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

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

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

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

Knowing \(a_0\) all other ionization fractions \(a_j\) are then calculated by Eq. (1.55). The set of ionization fractions – as the normalized species distribution – contain all information about the ‘pure acid’ subsystem. More interesting features about the ionization fraction will be provided in § 1.5.

\(^4\)\(C_T\) is only relevant when other components or subsystems, in addition to \(H_nA\), are present.
The inverse task is to calculate $x$ (or pH) from $a_0$ (or any other $a_j$). This leads to a polynomial of order $N$; its derivation is presented in § B.1.1.

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

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

Vice versa, given a constant value of $a_0$ (or any other $a_j$), the corresponding pH (or $x$) of the ‘pure acid’ subsystem is completely determined by a polynomial of order $N$ in $x$:

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

**Example.** For a diprotic acid $H_2A$, Eq. (1.59) reduces to a *quadratic* equation (and, thus, can be solved quite easily). Let’s assume we know the value of $a_0$ and want to calculate the corresponding $x$. The steps are as follows:

\[
0 = x^2 + \alpha K_1 x + \alpha K_2 \quad \text{with} \quad \alpha = \frac{a_0}{1-a_0}
\]

The positive root of this quadratic equation is

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

The approximation on the right-hand side is valid for $K_1/K_2 << 1$. 
1.4 Equivalence Points of Subsystem “Pure Acid”

1.4.1 Definition of $EP_n$

An equivalence point (EP) is defined as the point at which chemically equivalent quantities of acids and bases have been mixed:

\[(1.62) \quad \text{equivalence point:} \quad [\text{acid}] = [\text{base}]\]

This concept applies to *conjugate* acids and bases, too:

\[(1.63) \quad \text{equivalence point:} \quad [\text{conjugate acid}] = [\text{conjugate base}]\]

For a polyprotic-acid this gives rise to a whole series of EPs, because – as we have seen in Eqs. (1.41) to (1.43) – each dissociation step (by releasing protons) relates a conjugate acid to its conjugate base. In particular, two types of equivalence points are distinguished:

\[(1.64) \quad EP_j: \quad [j-1] = [j+1]\]
\[(1.65) \quad \text{semi-EP}_j: \quad [j] = [j+1]\]

This definition even remains valid for $EP_j$ with $j=0$ and $j=N$, when we identify $[-1]$ by $[H^+]$ and $[N+1]$ by $[OH^-]$. This yields:

\[(1.66) \quad EP_0: \quad [H^+] = [1] \quad \text{(for } j = 0)\]
\[(1.67) \quad EP_j: \quad [j-1] = [j+1] \quad \text{(for } j = 1, 2, \ldots, N-1)\]
\[(1.68) \quad EP_N: \quad [N-1] = [OH^-] \quad \text{(for } j = N)\]

and

\[(1.69) \quad \text{semi-EP}_j: \quad [j] = [j+1] \quad \text{(for } j = 0, 1, \ldots, N-1)\]

Each EP is the midpoint between two adjacent semi-EPs (as it will be shown in § 1.4.2). An 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, which can be denoted by $EP_n$, where $n$ runs over all integer and half-integer values:\(^5\)

\[(1.70) \quad n = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \ldots, N-\frac{1}{2}, N\]

According to Eqs. (1.66) to (1.69), $EP_n$ is defined by

\[(1.71) \quad EP_n = \begin{cases} [n-1] = [n+1] & \text{for } n = 0, 1, 2, \ldots, N \quad (EP_{j=n}) \\ [n-\frac{1}{2}] = [n+\frac{1}{2}] & \text{for } n = \frac{1}{2}, \frac{3}{2}, \ldots, N-\frac{1}{2} \quad (\text{semi EP}_{j=n-\frac{1}{2}}) \end{cases}\]

---

\(^5\) The choice of the small latter $n$ as index in $EP_n$ 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.
In fact, by inserting half-integer values of $n$ into the last line the definition of the semi-EP in Eq. (1.69) is fully established.

### 1.4.2 Correspondence between $\text{EP}_n$ and $\text{pH}_n$

Equivalence points are usually identified with the corresponding $\text{pH}$ values (e.g. in titration experiments): $\text{EP}_n \leftrightarrow \text{pH}_n$, or $\text{EP}_n \leftrightarrow x_n$. These relationships can be easily established. For this purpose, however, it is useful to make a distinction between so-called ‘external’ and ‘internal’ EPs, that separates the two outermost equivalence points $\text{EP}_0$ and $\text{EP}_N$ from the rest:

- **external** equivalence points  
  $\text{EP}_0$ and $\text{EP}_N$

- **internal** equivalence points  
  all other $\text{EP}_n$ (for $\frac{1}{2} \leq n \leq N-\frac{1}{2}$)

#### Internal EPs

The internal equivalence points deliver especially simple formulas. From Eqs. (1.50) and (1.51) we get immediately (valid for $0 < j < N$):

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

This yields the following sequence:

\[
\begin{align*}
\text{semi-EP}_{1/2}: & \quad \text{EP}_{1/2} \leftrightarrow \text{pH}_{1/2} = pK_1 \\
\text{EP}_1: & \quad \text{EP}_1 \leftrightarrow \text{pH}_1 = \frac{1}{2} (pK_1 + pK_2) \\
\text{EP}_{3/2}: & \quad \text{EP}_{3/2} \leftrightarrow \text{pH}_{3/2} = pK_2 \\
\text{EP}_2: & \quad \text{EP}_2 \leftrightarrow \text{pH}_2 = \frac{1}{2} (pK_2 + pK_3) \\
& \vdots \\
\text{EP}_{N-1/2}: & \quad \text{EP}_{N-1/2} \leftrightarrow \text{pH}_{N-1/2} = pK_N \\
\end{align*}
\]

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, $\text{EP}_n$ with whole-integer $n$ are the midpoints between two adjacent semi-EPs. This can be summarized as follows:

\[
\begin{align*}
\text{pH}_n = \begin{cases} 
\frac{1}{2} (pK_n + pK_{n+1}) & \text{for } n = 1, 2, \ldots, N-1 \\
\frac{1}{2} K_{n+1/2} & \text{for } n = \frac{1}{2}, \frac{3}{2}, \ldots, N-\frac{1}{2} 
\end{cases} \\
\text{(EP}_n = \text{EP}_{n+1/2} = \text{semi EP}_j)
\end{align*}
\]

#### Tab. 1.3  
Internal equivalence points for four acids (based on $pK$ values in Tab. 1.1 on page 10)

<table>
<thead>
<tr>
<th>$N$</th>
<th>Acid H$_n$A</th>
<th>$\text{pH}_{1/2}$</th>
<th>$\text{pH}_1$</th>
<th>$\text{pH}_{3/2}$</th>
<th>$\text{pH}_2$</th>
<th>$\text{pH}_{5/2}$</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>4</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>
To give an example, Tab. 1.3 lists all *intrinsic* equivalence points of four common acids. In general, the fixed-valued *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, too.

**External EPs.** The formulas for the two *external* equivalence points EP_0 and EP_N (which are related to H⁺ or OH⁻ via Eqs. (1.66) and (1.68)) are not quite so simple. From Eqs. (1.53) to (1.55) follows

\[
\begin{align*}
\text{EP}_0: & \quad [H^+] = [1] \quad \Rightarrow \quad x = C_T a_1 \quad \Rightarrow \quad C_T = \frac{x^2}{K_1} \cdot \frac{1}{a_0(x)} \\
\text{EP}_N: & \quad [N-1] = [OH^-] \quad \Rightarrow \quad C_T a_{N-1} = \frac{K_w}{x} \quad \Rightarrow \quad C_T = \frac{K_w K_N}{x^2} \cdot \frac{1}{a_N(x)}
\end{align*}
\]

Now, the related pH values (or x) depend on the total amount of acid, C_T. Unfortunately, the corresponding equations on the right-hand side can only be presented 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 polynomial of (higher) order.]

### 1.4.3 Summary and Examples

As shown in the foregoing paragraph, there are distinct types of equivalence points, whereas each EP_n is associated with a specific pH_n value. The so-called *internal* equivalent points refer to fixed pH values as defined in Eq. (1.79):

- ‘common’ EP_n with integer n \((EP_1, EP_2, ..., EP_{N-1})\) at pH_n
- semi-EP_n 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:\(^6\)

- **EP_0**: approaching pH \(\rightarrow 0\) \((or \ x \rightarrow \infty)\) when C_T \(\rightarrow \infty\)
- **EP_N**: approaching pH \(\rightarrow 14\) \((or \ x \rightarrow 0)\) when C_T \(\rightarrow \infty\)

The pH_n values (external and internal) are arranged on the pH scale in the sequence of increasing n, exactly in the way as given in Eq. (1.70):

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

An example of such a sequence is shown schematically in Fig. 1.5 for the triprotic acid H_3PO_4. As we will learn in § 2.4.1, the fixed-valued EPs are the large-C_T limit when the subsystem ‘pure acid’ is coupled to the subsystem ‘pure H_2O’.

---

\(^6\) These limits result directly from the asymptotic behavior of a_0 and a_N given in Eqs. (1.95) and (1.96).
Acids & Buffer Systems

Another example is given in Fig. 1.6. It shows all equivalence points of carbonic acid (upper diagram) and phosphoric acid (lower diagram). The *intrinsic* equivalence points (red lines) are independent of $C_T$ while the two *extrinsic* EPs (blue and green curves) are not.

The *dashed* curves (instead of full-line curves) in Fig. 1.6 remind us that these are approximations valid for the isolated subsystem ‘pure acid’ (i.e. without coupling to the subsystem ‘pure H$_2$O’). The general case will be discussed in § 2.4.1. There we will learn that all *internal* EPs are the large-$C_T$ limit of the combined system ‘H$_3$A + H$_2$O’.
1.5 Ionization Fractions

1.5.1 Definition of $a_j$

An $N$-protic acid comprises $N+1$ acid species $[j]$. Instead of $[j]$, however, it is often convenient to use ionization fractions $a_0$, $a_1$ to $a_N$:

\[(1.83) \quad a_j = \frac{[j]}{C_T} \quad \text{for } j = 0, 1, 2, \ldots, N\]

They form the mathematical skeleton of the subsystem ‘pure acid’ with their typical dependence on $x$ (or pH) derived in § 1.3.4, Eq. (1.58):

\[(1.84) \quad a_j = \left(\frac{k_j}{x^j}\right) a_0 \quad \text{with} \quad a_0 = \left(1 + \frac{k_1}{x} + \frac{k_2}{x^2} + \ldots + \frac{k_N}{x^N}\right)^{-1}\]

Combining the left and right equations yields:

\[(1.85) \quad a_j = a_0 \left(\frac{k_j}{x^j}\right) = \frac{k_j / x^j}{\sum_{j=0}^{N} k_j / x^j} \quad \text{for } j = 0, 1, 2, \ldots, N\]

The ionization fractions are solely functions of $x$ (or pH = $-\lg x$); the only other ingredients are the equilibrium constants, introduced in Eq. (1.46):

\[(1.86) \quad k_0 = 1, \quad k_1 = K_1, \quad k_2 = K_1 K_2, \quad \text{to} \quad k_N = K_1 K_2 \ldots K_N\]

Due to its very definition in Eq. (1.83) the ionization fractions are independent of the total concentration $C_T$, which is very convenient in graphical representations as shown in Fig. 1.7, for example.

