

Chemical Equilibria and pH Calculations

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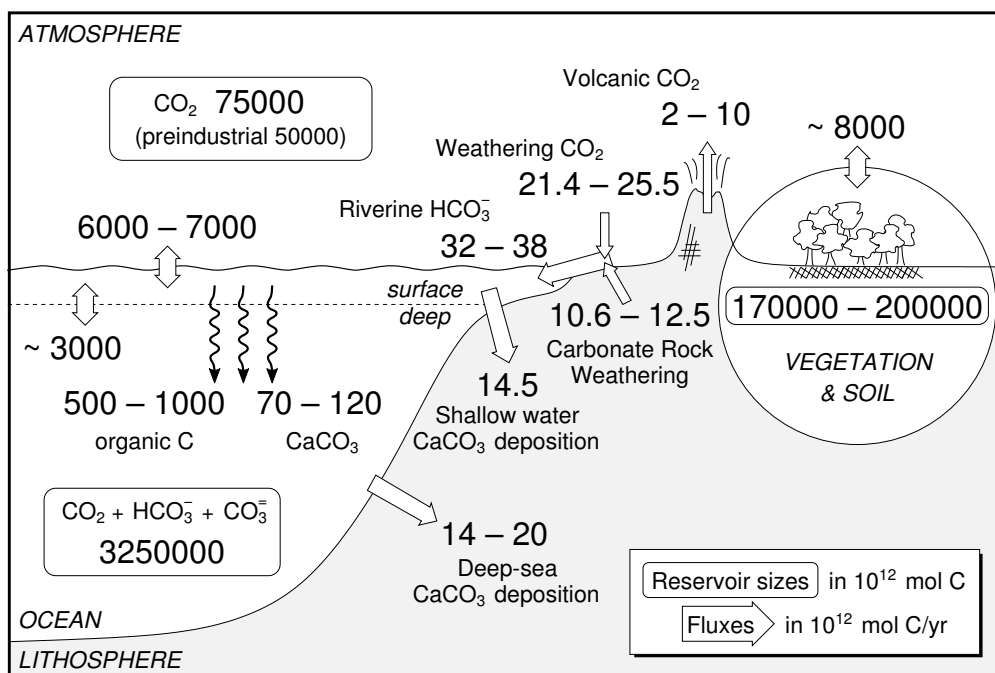
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Plan

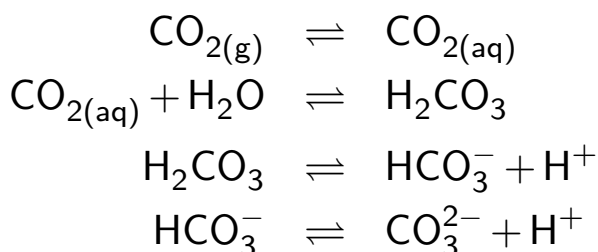
- Chemistry of the carbon dioxide system
- Chemical equilibria
- pH scales
- Conservative state variables:
dissolved inorganic carbon and alkalinity
- Carbonate: calculation

Processes and Exchange Fluxes



Carbonate Chemistry

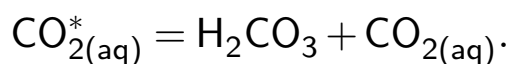
Dissolution of atmospheric CO₂ in water



Actually

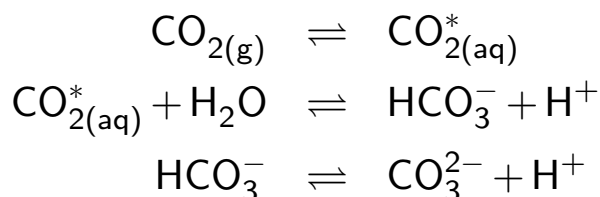
$$\frac{[\text{H}_2\text{CO}_3]}{[\text{H}_2\text{CO}_3] + [\text{CO}_{2(\text{aq})}]} \ll 1$$

For practical usage, we define



Carbonate Chemistry

Equilibrium system actually used:



Equilibrium relationships

$$\begin{aligned} K_H^* &= \frac{[\text{CO}_{2(aq)}^*]}{f_{\text{CO}_2}} \quad (\text{Henry's Law}) \\ K_1^* &= \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_{2(aq)}^*]} \\ K_2^* &= \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \end{aligned}$$

pK Values of the Equilibrium Constants

- $pK := -\log_{10}(K)$, by analogy with $pH := -\log_{10}([\text{H}^+])$
- Consider, e. g., the equilibrium between $\text{CO}_{2(aq)}^*$ and HCO_3^- in a solution containing dissolved CO_2 :

$$K_1^* = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_{2(aq)}^*]}$$

When $[\text{CO}_{2(aq)}^*] = [\text{HCO}_3^-]$ (\rightarrow *equivalence point*), we have

$$K_1^* = [\text{H}^+] \quad \Leftrightarrow \quad pK_1^* = pH$$

\Rightarrow equivalence points located at the pK values

Stoichiometric vs. Thermodynamic Constants

- K_H^* , K_1^* and K_2^* are *stoichiometric constants* as they link concentrations
- The corresponding *thermodynamic equilibrium constants* K_H , K_1 and K_2
 - link *activities* instead of concentrations
 - only depend on temperature and pressure
 - have been determined for a large number of reactions
- The activity $\{A\}$ and the concentration $[A]$ of a chemical species A are related by the activity coefficient γ_A

$$\{A\} = \gamma_A[A]$$

- γ_A depends on the chemical composition of the solution

Chemical Composition of Seawater

Composition of
 one kilogram of
 average seawater
 ($S = 35$)

