

Short Lecture 2023

Acid-Base Systems — Math Background —

Harald Kalka
Dresden, Germany

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Contents

1	Introduction	1
1.1	Short History & State of the Art	1
1.1.1	Three Concepts	1
1.1.2	State of the Art	2
1.2	Motivation	4
1.3	Structure of the Lecture	6
2	Polyprotic Acids	7
2.1	What is an Acid?	7
2.1.1	Proton Transfer	7
2.1.2	Acidity Constants	8
2.1.3	Mono-, Di-, and Triprotic Acids	10
2.1.4	Strong Acids vs Weak Acids	11
2.1.5	Weak Acids vs Dilute Acids	12
2.2	Basic Set of Equations	12
2.2.1	Special Case: Diprotic Acids (H_2A)	12
2.2.2	General Case: Polyprotic Acids (H_NA)	14
3	1-Component System: “H_NA”	17
3.1	The Subsystem “Pure Acid”	17
3.1.1	Streamlined Notation	17
3.1.2	Stepwise vs Cumulative Dissociation	18
3.1.3	Generalized HENDERSON-HASSELBACH Equations	20
3.1.4	Closed-Form Expressions	21
3.1.5	Inverse Task	21
3.2	Equivalence Points	22
3.2.1	Definition of Equivalence Points	22
3.2.2	Assignment between EP _n and pH _n	23
3.2.3	Summary & Examples	24
3.3	Ionization Fractions: Degree of Dissociation	26
3.3.1	Definition of a_j	26
3.3.2	BJERRUM Plots & Special Features of a_j	26
3.3.3	Two Types of a_j : S-Shaped vs Bell-Shaped	28

3.3.4	Two Types of Approximations	29
3.4	Moments Y_L : Weighted Sums over a_j	32
3.4.1	Definition of Y_L	32
3.4.2	Moments and EPs	34
4	2-Component System: “$\text{H}_\text{N}\text{A} + \text{H}_2\text{O}$”	37
4.1	Basic Set of Equations	37
4.2	Closed-Form Equations	38
4.2.1	Forward and Inverse Task	38
4.2.2	Examples	39
5	Acid-Base System	41
5.1	Introduction	41
5.1.1	Definitions	41
5.1.2	Special Case: Diprotic Acid	42
5.2	Basic Set of Equations	44
5.2.1	The 3-Component System	44
5.2.2	Closed-Form Expressions	45
5.2.3	Polynomials for $x = 10^{-\text{pH}}$	47
5.2.4	Lego-Set of Building Blocks	48
5.3	Titration Curves	48
5.4	Equivalence Points: General Approach	50
5.4.1	Definitions	50
5.4.2	EP _n as Trajectories in pH- C_T Diagrams	52
5.4.3	Summary: Systematics & Classification	53
6	Buffer Capacities	57
6.1	ANC and BNC	57
6.1.1	EPs as Reference Points of ANC and BNC	57
6.1.2	Titration Example	58
6.1.3	Alkalinity and Acidity	59
6.1.4	pH as Reference Point of ANC and BNC	61
6.2	Buffer Intensity	61
6.2.1	From Buffer Capacity to Buffer Intensity	61
6.2.2	Minima and Maxima (High- C_T Limit)	63
6.2.3	The General Case	65
7	Application: Carbonate System	69
7.1	Relationships between pH, C_T , and Alkalinity	69
7.2	Three Equivalence Points	70
7.3	Acid–Base Titration with H_2CO_3 as Titrant	72
7.4	Open vs Closed CO_2 System	73
7.5	Seawater	75
7.6	From Ideal to Real Solutions	75

8 Additional Topics	77
8.1 Strong Polyprotic Acids	77
8.2 Mixtures of Acids	79
8.3 H _N A as Superposition of N Monoprotic Acids	79
 Appendices	
A Activity Models	85
A.1 Activity vs Concentration	85
A.2 Activity Corrections	86
A.2.1 Four Activity Models	86
A.2.2 The Prefactors A and B	87
B Math Relationships	89
B.1 Polynomials in x	89
B.1.1 The Subsystem H _N A	89
B.1.2 The General Case: H _N A + H ₂ O + Strong Base	90
B.2 Approximations for a_j	91
B.2.1 Piecewise Linearization of $\lg a_j$	91
B.2.2 Strong Polyprotic Acids	92
B.3 Simple Relationships between a_j and Y_L	93
B.3.1 Relationships for Y_L	93
B.3.2 Maximum of a_j	94
B.4 Derivatives with Respect to pH	95
B.4.1 Basic Equations	95
B.4.2 First Derivative of a_j and Y_L	96
B.4.3 Higher Derivatives of a_j and Y_L	96
C Proton Balance	99
C.1 Diprotic Acid	99
C.2 General Case: N-protic Acid	101
References	103

List of Symbols & Abbreviations

a_j	ionization fractions, $a_j = [j]/C_T$	—
Acy	acidity	mol/L
Alk	total alkalinity (M-alkalinity)	mol/L
ANC	acid-neutralizing capacity	mol/L
BNC	base-neutralizing capacity	mol/L
C_A	concentration of strong monoprotic acid, $C_A = [\text{HX}]_T$	mol/L
C_B	concentration of strong monoacidic base, $C_B = [\text{BOH}]_T$	mol/L
C_T	total concentration of N -protic acid, $C_T = [\text{H}_N\text{A}]_T$	mol/L
EP_j	equivalence point (for integer j)	—
EP_n	equivalence point (for integer and half-integer n)	—
G	molar GIBBS energy	J/mol
I	ionic strength	mol/L
j	index denoting the aqueous species $j = 0, 1, \dots, N$	—
$[j]$	molar concentration of aqueous species j : $[j] = [\text{H}_{N-j}\text{A}^j]$	mol/L
$\{j\}$	activity of aqueous species j : $\{j\} = \{\text{H}_{N-j}\text{A}^j\}$	mol/L
$\langle j \rangle$	mean value of j (real number between 0 and N)	—
K_a	acidity constant (general abbreviation)	mol/L
${}^c K_a$	conditional acidity constant (non-thdyn quantity)	mol/L
K_j	acidity constant of dissociation step j	mol/L
K_H	HENRY constant	mol/(L·atm)
k_j	cumulative acidity constant, $k_j = K_1 K_2 \cdots K_j$	(mol/L) j
K_w	equilibrium constant of self-ionization of H_2O	(mol/L) 2
n	equivalent fraction, $n = (C_B - C_A)/C_T$	—
N	number of protons (H^+ ions) of the N -protic acid H_NA	—
P	pressure	atm
pH	$= -\lg \{\text{H}\equiv\} = -\lg x$	—
pH_j	pH of equivalence point EP_j : $\text{pH}_j = \frac{1}{2} (\text{pK}_j + \text{pK}_{j+1})$	—
pH_n	pH of equivalence point EP_n	—
pk_j	$= -\lg k_j$	—
pK_j	$= -\lg K_j$	—
R	universal gas constant	J/(mol K)
x	activity of H^+ , $x \equiv \{\text{H}^+\}$	mol/L
T	temperature	K or °C
Y_L	L^{th} moment constructed from a_j : $Y_L = \sum_j j^L a_j$	—
$w(x)$	pure water balance: $w \equiv [\text{OH}^-] - [\text{H}^+] = K_w/x - x$	mol/L
Z	charge of highest protonated acid species	—
z_{av}	average charge of acid: $z_{\text{av}} = Z_T/C_T$	—
z_j	charge of species j : $z_j = Z - j$	—

Z_T	total charge of acid	—
β	(unitless) buffer intensity, $\beta = dn//d \text{pH}$	—
β_C	buffer intensity, $\beta_C = dC_B/d \text{pH} = C_T\beta$	mol/L
β_j	cumulative formation constants	$(\text{mol}/\text{L})^{-j}$
γ_j	activity correction for species j	—

Units and Conversions

L	liter ($1 \text{ L} = 1 \text{ dm}^3 = 10^{-3} \text{ m}^3$)	
M	molarity ($1 \text{ M} = 1 \text{ mol/L}$)	
mM	$1 \text{ mM} = 10^{-3} \text{ mol/L}$	
$\lg x$	decadic logarithm ($= \log_{10} x$)	conversion: $\lg x = (\ln x)/(\ln 10)$
$\ln x$	natural logarithm ($= \log_e x$)	conversion: $\ln x = (\ln 10) \cdot (\lg x)$
$\ln 10$	= 2.303	

Abbreviations

EDTA	ethylenediaminetetraacetic acid
EP	equivalence point
GEM	GIBBS energy minimization
LMA	law of mass action
NTA	nitrolotriacetic acid
PRL	proton reference level
thdyn	thermodynamics, thermodynamical

Some Definitions

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

$$[j] \equiv [\text{H}_{N-j}\text{A}^{Z-j}] \quad \text{for } j = 0, 1, 2, \dots N \quad (1)$$

Here the integer j also labels the electric charge of species j :

$$z_j = Z - j \quad \text{with} \quad \begin{cases} Z = 0 & \text{for common acids} \\ Z \geq j & \text{for zwitterionic acids (e.g. amino acids)} \end{cases} \quad (2)$$

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

$$C_T \equiv [\text{H}_N\text{A}]_T = \sum_{j=0}^N [j] \quad (\text{mass balance}) \quad (3)$$

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

$$a_j \equiv \frac{[j]}{C_T} \quad \text{for } j = 0, 1, 2, \dots N \quad (4)$$

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

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

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

$$x \equiv \{\text{H}^+\} = 10^{-\text{pH}} \quad \iff \quad \text{pH} = -\lg x \quad (5)$$

*The difference between theory and practice is
smaller in theory than it is in practice*

— Folklore

1

Introduction

Contents

1.1	Short History & State of the Art	1
1.2	Motivation	4
1.3	Structure of the Lecture	6

This lecture provides a detailed math description of the acid-base system, leading to analytical formulas that anyone can easily apply without effort to plot titration curves, BJERRUM plots and other diagrams. It covers and explains the first part of the review article [1].

1.1 Short History & State of the Art

1.1.1 Three Concepts

The theory of acid-base reactions in water is not new; the subject has been studied for more than 100 years. Three main concepts were successively developed during this period:

- In 1884, ARRHENIUS provided the first modern, molecular-based definition: An acid is a substance that releases H^+ in water; a base is a substance that releases OH^- . In this way, he predicted the dissociation into *ions* even before charged elementary particles were accepted and established (in the late 1890s). H^+ ions are just protons.
- In 1923, BRØNSTED and LOWRY extended the concept with the idea that an acid-base reaction involves a proton transfer from a proton donor (the acid) to a proton acceptor (the base). The solvent no longer has to be water, as the new concept also applies to liquid ammonia, alcohol, benzene, and other non-aqueous solutions.

- About 15 years later, LEWIS went one step further and stretched the “proton-transfer” concept of conventional acids and bases to the much broader concept of “electron-pair transfer”: Acids are substances able to “accept” a lone pair of electrons from another molecule, designated as a base. The latter can also be used for ligand-metal ion coordination reactions and substitution reactions in organic chemistry.

The three concepts in Table 1.1 are shown as VENN diagram in Fig 1.1, where the LEWIS concept encompasses both BRØNSTED-LOWRY and ARRHENIUS theories.¹

Table 1.1: Three acid-base concepts.

	acid	base
ARRHENIUS (1884)	contains H ⁺	contains OH ⁻
BRØNSTED-LOWRY (1923)	proton (H ⁺) donor	proton (H ⁺) acceptor
LEWIS (1938)	e ⁻ pair acceptor	e ⁻ pair donor

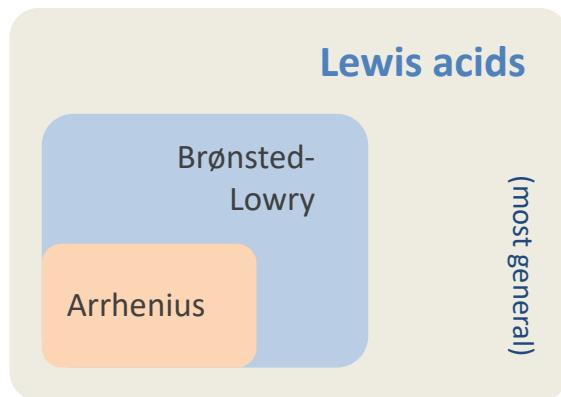


Figure 1.1: Relationship between acid-base concepts.

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

1.1.2 State of the Art

Acid-Base Equilibria

The topic of acid–base equilibria is covered in an extensive bibliography, usually focusing on mono- and diprotic acids, which is the entry point to understanding

¹While acid-base reactions interchange electron-*pairs*, redox reactions are based on the exchange (of a sequence) of *single* electrons.

chemical equilibrium reactions *per se*. The list of classical textbooks and monographs is long and stems from various subfields, such as hydrochemistry [2–4] as well as general and analytical chemistry [5–8]. This is accompanied with several modeling approaches, e.g., [9–11]. More advanced modeling approaches can be found for polyprotic acids.

Polyprotic Acids

The mathematical description of polyprotic acids H_NA (with $N \geq 3$) is a special topic that extends the traditional view on acid–base reactions. Algebraic equations are presented in [12–18]; their application to titration and buffer capacities can be found in [19–22] and in [23–28]. Many of the developments come from areas outside conventional hydrochemistry (e.g., organic and bio/med chemistry), which is the playground of proton-binding macromolecules such as nucleic acids and fulvic/humic acids. This also encourages a statistical description [29–32].

Dissociation vs Association Reactions

There are two principal ways of math description:

- the approach in hydrochemistry (based on *dissociation* reactions with reference state H_NA)
- the approach employed in organic and biochemistry (based on *association* reactions with reference state A^{-N})

The present lecture follows the first approach. [The interrelationship with the second approach is established in [1], Section 2.5.]

Titration & Buffer Capacities

Titration and buffer capacities are summarized in an excellent review article by Asuero and Michałowski [24]. This and other papers [22–26, 28] rely on association reactions (with reference state A^{-N}), so one has to be careful when comparing the formulas with the present approach.

[Most of these papers take the *dilution* during titration into account by explicitly using the volume of the titrant. This effect is ignored in this lecture to keep the formulas simple.]

LMA vs GEM

For the general case of aquatic systems (as mixtures of any number of acids and bases plus solid and gaseous phases), there are two prototypes of numerical approaches:

- **LMA:** models that are based on the law of mass action (LMA) (e.g., PhreeqC [33, 34] and many others)
- **GEM:** models that are based on GIBBS energy minimization [35, 36]

1.2 Motivation

Today, computers solve nonlinear systems numerically in the shortest time with high quality, which is a great help in dealing with complex real-world tasks (and we are grateful for that). However, by delegating everything to computers, we sometimes lose the overview of the underlying principles and functional relationships (digital data are too incomplete/imprecise to understand the deeper aspects of reality). Starting from the laws of mass action and mass/charge balance, a mathematical solution is provided in the form of simple and smooth analytical formulas for acid–base reactions. This is performed for the general case of N -protic acids, where N can be any integer ($N \geq 1$).

[In [1], the approach was applied to the broad class of zwitterionic acids H_NA^{+Z} (amino acids, NTA, EDTA, etc.), which embeds all “ordinary acids” as a special sub-class characterized by $Z = 0$.]

Why do we need equations/formulas for $N > 2$?

Usually (and this is the first that comes to mind) N is a small number: 1, 2 or 3 for monoprotic, diprotic and triprotic acids. However, in reality, there are compounds with more protons, such as EDTA with $N = 6$ (discussed in [1], Section 4.1.6) or other macromolecules in biochemistry and/or mixtures thereof. Moreover, when N is treated as a *variable* integer, the equations teach us things that might otherwise be non-obvious (e.g., classification of equivalence points in § 5.4).

Is the approach mathematically strict?

The math derivation is strict. For this purpose, it is assumed that the activities (that enter the mass action laws) are replaced by molar concentrations, which is justified either for dilute systems or for non-dilute systems using *conditional* equilibrium constants (cf. seawater example in § 7.5). Deviations in the analytical model from numerical activity-based calculations are discussed in § 7.6.

What is the difference to standard approaches given in textbooks?

In textbooks [2–7], an algebraic solution of the acid–base problem is usually provided for diprotic acids ($N = 2$) in *implicit* form, namely as a polynomial of degree 4 in $x = 10^{-\text{pH}}$ (quartic equation!) — see, e.g., [2] (p. 107) or Eq (5.38) below. That is the common way to handle the acid–base problem. In the general case of N -protic acids, this procedure leads to polynomials of order $N + 2$, where, for $N > 4$, there is *principally* no algebraic solution (according to the ABEL–RUFFINI theorem). This dilemma will be avoided in the present approach. However, before we start, let us explain this in another way.

In titration, a *titrant* (strong base of amount C_B) is added to the *analyte* (N -protic acid with amount C_T), resulting in a certain pH value. So, one is tempted to write the pH as a function of C_T and C_B , that is:

$$\text{pH} = \text{pH}(\text{analyte, titrant}) = \text{pH}(C_T, C_B) \quad \text{or} \quad \text{pH} = \text{pH}(C_T, n) \quad (1.1)$$

where $n = C_B/C_T$. However, as mentioned above, these relations cannot be expressed in the form of an *explicit* function; they only exist *implicitly* in the form of polynomials of degree $N+2$ (see (4.11) on page 39). So we put the whole thing “from head to toe” by providing a strict algebraic solution in the form of the

$$\text{explicit function: } n = n(\text{pH}, C_T) \quad \text{or} \quad n = n(x, C_T) \quad (1.2)$$

From the viewpoint of (1.2), the polynomials are then considered as the inverse task in § 4.2.1.

The lecture contains over 100 formulas. What is the central formula?

The central formula is the analytical formula for the explicit function (1.2):

$$n(x, C_T) = Y_1(x) + \frac{w(x)}{C_T} \quad (1.3)$$

(symbols are explained in the text). This formula contains all information about the acid–base system in condensed form.

In this lecture, the function $n(x)$ appears under several names: equivalence fraction, titration function/curve, and normalized buffer capacity (because it measures the distance to EP_0).

As sketched in Fig 1.2, depending on whether n is a specific discrete number or a real function, different aspects appear: the equivalence points (as “special equilibrium states”) or buffer capacities as “distances” between two equilibrium states.

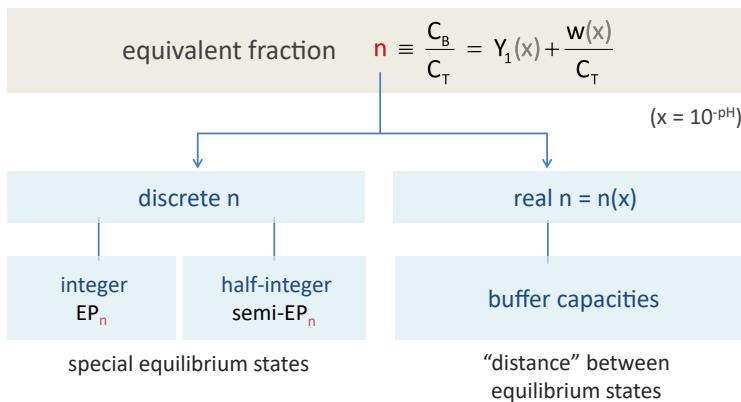


Figure 1.2: Equivalent fraction n as the central quantity from which all other quantities and formulas will be derived in this lecture.

What does it mean to be a simple and smooth analytical formula?

“Simple” means that the analytical formulas are easy to handle in a Lego-like manner from plain constructs, as summarized in § 5.2.4. There is no need for programming or root-solving methods. All results and diagrams in this lecture were created with Excel, and anyone can easily reproduce them.

“Smooth” means that the analytical formula $n = n(x)$ or $n = n(\text{pH})$ — as well as its building blocks — are infinitely derivable functions that offer calculus in the form of pH derivatives and integrals (a feature that is not possible for numerical solutions/data). The pH derivatives convert buffer capacities to buffer intensities; pH derivatives are also used to identify equivalence points (EPs) as local minima/maxima and/or inflection points.

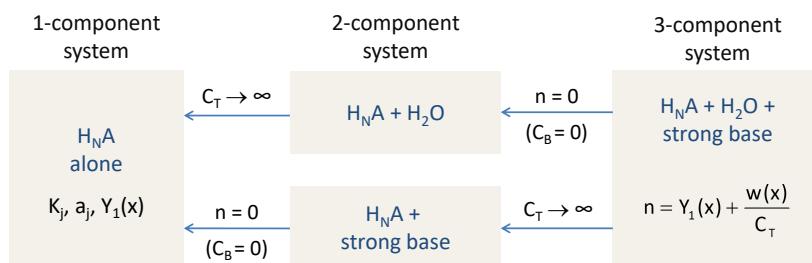
1.3 Structure of the Lecture

Chapter 2 introduces the concept of polyprotic acids H_NA for any number of protons N (including all common mono-, di-, and triprotic acids characterized by $N = 1, 2, 3$). Mathematically, this results in a system of $N+3$ nonlinear equations (cf. (2.32) to (2.37) on page 15). The goal of the next three Chapters is to bundle this set of $N+3$ equations into a single analytical formula. This is done in three subsequent steps (see also Fig 1.3):

- Chapter 3: 1-component system “ H_NA ”
- Chapter 4: 2-component system “ $H_NA + H_2O$ ”
- Chapter 5: 3-component system “ $H_NA + H_2O + \text{base}$ ” (acid-base system)

In Chapter 3, we start with the 1-component system i.e., the N -protic acid itself, which is fully determined by N acidity constants K_1 to K_N . In Chapter 4, H_2O is included (by incorporating the self-ionization of water). In Chapter 5, the 2-component system is extended to a 3-component “acid–base system”, which opens the door to the description of acid–base titrations. In all of these considerations, attention is drawn to the *equivalence points* (definition and classification), which can hardly be overestimated.

Figure 1.3:
Relationships
between 1-, 2-, and
3-component systems.



[Note. Regarding the connection between the three subsystems in Fig 1.3, the numbers $1/C_T$ and C_B/C_T act as “coupling constants” of the acid to the water (autoprotolysis) and to the base.]

The concept of buffer capacities is introduced in Chapter 6. In Chapter 7, the derived concepts and formulas are applied to the carbonate system, such as alkalinity, open vs closed CO_2 -system, seawater, etc.

Chapter 8 briefly discusses some special/additional topics: (i) strong polyprotic acids, (ii) mixtures of acids, and (iii) the superposition of N monoprotic acids (in order to generate an N -protic acid).

Final Note

The presented mathematical framework is based on *analytical* formulas. In this way, it widens our understanding of the acid-base system. However, it will and can never replace numerical models like PhreeqC [33, 34], aqion [37] or other software, which are able to handle real-world problems (including activity corrections, an arbitrary number of species and phases, aqueous complex formation, etc.).

Lots of things get better as they get shorter.

— Anonymous

2

Polyprotic Acids

Contents

2.1	What is an Acid?	7
2.2	Basic Set of Equations	12

2.1 What is an Acid?

2.1.1 Proton Transfer

An acid HA is a *proton donor*; it releases H⁺ ions (more precisely: H₃O⁺) when dissolved in water:



which is a shorthand for $\text{HA(aq)} + \text{H}_2\text{O(l)} = \text{H}_3\text{O}^+(\text{aq}) + \text{A}^-(\text{aq})$.

The definition of acids as proton donors is fully consistent with ARRHENIUS' conception that acids are substances that contain and release H⁺ ions. In the case of bases, however, the concepts of ARRHENIUS and BRØNSTED-LOWRY differ:

ARRHENIUS base	contains OH ⁻	(e.g. NaOH, KOH, NH ₄ OH)
BRØNSTED-LOWRY base	H ⁺ acceptor	(e.g. OH ⁻ , Cl ⁻ , NH ₃)

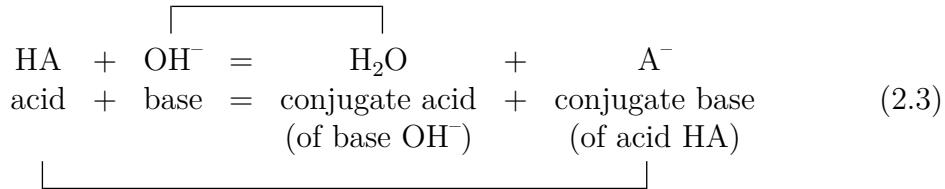
This allows all ARRHENIUS bases¹ to be combined into a single H⁺ acceptor equation:



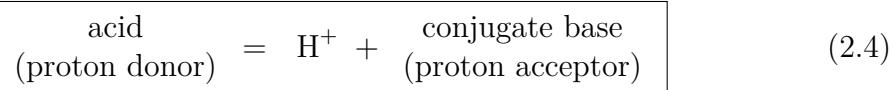
¹For example, an ARRHENIUS base can be abbreviated by BOH, where the cation B⁺ stands for Na⁺, K⁺, NH₄⁺ etc.

Conjugate Acids

Now something new comes into play (that the ARRHENIUS concept does not have): *conjugate* acid-base pairs. Adding (2.2) to (2.1) yields:



Note that H^+ ions do not occur in this overall reaction because they are transferred between conjugate acid-base pairs. H^+ ions occur only in “half reactions”, such as in (2.1) or (2.2):



Eq (2.4) is a general concept that applies to any polyprotic acid, namely for each individual dissociation step (as shown in (2.15) to (2.17) on page 10).

Autoprotolysis

One special case of (2.3) is the self-dissociation of water:



Here, the water acts simultaneously as an acid and a base. Such substances are termed *ampholytes*.

2.1.2 Acidity Constants

The equilibrium constant of reaction (2.1) is called *acidity constant*. There are two types of acidity constants:

$$\text{thermodynamic acidity constant:} \quad K_a = \frac{\{\text{H}^+\}\{\text{A}^-\}}{\{\text{HA}\}} \quad (\text{based on activities}) \quad (2.6)$$

$$\text{conditional acidity constant (of mixed type):} \quad {}^cK_a = \frac{\{\text{H}^+\} [\text{A}^-]}{[\text{HA}]} \quad (\text{based on concentrations}) \quad (2.7)$$

The last equation represents a *mixed-type* constant since we use the activity for H^+ but the concentrations for all other components.

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

Activities

Activities are “effective concentrations” which can be calculated by semi-empirical activity corrections γ_j for each species j (cf. Appendix A):

$$\text{activity (effective concentration):} \quad \{j\} = \gamma_j [j] \quad (2.8)$$

The activity corrections increase with the ionic strength I of the solution. In ideal or near-ideal solutions (i.e. diluted systems) we have $I \simeq 0$ and $\gamma_j \simeq 1$, so that activities and concentrations are (almost) the same.

Note. The derivations in this lecture rely on concentrations (except for H^+ , where we use the activity). Thus, the obtained results are valid either in dilute systems or by using the conditional acidity constant ${}^c K_a$. We consider it as an assumption that applies to the whole text (and skip the small-letter superscript c on ${}^c K_a$).

lg K Value

In practice, it is convenient to use the decadic logarithm of (2.7):

$$\lg K_a = \lg \{\text{H}^+\} + \lg [\text{A}^-] - \lg [\text{HA}] \quad (2.9)$$

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

$$\text{pK}_a = -\lg K_a \quad (2.10)$$

which parallels the definition of pH as $\text{pH} = -\lg \{\text{H}^+\}$. With pK_a , Eq (2.9) converts to

$$\text{pK}_a = \text{pH} - \lg [\text{A}^-] + \lg [\text{HA}] \quad (2.11)$$

Henderson-Hasselbach Equation

Eq (2.11) can also be written as the so-called HENDERSON-HASSELBACH equation:

$$\text{pH} = \text{pK}_a + \lg \frac{[\text{A}^-]}{[\text{HA}]} = \text{pK}_a + \lg \frac{[\text{proton acceptor}]}{[\text{proton donor}]} \quad (2.12)$$

Here, the term $\lg [\text{A}^-]/[\text{HA}]$ vanishes for equal 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 the species HA is dissociated into species A^- . Therefore, it is no surprise that the pK_a value is also called the “semi-equivalence point” — more on this topic in § 3.2.2 and particularly in (3.44) below.

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 (cf. (2.18) below).

Gibbs Energy

In chemical thermodynamics, there is a fundamental link between the equilibrium constant K and the (change of) GIBBS energy:

$$\Delta G^0 = -RT \ln K \quad (2.13)$$

where $R = 8.314 \text{ J}/(\text{mol}\cdot\text{Kelvin})$ is the gas constant and T the temperature in Kelvin. This equation can be rearranged to $\lg K$:

$$\lg K = -\frac{\Delta G^0}{\ln 10 \cdot RT} = -\frac{\Delta G^0}{2.303 \cdot RT} \quad \text{or} \quad \text{pK}_a = \frac{\Delta G^0}{2.303 \cdot RT} \quad (2.14)$$

An example for the relationship between ΔG^0 and several pK values (of a triprotic acid) is given in Fig 3.1 on page 20.

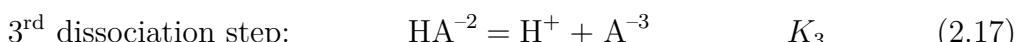
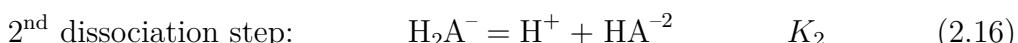
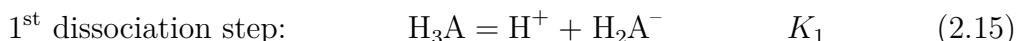
2.1.3 Mono-, Di-, and Triprotic Acids

Acids can donate one, two, or more protons H^+ . Typical examples are listed in Table 2.1.

Table 2.1: Typical mono-, di-, and triprotic acids.

monoprotic acid (HA)	diprotic acid (H_2A)	triprotic acid (H_3A)
HCl	H_2CO_3	H_3PO_4
HNO_3	H_2SO_4	H_3AsO_4
HI	H_2CrO_4	citric acid
HF	H_2SeO_4	
formic acid	oxalic acid	

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



Ranking

Protons are released sequentially one after the other, with the first proton being the fastest and most easily lost, then the second, and then the third (which is the most strongly bound). This yields the following ranking of acidity constants of a polyprotic acid:²

$$K_1 > K_2 > K_3 \quad \text{or} \quad pK_1 < pK_2 < pK_3 \quad (2.18)$$

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 Table 2.2.

Table 2.2: pK values of four common N -protic acids at 25°C.

N	acid	formula	type	pK_1	pK_2	pK_3	Ref
1	acetic acid	CH_3COOH	HA	4.76			[38]
2	(composite) carbonic acid	H_2CO_3	H_2A	6.35	10.33		[39]
3	phosphoric acid	H_3PO_4	H_3A	2.15	7.21	12.35	[38]
3	citric acid	$C_6H_8O_7$	H_3A	3.13	4.76	6.4	[38]

Note 1. In Table 2.2, the *composite* carbonic acid is the sum of the unionized species $CO_2(aq)$ and the pure acid: $H_2CO_3^* = CO_2(aq) + H_2CO_3$; to simplify the notation, we omit the asterisk (*) on $H_2CO_3^*$ throughout the text.

Note 2. The acids in the table are so-called “common acids”. Additionally, there are also zwitterionic acids (amino acids). The latter are described in [1].

²In organic acids, the second and third acidity constants can be similar.

2.1.4 Strong Acids vs Weak Acids

Monoprotic Acids

Unlike weak acids, strong acids dissociate completely in water. Let us consider a monoprotic acid specified by K_a and the amount $C_T \equiv [\text{HA}]_T$ (which is de facto the acid's initial concentration before it dissolves). In the equilibrium state, the total concentration splits into an undissociated and a dissociated part:

$$C_T = [\text{HA}] + [\text{A}^-] \quad \text{or} \quad 1 = a_0 + a_1 \quad (2.19)$$

where $a_0 = [\text{HA}]/C_T$ and $a_1 = [\text{A}^-]/C_T$ are the “ionization fractions”. The difference between strong and weak acids is summarized in Table 2.3.

Table 2.3: Strong vs weak acids (greatly simplified).

	strong acid	weak acid
acidity constant	$K_a \gg 1$	$K_a \leq 1$
$\text{p}K_a = -\lg K_a$	$\text{p}K_a < 0$	$\text{p}K_a > 0$
$\{\text{H}^+\} \simeq [\text{H}^+] = 10^{-\text{pH}}$	$[\text{H}^+] \simeq C_T$	$[\text{H}^+] \ll C_T$
undissociated acid	$[\text{HA}] \simeq 0$ or $a_0 \simeq 0$	$[\text{HA}] \simeq C_T$ or $a_0 \simeq 1$
dissociated acid	$[\text{A}^-] \simeq C_T$ or $a_1 \simeq 0$	$[\text{A}^-] \ll C_T$ or $a_1 \ll 1$

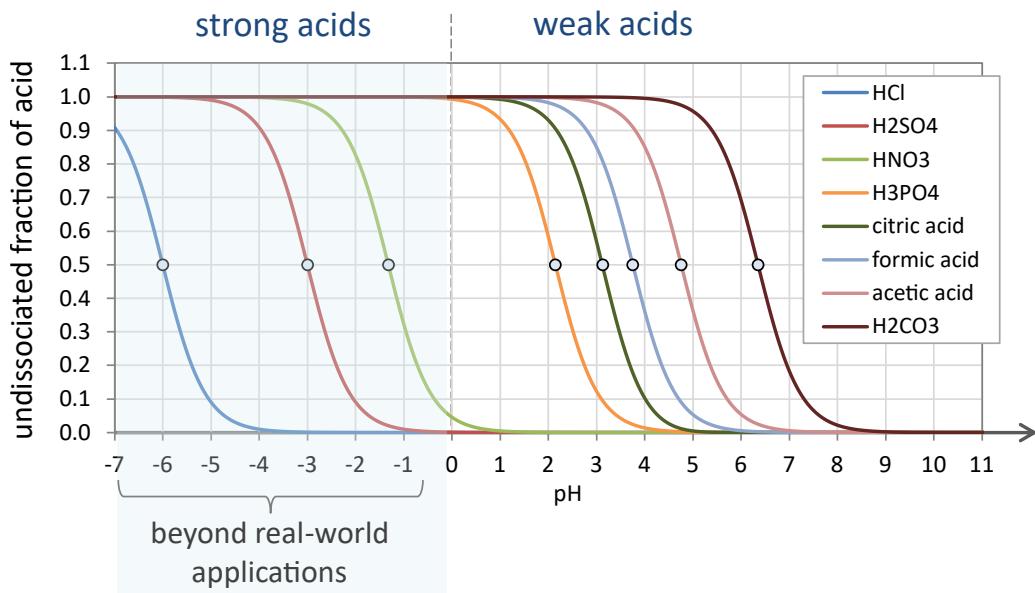


Figure 2.1: Undissociated fraction a_0 for strong and weak acids. Strong acids are completely dissociated in the pH range above $\text{pH} \simeq 0$.

Polyprotic Acids

The classification in Table 2.3 can also be applied to N -protic acids if we rename the acidity constant K_a by the 1st dissociation constant K_1 .

Undissociated Fraction

Weak acids are characterized by a non-negligible amount of undissolved acid. Mathematically, the undissociated part is equivalent to the ionization fraction a_0 :

$$\text{undissociated acid: } a_0 \equiv \frac{[\text{H}_\text{NA}]}{C_T} \simeq \frac{1}{1 + K_a/x} \quad \text{with } x = 10^{-\text{pH}} \quad (2.20)$$

This quantity as a function of pH is displayed in Fig 2.1 for several acids. As expected, strong acids are completely dissociated in real-world applications (where $\text{pH} \geq 0$). The small circles mark the position of the corresponding pK_1 values (which are the inflection points of a_0).