To explicitly exhibit the pH dependence of $a_j$, Eq. (1.85) can also be written as

\[(1.87) \quad a_j(pH) = a_0 \cdot k_j 10^{j \cdot pH} = \frac{k_j 10^{j \cdot pH}}{\sum_{j=0}^{N} k_j 10^{j \cdot pH}}\]

In the further treatment, the ionization fractions will become the building blocks of all relevant quantities and relationships. Once we know $a_j$, the concentration of the acid species is immediately obtained by multiplication with $C_T$:

\[(1.88) \quad [j] = C_T a_j(x) \quad \text{for } j = 0, 1, \ldots, N\]
1.5.2 Special Features of $a_j$

Ionization fractions have several nice and interesting features, two among them are:

- they are independent of the amount of acid $C_T$
- they remain unchanged when the system is titrated by a strong base or acid – as it will be done in Chapter 2.

**Examples.** The pH dependence of the ionization fractions for four acids (based on $pK$ in Tab. 1.1) is shown in Fig. 1.7.

![Fig. 1.7 Ionization fractions for four acids (blue circles denote semi-EPs)](image)

**Mass Balance.** For each chosen value of $x$ (or pH) the sum over 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 bounded between 0 and 1:

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

They neither become negative nor greater than 1. Strictly speaking, the functions will come very close to the boundaries, but will never actually reach the values 0 and 1.
Equivalence Points. The equivalence points, introduced in Eqs. (1.72) and (1.73), can also be defined by

\begin{align*}
(1.91) \quad \text{semi-EP}: \quad [j] &= [j+1] \quad \Leftrightarrow \quad a_j = a_{j+1} \quad \Rightarrow \quad x = K_j \\
(1.92) \quad \text{EP}: \quad [j-1] &= [j+1] \quad \Leftrightarrow \quad a_{j-1} = a_{j+1} \quad \Rightarrow \quad x = (K_j K_{j+1})^{1/2}
\end{align*}

This holds for the internal equivalence points and can be summarized as:

<table>
<thead>
<tr>
<th>Condition</th>
<th>Range</th>
<th>pH</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>semi-EP_j</td>
<td>$a_j = a_{j+1}$</td>
<td>$j = 0, 1, \ldots, N$</td>
<td>$pK_j$</td>
</tr>
<tr>
<td>EP_j</td>
<td>$a_{j-1} = a_{j+1}$</td>
<td>$j = 1, 2, \ldots, N-1$</td>
<td>$pH_j \equiv \frac{1}{2} (pK_j + pK_{j+1})$</td>
</tr>
</tbody>
</table>

The equivalence points are easily noticeable in the diagrams of Fig. 1.7: The semi-EPs are located at the intersection of two adjacent ionization fractions, $a_j$ and $a_{j+1}$ (marked as blue circles); the whole-integer EPs are intersections of next-but-one adjacent ionization fractions, $a_{j-1}$ and $a_{j+1}$ (marked as yellow circles). Notice that the latter are located at the maximum of each $a_j$ (which is proofed mathematically in Eq. (B.23) of Appendix B.2.2).

The actual values at the points of intersection are (cf. Eq. (B.25)):

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

which can be brought into a compact mathematical form

\begin{align*}
(1.97) \quad \text{semi-EP}_j \quad &a_j (pK_j) = \frac{1}{2} (\delta_{0j} + \delta_{j+1}) \\
(1.98) \quad \text{EP}_j \quad &a_j (pH_j) = (1 - 2a_{j-1}) \delta_p
\end{align*}

using the KRONECKER delta:

\begin{align*}
(1.99) \quad \delta_{ij} &= \begin{cases} 
1 & \text{for } i = j \\
0 & \text{for } i \neq j
\end{cases}
\end{align*}

Asymptotic Values. Instead of the two extrinsic EPs, we consider asymptotic values of $a_j$ for two extreme conditions (opposite ends of pH scale):

\begin{align*}
(1.100) \quad \text{strong acidic:} \quad &pH \to 0 \quad (\text{or } x \to \infty): \quad a_0 = 1 \quad \text{all other } a_i = 0 \\
(1.101) \quad \text{strong basic:} \quad &pH \to 14 \quad (\text{or } x \to 0): \quad a_N = 1 \quad \text{all other } a_i = 0
\end{align*}
1.5.3 Moments $Y_k$ – Sums over $a_i$

By summation over ionization fractions $a_i$ we get some kind of $k^{th}$ moment:

$$Y_k = \sum_{j=0}^{N} j^k a_j$$

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

$$Y_0 = a_0 + a_1 + ... + a_N = 1 \quad \text{for } k = 0$$

For all other positive integers we have:

$$Y_k = a_1 + 2^k a_2 + 3^k a_3 + ... + N^k a_N \quad \text{for } k \geq 1$$

$Y_0$ represents the mass balance; $Y_1$ will turn out to be the key quantity in the description of proton balance and acid-base titration in Chapter 2; $Y_2$ and $Y_3$ will describe the buffer intensity and its derivative in Chapter 3.

All $Y_k$ are positive functions, living in the range $0 < Y_k \leq N^k$ (here the equal sign holds only for $Y_0$, all other $Y_k$ never reach the upper limit of $N^k$).

**pH Dependence.** The moments, just like the ionization fractions, are solely functions of $x$ (or $\text{pH} = -\lg x$); the only other ingredients are the equilibrium constants of the acid. From Eq. (1.85) we obtain:

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

(In order to get the equation on the right-hand side, you should multiply both nominator and denominator with $x^N$.) Converting $x$ to $\text{pH}$ yields:

$$Y_1(\text{pH}) = \frac{\sum_{j=0}^{N} j k_j 10^{j \cdot \text{pH}}}{\sum_{j=0}^{N} k_j 10^{j \cdot \text{pH}}}$$

**Equivalent Points.** For the two types of equivalence points the following simple relationships are obtained (see Eqs. (B.16) and (B.17) in Appendix B.2.1):

$$\text{semi-EP}_j \quad pK_j \quad a_j = a_{j-1} \approx \frac{1}{2} \quad Y_k = \frac{1}{2} \{ (j-1)^k + j^k \}$$

$$\text{EP}_j \quad pH_j \equiv \frac{1}{2} (pK_j + pK_{j+1}) \quad a_j = 1 - 2a_{j-1} \approx 1 \quad Y_k \approx j^k$$

This is valid only for the so-called *internal* equivalence points ($j = 1$ to $N-1$), and for $k \geq 1$. Applying it, the following special values are obtained for $Y_k$: 
Acids & Buffer Systems

<table>
<thead>
<tr>
<th>Semi-EP</th>
<th>EP</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Y_i(pK_1) = \frac{1}{2}$</td>
<td>$Y_i(pH) = 1$</td>
</tr>
<tr>
<td>$Y_i(pK_2) = \frac{1}{2} (1 + 2^j)$</td>
<td>$Y_i(pH) = 2^k$</td>
</tr>
<tr>
<td>$Y_i(pK_3) = \frac{1}{2} (2^k + 3^k)$</td>
<td>$Y_i(pH) = 3^k$</td>
</tr>
<tr>
<td>$Y_i(pK_j) = j - \frac{1}{2}$</td>
<td>$Y_i(pH) = j$</td>
</tr>
<tr>
<td>$Y_i(pK_j) = (j - 1) j - \frac{1}{2}$</td>
<td>$Y_i(pH) = j^2$</td>
</tr>
</tbody>
</table>

The two relations in Eq. (1.112) can be combined into the remarkable formula valid for all internal EPs and semi-EPs:

(1.114) \[ Y_i(pH) = n \] for \( n = \frac{1}{2}, 1, ..., N - \frac{1}{2} \)

**Asymptotic Values.** The asymptotic behavior results from Eqs. (1.100) and (1.101):

(1.115) \[ Y_k (pH \to 0) = 0 \] or \[ Y_k (x \to \infty) = 0 \]

(1.116) \[ Y_k (pH \to 14) = N^k \] or \[ Y_k (x \to 0) = N^k \]

**Examples.** Fig. 1.8 displays the pH dependence of $Y_1$ to $Y_4$ for four acids (based on pK values taken from Tab. 1.1).

Fig. 1.8  Moments $Y_1$ to $Y_4$ (build from ionization fractions) for four acids
### 1.6 The Coupled System “H₂O + HₙA”

#### 1.6.1 Basic Set of Equations

Based on the preparatory work done in the foregoing paragraphs we are able to solve the complete system ‘H₂O + HₙA’ in an efficient way. The basic set of \( N+3 \) equations, formerly given in Eqs. (1.33) to (1.38), becomes now (after replacing the acid species \([j]\) by the ionization fractions \( a_j = [j]/C_T \)):

\[
\begin{align*}
(1.117) \quad & K_w = x (x + w) \quad \text{(subsystem ‘H₂O’)} \\
(1.118) \quad & k_1 = x (a_1/a_0) \quad \text{or} \quad a_1 = (k_1/x) a_0 \\
(1.119) \quad & k_2 = x (a_2/a_0) \quad \text{or} \quad a_2 = (k_2/x^2) a_0 \\
& \quad \vdots \\
(1.120) \quad & k_N = x (a_N/a_0) \quad \text{or} \quad a_N = (k_N/x^N) a_0 \\
(1.121) \quad & 1 = a_0 + a_1 + a_2 + \ldots + a_N \\
(1.122) \quad & 0 = w/C_T - (a_1 + 2a_2 + \ldots + Na_N) = -w/C_T - Y_1 \quad \text{(charge balance)}
\end{align*}
\]

**H₂O.** The subsystem ‘pure H₂O’ with its two variables [H⁺] and [OH⁻] is expressed by \( x = [H^+] \) and \( w(x) \). The latter variable already includes the self-ionization of water:

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

**HₙO.** The subsystem ‘pure acid’ (Hₙ/A) with its \( N+1 \) species \([j]\) comprises \( N+1 \) equations – Eqs. (1.118) to (1.121). As shown in § 1.3, it is completely described by a set of \( N+1 \) ionization fractions:

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

**H₂O + HₙO.** Both subsystems are linked by the charge-balance equation (1.122). The schema in Fig. 1.9 (for an \( N \)-protic acid) is a generalization of Fig. 1.3 (for H₂A).
1.6.2 Closed-Form Expressions

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

- given pH ⇒ calculate Cₜ (and equilibrium speciation [j] = Cₜ aₗ)
- given Cₜ ⇒ calculate pH (and equilibrium speciation [j] = Cₜ aₗ)

**From pH to Cₜ.** For a given pH (or x = 10⁻ᵖᴴ) the composition of the equilibrium system is obtained by

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

\[
(1.125) \quad \text{amount of acid: } Cₜ(x) = -\frac{w}{Y_l} \quad \text{with } Y_l = \sum_{j=0}^{N} j a_j(x)
\]

\[
(1.126) \quad \text{speciation: } [j] = Cₜ(x) a_j(x) \quad \text{for } j = 0, 1, \ldots N
\]

**From Cₜ to pH.** The inverse task to calculate pH (or x) from a given Cₜ is more tricky. As shown in Appendix B.1.2 and Eq. (B.10), it leads to a polynomial of order N+2:

\[
(1.127) \quad 0 = \sum_{j=0}^{N} \left\{ x^2 - jCₜ - Kw \right\} k_j x^{N-j}
\]

In comparison with the polynomial for the pure-acid subsystem in Eq. (1.59), this polynomial has a higher degree by 2 (from N to N+2), which make a solution much harder. [Note: There is no algebraic expression for solving polynomials of degree higher than 4. Thus, numerical root-finding methods should be applied.]