Solute	mol
Na^+	0.46900
Mg^{2+}	0.05282
Ca^{2+}	0.01028
K^+	0.01021
Sr^{2+}	0.00009
Cl^-	0.54588
SO_4^{2-}	0.02823
HCO_3^-	0.00186
Br^-	0.00084
CO_3^{2-}	0.00019
$\text{B}(\text{OH})_4^-$	0.00008
F^-	0.00007
$\text{B}(\text{OH})_3$	0.00033

After Millero (1982)

Activity Coefficients

- Influence of activity coefficients not negligible in seawater

Ion	γ
Na ⁺	0.666
Cl ⁻	0.668
H ⁺	0.590
HCO ₃ ⁻	0.570
CO ₃ ²⁻	0.039

Conditions:
 seawater at 25°C and $S = 35$
 After Zeebe and Wolf-Gladrow
 (2003, Tab. 1.1.3)

- Two ways to address this complication
 - calculation of γ values from solute interaction models
 ⇒ difficult and tedious
 - empirical determination of stoichiometric coefficients including effects of γ , as a function of temperature, pressure and salinity
 ⇒ adopted in practice

pH Scales

- Classically $pH = -\log_{10}[H^+]$
- However, even in freshwater solutions, free H⁺ ions present only in negligible amounts: most are complexed by water molecules
- In seawater, this complexing extends to other solutes as well
- In seawater, it would be best to adopt $pH = -\log_{10}\{H^+\}$
 ⇒ useless as $\{H^+\}$ cannot be individually measured
- Definition of operational pH scales that take into account the presence of extra ions able to release H⁺ ions
- Motivations essentially experimentally oriented

pH Scales: Free, Total, . . .

- *Free Scale* – based upon $[\text{H}^+]_{\text{F}}$, the concentration of free and hydrated H^+ ions
- *Total Scale* – takes into account the role of HSO_4^- :

$$\begin{aligned} \text{pH}_{\text{T}} &:= -\log_{10} [\text{H}^+]_{\text{T}} \\ [\text{H}^+]_{\text{T}} &:= [\text{H}^+]_{\text{F}} (1 + S_{\text{T}}/K_{\text{S}}) \end{aligned}$$

where

- $S_{\text{T}} = [\text{SO}_4^{2-}] + [\text{HSO}_4^-]$ is the total sulphate concentration
- $K_{\text{S}} = \frac{[\text{H}^+]_{\text{F}} [\text{SO}_4^{2-}]}{[\text{HSO}_4^-]}$ is the dissociation constant of HSO_4^-
- $[\text{H}^+]_{\text{T}} \simeq [\text{H}^+]_{\text{F}} + [\text{HSO}_4^-]$

pH Scales: . . . Seawater

- *Seawater Scale* – takes into account the roles of HSO_4^- and HF:

$$\begin{aligned} \text{pH}_{\text{SWS}} &:= -\log_{10} [\text{H}^+]_{\text{SWS}} \\ [\text{H}^+]_{\text{SWS}} &:= [\text{H}^+]_{\text{F}} (1 + S_{\text{T}}/K_{\text{S}} + F_{\text{T}}/K_{\text{F}}) \end{aligned}$$

where

- S_{T} and K_{S} as for the Total Scale
- $F_{\text{T}} = [\text{HF}] + [\text{F}^-]$ is the total concentration of fluorine
- $K_{\text{F}} = \frac{[\text{H}^+]_{\text{F}} [\text{F}^-]}{[\text{HF}]}$ is the dissociation constant of HF
- $[\text{H}^+]_{\text{SWS}} \simeq [\text{H}^+]_{\text{F}} + [\text{HSO}_4^-] + [\text{HF}]$

Carbonate Speciation

Why are these precisions important?