2.1.5 Weak Acids vs Dilute Acids

A *weak* acid and a *dilute* acid are two different things. The first relies on the acidity constants K_a (which is a thermodynamic property of the acid that nobody can change), while the second relies on the amount C_T of a given acid:

$$\begin{array}{lll} \text{weak acid} \leftrightarrow \text{strong acid} & \Leftrightarrow & \text{small } K_a \leftrightarrow \text{large } K_a \\ \text{dilute acid} \leftrightarrow \text{concentrated acid} & \Leftrightarrow & \text{small } C_T \leftrightarrow \text{large } C_T \end{array}$$

One cannot make a weak acid strong, but one can change the degree of dilution (or concentration). Table 2.4 summarizes the principal difference between the degree of strength and the degree of dilution. The basic idea behind this is also sketched in Fig 2.2. For polyprotic acids, replace K_a by K_1 .

Table 2.4: Degree of strength vs degree of dilution.

	degree of strength	degree of dilution
determined by:	acidity constant K_a	amount of acid C_T
relationships:	weak acid \leftrightarrow strong acid small $K_a \leftrightarrow$ large K_a (positive $\text{pK}_a \leftrightarrow$ negative pK_a)	dilute acid \leftrightarrow concentr. acid small $C_T \leftrightarrow$ large C_T
compares:	two different acids	dilution of the same acid
describes:	release of H^+	dilution of H^+
type:	fundamental property (cannot be changed)	control parameter (can be changed)

2.2 Basic Set of Equations

2.2.1 Special Case: Diprotic Acids (H_2A)

Before turning to N -protic acids, let us start with the simple case of diprotic acids ($N = 2$).

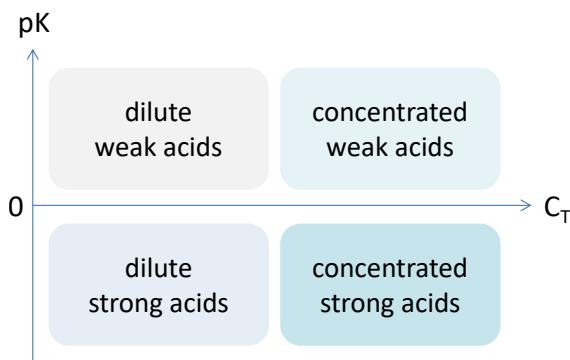


Figure 2.2: Weak/strong vs dilute/concentrated acid.

When a diprotic acid H_2A (the solute) is added to pure water (the solvent), the equilibrium state of the solution is characterized by five dissolved species: H^+ , OH^- , H_2A , HA^- , and A^{-2} (see Fig 2.3). Thus, five equations are required for its math description:

$$K_w = \{\text{H}^+\} \cdot \{\text{OH}^-\} \quad (\text{self-ionization of H}_2\text{O}) \quad (2.21)$$

$$K_1 = \{\text{H}^+\} \cdot \{\text{HA}^-\} / \{\text{H}_2\text{A}\} \quad (1^{\text{st}} \text{ dissociation step}) \quad (2.22)$$

$$K_2 = \{\text{H}^+\} \cdot \{\text{A}^{-2}\} / \{\text{HA}^-\} \quad (2^{\text{nd}} \text{ dissociation step}) \quad (2.23)$$

$$C_T = [\text{H}_2\text{A}] + [\text{HA}^-] + [\text{A}^{-2}] \quad (\text{mass balance}) \quad (2.24)$$

$$0 = [\text{HA}^-] + 2[\text{A}^{-2}] + [\text{OH}^-] - [\text{H}^+] \quad (\text{charge balance}) \quad (2.25)$$

The first three equations are *mass-action laws* (of type (2.6)); the two last equations represent the *mass balance* and the *charge balance*. While the mass-action laws are based on activities (denoted by braces), the mass-balance and charge-balance equations rely on molar concentrations (denoted by square brackets) — see Fig 2.4.

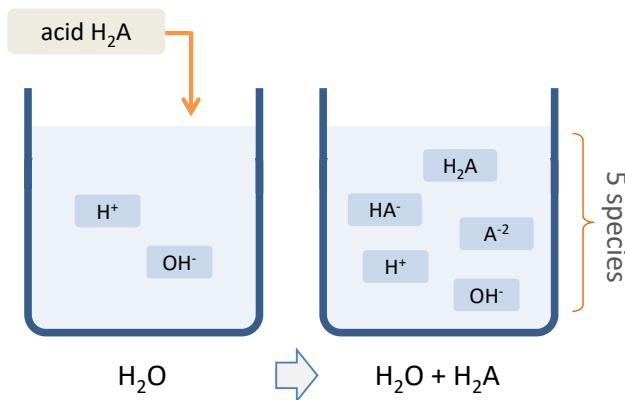


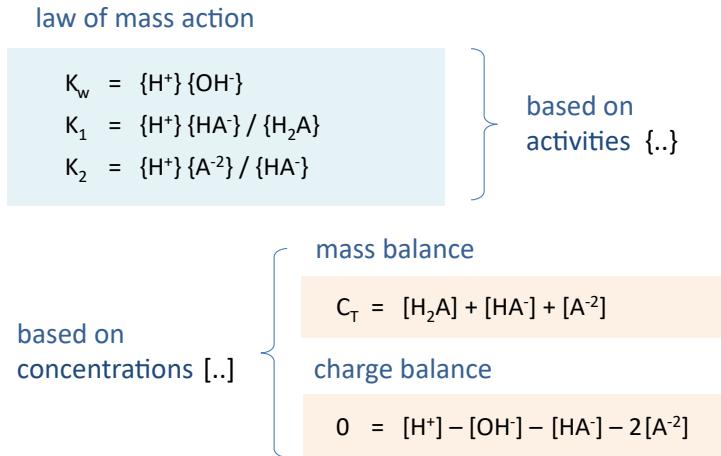
Figure 2.3: Addition of a diprotic acid to water results in an equilibrium state with five species.

Note. The total concentration of a diprotic acid is abbreviated by $C_T = [\text{H}_2\text{A}]_T$. This quantity should not be confused with the *neutral* dissolved species $\text{H}_2\text{A}(\text{aq})$ and its molar concentration $[\text{H}_2\text{A}]$.³

As summarized in Fig 2.5, the math description of the diprotic acid system is based on two components (or subsystems) plus a coupling term:

³The dissolved but undissociated neutral species is sometimes also abbreviated as H_2A^0 .

Figure 2.4: Diprotic acid: activity-based equations vs concentration-based equations.



- component H_2O (subsystem “pure water”) described by (2.21)
- component H_2A (subsystem “acid”) described by (2.22) to (2.24)
- coupling of both subsystems described by (2.25)

The two subsystems are linked together by the charge-balance equation (2.25).

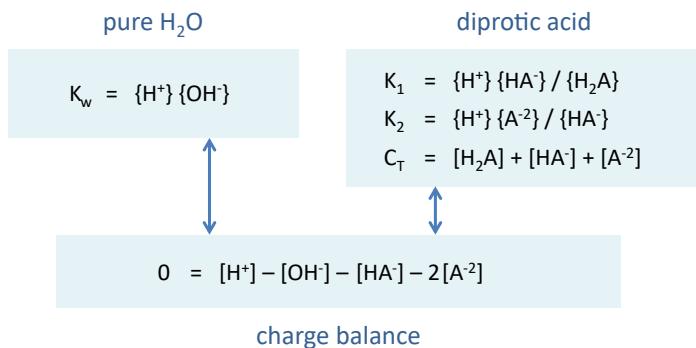


Figure 2.5: Diprotic-acid system: The subsystem “ H_2O ” and the subsystem “acid” are coupled by the charge-balance equation.

2.2.2 General Case: Polyprotic Acids (H_NA)

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

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

Hence, a complete math description requires a set of $N+3$ equations:

$$K_w = \{H^+\} \cdot \{OH^-\} \quad (\text{self-ionization } H_2O) \quad (2.26)$$

$$K_1 = \{H^+\} \cdot \{H_{N-1}A^-\} / \{H_NA\} \quad (1^{\text{st}} \text{ diss step}) \quad (2.27)$$

$$K_2 = \{H^+\} \cdot \{H_{N-2}A^{2-}\} / \{H_{N-1}A^-\} \quad (2^{\text{nd}} \text{ diss step}) \quad (2.28)$$

⋮

$$K_N = \{H^+\} \cdot \{A^{-N}\} / \{HA^{-(N-1)}\} \quad (N^{\text{th}} \text{ diss step}) \quad (2.29)$$

$$C_T = [H_NA] + [H_{N-1}A^-] + \dots + [A^{-N}] \quad (\text{mass balance}) \quad (2.30)$$

$$0 = [H_{N-1}A^-] + 2[H_{N-2}A^{2-}] + \dots + N[A^{-N}] + [OH^-] - [H^+] \quad (2.31)$$

Here the last equation represents the charge balance.

The math structure is analogous to that of diprotic acids in § 2.2.1. All mass-action laws, i.e. the first $N+1$ equations, are based on activities, $\{j\}$, while the mass balance and charge balance, i.e. the last two equations, are based on molar concentrations, $[j]$.

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

Preconditions for Analytical Formulas

In order to deduce closed-form expressions (i.e. analytical formulas), we have to replace all activities by molar concentrations (except for H^+):

$$\{j\} \longrightarrow [j]$$

This approximation is valid either in very dilute systems or by using conditional equilibrium constants cK as introduced in (2.7). In the following we assume that this has been done (without explicitly specifying it by cK in the notation). Thus we have for the system of $N+3$ equations:

$$K_w = \{\text{H}^+\} \cdot [\text{OH}^-] \quad (\text{self-ionization H}_2\text{O}) \quad (2.32)$$

$$K_1 = \{\text{H}^+\} \cdot [\text{H}_{N-1}\text{A}^-] / [\text{H}_N\text{A}] \quad (1^{\text{st}} \text{ diss step}) \quad (2.33)$$

$$K_2 = \{\text{H}^+\} \cdot [\text{H}_{N-2}\text{A}^{-2}] / [\text{H}_{N-1}\text{A}^-] \quad (2^{\text{nd}} \text{ diss step}) \quad (2.34)$$

:

$$K_N = \{\text{H}^+\} \cdot [\text{A}^{-N}] / [\text{H}\text{A}^{-(N-1)}] \quad (N^{\text{th}} \text{ diss step}) \quad (2.35)$$

$$C_T = [\text{H}_N\text{A}] + [\text{H}_{N-1}\text{A}^-] + \dots + [\text{A}^{-N}] \quad (\text{mass balance}) \quad (2.36)$$

$$0 = [\text{H}_{N-1}\text{A}^-] + 2[\text{H}_{N-2}\text{A}^{-2}] + \dots + N[\text{A}^{-N}] + [\text{OH}^-] - [\text{H}^+] \quad (2.37)$$

Comparing this to the set of equations (2.26) to (2.31), the mass and charge balance (i.e. the last two equations) remain unchanged. And as for the rest of the equations, you have to look closely to see the small but so fundamental change: the transition from activities to concentrations (by changing the type of brackets).

The new set of equations is the basis for all subsequent investigations. As a warm-up, the next paragraph starts with the subset of equations (2.33) to (2.36) that defines the 1-component subsystem “acid”. It exhibits the math features of the acid in its clearest form.

Things will seem difficult when simple and simple when difficult. The intelligent understand this and maintain control through manipulation.

— Sun Tzu: The Art of War

3

1-Component System: “H_NA”

Contents

3.1	The Subsystem “Pure Acid”	17
3.2	Equivalence Points	22
3.3	Ionization Fractions: Degree of Dissociation	26
3.4	Moments Y_L: Weighted Sums over a_j	32

3.1 The Subsystem “Pure Acid”

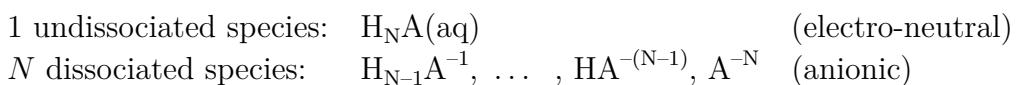
This Chapter focuses on the 1-component system “acid” defined by the subset of $N+1$ equations (2.33) to (2.36). In other words, we ignore the self-ionization of water in (2.32) and the charge balance equation (2.37).

3.1.1 Streamlined Notation

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

$$C_T \equiv [\text{H}_N\text{A}]_T = \text{TOT H}_N\text{A} \quad (3.1)$$

The N -protic acid is characterized by $N+1$ species:



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

$$[j] \equiv [\text{H}_{N-j}\text{A}^{-j}] \quad \text{for } j = 0, 1, 2, \dots, N \quad (3.2)$$

The symbol j is an integer, which also indicates the negative charge of the species (which is equal to the number of H^+ released):

$$z_j = 0 - j \quad (3.3)$$

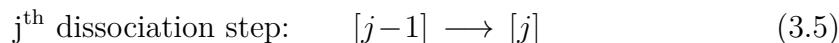
Thus, the species $[0]$ stands for the uncharged, undissociated compound $\text{H}_\text{N}\text{A}$ (aq). Note: This quantity should not be confused with the acid’s total amount, $[\text{H}_\text{N}\text{A}]_T$.

The sum of all species yields the total concentration C_T :

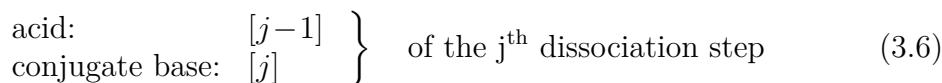
$$\text{mass balance: } C_T = \sum_{j=0}^N [j] = [0] + [1] + \cdots + [N] \quad (3.4)$$

Dissociation Steps

In each successive dissociation step, j is enhanced by 1 (due to the release of one H^+ ion):



where, according to (2.4), the conjugate acid-base pair is composed of:



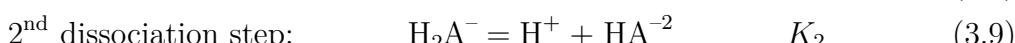
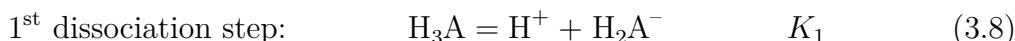
Ionization Fractions

Instead of using the $N+1$ acid species $[j]$, it is more convenient to work with ionization fractions (as the ratio of the acid-species concentration to the total amount of acid):

$$a_j \equiv \frac{[j]}{C_T} \quad \text{for } j = 0, 1, 2, \dots, N \quad (3.7)$$

3.1.2 Stepwise vs Cumulative Dissociation

As we know from § 2.1.3, a monoprotic acid is characterized by *one* acidity constant $K_1 (= K_a)$, a diprotic acid by *two* acidity constants (K_1, K_2), and a triprotic acid by *three* acidity constants (K_1, K_2 , and K_3):



The three reactions can also be written as:



with k_j as the *cumulative* acidity constants.

So we have two types of representation: The first representation describes the *step-by-step* release of a single H⁺ in each dissociation step (it's the way nature works); the second relates each dissociated species to the undissociated acid by a “many-proton” or *cumulative* release. The latter is a math trick to simplify calculations.

The second representation (in Table 3.1) requires a new set of mass-action laws based on cumulative acidity constants k_1 , k_2 , to k_N :

$$\left. \begin{array}{l} K_1 = \{\text{H}^+\} [\text{H}_{\text{N}-1}\text{A}^-] / [\text{H}_\text{NA}] \\ K_2 = \{\text{H}^+\} [\text{H}_{\text{N}-2}\text{A}^{-2}] / [\text{H}_{\text{N}-1}\text{A}^-] \\ \vdots \\ K_N = \{\text{H}^+\} [\text{A}^{-\text{N}}] / [\text{H}\text{A}^{-(\text{N}-1)}] \end{array} \right\} \Rightarrow \begin{array}{l} k_1 = \{\text{H}^+\} [\text{H}_{\text{N}-1}\text{A}^-] / [\text{H}_\text{NA}] \\ k_2 = \{\text{H}^+\}^2 [\text{H}_{\text{N}-2}\text{A}^{-2}] / [\text{H}_\text{NA}] \\ \vdots \\ k_N = \{\text{H}^+\}^N [\text{A}^{-\text{N}}] / [\text{H}_\text{NA}] \end{array}$$

which are products of K_1 , K_2 , and so on:

$$k_j = \begin{cases} 1 & \text{for } j = 0 \\ K_1 K_2 \cdots K_j & \text{for } 1 \leq j \leq N \end{cases} \quad (3.14)$$

For values of j outside this range (i.e. either for negative j or for $j > N$), we set $k_j = 0$. In logarithmic form, using the definition $\text{pk}_j \equiv -\lg k_j$, it becomes:

$$\text{pk}_j = \begin{cases} 1 & \text{for } j = 0 \\ \text{pK}_1 + \text{pK}_2 + \cdots + \text{pK}_j & \text{for } 1 \leq j \leq N \end{cases} \quad (3.15)$$

This additive relationship is illustrated in Fig 3.1 for the triprotic acid, where the pk_j and pK_j values are plotted along a GIBBS energy axis.

Table 3.1: Acid species and their cumulative acidity constants (in the new representation).

j	species	equilibrium reaction	cumulative acidity constant
0	[0] $\equiv [\text{H}_\text{NA}]$	$\text{H}_\text{NA} = \text{H}_\text{NA}$	$k_0 = [\text{H}_\text{NA}] / [\text{H}_\text{NA}] = 1$
1	[1] $\equiv [\text{H}_{\text{N}-1}\text{A}^-]$	$\text{H}_\text{NA} = \text{H}^+ + \text{H}_\text{NA}^-$	$k_1 = \{\text{H}^+\} [\text{H}_{\text{N}-1}\text{A}^-] / [\text{H}_\text{NA}] = K_1$
2	[2] $\equiv [\text{H}_{\text{N}-2}\text{A}^{-2}]$	$\text{H}_\text{NA} = 2\text{H}^+ + \text{H}_{\text{N}-2}\text{A}^{-2}$	$k_2 = \{\text{H}^+\}^2 [\text{H}_{\text{N}-2}\text{A}^{-2}] / [\text{H}_\text{NA}] = K_1 K_2$
\vdots			
N	[N] $\equiv [\text{A}^{-\text{N}}]$	$\text{H}_\text{NA} = N\text{H}^+ + \text{A}^{-\text{N}}$	$k_N = \{\text{H}^+\}^N [\text{A}^{-\text{N}}] / [\text{H}_\text{NA}] = K_1 K_2 \cdots K_N$

In contrast to the pk_j values, which are arranged on the energy scale (like in Fig 3.1), the pK_j values can be arranged on a pH scale — see Fig 3.2 on page 25.

Note. The cumulative acidity constant k_j should not be confused with the cumulative equilibrium constant for complex formation denoted by β_j (stability constants). Acidity constants are *dissociation* constants, while complex-formation constants are *association* constants. For more details see [1].

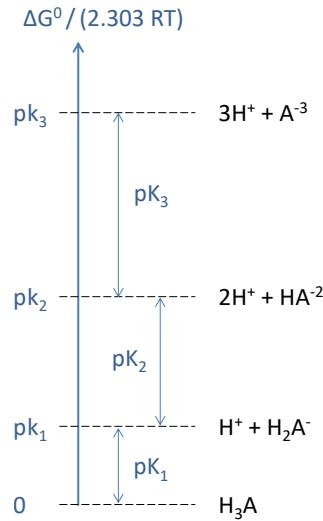


Figure 3.1: Relationship between p_k and pK values of a triprotic acid on a GIBBS-energy axis.

3.1.3 Generalized Henderson-Hasselbach Equations

The two representations (i.e. the stepwise and the cumulative dissociation introduced in § 3.1.2) can be brought into a compact form (using $x = \{\text{H}^+\}$):

	reaction formula	law-of-mass action
stepwise:	$\text{H}_{N-(j-1)}\text{A}^{-(j-1)} = \text{H}^+ + \text{H}_{N-j}\text{A}^{-j}$	$K_j = \frac{x[j]}{[j-1]}$

(3.16)

cumulative:	$\text{H}_N\text{A} = j\text{H}^+ + \text{H}_{N-j}\text{A}^{-j}$	$k_j = \frac{x^j[j]}{[0]} = K_1 K_2 \cdots K_j$
-------------	--	---

(3.17)

Here, (3.16) represents the j^{th} dissociation step characterized by K_j ; these are N reactions (where j runs from 1 to N). In (3.17), the number of reactions is $N+1$ (where j runs from 0 to N), including the trivial case $\text{H}_N\text{A} = \text{H}_N\text{A}$ with $k_0=1$.

Eqs (3.16) and (3.17) provide the pH (or x) at particular concentration ratios:

$$\frac{[j]}{[j-1]} = \frac{K_j}{x} \quad \xrightarrow{[j]=[j-1]} \quad x = K_j \quad (3.18)$$

$$\frac{[j+1]}{[j-1]} = \frac{K_j}{x} \frac{K_{j+1}}{x} \quad \xrightarrow{[j+1]=[j-1]} \quad x = (K_j K_{j+1})^{1/2} \quad (3.19)$$

$$\frac{[j]}{[0]} = \frac{k_j}{x^j} = \frac{K_1}{x} \frac{K_2}{x} \cdots \frac{K_j}{x} \quad (3.20)$$

Thus, once we know the concentration of one species, say $[j]$, we are able to calculate all other concentrations in turn, i.e. the equilibrium distribution of *all* species for a given pH (or x). Under specific conditions (indicated by the arrows) the first two equations define two types of equivalence points, which will be discussed in § 3.2.1.

In logarithmic form, the first two equations are generalizations of the HENDERSON-HASSELBACH formula introduced in (2.12):

$$\text{pH} = \text{pK}_j + \lg \frac{[j]}{[j-1]} \quad \xrightarrow{[j]=[j-1]} \quad \text{pH} = \text{pK}_j \quad (3.21)$$

$$\text{pH} = \frac{\text{pK}_j + \text{pK}_{j+1}}{2} + \lg \frac{[j+1]}{[j-1]} \quad \xrightarrow{[j+1]=[j-1]} \quad \text{pH} = \frac{1}{2} (\text{pK}_j + \text{pK}_{j+1}) \quad (3.22)$$

3.1.4 Closed-Form Expressions

Using (3.17), the subset of the $N+1$ equations (2.33) to (2.36) collapses to:

$$[j] = \left(\frac{k_j}{x^j} \right) [0] \quad (N \text{ dissociation steps, } j = 1 \text{ to } N) \quad (3.23)$$

$$C_T = \sum_{j=0}^N [j] = [0] \sum_{j=0}^N \frac{k_j}{x^j} \quad (\text{mass balance}) \quad (3.24)$$

As long as we consider the subsystem "acid" alone, C_T itself is irrelevant.¹ Dividing both equations by C_T , we obtain the ionization fractions defined by $a_j = [j]/C_T$:

$$a_j = \left(\frac{k_j}{x^j} \right) a_0 \quad (3.25)$$

$$1 = \sum_{j=0}^N a_j = a_0 \sum_{j=0}^N \frac{k_j}{x^j} = a_0 \left(1 + \frac{k_1}{x} + \frac{k_2}{x^2} + \cdots + \frac{k_N}{x^N} \right) \quad (3.26)$$

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

$$a_0 = \left(1 + \frac{k_1}{x} + \frac{k_2}{x^2} + \cdots + \frac{k_N}{x^N} \right)^{-1} \quad (3.27)$$

$$= \left(1 + \frac{K_1}{x} + \frac{K_1 K_2}{x^2} + \cdots + \frac{K_1 K_2 \cdots K_N}{x^N} \right)^{-1} \quad (3.28)$$

If a_0 is known, all other ionization fractions a_j can be calculated from (3.25). The set of ionization fractions — i.e. the *normalized* acid-species distribution — contains the complete information about the subsystem "acid". The fascinating features of the ionization fractions will be discussed and presented in § 3.3.

Summary

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

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

(3.29)

3.1.5 Inverse Task

The inverse task is to calculate x or pH starting from a given a_0 (or any other a_j). Unfortunately, the inverse task does not hold a simple equation in store for us. On the contrary, it leads to a polynomial of high degree, namely of degree N (as derived in Appendix B.1.1):

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

(3.30)

¹ C_T becomes relevant only if, in addition to H_{NA}, H₂O and/or other acids and bases are present.

If we move from the 1-component system “acid” to the 2-component system “acid + H₂O”, the degree of the polynomial increases to $N+2$, as it will be shown in (4.11) below.

Special Case: H₂A

For a diprotic acid H₂A, (3.30) becomes a *quadratic* equation (which can be solved easily). Let’s assume we know the value of a_0 and want to calculate the corresponding x . The steps are as follows (note that $k_0 = 1$):

$$0 = -\left(\frac{1-a_0}{a_0}\right)x^2 + K_1x + K_1K_2 \quad (3.31)$$

$$0 = x^2 - \alpha K_1x - \alpha K_1K_2 \quad \text{with} \quad \alpha = \frac{a_0}{1-a_0} \quad (3.32)$$

The positive root of this quadratic equation is

$$x = \frac{\alpha K_1}{2} \left(1 + \sqrt{1 + \frac{4 K_2}{\alpha K_1}} \right) \quad (3.33)$$

Usually $K_2/K_1 \ll 1$ applies, so that the second term inside the square root disappears. Then, for $a_0 = \frac{1}{2}$ (i.e. $\alpha = 1$) we obtain the simple result: $x = K_1$.

3.2 Equivalence Points

3.2.1 Definition of Equivalence Points

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

$$\text{equivalence point: } [\text{acid}] = [\text{base}] \quad (3.34)$$

This concept applies to any conjugate acid-base pair:

$$\text{equivalence point: } [\text{acid}] = [\text{conjugate base}] \quad (3.35)$$

Thus, a polyprotic acid gives rise to a whole series of EPs, because — as we have seen in (3.5) to (3.6) — each dissociation step (by releasing 1 proton) relates an acid species to its conjugate base. Thereby, two types of equivalence points emerge:

$$\text{EP}_j : \quad [j-1] = [j+1] \quad (3.36)$$

$$\text{semi-EP}_j : \quad [j-1] = [j] \quad (3.37)$$

The definition of EP_j applies for $j=0$ and $j=N$ too, if we extend our notation and identify $[-1]$ by $[\text{H}^+]$ and $[N+1]$ by $[\text{OH}^-]$. Taken together, it yields:

$$\text{EP}_0 : \quad [\text{H}^+] = [1] \quad (\text{for } j = 0) \quad (3.38)$$

$$\text{EP}_j : \quad [j-1] = [j+1] \quad (\text{for } j = 1, 2, \dots, N) \quad (3.39)$$

$$\text{EP}_N : \quad [N-1] = [\text{OH}^-] \quad (\text{for } j = N) \quad (3.40)$$

and

$$\text{semi-EP}_j : \quad [j-1] = [j] \quad (\text{for } j = 1, 2, \dots, N) \quad (3.41)$$

On the pH scale, each EP is the midpoint between two adjacent semi-EPs (as shown later in § 3.2.2). The acid H_{NA} has $N+1$ EPs (the same number as the number of acid species) plus N semi-EPs. In total there are $2N+1$ equivalence points, called EP_n, where n runs over all integer and half-integer values:

$$n = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \dots, N - \frac{1}{2}, N \quad (3.42)$$

According to the equations (3.38) to (3.41), EP_n is defined by

$$\text{EP}_n \Leftrightarrow \begin{cases} [n-1] = [n+1] & \text{for } n = 0, 1, 2, \dots, N \Leftrightarrow \text{EP}_{j=n} \\ [n-\frac{1}{2}] = [n+\frac{1}{2}] & \text{for } n = \frac{1}{2}, \frac{3}{2}, \dots, N - \frac{1}{2} \Leftrightarrow \text{semi-EP}_{j=n+1/2} \end{cases} \quad (3.43)$$

Note 1. Comparing (3.36) and (3.37) based on j with (3.43) based on n , we see that introducing n makes the equations more “symmetric”.

Note 2. The choice of the lowercase letter n as the subscript on EP_n is not accidental. The deep relationship between EP_n and the variable $n = C_B/C_T$, where C_B is the amount of strong base, will be discussed in Chapter 5.

3.2.2 Assignment between EP_n and pH_n

The equivalence point as a *special* equilibrium state is characterized by a specific pH value: EP_n \Leftrightarrow pH_n (or EP_n \Leftrightarrow x_n). This assignment can be easily established. But before we start, it is useful to make a distinction between so-called *external* and *internal* EPs, which separate the two outermost equivalence points EP₀ and EP_N from the rest:

- *external* equivalence points EP₀ and EP_N (only two)
- *internal* equivalence points all other EP_n (for $\frac{1}{2} \leq n \leq N - \frac{1}{2}$)

Internal EPs

The *internal* equivalence points deliver particularly simple formulas. From (3.18) and (3.19), or from (3.21) and (3.22), we obtain (valid for $0 < j < N$):

$$\text{semi-EP}_j : [j-1] = [j] \Rightarrow \text{pH} = \text{pK}_j \Leftrightarrow x = K_j \quad (3.44)$$

$$\text{EP}_j : [j-1] = [j+1] \Rightarrow \text{pH} = \frac{1}{2}(\text{pK}_j + \text{pK}_{j+1}) \Leftrightarrow x = \sqrt{K_j K_{j+1}} \quad (3.45)$$

It gives the following sequence:

$$n = \frac{1}{2} : \text{EP}_{1/2} \Leftrightarrow \text{pH}_{1/2} = \text{pK}_1 \quad (3.46)$$

$$n = 1 : \text{EP}_1 \Leftrightarrow \text{pH}_1 = \frac{1}{2}(\text{pK}_1 + \text{pK}_2) \quad (3.47)$$

$$n = \frac{3}{2} : \text{EP}_{3/2} \Leftrightarrow \text{pH}_{3/2} = \text{pK}_2 \quad (3.48)$$

$$n = 2 : \text{EP}_2 \Leftrightarrow \text{pH}_2 = \frac{1}{2}(\text{pK}_2 + \text{pK}_3) \quad (3.49)$$

⋮

$$n = N - \frac{1}{2} : \text{EP}_{N-1/2} \Leftrightarrow \text{pH}_{N-1/2} = \text{pK}_N \quad (3.50)$$

Here the close relationship between equivalence points and pK values becomes evident. Each acid's pK value represents exactly one semi-EP (characterized by

half-integer n). On the other hand, EP_n with integer n are the midpoints between two adjacent semi-EPs. It can be summarized as follows:²

$$\text{pH}_n = \begin{cases} \frac{1}{2}(\text{pK}_n + \text{pK}_{n+1}) & \text{for } n = 1, 2, \dots, N-1 \quad (\text{EP}_{j=n}) \\ \text{pK}_{n+1/2} & \text{for } n = \frac{1}{2}, \frac{3}{2}, \dots, N-\frac{1}{2} \quad (\text{semi-EP}_{j=n+1/2}) \end{cases} \quad (3.51)$$

Table 3.2 lists the *internal* EPs of four common acids, which 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 .

Table 3.2: Internal equivalence points of four acids (based on pK values in Table 2.2).

N	acid	$\text{pH}_{1/2}$	pH_1	$\text{pH}_{3/2}$	pH_2	$\text{pH}_{5/2}$
1	acetic acid	4.76				
2	(composite) carbonic acid	6.35	8.34	10.33		
3	phosphoric acid	2.15	4.68	7.21	9.78	12.35
3	citric acid	3.13	3.94	4.76	5.58	6.4

External EPs

There are only two *external* equivalence points: EP_0 and EP_N . The formulas which refer to H^+ or OH^- via (3.38) or (3.40) are a bit trickier than for the internal EPs. From (3.23) to (3.27) follows:³

$$\text{EP}_0 : \quad [\text{H}^+] = [1] \quad \Rightarrow \quad x = C_T a_1 \quad \Rightarrow \quad C_T = \frac{x^2}{K_1} \cdot \frac{1}{a_0(x)} \quad (3.52)$$

$$\text{EP}_N : \quad [N-1] = [\text{OH}^-] \quad \Rightarrow \quad C_T a_{N-1} = \frac{K_w}{x} \quad \Rightarrow \quad C_T = \frac{K_w K_N}{x^2} \cdot \frac{1}{a_N(x)} \quad (3.53)$$

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

The only thing we can offer are values for the asymptotic case. As shown later in (3.71) and (3.72), we have $a_0 = 1$ for $x \rightarrow \infty$ and $a_N = 1$ for $x \rightarrow 0$. The last two equations then yield:

$$\text{EP}_0 : \quad \text{approaching pH} \rightarrow 0 \quad (\text{or } x \rightarrow \infty) \quad \text{if } C_T \rightarrow \infty \quad (3.54)$$

$$\text{EP}_N : \quad \text{approaching pH} \rightarrow 14 \quad (\text{or } x \rightarrow 0) \quad \text{if } C_T \rightarrow \infty \quad (3.55)$$

3.2.3 Summary & Examples

The same acidity constants (or pK values) that characterize the N -protic acid represent the pH values of the *internal* equivalent points in the form of (3.43):

²The index j is always an integer; the index n is both integer and half-integer.

³For simplicity we set here $x \simeq [\text{H}^+]$, which deviates from our definition of x as $\{\text{H}^+\}$.

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

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

- EP_0 : $pH \rightarrow 0$
- EP_N : $pH \rightarrow 14$

On the pH scale, all equivalence points EP_n (*external* and internal) are arranged from left to right when n is increased stepwise as in (3.42):

$$pH_0, pH_{1/2}, pH_1, pH_{3/2}, \dots, pH_N \quad (3.56)$$

Such a sequence is shown schematically in Fig 3.2 for the triprotic acid H_3PO_4 .

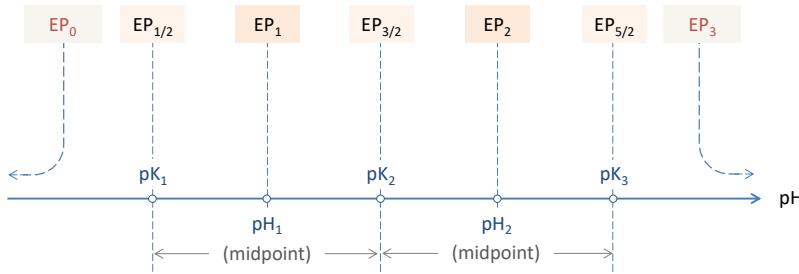


Figure 3.2:
Equivalence points
of a triprotic acid
 H_3A arranged on
the pH scale.

pH- C_T Plots

Fig 3.3 shows all equivalence points of the carbonic acid (left diagram) and the phosphoric acid (right diagram) in the pH- C_T diagram. The *internal* equivalence points (in red color) are independent of C_T and therefore straight lines, the two *external* EPs (blue and green curves) are not.

