



ALKALINITY IN THEORY AND PRACTICE

Nicholas J. Tosca^{1*} and Benjamin M. Tutolo²

DOI: 10.2138/gselements.19.1.7

The articles in this issue highlight interdisciplinary approaches to the science of alkaline lakes, but one important concept links all of them together: alkalinity. Here, we discuss what alkalinity is, why it is important, and how it is typically measured. We review two different but complementary definitions of alkalinity that offer an intuitive starting point for understanding how this critical parameter responds to biogeochemical processes.

INTRODUCTION

Alkalinity is fundamental to understanding the geochemistry of natural waters. It is central to the quantitative treatment of the dissolved carbon dioxide system because it is unchanged by temperature or pressure, it encompasses the net effect of multiple chemical equilibria, and it is a directly measurable quantity that can be used in constraining these systems. Indeed, collected measurements (TABLE 1) show how widely alkalinity can vary among natural waters, and how this single parameter can reveal much about the lithospheric, biospheric, and atmospheric interactions that shape them.

Despite its importance, the concept of alkalinity can potentially be quite confusing, partially because of the multiple methods by which it is defined. Here, we focus on two commonly used definitions that are each applicable to alkaline lakes, but together provide a basis for understanding how natural waters become alkaline and how alkalinity might respond to various biogeochemical processes.

TABLE 1 REPRESENTATIVE ALKALINITIES OF NATURAL WATERS.

Fluid	Alkalinity [mEq/kg]	Reference
Black Smokers	-0.19 to -0.5	1
Seawater	2.3	2
Rivers	1.13 ± 1.07	3
Groundwaters	4.34 ± 1.97	3
East African Rift alkaline lakes	4.44 to 3170	4

References: ¹Von Damm et al. (1985); ²Holland (1978); ³Zhang and Planavsky (2020); ⁴Cerling (1979).

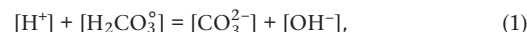
ALKALINITY AS THE EQUIVALENT SUM OF TITRATABLE BASES

Most rigorous definitions of alkalinity are necessarily based on acid-base equilibria. However, rather than beginning with a definition of alkalinity, in our experience it is perhaps more intuitive to first consider the changes that take place during the titration of a natural water with a strong acid, from which point a rigorous definition logically

1 Department of Earth Sciences
University of Cambridge
Cambridge, CB2 3EQ, United Kingdom
* E-mail: njt41@cam.ac.uk

2 Department of Geoscience
University of Calgary
Calgary, T2N 1N4, Canada

follows. During a so-called “acidometric” titration, strong acid is added to a solution until all aqueous species capable of accepting protons are completely converted to uncharged species. If these “proton acceptors,” or more generally, bases, are present in concentrations in excess relative to the “proton donors” (i.e., acids with relatively large dissociation constants), some of the H⁺ added during the titration will be consumed, resulting in a characteristic relationship between the amount of acid added and the resulting pH (FIG. 1A). For instance, consider a 5 mmol·L⁻¹ Na₂CO₃ solution, where dissolved carbonate species (i.e., HCO₃⁻ and CO₃²⁻) and the OH⁻ anion, are the species capable of accepting protons. As acid is added to this solution, the initially high pH (10.96 at 25 °C) begins to decrease systematically until a maximum is reached with respect to the rate of pH change as a function of the acid added (FIG. 1A). This maximum can be identified as an inflection point on a titration curve (FIG. 1A), or by inspecting the first derivative of pH with respect to the acid added (FIG. 1B). At this point in the titration,



which, because of the negligibly low concentration of OH⁻ and H⁺ at this pH (FIG. 1C), may be simplified to

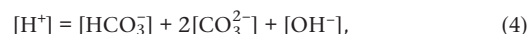


By mass balance with respect to protons, this condition is equivalent to that which would be achieved if an equivalent amount (5 mmol·L⁻¹ in this example) of NaHCO₃ salt were added to the solution (H₂O). In other words, the sum of the concentrations of all species that have excess protons relative to HCO₃⁻ and H₂O is equivalent to the sum of the concentrations of all species that are deficient in protons relative to HCO₃⁻ and H₂O. Because of the equivalence of CO₃²⁻ and H₂CO₃^{*} in Eq. (2), this is referred to as the first equivalence point (EP1 in FIG. 1A).

