Acid and Bases: Alkalinity and pH in Natural Waters.

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OBJECTIVES

To understand the processes that control the pH of natural waters, *i.e.*, the balance between acids and bases. We shall focus our attention on the carbonate system, and on defining the sources of acids and bases in either natural or perturbed (because of anthropogenic activities) environments. Proton exchange reactions are usually fast, and are therefore conveniently treated at equilibrium.
Introduction

The pH of most natural waters is comprised between 6 and 9. However, various exceptions to this “rule” exist, e.g., acid mine drainage, acid rain, and hydrothermal solutions. The presence of ions in natural aqueous solutions results primarily from the weathering, along the hydrologic cycle, of rock minerals present at the surface of the earth. We can view this process as a gigantic acid/base titration occurring within the hydrosphere. Other processes, such as hydrothermal circulation, lead to changes in the chemical composition of natural waters but we shall limit our discussion here to surficial processes, e.g., the exogenic hydrologic cycle.
The Weathering Agent: CO$_2$

At the surface of the earth CO$_2$ is the main weathering agent, *i.e.*, the acid, that dissolves rock minerals. A very simple reaction is the weathering of carbonates, such as calcium carbonates, in presence of CO$_2$ that leads to the formation of bicarbonates and calcium ions.

\[
\text{CaCO}_3(\text{s}) + \text{H}_2\text{CO}_3 \rightleftharpoons \text{Ca}^{2+} + 2\text{HCO}_3^-
\]

This reaction summarizes a more complex set of chemical reactions that expresses the solubility of calcium carbonate as well as the acid/base equilibria in the carbonate system. These equations are:
\[
\text{CaCO}_3(\text{s}) \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-} \\
\text{CO}_2(\text{g}) + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 \\
\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \\
\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}
\]
The Bases: Rock Minerals!

The rocks present at the surface of the earth have different origins (genesis), and are classified according to these origins. One can distinguish:

**Igneous Rocks** that are formed as a result of the cooling of a magma. These rocks are up-lifted to the surface of the earth by tectonic movements.

**Sedimentary Rocks** that are formed as a result of a sedimentation process, *i.e.*, the deposition of particles. Biological processes play an important role in the formation of aquatic sediments.
Metamorphic Rocks that results from the transformation (i.e., metamorphosis) of rocks under high temperature and pressure.

We shall discuss rock minerals in more details in the next weeks (see Chapter 5 in your book). As an example, we can write here the weathering reaction of a common mineral (albite, a sodium-plagioclase) present in some igneous rocks by our “favourite” weathering agent:

\[
2\text{H}_2\text{CO}_3 + 9\text{H}_2\text{O} + 2\text{NaAlSi}_3\text{O}_8(s) \quad \rightleftharpoons \quad \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4(s) + 2\text{Na}^+ + 2\text{HCO}_3^- + 4\text{H}_4\text{SiO}_4
\]
Formation of soils

This reaction results in the formation of a secondary mineral (kaolinite) that is quite common in soils. Actually, the processes of chemical and physical weathering lead to the formation of soils. The dissolution of albite is termed incongruent because it leads to the formation of another solid phase: kaolinite. Congruent dissolution reactions result only in the release of soluble species. We shall see more on this topic later on.
The proton, Acid & Bases that are either strong or weak

At the beginning of the past century (ca. 1920), chemists established the conceptual framework for dealing with acid-base reactions. They realized the important role of the proton, $H^+$, and the fact that this proton was actually hydrated when in solution, i.e. present with a certain number of water molecules: $H_3O^+$ or $H_5O_2^+$. In 1923, Bronsted and Lowry proposed independently to call acids the chemical species that demonstrate the propensity to release protons, and bases the chemical species that accept protons. Depending on the “strenght” of this propensity acid and bases are ranked from strong to weak. Around the same time, Sorensen proposed to define the acidity of the medium by the measure of its pH:

$$\text{pH} = -\log[H^+] \text{ also } \text{pH} = -\log\{H^+\}$$
The strength of acid and bases

How can we characterize whether acids or bases are strong, relatively strong, weak, relatively weak, or... We shall say that an acid is strong when its propensity to release protons is high, and weak conversely. Acids that completely dissociate in water are therefore strong acids, *e.g.*, HClO$_4$, HCl, HNO$_3$, and acids that do not have a strong propensity to release protons are therefore weak, *e.g.* Acetic Acid (Ethanoic: CH$_3$COOH) that we studied in class.