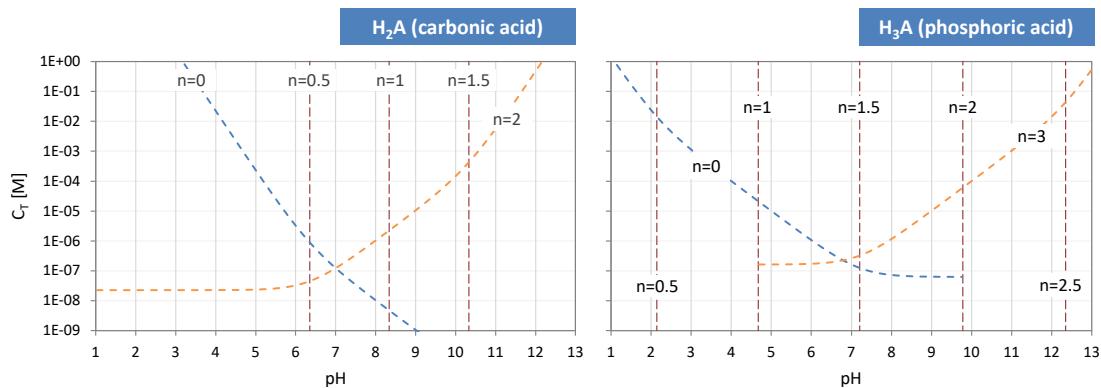


Figure 3.3: pH dependence of EPs and semi-EPs for two acids plotted as $C_T = f(pH)$. The curves are approximations valid for the subsystem "acid" (i.e. without coupling to the subsystem " H_2O ").

The representation as *dashed* curves (and not as solid lines) in Fig 3.3 reminds us that these are approximations, valid for the isolated subsystem "acid" (i.e. without coupling to the subsystem " H_2O "). The general case will be discussed later in § 5.4.2, where we learn that all *internal* EPs represent the large- C_T limit of the " $H_N A + H_2O$ " system.

3.3 Ionization Fractions: Degree of Dissociation

3.3.1 Definition of a_j

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

$$a_j \equiv \frac{[j]}{C_T} \quad \text{for } j = 0, 1, 2, \dots, N \quad (3.57)$$

They form the math skeleton of the subsystem “acid” with its typical dependence on x (or pH):⁴

$$a_j = \left(\frac{k_j}{x^j} \right) a_0 \quad \text{with} \quad a_0 = \left(1 + \frac{k_1}{x} + \frac{k_2}{x^2} + \dots + \frac{k_N}{x^N} \right)^{-1} \quad (3.58)$$

Merging the left and right equations yields:

$$a_j = \left(\frac{k_j}{x^j} \right) a_0 = \frac{k_j/x^j}{\sum_{j=0}^N k_j/x^j} \quad \text{for } j = 0, 1, 2, \dots, N \quad (3.59)$$

The ionization fractions are solely functions of x (or pH = $-\lg x$); the only other ingredients are the cumulative equilibrium constants, introduced in (3.14):

$$k_0 = 1, k_1 = K_1, k_2 = K_1 K_2, \dots, k_N = K_1 K_2 \cdots K_N \quad (3.60)$$

Due to the definition in (3.57), the ionization fractions are independent of the total concentration C_T , which is useful in graphical presentations, as shown in Fig 3.4. On the other hand, once we know a_j , the molar concentration of the acid species is obtained by multiplication with C_T :

$$[j] = C_T a_j(x) \quad \text{for } j = 0, 1, 2, \dots, N \quad (3.61)$$

To make the pH dependence of a_j more apparent, (3.59) can be written as

$$a_j(\text{pH}) = a_0 k_j \cdot 10^{j \cdot \text{pH}} = \frac{k_j 10^{j \cdot \text{pH}}}{\sum_{j=0}^N k_j 10^{j \cdot \text{pH}}} \quad (3.62)$$

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

3.3.2 Bjerrum Plots & Special Features of a_j

BJERRUM plots (dissociation diagrams) are a convenient way to visualize the pH dependence of the ionization fractions a_j . This is demonstrated in Fig 3.4 for four acids (based on pK values taken from Table 2.2).

⁴It was derived in § 3.1.4, see (3.29).

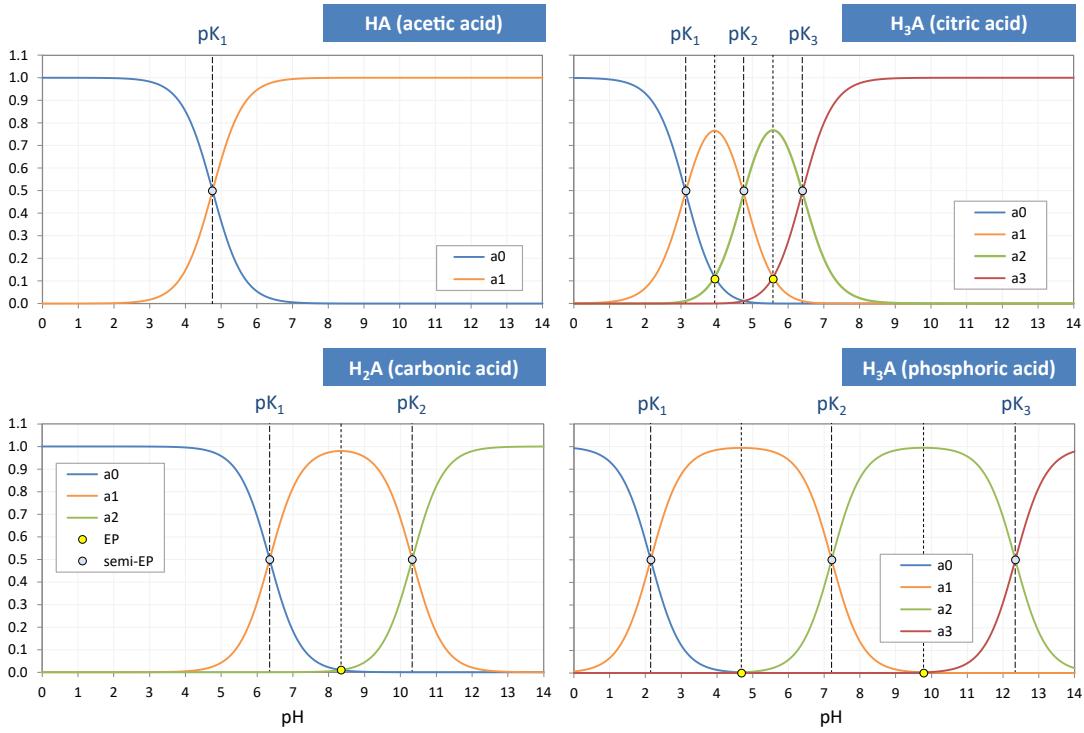


Figure 3.4: BJERRUM plots of ionization fractions for four acids (blue circles denote semi-EPs).

Universality

Ionization fractions have the nice feature that they are independent of the acid’s total amount C_T . Regardless of the assumed C_T (either constant or pH-dependent), the shapes of the ionization-fractions remain the same — see examples in § 7.3 (H_2A as titrant vs H_2A as analyte) and § 7.4 (open vs closed CO_2 system).

Mass Balance

For any chosen value of x (or pH) the sum of all ionization fractions equals 1:

$$1 = a_0 + a_1 + a_2 + \dots + a_N = \sum_{j=0}^N a_j(x) \quad (\text{for any } x \text{ or pH}) \quad (3.63)$$

Value Range

The ionization fractions are bound between 0 and 1:

$$0 < a_j < 1 \quad (\text{for all } j) \quad (3.64)$$

They never become negative or greater than 1. [Strictly speaking: The functions will come very close to the values 0 and 1, but they never really reach them.]

Equivalence Points

The equivalence points introduced in (3.44) and (3.45) can also be defined by equating two ionization fractions:

$$\text{semi-EP}_j : [j-1] = [j] \iff a_{j-1} = a_j \Rightarrow x = K_j \quad (3.65)$$

$$\text{EP}_j : [j-1] = [j+1] \iff a_{j-1} = a_{j+1} \Rightarrow x = \sqrt{K_j K_{j+1}} \quad (3.66)$$

This applies only for the *internal* equivalence points:

condition	range	pH	n
semi-EP _j	$a_{j-1} = a_j$	$j = 1, 2, \dots, N$	pK_j
EP _j	$a_{j-1} = a_{j+1}$	$j = 1, 2, \dots, N-1$	$\text{pH}_j = \frac{1}{2}(\text{pK}_j + \text{pK}_{j+1})$

Equivalence points are easily recognizable in the diagrams of Fig 3.4: The semi-EPs are located at the intersection of two adjacent ionization fractions, a_{j-1} and a_j (marked as blue circles); the EPs for integer n are at intersections of ionization fractions a_{j-1} and a_{j+1} (marked as yellow circles). Notice that the latter are located at the maximum of a_j (whose mathematical verification is given in (B.33) of Appendix B.3.2).

The actual values at the points of intersection are (cf. (B.35)):

$$\text{semi-EP}_j \quad a_j = a_{j-1} \simeq \frac{1}{2} \quad (\text{all other } a_j \simeq 0) \quad (3.69)$$

$$\text{EP}_j \quad a_j = 1 - 2a_{j-1} \simeq 1 \quad (\text{all other } a_j \simeq 0) \quad (3.70)$$

3.3.3 Two Types of a_j : S-Shaped vs Bell-Shaped

The acidity constants in the form of pK_j values subdivide the entire pH domain into $N+1$ distinct intervals, as shown in Fig 3.5. The j^{th} interval is the subdomain in which the ionization fraction a_j exercises its full dominance — see right diagrams in Fig 3.5. As indicated by colors, there are two types of curves: (i) S-shaped curves (sigmoid curves) in the 0-th and the N^{th} interval at the opposite ends of the pH scale (red color) and (ii) bell-shaped curves in all other intervals (blue color), with their maxima in the middle of the interval.

Note 1. For $N=1$, the red curves a_0 and a_1 bear a striking similarity to logistic functions or to the FERMI–DIRAC distribution in statistical physics.

Note 2. The S-shaped curves appear as the two halves of a bell-shaped curve when the opposite ends are glued together at $\pm\infty$.⁵

Table 3.3 contrasts the two types of ionization fractions. Their otherness implies the distinction between external (outer) and internal (inner) equivalence points (cf. § 3.2.2).

⁵For a mathematician this isn't even as crazy as it seems (when acting on the complex RIEMANN sphere, for example).

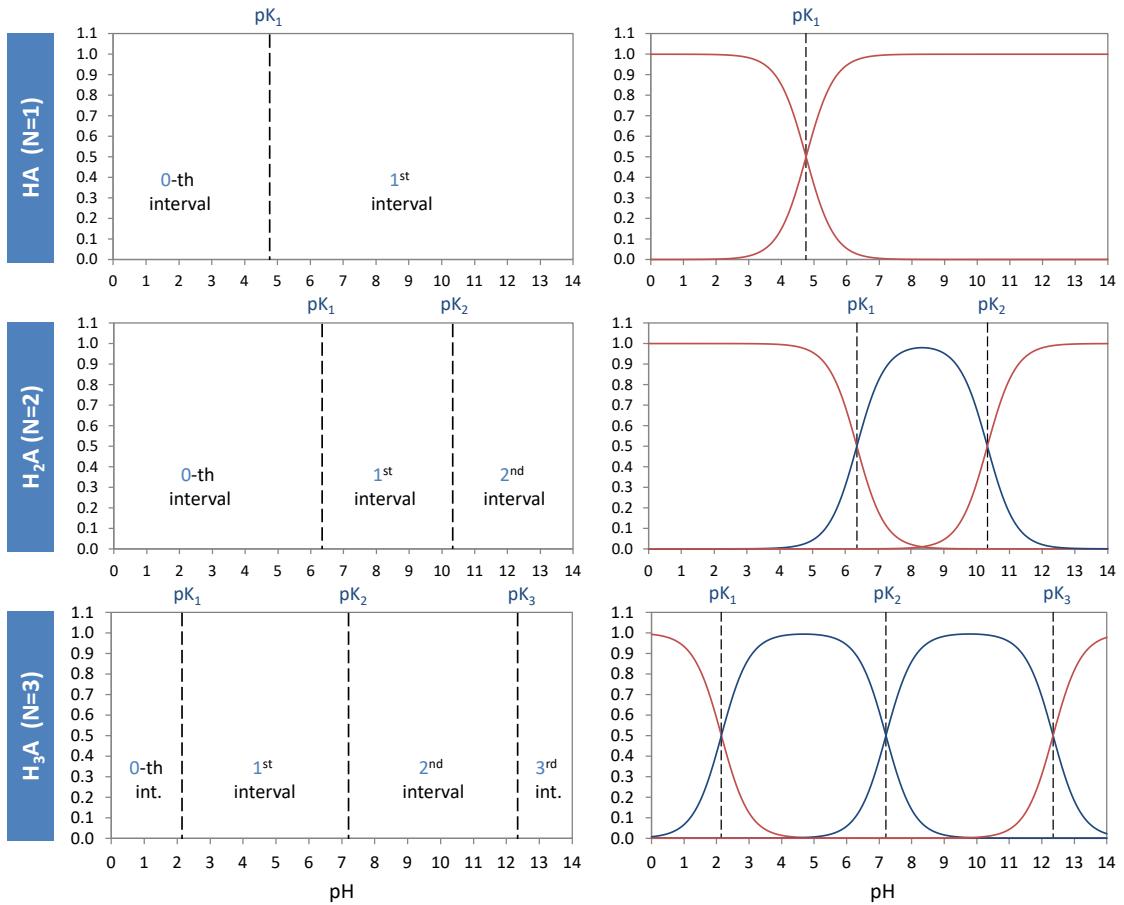


Figure 3.5: Each ionization fraction a_j has its own domain in the pH interval between two adjacent pK_j values. (HA – acetic acid, H_2A – carbonic acid, H_3A – phosphoric acid).

Asymptotic Behavior

At the opposite ends of the pH scale, the two ionization fractions a_0 and a_N attain the maximum value 1:

$$\text{strongly acidic: } \text{pH} < 0 \quad (\text{or } x \rightarrow \infty) \quad a_0 = 1 \quad \text{all other } a_j = 0 \quad (3.71)$$

$$\text{strongly alkaline: } \text{pH} > 14 \quad (\text{or } x \rightarrow 0) \quad a_N = 1 \quad \text{all other } a_j = 0 \quad (3.72)$$

This behavior is an important fact to identify them as cumulative distribution functions in [1]. [Note: The pH scale does not end at 0 or 14, but extends to $\text{pH} < 0$ and $\text{pH} > 14$ (in theory, even up to $-\infty$ and to $+\infty$).]

3.3.4 Two Types of Approximations

The formula for the ionization fractions in (3.58) can be approximated in two radically different ways:

- approximation 1: “piecewise log-scale approximation” for $\lg a_j$
- approximation 2: “midpoint approximation” for a_j

Table 3.3: Two types of ionization fractions.

	Type 1 (S-shaped)	Type 2 (bell-shaped)
ionization fraction:	a_0 and a_n	a_1, a_2, \dots, a_{N-1} (does not exist for 1-protic acids)
domain (pH interval):	$pH < pK_1$ (for a_0) $pH > pK_N$ (for a_N)	$pK_j < pH < pK_{j+1}$
maximum at pH:	$-\infty$ (for a_0) $+\infty$ (for a_N)	$\frac{1}{2}(pK_j + pK_{j+1})$
strongly acidic ($pH \rightarrow 0$):	$a_0 = 1, a_N = 0$	$a_j = 0$
strongly alkaline ($pH \rightarrow 14$):	$a_0 = 0, a_N = 1$	$a_j = 0$
integral (area below curve):	infinite	finite
associated EPs:	two <i>external</i> EPs: EP_0 and EP_N	$N-1$ <i>internal</i> EPs: $EP_1, EP_2, \dots, EP_{N-1}$

Approximation 1

This approach focuses on the *logarithm* of a_j (i.e., on $\lg a_j$ instead of a_j itself). It is the approach that is used in textbooks as a graphical method for solving the algebraic equations of equilibrium systems (in double-logarithmic diagrams).

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

$$\lg a_j \simeq (j - i) \text{ pH} + (pk_i - pk_j) \quad \text{for the } i^{\text{th}} \text{ interval} \quad (3.73)$$

where $pk_i = pK_1 + pK_2 + \dots + pK_i$ and $pk_0 = 0$. (For the derivation we refer to Appendix B.2.1) Note: In the special case of $j=i$ we get $\lg a_j=0$, that is $a_j=1$.

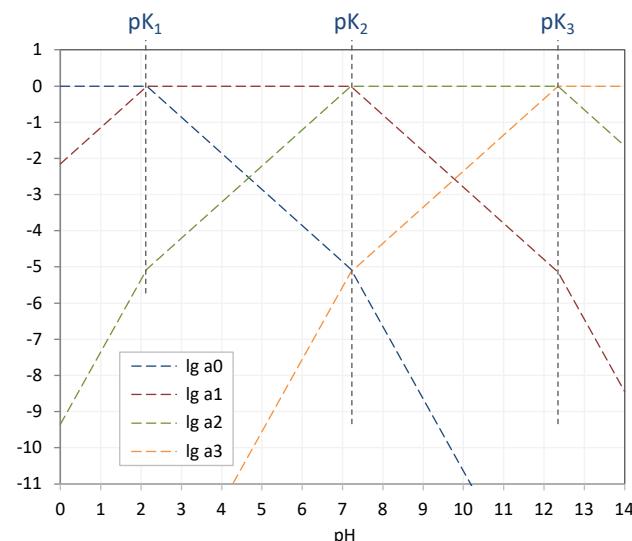


Figure 3.6: HÄGG's diagram: ionization fractions $\lg a_j$ for phosphoric acid based on the piecewise approximation in (3.73).

Fig 3.6 shows the approximation for phosphoric acid (as a triprotic acid). There are three pK values that subdivide the pH domain into four intervals. In each i^{th}

interval, $\lg a_j$ represents a straight line with integer-valued slope ($j-i$) and offset ($\text{pk}_i - \text{pk}_j$). For example, for a_2 (green dashed curve) we have:

$$\lg a_2 \simeq (2-i) \text{ pH} + (\text{pk}_i - \text{pk}_2)$$

with the following segments (straight lines) in the i^{th} intervals:

$$\begin{aligned} i = 0: \quad (2-0) \text{ pH} + (0 - \text{pk}_2) &= 2 \text{ pH} - (\text{pK}_1 + \text{pK}_2) = 2 \text{ pH} - 9.35 \\ i = 1: \quad (2-1) \text{ pH} + (\text{pk}_1 - \text{pk}_2) &= \text{pH} - \text{pK}_2 = \text{pH} - 7.21 \\ i = 2: \quad (2-2) \text{ pH} + (\text{pk}_2 - \text{pk}_2) &= 0 = 0 \\ i = 3: \quad (2-3) \text{ pH} + (\text{pk}_3 - \text{pk}_2) &= -\text{pH} + \text{pK}_3 = -\text{pH} + 12.35 \end{aligned}$$

Approximation 2

This approach is based on the fact that the curves in Fig 3.4 look so elementary that one wonders whether these cannot be described by a much simpler formula. And this is indeed so; one can replace the exact formulas in (3.58) by simpler ones:

$$a_0 \simeq \left(1 + \frac{K_1}{x}\right)^{-1} \quad (3.74)$$

$$a_j \simeq \left(\frac{x}{K_j} + 1 + \frac{K_{j+1}}{x}\right)^{-1} \quad (\text{for } j = 1 \text{ to } N) \quad (3.75)$$

$$a_N \simeq \left(\frac{x}{K_N} + 1\right)^{-1} \quad (3.76)$$

This approach relies on no more than *two* (adjacent) pK values; all other pK values are ignored. In fact, for diprotic acids it just coincides with the exact formula,⁶ but for N -protic acids with $N > 2$ it deviates slightly. The small deviations from the exact description can only be recognized in logarithmic plots of a_j — as shown for phosphoric acid ($N = 3$) in Fig 3.76.

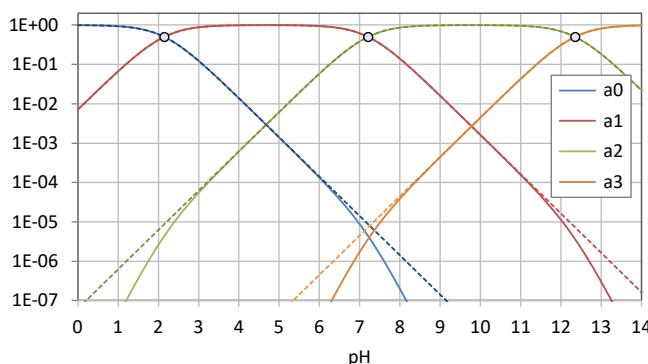


Figure 3.7: HÄGG's diagram: ionization fractions for phosphoric acid. Solid lines — exact description based on (3.58); dashed lines — approximations in (3.74) to (3.76).

⁶Of course, it also provides an exact solution for monoprotic acids ($N=1$), where a_0 and a_1 are given by (3.74) and (3.76).

Summary

The two approaches are *complementary*, as demonstrated in Fig 3.8 (for phosphoric acid). Approach 1 offers a very nice approximation in logarithmic plots, but fails to reproduce the S-shaped and bell-shaped curves in pH- a_j diagrams (dashed curves in bottom-left diagram). Conversely, Approach 2 reproduces the a_j curves perfectly, but if we look more closely, we see deviations in the log-plots for values below 10^{-4} (dashed curves in the top-right diagram).

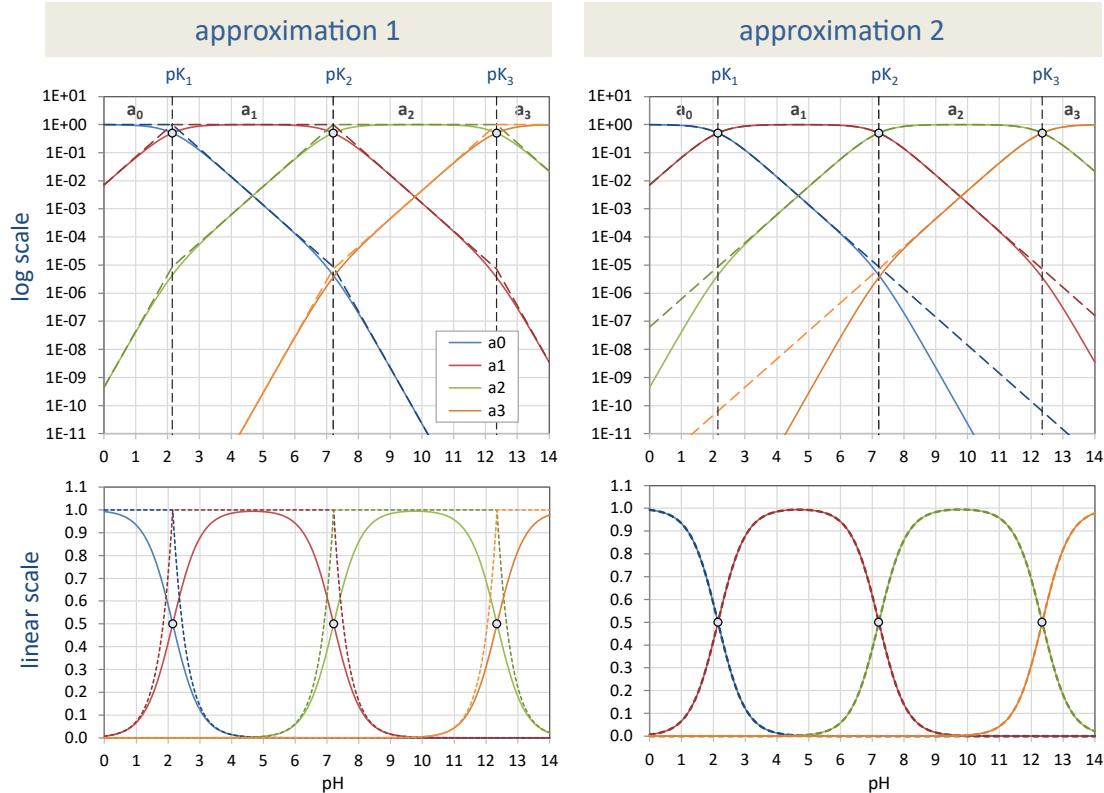


Figure 3.8: Ionization fractions for phosphoric acid in the two approximations (dashed lines). Solid lines: exact description based on (3.58).

3.4 Moments Y_L : Weighted Sums over a_j

3.4.1 Definition of Y_L

The ionization fractions a_j are the building blocks for the construction of so-called *moments*. The L^{th} -moment Y_L is defined as the weighting sum over a_j :

$$Y_L \equiv \sum_{j=0}^N j^L a_j \quad (3.77)$$

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

$$Y_0 = a_0 + a_1 + \cdots + a_N \quad (\text{for } L = 0) \quad (3.78)$$

For all other positive integers we have:

$$Y_L = a_1 + 2^L a_2 + 3^L a_3 + \dots + N^L a_N \quad (\text{for } L \geq 1) \quad (3.79)$$

As indicated in Fig 3.9, the moments itself are the building blocks of a whole series of relevant quantities: Y_0 represents the mass balance; Y_1 will turn out to be the key quantity in the description of acid-base titration curves in § 5.3; Y_2 and Y_3 will enter the buffer intensity and its derivative in § 6.2 (cf. equations (6.19) and (6.20) on page 61).

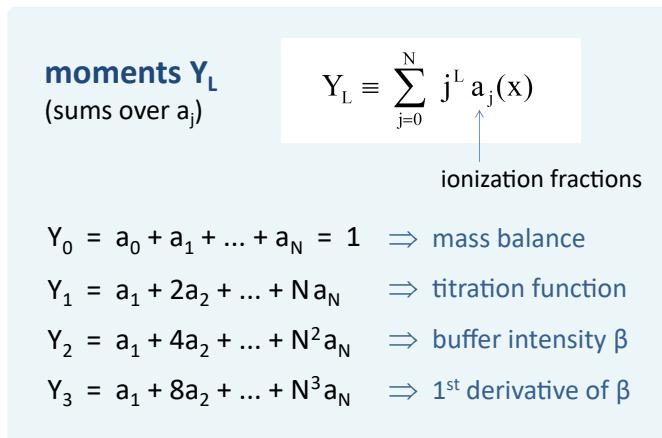


Figure 3.9: Moments Y_L as building blocks for relevant quantities that will be introduced in equations (6.18) to (6.20) on page 61.

The moments Y_L are *non-negative* functions, living in the range $0 < Y_L \leq N^L$ (whereby the equals sign only applies to Y_0 , all other Y_L approach the upper limit of N^L asymptotically).

Fig 3.10 illustrates how the “titration curve” Y_1 emerges from the set of (three) ionization fractions a_j (for phosphoric acid as a triprotic acid).

Fig 3.11 displays the pH dependence of Y_1 to Y_4 for four acids (with pK values taken from Table 2.2). Note that for monoprotic acids (top-left diagram) all moments are equal, i.e. the four Y_L -curves cover each other.

pH Dependence

The moments, just like the ionization fractions, are solely functions of x (or pH = $-\lg x$); the only other ingredients are the (cumulative) equilibrium constants of the acid. From (3.59) we obtain:⁷

$$Y_1(x) = \frac{\sum_{j=0}^N j \cdot (k_j/x^j)}{\sum_{j=0}^N (k_j/x^j)} = \frac{\sum_{j=0}^N j \cdot k_j x^{N-j}}{\sum_{j=0}^N k_j x^{N-j}} \quad (3.80)$$

Converting x to pH yields:

$$Y_1(\text{pH}) = \frac{\sum_{j=0}^N j \cdot k_j 10^{j \cdot \text{pH}}}{\sum_{j=0}^N k_j 10^{j \cdot \text{pH}}} \quad (3.81)$$

⁷To obtain the last equation you should multiply both nominator and denominator by x^N .

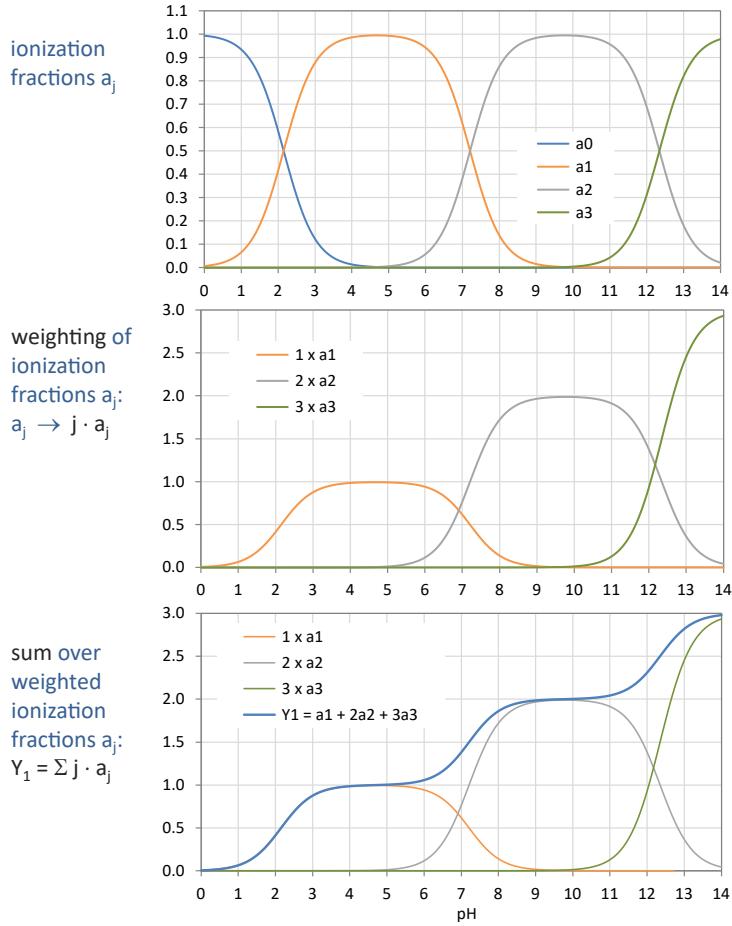


Figure 3.10:
Construction of Y_1 (blue curve in bottom diagram) from summation over three weighted ionization fraction a_j . (Example: phosphoric acid as a triprotic acid).

3.4.2 Moments and EPs

Internal EPs

For the equivalence points, the following simple relationships are obtained (see (B.26) and (B.27) in Appendix B.3.1):

$$\text{semi-EP}_j : \quad pK_j \quad a_j = a_{j-1} \simeq \frac{1}{2} \quad Y_L = \frac{1}{2}\{(j-1)^L + j^L\} \quad (3.82)$$

$$\text{EP}_j : \quad pH_j \equiv \frac{1}{2}(pK_j + pK_{j+1}) \quad a_j = 1 - 2a_{j-1} \simeq 1 \quad Y_L \simeq j^L \quad (3.83)$$

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

$$Y_L \text{ at semi-EP}_j :$$

$$Y_L(pK_1) = \frac{1}{2}$$

$$Y_L(pK_2) = \frac{1}{2}(1 + 2^L)$$

$$Y_L(pK_3) = \frac{1}{2}(2^L + 3^L)$$

$$Y_1(pK_j) = j - \frac{1}{2}$$

$$Y_2(pK_j) = (j-1)j + \frac{1}{2}$$

$$Y_L \text{ at EP}_j :$$

$$Y_L(pH_1) = 1 \quad (3.84)$$

$$Y_L(pH_2) = 2^L \quad (3.85)$$

$$Y_L(pH_3) = 3^L \quad (3.86)$$

$$Y_1(pH_j) = j \quad (3.87)$$

$$Y_2(pH_j) = j^2 \quad (3.88)$$

The two relations in (3.87) can be combined into the remarkable formula valid for all internal EPs and semi-EPs to a very good approximation (though not exactly):

$$Y_1(pH_n) - n = 0 \quad \text{for } n = \frac{1}{2}, 1, \dots, N - \frac{1}{2} \quad (3.89)$$

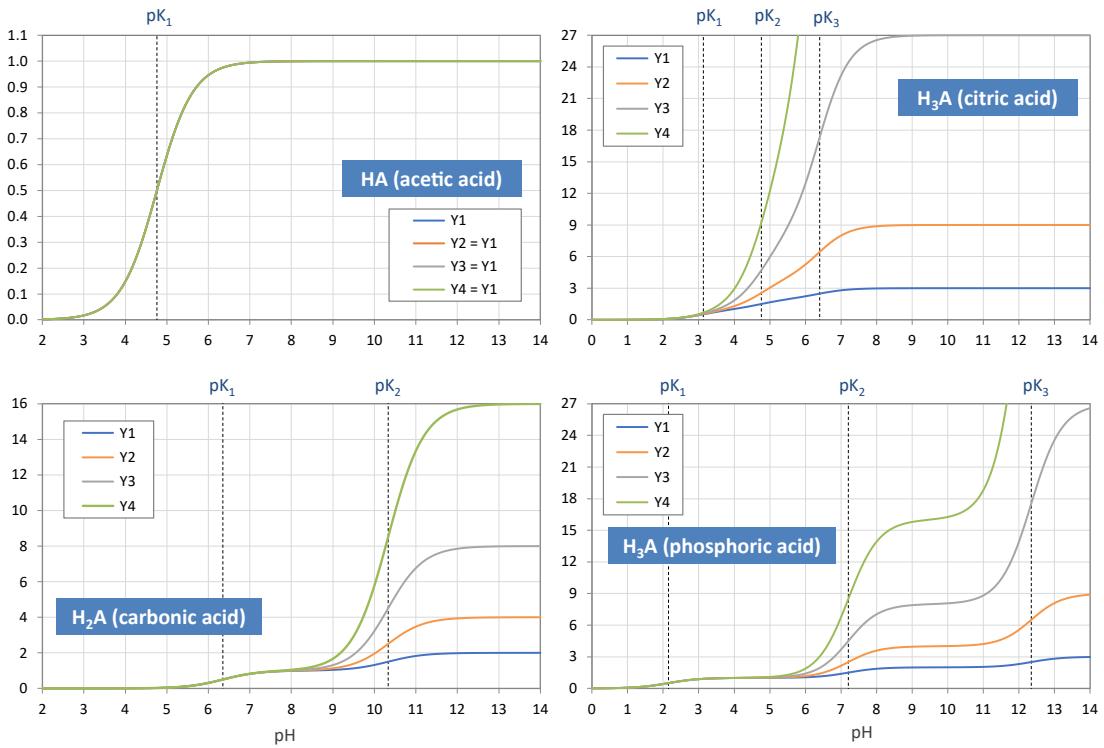


Figure 3.11: pH dependence of Y_1 to Y_4 for four acids. In the case of monoprotic acids (top-left diagram) all Y_L are equal; the four curves lie on top of each other.

In fact, it establishes the link between EP_n and pH_n defined in (3.51). A graphical representation is provided by the small circles in Fig 3.12.

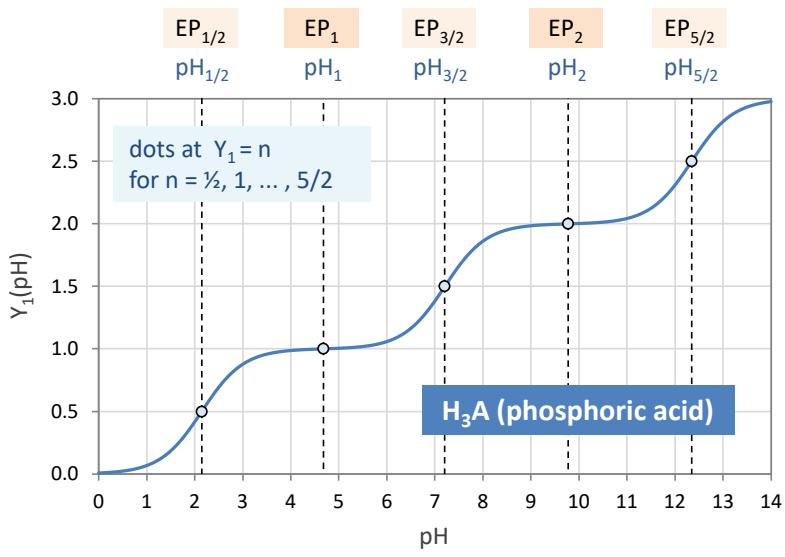


Figure 3.12:
Moment $Y_1(pH)$ for phosphoric acid. The small circles (dots) indicate the relationship in (3.89).