**Example.** For a diprotic acid (N=2) we get from Eq. (1.127), and with k₁=K₁ and k₂=K₁K₂, a quartic equation you find in many textbooks [SM96]:

\[
(1.128) \quad 0 = x^4 + K_1 x^3 + (K_1 K_2 - Cₜ K_1 - Kw) x^2 - K_1 (2Cₜ K_2 + Kw) x + K_1 K_2 K_w
\]
2 ACID-BASE TITRATION

2.1 Introduction

2.1.1 Definitions

Chapter 1 was focused on the mathematical description of the acid system, $H_NA + H_2O$, starting from the set of equations (1.26) to (1.31) towards a simple analytical formula in Eq. (1.125). It 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. Here, ‘strong’ means complete dissociation in water:

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

For example, BOH stands for NaOH, KOH, or NH$_4$OH (i.e. $B^+ = Na^+$, $K^+$, or NH$_4^+$) and HX represents HCl, HI, or HBr (i.e. $X^- = Cl^-$, $I^-$, or Br$^-$).

The addition of a strong base or strong acid is usually known as acid-base titration:

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

The amount of the added strong base and strong acid are denoted by $C_B$ and $C_A$. This can be related to the total amount of $H_NA$ by the ratios

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

Since the strong acid and strong base operate in exactly opposite direction (and both canceling each other) we are able to combine the two equations into one:

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

where either $C_B$ or $C_A$ is zero. In this way, the equivalent fraction of the titrant, $n$, is positive for the alkalimetric titration and negative for the acidimetric titration.

Example. Fig. 2.1 provides the acid-base titration of a 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 by addition of NaOH ($n$ is positive); lower $pH$ values by addition of HCl ($n$ is negative).

---

7 In Sigg and Morgan [SM96], the equivalent fractions $n$ is abbreviated by $f$. 
The small circles at the three integer values \( n = 0, 1, \) and \( 2 \) indicate the so-called equivalence points.

![Fig. 2.1 Titration curve \( n(pH) \) of the carbonate system (10 mM H\(_2\)CO\(_3\)).](image)

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 other curves for \( C_T = 1 \text{ mM} \) and \( 100 \text{ mM} \). The two diagrams in Fig. 2.2 differ only by the choice of x-axis (the x-axis and y-axis are interchanged).

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

Let’s consider a diprotic acid \( H_2A \) of amount \( C_T \) to which a monoacidic strong base \( BOH \) (with \( B^+ = Na^+, K^+, \) or \( NH_4^+ \)) is added:

\[
(2.7) \quad H_2A + n BOH = B_nH_{2-n}A + n H_2O
\]

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

While \( C_B \) and \( C_T \) are given in molar units (mol/L), \( n \) is a dimensionless number (unit-free).

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.

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

The variation of \( n \) (or \( C_B \)) in reaction formula (2.7) by adding a strong base is called *alkalimetric* titration.

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

\[
(2.8) \quad n = 0: \quad \text{pure } H_2A \text{ solution (acid)} \quad \Leftrightarrow \quad H_2A \quad \text{EP}
\]
\[
(2.9) \quad n = 1: \quad \text{pure } BHA \text{ solution (ampholyte)} \quad \Leftrightarrow \quad H^-A^+ \quad \text{EP}
\]
\[
(2.10) \quad n = 2: \quad \text{pure } B_2A \text{ solution (base)} \quad \Leftrightarrow \quad A^{2-} \quad \text{EP}
\]

In fact, \( n = 0, 1, \) and \( 2 \) define the three equivalence points (EP\(_0\), EP\(_1\), EP\(_2\)) of a diprotic acid – introduced in § 1.4. [Example: For \( H_2CO_3 \) and the strong acid NaOH we obtain pure solutions of \( H_2CO_3, NaHCO_3 \) and \( Na_2CO_3 \).]

In addition, the half-integer values \( n = 1/2, 3/2, \) and \( 5/2 \) define the semi equivalence points EP\(_{1/2}\), EP\(_{3/2}\), and EP\(_{5/2}\).
Basic Equations. The set of mathematical equations to describe the alkalimetric titration is a generalization of Eqs. (1.21) to (1.25) introduced for diprotic acids in § 1.2.1:

\begin{align*}
(2.11) \quad K_w &= \{H^+\} \{OH^-\} \quad \text{(self-ionization of H}_2\text{O)} \\
(2.12) \quad K_1 &= \{H^+\} \{HA^-\} / \{H_2A\} \quad \text{(1st diss. step)} \\
(2.13) \quad K_2 &= \{H^+\} \{A^{2-}\} / \{HA^-\} \quad \text{(2nd diss. step)} \\
(2.14) \quad C_T &= \{H_2A\} + \{HA^-\} + \{A^{2-}\} \quad \text{(mass balance)} \\
(2.15) \quad 0 &= \{H^+\} + n \{H_2A\} + (n-1) \{HA^-\} + (n-2) \{A^{2-}\} - \{OH^-\} \quad \text{(proton balance)}
\end{align*}

It differs from the set of equations (1.21) to (1.25) only by the last equation, where ‘charge balance’ is replaced by the more general concept of ‘proton balance’ (which will be explained in § 2.2). For n=0, the set reduces to the description of the pure diprotic-acid system. Also, for n=0, the concept of ‘proton balance’ reduces to the electro-neutrality condition (charge balance).

Remarkably enough, the last equation (2.15) is the sole equation that explicitly depends on \( n \). The other four equations are independent on the type of reactant we add to water (acid, ampholyte or base).
2.2 Proton Balance

2.2.1 Special Case: Diprotic Acid

The proton balance is of great significance in acid-base systems. 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):

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

Subsystem H\(_2\)O. The simplest case is pure water with its three species H\(^+\), OH\(^-\), and H\(_2\)O. Choosing H\(_2\)O as the reference level, the species H\(^+\) is richer in 1 proton (excess proton), while OH\(^-\) is 1 proton poorer (deficient proton):

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

\[ (2.17) \quad \text{H}_2\text{O} \quad [H^+] = [OH^-] \]

The proton balance of the subsystem ‘pure water’ (here indicated by the subscript w) is then expressed by:

\[ (2.18) \quad TOTH_w = [H^+] - [OH^-] = 0 \]

Because water is ever-present in any acid-base system, H\(^+\) and OH\(^-\) always enter the proton balance – see Eqs. (2.32) to (2.34) below.

Subsystem H\(_2\)A. The diprotic acid H\(_2\)A has three distinct reference levels denoted by \( n = 0, 1, \) and 2:

\[
\text{PRL} \quad \text{excess protons} \quad \text{deficient protons} \\
(2.19) \quad n = 0: \quad \text{H}_2\text{A} \quad 0 \quad [\text{HA}^-] + 2[\text{A}^{2-}] \quad TOTH_0 = -[\text{HA}^-] - 2[\text{A}^{2-}] \\
(2.20) \quad n = 1: \quad \text{HA}^- \quad [\text{H}_2\text{A}] \quad [\text{A}^{2-}] \quad TOTH_1 = [\text{H}_2\text{A}] - [\text{A}^{2-}] \\
(2.21) \quad n = 2: \quad \text{A}^{2-} \quad 2[\text{H}_2\text{A}] + [\text{HA}^-] \quad 0 \quad TOTH_2 = 2[\text{H}_2\text{A}] + [\text{HA}^-] \\
\]

How to write down these equations? In Eq. (2.19), H\(_2\)A is the reference level. There are no species that have more protons than H\(_2\)A, 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. (2.20), HA\(^-\) is the reference level. From this perspective, H\(_2\)A 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. (2.21), A\(^{2-}\) is the reference level. Now, H\(_2\)A 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 PRLs of the subsystem ‘diprotic acid’, denoted by H\textsubscript{2-n}A\textsuperscript{n} (for \(n = 0, 1, 2\)), yields the following proton balance equation:

\[
PRL_{H_{2-n}A^n} \quad \text{TOT}H_{n} = \text{excess protons} - \text{deficient protons}
\]

(2.22) \(H_{2-n}A^n \quad \text{TOT}H|_n = n[H_2A] + (n-1)[HA^-] + (n-2)[A^{2-}] = 0\)

This one-liner comprises all three equations (2.19) to (2.21). [Example: In the case of a carbonic acid system the three PRLs correspond to H\textsubscript{2}CO\textsubscript{3}, HCO\textsubscript{3}\textsuperscript{-}, and CO\textsubscript{3}\textsuperscript{2-}.

Fig. 2.4 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 a mono-, di-, and tri-protic acid we have

(2.23) \(N=1:\quad \text{TOT}H|_0 = -[A^-] = 0\)
(2.24) \(N=2:\quad \text{TOT}H|_0 = -[HA^-] - 2[A^{2-}] = 0\)
(2.25) \(N=3:\quad \text{TOT}H|_0 = -[H_2A^-] - 2[HA^{2-}] - 3[A^{3-}] = 0\)

\(H_2A + H_2O\). The combined system as the sum of subsystem ‘pure water’ and subsystem ‘diprotic acid’ obeys the proton balance for the three PRLs \(H_{2-n}A^n\) (with \(n = 0, 1, 2\)):

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

(2.26)

The two species, \(H^+\) and \(OH^-\), that appear in this equation trace back from the H\textsubscript{2}O-reference level in Eq. (2.17). They have their permanent place in any H\textsubscript{2}O containing system.

One fact is of relevance: The PRLs are usually chosen at equivalence points EP\textsubscript{n} (with integer n). There is a direct correspondence between PRL at n and EP\textsubscript{n}.  