As more acid is added, pH continues to decrease until a second equivalence point is reached (EP2 in FIG. 1A), where



Again, considering proton mass balance, this condition is equivalent to that which would be achieved if an equivalent amount (again, 5 mmol·L⁻¹ in this example) of H₂CO₃^{*} were added to the solution (H₂O) because



which can be simplified to Eq. (3) because of the negligibly low concentrations of OH⁻ and CO₃²⁻ at this pH (FIG. 1C). Equation (4) represents the “proton condition” for carbonic acid (H₂CO₃^{*}), or simply the point at which the concentrations of all species that have excess protons relative to H₂CO₃^{*} and H₂O are equivalent to the concentration of all species that are deficient in protons relative to H₂CO₃^{*} and H₂O. Writing the proton condition in this way demonstrates why it must be defined with reference to a specific species (e.g., HCO₃⁻ in Eq. (1) and H₂CO₃^{*} in Eq. (4)). While similar to Eq. (1), Eq. (4) includes H⁺ and OH⁻ (i.e., H₂O that has accepted or donated protons, respectively) and the inorganic carbon species are distinct. Equation (4) defines the “zero level” reference condition for the dissolved carbonate system, where the number of excess protons is equal to [H⁺], and the number of proton deficiencies is equal to [HCO₃⁻] + 2[CO₃²⁻] + [OH⁻]. Rearranging Eq. (4) also leads to the definition of titration (or total) alkalinity (TA), which is the excess of proton acceptors over proton donors. For the CO₂-H₂O system,



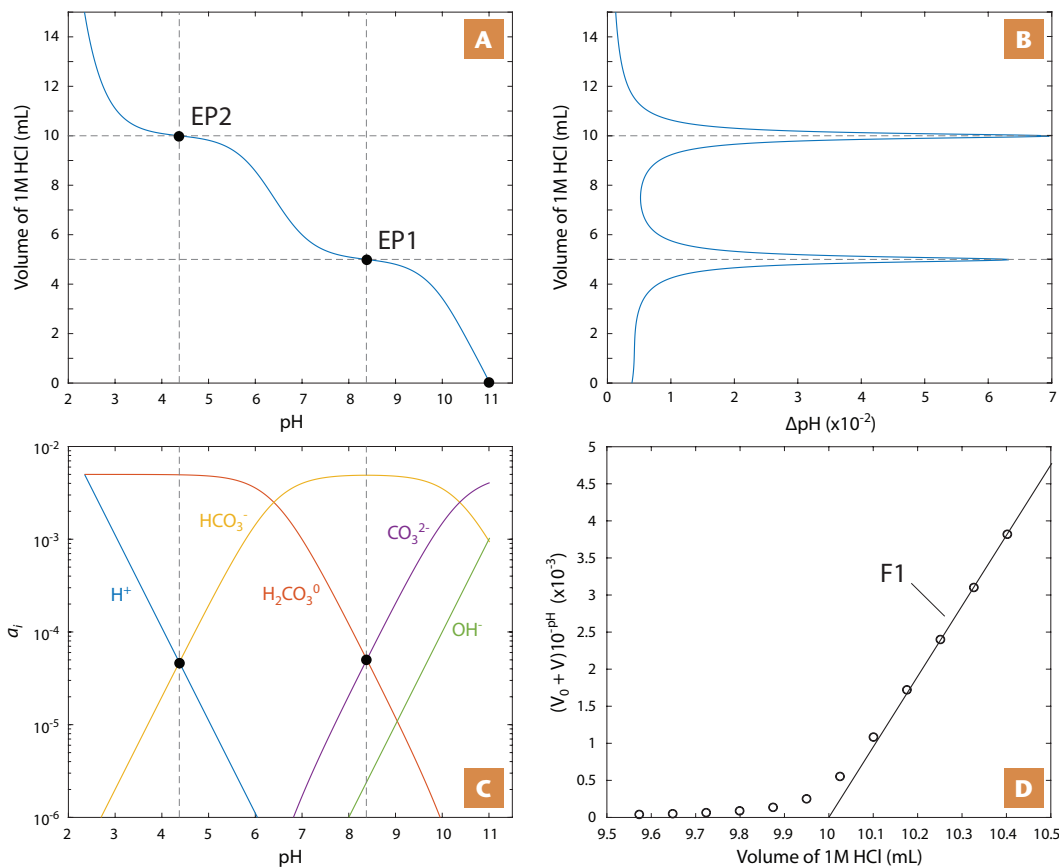


FIGURE 1 (A) Calculated titration curve of a 5 mmol·L⁻¹ Na₂CO₃ solution with 1 mol·L⁻¹ HCl. As acid is added, the pH decreases until the first equivalence point (EP1) is reached; this is where [H₂CO₃⁰] = [CO₃²⁻] and HCO₃⁻ is the dominant carbon species in solution. Further acid addition decreases the pH until a second equivalence point (EP2) is reached, where [H⁺] = [HCO₃⁻] and [H₂CO₃⁰] is the dominant carbon species in solution. The pH of the equivalence points is determined by the Na₂CO₃ concentration; the dissociation constants, K₁ and K₂, for carbonic acid; and K_w, the dissociation constant for H₂O. (B) The approximate derivative of the pH is calculated by taking the difference between adjacent values along the titration curve. The two maxima correspond to EP1 and EP2 in (A). (C) Bjerrum plot of the activities of proton donors and acceptors corresponding to the titration curve illustrated in (A). (D) Gran plot of titration data showing the linear Gran function F₁ and extrapolation to zero, which indicates the volume corresponding to the titration endpoint.