External EPs (Asymptotic Behavior)

The asymptotic behavior results from (3.71) and (3.72):

$$Y_L(\text{pH} \rightarrow 0) = 0 \quad \text{or} \quad Y_L(x \rightarrow \infty) = 0 \quad (3.90)$$

$$Y_L(\text{pH} \rightarrow 14) = N^L \quad \text{or} \quad Y_L(x \rightarrow 0) = N^L \quad (3.91)$$

In particular, for Y_1 we get the asymptotic values 0 and 3 at the opposite ends of the pH scale, as shown Fig 3.12. These values correspond to the two external EPs (EP_0 and EP_3). In this case, (3.89) seems to be applicable even to *external* EPs defined by the indices $n = 0$ and $n = N$.

No one regards what is at his feet; we all
gaze at the stars.

— Quintus Ennius, 239-169 BC

4

2-Component System: “H_NA + H₂O”

Contents

4.1 Basic Set of Equations	37
4.2 Closed-Form Equations	38

4.1 Basic Set of Equations

In this Chapter we consider the coupled system “H_NA + H₂O”. The basic set of $N+3$ equations, given in (2.32) to (2.37), becomes (after replacing the acid species $[j]$ by the ionization fractions $a_j = [j]/C_T$):

$$K_w = x(x+w) \quad (\text{subsystem H}_2\text{O}) \quad (4.1)$$

$$k_1 = x(a_1/a_0) \quad \text{or} \quad a_1 = (k_1/x)a_0 \quad (\text{H}_\text{N}\text{A: 1}^{\text{st}} \text{ diss step}) \quad (4.2)$$

$$k_2 = x(a_2/a_0) \quad \text{or} \quad a_2 = (k_2/x^2)a_0 \quad (\text{H}_\text{N}\text{A: 2}^{\text{nd}} \text{ diss step}) \quad (4.3)$$

⋮

$$k_N = x(a_N/a_0) \quad \text{or} \quad a_N = (k_N/x^N)a_0 \quad (\text{H}_\text{N}\text{A: } N^{\text{th}} \text{ diss step}) \quad (4.4)$$

$$1 = a_0 + a_1 + a_2 + \dots + a_N \quad (\text{H}_\text{N}\text{A: mass balance}) \quad (4.5)$$

$$0 = (a_1 + 2a_2 + \dots + Na_N) + w/C_T = Y_1 + \frac{w}{C_T} \quad (\text{charge bal.}) \quad (4.6)$$

Subsystem H₂O

The subsystem H₂O with its two components H⁺ and OH⁻ is expressed by $x = \{\text{H}^+\}$ and $w(x)$. The latter includes the self-ionization of water controlled by K_w :

$$w = [\text{OH}^-] - [\text{H}^+] \simeq \frac{K_w}{x} - x \quad (4.7)$$

Subsystem H_NA

The 1-component system “acid” (H_NA) was introduced and discussed in Chapter 3. The N -protic acid comprises $N+1$ acid species [j], which are described by the subset of $N+1$ equations (4.2) to (4.5).

Coupling: H_NA + H₂O

Both subsystems are linked together by the charge-balance equation (4.6). The schema in Fig 4.1 (for an N -protic acid H_NA) is a generalization of Fig 2.5 (for the diprotic acid H₂A).

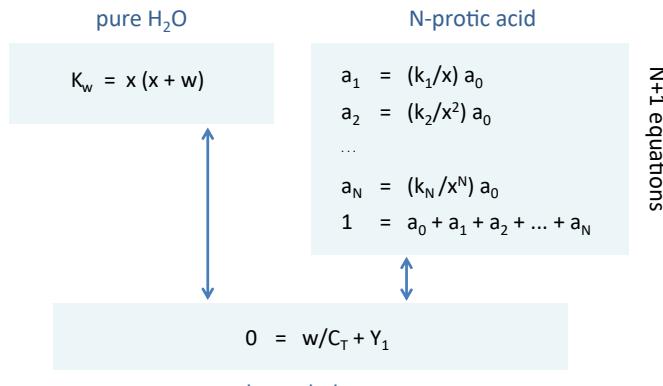


Figure 4.1: The two subsystems “H₂O” and “H_NA” are coupled via the charge-balance equation.

4.2 Closed-Form Equations

4.2.1 Forward and Inverse Task

The 2-component system “H_NA + H₂O” is controlled by two “master variables”: pH and the amount of acid C_T , but only one of them can be freely chosen. Hence, two tasks emerge:

- given pH \Rightarrow calculate C_T
 - given C_T \Rightarrow calculate pH
- } and equilibrium speciation $[j] = C_T a_j$

Forward Task: $C_T = C_T(\text{pH})$

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

$$\text{pH (or } x \text{)} \Rightarrow \text{amount of acid: } C_T(x) = -\frac{w}{Y_1} \quad \text{with } Y_1 = \sum_{j=0}^N j a_j(x) \quad (4.8)$$

$$\Rightarrow \text{speciation (} 0 \leq j \leq N \text{): } [j] = C_T(x) a_j(x) = \left(-\frac{w}{Y_1} \right) a_j(x) \quad (4.9)$$

Eq (4.8) represents an *explicit* function:

$$C_T = f(\text{pH}) \quad (4.10)$$

This dependence is displayed in the left diagram of Fig 4.2. [Note: Exactly the same functions represent the pH dependence of the equivalence points EP_0 plotted as blue curves in the diagrams of Fig 5.10 on page 53.]

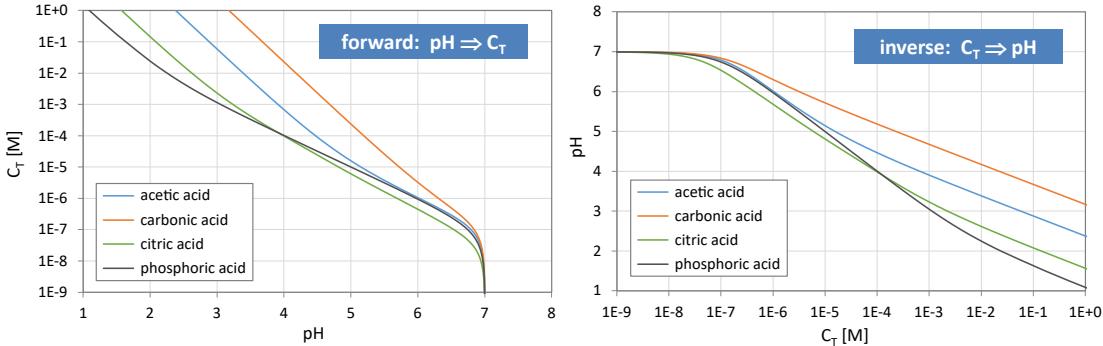


Figure 4.2: Functional relationship between pH and the amount of acid C_T . The left diagram is based on (4.8); right diagram: same as left diagram, only axes interchanged.

Inverse Task: $pH = pH(C_T)$

The *inverse* task to calculate the pH (or x) for a given C_T is intricate because an *explicit* function, such as $pH = f(C_T)$, does not exist for $N > 1$. The only thing we can offer is an *implicit* function in the form of a polynomial¹ of degree $N+2$:

$$0 = \sum_{j=0}^N \{x^2 - j C_T x - K_w\} k_j x^{N-j} \quad (4.11)$$

Compared to the polynomial for the 1-component system “ H_NA ” in (3.30), this polynomial is two degrees higher ($N+2$ rather than N), which makes the solution more difficult. In principle, there is no algebraic expression for solving polynomials with a degree higher than 4, no matter how hard we try. Thus, numerical root-finding methods should be applied. The curves in the right diagram of Fig 4.2 were plotted by a trick: Take the left diagram and interchange the axes.

Note. What is called here “forward task” and what is called “inverse task” is arbitrary. In this case we call “forward task” the simpler calculation method.

4.2.2 Examples

Example $N = 1 \implies$ Cubic Equation

The monoprotic acid represents the simplest case, where the sum in (4.11) runs over two terms only, $j=0$ and 1. With $k_0=1$ and $k_1=K_1$ we get a cubic equation:

$$0 = x^3 + K_1 x^2 - (C_T K_1 + K_w) x - K_1 K_w \quad (4.12)$$

¹The derivation is presented in Appendix B.1.2 — see (B.8) for the special case $n=0$.

Example $N = 2 \implies$ Quartic Equation

For a diprotic acid, we get from (4.11) with $k_0 = 1$, $k_1 = K_1$, and $k_2 = K_1 K_2$ a quartic equation:

$$0 = x^4 + K_1 x^3 + (K_1 K_2 - C_T K_1 - K_w) x^2 - K_1 (2C_T K_2 + K_w) x - K_1 K_2 K_w \quad (4.13)$$

This equation can be found in textbooks, e.g. [2]. If you set $K_2 = 0$, you arrive at (4.12).

The greatest, and most robust, contribution to knowledge consists in removing what we think is wrong.

— Nassim Nicholas Taleb

5

Acid-Base System

Contents

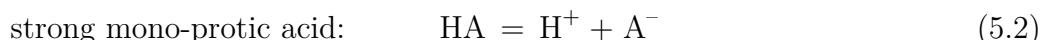
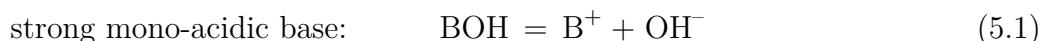
5.1	Introduction	41
5.2	Basic Set of Equations	44
5.3	Titration Curves	48
5.4	Equivalence Points: General Approach	50

5.1 Introduction

5.1.1 Definitions

The previous Chapter provided the algebraic description of the 2-component system “ $H_NA + H_2O$ ” (polyprotic acid in water). Starting from the set of equations (2.32) to (2.37) we arrived at an analytical formula in (4.9) which predicts the amount of C_T for a given pH and vice versa.

A new degree of freedom comes into play when a *strong* base (or *strong* acid) is added to this “undisturbed” system: the 2-component system becomes a 3-component system. The term “strong” means *complete* dissociation in water:



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

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



C_B and C_A denote the amounts of strong base and strong acid. They can be related to the total amount of $\text{H}_\text{N}\text{A}$ by

$$n_B = \frac{C_B}{C_T} \quad \text{and} \quad n_A = \frac{C_A}{C_T} \quad (5.5)$$

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

$$\text{equivalent fraction: } n = \frac{C_B - C_A}{C_T} \quad (5.6)$$

where either C_B or C_A is zero. In this way, the equivalent fraction n of the titrant is *positive* for the alkalimetric titration and *negative* for the acidimetric titration.¹ Note that $n = 0$ represents the “undisturbed” system.

Example

Fig 5.1 provides the acid-base titration of the carbonate system with $C_T = 10 \text{ mM H}_2\text{CO}_3$. The pure H_2CO_3 system is characterized by $\text{pH} = 4.17$ (at $n=0$). Larger pH values are obtained through the addition of NaOH (n is positive); lower pH values through the addition of HCl (n is negative). The small circles at the three integer values $n = 0, 1$, and 2 indicate the equivalence points EP_0 , EP_1 , and EP_2 .

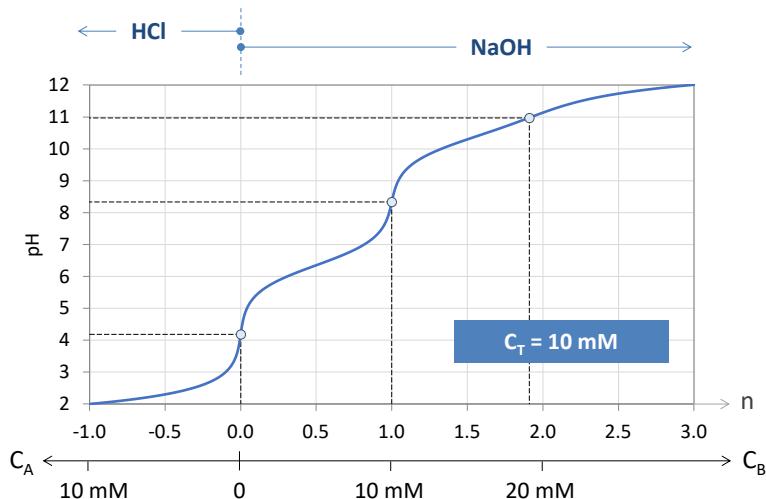
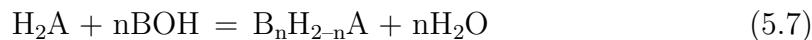


Figure 5.1: Titration curve $\text{pH} = \text{pH}(n)$ of the carbonate system ($10 \text{ mM H}_2\text{CO}_3$).

The same titration curve as in Fig 5.1 (valid for $C_T = 10 \text{ mM}$) is shown in Fig 5.2 together with two additional curves for $C_T = 1 \text{ mM}$ and 100 mM . The only difference between the left and right diagrams in Fig 5.2 is that the x - and y -axes are swapped. [The curves are calculated using (5.32) on page 46.]

5.1.2 Special Case: Diprotic Acid

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



¹In [2], the equivalent fractions n is abbreviated by f .

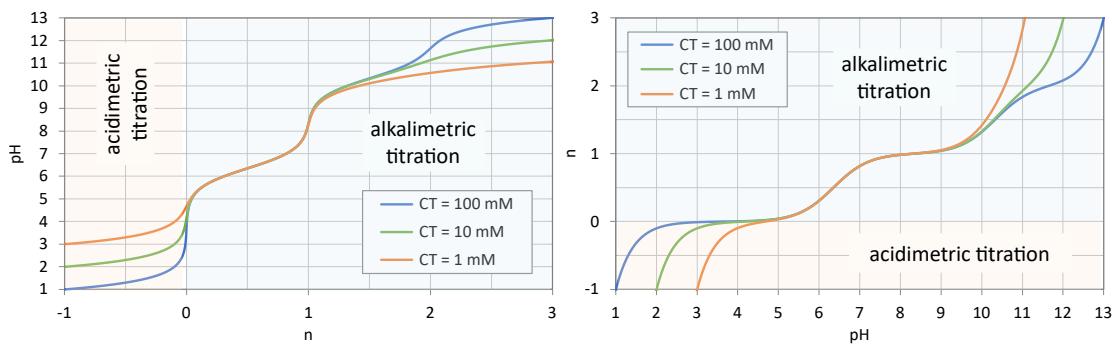


Figure 5.2: Titration curves of the carbonate system (for 1, 10, and 100 mM H_2CO_3). Left diagram: $n = n(\text{pH})$, right diagram: $\text{pH} = \text{pH}(n)$.

Here n acts as a stoichiometric coefficient that embodies the ratio of the added strong base to the amount of the diprotic acid: $n = C_B/C_T$ as introduced in (5.5) and (5.6).

The entity $\text{B}_n\text{H}_{2-n}\text{A}$ in the reaction formula (5.7) does not survive in water; it dissociates into several aqueous species — as indicated in Fig 5.3.

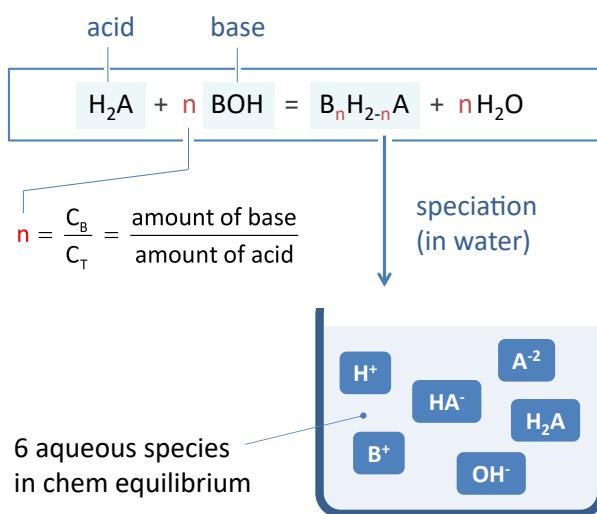


Figure 5.3: Alkalimetric titration of a diprotic acid with a strong base.

The variation of n (or C_B) in the reaction formula (5.7) by adding a strong base is called *alkalimetric titration*. Because strong bases dissociate completely, we have:

$$C_B \equiv [\text{BOH}]_T = \text{B}^+ \quad (\text{strong base}) \quad (5.8)$$

The special cases $n = 0, 1$, and 2 are of particular interest. When these three integers are inserted into the reaction formula (5.7), the entity $\text{B}_n\text{H}_{2-n}\text{A}$ becomes a pure acid, an amphotolyte and a (conjugate) base:

$$n = 0 : \quad \text{pure } \text{H}_2\text{A} \text{ solution} \quad (\text{acid}) \quad \iff \quad \text{H}_2\text{A EP} \quad (5.9)$$

$$n = 1 : \quad \text{pure BHA solution} \quad (\text{amphotolyte}) \quad \iff \quad \text{HA}^- \text{ EP} \quad (5.10)$$

$$n = 2 : \quad \text{pure B}_2\text{A solution} \quad (\text{base}) \quad \iff \quad \text{A}^{2-} \text{ EP} \quad (5.11)$$

In fact, $n = 0, 1$, and 2 define the three equivalence points ($\text{EP}_0, \text{EP}_1, \text{EP}_2$) of a diprotic acid — introduced in § 3.2.1 and discussed in § 7.2 below. [Example: For “ H_2CO_3 plus NaOH ” we obtain pure solutions of H_2CO_3 , NaHCO_3 and Na_2CO_3 .]

Charge Balance

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

$$[\text{H}^+] + [\text{B}^+] = [\text{HA}^-] + 2[\text{A}^{-2}] + [\text{OH}^-] \quad (5.12)$$

Replacing $[\text{B}^+]$ by C_B , as stated in (5.8), we get

$$C_B = [\text{HA}^-] + 2[\text{A}^{-2}] + [\text{OH}^-] - [\text{H}^+] \quad (5.13)$$

Base Equations

The set of algebraic equations to describe the alkalimetric titration of a diprotic acid by a strong base generalizes the equations (2.21) to (2.25) introduced in § 2.2.1:

$$K_w = \{\text{H}^+\} \cdot \{\text{OH}^-\} \quad (\text{self-ionization of H}_2\text{O}) \quad (5.14)$$

$$K_1 = \{\text{H}^+\} \cdot \{\text{HA}^-\} / \{\text{H}_2\text{A}\} \quad (\text{1}^{\text{st}} \text{ diss step}) \quad (5.15)$$

$$K_2 = \{\text{H}^+\} \cdot \{\text{A}^{-2}\} / \{\text{HA}^-\} \quad (\text{2}^{\text{nd}} \text{ diss step}) \quad (5.16)$$

$$C_T = [\text{H}_2\text{A}] + [\text{HA}^-] + [\text{A}^{-2}] \quad (\text{mass balance}) \quad (5.17)$$

$$C_B = [\text{HA}^-] + 2[\text{A}^{-2}] + [\text{OH}^-] - [\text{H}^+] \quad (\text{charge balance}) \quad (5.18)$$

It differs from the original set by the last equation only, which is the charge balance taken from (5.13). In fact, it is the sole equation into which the “strong base” creeps into this set of equations; the other four equations in this set are completely unrelated to C_B . For $C_B = 0$ the set reduces to the description of the base-free diprotic-acid system.

Proton Balance

In textbooks, (5.18) is sometimes introduced through the concept of “proton balance”—a special topic which is explained in Appendix C. For diprotic acids the proton balance yields:

$$0 = [\text{H}^+] + n[\text{H}_2\text{A}] + (n - 1)[\text{HA}^-] + (n - 2)[\text{A}^{-2}] - [\text{OH}^-] \quad (5.19)$$

Using $n = C_B/C_T$ and $C_T = [\text{H}_2\text{A}] + [\text{HA}^-] + [\text{A}^{-2}]$, this formula converts to (5.18).

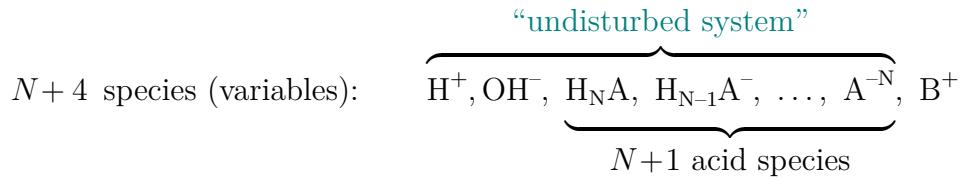
5.2 Basic Set of Equations

5.2.1 The 3-Component System

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

- pure water
 - weak N -protic acid H_NA
 - strong mono-acidic base BOH
- } the “base-free” or “undisturbed” system
of Chapter 4

It is characterized by



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

$$K_w = \{\text{H}^+\} \cdot \{\text{OH}^-\} \quad (\text{self-ionization of H}_2\text{O}) \quad (5.20)$$

$$K_1 = \{\text{H}^+\} \cdot \{\text{H}_{\text{N}-1}\text{A}^-\} / \{\text{H}_\text{N}\text{A}\} \quad (1^{\text{st}} \text{ diss step}) \quad (5.21)$$

$$K_2 = \{\text{H}^+\} \cdot \{\text{H}_{\text{N}-2}\text{A}^{-2}\} / \{\text{H}_{\text{N}-1}\text{A}^-\} \quad (2^{\text{nd}} \text{ diss step}) \quad (5.22)$$

⋮

$$K_N = \{\text{H}^+\} \cdot \{\text{A}^{-\text{N}}\} / \{\text{H}\text{A}^{-(\text{N}-1)}\} \quad (\text{N}^{\text{th}} \text{ diss step}) \quad (5.23)$$

$$C_T = [\text{H}_\text{N}\text{A}] + [\text{H}_{\text{N}-1}\text{A}^-] + \dots + [\text{A}^{-\text{N}}] \quad (\text{mass balance}) \quad (5.24)$$

$$\textcolor{red}{C_B} = [\text{H}_{\text{N}-1}\text{A}^-] + 2[\text{H}_{\text{N}-2}\text{A}^{-2}] + \dots + N[\text{A}^{-\text{N}}] + [\text{OH}^-] - [\text{H}^+] \quad (5.25)$$

This set of equations is an extension of the diprotic-acid case in (5.14) to (5.18) from $N=2$ to any large N . This is also an extension of the “undisturbed $\text{H}_\text{N}\text{A}$ system” defined by the set of $N+3$ equations (2.26) to (2.31). The latter is re-established when $\textcolor{red}{C_B}$ is set to zero (in the last equation). In fact, the only difference to the original set of equations (2.26) to (2.31) is just the charge-balance equation in the last line.

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

Two assumptions are necessary to derive closed-form expressions (one-line formulas) from the set of equations (5.21) to (5.25):

- activities should be replaced by concentrations: $\{\cdot\} \rightarrow [\cdot]$
- the strong base BOH dissolves completely without forming aqueous species (such as NaCO_3^- or $\text{NaHCO}_3(\text{aq})$)

The first assumption is fulfilled either in dilute systems or by switching to *conditional* equilibrium constants ${}^c K$ introduced in (2.7). These are so-called “ideal conditions”; counterexamples for “real conditions” will be given in § 7.6.

5.2.2 Closed-Form Expressions

The procedure for solving the set of algebraic equations (5.21) to (5.25) is the same as that we used in previous paragraphs (cf. in § 4.2):

- replace activities by concentrations: $\{\cdot\} \rightarrow [\cdot]$ in (5.21) to (5.23)
- replace acid species $[j]$ by ionization fractions a_j in (5.21) to (5.25)
- replace $\{\text{H}^+\}$ by x and $[\text{OH}^-]$ by $K_w/x-x$, and use $w(x)$ defined in (4.7)
- use the compact notation Y_1 for the sums over a_j in (5.25)

In this way, the set of $N + 3$ equations simplifies to:

$$K_w = x(x+w) \quad (\text{subsystem H}_2\text{O}) \quad (5.26)$$

$$k_1 = x(a_1/a_0) \quad \text{or} \quad a_1 = (k_1/x)a_0 \quad (\text{H}_N\text{A: 1}^{\text{st}} \text{ diss step}) \quad (5.27)$$

$$k_2 = x(a_2/a_0) \quad \text{or} \quad a_2 = (k_2/x^2)a_0 \quad (\text{H}_N\text{A: 2}^{\text{nd}} \text{ diss step}) \quad (5.28)$$

\vdots

$$k_N = x(a_N/a_0) \quad \text{or} \quad a_N = (k_N/x^N)a_0 \quad (\text{H}_N\text{A: } N^{\text{th}} \text{ diss step}) \quad (5.29)$$

$$1 = a_0 + a_1 + a_2 + \dots + a_N \quad (\text{H}_N\text{A: mass balance}) \quad (5.30)$$

$$\textcolor{red}{n} = Y_1 + w/C_T \quad (\text{charge balance}) \quad (5.31)$$

This set of equations upgrades (4.1) to (4.6) from an acid system to an *acid-base system* with the parameter n as the new ingredient.

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

$$n(x) = Y_1(x) + \frac{w(x)}{C_T} \quad (5.32)$$

The information contained in all other equations — i.e. equations (5.26) to (5.30) — is encapsulated in the definition of Y_1 and w :

$$Y_L = \sum_{j=0}^N j \cdot a_j = a_1 + 2a_2 + 3a_3 + \dots + Na_N \quad (5.33)$$

$$w = [\text{OH}^-] - [\text{H}^+] \simeq \frac{K_w}{x} - x \quad (5.34)$$

In (5.32), each of the three terms represents one of the three components (subsystems): n — the strong base, w/C_T — the water, and Y_1 — the acid. This is summarized in Fig 5.4, which illustrates how the three components “pure H_2O ”, “ N -protic acid”, and “strong base” are coupled via one single equation: the charge-balance equation.

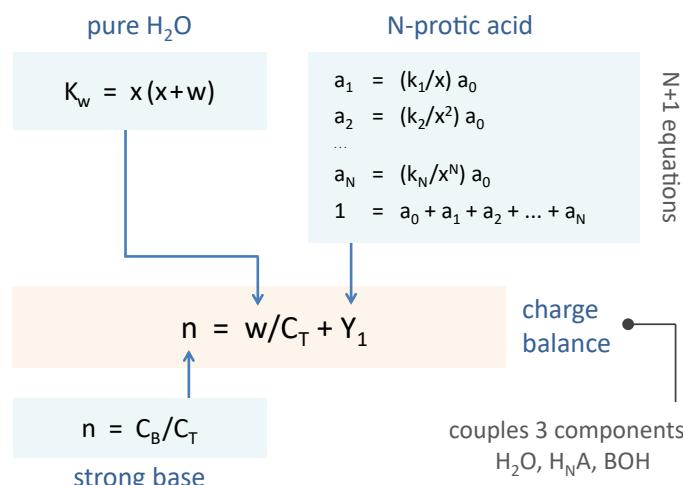


Figure 5.4: The acid-base system: The three components “ H_2O ”, “acid”, and “strong base” are coupled via the charge-balance equation.

5.2.3 Polynomials for $x = 10^{-\text{pH}}$

Eq (5.32) can be solved for x (or pH). This is done in Appendix B.1.2 with the final result in (B.8), which is a polynomial of degree $N+2$ in x :

$$0 = \sum_{j=0}^N \{x^2 + (n-j)C_T x - K_w\} k_j x^{N-j} \quad (5.35)$$

For $n=0$ it falls back to (4.11) on page 39. Theoretically, this equation can be used to calculate x , but in practice it's a difficult task, even for a cubic equation. For higher-order polynomials, numerical root-finding methods should be used.

Example $N = 1$

The monoprotic acid represents the simplest case, where the sum in (5.35) runs over two terms only, $j=0$ and 1. With $k_0=1$ and $k_1=K_1$ we get a *cubic* equation, i.e. a polynomial of degree 3 in x ($= 10^{-\text{pH}}$):

$$0 = x^3 + \{K_1 + nC_T\} x^2 + \{(n-1)C_T K_1 - K_w\} x - K_1 K_w \quad (5.36)$$

which generalizes (4.12) for $n \neq 0$. It predicts x (or pH) for any given pair of C_T and n . Alternatively, replacing n by $C_B = nC_T$ yields:

$$0 = x^3 + \{K_1 + C_B\} x^2 + \{(C_B - C_T) K_1 - K_w\} x - K_1 K_w \quad (5.37)$$

Example $N = 2$

For a diprotic acid, we get from (5.35) with $k_0 = 1$, $k_1 = K_1$, and $k_2 = K_1 K_2$ a *quartic* equation:

$$\begin{aligned} 0 = x^4 &+ \{K_1 + nC_T\} x^3 + \{K_1 K_2 - (n-1)C_T K_1 - K_w\} x^2 \\ &+ K_1 \{(n-2)C_T K_2 + K_w\} x - K_1 K_2 K_w \end{aligned} \quad (5.38)$$

which generalizes (4.13) for $n \neq 0$. It predicts x (or pH) for any given pair of C_T and n . Replacing n by $C_B = nC_T$ yields:

$$\begin{aligned} 0 = x^4 &+ \{K_1 + C_B\} x^3 + \{K_1 K_2 - (C_B - C_T) K_1 - K_w\} x^2 \\ &+ K_1 \{(C_B - 2C_T) K_2 + K_w\} x - K_1 K_2 K_w \end{aligned} \quad (5.39)$$

Setting $K_2=0$, we arrive at (5.36) and (5.37). As will be shown later in § 8.1, in the case of strong acids all polynomials simplify (their degree decreases by one unit).

Summary

Either the closed-form expression in (5.32) or the polynomial in (5.35) are self-sufficient ways to describe the acid-base titration completely. Both are different encodings of one and the same thing, namely the set of $N+3$ equations (5.26) to (5.31).

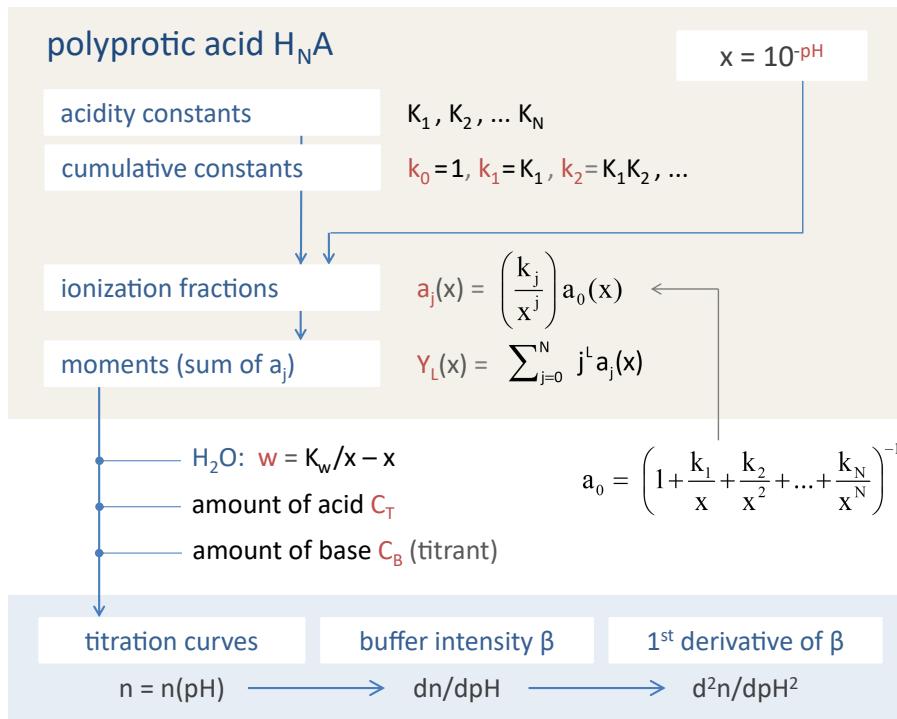


Figure 5.5: The analytical solution in (5.32) is constructed from acidity constants and ionization fractions.

5.2.4 Lego-Set of Building Blocks

The analytical solution in (5.32) can be constructed “Lego-like” from building blocks of increasing complexity (acidity constants K_j , ionization fractions a_j , moments Y_L). The hierarchy is sketched in Fig 5.5.

At the lowest level there are the N acidity constants K_1 to K_N (as irreducible essence of acid H_NA), which — after multiplication — form cumulative equilibrium constants k_1 to k_N . These constants, in combination with the variable $x = \{\text{H}^+\}$, enter the ionization fractions a_j (which embody the law of mass action in each dissociation step). Then, the ionization fractions are summed up to form the moment Y_L as the central part of the final equation. The only other ingredient is the quantity $w(x) = K_w/x - x$ describing the self-ionization of water.

The usefulness of the higher moments Y_L (i.e. for $L \geq 2$) becomes clear later on, when the moments are used as building blocks for other key quantities:

- $Y_0 \Rightarrow$ mass balance $(Y_0 = 1)$
- $Y_1 \Rightarrow$ enters buffer capacity $n(x)$ in (5.32)
- $Y_2 \Rightarrow$ enters buffer intensity $\beta = dn/dx$ in (6.22)
- $Y_3 \Rightarrow$ enters 1st derivative of β in (6.23)

5.3 Titration Curves

The closed-form expression in (5.32) contains all the information about the acid-base system. Plotting the equivalent fraction as a function of pH, i.e. $n = n(\text{pH})$,

provides titration curves:

$$n = Y_1(\text{pH}) + \frac{w(\text{pH})}{C_T} \xrightarrow{C_T \rightarrow \infty} n = Y_1(\text{pH}) \quad (5.40)$$

This formula for n consists of two parts: $Y_1(x)$ as the contribution from the subsystem “acid” and $w(x)$ as the contribution from the subsystem “H₂O”. As indicated by the arrow, the latter term vanishes for large C_T values. In other words, for high-concentrated acids the formula simplifies to $n = Y_1$.

Example: Carbonic Acid

The upper diagram in Fig 5.6 shows the titration curve of carbonic acid in the high- C_T limit, where the simplified formula $n(\text{pH}) = Y_1 = a_1 + 2a_2$ applies. The corresponding ionization fractions a_j — as the building blocks of Y_j — are displayed in the bottom diagram.

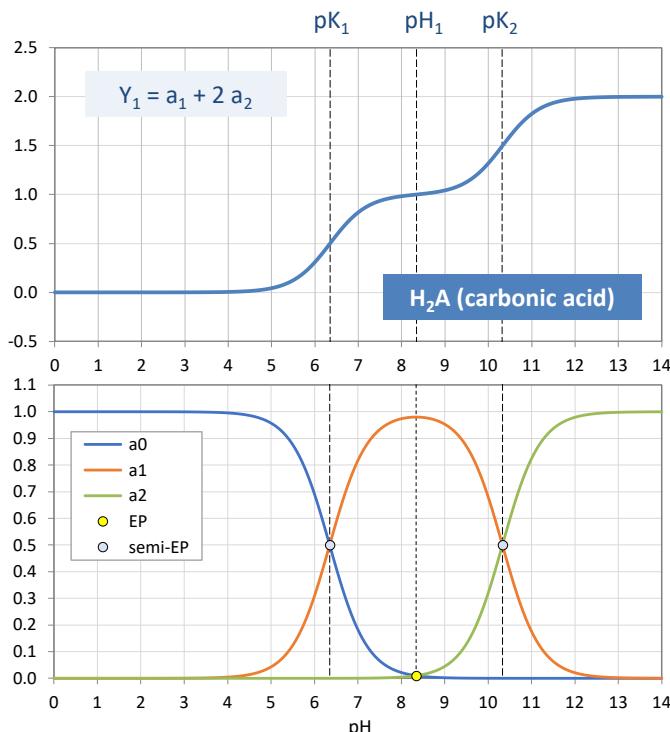


Figure 5.6: Titration curve of carbonic acid in the “high- C_T limit”: $Y_1(\text{pH}) = a_1 + 2a_2$ (top diagram); ionization fractions a_0 , a_1 , and a_2 (bottom diagram).