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2.2.2 General Case: $N$-Protic Acid

Subsystem $H_NA$. It’s not difficult to generalize the results of the previous paragraph to an $N$-protic acid $H_NA$. It has $N+1$ distinct PRLs (i.e. for each species $H_NA^{n-}$ one proton reference level, or the corresponding $EP_n$):

(2.27) PRL $H_{N-n}A^n$: $TOTH|_n = n [H_NA] + (n-1) [H_{N-1}A] + (n-2) [H_{N-2}A^2] + ... + (n-N) [A^{-N}] = 0$

or in compact notation:

(2.28) PRL $H_{N-n}A^n$: $TOTH|_n = \sum_{j=0}^{N} (n-j) [j] = 0$

Per definition, $TOTH|_n$ is always zero. According to Eq. (B.13), the last equation can also be expressed by

(2.29) PRL $H_{N-n}A^n$: $TOTH|_n = (n-Y_1) C_T = 0$

An alternative representation of Eq. (2.28) is given by

(2.30) $TOTH|_n = n \sum_{j=0}^{N} [j] + TOTH|_0 = nC_T + TOTH|_0 = 0$

with

(2.31) $TOTH|_0 = -\sum_{j=0}^{N} j [j] = -Y_1 C_T$

In contrast to $TOTH|_n$, which is always zero (per definition), $TOTH|_0$ is greater than zero.

$H_NA + H_2O$. The proton balance of the whole system (at PRL $n=0$, or $EP_0$) is defined by

(2.32) $TOTH = TOTH|_w + TOTH|_0$

which – according to Eqs. (2.18) and (2.31) – is equivalent to

(2.33) $TOTH = [H^+] - [OH^-] - Y_1 C_T$

As can be seen from Eq. (2.30), in the general case for $n \neq 0$, $TOTH$ becomes nonzero:

(2.34) $TOTH = [H^+] - [OH^-] - Y_1 C_T = -n C_T$

This proton-balance equation, in form of $0 = [H^+] - [OH^-] - Y_1 C_T - n C_T$, will enter the basic set of equations in § 2.3 – as Eq. (2.43) or Eq. (2.49).


2.2.3 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 conceptions coincide.

In case of pure water, $TOT\ H_w$, we have the trivial result:

\[(2.35) \quad \text{charge balance: } 0 = [H^+] - [OH^-] = TOT\ H_w\]

For the combined system, acid $+ H_2O$, we have

\[(2.36) \quad \text{charge balance: } 0 = [H^+] - [OH^-] - [H_{N-1}A^-] - 2[H_{N-2}A^2] - ... - N[A^{-N}] = TOT\ H_w + TOT\ H_0\]

According to Eqs. (2.33) and (2.34) it yields

\[(2.37) \quad n = 0: \ TOT\ H = 0 \iff \text{charge balance}\]
2.3 Basic Set of Equations

2.3.1 Exact Description

The mathematical description of the acid-base titration represents an \(N\)-protic acid \(H_NA\) (the ‘undisturbed system’) plus a strong base \(BOH\). It is characterized by

\[
\text{the ‘undisturbed system’}
\]

\[
\text{\(N+4\) species (variables): \(H^+, OH^-, H_NA, H_{N-1}A^-, \ldots A^{-N}, B^+\)}
\]

\[
\text{\(N+1\) acid species}
\]

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

(2.38) \[ K_w = [H^+] \{OH^-\} \quad \text{(self-ionization \(H_2O\))} \]

(2.39) \[ K_1 = [H^+] \{H_{N-1}A^-\} / \{H_NA\} \quad \text{(1st diss. step)} \]

(2.40) \[ K_2 = [H^+] \{H_{N-2}A^{2-}\} / \{H_{N-1}A^-\} \quad \text{(2nd diss. step)} \]

\[
\ldots
\]

(2.41) \[ K_N = [H^+] \{A^{-N}\} / \{HA^{(N-1)}\} \quad \text{(Nth diss. step)} \]

(2.42) \[ C_T = [H_NA] + [H_{N-1}A^-] + \ldots + [A^{-N}] \quad \text{(mass balance)} \]

(2.43) \[ 0 = [H^+] – [OH^-] + n [H_NA] + (n-1) [H_{N-1}A^-] + \ldots + (n-N) [A^{-N}] \quad \text{(proton balance)} \]

This set of equations is an extension of the diprotic-acid case in Eqs (2.11) to (2.15) 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 (1.26) to (1.31). The latter is re-established when \(n\) is put to zero (in the last equation).

In fact, the only difference to the set of equations (1.26) to (1.31) is just the last line, where charge balance is replaced by proton balance.

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

Two assumptions are necessary to derive closed-form expressions from the set of equations (2.38) to (2.43) in the next paragraph:

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

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

The first assumption is fulfilled either in very dilute systems or by switching to conditional equilibrium constants \(^cK\) as introduced in Eq. (1.9). When these assumptions are

\(\text{such like NaCO}_3^- \text{ or NaHCO}_3(aq) – \text{which are really existent, but in small concentrations only}\)
valid, we speak about ‘ideal conditions’ (examples for real ‘real’ conditions will be given in §2.4.4).

2.3.2 Closed-Form Expressions

The procedure to solve the set of mathematical equations (2.38) to (2.43) is the same we already used in the previous paragraphs (cf. in §1.6.1):

- replace activities by concentrations: \{..\} \Rightarrow [..] in Eqs. (2.38) to (2.41)
- replace acid species \([j]\) by ionization fractions \(a_j\) in Eqs. (2.39) to (2.43)
- replace \([H^+]\) by \(x\) and \([OH^-]\) by \(K_w/x – x\), and use \(w(x)\) defined in Eq. (1.123)
- use the compact notation \(Y_1\) for sums over \(a_j\)

In this way, we obtain a new set of \(N+3\) equations:

<table>
<thead>
<tr>
<th>Equation</th>
<th>Expression</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2.44)</td>
<td>(K_w = x (x + w))</td>
<td>(self-ionization)</td>
</tr>
<tr>
<td>(2.45)</td>
<td>(k_1 = x (a_1/a_0)) or (a_1 = (k_1/x) a_0)</td>
<td>subsystem ‘strong base’</td>
</tr>
<tr>
<td>(2.46)</td>
<td>(k_2 = x (a_2/a_0)) or (a_2 = (k_2/x^2) a_0)</td>
<td>subsystem ‘pure water’</td>
</tr>
<tr>
<td>(2.47)</td>
<td>(k_N = x (a_N/a_0)) or (a_N = (k_N/x^N) a_0)</td>
<td>subsystem ‘pure acid’</td>
</tr>
<tr>
<td>(2.48)</td>
<td>(1 = a_0 + a_1 + a_2 + ... + a_N)</td>
<td></td>
</tr>
<tr>
<td>(2.49)</td>
<td>(0 = – w/C_T + na_0 + (n-1)a_1 + (n-2)a_2 + ... + (n-N)a_N = – w/C_T + n – Y_1)</td>
<td></td>
</tr>
</tbody>
</table>

This set of equations is a generalization of Eqs. (1.117) to (1.122) for nonzero values of \(n\).

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

(2.50) \[ 0 = n – w(x)/C_T – Y_1(x) \]

The information contained in all other equations (i.e. the equations above the last line) is condensed in the definition of \(Y_1\) and \(w\).

(2.51) \[ Y_1 = \sum_{j=0}^{N} j a_j = a_1 + 2a_2 + ... + Na_N \]

(2.52) \[ w \equiv [OH^-] – [H^+] = \frac{K_w}{x} – x \]

Each of the three terms in Eq. (2.50) represents one of the three subsystems: \(n\) – the strong base, \(w/C_T\) – the pure water, and \(Y_1\) – the pure acid (see also Fig. 2.5).
Polynomial. Eq. (2.50) can be solved for $x$. As shown in Appendix B.1.2, Eq. (B.9), it leads to a polynomial of order $N+2$ in $x$ (i.e. $N+2$ is the highest power of $x$):

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

For $n = 0$ it falls back to Eq. (1.127) on page 28. Theoretically, one can use this equation to calculate $x$. Practically, however, it is a non-trivial task even for a cubic equation (for higher polynomials numerical root-finding methods should be applied).

Example. For the special case of a diprotic acid ($N=2$), the polynomial in Eq. (2.53) becomes a quartic equation, i.e. a polynomial of 4th order in $x$ ($=10^{-pH}$):

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

It generalizes the quartic equation (1.128) for nonzero values of $n$. It predicts $x$ (or $pH$) for any given pair of $C_T$ and $n$. Alternatively, replacing $n$ by $C_B = nC_T$ yields:

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

Summary. Either closed-form expression in Eq. (2.50) or the polynomial in Eq. (2.53) 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 (2.44) to (2.49).

Fig. 2.5 Equations of the acid-base titration. The three subsystems ‘acid’, ‘H$_2$O’, and ‘strong base’ are coupled via the proton-balance equation.

Fig. 2.5 illustrates how the three subsystems ‘pure acid’, ‘pure H$_2$O’, and ‘strong base’ are coupled via one central equation: the proton balance.
2.3.3 Example: Carbonic Acid System (N=2)

In the case of a diprotic acid H$_2$A, the set of Eqs. (2.44) to (2.49) reduces to five equations. The actual equilibrium state (i.e. the concentrations of the 3 aqueous species [j]: H$_2$A, HA$^-$, and A$^2$) is completely controlled by two parameters chosen from the triple (C$_T$, n, pH) or (C$_T$, C$_B$, pH), where C$_B$ = nC$_T$ which is also known as alkalinity: Alk = C$_B$ (see Eq. (3.19)). Once one knows two of them, the third is automatically determined:

(2.56) \[ \text{pH (C}_T, n) = -\log x_n \text{ with } x_n \text{ as positive root of Eq. (2.54)}; \quad [j] = C_T a_j \]

(2.57) \[ \text{pH (C}_T, \text{Alk)} = -\log x_n \text{ with } x_n \text{ as positive root of Eq. (2.55)}; \quad [j] = C_T a_j \]

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

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

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

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

Fig. 2.6 Relationships between pH, C$_T$, and n for the carbonic acid system (at 25 °C)
It’s quite instructive to exhibit the non-linearity of all these equations graphically. The diagrams Fig. 2.6 display all possible combinations of one dependent and two independent variables (taken from the triplet $C_T$, $n$, and pH) for the carbonate system.

All diagrams are redrawn in Fig. 2.7 for the case when the normalized amount of added strong base, $n = C_B/C_T$, is replaced by the total alkalinity ($\text{Alk} = n C_T$).