- Stoichiometric dissociation acid dissociation constant (such as K_1^* and K_2^* , e. g.) have the same units as $[H^+]$
 \Rightarrow need to know on which pH scale these constants are given
- Dialogue between modellers and experimentalists easier if concepts used in common are known and agreed upon

Carbonate Chemistry

Let $C_T = [CO_{2(aq)}^*] + [HCO_3^-] + [CO_3^{2-}]$. Equilibrium relationships lead to the following *speciation relationships*

$$\frac{[CO_{2(aq)}^*]}{C_T} = \frac{[H^+]^2}{[H^+]^2 + K_1^*[H^+] + K_1^*K_2^*}$$

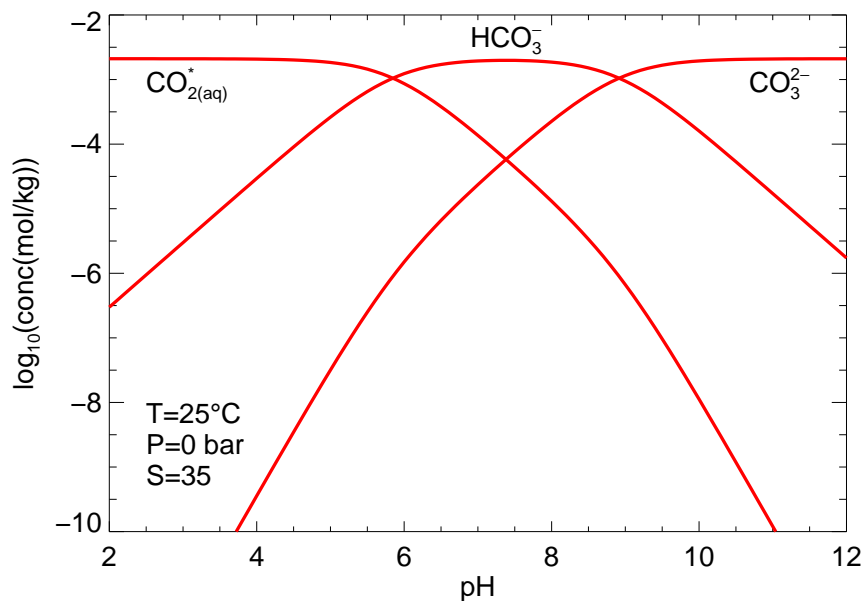
$$\frac{[HCO_3^-]}{C_T} = \frac{K_1^*[H^+]}{[H^+]^2 + K_1^*[H^+] + K_1^*K_2^*}$$

$$\frac{[CO_3^{2-}]}{C_T} = \frac{K_1^*K_2^*}{[H^+]^2 + K_1^*[H^+] + K_1^*K_2^*}$$

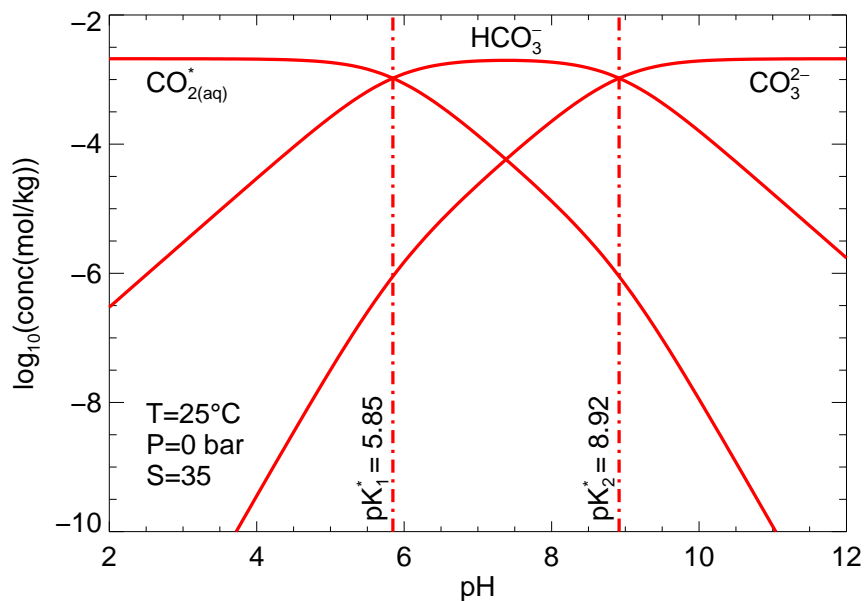
\Rightarrow

pH plays a central role for the *speciation* of the CO_2 - HCO_3^- - CO_3^{2-} system