Fig 5.7 compares the titration curves in the “high- C_T limit” (top diagram is the same as in Fig 5.6) with the general case, $n = Y_1 + w/C_T$, for different values of C_T (bottom diagram). Here too, the dark blue curve represents Y_1 as the “high- C_T limit”, i.e. $C_T/w \gg 1$.

Example: HA, H₂A, H₃A

Titration curves of four common acids for different values of C_T (including the high- C_T case $n(\text{pH}) = Y_1$ as a dark blue curve) are shown in Fig 5.8.

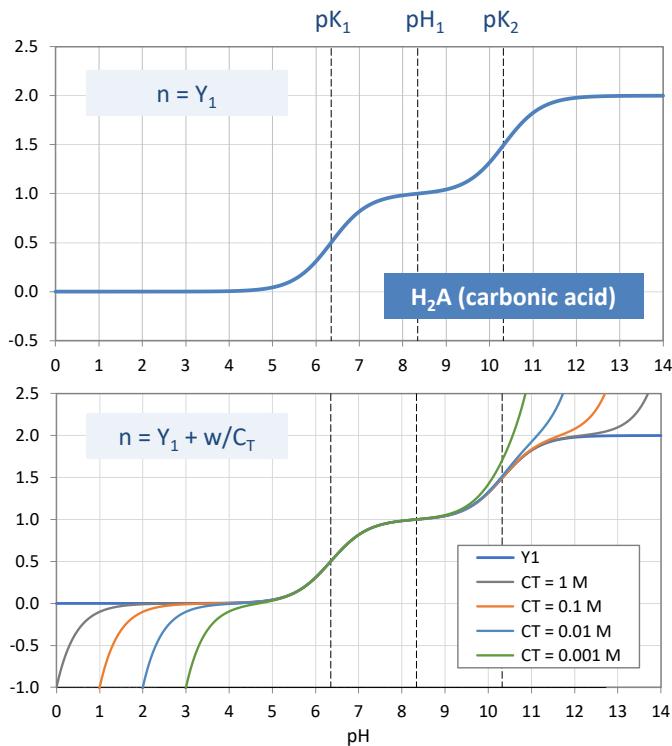


Figure 5.7: Titration curves of carbonic acid for different C_T values. Top diagram: the “pure-acid” case: $n(\text{pH}) = Y_1 = a_1 + 2a_2$; bottom diagram: the “pure-acid” case ($C_T \rightarrow \infty$) together with four finite C_T values.

5.4 Equivalence Points: General Approach

5.4.1 Definitions

In § 3.2, equivalence points were introduced by equating two adjacent *acid species* [j]:²

$$\text{EP}_j : [j-1] = [j+1] \Leftrightarrow \text{EP}_n : [n-1] = [n+1] \quad (\text{for integer } n=j) \quad (5.41)$$

$$\text{semi-EP}_j : [j-1] = [j] \Leftrightarrow \text{EP}_n : [n - \frac{1}{2}] = [n + \frac{1}{2}] \quad (\text{for half-integer } n=j - \frac{1}{2}) \quad (5.42)$$

This definition leads to simple formulas for the corresponding pH values (cf. § 3.2.2), whereby the so-called internal EPs are directly related to the acidity constants K_j :

$$\text{EP}_n \Leftrightarrow \text{pH}_n = \begin{cases} \frac{1}{2}(\text{pK}_n + \text{pK}_{n+1}) & \text{for } n = 1, 2, \dots, N-1 \quad (\text{EP}) \\ \text{pK}_{n+1/2} & \text{for } n = \frac{1}{2}, \frac{3}{2}, \dots, N - \frac{1}{2} \quad (\text{semi-EP}) \end{cases} \quad (5.43)$$

General Approach

The general approach is based on the equality of two chemical *compounds* (and not on the equality of two *acid species* as done in (5.41) and (5.42)):

$$\text{EP: } [\text{N-protic acid}]_T = [\text{strong base}]_T \quad (5.44)$$

which can be written as

$$\text{EP: } C_T = C_B \quad \text{or} \quad n = \frac{C_B}{C_T} = 1 \quad (5.45)$$

²Here, the notation is extended to include the two external EPs by setting $[-1] = [\text{H}^+]$ and $[N+1] = [\text{OH}^-]$.

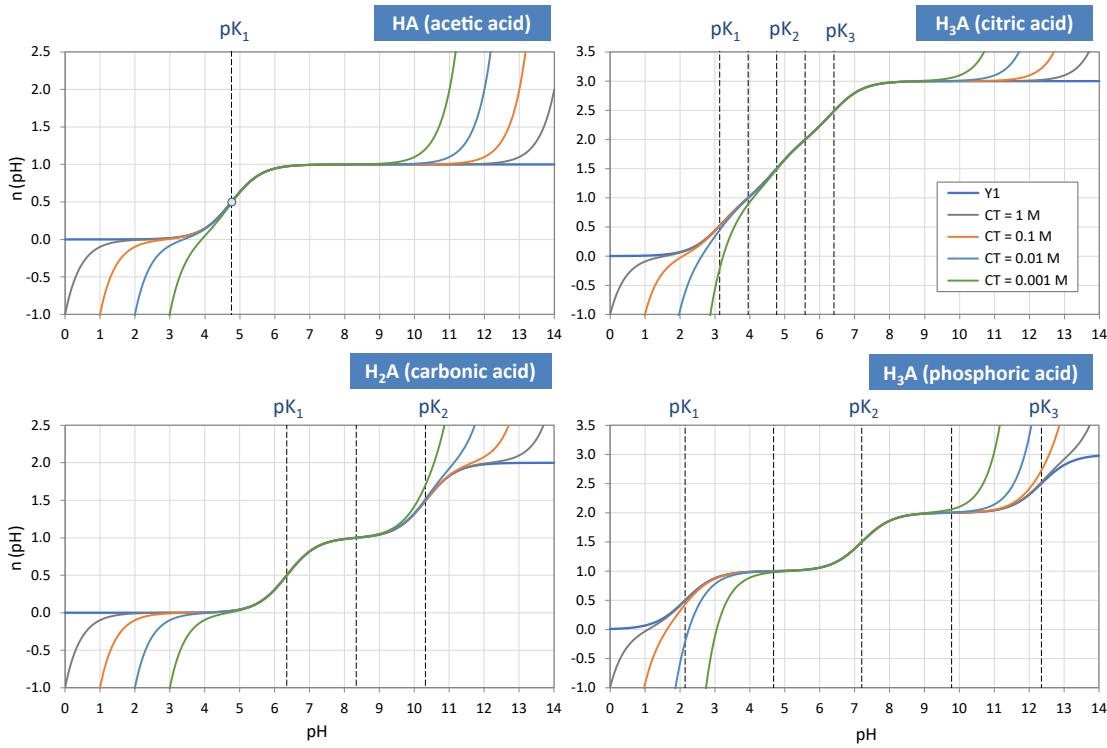


Figure 5.8: Titration curves of four common acids for different values of C_T (including the “pure-acid case” $n(\text{pH}) = Y_1$).

This defines the equivalence point EP_1 . The extension to other EPs and semi-EPs (for integer and half-integer n) is easy:

$$\boxed{\text{EP}_n : n = \frac{C_B}{C_T} \quad \text{for } n = 0, \frac{1}{2}, 1, \frac{3}{2}, \dots N} \quad (5.46)$$

The math relationship between the EP_n and the corresponding pH_n value is provided by the equivalence-fraction formula (5.32):

$$n = Y_1(\text{pH}) + \frac{w(\text{pH})}{C_T} \quad \text{for } n = 0, \frac{1}{2}, 1, \frac{3}{2}, \dots N \quad (5.47)$$

Plotting it as a function of pH yields the blue titration curve in Fig 5.9 (for H_2CO_3 with $C_T = 100 \text{ mM}$). The small circles at integer and half-integer values of n mark the assignment between EP_n and pH_n . Since H_2CO_3 is a 2-protic acid there are $2 \times 2 + 1 = 5$ equivalence points in total.

Asymptotic Behavior: $C_T \rightarrow \infty$

If C_T increases steadily, the second term in (5.47) approaches zero and we get the simple relationship:

$$\text{EP}_n \text{ for } C_T \rightarrow \infty \iff 0 = n - Y_1(\text{pH}_n) \quad (\text{“pure-acid case”}) \quad (5.48)$$

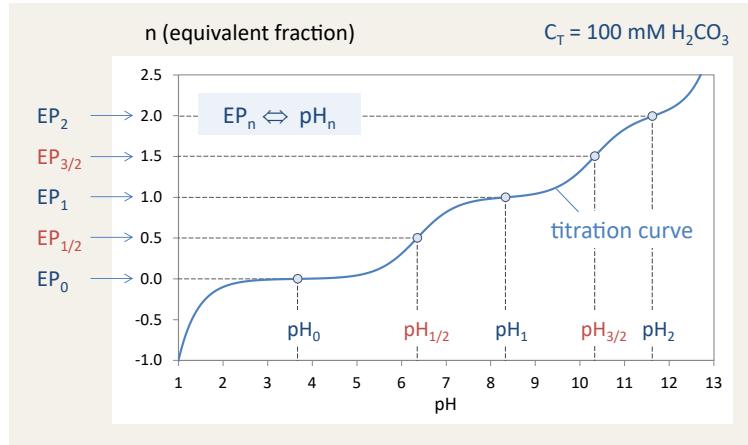


Figure 5.9: Titration curve of the diprotic acid H_2CO_3 based on (5.47) with EPs and semi-EPs located at integer and half-integer values of n .

In fact, according to (3.89), it offers the intimate relationship between the pH of an *internal* equivalence point and the acidity constants, as stated in (5.43).³ In other words, the “pure-acid case” from § 3.2 is immanent in (5.47) and comes to light when the “coupling term” w/C_T disappears.

5.4.2 EP_n as Trajectories in pH-C_T Diagrams

Eq (5.47) can be rearranged into the form

$$C_T = \frac{w(\text{pH}_n)}{n - Y_1(\text{pH}_n)} \quad (5.49)$$

Now it is possible to plot all EP_n as distinct curves into a pH- C_T diagram (one curve for one integer or half-integer value of n). This is done in Fig 5.10 for four acids. The dashed curves and lines are approximations corresponding to the high- C_T limit as displayed in Fig 3.3 on page 25.

Let’s explain the general behavior of the EP_n curves using the phosphoric acid (as a triprotic acid). This example is shown in Fig 5.11 and consists of two diagrams. In the top diagram, we have the two uncoupled (isolated) subsystems located at opposite ends of the C_T scale:

- subsystem “acid”: $C_T \rightarrow \infty$
- subsystem “ H_2O ”: $C_T \rightarrow 0$

The bottom diagram in Fig 5.11 shows the situation in which both subsystems are coupled. Starting at pH 7, the curves fan out when C_T increases until they fit the “pure-acid” values at the top of the chart. The whole behavior is determined by (5.49).

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

The two extremes (i.e. the two isolated subsystems) can be deduced from Eq (5.49) by setting either the nominator or the denominator to zero:

$$C_T = \frac{w}{n - Y_1} \iff \begin{cases} w = 0 & \Rightarrow C_T = 0 \\ n - Y_1 = 0 & \Rightarrow C_T \rightarrow \infty \end{cases} \quad (5.50)$$

³Eq (5.48) is more general than (5.43). Both equations are equivalent for $N \leq 2$, but deviate for higher N (albeit the deviation is very small).

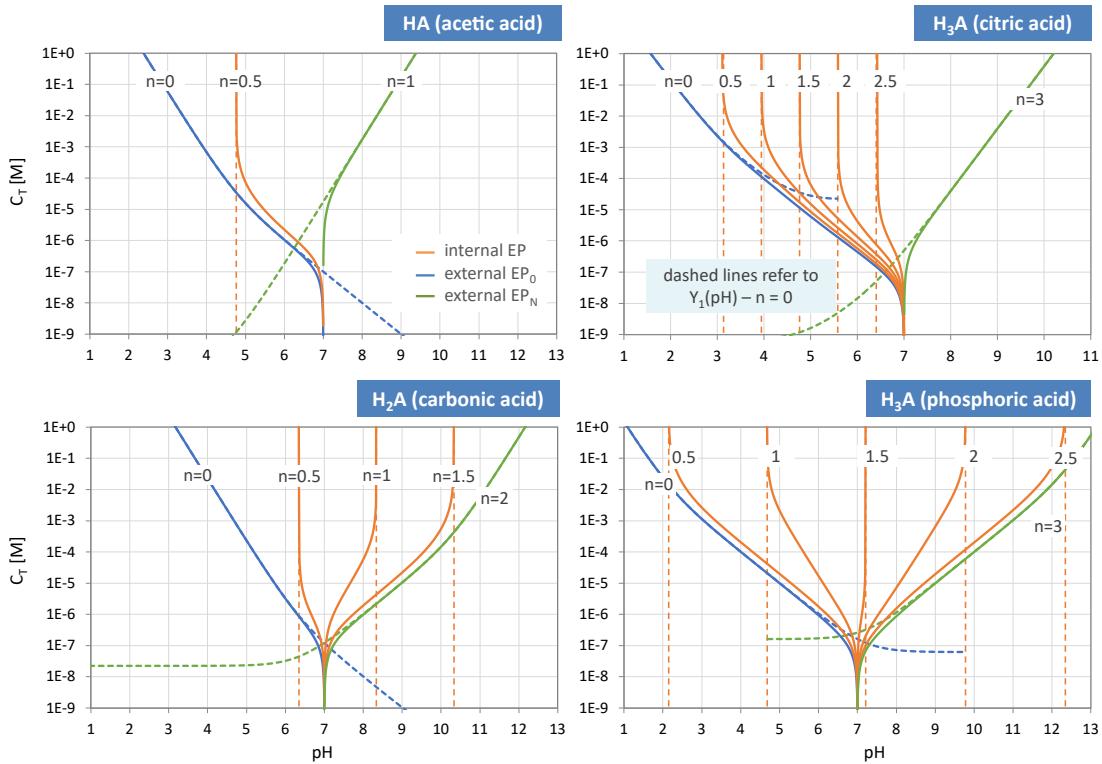


Figure 5.10: pH dependence of EPs and semi-EPs plotted as $C_T = f(\text{pH})$ for four acids.

In math jargon, the corresponding pH values of the “pure acid” system (listed in Tab 3.2) are the poles (or singularities) of (5.49) or (5.50). On the other hand, the single EP of “pure H_2O ” is at the position where the nominator in (5.49) or (5.50) becomes zero (which is exactly at $\text{pH} = 7$):

$$\text{EP of } \text{H}_2\text{O} \iff 0 = w(x) \iff C_T = 0 \quad (5.51)$$

5.4.3 Summary: Systematics & Classification

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

$$\text{EP}_n : \quad C_B/C_T = \textcolor{red}{n} \quad \text{for } \textcolor{red}{n} = 1, 2, \dots, N \quad (5.52)$$

$$\text{semi-EP}_{\frac{n}{2}} : \quad C_B/C_T = \frac{\textcolor{red}{n}}{2} \quad \text{for } \textcolor{red}{n} = \frac{1}{2}, \frac{3}{2}, \dots, \left(N - \frac{1}{2}\right) \quad (5.53)$$

The *trivial* case EP_0 refers to the base-free system with pH_0 as the pH value of the acid with amount C_T dissolved in water.

Second. Each EP_n is characterized by a specific pH value, which we call pH_n . The algebraic relationship $\text{EP}_n \Leftrightarrow \text{pH}_n$ is given by $n = Y_1(\text{pH}) + w(\text{pH})/C_T$, i.e. (5.47), where Y_1 describes the acid and w the water.

Third. The equivalent fraction $n = Y_1(\text{pH}) + w(\text{pH})/C_T$ (titration curve) represents the buffer capacity, as it will be shown later in Chapter 6. Its first pH-derivative is

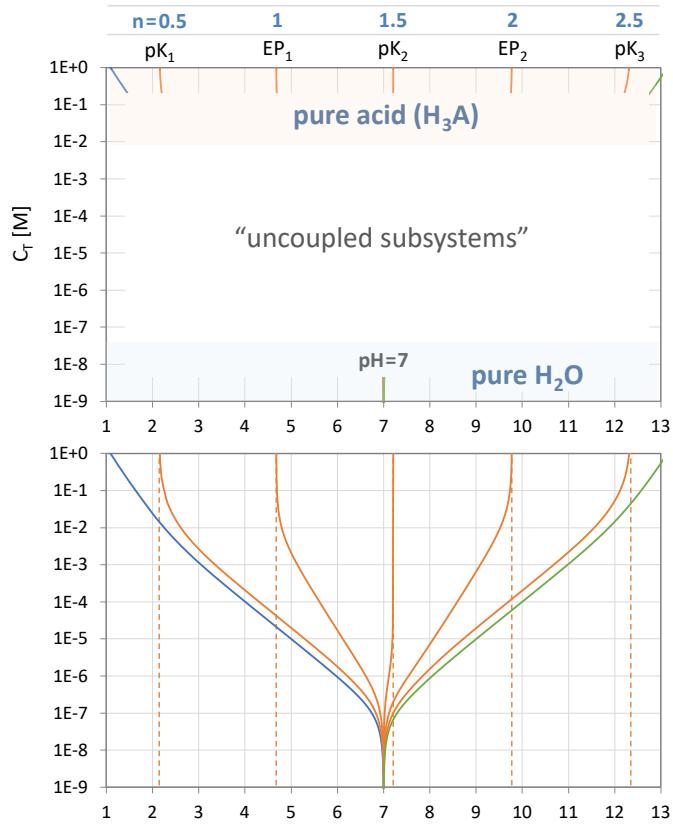


Figure 5.11: pH dependence of EPs and semi-EPs of phosphoric acid (H_3PO_4) for the uncoupled (top diagram) and the coupled system (bottom diagram).

the buffer intensity $\beta = dn/d\text{pH}$. The EPs are the extreme points of β :

$$\begin{array}{lll} \text{EP}_n & \text{integer } n & \iff \text{minimum buffer intensity } \beta \\ \text{semi-EP}_n & \text{half-integer } n & \iff \text{maximum buffer intensity } \beta \end{array}$$

Fourth. In the limiting case of high-concentrated acids ($C_T \rightarrow \infty$), the general relationship simplifies to:

$$Y_1(\text{pH}) - n = 0 \quad (5.54)$$

This equation asserts the direct link between pH_n and the acidity constants:⁴

$$\begin{array}{lll} \text{pH}_n = \frac{1}{2} (\text{pK}_n + \text{pK}_{n+1}) & \text{for integer } n & (\text{EP}_n) \\ \text{pH}_n = \text{pK}_{n+1/2} & \text{for half-integer } n & (\text{semi-EP}_n) \end{array}$$

These simple relationships are applicable for $C_T > 10^{-3} \text{ M}$, but fail in very dilute acids when the influence of the water becomes dominant (and the general formula (5.47) must be used instead of (5.54)).

Fifth. An alternative definition of EPs is based on the equality of the concentrations of the species, as done in (5.41) and (5.42), and originally established in § 3.2.1. This definition is an approximation which, strictly speaking, only applies to the high- C_T

⁴It is strictly valid for diprotic acids, but remains a very good approximation for N -protic acids with $N \geq 3$.

case. (Nonetheless, in carbonate systems, for example, EP₁ is often introduced as the equilibrium state for which $[CO_2] = [CO_3^{2-}]$ applies.)

Table 5.1 compares the two approaches to equivalence points. The left column summarizes the alternative definition based on the equality of species concentrations (as introduced in § 3.2.1 for the simplified “pure acid” case). This is in sharp contrast to the general approach (right column in Table 5.1) where real chemical compounds are set equal.

Table 5.1: Comparison of two approaches to equivalence points.

	1-component system (H _N A alone)	3-component system (H _N A + H ₂ O + strong base)
common, but approximate		general and strict
based on acid species EP _n : $[n-1] = [n+1]$ semi-EP _n : $[n-\frac{1}{2}] = [n+\frac{1}{2}]$	based on total amount of compounds EP _n : $n = \frac{[\text{strong base}]_T}{[H_N A]_T} = \frac{C_B}{C_T}$	
$pH_n = \begin{cases} \frac{1}{2}(pK_n + pK_{n+1}) & \Leftrightarrow \text{EP} \\ pK_{n+1/2} & \Leftrightarrow \text{semi-EP} \end{cases}$	$C_T = \frac{w(x)}{n - Y_1(x)}$	

\uparrow $C_T \rightarrow \infty$ \downarrow
 $(n - Y_1 = 0)$

Sixth. The concept was extended to zwitterionic acids in [1] (where (5.47) will become (4.7) in [1]). This provides a new perspective on Table 5.1: The simplified approach in the left column is related to *isoelectric* points (i.e. points that only exist for zwitterions, but not for common acids), while the approach in the right column refers to *isoionic* points.

Perfect is the enemy of Good Enough.

*"Good for everything" is the same as
"particularly good at nothing".*

— two proverbs

6

Buffer Capacities

Contents

6.1 ANC and BNC	57
6.2 Buffer Intensity	61

6.1 ANC and BNC

6.1.1 EPs as Reference Points of ANC and BNC

The starting-point is the acid-base system of Chapter 5. An equilibrium state of the acid–base system with a given amount of C_T is completely specified by the parameter C_B or $n = C_B/C_T$. The main relationship is presented by (5.32) in § 5.2.2.

Buffer capacities are *distances* between two equilibrium states, expressed as the deviation from a reference point:

$$\Delta n = n - n_{\text{ref}} \quad \text{or} \quad \Delta C_B = C_B - n_{\text{ref}} C_T \quad (6.1)$$

The reference point is usually an equivalence point $\text{EP}_n=j$ (with integer j). Thus we can set $n_{\text{ref}} = j$ and write:

$$\Delta n = n(x) - j \quad \text{or} \quad \Delta C_B = C_B - j \cdot C_T \quad (\text{with } j = 0, 1, \dots) \quad (6.2)$$

If $n_{\text{ref}}=0$, the equations collapse to $\Delta n=n$ and $\Delta C_B=C_B$. This legitimizes calling n and C_B *buffer capacities*; they measure the distance to EP_0 .

Two types of buffer capacities are in common use: the acid-neutralizing capacity (ANC) and the base-neutralizing capacity (BNC). The ANC is the amount of *basicity* of the system that can be titrated with a *strong acid* to a chosen equivalence point EP_j (at pH_j):

$$[\text{ANC}]_{n=j} = C_B(\text{pH}) - j \cdot C_T \quad (6.3)$$

The small subscript n in the symbol $[\text{ANC}]_n$ refers to the chosen reference point, usually EP_n (with an integer n). In the special case of $n=0$, which corresponds to the base-free 2-component system, the last term vanishes and the ANC becomes

$$[\text{ANC}]_0 = C_B(\text{pH}) \quad (6.4)$$

The BNC is the exact opposite of ANC:

$$[\text{BNC}]_n = -[\text{ANC}]_n \quad (6.5)$$

The definition in (6.3) leads to a simple formula for ANC. Using (5.32) for $C_B(\text{pH}) = n C_T$ yields:

$$[\text{ANC}]_{n=j} = \{Y_1(x) - j\} C_T + w(x) \quad (6.6)$$

For example, the amount of strong acid (say HCl) required to neutralize the system *from* startpoint x ($= 10^{-\text{pH}}$) *to* a particular EP_n (titration endpoint) is:

$$[\text{ANC}]_0 = \{Y_1(x) - 0\} C_T + w(x) = \{Y_1(x)C_T + w(x)\} - 0 \cdot C_T \quad (6.7)$$

$$[\text{ANC}]_1 = \{Y_1(x) - 1\} C_T + w(x) = \{Y_1(x)C_T + w(x)\} - 1 \cdot C_T \quad (6.8)$$

$$[\text{ANC}]_2 = \{Y_1(x) - 2\} C_T + w(x) = \{Y_1(x)C_T + w(x)\} - 2 \cdot C_T \quad (6.9)$$

The three ANC curves are shown in the top diagram of Fig 6.1 for carbonic acid ($C_T = 10 \text{ mM}$). The small circles at $\text{pH}_0 = 4.2$, $\text{pH}_1 = 8.2$, and $\text{pH}_2 = 11.1$ mark the corresponding EP_n . The curves display the amount of strong acid (normalized by C_T) required to remove the inherent basicity and to attain pH_0 (blue curve), pH_1 (green curve), and pH_2 (red curve). Of course, the highest amount (blue curve) is required to attain the lowest pH, namely $\text{pH}_0 = 4.2$.

Negative ANC values indicate that the system's acidity should be *removed* to attain the EP_n (which is the same as the *addition* of a strong base — see (6.5) for BNC). Curves of BNC are shown in the bottom diagram of Fig 6.1, which is the mirror image of the top diagram.

6.1.2 Titration Example

Given is a carbonic-acid system with $C_T = 10 \text{ mM}$. The titration curve — based on (5.32) — is displayed in Fig 6.2. The three EPs for $n = 0, 1, 2$ are marked by small yellow circles at $\text{pH}_0 = 4.2$, $\text{pH}_1 = 8.2$, and $\text{pH}_2 = 11.1$.

Let's select two points on the titration curve as displayed in Fig 6.2:

- point (A) at $\text{pH} = 11.7$ (belongs to equivalent fraction $n(\text{pH}) = 5/2$)
- point (B) at $\text{pH} = 2.3$ (belongs to equivalent fraction $n(\text{pH}) = -1/2$)

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

- acidimetric titration with strong acid from (A) at $\text{pH} = 11.2 \Rightarrow \text{pH}_n$
- alkalimetric titration with strong base from (B) at $\text{pH} = 2.3 \Rightarrow \text{pH}_n$

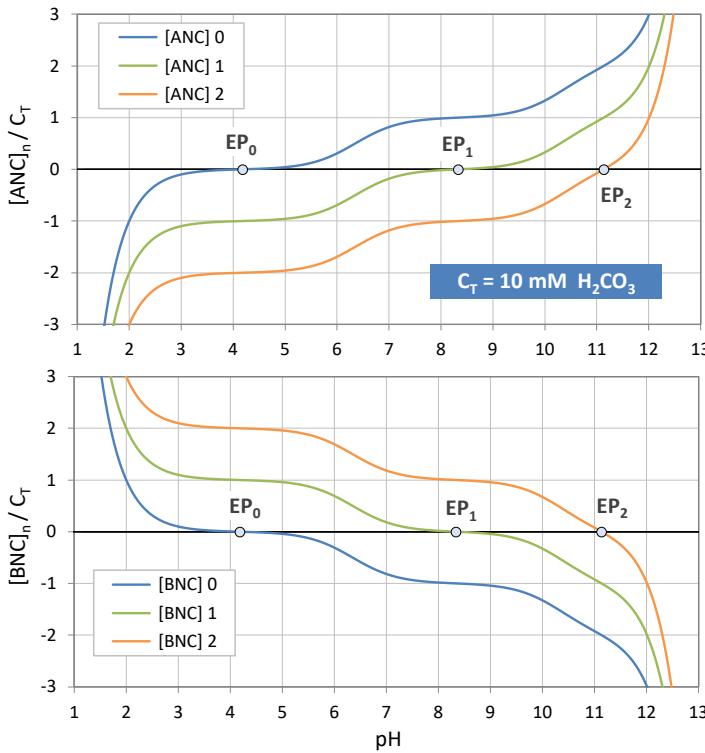


Figure 6.1: Normalized $[ANC]_n$ and $[BNC]_n$ for carbonic acid with $C_T = 10 \text{ mM}$.

ANC. The required amount of *strong acid* (indicated by the green arrows in Fig 6.2) to attain EP₁, EP₂ and EP₃ is just the acid-neutralizing capacity given in equations (6.7) to (6.9):

$$[ANC]_0 = \{5/2 - 0\} \cdot C_T = 25 \text{ mM} \quad (6.10)$$

$$[ANC]_1 = \{5/2 - 1\} \cdot C_T = 15 \text{ mM} \quad (6.11)$$

$$[ANC]_2 = \{5/2 - 2\} \cdot C_T = 5 \text{ mM} \quad (6.12)$$

BNC. The required amount of *strong base* (indicated by the red arrows in Fig 6.2) to attain EP₁, EP₂ and EP₃ is just the base-neutralizing capacity given in equations (6.7) to (6.9):

$$[BNC]_0 = \{-1/2 - 0\} \cdot C_T = 5 \text{ mM} \quad (6.13)$$

$$[BNC]_1 = \{-1/2 - 1\} \cdot C_T = 15 \text{ mM} \quad (6.14)$$

$$[BNC]_2 = \{-1/2 - 2\} \cdot C_T = 25 \text{ mM} \quad (6.15)$$

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

6.1.3 Alkalinity and Acidity

In carbonate systems, ANC is known as *alkalinity* and BNC as *acidity*. Again, we have to distinguish between different types of alkalinity and acidity depending on the reference point EP_n chosen. The carbonic acid has three integer-valued EPs; hence there are three types of *alkalinity* (cf. Fig 6.3):

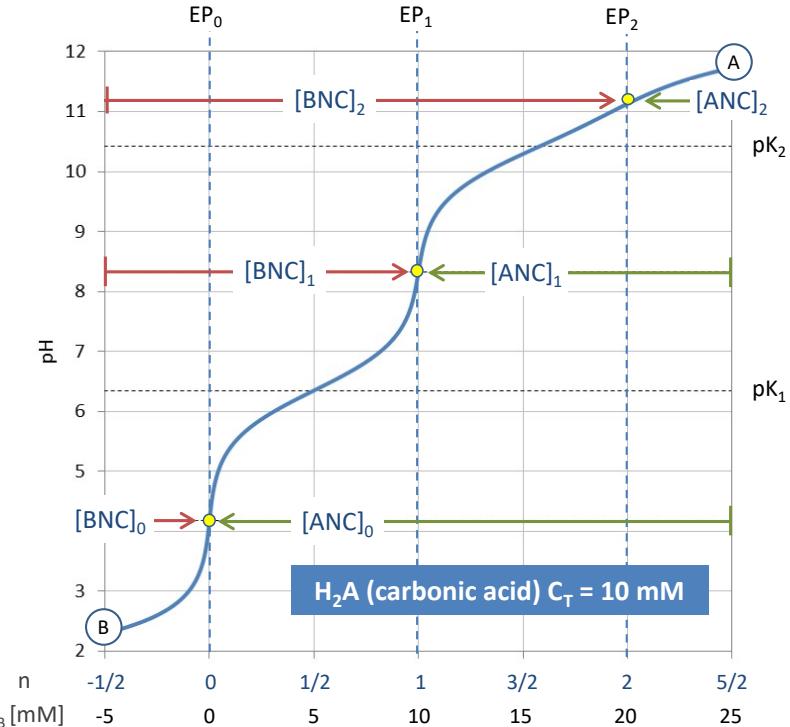


Figure 6.2:
Titration curve for carbonic acid with $[\text{ANC}]$ and $[\text{BNC}]$ values.

total alkalinity (M alkalinity): $[\text{Alk}] = [\text{ANC}]_{n=0}$

P alkalinity: $[\text{P-Alk}] = [\text{ANC}]_{n=1}$

caustic alkalinity: $[\text{OH-Alk}] = [\text{ANC}]_{n=2}$

Correspondingly, there are three types of *acidity*:

mineral acidity: $[\text{H-Acy}] = [\text{BNC}]_{n=0}$

CO_2 acidity: $[\text{CO}_2\text{-Acy}] = [\text{BNC}]_{n=1}$

acidity: $[\text{Acy}] = [\text{BNC}]_{n=2}$

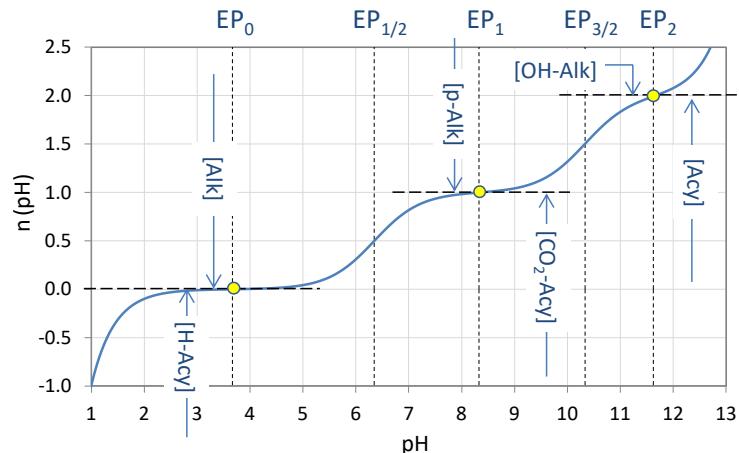


Figure 6.3: Titration curve $n=n(\text{pH})$ for carbonic acid ($C_T = 10 \text{ mM}$) with equivalence points and the corresponding types of alkalinity and acidity.

Alkalinity and acidity are complementary. From (6.5) we get:

$$\begin{aligned} [\text{ANC}]_0 &= -[\text{BNC}]_0 \implies [\text{Alk}] &= -[\text{H-Acy}] \\ [\text{ANC}]_1 &= -[\text{BNC}]_1 \implies [\text{P-Alk}] &= -[\text{CO}_2\text{-Acy}] \\ [\text{ANC}]_2 &= -[\text{BNC}]_2 \implies [\text{OH-Alk}] &= -[\text{Acy}] \end{aligned}$$

Of all three types of alkalinity, *total alkalinity* is the most important; it is given by

$$[\text{Alk}] \equiv [\text{ANC}]_0 = C_B = n C_T \quad (6.16)$$

Using (6.6), the difference between total alkalinity (M-alkalinity) and P-alkalinity yields the amount of C_T as follows:

$$[\text{Alk}] - [\text{P-Alk}] = [\text{ANC}]_0 - [\text{ANC}]_1 = C_T \quad (= \text{DIC}) \quad (6.17)$$

In carbonate systems, this is just the molar concentration of dissolved inorganic carbon (DIC).