**Fig. 2.7** Relationships between pH, $C_T$, and Alk for the carbonic acid system (at 25 °C)
2.4 Equivalence Points

2.4.1 The Coupled System: $H_NA + H_2O$

**Starting-Point.** In § 1.4 equivalence points were introduced for the *isolated* subsystem ‘pure acid’ (i.e. unlinked to the subsystem ‘pure $H_2O$’). They were defined by relating two neighbor or next-but-one neighbor acid species $[j]$ together as

$$\text{(2.62)} \quad \text{EP: } \text{[conjugate acid]} = \text{[conjugate base]}$$

or, more explicitly,

$$\text{(2.63)} \quad \text{EP}_j: \quad [j-1] = [j+1] \quad \Leftrightarrow \quad \text{EP}_n: \quad [n-1] = [n+1] \quad \text{for integer } n$$

$$\text{(2.64)} \quad \text{semi-EP}_j: \quad [j] = [j+1] \quad \Leftrightarrow \quad \text{EP}_n: \quad [n-1] = [n+1] \quad \text{for half-integer } n$$

This lead to simple formulas for the corresponding $pH_n$ (cf. § 1.4.2), which for the so-called *internal* EPs are fixed values

$$\text{(2.65)} \quad \text{EP}_n \Leftrightarrow pH_n = \begin{cases} \frac{1}{2}(pK_n + pK_{n+1}) & \text{for } n = 1, 2, \ldots, N-1 \quad (\text{EP}) \\ pK_{n+\frac{1}{2}} & \text{for } n = \frac{3}{2}, \frac{5}{2}, \ldots, N-\frac{1}{2} \quad (\text{semi EP}) \end{cases}$$

**Redefinition.** Now we are in the position to discuss the coupled system ‘$H_NA + H_2O$’ and redefine (still better, generalize) the definition of the equivalence point as

$$\text{(2.66)} \quad \text{EP: } \text{[N-protic acid]} = \text{[strong base]}$$

which is equivalent to

$$\text{(2.67)} \quad \text{EP: } \ C_T = C_B \quad \text{or} \quad n = \frac{C_B}{C_T} = 1$$

In fact, this is the definition of EP$_1$. The definition of all other EPs and semi-EPs is similar:

$$\text{(2.68)} \quad \text{EP}_n: \quad \text{[N-protic acid]} = n \quad \text{[strong base]} \quad \text{or} \quad n = \frac{C_B}{C_T}$$

The formula to calculate the corresponding $pH_n$ values and the whole pH dependence of the equivalence points EP$_n$ is contained *implicitly* in Eq. (2.50):

$$\text{(2.69)} \quad \text{EP}_n \quad \text{for } n = 0, \frac{1}{2}, 1, \frac{3}{2}, \ldots, N \quad \Leftrightarrow \quad C_T(n,x) = \frac{w(x)}{n - Y_1(x)}$$

The EPs of the isolated subsystem ‘pure acid’ are at the position where the denominator in Eq. (2.69) becomes zero:

$$\text{(2.70)} \quad \text{EP}_n \quad \text{of ‘pure acid’} \quad \Leftrightarrow \quad 0 = n - Y_1(x) \quad \Leftrightarrow \quad C_T \rightarrow \infty$$
In mathematical jargon, the corresponding pH (or x) values – i.e. the pH\textsubscript{b} values listed in Tab. 1.3 – are the \textit{singularities} of Eq. (2.69). Note that Eq. (2.70) is equivalent to Eq. (1.114) on page 26.

On the other hand, the single EP of ‘pure H\textsubscript{2}O’ is at the position where the nominator in Eq. (2.69) becomes zero (which is at pH = 7):

\begin{equation}
\text{EP of ‘pure H}_2\text{O’} \iff 0 = w(x) \iff C_T = 0
\end{equation}

All in all, the following picture emerges. At first we have the two \textit{uncoupled} subsystems located at both ends of the C\textsubscript{T} scale (as shown in the upper diagram of Fig. 2.8):

- subsystem ‘pure acid’: \( C_T \to \infty \)
- subsystem ‘pure H\textsubscript{2}O’: \( C_T \to 0 \)

The situation becomes interesting only when both systems are linked together. Then Eq. (2.69) describes, how the EPs of the acid smoothly approach the EP of pure water (at pH 7) when C\textsubscript{T} decreases. Just this behavior is shown in the lower diagram of Fig. 2.8 (and in all four diagrams of Fig. 2.9, too).

\begin{itemize}
\item \textbf{Fig. 2.8} \textit{pH} dependence of EPs and semi-EPs of phosphoric acid (H\textsubscript{3}PO\textsubscript{4}) for the uncoupled (upper diagram) and the coupled system (lower diagram)
\end{itemize}

Obviously, the subsystem ‘pure H\textsubscript{2}O’ overtakes the rule when C\textsubscript{T} drops below 10\textsuperscript{-7} M, which is the amount of H\textsuperscript{+} and OH\textsuperscript{-} in pure water.
**Examples.** The pH dependence of all these EPs is plotted as $C_T = f(pH)$ in Fig. 2.9 for four common acids. The dashed curves correspond to the isolated subsystem ‘pure acid’ displayed in Fig. 1.6 on page 21.

**2.4.2 Example: Carbonic Acid System**

As stated in § 1.4 (for the isolated subsystem ‘pure acid’), equivalence points are pH values at which the amount of two molar concentrations coincide

\[ \text{EP: } [\text{conjugate acid}] = [\text{conjugate base}] \]

In the case of carbonic acid we have three such equivalence points:

- **EP\(_0\):** (EP $\text{H}_2\text{CO}_3$): $[\text{H}^+] = [\text{HCO}_3^-]$  
- **EP\(_1\):** (EP $\text{HCO}_3^-$): $[\text{H}_2\text{CO}_3] = [\text{CO}_3^{2-}]$  
- **EP\(_2\):** (EP $\text{CO}_3^{2-}$): $[\text{HCO}_3^-] = [\text{OH}^-]$  

Fig. 2.10 comprises three diagrams. The upper diagram displays the pH dependence of the three EPs as $C_T = C_T(n, \text{pH})$, given in Eq. (2.69), for $n = 0, 1, \text{ and } 2$. The two diagrams below show the equilibrium distribution of the three acid species $[j]$ together with $[\text{H}^+]$ and $[\text{OH}^-]$; one diagram for $C_T = 10^{-3}$ M and one for $10^{-4}$ M.
**Acids & Buffer Systems**

**Short Lecture**

**EP<sub>0</sub> and EP<sub>2</sub>.** The selected points for EP<sub>0</sub> and EP<sub>2</sub> (so-called two *external* EPs) in the upper diagram refer just to the points of intersection (in the diagrams below), that is, to points where two concentrations coincide, which happens at the following pH values:

<table>
<thead>
<tr>
<th></th>
<th>$C_T = 10^{-4}$ M</th>
<th>$C_T = 10^{-3}$ M</th>
</tr>
</thead>
<tbody>
<tr>
<td>EP&lt;sub&gt;0&lt;/sub&gt; at pH</td>
<td>5.18</td>
<td>4.68</td>
</tr>
<tr>
<td>EP&lt;sub&gt;2&lt;/sub&gt; at pH</td>
<td>9.86</td>
<td>10.56</td>
</tr>
</tbody>
</table>

**EP<sub>1</sub>.** The *internal* equivalence point EP<sub>1</sub> obeys a slightly different behavior. According to Eq. (1.79), EP<sub>1</sub> refers to the *fixed* value $pH_1 = \frac{1}{2}(pK_1 + pK_2) = 8.34$. In fact, the curves of $H_2CO_3$ and $CO_3^{2-}$ intersect each other – in both diagrams – at exactly this ‘asymptotic’ value, that corresponds to $C_T \to \infty$ (but not to $C_T = 10^{-3}$ M or $10^{-4}$ M).

![Fig. 2.10 Equivalence points and species distribution (as a function of pH) for the carbonate system](image-url)
2.4.3 Example: Seawater

The closed-form expressions in Eqs. (2.50) and (2.69) are based on the assumption that activities could be replaced by concentrations, \( [j] \rightarrow [j] \). This holds either for dilute systems with zero ionic strength \( (I=0) \), or for non-dilute systems when thermodynamic equilibrium constants are replaced by conditional constants, \( K \rightarrow c_K \).

Seawater has \( I \approx 0.7 \text{ M} \), which is just on the upper bound of the validity range of common activity models (as discussed in Appendix A.2). Hence, in oceanography, chemists prefer conditional equilibrium constants \( c_K \). There are several compilations for \( c_K \) in literature; one example is given in Tab. 2.1.

| Tab. 2.1 Thermodynamic and conditional equilibrium constants for the carbonic acid system in pure water and seawater (at 25 °C, 1 atm) |
|---|---|
| | thermodynamic \( K \) (pure water, \( I = 0 \)) | conditional \( c_K \) [Mi95] (seawater, \( I = 0.7 \text{ M} \)) |
| \( pK_1 \) | 6.35 | 6.00 |
| \( pK_2 \) | 10.33 | 9.10 |
| \( pK_w \) | 14.0 | 13.9 |

Fig. 2.11 compares the results calculated by Eq. (2.69) for both the standard case (solid lines based on thermodynamic equilibrium constants \( K \)) and seawater (dashed lines based on conditional constants \( c_K \)). The solid curves are identical with the solid curves displayed in Fig. 2.10.
### 2.4.4 From Ideal to Real Conditions

All calculations so far were performed for the *ideal* case (no activity corrections, no complexation – cf. Assumption 1 and 2 at the end of § 2.3.1). Modern hydrochemistry programs do not adhere to those restrictions; they always perform activity corrections (cf. Appendix A). In this way, they are more accurate in predicting the relationship between pH and a given $C_T$.

Given is a carbonic acid system that will be titrated with NaOH. Fig. 2.12 compares the results of the closed-form equation (2.69) (solid lines) with the numerical-model predictions (dots).[^9]

![Equivalence points](image)

**Fig. 2.12** Equivalence points (as a function of pH): closed-form equation (2.69) vs. numerical model (dots)

As expected, deviations between the ideal and real case occur at high $C_T$. There are two reasons:

- With increasing $C_T$ the ionic strength $I$ increases, and hence also the activity corrections.^[10]
- Numerical models consider the formation of additional aquatic complexes such as NaHCO$_3^-$ and Na$_2$CO$_3$(aq) (which are ignored in the present approach). These aquatic complexes become especially relevant at high concentrations for $n = 1$ and 2.

[Note: Similar results are obtained when Na is replaced by K or NH$_4$.]

[^9]: Such calculations can be performed by free hydrochemistry software like PhreeqC or aqion.

[^10]: At values of $C_T$ between 1 and 10 M Na$_2$CO$_3$ (i.e. the most upper part of the green curve) we are even outside the applicability range of common activation models.
2.5 Titration Curves

2.5.1 The Pure-Acid Limit

The closed-form expression for titration curves \( n = n(pH) \) is given in Eq. (2.50), where \( x = 10^{-pH} \):

(2.73) \[
    n(x) = Y_1(x) + \frac{w(x)}{C_T}
\]

or

(2.74) \[
    C_B = Y_1(x) C_T + w(x)
\]

The latter predicts the amount of strong base, \( C_B = n C_T \), that is required to neutralize the acid \( H_NA \) to a given \( pH = -\lg x \).

The formulas for the titration curves consist of two parts: \( Y_1(x) \) as the contribution of the subsystem ‘pure acid’ and \( w(x) \) as the contribution from ‘pure water’. It is self-evident, that for increasing \( C_T \) values, the second term becomes more and more irrelevant. In the ‘pure acid’ limit the titration curve then simplifies to

(2.75) \[
    C_T \to \infty: \quad n(x) = Y_1(x)
\]

The upper diagram in Fig. 2.13 shows the titration curve of carbonic acid in the high-C\(_T\) limit, \( n(pH) = Y_1 = a_1 + 2a_2 \). The corresponding ionization fractions – as the building blocks of \( Y_1 \) – are displayed in the lower diagram.