Speciation: Bjerrum Plot

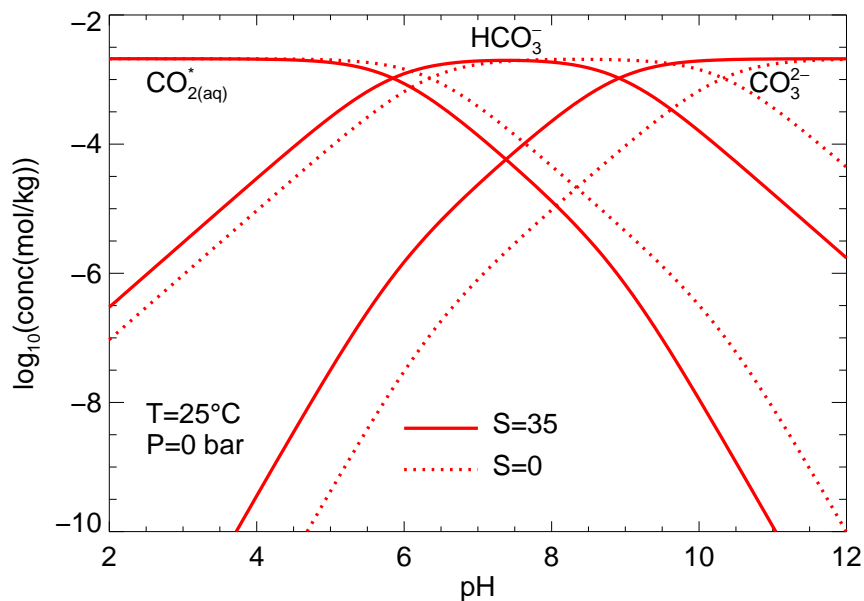


Speciation: Bjerrum Plot



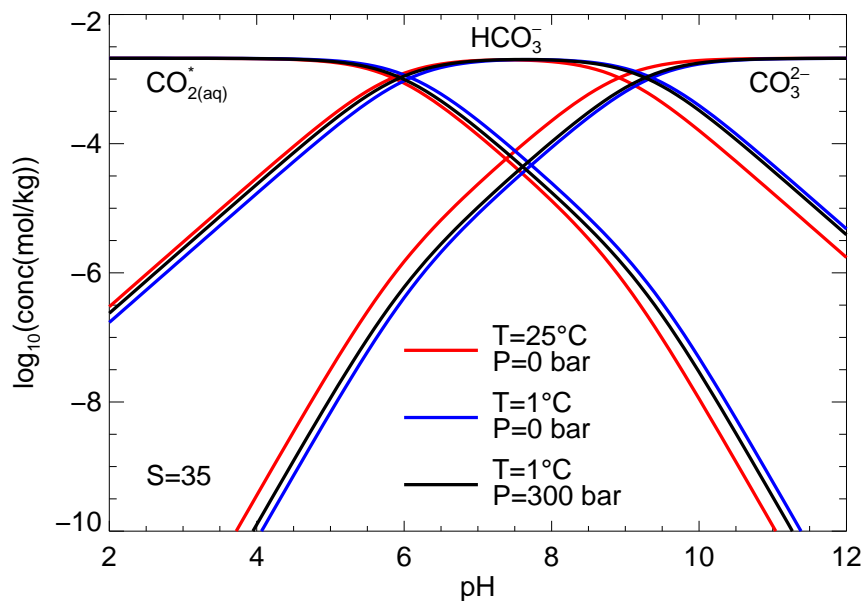
Points d'équivalence

Speciation: Bjerrum Plot



Seawater – freshwater

Speciation: Temperature and Pressure Effects



Temperate and cold surface waters, deep water (3000 m)

Carbonate Chemistry

Special Roles of Different Species

- $\text{CO}_{2(\text{aq})}$: air-sea exchange
- CO_3^{2-} : carbonate dissolution

Measurables

- $\text{CO}_{2(\text{aq})}$: by IR absorption (under favourable conditions)
- pH: after consideration of all the complications
- CO_3^{2-} : UV spectrophotometry of Pb(II) complexation
- C_T : by degassing via acidification
- Alkalinity: by titration with a strong acid (e. g., HCl)

State Variables of the Carbonate System

- H^+ (or pH), $\text{CO}_{2(\text{aq})}$ (or pCO_2) and CO_3^{2-} are the only species participating in the carbonate equilibria that can be directly measured
- Neither H^+ nor pCO_2 nor CO_3^{2-} are conservative: variations are not only controlled by sources and sinks in the system, but also by other state variables of the system (temperature, pressure) or other solutes, ...

⇒ pH , pCO_2 and CO_3^{2-} are unsuitable as state variables in models

- C_T is conservative and measurable
- 4 unknowns and 2 equilibrium relationships would require a second conservative and measurable parameter ... alkalinity

Alkalinity: a First Tour

- Alkalinity measures the capacity of a solution to neutralize acid to the bicarbonate equivalence point (where $[\text{HCO}_3^-] = [\text{H}^+]$), also called *second equivalence point*
- Measured by titration of a sample with a strong acid (generally HCl) until the equivalence point is reached; the *titration curve* (evolution of pH as a function of the added amount of acid) has an inflection point at this point, which must be determined with precision
- The alkalinity of the sample is then defined as the mole equivalent of acid added to reach the equivalence point \Rightarrow at the equivalence point, alkalinity is reduced to zero

Alkalinity: Exact Definition

Dickson (1981):

“The total alkalinity of a natural water is thus defined as the number of moles of hydrogen ion equivalent to the excess of proton acceptors (bases formed from weak acids with a dissociation constant $K \leq 10^{-4.5}$, at 25 °C and zero ionic strength) over proton donors (acids with $K > 10^{-4.5}$) in one kilogram of sample.”