6.1.4 pH as Reference Point of ANC and BNC

In § 6.1.1, ANC and BNC have been defined with respect to an equivalence point EP_n . ANC and BNC can also be defined with respect to a particular pH value (which can be any chosen value). In practice it is common to use the pH of the equivalence points EP_0 and EP_1 of the carbonate system:

$$\text{EP}_0: \quad \text{pH} = 4.3$$

$$\text{EP}_1: \quad \text{pH} = 8.2$$

The two EPs are shown as yellow dots in Fig 6.3. The usefulness of this choice is that these are the pH values of common indicators: indicator *methylorange* (titration endpoint 4.2 to 4.5) and indicator *phenolphthalein* (titration endpoint 8.2 to 8.3). The measured amount of strong acid or strong base to reach these endpoints are called:

$$\begin{aligned} \text{ANC to pH 4.3:} \quad & [\text{ANC}]_{\text{pH } 4.3} \simeq [\text{Alk}] \\ \text{ANC to pH 8.2:} \quad & [\text{ANC}]_{\text{pH } 8.2} \simeq [\text{P-Alk}] \\ \text{BNC to pH 4.3:} \quad & [\text{BNC}]_{\text{pH } 4.3} \simeq -[\text{Alk}] \\ \text{BNC to pH 8.2:} \quad & [\text{BNC}]_{\text{pH } 8.2} \simeq -[\text{P-Alk}] \end{aligned}$$

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

6.2 Buffer Intensity

6.2.1 From Buffer Capacity to Buffer Intensity

Let us start with the normalized buffer capacity in (6.2). Using (5.32) yields:

$$\text{normalized buffer capacity: } \Delta n(\text{pH}) = \{ Y_1(\text{pH}) - j \} + \frac{w(\text{pH})}{C_T} \quad (6.18)$$

The derivative with respect to pH gives:

$$\text{normalized buffer intensity: } \beta \equiv \frac{d \Delta n}{d \text{pH}} = \frac{dn}{d \text{pH}} \quad (\text{unitless}) \quad (6.19)$$

$$\text{buffer intensity: } \beta_C \equiv \frac{d C_B}{d \text{pH}} = \beta C_B \quad (\text{in mM}) \quad (6.20)$$

[Note: The last equation is valid if $C_T = \text{const}$ (standard case), otherwise we have to use $dC_B/d\text{pH} = \beta C_T + n(dC_T/d\text{pH})$.]

The acid-neutralizing capacity is re-established by integrating β_C over a definite pH interval (usually starting from an equivalence point EP_n):

$$[\text{ANC}]_n = \int_{\text{pH}_n}^{\text{pH}} \beta_C(\widetilde{\text{pH}}) d\widetilde{\text{pH}} \quad (6.21)$$

To perform the 1st and 2nd pH derivative of (6.18) we apply the formulas in Appendix B.4, in particular (B.40) and (B.41) for $w(\text{pH})$ as well as (B.50) and (B.53) for $Y_1(\text{pH})$. We get:

$$\text{norm. buffer intensity: } \beta(x) \equiv \frac{dn}{d\text{pH}} = (\ln 10) \left(Y_2 - Y_1^2 + \frac{w + 2x}{C_T} \right) \quad (6.22)$$

$$1^{\text{st}} \text{ derivative of } \beta: \quad \frac{d\beta}{d\text{pH}} = (\ln 10)^2 \left(Y_3 - 3Y_1Y_2 + 2Y_1^3 + \frac{w}{C_T} \right) \quad (6.23)$$

Fig 6.4 displays the titration curve (blue) together with the buffer intensity β (green) and its 1st derivative (red) for the H₂CO₃ system with $C_T = 100$ mM. The calculations are performed using equations (6.18), (6.22), and (6.23). The small circles indicate the EPs and semi-EPs. The EPs are the extremum points of β :

$$\begin{aligned} \text{EP}_n: \quad (\text{integer } n) &\Leftrightarrow \text{minimum buffer intensity } \beta \\ \text{semi-EP}_j: \quad (\text{half-integer } n) &\Leftrightarrow \text{maximum buffer intensity } \beta \end{aligned}$$

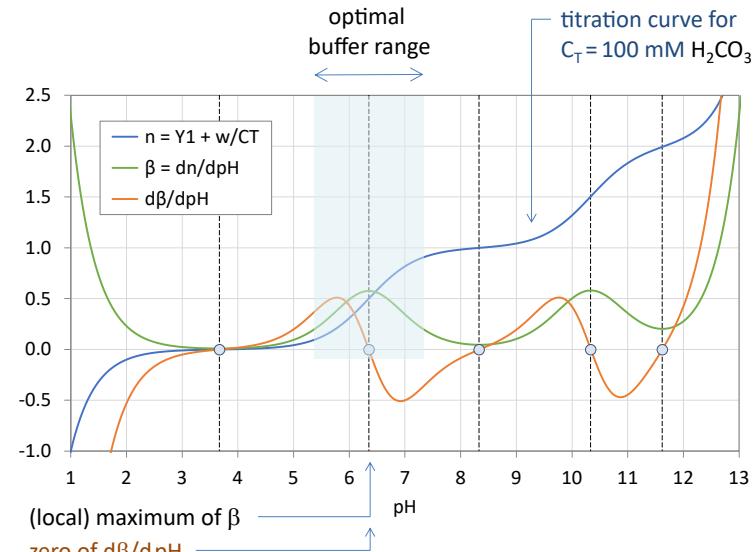


Figure 6.4: Optimal buffer range of the H₂CO₃ system with $C_T = 100$ mM.

A good pH buffer should mitigate pH changes when the system is attacked by a strong base or strong acid. It means that the pH change, ΔpH , should be small when $n = C_B/C_T$ changes by Δn . In other words, the *slope* of the titration curve in Fig 6.4, $\Delta n/\Delta\text{pH}$, should be large for maximum buffering capability. The buffer intensity,

$\beta = dn/dpH$, is just the measure of this slope. Thus, the pH at the point where β reaches its maximum signals the optimal buffer range (bounded by $pH_{max} \pm 1$).

More examples are given in Fig 6.5 and Fig 6.7. Since each titration curve (blue) is an ever-increasing function, its pH derivative, i.e. the buffer intensity β , is always positive (green curves).

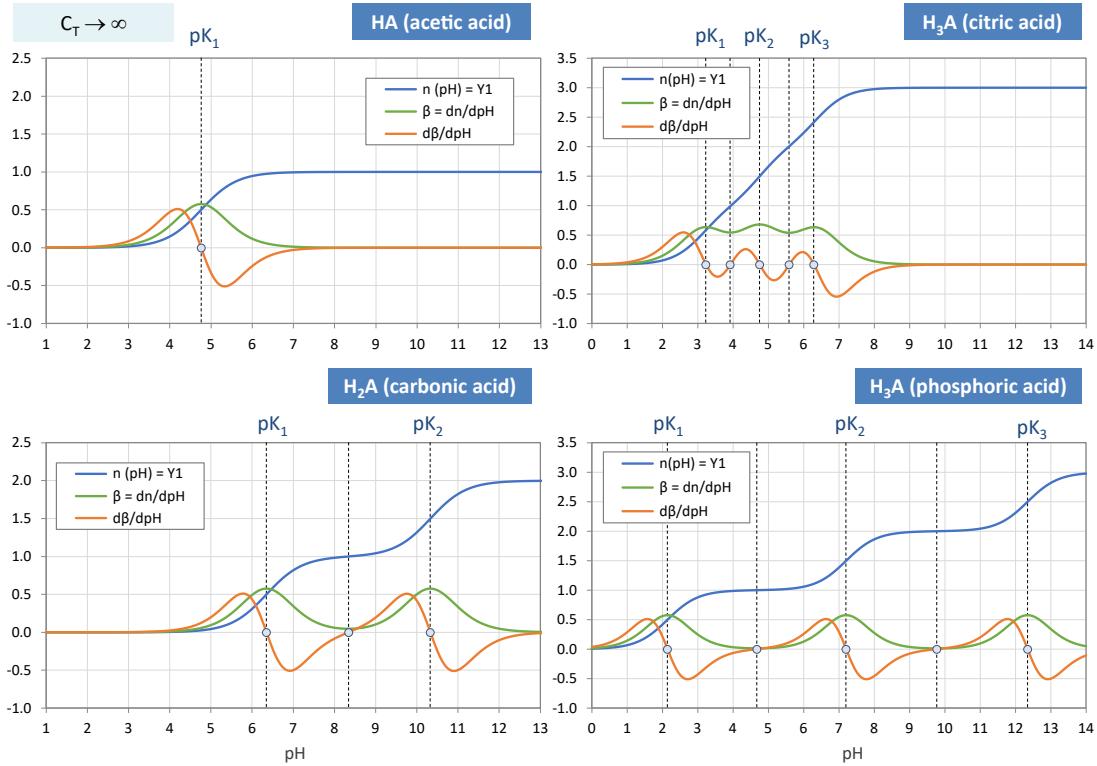


Figure 6.5: Normalized buffer capacity (blue), buffer intensity (green), and $d\beta/dpH$ (red) for four acids and $C_T \rightarrow \infty$ (i.e. $C_T/w \gg 1$). Maxima and minima of the buffer intensity β (green) are located at zeros of $d\beta/dpH$ (small circles on red curves).

6.2.2 Minima and Maxima (High- C_T Limit)

Equations (6.18), (6.22) and (6.23) simplify for large values of C_T (“high- C_T limit”), where the last term in the above equations (containing C_T in the denominator) vanish. Hence, for $C_T \gg w$ we have:

$$\text{norm. buffer capacity: } \Delta n(pH) = Y_1(pH) - j \quad (6.24)$$

$$\text{norm. buffer intensity: } \beta(pH) = (\ln 10) (Y_2 - Y_1^2) \quad (6.25)$$

$$\text{1st derivative of } \beta: \frac{d\beta}{dpH} = (\ln 10)^2 (Y_3 - 3Y_1 Y_2 + 2Y_1^3) \quad (6.26)$$

These are smooth functions made of Y_1 , Y_2 , and Y_3 alone. The behavior of Y_L is entirely determined by the set of the acid’s equilibrium constants K_j , or alternatively, by the *internal* equivalence points EP_n as given in (3.82) and (3.83):

$$\text{semi-EP}_j \text{ at } pK_j : \quad Y_L = \frac{1}{2} \{(j-1)^L + j^L\} \quad (n = j - \frac{1}{2}) \quad (6.27)$$

$$\text{EP}_j \text{ at } pH_j \equiv \frac{1}{2} (pK_j + pK_{j+1}) : \quad Y_L \simeq j^L \quad (n = j) \quad (6.28)$$

Inserting it into (6.25) yields

$$\frac{\beta(pK_j)}{\ln 10} = Y_2(pK_j) - Y_1^2(pK_j) = \{j(j-1) + \frac{1}{2}\} - \{j(j-1) + \frac{1}{4}\} = \frac{1}{4} \quad (6.29)$$

$$\frac{\beta(pH_j)}{\ln 10} = Y_2(pH_j) - Y_1^2(pH_j) = j^2 - j^2 = 0 \quad (6.30)$$

Now, we prove that these equivalence points are *extremum points* of the buffer intensity. In math, the maximum or minimum is known to be the point at which the slope (i.e. the derivative) of a function becomes zero. Hence, local maxima and minima of the buffer intensity $\beta(pH)$ occur at pH values where $d\beta/dpH = 0$. The derivative itself is given in (6.26), 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 (6.27):

$$\begin{aligned} Y_3 - 3Y_1Y_2 + 2Y_1^3 &= \frac{1}{2}\{(j-1)^3 + j^3\} - 3(j-\frac{1}{2})\{j(j-1) + \frac{1}{2}\} + 2(j-\frac{1}{2})^3 \\ &= 0 \quad \text{at } pH = pK_j \quad \text{for } j = 1, 2, \dots N \end{aligned} \quad (6.31)$$

For the EP_n with integer $n = j$, we get from (6.28):

$$\begin{aligned} Y_3 - 3Y_1Y_2 + 2Y_1^3 &= j^3 - 3j j^2 + 2j^3 \\ &= 0 \quad \text{at } pH = pH_j \quad \text{for } j = 1, 2, \dots N-1 \end{aligned} \quad (6.32)$$

Hence, the zeros of $d\beta/dpH$ occur exactly at the *internal* equivalence points EP_n for both integer and half-integer n . To decide whether the zeros indicate a *maximum* or *minimum*, we need the next higher derivative $d^2\beta/dpH^2$ (or d^3Y_1/dpH^3 , which is presented in (B.54) in Appendix B.4.3).

Summary

The following assignment is valid for $C_T/w \gg 1$:

$$\text{semi-EP}_j \text{ at } pK_j \iff \text{maximum of } \beta \quad (d^3Y_1/dpH^3|_{pK_j} < 0) \quad (6.33)$$

$$\text{EP}_j \text{ at } pH_j \iff \text{minimum of } \beta \quad (d^3Y_1/dpH^3|_{pH_j} > 0) \quad (6.34)$$

The buffer intensity attains its maximum at semi-equivalence points located at pK_j . The actual values of β at this extrema were already presented in (6.29) and (6.30):

$$\text{maxima of } \beta \text{ at semi-EP}_j : \beta_{\max} = \frac{\ln 10}{4} \simeq 0.576 \quad \text{for half-integer } n \quad (6.35)$$

$$\text{minima of } \beta \text{ at EP}_j : \beta_{\min} = 0 \quad \text{for } n = 1, 2, \dots N-1 \quad (6.36)$$

This behavior of the buffer intensity is illustrated in Fig 6.5 for four acids. The maxima of β (green curve) are indicated by the corresponding pK_j values, while the zeros of $d\beta/dpH$ (red curve) are marked by small blue dots.

Example: Carbonate System

The carbonate system, as shown in the bottom-left diagram of Fig 6.5, 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 β is located at $pH_1 = \frac{1}{2}(pK_1 + pK_{j+1}) = 8.34$ (which is an integer-valued EP).

6.2.3 The General Case

§ 6.2.2 was focused on large values of C_T ($\gg w$). Now, the more realistic case of small C_T values considers the effect of the autoprotolysis of H₂O through the last term in (6.18), (6.22) and (6.23). The results are displayed in diagrams, each containing three curves:

- $n(\text{pH})$ buffer capacity Eq (6.18) (blue curve)
- $\beta = dn/d\text{pH}$ buffer intensity Eq (6.22) (green curve)
- $d\beta/d\text{pH}$ 1st derivative of β Eq (6.23) (red curve)

All three quantities are unitless. The small blue circles mark the zeros of $d\beta/d\text{pH}$, which correspond to the minima and maxima of the buffer intensity β .

Example: Carbonate System

Given is the carbonic acid system with $C_T = 100 \text{ mM}$, 10 mM , and 1 mM H₂CO₃; the results are shown in Fig 6.6.

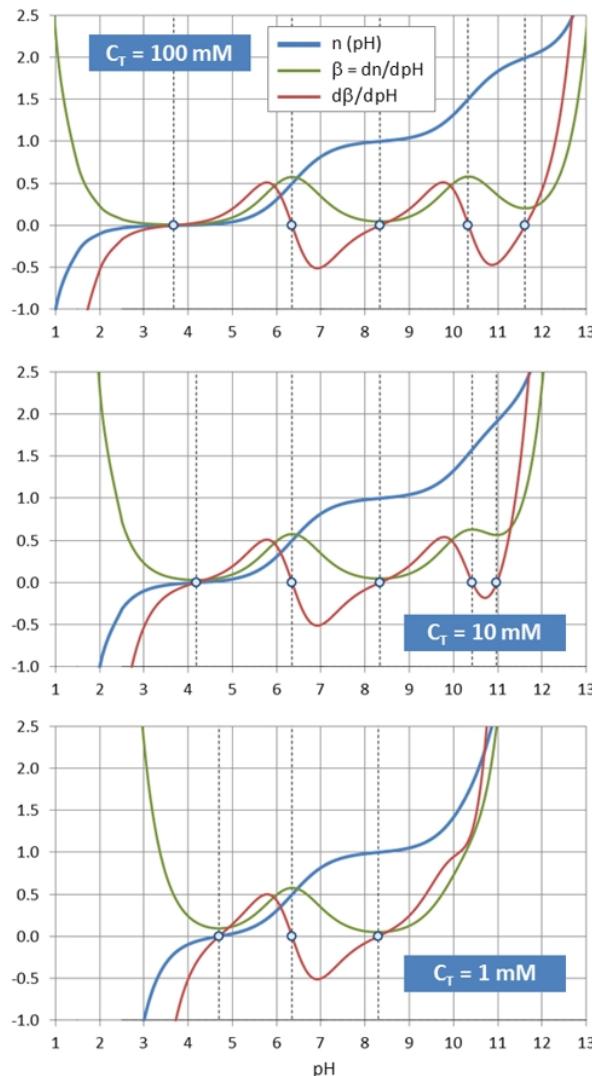


Figure 6.6: Titration curve $n(\text{pH})$, buffer intensity β , and $d\beta/d\text{pH}$ for three C_T values of the carbonate system.

Example: Four Common Acids

Fig 6.7 to Fig 6.9 displays the results for four common acids with an amount of $C_T = 100 \text{ mM}$, 10 mM , and 1 mM . These results should be compared with the curves for the case $C_T \rightarrow \infty$ in Fig 6.5 on page 63.

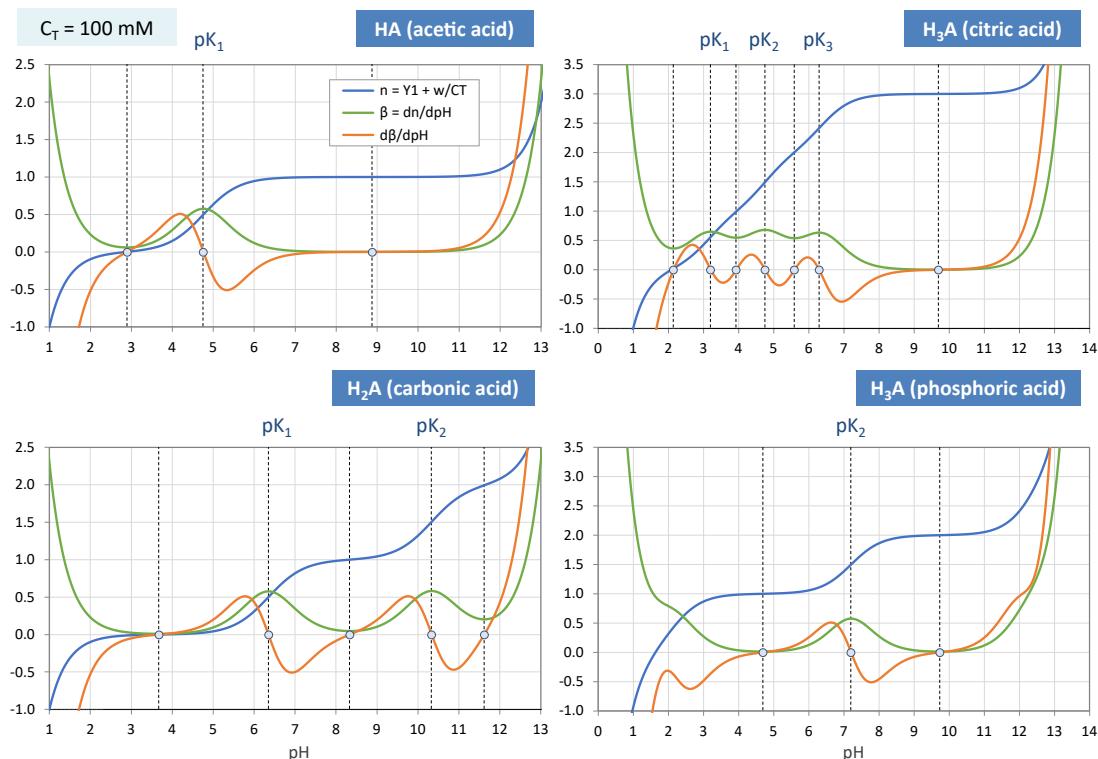


Figure 6.7: Titration curve (blue), buffer intensity (green), and $d\beta/dpH$ (red) for four common acids with $C_T = 100 \text{ mM}$.

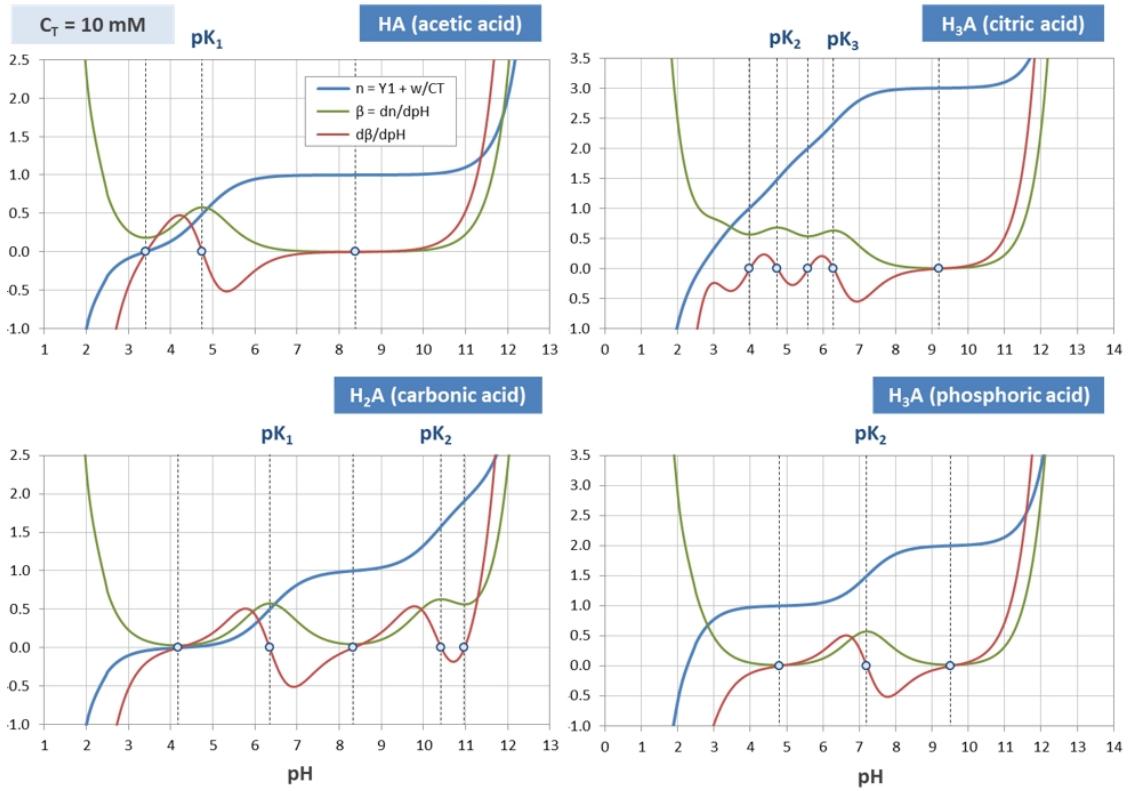


Figure 6.8: Titration curve (blue), buffer intensity (green), and $d\beta/d\text{pH}$ (red) for four common acids with $C_T = 10 \text{ mM}$.

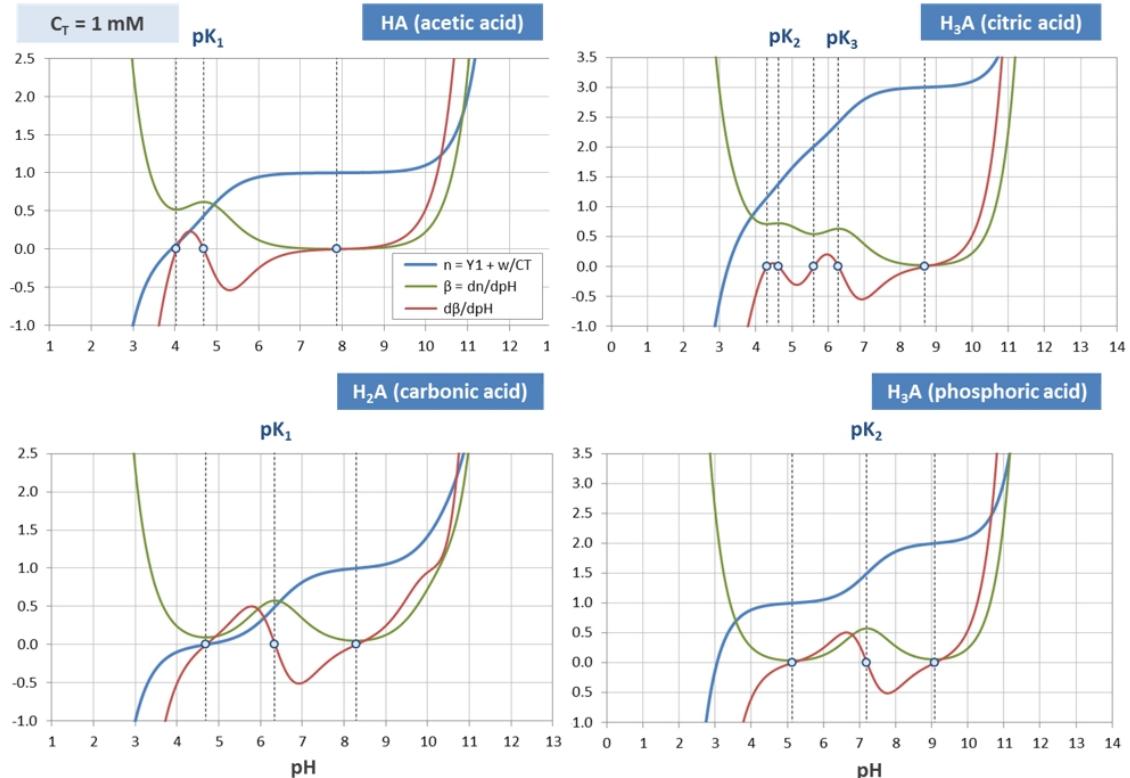


Figure 6.9: Titration curve (blue), buffer intensity (green), and $d\beta/d\text{pH}$ (red) for four common acids with $C_T = 1 \text{ mM}$.

*The archer who overshoots the target misses
as much as the one who does not reach it.*

— Montaigne

7

Application: Carbonate System

Contents

7.1	Relationships between pH, C_T , and Alkalinity	69
7.2	Three Equivalence Points	70
7.3	Acid–Base Titration with H_2CO_3 as Titrant	72
7.4	Open vs Closed CO_2 System	73
7.5	Seawater	75
7.6	From Ideal to Real Solutions	75

7.1 Relationships between pH, C_T , and Alkalinity

The actual equilibrium state of a diprotic acid H_2A (i.e. the concentrations of the three aqueous species $[j]$: H_2A , HA^- , and A^{2-}) is completely controlled by two parameters chosen from the triple (C_T, n, pH) or (C_T, C_B, pH) , where $C_B = n C_T = \text{Alk}$ (see (6.16)). Once we know two of them, the third is inevitably fixed:

$$\text{pH}(C_T, n) = -\lg x_n \text{ with } x_n \text{ as positive root of (5.38), } [j] = C_T a_j \quad (7.1)$$

$$\text{pH}(C_T, \text{Alk}) = -\lg x_n \text{ with } x_n \text{ as positive root of (5.39), } [j] = C_T a_j \quad (7.2)$$

$$n(C_T, \text{pH}) = a_1 + 2a_2 + w/C_T, \quad [j] = C_T a_j \quad (7.3)$$

$$\text{Alk}(C_T, \text{pH}) = C_T (a_1 + 2a_2) + w, \quad [j] = C_T a_j \quad (7.4)$$

$$C_T(n, \text{pH}) = w/(n - a_1 - 2a_2), \quad [j] = (w/(n - a_1 - 2a_2)) a_j \quad (7.5)$$

$$C_T(\text{Alk}, \text{pH}) = (\text{Alk} - w)/(a_1 + 2a_2), \quad [j] = (\text{Alk} - w)/(a_1 + 2a_2) a_j \quad (7.6)$$

These nonlinear relationships are displayed for carbonic acid in Fig 7.1 and Fig 7.2. The diagrams show all possible combinations of 1 dependent and 2 independent variables taken from the triple C_T , pH, and n (or $\text{Alk} = nC_T$). Note how the “simple transformation” of the variable n into $\text{Alk} = nC_T$ dramatically changes the shape of the curves in Fig 7.2 (compared to Fig 7.1).

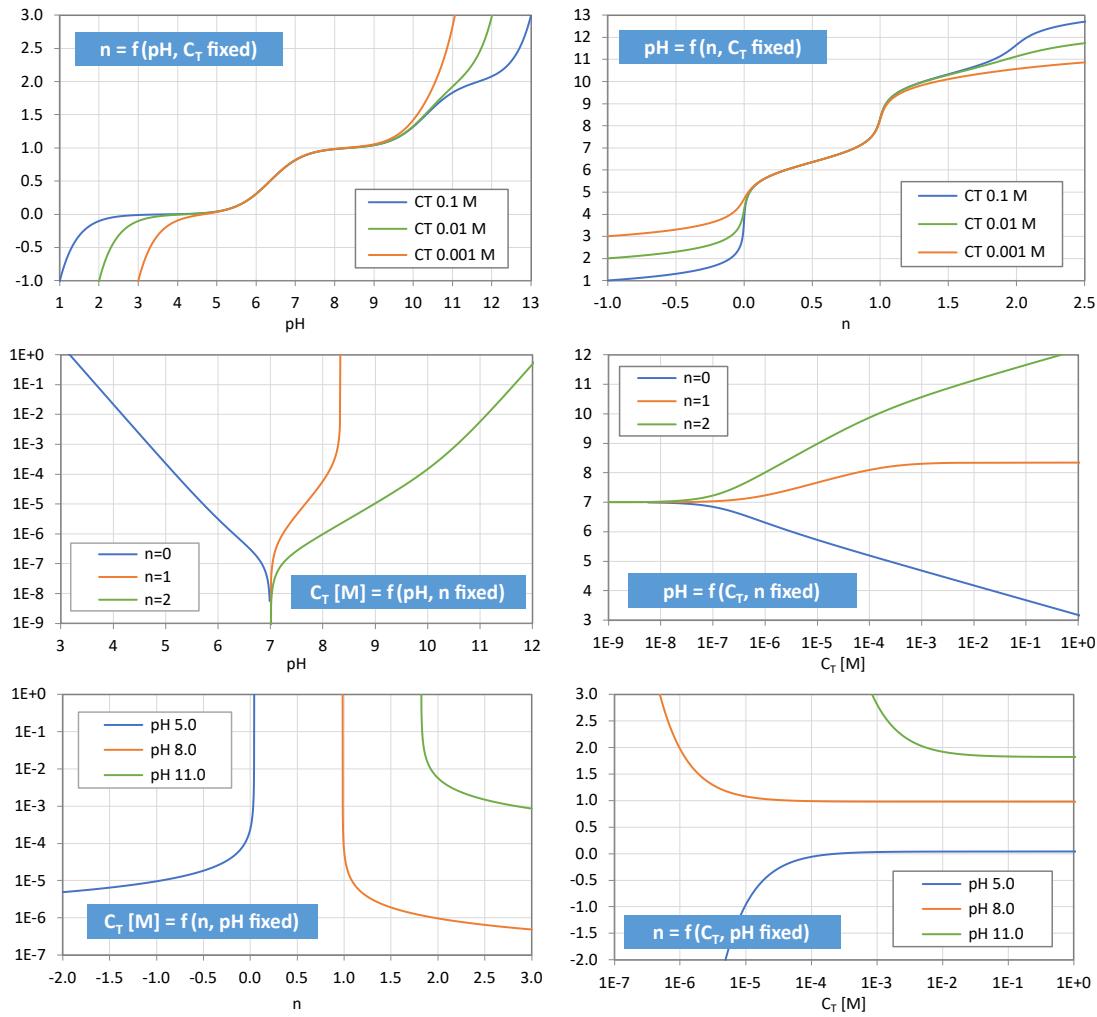


Figure 7.1: Relationships between pH, C_T , and n for the carbonic acid system (at 25 °C).

7.2 Three Equivalence Points

The carbonate system controls the pH in most natural waters. Due to the existence of three major carbonate species (CO_2 , HCO_3^- , CO_3^{2-}), textbooks usually focus on three equivalence points:

- EP₀ (also known as EP of CO_2): $[\text{H}^+] = [\text{HCO}_3^-]$
- EP₁ (also known as EP of HCO_3^-): $[\text{H}_2\text{CO}_3] = [\text{CO}_3^{2-}]$
- EP₂ (also known as EP of CO_3^{2-}): $[\text{HCO}_3^-] = [\text{OH}^-]$

The identification of EPs as points of equal species concentrations, as done here on the right-hand side, is an approximation, albeit a very good one. In BJERRUM plots, these are points of intersections of two concentration curves. Fig 7.3 maps the intersection points from the two lower diagrams (one for $C_T = 10^{-3} \text{ M}$ and one for 10^{-4} M) upwards into the pH- C_T diagram where they constitute the small circles on the EP trajectories.

Here, we observe a different behavior for the two *external* equivalence points (EP₀ and EP₂) on the one hand and for the single *internal* equivalence point EP₁ on the other hand.

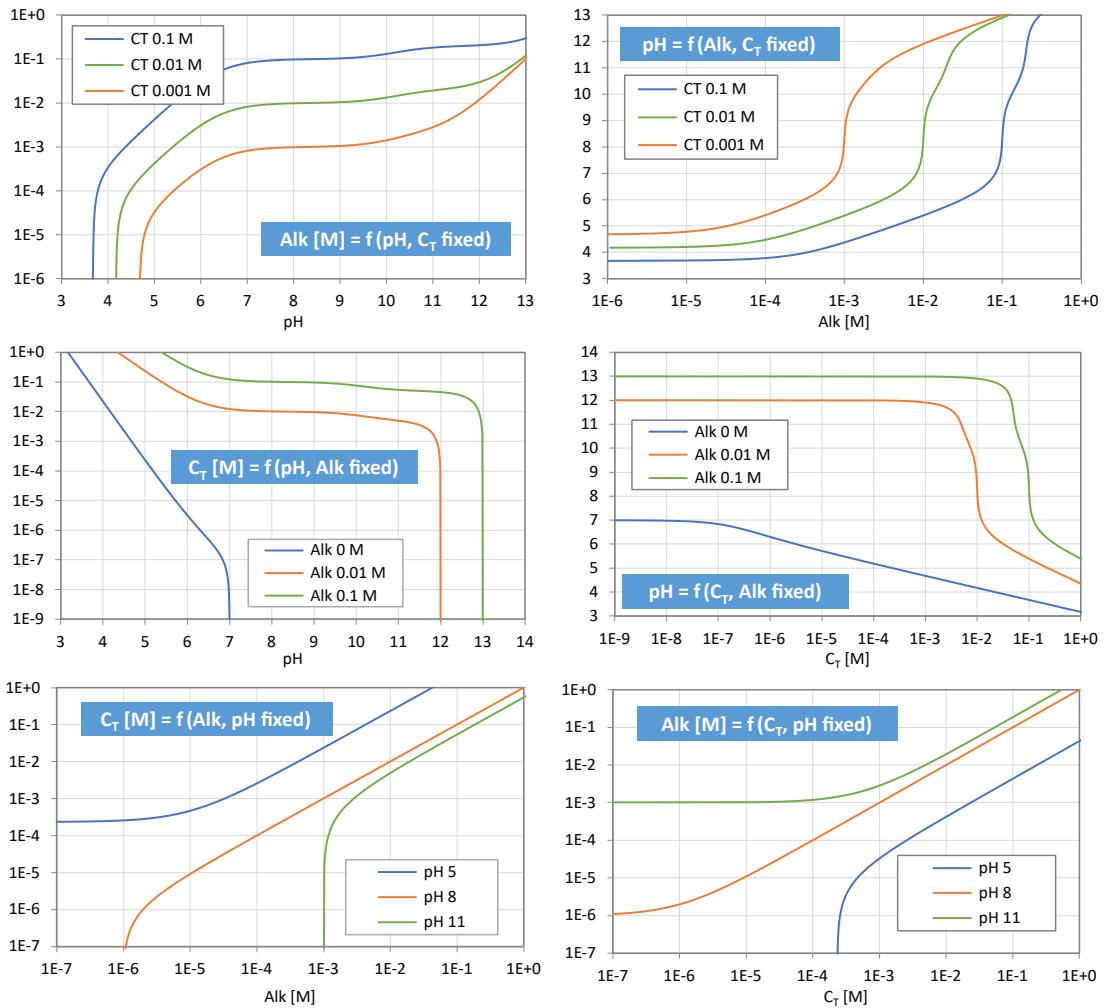


Figure 7.2: Relationships between pH, C_T , and Alk for the carbonic acid system (at 25 °C).