The same will hold for bases with respect to their ability to capture protons. It is important to stress here that these definitions are related to the solvent, water in our case. Water is an amphoteric species, *i.e.* it behaves as an acid and a base. Therefore,
any chemical species that has the propensity to release protons but that is weaker than water in water will not influence the acid-base equilibrium of the medium that will be primarily determined by the dissociation of water

\[ \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \quad \text{or} \quad 2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^- \]

**How can we gauge this strength?**

We can look at the $pK_A = -\log K_A$ of the acid. Acid strength will increase as the $pK_A$ decreases. Acids with negative $pK_A$ will therefore be strong acids. Acids with $pK_A$ around 4 or 6 will therefore be considered weak. However these notions are linked to the concentration of the acid.
Another convenient way is to use the **Henderson-Hasselbach equation**.

\[
pH = pK_A + \log \frac{[A^-]}{[AH]}
\]

This equation is just a re-arrangement of the acid-base constant equation, but provides valuable insights. Intuitively, at a pH equal to the \( pK_A \) the concentrations of the acid and its conjugate base are equal. At precisely one (1) pH unit above the \( pK_A \), most of the acid is present under its conjugate base form, i.e., 90% of the acid is present as \( A^- \). One can see also that when \( pH > pK_A \), then \( A^- \) is the predominant species.
Biological Processes: A first look at Alkalinity

Until now we have primarily explored the abiotic part of the processes that affect the balance of acid and bases. Actually, the global CO$_2$ cycle is strongly dependent on biological processes. To illustrate this point, let’s consider for a moment the influence of photosynthesis on the carbonate system. The net result of photosynthesis is to form organic matter, CH$_2$O, and produce O$_2$, using as reactants CO$_2$ and H$_2$O, according to:

$$\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_2\text{O} + \text{O}_2$$

If now, we combine this reaction with the carbonate equilibrium equations:
\[
\begin{align*}
\text{CO}_2 + \text{H}_2\text{O} & \rightleftharpoons \text{H}_2\text{CO}_3 \\
\text{H}_2\text{CO}_3 & \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \\
\text{HCO}_3^- & \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}
\end{align*}
\]

and were to predict the influence of photosynthesis - that, according to the above equation, consumes \(\text{CO}_2\) - using the customary equilibrium displacement view and on the suite of carbonate equilibrium reactions, we would conclude that all the equilibria should be displaced towards the left. That is, the pH of the solution should decrease since we are moving towards the formation of the acid, \(\text{H}_2\text{CO}_3\) to compensate its lost.

This reasoning turns out to be wrong. Actually, if one were to observe the change in pH in surface waters of a Lake during a sunny and quiet day, i.e., stagnant surface waters and therefore
limited CO$_2$ transfer between the water and the atmosphere, we would observe an increase in pH. Our previous conclusion turns out to be incorrect because we did forget that we were dealing with charged species in solution, i.e., HCO$_3^-$ and CO$_3^{2-}$. So, now let’s consider a natural water that contains the major ions:

$$\text{Na}^+, \text{K}^+, \text{Ca}^{2+}, \text{Mg}^{2+}, \text{Cl}^-, \text{and} \text{SO}_4^{2-}$$

in addition to the carbonate ions. The electro-neutrality of the solution entails that:

$$[\text{Na}^+] + [\text{K}^+] + 2[\text{Ca}^{2+}] + 2[\text{Mg}^{2+}] + [\text{H}^+] =$$

$$[\text{Cl}^-] + 2[\text{SO}_4^{2-}] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-]$$
In this equation, and during photosynthesis, only the concentrations of the carbonate species are affected, that is $\sum CO_2$ diminishes, with:

$$\sum CO_2 = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$$

we can regroup in the electro-neutrality equation, on the same hand side, all the species that are not involved in any of the acid/base reactions, one gets:

$$[Na^+] + [K^+] + 2[Ca^{2+}] + 2[Mg^{2+}] − [Cl^-] − 2[SO_4^{2-}]$$

\[=\]

$$[HCO_3^-] + 2[CO_3^{2-}] + [OH^-] − [H^+]$$

As we can see, the left hand side of this equation does not change during the removal of CO$_2$ as a result of photosynthesis.
Therefore, since the left hand side remains constant, the only way to maintain the right hand side also constant is to modify the concentration of the species. Given that $\sum CO_2$ decreases the concentration of $H^+$ must decrease and consequently the pH will increase. This pH increase will also compensate the diminution of $HCO_3^-$ and $CO_3^{2-}$ as a result of the decrease of $\sum CO_2$, since:

$$\frac{K_1}{[H^+]} = \frac{[HCO_3^-]}{[H_2CO_3]} \quad \text{and} \quad \frac{K_2}{[H^+]} = \frac{[CO_3^{2-}]}{[HCO_3^-]}$$