![Titration curve for the 'pure acid' case](image)
The general case is shown in Fig. 2.14. It compares titration curves of carbonic acid for different \( C_T \) values (including the ‘pure-acid’ case: \( n(pH) = Y_1 \)).

![Titration curves of carbonic acid for different \( C_T \) values. Upper diagram: the ‘pure-acid’ case: \( n(pH) = Y_1(pH) = a_1 + 2a_2 \); lower diagram: the ‘pure-acid’ case (as \( C_T = \infty \)) together with four finite \( C_T \) values.](image-url)
2.5.2 Titration Curves for HA, H₂A, and H₃A

Fig. 2.15 displays titration curves of four common acids for different values of CT (including the ‘pure-acid’ case n(pH) = Y₁ as blue curve). The calculations are based on Eq. (2.73).

![Titration curves of four common acids for different values of CT (including the ‘pure-acid’ case n(pH) = Y₁ as blue curve). The calculations are based on Eq. (2.73).]
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{NA} (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 full relationship is established by Eq. (2.50) in § 2.3.2.

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

\begin{equation}
[\text{ANC}]_n = \text{amount of base in initial system} - \text{amount of base at EP}_n
\end{equation}

\begin{equation}
[\text{ANC}]_n = C_B(pH) - C_B(pH_n)
\end{equation}

The subscript n on the symbol [ANC]\textsubscript{n} remind us that the neutralizing capacity always refers to a chosen equivalence point. In the special case of n = 0, which corresponds to the base-free system, i.e. C\textsubscript{B}(pH\textsubscript{0}) = 0, it simplifies to\textsuperscript{11}

\begin{equation}
[\text{ANC}]_0 = C_B(pH)
\end{equation}

Eq. (3.2) can also be written as

\begin{equation}
\frac{[\text{ANC}]_n}{C_T} = \frac{n(pH) - n(pH_n)}{Y_1(x) + w(x)/C_T}
\end{equation}

For the function n(pH) we apply Eq. (2.73):

\begin{equation}
n(x) = Y_1(x) + w(x)/C_T
\end{equation}

while n(pH\textsubscript{n}) – as the definition of equivalence points (cf. Eq. (2.69)) – provides a fixed integer value: n(pH\textsubscript{n}) = n (= 0, 1, 2, ...). Thus, Eq. (3.4) becomes

\begin{equation}
\frac{[\text{ANC}]_n}{C_T} = Y_1(x) + \frac{w(x)}{C_T} - n
\end{equation}

or

\begin{equation}
[\text{ANC}]_n = \{ Y_1(x) - n \} C_T + w(x)
\end{equation}

\textsuperscript{11} pH\textsubscript{0} is the pH value of acid H\textsubscript{NA} with amount C\textsubscript{T}. In other words, pH\textsubscript{0} is the root of polynomial (1.127).
The base-neutralizing capacity \([\text{BNC}]\) is just the opposite of \([\text{ANC}]\):

\[(3.8) \quad [\text{BNC}]_n = - [\text{ANC}]_n\]

which leads to

\[(3.9) \quad [\text{BNC}]_n = \{ n - Y_1(x) \} C_T - w(x)\]

### 3.1.2 Alkalinity and Acidity

In carbonate systems, \([\text{ANC}]\) is named *alkalinity*, while \([\text{BNC}]\) *acidity*. Also here we have to distinguish between different types of alkalinity and acidity depending on the chosen reference point \(EP_n\). The carbonic acid has three EPs, hence there are three types of alkalinity (cf. Fig. 3.1):

\[(3.10) \quad \text{total alkalinity (m alkalinity):} \quad [\text{Alk}] = [\text{ANC}]_{n=0}\]
\[(3.11) \quad \text{p alkalinity:} \quad [\text{p-Alk}] = [\text{ANC}]_{n=1}\]
\[(3.12) \quad \text{caustic alkalinity:} \quad [\text{OH-Alk}] = [\text{ANC}]_{n=2}\]

Correspondingly, there are three types of acidity:

\[(3.13) \quad \text{mineral acidity:} \quad [\text{H-Acy}] = [\text{BNC}]_{n=0}\]
\[(3.14) \quad \text{CO}_2\text{ acidity:} \quad [\text{CO}_2\text{-Acy}] = [\text{BNC}]_{n=1}\]
\[(3.15) \quad \text{acidity:} \quad [\text{Acy}] = [\text{BNC}]_{n=2}\]

Alkalinity and acidity are complementary. In particular, from Eq. (3.8) we get:

\[(3.16) \quad [\text{ANC}]_0 = - [\text{BNC}]_0 \quad \Rightarrow \quad [\text{Alk}] = - [\text{H-Acy}]\]
\[(3.17) \quad [\text{ANC}]_1 = - [\text{BNC}]_1 \quad \Rightarrow \quad [\text{p-Alk}] = - [\text{CO}_2\text{-Acy}]\]
\[(3.18) \quad [\text{ANC}]_2 = - [\text{BNC}]_2 \quad \Rightarrow \quad [\text{OH-Alk}] = - [\text{Acy}]\]

![Fig. 3.1 Titration curve of carbonic acid, \(n = n(pH)\), with equivalence points and the corresponding types of alkalinity and acidity](image-url)
Probably the most important quantity is the total alkalinity; according to Eq. (3.19) it is given by

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

Plots of alkalinity were presented in Fig. 2.7 on page 41.

### 3.2 Buffer Intensity

#### 3.2.1 Definitions

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

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

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

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

The latter is just the formula for the ‘normalized’ titration curve of an \( N \)-protic acid (see Eq. (2.73)). To exhibit its pH dependence we replace \( x \) by \( 10^{pH} \) and write:

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

The buffer intensity is the derivative of the buffer capacity with respect to pH. Depending on the expression for the buffer capacity (either its normalized form, \( n(pH) \), or as \( C_B \) as in Eq. (3.20)) we distinguish between two types of buffer intensities:

(3.23) buffer intensity (normalized): \[ \beta = \frac{d n}{d pH} \quad \text{[unitless]} \]

(3.24) buffer intensity: \[ \beta_C = \frac{d C_B}{d pH} = \beta C_T \quad \text{[mol/L]} \]

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

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

(3.25) \[ [\text{ANC}]_n = \int_{pH_n}^{pH} \beta_C(pH') \, d pH' \]
3.2.2 Optimal Buffer Range

Before we present closed-form expressions for the buffer intensity $\beta$ in the next paragraph some qualitative considerations are appropriate. A good pH buffer should mitigate pH changes when the system is attacked by a strong base or acid. That is, $\Delta p\text{H}$ should be small for any changes of $n = C_B/C_T$, i.e. any $\Delta n$. In other words, the slope of the titration curve, $\Delta n/\Delta p\text{H}$, should be as large as possible for maximum buffering. The buffer intensity, $\beta = dn/dp\text{H}$, itself is just the measure of this slope.

To sum up: the steeper the slope of a titration curve – as sketched in Fig. 3.2 – the higher is the buffer intensity $\beta = dn/dp\text{H}$, i.e. the higher is the system’s resistance to pH changes (caused by a strong base). Thus, the pH where $\beta$ reaches its maximum represents the optimal buffer range (bounded by $p\text{H}_{\text{max}} \pm 1$) – see example in Fig. 3.3.

**Fig. 3.2** The steeper the slope of a titration curve the higher is the system’s buffer intensity

**Fig. 3.3** Optimal buffer range ($\text{H}_2\text{CO}_3$ system). The mathematical equations for $\beta$ and $d\beta/dp\text{H}$ will be derived in § 3.2.3.
Since the titration curve (in blue color) is an ever-increasing function, its derivation, i.e. the buffer intensity $\beta$, is always positive (green curve). This is in full accord with Le CHÂTELIER’s principle that 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 $pH_{\text{max}}$ are related to the semi-equivalence points at $pK_j$.

### 3.2.3 Closed-Form Expressions

The starting-point is the analytical formula of the titration curve, $n(pH)$, given in Eq. (3.22). Its first derivative with respect to pH yields the buffer intensity $\beta(pH)$; it can be obtained with help of Eqs. (B.40) and (B.30). The next higher derivative yields $d\beta/dpH$, which can be obtained using Eqs. (B.42) and (B.31). Putting all together (and using the abbreviation $x = 10^{-pH}$), the results are:

\[
\begin{align*}
\text{(3.26) titration curve:} & \quad n(x) = Y_i(x) + \frac{w(x)}{C_T} \\
\text{(3.27) buffer intensity:} & \quad \beta(x) = \frac{dn}{dpH} = \ln 10 \left( Y_2 - Y_i^2 + \frac{w + 2x}{C_T} \right) \\
\text{(3.28) 1st derivative of } \beta: & \quad \frac{d\beta}{dpH} = \frac{d^2n}{dpH^2} = (\ln 10)^2 \left( Y_3 - 3Y_1Y_2 + 2Y_i^3 + \frac{w}{C_T} \right) 
\end{align*}
\]

These three functions are displayed in Fig. 3.3 and in all subsequent diagrams. Since $Y_2 \geq Y_i^2$, the buffer intensity is a positive function which never drops below zero. The maxima and minima of the buffer intensity are identified by the zeros of its derivative, i.e. they are located at pH values where $d\beta/dpH = 0$.

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

\[
\begin{align*}
\text{(3.29) titration curve:} & \quad n(x) = Y_i(x) \\
\text{(3.30) buffer intensity:} & \quad \beta(x) = \frac{dn}{dpH} = \ln 10 \left( Y_2 - Y_i^2 \right) \\
\text{(3.31) 1st derivative of } \beta: & \quad \frac{d\beta}{dpH} = \frac{d^2n}{dpH^2} = (\ln 10)^2 \left( Y_3 - 3Y_1Y_2 + 2Y_i^3 \right) 
\end{align*}
\]

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

---

12 The maximum or minimum is where the slope (i.e. the derivative) of a function becomes zero.
3.2.4 Minima and Maxima (Pure-Acid Limit)

This paragraph relies on the buffer intensity $\beta$ and its derivative $d\beta/d\text{pH}$ as given in Eqs. (3.30) and (3.31) for the pure-acid limit, $C_T >> w$ (where the contribution from ‘$H_2O$’ is neglected):

\begin{equation}
\beta(x) = \ln 10 \left(Y_2 - Y_1^2\right)
\end{equation}

\begin{equation}
\frac{d\beta}{dp\text{H}} = (\ln 10)^2 \left(Y_2 - 3Y_1Y_2 + 2Y_1^3\right)
\end{equation}

These are smooth functions made of $Y_1$, $Y_2$, and $Y_3$. The behavior of $Y_3$ is completely determined by the acid’s equilibrium constants $K_j$, or alternatively, by the internal equivalence points $EP_n$ as given in Eqs. (1.107) and (1.108):

\begin{align}
(3.34) & \quad \text{semi-EP}_j \quad \text{at } pK_j \quad Y_k = \frac{1}{2} \{(j-1)^k + j^k\} \quad (n = j^{\frac{1}{2}}) \\
(3.35) & \quad \text{EP}_j \quad \text{at } pH_j = \frac{1}{2}(pK_j + pK_{j+1}) \quad Y_k = j^k \quad (n = j)
\end{align}

Inserting it into Eq. (3.32) we get

\begin{align}
(3.36) \quad \frac{\beta(pK_j)}{\ln 10} &= Y_2(pK_j) - Y_1^2(pK_j) = \{j(j-1) + j\} - \{j(j-1) + \frac{1}{2}\} = \frac{1}{4} \\
(3.37) \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 proof that just these equivalence points are extrema points of the buffer intensity. As is known, the maximum or minimum is where the slope (i.e. the derivative) of a function becomes zero. Hence, local maxima and minima of the buffer intensity $\beta(pH)$ occur at pH values where $d\beta/dpH = 0$. The derivative itself is given by Eq. (3.33) above, where we focus on $Y_3 - 3Y_1Y_2 + 2Y_1^3$.