Two External Equivalence Points: EP_0 and EP_2

The two external EPs depend on C_T :

	$C_T = 10^{-4}$ M	$C_T = 10^{-3}$ M
EP_0 at pH	5.18	4.68
EP_2 at pH	9.86	10.56

One Internal Equivalence Point: EP_1

The EP_1 does not depend on C_T . The intersection points of the CO_2 and CO_3^{2-} curves in the two lower diagrams in Fig 7.3 are both at the same fixed pH value of $\frac{1}{2} (\text{p}K_1 + \text{p}K_2) = 8.34$, which belongs to the high- C_T limit of the red curve in the upper diagram. Only when we decrease C_T further below 10^{-4} M, i.e. for very dilute acids, the simple relationship $[\text{CO}_2] = [\text{CO}_3^{2-}]$ no longer works correctly.

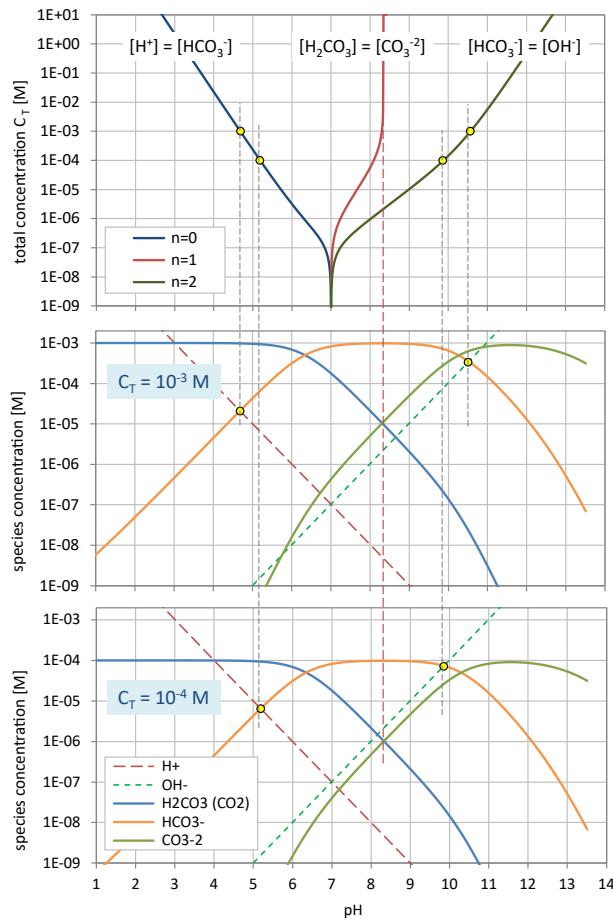


Figure 7.3: Equivalence points of the carbonate system. Assignment of the EPs in the upper pH- C_T diagram to the intersection points of curves of species concentrations (two lower diagrams).

7.3 Acid–Base Titration with H_2CO_3 as Titrant

During titration, a *titrant* is added to the *analyte* to reach the target pH or equivalence point. Two cases (which are opposite of each other) will be considered:

var A: 100 mM H_2CO_3 solution is titrated by a strong base/acid (NaOH and HCl)

var B: 100 mM NaOH solution is titrated by H_2CO_3

In **var A** the C_T is kept fixed (and C_B is varied), while in **var B** the C_B is kept fixed (and C_T is varied). The aim is to calculate the carbonate speciation as a function of pH. In both cases, we start with the ionization fractions a_j (based on (3.58) and shown in the bottom left diagram in Fig 3.4), which are the same for **var A** and **var B**. From each a_j , we then get the species concentration by multiplication with C_T : $[j] = C_T a_j$. The main point is that **var A** and **var B** differ in the C_T value:

var A: $C_T = \text{const}$ with $C_T = 100 \text{ mM}$

var B: $C_T = (C_B - w)/Y_1$ with $C_B = 100 \text{ mM}$

where the last line is taken from (5.32).

The obtained species distribution is displayed in Fig 7.4: **var A** (left) and **var B** (right). The gray curve represents the total concentration C_T as the sum of all

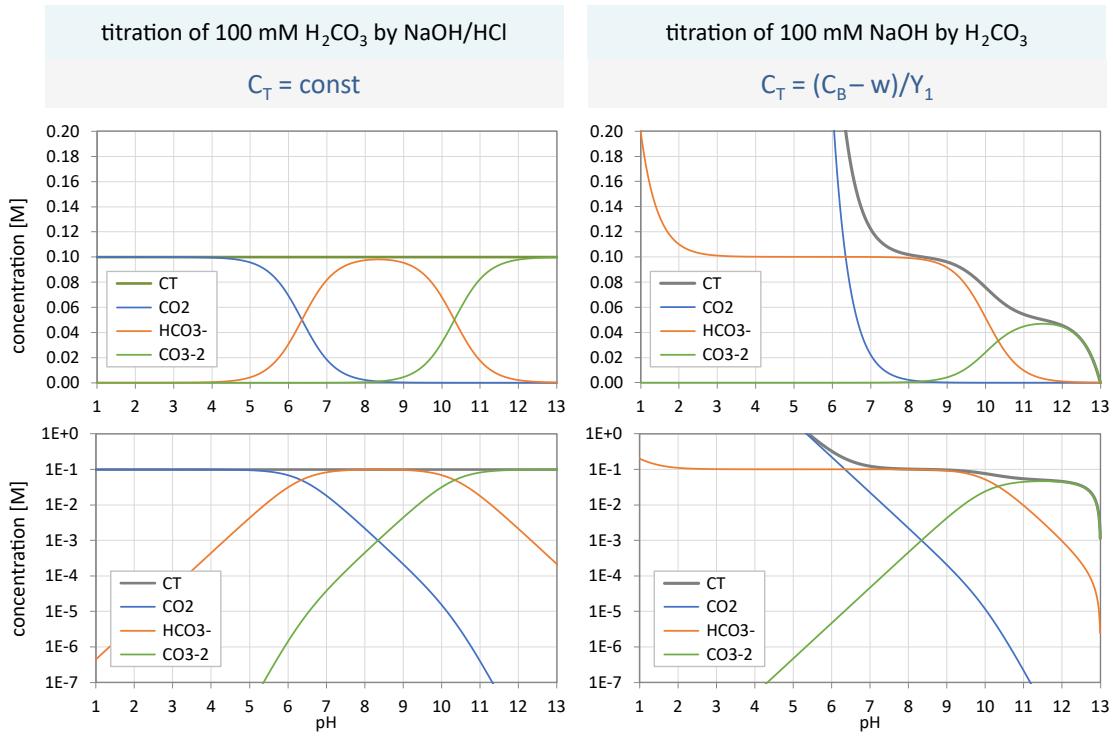


Figure 7.4: Species distribution of H_2CO_3 as a function of pH for **var A** (left) and **var B** (right). Top diagrams: concentrations in linear scale; bottom diagrams: logarithmic scale.

carbonate species. The top and bottom diagrams only differ by the concentration scale: the y -axis is linear or logarithmic, respectively.

Although both variants rely on exactly the same ionization fractions, the pH dependence of the species in **var A** (left) and **var B** differ significantly. While the species distribution in **var A** (top left) replicates the shapes of the ionization fractions, **var B** is completely out of line. [Note: In **var B**, pH < 5 is not available in practice.]

7.4 Open vs Closed CO₂ System

In an *open* CO₂ system, the solution is in equilibrium with the CO₂ of the atmosphere. Let us compare it with the closed system:

var A: titration of 100 mM H₂CO₃ solution as “closed CO₂ system”
 (same as in § 7.3)

var C: titration of 100 mM H₂CO₃ solution as “open CO₂ system”

As in § 7.3, we start with the same ionization fractions a_j for both **var A** and **var C**, as shown in the left bottom diagram in Fig 3.4. As in § 7.3, the two variants differ only in the functional dependence of C_T , which will be derived now.

The “open system” is described by HENRY’s law that partitions the CO₂ between the aqueous and gas phase: CO₂(aq) is proportional to CO₂(g), whereas CO₂(aq) is the undissociated acid H₂CO₃, i.e., the uncharged species [0]. Thus, we can write:

$$[0] = K_H \cdot P \quad \text{with} \quad K_H = 10^{-1.47} \text{ M/atm (at } 25^\circ\text{C}) \quad (7.7)$$

and with P as the partial CO_2 pressure. Using $[0] = C_T a_0$, we obtain:

$$\text{open } \text{CO}_2 \text{ system : } C_T = \frac{K_H P}{a_0} \quad (7.8)$$

Thus, the two variants differ in the C_T value:

var A: $C_T = \text{const}$ with $C_T = 100 \text{ mM}$

var C: $C_T = K_H P/a_0$ with $P = 0.00039 \text{ atm} (= 10^{-3.408} \text{ atm})$

The carbonate speciation is displayed in Fig 7.5: **var A** (left) and **var C** (right).

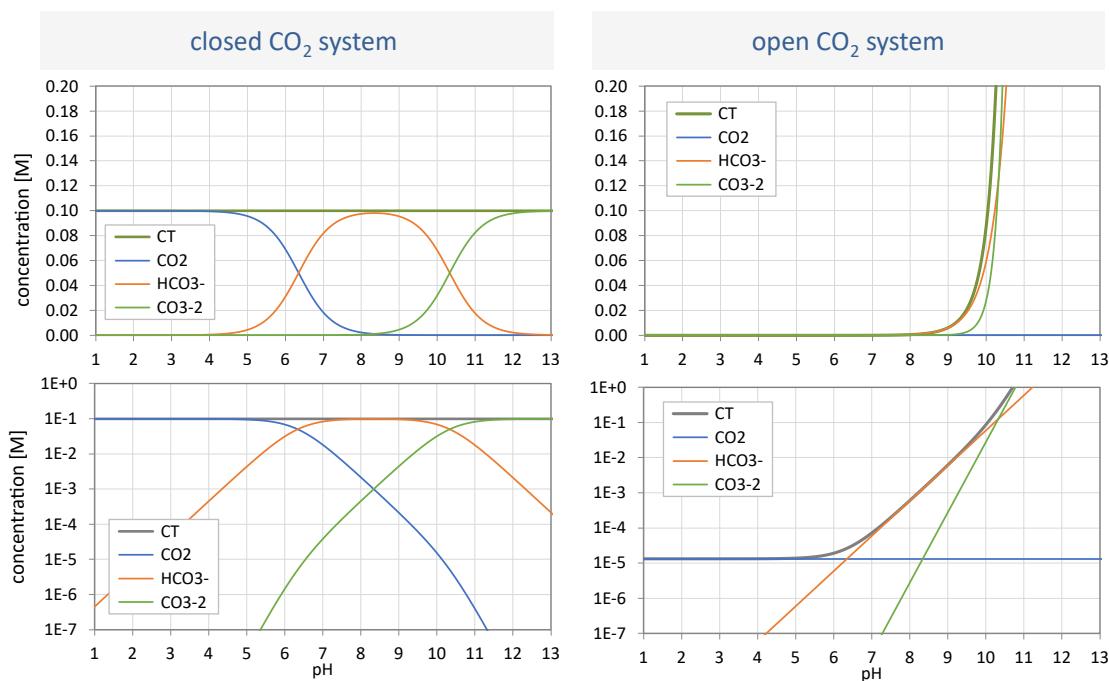


Figure 7.5: Species distribution of H_2CO_3 as a function of pH for **var A** (left) and **var C** (right). Top diagrams: concentrations in linear scale; bottom diagrams: log scale.

The conclusions are similar to § 7.3. Although both variants rely on exactly the same ionization fractions, the pH dependence of the species in **var A** and **var C** is completely different. While the species distribution in **var A** (top left) replicates the shapes of the ionization fractions, **var C** does not. The more alkaline the solution becomes, the more CO_2 is sucked out of the atmosphere (which increases the C_T exponentially). [Note: In **var C**, $\text{pH} < 5$ is not available in practice.]

Resume

The three variants (**var A**, **var B**, **var C**) discussed in the last two Sections exhibit the *universality* of the ionization fractions a_j (shown in the bottom left diagram in Fig 3.4). They are independent of the chosen model, i.e. the functional dependence of C_T .

7.5 Seawater

The analytical formulas in (5.32) and (5.49) are based on the assumption that activities could be replaced by concentrations, $\{j\} \rightarrow [j]$. This is valid either for dilute systems with near-zero ionic strength ($I \simeq 0$), or for non-dilute systems when the thdyn equilibrium constants are replaced by conditional constants, $K \rightarrow {}^c K$.

Seawater has $I \simeq 0.7$ M, which is at the upper limit of the validity range of common activity models (as discussed in Appendix A.2). Hence, in oceanography, chemists prefer conditional equilibrium constants ${}^c K$. In the literature, there are several compilations for ${}^c K$; one example is given in Table 7.1.

Table 7.1: Thermodynamic and conditional equilibrium constants for H_2CO_3 in pure water and seawater (at 25 °C, 1 atm); ${}^c K$ values from [40].

	thdyn K (pure water, $I = 0$)	conditional ${}^c K$ (seawater, $I = 0.7$ M)
pK ₁	5.18	6.0
pK ₂	10.33	9.1
pK _w	14.0	13.1

Fig 7.6 (left diagram) compares the results calculated by (5.49) for both the standard case (solid lines based on thdyn equilibrium constants K) and seawater (dashed lines based on conditional constants ${}^c K$). The solid curves in Fig 7.6 are identical to the solid curves for $n = 0, 1$, and 2 shown in the bottom left diagram in Fig 5.10.

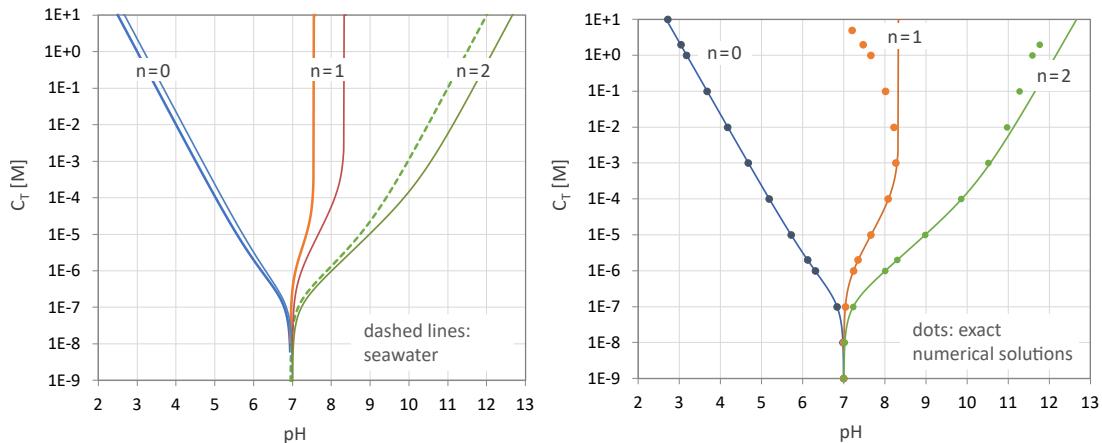


Figure 7.6: pH– C_T diagrams of the carbonic-acid system. Left: H_2CO_3 in pure water (solid lines) vs H_2CO_3 in seawater (dashed lines). Right: closed-form expression (5.49) vs numerical model (dots).

7.6 From Ideal to Real Solutions

All calculations so far (except in § 7.5) were performed for the *ideal* case (i.e., no activity corrections, no aqueous complexation). Modern hydrochemistry software

does not adhere to those restrictions; they perform activity corrections “automatically”. In this respect, they are able to predict the relationship between pH and a given C_T for *real* systems more accurately.

Given is a carbonic acid system titrated with NaOH. Fig 7.6 (right diagram) compares the results of the analytical formula (5.49) (solid lines) with the numerical-model predictions (dots) using PhreeqC [33] or aqion [37]. (Similar results are obtained when NaOH is replaced by KOH.)

As expected, deviations between the ideal and the real case only occur at high C_T values. There are two reasons: (i) with rising C_T , the ionic strength increases; consequently, the activity corrections are large and cannot be ignored; and (ii) numerical models consider the formation of aquatic complexes such as NaHCO_3^- and $\text{Na}_2\text{CO}_3(\text{aq})$, which are absent in the analytical approach. The aquatic complexes become particularly relevant at high concentrations for $n = 1$ and 2. [Note: At very high values of C_T between 1 and 10 M Na_2CO_3 (i.e., the most upper part of the green curve), we exit the applicability range of common activation models.]

Our best advice is surely that offered by WITTGENSTEIN: to pass over in silence what we cannot talk about.

— Folklore

8

Additional Topics

Contents

8.1 Strong Polyprotic Acids	77
8.2 Mixtures of Acids	79
8.3 H_NA as Superposition of N Monoprotic Acids	79

8.1 Strong Polyprotic Acids

The math description of *strong* polyprotic acids is simpler than that of weak polyprotic acids, since strong acids never occur in the undissociated state at pH $\gtrsim 0$ (at least one H⁺ is always released).¹

Because the amount of the undissociated species is zero, $[0] = 0$ or $a_0 = 0$, it is not necessary to explicitly calculate the first dissociation step. In other words, we can remove (5.21) or (5.27) from our set of $N+3$ equations and completely forego the first dissociation constant K_1 (keeping in mind that K_1 is a large number — as discussed in § 2.1.4). That is good news, because the first dissociation constant of strong acids is often not known precisely enough.

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

$$\text{strong acid: } \frac{x}{K_1} \rightarrow 0 \quad \text{for all practice relevant } x \text{ (i.e. } x \leq 1\text{)} \quad (8.1)$$

Thus, we divide our analytical formulas by K_1 and then set all terms containing x/K_1 to zero (this is demonstrated, for example, in Appendix B.2.2 for the ionization fractions). In this way, K_1 disappears from all equations:

¹as shown in Fig 2.1 on page 11

general case	strong acid
$K_1, K_2, \dots, K_N \Rightarrow \cancel{K_1}, K_2, \dots, K_N$	

The cumulative acidity constants k_j in (3.60) are also redefined:

$$k_1 = K_1 \quad \Rightarrow \quad k_1 = 1 \quad (8.2)$$

$$k_2 = K_1 K_2 \quad \Rightarrow \quad k_2 = K_2 \quad (8.3)$$

$$k_3 = K_1 K_2 K_3 \quad \Rightarrow \quad k_3 = K_2 K_3 \quad (8.4)$$

and so on.

Ionization Fractions

The ionization fractions a_j , originally defined in (3.58), simplify as follows:

general case	strong acid
$a_0 = \left(1 + \frac{K_1}{x} + \frac{K_1 K_2}{x^2} + \dots\right)^{-1}$	$\Rightarrow a_0 = 0$
$a_1 = \left(\frac{x}{K_1} + 1 + \frac{K_2}{x} + \dots\right)^{-1}$	$\Rightarrow a_1 = \left(1 + \frac{K_2}{x} + \frac{K_2 K_3}{x^2} + \dots\right)^{-1}$
$a_j = \left(\frac{k_j}{x^j}\right) a_0$	$\Rightarrow a_j = \left(\frac{k_j}{x^{j-1}}\right) a_1 \quad \text{for } j > 1$

For the derivation see Appendix B.2.2.

Polynomials

For strong acids, the polynomial in (5.35) becomes one degree less in x (Note that the summation now starts with $j = 1$):

$$0 = \sum_{j=1}^N \{x^2 + (n-j)C_T x - K_w\} k_j x^{N-j} \quad (8.8)$$

Example $N = 1$

For a strong monoprotic acid, the sum in (8.8) runs only over one single term, namely $j = 1$. With $k_1 = 1$, we get a *quadratic* equation:

$$0 = x^2 + (n-1)C_T x - K_w \quad (8.9)$$

Note that this equation does not contain any acidity constant.

Example $N = 2$

For a strong diprotic acid, the polynomial in (8.8) becomes a *cubic* equation:

$$0 = x^3 + \{(n-1)C_T + K_2\} x^2 + \{(n-2)C_T K_2 - K_w\} x - K_2 K_w \quad (8.10)$$

This equation can also be derived from (5.38) by applying the condition $x/K_1 = 0$ from (8.1).

8.2 Mixtures of Acids

Until now we considered acid–base systems with *one* polyprotic acid. It is not difficult to extend the approach to mixtures of several polyprotic acids:

$$\text{acid a} + \text{acid b} + \text{acid c} + \dots \quad \text{with amounts of } C_a, C_b, C_c, \dots$$

The total sum of all acids will be abbreviated by $C_T = C_a + C_b + C_c + \dots$. The equivalent fraction $n = n(x)$, i.e. the titration curve, of the multi-acid system (plus a strong base of amount $C_B = nC_T$) is then described by:

$$n = \tilde{Y}_1(x) + \frac{w(x)}{C_T} \quad (8.11)$$

It has the same structure as (5.32), except Y_1 is replaced by the *generalized* moment \tilde{Y}_1 as a superposition of the individual acid's Y_1 :

$$\tilde{Y}_1 = n_a Y_1^{(a)} + n_b Y_1^{(b)} + n_c Y_1^{(c)} + \dots \quad \text{with coefficients } n_\alpha = \frac{C_\alpha}{C_T} \quad (8.12)$$

The generalized moments \tilde{Y}_L (here for $L=1$) are built in the usual way from the ionization fractions (i.e. according to (3.77)):

$$Y_L^{(\alpha)} \equiv \sum_{j=0}^{N_\alpha} j^L a_j^{(\alpha)} \quad (8.13)$$

Here the ionization fractions $a_j^{(\alpha)}$ are determined by the (cumulative) acidity constants $k_j^{(\alpha)}$ of the individual acids, according to (3.25). The sum runs from $j = 1$ to N_α , which is the number of protons of acid α ($= a, b, c$).

Example: $\text{H}_3\text{PO}_4 + \text{H}_2\text{CO}_3$

Given is a mixture of two acids: phosphoric acid plus carbonic acid with equal amounts: $C_{\text{phos}} = C_{\text{carb}} = C_T/2$. The first moment \tilde{Y}_1 of the two-acid system is displayed as the blue curve in the upper diagram of Fig 8.1. It is simply the sum of $Y_1^{(\text{phos})}$ and $Y_1^{(\text{carb})}$. This curve approaches the value 5 when $\text{pH} \rightarrow 14$, which is the degree of the two-acid system: $N = 3 + 2 = 5$.

The bottom diagram in Fig 8.1 displays the individual ionization fractions of the two acids. To recall: The blue curve (Y_1) in the top diagram represents the “titration curve” in the high- C_T limit.

8.3 H_NA as Superposition of N Monoprotic Acids

Is it possible to generate the titration curve of an N -protic acid (defined by K_1, K_2 to K_N) by a superposition of “virtual” N monoprotic acids having the acidity constants K_1, K_2 to K_N ? Answer: This is only possible approximately (never exactly). The underlying math will be demonstrated for the diprotic acid H_2A .

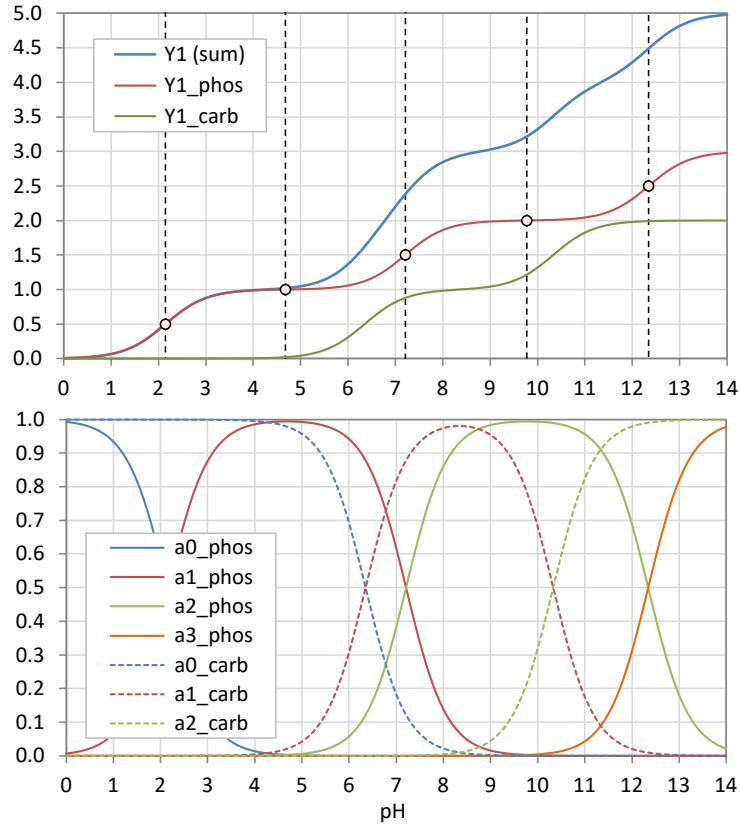


Figure 8.1: Y_1 and a_j for a system composed of phosphoric and carbonic acid.

Since the general formula for the titration curve $n(x)$ is $n = Y_1 + w/C_T$ (see (5.32)), it is sufficient to focus on Y_1 :

$$Y_1 = a_1 + 2a_2 = (a_1 + a_2) + a_2 \quad (8.14)$$

From (3.58) we then get:

$$a_1 + a_2 = \left(\frac{K_1}{x} + \frac{K_1 K_2}{x^2} \right) \left(1 + \frac{K_1}{x} + \frac{K_1 K_2}{x^2} \right)^{-1} = \frac{K_1^{(a)}}{x} \left(1 + \frac{K_1^{(a)}}{x} \right)^{-1} \equiv a_1^{(a)} \quad (8.15)$$

$$a_2 = \frac{K_2}{x} \left(\frac{x}{K_1} + 1 + \frac{K_2}{x} \right)^{-1} = \frac{K_1^{(b)}}{x} \left(1 + \frac{K_1^{(b)}}{x} \right)^{-1} \equiv a_1^{(b)} \quad (8.16)$$

Here we have introduced new acidity constants $K_1^{(a)}$ and $K_1^{(b)}$, which are (almost) identical with the two acidity constants of H_2A :

$$K_1^{(a)} = K_1 \left(1 + \frac{K_2}{x} \right) \xrightarrow[\text{pH} \rightarrow 0]{K_2/x \ll 1} K_1^{(a)} \simeq K_1 \quad (8.17)$$

$$K_1^{(b)} = K_2 \left(1 + \frac{x}{K_1} \right) \xrightarrow[\text{pH} \rightarrow 14]{x/K_1 \ll 1} K_1^{(b)} \simeq K_2 \quad (8.18)$$

In fact, $a_1^{(a)}$ and $a_1^{(b)}$ are just the ionization fractions of the two monoprotic acids that

define their first moments $Y_1^{(a)} = a_1^{(a)}$ and $Y_1^{(b)} = a_1^{(b)}$. This leads to the conclusion:

$$\underbrace{Y_1 = a_1 + 2a_2}_{\text{diprotic acid}} \iff \underbrace{Y_1 = Y_1^{(a)} + Y_1^{(b)}}_{\text{superposition of 2 monoprotic acids}}$$

which can be extended to any N -protic acid:

$$\underbrace{Y_1 = a_1 + 2a_2 + 3a_3 + \dots}_{N\text{-protic acid}} \iff \underbrace{Y_1 = Y_1^{(a)} + Y_1^{(b)} + Y_1^{(c)} + \dots}_{\text{superposition of } N \text{ monoprotic acids}}$$

Note that this is only an approximation, as indicated by the arrows in Eqs. (8.17) and (8.18). The “quality” of this approximation will be demonstrated in the following two examples.

Two Examples

Two examples are presented in Fig 8.2 where Y_1 of carbonic acid (H_2A) and phosphoric acid (H_3A) are generated from two and three “virtual” monoprotic acids:

carbonic acid :	$Y_1 = a_1^{(a)} + a_1^{(b)}$
phosphoric acid :	$Y_1 = a_1^{(a)} + a_1^{(b)} + a_1^{(c)}$

The blue curves in the present diagram are de facto indistinguishable from the blue curves (showing Y_1) in Fig 5.8.

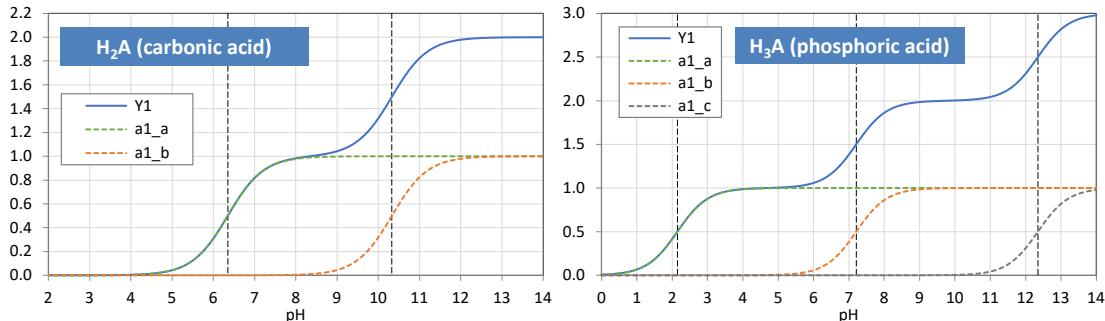


Figure 8.2: Y_1 of carbonic and phosphoric acids generated as superposition of two and three “virtual” monoprotic acids.

Appendices

One small observation can disprove a statement, while millions can hardly confirm it.

— Scientific principle

A

Activity Models

Contents

A.1 Activity vs Concentration	85
A.2 Activity Corrections	86

A.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 actually are (or measured). This *effective* concentration, which is available for reactions, is called *activity*:

$$\text{activity} = \text{effective concentration} \leq \text{real concentration}$$

The concentration [j] of the aqueous species j is converted to the activity {j} using the activity coefficient γ_j :

$$\{j\} = \gamma_j [j] \tag{A.1}$$

In the limit of infinitely dilute systems, the activity coefficient becomes 1:

$$\text{ideal solution: } \gamma_j = 1 \implies \{j\} = [j] \tag{A.2}$$

Since γ_j corrects for electrostatic shielding by other ions, γ_j depends on the *ionic strength*:

$$I = \frac{1}{2} \sum_j z_j^2 [j] \tag{A.3}$$

The sum runs over all ions in the solution. Due to the square of charge z_j , multivalent ions contribute particularly strongly to the ionic strength.

A.2 Activity Corrections

A.2.1 Four Activity Models

For the activity corrections γ or $\lg \gamma$, several semi-empirical approaches are available (each with its own validity range dictated by the ionic strength):

model	equation	validity range
DEBYE-HÜCKEL (DH):	$\lg \gamma_j = -Az_j^2 \sqrt{I}$	$I < 10^{-2.3} \text{ M}$ (A.4)
Extended DH:	$\lg \gamma_j = -Az_j^2 \left(\frac{\sqrt{I}}{1+B\alpha_j \sqrt{I}} \right)$	$I < 0.1 \text{ M}$ (A.5)
DAVIES:	$\lg \gamma_j = -Az_j^2 \left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3I \right)$	$I \leq 0.5 \text{ M}$ (A.6)
TRUESESELL-JONES:	$\lg \gamma_j = -Az_j^2 \left(\frac{\sqrt{I}}{1+B\alpha_j^0 \sqrt{I}} \right) + b_j I$	$I < 1 \text{ M}$ (A.7)

All quantities carrying the subscript j are ion-specific parameters (α_j , α_j^0 , and b_j). On the other hand, the two prefactors A and B depend on the temperature T and the dielectric constant ε_r :

$$A = A_0 \cdot (\varepsilon_r T)^{-3/2} \quad \text{with } A_0 = 1.824 \cdot 10^6 \text{ K}^{3/2} \text{ M}^{-1/2} \quad (\text{A.8})$$

$$B = B_0 \cdot (\varepsilon_r T)^{-1/2} \quad \text{with } B_0 = 50.28 \text{ nm}^{-1} \text{ K}^{1/2} \text{ M}^{-1/2} \quad (\text{A.9})$$

For water at 25°C ($T = 298.15$ K) and with $\varepsilon_r = 78.54 \text{ C}^2/(\text{J}\cdot\text{m})$, we get

$$A = 0.5089 \text{ M}^{-1/2} \quad (\text{A.10})$$

$$B = 3.286 \text{ nm}^{-1} \text{ M}^{-1/2} \quad (\text{A.11})$$

Please note the length unit in the last equation: 1 nm = 10^{-9} m = 10 Ångström. The derivation of the prefactors A and B is given in § A.2.2.

Alternative Definitions (Two Pitfalls)

The prefactors A and B depend on the units chosen (and other conventions). So be careful when comparing them with other prefactors given in the literature.