**Conclusion:** From the chemical stand point, we can view photosynthesis, in this simple form, as a reaction leading to the decrease in the total concentration of acid, *i.e.*, $\sum CO_2$, at a constant “reserve of base”, *i.e.*, alkalinity. We shall next refine our definition of alkalinity.
Titration Alkalinity

One needs to relate our chemical calculations to observable, i.e., measurable quantities. If the concentrations of cations can be readily determined by atomic spectroscopy techniques, the concentrations of “inactive anions”, e.g., chloride and sulfate are usually measured either by colorimetric methods or using separation techniques such as ion chromatography or capillary electrophoresis. The most convenient way to determine acid/base species such as $\text{HCO}_3^-$ and $\text{CO}_3^{2-}$ is to perform a titration. In the case of natural waters, and in most instances, the carbonate system dominates. Therefore, the end point of the acid titration of a natural water sample will be primarily determined by this acid/base system. We shall see that the pH of the end point (the pH of the equivalence point) lies actually between
$4 < \text{pH} < 5$, ca. pH = 4.5. At this pH, the dominant base species are **quantitatively** titrated, that entails that the concentrations of $\text{CO}_3^{2-}$ and $\text{HCO}_3^-$ are negligible. A figure is worth a thousand words... lets build pH=pK lines - 1D pC-pH diagrams if you wish - where we position the location of the pH of the end point, the pH$_{(eq)}$ in the graph.

![pH=pK diagram](image)

We shall call Alk$_t$: **Titration Alkalinity**. It is the quantity that results from the process of titrating with a strong acid, e.g., HCl, a natural water sample to the end point of the carbonate system. From the graph above, we can see that both $\text{CO}_3^{2-}$ and
HCO$_3^-$ will be protonated leading to the following contribution to the titration alkalinity, also called carbonate alkalinity, Alk$_C$:

$$\text{Alk}_C = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]$$

Now let's expand this approach to the other acid/base systems present in natural waters, even though they are not dominant species in most cases they will contribute to the titration alkalinity. Let's first consider the phosphate system and draw again the pH=pK line with the location of the pH of the equivalent volume.

At the pH of the equivalent point H$_2$PO$_4^-$ is not titrated, therefore the contribution of the phosphate system to the titration
alkalinity is:

\[ \text{Alk}_p = [\text{HPO}_4^{2-}] + 2[\text{PO}_4^{3-}] - [\text{H}_3\text{PO}_4] \]

since the acid \( \text{H}_3\text{PO}_4 \) contributes protons in this case. *Note that the factor and the charge of the species differ in this case. Why do you think that is?*

We can also add the contributions of the various other acid/base systems of relevance in natural waters. For example, in anoxic waters the presence of amonia and sulfides provide additional terms to \( \text{Alk}_t \) since, for amomia one has:

\[
\begin{align*}
\text{NH}_4^+ \quad & \text{pH}_{\text{eq}} \quad \text{pK}_1 = 9.24 \quad \text{NH}_3 \\
\text{pH} = \text{pK} \quad &
\end{align*}
\]
and for the sulfidic system:

\[
\begin{align*}
\text{H}_2\text{S} & \quad p\text{Heq} \quad pK_1 = 7.02 \quad \text{HS}^- \\
\text{pH} = pK
\end{align*}
\]

In the special case of sea water, one needs to consider the presence of the borate system.

\[
\begin{align*}
\text{H}_5\text{BO}_4^- & \quad p\text{Heq} \quad pK_1 = 9.24 \quad \text{H}_4\text{BO}_4^- \\
\text{pH} = pK
\end{align*}
\]

In addition, the silicilic system also presents acid/base properties - please draw yourself the relevant pH=pK line. Hence, the final expression for Alk_t becomes:
\[ \text{Alk}_t = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{HPO}_4^{2-}] + 2[\text{PO}_4^{3-}] + [\text{NH}_3] + [\text{HS}^-] + [\text{B(OH)}_4^-] + [\text{H}_3\text{SiO}_4^-] + 2[\text{H}_2\text{SiO}_4^{2-}] + [\text{OH}^-] - [\text{H}^+] - [\text{H}_3\text{PO}_4] \]