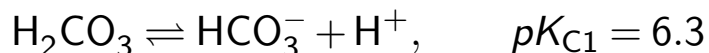
$$\text{Alk}_T := \sum_i [\text{proton acceptor}_i] - \sum_j [\text{proton donor}_j]$$

Notice that

$$K \leq 10^{-4.5} \Leftrightarrow pK \geq 4.5 \quad \text{and} \quad K > 10^{-4.5} \Leftrightarrow pK < 4.5$$

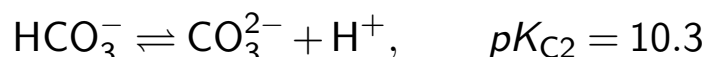
Alkalinity Contributions: Carbonic Acid Example

- Carbonic Acid H_2CO_3



$pK_{C1} \geq 4.5 \Rightarrow$ base is an acceptor, contributing $+\text{[HCO}_3^-]$

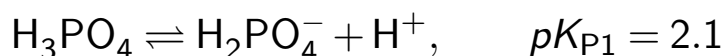
- Bicarbonate ion HCO_3^-



$pK_{C2} \geq 4.5 \Rightarrow$ base is an acceptor, contributing $+2 \times [\text{CO}_3^{2-}]$:
by accepting a proton, the base CO_3^{2-} is converted to HCO_3^- ,
another acceptor, which must also be accounted for.

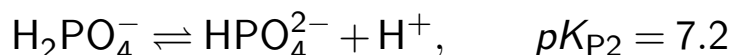
Alkalinity Contributions: Phosphoric Acid Example

- Orthophosphoric Acid H_3PO_4



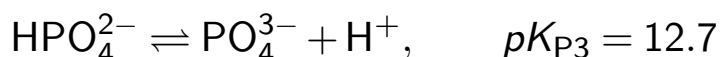
$pK_{P1} < 4.5 \Rightarrow$ acid is a donor and contributes $-\text{[H}_3\text{PO}_4]$

- Dihydrogen phosphate H_2PO_4^-



$pK_{P2} \geq 4.5 \Rightarrow$ base is an acceptor and contributes $+\text{[HPO}_4^{2-}]$

- Hydrogen phosphate HPO_4^{2-}



$pK_{P3} \geq 4.5 \Rightarrow$ base is an acceptor, contributing $+2 \times [\text{PO}_4^{3-}]$

Alkalinity

Acide	pK_A	Type provided	Species	H^+ eq/mol
H_2O	14.0	acceptor	OH^-	$[OH^-]$
H_2CO_3	6.3	acceptor	HCO_3^-	$[HCO_3^-]$
HCO_3^-	10.3	acceptor	CO_3^{2-}	$2 \times [CO_3^{2-}]$
$B(OH)_3$	9.2	acceptor	$B(OH)_4^-$	$[B(OH)_4^-]$
HSO_4^-	2.0	donor	HSO_4^-	$-[HSO_4^-]$
HF	3.2	donor	HF	$-[HF]$
H^+	—	donor	H^+	$-[H^+]$
H_3PO_4	2.1	donor	H_3PO_4	$-[H_3PO_4]$
$H_2PO_4^-$	7.2	acceptor	HPO_4^{2-}	$[HPO_4^{2-}]$
HPO_4^{2-}	12.7	accepteur	PO_4^{3-}	$2 \times [PO_4^{3-}]$
H_4SiO_4	9.7	acceptor	$H_3SiO_4^-$	$[H_3SiO_4^-]$
H_2S	7.0	acceptor	HS^-	$[HS^-]$
HS^-	12.0	acceptor	S^{2-}	$2 \times [S^{2-}]$
NH_4^+	9.3	acceptor	NH_3	$[NH_3]$

Compiled from data reported by Dickson (1981)

Alkalinity in Detail

We thus obtain the following expression for alkalinity

$$\begin{aligned}
 \text{Alk}_T = & [HCO_3^-] + 2 \times [CO_3^{2-}] + [B(OH)_4^-] + [OH^-] \\
 & + [HPO_4^{2-}] + 2 \times [PO_4^{3-}] + [H_3SiO_4^-] \\
 & + [NH_3] + [HS^-] + 2 \times [S^{2-}] + \dots \\
 & - [H^+]_F - [HSO_4^-] - [HF] - [H_3PO_4] - \dots
 \end{aligned}$$

where the ... stand for the concentrations of additional negligible proton donors and acceptors.

Alkalinity in Practice

Alkalinity can generally be approximated to excellent precision by

$$\text{Alk}_T \simeq [\text{HCO}_3^-] + 2 \times [\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] + [\text{OH}^-] - [\text{H}^+] \equiv \text{Alk}_{\text{CBW}}$$

Often, it is even sufficient to adopt

$$\text{Alk}_T \simeq [\text{HCO}_3^-] + 2 \times [\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] \equiv \text{Alk}_{\text{CB}}$$

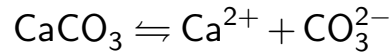
However, under certain particular conditions, it may be necessary to take additional contributors into account, such as, e. g., the conjugate bases of phosphoric or silicic acids