For the semi-EP$_n$ with half-integer $n = j^{\frac{1}{2}}$ we get from Eq. (3.34):

\begin{equation}
Y_3 - 3Y_1Y_2 + 2Y_1^3 = \frac{1}{2} \{(j-1)^3 + j^3\} - 3(j-1)^{3/2}(j(j-1)^{1/2}) + 2(j^{3/2})^3 \\
= 0 \quad \text{at } \text{pH} = pK_j \quad \text{for } j = 1, 2, ..., N
\end{equation}

For EP$_n$ with integer $n = j$ we get from Eq. (3.35):

\begin{equation}
Y_3 - 3Y_1Y_2 + 2Y_1^3 = j^3 - 3j^2 + 2j^3 \\
= 0 \quad \text{at } \text{pH} = pH_j \quad \text{for } j = 1, 2, ..., N-1
\end{equation}

Hence, the zeros of $d\beta/dpH$ occur exactly at the internal equivalence points of both types: integer and half-integer EP$_n$. In order to decide whether the zero indicates a maximum or minimum we need the next-higher derivative, $d^3\beta/dpH^3$ (or $d^3Y/dpH^3$ which is presented in Eq. (B.43).
In summary, we get the following assignment:

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

The buffer intensity attains its maximum at semi-equivalence points at \( pK_j \). The actual values of \( \beta \) at this extrema were already presented in Eqs. (3.36) and (3.37):

\[ \text{maxima of } \beta \text{ at EP}_n \quad \beta_{\text{max}} = \frac{\ln 10}{4} \approx 0.576 \quad \text{for } n = 1, 2, \ldots N-1 \]
\[ \text{minima of } \beta \text{ at semi-EP}_n \quad \beta_{\text{min}} = 0 \quad \text{for half-integer } n \]

This behavior of the buffer intensity is shown in Fig. 3.4 for four common acids. The maxima of \( \beta \) (green curve) are indicated with the corresponding \( pK_j \) values. The zeros of \( d\beta/dpH \) (red curve) are marked by small blue dots.

**Example.** The carbonate system, as shown in the bottom-left diagram of Fig. 3.4, 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).

---

**Fig. 3.4** Maxima and minima of the buffer intensity \( \beta \) (green curves) are located at zeros of \( d\beta/dpH \) (red curves). Calculations for the pure-acid case, \( C_T/w \gg 1 \).
3.2.5 Examples for the General/Realistic Case

The foregoing paragraph was focused on the pure-acid case valid for \( C_T \to \infty \). The general case (for finite and realistic values of \( C_T \)) should incorporate the influence of water embodied in the quantity \( w(x) \) that enters the Eqs. (3.26) to (3.28). The results for the general/realistic case are plotted in diagrams, each of which contains three curves:

- \( n(pH) \)  titration curve  Eq. (3.26)  (blue curve)
- \( \beta = dn/dpH \)  buffer intensity  Eq. (3.27)  (green curve)
- \( d\beta /d\text{pH} \)  \(^1\)st derivative of \( \beta \)  Eq. (3.28)  (red curve)

All three quantities are unitless. The small blue dots mark the zeros of \( d\beta /d\text{pH} \); they correspond to minima and maxima of the buffer intensity.

**Example 1.** Given is a pure \( \text{CO}_2 \) system with \( C_T = 100 \text{ mM}, 10 \text{ mM}, \) and \( 1 \text{ mM} \) \( \text{H}_2\text{CO}_3 \); the results are shown in Fig. 3.5.

![Diagram](image.png)
Acids & Buffer Systems

**Short Lecture**

Fig. 3.6 Titration curve (blue), buffer intensity (green), and dβ/dpH (red) for four common acids with $C_T = 100$ mM

Fig. 3.7 Titration curve (blue), buffer intensity (green), and dβ/dpH (red) for four common acids with $C_T = 10$ mM

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Fig. 3.8 Titration curve (blue), buffer intensity (green), and $d\beta/dpH$ (red) for four common acids with $C_T = 1$ mM

Example 2. Fig. 3.6 to Fig. 3.8 displays the results for four common acids with an amount of $C_T = 100$ mM, 10 mM, and 1 mM. These results should be compared with pure-acid case in Fig. 3.4, which is obtained when $C_T$ is increased to infinity.
REFERENCES


ADDITIONAL LINKS

PowerPoint Presentations:

- Aqueous Speciation  
  [www.slideshare.net/aqion/aqueous-speciation](http://www.slideshare.net/aqion/aqueous-speciation)
- Open vs Closed CO₂ System  
  [www.slideshare.net/aqion/open-vs-closed-carbonate-system](http://www.slideshare.net/aqion/open-vs-closed-carbonate-system)
- Diprotic Acids & Equivalence Points  
  [www.slideshare.net/aqion/diprotic-acids-and-equivalence-points](http://www.slideshare.net/aqion/diprotic-acids-and-equivalence-points)
- Buffer Systems & Titration  
  [www.slideshare.net/aqion/buffer-systems-and-titration](http://www.slideshare.net/aqion/buffer-systems-and-titration)
- Composite Carbonic Acid (Kinetics)  
  [www.slideshare.net/aqion/composite-carbonic-acid-and-carbonate-kinetics](http://www.slideshare.net/aqion/composite-carbonic-acid-and-carbonate-kinetics)
APPENDIX
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:

\[(A.1) \quad \text{activity} = \text{effective concentration} \leq \text{real concentration}\]

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

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

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

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

\[(A.2) \quad \{j\} = \gamma_j [j] \quad \text{(activity} = \gamma_j \times \text{concentration)}\]

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:

\[(A.3) \quad \text{ideal solution:} \quad \gamma_i = 1 \quad \text{(infinitely diluted system)}\]

that is, activity and concentration coincide:

\[(A.4) \quad \text{ideal solution:} \quad \{i\} = [i]\]

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

A.1.2 Ionic Strength

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

\[(A.5) \quad I = \frac{1}{2} \sum_j z_j^2 [j]\]
Here, \([j]\) and \(z_j\) are the molar concentration and the charge of ion \(j\). The sum is taken over all ions in the solution. Due to the square of \(z_j\), multivalent ions contribute strongly to the ionic strength. [Note: In literature the ionic strength, \(I\), is also abbreviated by the Greek symbol \(\mu\).]

For comparison: Typical ionic strengths of natural waters are

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

### A.2 Activity Models

The step from molar concentrations (analytical data) to activities (that enter law-of-mass-action calculations) requires the calculation of activity coefficients \(\gamma_j\). For this task several approaches are available, whereas each activity model has its own range of validity defined by the ionic strength \(I\) as shown here:

\[
\text{(A.6) DEBYE-HÜCKEL (DH) } \quad \lg \gamma_j = -A z_j^2 \sqrt{I} \quad \text{for } I < 10^{-2.3} \text{ M} \\
\text{(A.7) Extended DH } \quad \lg \gamma_j = -A z_j^2 \left( \frac{\sqrt{I}}{1 + B \alpha_j \sqrt{I}} \right) \quad \text{for } I < 0.1 \text{ M} \\
\text{(A.8) DAVIES } \quad \lg \gamma_j = -A z_j^2 \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right) \quad \text{for } I \leq 0.5 \text{ M} \\
\text{(A.9) TRUESDELL-JONES } \quad \lg \gamma_j = -A z_j^2 \left( \frac{\sqrt{I}}{1 + B \alpha_j^0 \sqrt{I} + b_j I} \right) \quad \text{for } I < 1 \text{ M}
\]

Here, \(z_j\) is the valence of ion \(j\). All quantities carrying the subscript \(j\) are ion-specific parameters (\(\alpha_j\), \(\alpha_j^0\) and \(b_j\)). On the other hand, the parameters \(A\) and \(B\) depend on temperature \(T\) and the dielectric constant \(\varepsilon\):

\[
\text{(A.10) } A = 1.82 \cdot 10^6 (\varepsilon T)^{3/2} \\
\text{(A.11) } B = 3.281 \text{ M}^{1/2} \text{ nm}^{-1}
\]

For standard conditions (water at 25 °C) we get

\[
\text{(A.12) } A = 0.5085 \text{ M}^{1/2} \\
\text{(A.13) } B = 3.281 \text{ M}^{1/2} \text{ nm}^{-1}
\]

Please note the length unit: 1 nm = 10^{-9} m = 10 Ångström.
B MATHEMATICAL RELATIONSHIPS

B.1 Polynomials in x

B.1.1 The Subsystem \( H_N A \)

The ionization fractions \( a_j \) of an \( N \)-protic acid, are functions of \( x \) (\( j = 1 \) to \( N \)):

\[
\begin{align*}
(B.1) \quad a_j(x) &= \left( \frac{k_j}{x} \right) a_0 \\
& \quad \text{with} \quad a_0(x) = \left( 1 + \frac{k_1}{x} + \frac{k_2}{x^2} + \ldots + \frac{k_N}{x^N} \right)^{-1}
\end{align*}
\]

The task is to solve it for \( x \), that is, to find a formula that calculates \( x \) for a given value of \( a_j \). This will lead to a polynomial of order \( N \) in \( x \).