Example 1. If the activity corrections are expressed in terms of $\ln \gamma$ (instead of $\lg \gamma$), then A should be multiplied by $\ln 10$:

$$A \implies A \cdot (\ln 10) = 1.172 \text{ M}^{-1/2} \quad (\text{A.12})$$

Example 2. If B in (A.11) is expressed using the (non-SI) unit Ångström (instead in nm), then B should be divided by 10:

$$B \implies B/10 = 0.3286 \text{ \AA}^{-1} \text{ M}^{-1/2} \quad (\text{A.13})$$

A.2.2 The Prefactors A and B

The calculation of the prefactors A and B in § A.2.1 is based on the following physical constants:

$$N_A = 6.022 \cdot 10^{23} \text{ mol}^{-1} \quad (\text{A.14})$$

$$e = 1.602 \cdot 10^{-19} \text{ C} \quad (\text{A.15})$$

$$k_B = 1.381 \cdot 10^{-23} \text{ J/K} \quad (\text{A.16})$$

$$\varepsilon_0 = 8.854 \cdot 10^{-12} \text{ C}^2 \text{J}^{-1} \text{m}^{-1} \quad (\text{A.17})$$

$$\varepsilon_r = 78.54 \quad (\text{for water}) \quad (\text{A.18})$$

Prefactor A

$$A = \frac{\sqrt{2\pi N_A}}{\ln 10} \left(\frac{e^2}{4\pi k_B \varepsilon_0 \varepsilon_r T} \right)^{3/2} = A_0 \cdot (\varepsilon_r T)^{-3/2} \quad (\text{A.19})$$

with

$$\begin{aligned} A_0 &= \frac{\sqrt{2\pi N_A}}{\ln 10} \left(\frac{e^2}{4\pi k_B \varepsilon_0} \right)^{3/2} \\ &= \frac{\sqrt{2\pi} 6.02 \cdot 10^{23} \text{ mol}^{-1}}{\ln 10} \cdot \left(\frac{2.57 \cdot 10^{-38} \text{ C}^2}{4\pi 1.38 \cdot 10^{-23} \text{ J/K} 8.85 \cdot 10^{-12} \text{ C}^2 / (\text{J} \cdot \text{m})} \right)^{3/2} \\ &= 8.45 \cdot 10^{11} \text{ mol}^{-1/2} \cdot (1.67 \cdot 10^{-5} \text{ m} \cdot \text{K})^{3/2} \\ &= 8.45 \cdot 10^{11} \text{ mol}^{-1/2} \cdot 6.83 \cdot 10^{-8} (\text{m} \cdot \text{K})^{3/2} \\ &= 5.77 \cdot 10^4 \text{ K}^{3/2} \left(\frac{\text{m}^3}{\text{mol}} \right)^{1/2} \\ &= 5.77 \cdot 10^4 \cdot 10^{3/2} \text{ K}^{3/2} \text{ M}^{-1/2} \quad \left(\text{with M} = \frac{\text{mol}}{\text{L}} = \frac{\text{mol}}{10^{-3} \text{ m}^3} \right) \\ &= 1.824 \cdot 10^6 \text{ K}^{3/2} \text{ M}^{-1/2} \end{aligned} \quad (\text{A.20})$$

For water at 25°C we have:

$$\varepsilon_r T = 78.54 \cdot 238.15 \text{ K} = 2.34 \cdot 10^4 \text{ K} \quad (\text{A.21})$$

which yields

$$(\varepsilon_r T)^{-3/2} = 2.79 \cdot 10^{-7} \text{ K}^{-3/2} \quad (\text{A.22})$$

Taken together, we obtain the result shown in (A.10):

$$A = A_0 \cdot (\varepsilon_r T)^{-3/2} = 0.5089 \text{ M}^{-1/2} \quad (\text{A.23})$$

Prefactor B

$$B = \sqrt{\frac{2N_A e^2}{k_B \varepsilon_0 \varepsilon_r T}} = B_0 \cdot (\varepsilon_r T)^{-1/2} \quad (\text{A.24})$$

with

$$\begin{aligned} B_0 &= \sqrt{\frac{2N_A e^2}{k_B \varepsilon_0}} \\ &= \left(\frac{2 \cdot 6.02 \cdot 10^{23} \cdot 2.57 \cdot 10^{-38}}{1.38 \cdot 10^{-23} \cdot 8.85 \cdot 10^{-12}} \cdot \frac{\text{m}\cdot\text{K}}{\text{mol}} \right)^{1/2} \\ &= \left(2.53 \cdot 10^{20} \frac{\text{m}\cdot\text{K}}{\text{mol}} \right)^{1/2} \\ &= 1.59 \cdot 10^{10} \frac{\text{m}^{1/2}}{\text{mol}^{1/2}} \cdot \text{K}^{1/2} \\ &= 1.59 \cdot 10^{10} \frac{1}{\text{m}} 10^{3/2} \frac{\text{K}^{1/2}}{\text{M}^{1/2}} \quad \left(\text{with } M = \frac{\text{mol}}{\text{L}} = \frac{\text{mol}}{10^{-3} \text{m}^3} \right) \\ &= 50.3 \text{ nm}^{-1} \text{ K}^{1/2} \text{ M}^{-1/2} \quad \left(\text{with } 1 \text{ m} = 10^9 \text{ nm} \right) \end{aligned} \quad (\text{A.25})$$

For water at 25°C, using (A.21), we obtain:

$$(\varepsilon_r T)^{-1/2} = 6.54 \cdot 10^{-3} \text{ K}^{-1/2} \quad (\text{A.26})$$

Taken together, we obtain the result shown in (A.11):

$$B = B_0 \cdot (\varepsilon_r T)^{-1/2} = 3.286 \text{ nm}^{-1} \text{ M}^{-1/2} \quad (\text{A.27})$$

The man who does not read good books has no advantage over the man who cannot read.

— Mark Twain

B

Math Relationships

Contents

B.1 Polynomials in x	89
B.2 Approximations for a_j	91
B.3 Simple Relationships between a_j and Y_L	93
B.4 Derivatives with Respect to pH	95

B.1 Polynomials in x

B.1.1 The Subsystem H_NA

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

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

The task is to solve it for x , that is, to find a formula that calculates x for a given value of a_j . This will lead to a polynomial of degree N in x . For this purpose, let's start with a_0 and transform it in the following way:

$$\begin{aligned} \frac{1}{a_0} &= \left(1 + \frac{k_1}{x} + \frac{k_2}{x^2} + \cdots \right) = \frac{1}{x_N} (x^N + k_1 x^{N-1} + \cdots + k_N) \quad \Big| \cdot x^N \\ \frac{x^N}{a_0} &= x^N + k_1 x^{N-1} + \cdots + k_N = \sum_{j=0}^N k_j x^{N-j} \end{aligned} \quad (\text{B.2})$$

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

$$0 = c_0 \cdot x^N + k_1 x^{N-1} + \cdots + k_N \quad \text{and} \quad c_0 \equiv -\left(\frac{1 - a_0}{a_0} \right) \quad (\text{B.3})$$

The result can be generalized to any other a_j . To do this, insert $a_0 = (x^j/k_j) a_j$ into the left-hand side of (B.2):

$$\left(\frac{k_j}{a_j}\right) x^{N-j} = \sum_{i=0}^N k_i x^{N-i} \quad (\text{B.4})$$

Again, the obtained polynomial is of degree N :

$$0 = c_j \cdot x^{N-j} + \sum_{i \neq j}^N k_i x^{N-i} \quad \text{and} \quad c_j \equiv -\left(\frac{1-a_j}{a_j}\right) k_j \quad (\text{B.5})$$

For $j = 0$ (and with $k_0 = 1$), this formula reduces to (B.3).

B.1.2 The General Case: $\text{H}_\text{N}\text{A} + \text{H}_2\text{O} + \text{Strong Base}$

The titration of a polyprotic acid $\text{H}_\text{N}\text{A}$ by a strong base is described by (5.32), which we now write as

$$Y_1(x) = n - \frac{w(x)}{C_T} \quad \text{with} \quad n = \frac{C_B}{C_T} \quad (\text{B.6})$$

For Y_1 on the left-hand side, we apply (3.80). That is,

$$Y_1(x) = \frac{\sum_{j=0}^N j \cdot k_j x^{N-j}}{\sum_{j=0}^N k_j x^{N-j}} \quad (\text{B.7})$$

Inserting it into (B.6) and multiplying both sides by $\sum k_j x^{N-j}$ yields:

$$\begin{aligned} \sum_{j=0}^N j \cdot k_j x^{N-j} &= \left\{ n - \frac{w}{C_T} \right\} \sum_{j=0}^N k_j x^{N-j} \\ 0 &= \sum_{j=0}^N \left\{ j - n + \frac{w}{C_T} \right\} k_j x^{N-j} \\ &= \sum_{j=0}^N \{C_T(j-n) + w\} k_j x^{N-j} \quad (\text{both sides are multiplied by } C_T) \\ &= \sum_{j=0}^N \left\{ C_T(j-n) - x + \frac{K_w}{x} \right\} k_j x^{N-j} \quad (w \text{ is replaced by (5.34)}) \end{aligned}$$

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

$$0 = \sum_{j=0}^N \{x^2 + (n-j)C_T x - K_w\} k_j x^{N-j} \quad (\text{B.8})$$

To show that the polynomial is indeed of degree $N+2$ you can rewrite (B.8) as

$$0 = \sum_{j=0}^{N+2} f_j x^{N+2-j} \quad \text{with} \quad f_j = k_j + k_{j-1}(n+1-j)C_T - K_w k_{j-2} \quad (\text{B.9})$$

The cumulative equilibrium constants k_j are defined in (3.14). The first and the last coefficients of this polynomial are: $f_0 = 1$ and $f_{N+2} = -K_w K_1 K_2 \cdots K_N$. [Note: k_j is per definition zero for negative values of j .]

Special Case: $C_T \rightarrow \infty$

Let us divide both sides of (B.8) by C_T :

$$0 = \sum_{j=0}^N \left\{ \frac{x^2}{C_T} + (n-j)x - \frac{K_w}{C_T} \right\} k_j x^{N-j} \quad (\text{B.10})$$

In the limit $C_T \rightarrow \infty$, only the second term in the curly braces survives and thus (B.8) simplifies to a polynomial of degree $N+1$:

$$0 = \sum_{j=0}^N (n-j) k_j x^{N+1-j} \quad (\text{B.11})$$

B.2 Approximations for a_j

B.2.1 Piecewise Linearization of $\lg a_j$

We start with the definition of a_0 in (3.58):

$$a_0^{-1} = \left(1 + \frac{k_1}{x} + \frac{k_2}{x^2} + \cdots + \frac{k_N}{x^N} \right) = \left(1 + \frac{K_1}{x} + \frac{K_1 K_2}{x^2} + \cdots + \frac{K_1 K_2 \cdots K_N}{x^N} \right) \quad (\text{B.12})$$

In each pH interval, as defined in the left diagrams in Fig 3.5 on page 29, we can approximate a_0 as follows (because $K_1 > K_2 > \dots > K_N$):

0 th interval ($\text{pH} < \text{pK}_1$)	where $x > K_1$	$\implies a_0^{-1} \simeq 1$
1 st interval ($\text{pK}_1 < \text{pH} < \text{pK}_2$)	where $K_1 > x > K_2$	$\implies a_0^{-1} \simeq k_1/x$
2 nd interval ($\text{pK}_2 < \text{pH} < \text{pK}_3$)	where $K_2 > x > K_3$	$\implies a_0^{-1} \simeq k_2/x^2$
...		
N th interval ($\text{pH} > \text{pK}_N$)	where $x < K_N$	$\implies a_0^{-1} \simeq k_N/x^N$

Thus, we can approximate $\lg a_0$ in the i^{th} interval by

$$\lg a_0 \simeq \lg \frac{x^i}{k_i} = i \lg x - \lg k_i = -i \text{pH} + \text{pk}_i \quad (\text{B.13})$$

where $\text{pk}_i = \text{pK}_1 + \text{pK}_2 + \cdots + \text{pK}_i$ and $\text{pK}_0 = 0$.

The generalization of this result to all other a_j is simple. Again, we refer to (3.58):

$$a_j = \left(\frac{k_j}{x^j} \right) a_0 \implies \lg a_j = \lg a_0 + j \text{pH} - \text{pk}_j \quad (\text{B.14})$$

Inserting the approximation (B.13) for $\lg a_0$ yields

$$\lg a_j \simeq (j-i) \text{pH} + (\text{pk}_i - \text{pk}_j) \quad \text{for the } i^{\text{th}} \text{ interval} \quad (\text{B.15})$$

This is a *linear* function of pH with integer-valued *slope* $(j-i)$ and *offset* $(\text{pk}_i - \text{pk}_j)$.

Example: Phosphoric Acid

Phosphoric acid is defined by $N=3$ equilibrium constants ($pK_1 = 2.15$, $pK_2 = 7.21$, $pK_3 = 12.35$). Equation (B.15) is plotted in Fig 3.6 on page 30. Each $\lg a_j$ consists of four *linear* segments, with one segment in each interval i . In particular, we have:

- $a_0 \simeq (0 - i) \cdot \text{pH} + (\text{pk}_i - \text{pk}_0)$ (blue dashed curve)

$i=0:$	$(0 - 0) \cdot \text{pH} + (0 - 0) = 0$	$= 0$
$i=1:$	$(0 - 1) \cdot \text{pH} + (\text{pk}_1 - 0) = -\text{pH} + \text{pK}_1$	$= -\text{pH} + 2.15$
$i=2:$	$(0 - 2) \cdot \text{pH} + (\text{pk}_2 - 0) = -2 \cdot \text{pH} + (\text{pK}_1 + \text{pK}_2)$	$= -2 \cdot \text{pH} + 9.35$
$i=3:$	$(0 - 3) \cdot \text{pH} + (\text{pk}_3 - 0) = -3 \cdot \text{pH} + (\text{pK}_1 + \text{pK}_2 + \text{pK}_3)$	$= -3 \cdot \text{pH} + 21.7$
- $a_1 \simeq (1 - i) \cdot \text{pH} + (\text{pk}_i - \text{pk}_1)$ (brown dashed curve)

$i=0:$	$(1 - 0) \cdot \text{pH} + (0 - \text{pk}_1) = \text{pH} - \text{pK}_1$	$= \text{pH} - 2.15$
$i=1:$	$(1 - 1) \cdot \text{pH} + (\text{pk}_1 - \text{pk}_1) = 0$	$= 0$
$i=2:$	$(1 - 2) \cdot \text{pH} + (\text{pk}_2 - \text{pk}_1) = -\text{pH} + \text{pK}_2$	$= -\text{pH} + 7.21$
$i=3:$	$(1 - 3) \cdot \text{pH} + (\text{pk}_3 - \text{pk}_1) = -2 \cdot \text{pH} + (\text{pK}_2 + \text{pK}_3)$	$= -2 \cdot \text{pH} + 19.55$
- $a_2 \simeq (2 - i) \cdot \text{pH} + (\text{pk}_i - \text{pk}_2)$ (green dashed curve)

$i=0:$	$(2 - 0) \cdot \text{pH} + (0 - \text{pk}_2) = 2 \cdot \text{pH} - (\text{pK}_1 + \text{pK}_2)$	$= 2 \cdot \text{pH} - 9.35$
$i=1:$	$(2 - 1) \cdot \text{pH} + (\text{pk}_1 - \text{pk}_2) = \text{pH} - \text{pK}_2$	$= \text{pH} - 7.21$
$i=2:$	$(2 - 2) \cdot \text{pH} + (\text{pk}_2 - \text{pk}_2) = 0$	$= 0$
$i=3:$	$(2 - 3) \cdot \text{pH} + (\text{pk}_3 - \text{pk}_2) = -\text{pH} + \text{pK}_3$	$= -\text{pH} + 12.35$
- $a_3 \simeq (3 - i) \cdot \text{pH} + (\text{pk}_i - \text{pk}_3)$ (orange dashed curve)

$i=0:$	$(3 - 0) \cdot \text{pH} + (0 - \text{pk}_3) = 3 \cdot \text{pH} - (\text{pK}_1 + \text{pK}_2 + \text{pK}_3)$	$= 3 \cdot \text{pH} - 21.7$
$i=1:$	$(3 - 1) \cdot \text{pH} + (\text{pk}_1 - \text{pk}_3) = 2 \cdot \text{pH} - (\text{pK}_2 + \text{pK}_3)$	$= 2 \cdot \text{pH} - 19.55$
$i=2:$	$(3 - 2) \cdot \text{pH} + (\text{pk}_2 - \text{pk}_3) = \text{pH} - \text{pK}_3$	$= \text{pH} - 12.35$
$i=3:$	$(3 - 3) \cdot \text{pH} + (\text{pk}_3 - \text{pk}_3) = 0$	$= 0$

B.2.2 Strong Polyprotic Acids

The ionization fractions a_j are defined in (3.58). They simplify for strong acids, where the condition $x/K_1 \rightarrow 0$ holds for all relevant x (as indicated in (8.1)).

Let's start with

$$\begin{aligned} a_0^{-1} &= \left(1 + \frac{k_1}{x} + \frac{k_2}{x^2} + \dots\right) = \frac{K_1}{x} \left(\frac{x}{K_1} + 1 + \frac{K_2}{x^2} + \dots\right) \\ &= \frac{K_1}{x} \left(1 + \frac{K_2}{x^2} + \dots\right) \quad \text{because } x/K_1 \simeq 0 \end{aligned}$$

It yields

$$a_0 = \frac{x}{K_1} \left(1 + \frac{K_2}{x^2} + \dots\right)^{-1} = 0 \quad \text{because } x/K_1 \simeq 0 \quad (\text{B.16})$$

According to the general formula $a_1 = (K_1/x) a_0$, the term in the brackets in (B.16) represents a_1 :

$$a_1 = \left(1 + \frac{K_2}{x^2} + \dots\right)^{-1} \quad (\text{B.17})$$

and we successively get

$$a_0 = 0 \quad (\text{B.18})$$

$$a_1 = \left(1 + \frac{K_2}{x^2} + \frac{K_2 K_3}{x^3} + \dots\right)^{-1} = \left(1 + \frac{\tilde{k}_2}{x^2} + \frac{\tilde{k}_3}{x^3} + \dots\right)^{-1} \quad (\text{B.19})$$

$$a_j = \left(\frac{\tilde{k}_j}{x^{j-1}}\right) a_1 \quad \text{for } j > 0 \quad (\text{B.20})$$

with “redefined” cumulative acidity constants \tilde{k}_j :

$$\tilde{k}_0 = 0, \quad \tilde{k}_1 = 1, \quad \tilde{k}_2 = K_2, \quad \dots \quad \tilde{k}_N = K_2 K_3 \cdots K_N \quad (\text{B.21})$$

In this way, K_1 disappeared from all equations.

B.3 Simple Relationships between a_j and Y_L

B.3.1 Relationships for Y_L

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

$$Y_L \equiv \sum_{j=0}^N j^L a_j = 0^L a_0 + 1^L a_1 + 2^L a_2 + \dots + N^L a_N \quad (\text{B.22})$$

with the special case $Y_0 = 1$ (mass balance) — see (3.63) and (3.78). [Note: $0^0 = 1$.]

An alternative relationship between a_j and Y_1 can be established in the following sequence of steps:

$$\begin{aligned} n &= n \\ n Y_0 &= n \quad (\text{because } Y_0 = 1) \\ n Y_0 - Y_1 &= n - Y_1 \quad (Y_1 \text{ subtracted from both sides}) \\ n \sum a_j - \sum j a_j &= n - Y_1 \quad (\text{using (B.22) on the left-hand side}) \end{aligned}$$

which finally yields the result:

$$\sum_{j=0}^N (n - j) a_j = n - Y_1 \quad \text{or} \quad \sum_{j=0}^N (n - j) [j] = (n - Y_1) C_T \quad (\text{B.23})$$

Equivalence Points

The two types of equivalence points are characterized by (c.f. (3.69) and (3.70)):

$$\text{semi-EP}_j : \quad \text{pH} = \text{pK}_j \quad \Rightarrow \quad a_j = a_{j-1} \simeq \frac{1}{2} \quad (\text{B.24})$$

$$\text{EP}_j : \quad \text{pH}_j \equiv \frac{1}{2}(\text{pK}_j + \text{pK}_{j+1}) \quad \Rightarrow \quad a_j(\text{pH}_j) \simeq 1 \quad (\text{B.25})$$

while all other ionization fractions are almost zero. In this way, the whole sum in (B.22) is reduced to one or two terms:

$$Y_L(\text{pK}_j) = (j-1)^L a_{j-1} + j^L a_j = \frac{1}{2} \{(j-1)^L + j^L\} \quad \text{for } L \geq 1 \quad (\text{B.26})$$

$$Y_L(\text{pH}_j) = j^L a_j \simeq j^L \quad \text{for } L \geq 1 \quad (\text{B.27})$$

B.3.2 Maximum of a_j

The maximum (extremum) of an ionization fraction a_j is obtained under the condition that its 1st derivative should vanish:

$$\frac{da_j}{d\text{pH}} = 0 \quad \iff \quad \text{extremum of } a_j \quad (\text{B.28})$$

According to (B.47) on page 96, this is equivalent to the condition:

$$(j - Y_1) a_j = 0 \quad \text{or} \quad j - Y_1 = 0 \quad (\text{B.29})$$

From (B.23) we get

$$\sum_{i=0}^N (j-i) a_i = 0 \quad (\text{B.30})$$

or, more explicitly,

$$-ja_0 - (j-1)a_1 - \cdots - a_{j-1} + 0 + a_{j+1} + \cdots + (N-j)a_N = 0 \quad (\text{B.31})$$

From the viewpoint of a_j , only its two neighbors a_{j-1} and a_{j+1} are of relevance (all other are nearly zero). Thus, (B.30) collapses to $-a_{j-1} + a_{j+1} = 0$, that is

$$\text{maximum of } a_j \quad \iff \quad a_{j-1} = a_{j+1} \quad \text{or} \quad \frac{a_{j+1}}{a_{j-1}} = 1 \quad (\text{B.32})$$

The pH at the maximum is obtained from (3.19):

$$\frac{a_{j+1}}{a_{j-1}} = \frac{[j+1]}{[j-1]} = \frac{K_j K_{j+1}}{x^2} \quad \Rightarrow \quad x_{\max} = (K_j K_{j+1})^{1/2} \quad (\text{B.33})$$

According to (3.45), the ionization fraction a_j has its maximum at the equivalence point:

$$\text{maximum of } a_j \quad \text{at EP}_j \quad \text{with } \text{pH} = \frac{1}{2}(\text{pK}_j + \text{pK}_{j+1}) \quad (\text{B.34})$$

From mass conservation, i.e. (3.63), one gets the value of a_j at the maximum as:

$$a_j(x_{\max}) = 1 - a_{j-1} - a_{j+1} = 1 - 2a_{j-1} \quad (\text{B.35})$$

which, in most cases, is close to 1.

B.4 Derivatives with Respect to pH

B.4.1 Basic Equations

Given is

$$x = \{H^+\} = 10^{-\text{pH}} = e^{-(\ln 10) \text{pH}} \quad (\text{B.36})$$

The 1st and the k^{th} derivative of x with respect to pH are:

$$\frac{dx}{d \text{pH}} = -(\ln 10) x \quad (\text{B.37})$$

$$\frac{d^k x}{d \text{pH}^k} = -(\ln 10)^k x \quad (\text{B.38})$$

This result is used to differentiate any given function $f(x)$ with respect to pH (by application of the chain rule):

$$\frac{df(x)}{d \text{pH}} = \frac{dx}{d \text{pH}} \frac{df(x)}{dx} = -(\ln 10)^k x \frac{df(x)}{dx} \quad (\text{B.39})$$

Example 1

For $w(x) = K_w/x - x$, introduced in (4.7), we get:

$$\frac{dw(x)}{d \text{pH}} = \ln 10 (K_w/x + x) = (\ln 10) (w + 2x) \quad (\text{B.40})$$

$$\frac{d^2 w(x)}{d \text{pH}^2} = (\ln 10)^2 (w + 2x - 2x) = (\ln 10)^2 w \quad (\text{B.41})$$

All higher derivatives repeat this pattern:

$$\frac{d^k w(x)}{d \text{pH}^k} = (\ln 10)^k \begin{cases} w & \text{for } k \text{ even} \\ w + 2x & \text{for } k \text{ odd} \end{cases} \quad (\text{B.42})$$

Example 2

Let us consider the function, $g = 1/a_0$, that is

$$g(x) = 1 + \frac{k_1}{x} + \frac{k_2}{x^2} + \cdots + \frac{k_N}{x^N} \quad (\text{B.43})$$

Its first derivative is then given by

$$\frac{dg(x)}{d \text{pH}} = \ln 10 \left(\frac{k_1}{x} + 2 \frac{k_2}{x^2} + \cdots + N \frac{k_N}{x^N} \right) = \frac{\ln 10}{a_0} (a_1 + 2a_2 + \cdots + Na_N) \quad (\text{B.44})$$

where on the right-hand side, (3.25) was applied. Using the definition of Y_1 in (3.79), it yields the interesting result:

$$\frac{dg(x)}{d \text{pH}} = \frac{d}{d \text{pH}} \frac{1}{a_0} = \ln 10 \frac{Y_1}{a_0} \quad (\text{B.45})$$

B.4.2 First Derivative of a_j and Y_L

Ionization Fractions

Let us start with the 1/st/ derivative of a_0 by applying the results of the last example (particularly (B.45)):

$$\frac{da_0(x)}{dpH} = \frac{d}{dpH} \frac{1}{g(x)} = -\frac{1}{g^2} \frac{dg(x)}{dpH} = -a_0^2 (\ln 10) \frac{Y_1}{a_0} = (-\ln 10) Y_1 a_0 \quad (\text{B.46})$$

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

$$\frac{da_j(x)}{dpH} = (-\ln 10) (Y_1 - j) a_j \quad (\text{B.47})$$

Moments

Applying the above results to the sums over a_j yields

$$\frac{d}{dpH} \sum_{j=0}^N a_j = (-\ln 10) \sum_{j=0}^N (Y_1 - j) a_j = (-\ln 10) (Y_1 - Y_1) = 0 \quad (\text{B.48})$$

$$\frac{d}{dpH} \sum_{j=0}^N j a_j = (-\ln 10) \sum_{j=0}^N j (Y_1 - j) a_j = (-\ln 10) (Y_1^2 - Y_2) \quad (\text{B.49})$$

The first relation, which gives zero, is obvious because it represents the derivation of a constant, namely $d1/dpH = 0$. Equation (B.49) is just the 1st derivative of Y_1 :

$$\frac{dY_1}{dpH} = (-\ln 10) (Y_1^2 - Y_2) \quad (\text{B.50})$$

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

$$\frac{dY_L}{dpH} = (-\ln 10) \sum_{j=0}^N j^L (Y_1 - j) a_j = (-\ln 10) (Y_1 Y_L - Y_{L+1}) \quad (\text{B.51})$$

B.4.3 Higher Derivatives of a_j and Y_L

The 2nd derivative of a_j is given by

$$\begin{aligned} \frac{d^2 a_j(x)}{dpH^2} &= (-\ln 10) \frac{d}{dpH} (Y_1 - j) a_j \\ &= (-\ln 10) \left\{ a_j \frac{dY_1}{dpH} + (Y_1 - j) \frac{da_j}{dpH} \right\} \quad (\text{use of (B.47) and (B.50)}) \\ &= (-\ln 10)^2 \{ (Y_1^2 - Y_2) + (Y_1 - j)^2 \} a_j \end{aligned} \quad (\text{B.52})$$

The 2nd derivative of Y_1 is given by

$$\begin{aligned}
 \frac{d^2Y_1}{dpH^2} &= (-\ln 10) \frac{d}{dpH} (Y_1^2 - Y_2) \\
 &= (-\ln 10) \left\{ 2Y_1 \frac{dY_1}{dpH} - \frac{dY_2}{dpH} \right\} \\
 &= (-\ln 10)^2 \left\{ 2Y_1 (Y_1^2 - Y_2) - (Y_1 Y_2 - Y_3) \right\} \\
 &= (-\ln 10)^2 \left\{ 2Y_1^3 - 3Y_1 Y_2 + Y_3 \right\}
 \end{aligned} \tag{B.53}$$

The 3rd derivative of Y_1 is:

$$\begin{aligned}
 \frac{d^3Y_1}{dpH^3} &= (-\ln 10)^2 \frac{d}{dpH} (2Y_1^3 - 3Y_1 Y_2 + Y_3) \\
 &= (-\ln 10)^2 \left\{ 3(2Y_1^2 - Y_2) \frac{dY_1}{dpH} - 3Y_1 \frac{dY_2}{dpH} + \frac{dY_3}{dpH} \right\} \\
 &= (-\ln 10)^3 \left\{ 3(2Y_1^2 - Y_2)(Y_1^2 - Y_2) - Y_1 (3Y_1 Y_2 - 4Y_3) - Y_4 \right\}
 \end{aligned} \tag{B.54}$$

The man who does not read good books has no advantage over the man who cannot read.

— Mark Twain

C

Proton Balance

Contents

C.1 Diprotic Acid	99
C.2 General Case: N-protic Acid	101

C.1 Diprotic Acid

PRL. The proton balance is often used in acid-base theory. It is a balance between the species that have excess protons versus those that are deficient in protons (relative to a defined proton reference level — PRL):

$$TOT H = \text{excess protons} - \text{deficient protons} \quad (\text{C.1})$$

Subsystem H_2O . The simplest case is pure water with its three species H^+ , OH^- , and H_2O . Choosing H_2O as the reference level, the species H^+ is enriched in 1 proton (excess proton), while OH^- is depleted in 1 proton (deficient proton):

PRL	excess protons	deficient protons	
H_2O	$[H^+]$	$[OH^-]$	(C.2)

The proton balance of the subsystem “pure water” is then expressed by:

$$TOT H|_w = [H^+] - [OH^-] = -w(x) \quad (\text{C.3})$$

where $w(x)$ was introduced in (4.7). Thus, for pure water we have $TOT H|_w = 0$.

Because water is ever-present in an acid-base system, H^+ and OH^- are always a part of the proton balance — see Eqs. (C.15) and (C.16) below.

Subsystem H₂A. The diprotic acid H₂A has three distinct reference levels denoted by $n = 0, 1$, and 2 :

PRL	excess protons	deficient protons	$TOT H _n$
$n = 0$	H ₂ A	0	$[HA^-] + 2[A^{-2}]$
$n = 1$	HA ⁻	[H ₂ A]	$[A^{-2}]$
$n = 2$	A ⁻²	2[H ₂ A] + [HA ⁻]	0

(C.4) (C.5) (C.6)

How to write down these equations?

In (C.4), H₂A is the reference level. There are no species that have more protons than H₂A, hence, there is nothing to add to the left-hand side. Conversely, HA⁻ is deficient by 1 proton and A⁻² by 2 protons; therefore, both species enter the right-hand side. (If a species has lost 2 protons relative to the PRL, its concentration is multiplied by 2.)

In (C.5), HA⁻ is the reference level. From this perspective, H₂A has 1 excess proton (the species enters the left-hand side), while A⁻² is deficient by 1 proton (the species enters the right-hand side).

In (C.6), A⁻² is the reference level. Now, H₂A has 2 excess protons and HA⁻ has 1 excess proton (both species enter the left-hand side); but there are no species that have less protons than A⁻² (i.e. no species enters the right-hand side).

Taken together, the three PRL of the subsystem “diprotic acid”, denoted by H_{2-n}A⁻ⁿ (for $n = 0, 1, 2$), yield the following proton balance equation:

$$\begin{aligned} \text{PRL} &\quad TOT H &= & \text{excess protons} - \text{deficient protons} \\ H_{2-n}A^{-n} &\quad TOT H|_n &= & n[H_2A] + (n-1)[HA^-] + (n-2)[A^{-2}] = 0 \end{aligned} \quad (\text{C.7})$$

This one-liner comprises all three equations (C.4) to (C.6). [Example: In the case of a carbonic-acid system the three PRL correspond to H₂CO₃, HCO₃⁻, and CO₃⁻².]

Fig C.1 illustrates how the choice of the origin (yellow dots) of a coordinate system (x axis: species; y axis: number of excess/deficient protons) alters the proton balance equation.

For example, given a mono-, di-, and tri-protic acid we have for $n = 0$:

$$N = 1 : \quad TOT H|_0 = -[A^-] \quad (\text{C.8})$$

$$N = 2 : \quad TOT H|_0 = -[HA^-] - 2[A^{-2}] \quad (\text{C.9})$$

$$N = 3 : \quad TOT H|_0 = -[H_2A^-] - 2[HA^{-2}] - 3[A^{-3}] \quad (\text{C.10})$$

H₂A + H₂O. The combined system as the sum of subsystem “pure water” and subsystem “diprotic acid” obeys the proton balance for the three PRL at H_{2-n}A⁻ⁿ (with $n = 0, 1, 2$):

$$\begin{aligned} TOT H_w + TOT H|_n &= \\ &[H^+] - [OH^-] + n[H_2A] + (n-1)[HA^-] + (n-2)[A^{-2}] \end{aligned} \quad (\text{C.11})$$

The two species, H⁺ and OH⁻, that appear in this equation trace back to the H₂O-reference level in (C.2). They have a permanent place in any H₂O containing system.

Note: The PRLs are usually chosen at equivalence points EP_n (with integer n). There is a direct correspondence between PRL at n and EP_n.

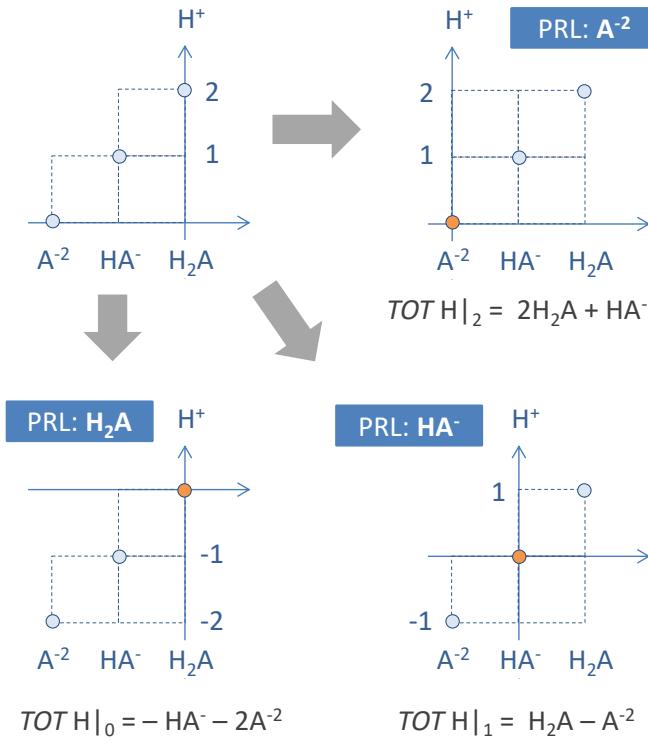


Figure C.1: PRL of a diprotic acid.

C.2 General Case: N-protic Acid

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

$$\begin{aligned} \text{PRL } H_{N-n}A^{-n}: \quad TOT H|_n^{(\text{acid})} &\equiv n[H_NA] + (n-1)[H_{n-1}A^-] + \\ &+ (n-2)[H_{n-2}A^{-2}] + \dots + (n-N)[H_{n-N}A^{-N}] = 0 \end{aligned} \quad (\text{C.12})$$

or in compact notation:

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

According to (B.23), the last equation can also be expressed by

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

$H_NA + H_2O$. The proton balance of the whole system is the sum of (C.3) and (C.14):

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

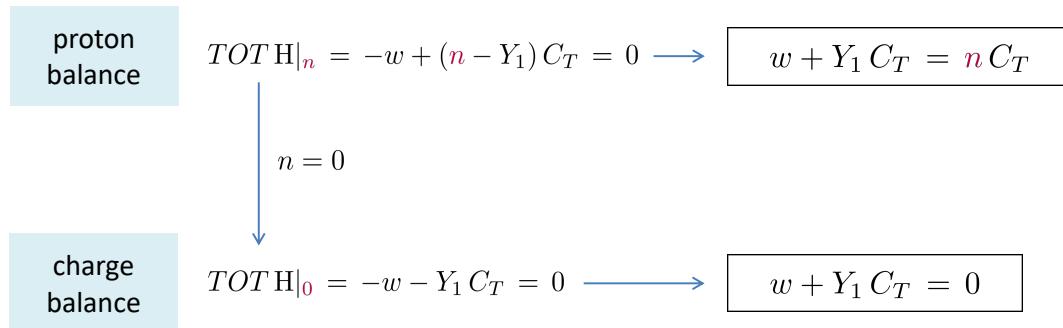
which is equivalent to

$TOT H|_n = -w + (n - Y_1) C_T = 0$

(C.16)

This proton-balance equation, in the form of $0 = [\text{H}^+] - [\text{OH}^-] + nC_T - Y_1C_T$, is equivalent to (5.25) and (5.31).

Charge Balance. The concept of proton balance is more general than the concept of charge balance (electro-neutrality). Only in the special case of $n = 0$ do the charge balance and proton balance coincide:



The last equation is equivalent to the charge-balance equation:

$$0 = [\text{H}^+] - [\text{OH}^-] - [\text{H}_{n-1}\text{A}^-] - 2[\text{H}_{n-2}\text{A}^{-2}] - \dots - N[\text{A}^{-N}] \quad (\text{C.17})$$

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