Alkalinity: a Few Comments

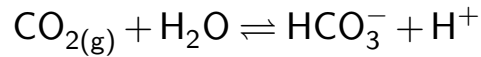
- Alkalinity is a complex concept, with an opaque definition
- In the literature, there are alternative definitions based upon electroneutrality, that define alkalinity as being equal to the charge difference between conservative cations and anions
- Alkalinity defined this way
 - is also conservative (by construction);
 - neglects contributions from non charged bases (e. g., NH_3) that may be important under some conditions (e. g., anoxic waters)
 - is equal to total alkalinity up to a sum of total concentrations (total phosphate, ammonium, sulphate), that are often, but not always, negligible
 - makes the concept even more confusing

Total Alkalinity: Properties

- Total alkalinity is conservative
 - affected by the precipitation and the dissolution of minerals



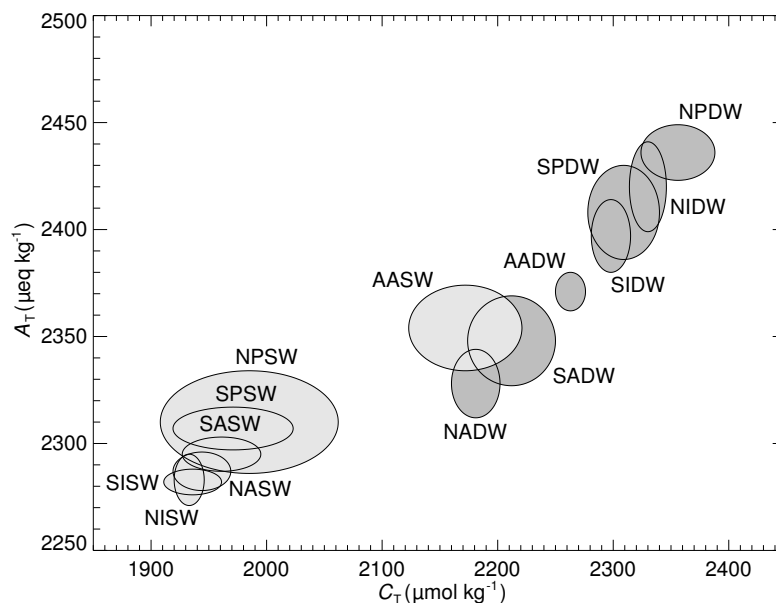
- not affected by the dissolution of gaseous CO_2 in water



- mixing two water samples, with masses M_1 and M_2 , and total alkalinities A_1 and A_2 , resp., produce a mixture of mass $M = M_1 + M_2$ and total alkalinity A , such that $MA = M_1A_1 + M_2A_2$
- The dominant alkalinity fraction in the most natural waters is *carbonate alkalinity*

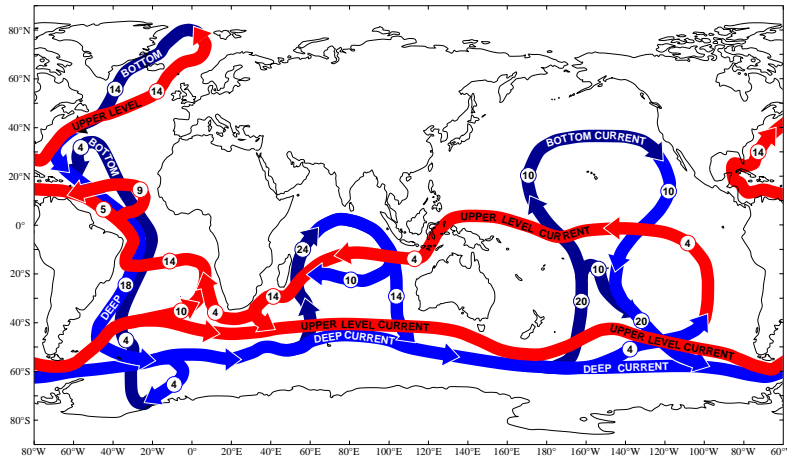
$$\text{Alk}_C = [\text{HCO}_3^-] + 2 \times [\text{CO}_3^{2-}]$$

C_T and Alk_T in the Ocean

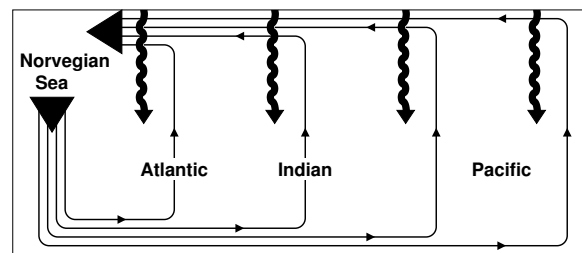


DIC: Dissolved Inorganic Carbon

C_T and Alk_T in the Ocean: Origin of Gradients



Vertical
 gradients



Inter-basin
 gradients

Following Broecker and Peng (1982)