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

\[
\begin{align*}
(B.2) \quad a_0^{-1} &= \left( 1 + \frac{k_1}{x} + \frac{k_2}{x^2} + \ldots \right) = \frac{1}{x^N} \left( x^N + k_1 x^{N-1} + \ldots + k_N \right) \\
(B.3) \quad \frac{x^N}{a_0} &= x^N + k_1 x^{N-1} + \ldots + k_N = \sum_{j=0}^{N} k_j x^{N-j}
\end{align*}
\]

It yields a polynomial of order \( N \) in \( x \) (i.e. the highest power of \( x \) is \( N \)):

\[
\begin{align*}
(B.4) \quad 0 &= \text{const} \cdot x^N + k_1 x^{N-1} + \ldots + k_N \quad \text{with} \quad \text{const} = -\left( \frac{1-a_0}{a_0} \right)
\end{align*}
\]

This result can be generalized to any other \( a_j \). To do this, insert \( a_0 = \left( x^j/k_j \right) a_j \) into the left-hand side of Eq. (B.3):

\[
\begin{align*}
(B.5) \quad \left( \frac{k_j}{a_0} \right) x^{N-j} &= \sum_{j=0}^{N} k_j x^{N-j}
\end{align*}
\]

Again, the obtained polynomial is of order \( N \) in \( x \)

\[
\begin{align*}
(B.6) \quad 0 &= \text{const} \cdot x^{N-j} + \sum_{i \neq j}^{N} k_i x^{N-i} \quad \text{with} \quad \text{const} = -\left( \frac{1-a_j}{a_j} \right)
\end{align*}
\]

For \( j = 0 \) this formula reduces to Eq. (B.4).

B.1.2 The General Case: \( H_N A + H_2 O + \text{Strong Base} \)

The titration of an polyprotic acid \( H_N A \) by a strong base is described by Eq. (2.50):

\[
\begin{align*}
(B.7) \quad 0 &= n - w(x)/C_T - Y_1(x) \quad \text{with} \quad n = \frac{C_B}{C_T}
\end{align*}
\]
The closed-form expression that describes the base-free system ‘H₂O + H₃A’ of § 1.6.2 is then obtained as a special case for \( n = 0 \):

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

The task is to find a formula that calculates \( x \) for a given value of \( C_T \) (and \( n \)). For this purpose, we start with Eq. (B.7) and get:

\[
0 = n - w/C_T - Y_1
\]

\[
= n - w/C_T - \sum_{j=0}^{N} j \frac{k_{j} x^{N-j}}{\sum_{j=0}^{N} k_{j} x^{N-j}} ~ \quad \text{(Eq. (1.105) is used for } Y_1) \]

\[
= \sum_{j=0}^{N} \left( n - \frac{W}{C_T} - j \right) k_{j} x^{N-j} ~ \quad \text{(both sides multiplied by } \sum k_j x^{N-j}) \]

\[
= \sum_{j=0}^{N} \left( n - \frac{K_w / x - x}{C_T} - j \right) k_{j} x^{N-j} ~ \quad \text{(Eq. (1.123) is applied for } w) \]

\[
= \sum_{j=0}^{N} \left( x^2 + (n - j) C_T x - K_w \right) k_{j} x^{N-j} \quad \text{(both sides multiplied by } x C_T) \]

In this way, we obtained a polynomial of order \( N+2 \) in \( x \):

\[
(B.9) \quad 0 = \sum_{j=0}^{N} \left( x^2 + (n - j) C_T x - K_w \right) k_{j} x^{N-j}
\]

In the special case of \( n = 0 \) it becomes:

\[
(B.10) \quad 0 = \sum_{j=0}^{N} \left( x^2 - j C_T x - K_w \right) k_{j} x^{N-j} \quad \text{(for } n = 0) \]

To make it more explicit that the polynomial in Eq. (B.9) is indeed of order \( N+2 \), it can be re-written as

\[
(B.11) \quad 0 = \sum_{j=0}^{N+2} f_j x^{N+2-j} \quad \text{with } \quad f_j = k_j + k_{j+1} (n + 1 - j) C_T - K_w k_{j+2}
\]

The combined equilibrium constants \( k_j \) defined in Eq. (1.46). The first and the last coefficients of this polynomial are: \( f_0 = -K_w K_1 K_2 ... K_N \) and \( f_{N+2} = 1 \), respectively. [Note: \( k_i \) is per definition zero for negative values i.]
B.2 Simple Relationships between $a_j$ and $Y_k$

B.2.1 Relationships for $Y_k$

The moments $Y_k$ are defined as finite sums over the ionization fractions $a_j$:

$$Y_k \equiv \sum_{j=0}^{N} j^k a_j = 0^k a_0 + 1^k a_1 + 2^k a_2 + \ldots + N^k a_N$$

with the special case $Y_0 = 1$ (mass balance) – see Eqs. (1.89) and (1.103).

One simple relationship between $a_j$ and $Y_k$ can be established in the following sequence of steps:

\[ n = n \]
\[ n Y_0 = n \quad \text{(because $Y_0 = 1$)} \]
\[ n Y_0 - Y_1 = n - Y_1 \quad \text{($Y_1$ subtracted from both sides)} \]
\[ n \sum a_j - \sum j a_j = n - Y_1 \quad \text{(using Eq. (B.12) on left-hand side)} \]

which finally yields the result

$$\sum_{j=0}^{N} (n - j) a_j = n - Y_1 \quad \text{or} \quad \sum_{j=0}^{N} (n - j) \left[ j \right] = (n - Y_1) C_T$$

**Equivalence Points.** The two types of equivalence points are characterized by (c.f. Eqs. (1.95) and (1.96)):

(B.14) semi-EP$_j$: $pH = pK_j \quad \Rightarrow \quad a_j = a_{j+1} = \frac{1}{2}$

(B.15) EP$_j$: $pH_j = \frac{1}{2} (pK_j + pK_{j+1}) \quad \Rightarrow \quad a_j (pH_j) \approx 1$

all other ionization fractions are almost zero. In this way, the whole sum in Eq. (B.12) downgrades to one or two terms:

(B.16) $Y_k (pK_j) = (j - 1)^k a_{j-1} + j^k a_j = \frac{1}{2} \{ (j - 1)^k + j^k \}$ for $k \geq 1$

(B.17) $Y_k (pH_j) = j^k a_j \approx j^k$ for $k \geq 1$

B.2.2 Maximum of $a_j$

The maximum (extrema) of an ionization fraction $a_j$ is obtained from the condition that its first derivative should vanish:

$$\frac{da_j}{d pH} = 0 \quad \Leftrightarrow \quad \text{extremum of } a_j$$

According to Eq. (B.37) this is equivalent to the condition:

(B.19) $(j - Y_1) a_j = 0 \quad \text{or} \quad j - Y_1 = 0$
From Eq. (B.13) one gets

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

or, more explicitly,

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

From the view point of \( a_i \) only its two neighbors, \( a_{j-1} \) and \( a_{j+1} \), are of relevance (all other are nearly zero). Thus, Eq. (B.20) collapses to \(-a_{j-1} + a_{j+1} = 0\), that is

\[ \text{maximum of } a_j \Leftrightarrow a_{j-1} = a_{j+1} \quad \text{or} \quad \frac{a_{j+1}}{a_{j-1}} = 1 \]

The pH at the maximum is obtained from Eq. (1.51),

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

According to Eq. (1.73), the ionization fraction \( a_j \) has its maximum at the equivalence point

\[ \text{maximum of } a_j \quad \text{at EP}_j \quad \text{with} \quad \text{pH} = \frac{1}{2}(pK_j + pK_{j+1}) \]

From mass conservation, i.e. Eqs. (1.89), one gets the value of \( a_j \) at the maximum as

\[ a_j(x_{\text{max}}) = 1 - a_{j-1} - a_{j+1} = 1 - 2a_{j-1} \]

which, in most cases, is very close to 1.

### B.3 Derivatives with Respect to pH

#### B.3.1 Basic Equations

Given is

\[ x = [H^+] = 10^{-\text{pH}} = e^{-\ln 10 \text{pH}} \]

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

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

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

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

**Example 1.** For \( w(x) = K_w/x - x \), introduced in Eq. (0.7), we get:

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

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

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

Its first derivative is then given by

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

where on the right-hand site Eq. (1.55) was applied. Using the definition of \( Y_1 \) in Eq. (1.104), it yields the interesting result:

\[
\frac{dg(x)}{dpH} = \frac{1}{a_0} = \ln 10 \frac{Y_1}{a_0}
\]

### B.3.2 Derivatives of Ionization Fractions \( a_j \) and \( Y_k \)

We start with the first derivative of \( a_0 \) by applying the results of the last example (especially Eq. (B.35)):

\[
\frac{da_0(x)}{dpH} = \frac{d}{dpH} \frac{1}{g(x)} = -\frac{1}{g^2} \frac{dg(x)}{dpH} = -a_0^2 (\ln 10) \frac{Y_1}{a_0} = -(\ln 10) Y_1 a_0
\]

In the same way, we get from \( a_j = (k_j/x^j) a_0 \) the general result for any ionization coefficient \( a_j \):
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(B.37) \( \frac{d a_j(x)}{d pH} = -\ln 10 \ (j - Y_i) a_j \)

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

(B.38) \( \frac{d}{d pH} \sum_{j=0}^{N} a_j = \ln 10 \sum_{j=0}^{N} (j - Y_i) a_j = \ln 10 (Y_i - Y_i) = 0 \)

(B.39) \( \frac{d}{d pH} \sum_{j=0}^{N} j a_j = \ln 10 \sum_{j=0}^{N} j(j - Y_i) a_j = \ln 10 (Y_2 - Y_i^2) \)

The first relation, which gives zero, is obvious because it represents the derivation of a constant, namely \( d \ln(d pH) = 0 \). Eq (B.39) is nothing else than the first derivative of \( Y_1 \):

(B.40) \( \frac{d Y_1(x)}{d pH} = \ln 10 (Y_2 - Y_i^2) \)

In the same way, for all higher moments \( Y_k \) we get:

(B.41) \( \frac{d Y_k(x)}{d pH} = \ln 10 \sum_{j=0}^{N} j^k (j - Y_i) a_j = \ln 10 (Y_{k+1} - Y_i Y_k) \)

**B.3.3 Higher Derivatives of \( Y_k \)**

The second derivative of \( Y_1 \) is given by

(B.42) \( \frac{d^2 Y_1}{d pH^2} = \ln 10 \frac{d}{d pH} (Y_2 - Y_i^2) \)

\( = (\ln 10)^2 (Y_3 - Y_1 Y_2 - 2Y_1 (Y_2 - Y_i^2)) \)

\( = (\ln 10)^2 (Y_3 - 3Y_1 Y_2 + 2Y_i^3) \)

The third derivative of \( Y_1 \) is:

(B.43) \( \frac{d^3 Y_1}{d pH^3} = (\ln 10)^3 \frac{d}{d pH} (Y_3 - 3Y_1 Y_2 + 2Y_i^3) \)

\( = (\ln 10)^3 \{ (Y_4 - Y_1 Y_3) - 3Y_2 (Y_2 - Y_i^2) - 3Y_1 (Y_3 - Y_1 Y_2) + 6Y_1 Y_2 (Y_2 - Y_i^2) \} \)

\( = (\ln 10)^3 \{ Y_4 - Y_1 (4Y_3 - 3Y_1 Y_2) - 3(Y_2 - 2Y_i^2) (Y_2 - Y_i^2) \} \)