For the example discussed above (and in FIG. 1), a 5 mmol·L⁻¹ Na₂CO₃ solution, Eq. (5) implies that, at pH values below EP2 (4.33), proton donors will be in excess of proton acceptors, whereas at pH values above this, the reverse is true. In addition, the total amount of monoprotic acid (HCl in this case) added to reach EP2 is equal to 10 mmol·L⁻¹, which indicates that the initial solution is characterized by an excess of proton acceptors over donors (or total alkalinity), expressed as a charge concentration of 10 meq·L⁻¹.

Because natural waters can include a wide variety of acids and bases, it is important to clarify what constitutes proton donors and acceptors. The definition of the total alkalinity of seawater provides a useful example. As the determination of alkalinity for seawater became more precise (Gran 1952; Edmond 1970; Dickson 1981), so did its definition. For example, Dickson (1981) defined alkalinity as we have above: the charge concentration of the excess of proton acceptors over proton donors. In this definition, however, a proton acceptor is defined as a base formed from a weak acid with a dissociation constant (K) < 10^{-4.5}. Conversely, proton donors are defined as acids with K ≥ 10^{-4.5}. This choice of dissociation constant was made to match the reference level of protons for carbonic acid with the pH of the equivalence point of a titration of modern seawater (which is 4.5). For natural waters, appropriate definitions of alkalinity can be written relative to a reference, which represents relevant species defining the chosen zero proton condition. This permits the inclusion of several other proton donors or acceptors defined relative to the reference point, such as

$$\text{TA} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] + 2[\text{HPO}_4^{2-}] + 3[\text{PO}_4^{3-}] + [\text{H}_3\text{SiO}_4^-] + [\text{NH}_3] + [\text{HS}^-] + 2[\text{S}^{2-}] - [\text{H}^+] - [\text{HF}] - [\text{HSO}_4^-] - [\text{H}_3\text{PO}_4] \quad (6)$$

It is important to note, however, that this is not exhaustive. Rather, it only represents a general example of a multi-component solution characterized by several acid–base species. In fact, most of the time, this complexity can be avoided because alkalinity is dominated by the carbonic acid system for many natural waters. In these cases, total alkalinity is often approximately equal to the carbonate alkalinity (CA), which is defined as

$$\text{CA} = [\text{HCO}_3^-] + [\text{CO}_3^{2-}]. \quad (7)$$

Similarly, the specific contributions to total alkalinity from other acid–base compounds may be defined in an analogous way, e.g., borate alkalinity, silicate alkalinity, water or “caustic” alkalinity (Zeebe and Wolf-Gladrow 2001).

The various forms of alkalinity can be determined for natural waters in a number of different ways (see, e.g., the United States Geological Survey National Field Manual (Rounds 2012)). One such method is to use indicating compounds, such as phenolphthalein or bromocresol green-methyl red, which change color at pH values that correspond approximately to the first and second equivalence points of a carbonic acid titration, respectively. While these indicator-based methods can produce robust data, titration is widely regarded as the most accurate and reliable method for the determination of total alkalinity (Rounds 2012). Even so, the identification of titration endpoints can be susceptible to significant error, especially for low alkalinity waters. For this reason, the well-known Gran titration method (Gran 1952) is commonly utilized because it is rapid, does not rely on the identification of inflection points, and typically yields precise results. The Gran method effectively linearizes a set of functions that describe segments of the full titration curve. Stumm and Morgan (1996) offer a detailed treatment of

the Gran method starting with the proton mass balance. For example, when H^+ is present in significant excess of equivalence point EP2 in the above titration, the proton mass balance can be expressed as follows:

$$(v_0 + v)[H^+]_{\text{excess}} = (v - v_{\text{EP2}})C_A, \quad (8)$$

where v_0 is the initial sample volume, v is the volume of acid added, v_{EP2} is the volume of acid added to reach the equivalence point (here EP2), C_A is the molar concentration of acid used, and $[H^+]_{\text{excess}}$ is the excess H^+ concentration of protons relative to the proton condition:

$$[H^+]_{\text{excess}} = [H^+] - [HCO_3^-] + 2[CO_3^{2-}] + [OH^-]. \quad (9)$$

When protons are added in significant excess of EP2, $[H^+]_{\text{excess}}$ can be considered approximately equal to $[H^+]$ because under these conditions,

$$[H^+] \gg [HCO_3^-] + 2[CO_3^{2-}] + [OH^-]. \quad (10)$$

This simplifies to

$$(v_0 + v)[H^+] \approx (v - v_{\text{EP2}})C_A. \quad (11)$$

Substituting pH into Eq. (11) results in the Gran function, F_1 :

$$F_1 = (v_0 + v)10^{-\text{pH}} \approx (v - v_{\text{EP2}})C_A. \quad (12)$$

The equivalence point (when $v = v_{\text{EP2}}$) can therefore be determined when $F_1 = 0$. In practice, this can be done by adding acid in significant excess of the titration end point, plotting F_1 versus v , and linearly extrapolating to $F_1 = 0$ (FIG. 1D).

ALKALINITY AS A CHARGE BALANCE PARAMETER

For many geochemists, a more intuitive definition for alkalinity may also be derived from the requirement that all solutions must be electrically neutral. For example, charge balance for a typical natural water may be written as

$$[H^+] + [Na^+] + [K^+] + 2[Ca^{2+}] + 2[Mg^{2+}] = [Cl^-] + 2[SO_4^{2-}] + [NO_3^-] + [HCO_3^-] + 2[CO_3^{2-}] + [OH^-]. \quad (13)$$

Of these dissolved species, the concentrations of Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , and NO_3^- do not change with changes in pH, pressure, or temperature encountered near the Earth's surface and are therefore considered "conservative" (Drever 1997). This leads to another definition for total alkalinity if the conservative cations and anions are separated from the "non-conservative" species that appear in charge balance equations such as Eq. (13):

$$\text{Alkalinity} = \frac{\text{Equivalent sum of conservative cations} - \text{Equivalent sum of conservative anions}}{1}, \quad (14)$$

or, more specifically,

$$\text{Alkalinity} = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [OH^+] = ([Na^+] + [K^+] + 2[Ca^{2+}] + 2[Mg^{2+}]) - ([Cl^-] + 2[SO_4^{2-}] + [NO_3^-]). \quad (15)$$

Treating alkalinity as a charge balance parameter offers an intuitive means of understanding how alkaline waters may be generated. First, because the concentrations of conservative cations and anions (or, more precisely, their total analytical concentrations) do not change with pH, temperature, or pressure, total alkalinity itself is also a conservative quantity that does not change with pH, temperature, or pressure, even though the individual concentrations of HCO_3^- , CO_3^{2-} , H^+ , and OH^- do (Stumm and Morgan 1996; Drever 1997). Second, this shows how the

relative abundance of cations (e.g., Na^+) and anions (e.g., SO_4^{2-}) generated through biogeochemical reactions affect alkalinity. To provide further examples of the utility of this definition, consider the evolution of meteoric water with dissolved atmospheric CO_2 as it is influenced by the chemical weathering of alkali feldspar. It is clear that the release of Na^+ and K^+ will increase the alkalinity of the system because conservative cations increase in concentration but conservative anions do not. Thus, charge balance must be maintained by titratable bases, which in this example (and for many natural waters) is dominated by HCO_3^- and CO_3^{2-} . This definition also provides insight into how, in some circumstances, alkalinity can increase with evaporation (Tosca and Tutolo 2023 this issue). For example, if water with an alkalinity of $2 \text{ mEq} \cdot \text{L}^{-1}$ were to become concentrated 10-fold through evaporation, the concentrations of conservative anions and cations would increase uniformly (assuming no minerals precipitate), therefore increasing the alkalinity accordingly to $20 \text{ mEq} \cdot \text{L}^{-1}$. Exactly the opposite would occur if the water were diluted by 10-fold.

SUMMARY

Along with its counterpart pH, alkalinity is arguably one of the most fundamentally important, yet commonly misunderstood, parameters in the field of aqueous geochemistry. In this *Toolkit*, we have discussed what alkalinity is, why it is important, and how it is typically measured. We reviewed two complementary definitions for alkalinity that offer an intuitive starting point for understanding how this critical parameter responds to, and helps elucidate, biogeochemical processes, including those affecting the alkaline lakes that are the subject of this issue.

ACKNOWLEDGMENTS

The authors thank Francis Albarède, William Seyfried, Joel Hurowitz, and Janne Blichert-Toft for sharing perspectives on teaching alkalinity and for suggestions that greatly improved the clarity of this manuscript.

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