Calculating pH and Speciation From Alk_T and C_T

Posing the problem

- select an appropriate approximation, such as, e. g.,

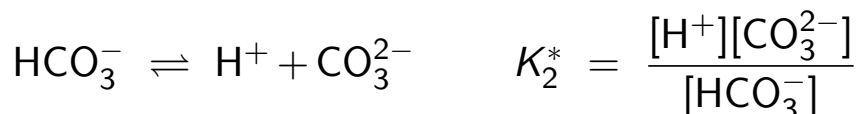
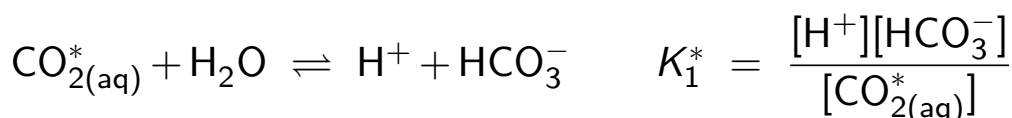
$$Alk_T \simeq [HCO_3^-] + 2 \times [CO_3^{2-}] + [B(OH)_4^-] + [OH^-] - [H^+]$$

- Alk_T , B_T and C_T are given
- temperature, salinity and pressure given
- determine
 - solution pH
 - $[CO_{2(aq)}^*]$, $[HCO_3^-]$, $[CO_3^{2-}]$ (speciation)
 - CO_2 partial pressure in the atmosphere in equilibrium with the solution (pCO_2)

⇒ express each concentration as a function of $[H^+]$...

Carbonate System Speciation

$$C_T = [\text{CO}_2^*_{(\text{aq})}] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$$



K_1^* and K_2^* (stoichiometric) equilibrium constants

Carbonate System Speciation

$$K_1^* = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2^*_{(\text{aq})}]} \Rightarrow [\text{HCO}_3^-] = \frac{K_1^*}{[\text{H}^+]} [\text{CO}_2^*_{(\text{aq})}]$$

$$K_2^* = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \Rightarrow [\text{CO}_3^{2-}] = \frac{K_2^*}{[\text{H}^+]} [\text{HCO}_3^-]$$

$$= \frac{K_1^* K_2^*}{[\text{H}^+]^2} [\text{CO}_2^*_{(\text{aq})}]$$

Hence

$$C_T = [\text{CO}_2^*_{(\text{aq})}] + \frac{K_1^*}{[\text{H}^+]} [\text{CO}_2^*_{(\text{aq})}] + \frac{K_1^* K_2^*}{[\text{H}^+]^2} [\text{CO}_2^*_{(\text{aq})}]$$

$$= [\text{CO}_2^*_{(\text{aq})}] \frac{[\text{H}^+]^2 + K_1^* [\text{H}^+] + K_1^* K_2^*}{[\text{H}^+]^2}$$

Carbonate System: Speciation Relationships

Accordingly

$$[\text{CO}_2^*(\text{aq})] = \frac{[\text{H}^+]^2}{[\text{H}^+]^2 + K_1^*[\text{H}^+] + K_1^*K_2^*} C_T.$$

Since

$$[\text{HCO}_3^-] = \frac{K_1^*}{[\text{H}^+]} [\text{CO}_2^*(\text{aq})] \quad \text{and} \quad [\text{CO}_3^{2-}] = \frac{K_1^*K_2^*}{[\text{H}^+]^2} [\text{CO}_2^*(\text{aq})]$$

we furthermore get

$$[\text{HCO}_3^-] = \frac{K_1^*[\text{H}^+]}{[\text{H}^+]^2 + K_1^*[\text{H}^+] + K_1^*K_2^*} C_T$$

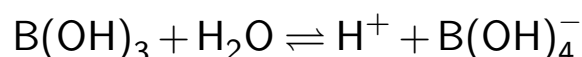
$$[\text{CO}_3^{2-}] = \frac{K_1^*K_2^*}{[\text{H}^+]^2 + K_1^*[\text{H}^+] + K_1^*K_2^*} C_T$$

Borate System Speciation

Total dissolved borate

$$B_T = [\text{B}(\text{OH})_3] + [\text{B}(\text{OH})_4^-]$$

Acid-base equilibrium



Equilibrium relationship

$$K_B^* = \frac{[\text{H}^+][\text{B}(\text{OH})_4^-]}{[\text{B}(\text{OH})_3]}$$

Borate System: Speciation Relationships

$$K_B^* = \frac{[\text{H}^+][\text{B}(\text{OH})_4^-]}{[\text{B}(\text{OH})_3]} \Rightarrow [\text{B}(\text{OH})_4^-] = \frac{K_B^*}{[\text{H}^+]} [\text{B}(\text{OH})_3]$$

$$\begin{aligned} B_T &= [\text{B}(\text{OH})_3] + \frac{K_B^*}{[\text{H}^+]} [\text{B}(\text{OH})_3] \\ &= [\text{B}(\text{OH})_3] \frac{[\text{H}^+] + K_B^*}{[\text{H}^+]} \end{aligned}$$

Hence

$$[\text{B}(\text{OH})_3] = \frac{[\text{H}^+]}{[\text{H}^+] + K_B^*} B_T \quad \text{and} \quad [\text{B}(\text{OH})_4^-] = \frac{K_B^*}{[\text{H}^+] + K_B^*} B_T$$

Calculating pH From Alk_T and C_T

Processing of the Alk_T terms related to the carbonate system

$$[\text{HCO}_3^-] = \frac{K_1^*[\text{H}^+]}{[\text{H}^+]^2 + K_1^*[\text{H}^+] + K_1^*K_2^*} C_T$$

$$2[\text{CO}_3^{2-}] = \frac{2K_1^*K_2^*}{[\text{H}^+]^2 + K_1^*[\text{H}^+] + K_1^*K_2^*} C_T$$

$$[\text{B}(\text{OH})_4^-] = \frac{K_B^*}{[\text{H}^+] + K_B^*} B_T$$

$$[\text{OH}^-] = \frac{K_W^*}{[\text{H}^+]}$$

Calculating pH From Alk_T and C_T

$$\frac{K_1^*[\text{H}^+] + 2K_1^*K_2^*}{[\text{H}^+]^2 + K_1^*[\text{H}^+] + K_1^*K_2^*} C_T + \frac{K_B^*}{[\text{H}^+] + K_B^*} B_T + \frac{K_W^*}{[\text{H}^+]} - [\text{H}^+] - \text{Alk}_T = 0$$

- Equation of the form $f([\text{H}^+]) = 0$, where $[\text{H}^+] > 0$
- First term
 - strictly decreasing with $[\text{H}^+]$ for $C_T > 0$
 - $\lim_{[\text{H}^+] \rightarrow 0} = 2C_T$
 - $\lim_{[\text{H}^+] \rightarrow +\infty} = 0$

Calculating pH From Alk_T and C_T

$$\frac{K_1^*[\text{H}^+] + 2K_1^*K_2^*}{[\text{H}^+]^2 + K_1^*[\text{H}^+] + K_1^*K_2^*} C_T + \frac{K_B^*}{[\text{H}^+] + K_B^*} B_T + \frac{K_W^*}{[\text{H}^+]} - [\text{H}^+] - \text{Alk}_T = 0$$

- Second term
 - strictly decreasing with $[\text{H}^+]$ for $B_T > 0$
 - $\lim_{[\text{H}^+] \rightarrow 0} = B_T$
 - $\lim_{[\text{H}^+] \rightarrow +\infty} = 0$
- Third and fourth terms
 - strictly decreasing with $[\text{H}^+]$
 - $\lim_{[\text{H}^+] \rightarrow 0} = +\infty$
 - $\lim_{[\text{H}^+] \rightarrow +\infty} = -\infty$

Calculating pH From Alk_T and C_T

$$\frac{K_1^*[\text{H}^+] + 2K_1^*K_2^*}{[\text{H}^+]^2 + K_1^*[\text{H}^+] + K_1^*K_2^*} C_T + \frac{K_B^*}{[\text{H}^+] + K_B^*} B_T + \frac{K_W^*}{[\text{H}^+]} - [\text{H}^+] - \text{Alk}_T = 0$$

Equation of the form $f([\text{H}^+]) = 0$, where $[\text{H}^+] > 0$ and

- f strictly decreasing with $[\text{H}^+]$
- f unbounded: $\sup = +\infty$, $\inf = -\infty$

\Rightarrow one and only one positive root for any Alk_T .

Calculating pH From Alk_T and C_T

$$\frac{K_1^*[\text{H}^+] + 2K_1^*K_2^*}{[\text{H}^+]^2 + K_1^*[\text{H}^+] + K_1^*K_2^*} C_T + \frac{K_B^*}{[\text{H}^+] + K_B^*} B_T + \frac{K_W^*}{[\text{H}^+]} - [\text{H}^+] - \text{Alk}_T = 0$$

Root H has an intrinsic lower bound:

- consider the infimum of non-water alkalinity: $A_{nW\text{inf}} = 0$
- let H_{inf} be the positive root of $A_{nW\text{inf}} + \frac{K_W^*}{H_{\text{inf}}} - H_{\text{inf}} - \text{Alk}_T = 0$
- $f(H_{\text{inf}}) > A_{nW\text{inf}} + \frac{K_W^*}{H_{\text{inf}}} - H_{\text{inf}} - \text{Alk}_T = 0$
- accordingly: $H_{\text{inf}} < H \dots$

Calculating pH From Alk_T and C_T

$$\frac{K_1^*[\text{H}^+] + 2K_1^*K_2^*}{[\text{H}^+]^2 + K_1^*[\text{H}^+] + K_1^*K_2^*} C_T + \frac{K_B^*}{[\text{H}^+] + K_B^*} B_T + \frac{K_W^*}{[\text{H}^+]} - [\text{H}^+] - \text{Alk}_T = 0$$

... and the root H has an intrinsic upper bound:

- consider the supremum of non-water alkalinity:

$$A_{\text{nWsup}} = 2C_T + B_T$$

- let H_{sup} be the positive solution of

$$A_{\text{nWsup}} + \frac{K_W^*}{H} - H - \text{Alk}_T = 0$$

- $f(H_{\text{sup}}) < A_{\text{nWsup}} + \frac{K_W^*}{H_{\text{sup}}} - H_{\text{sup}} - \text{Alk}_T = 0$

$$\Rightarrow \boxed{H_{\text{inf}} < H < H_{\text{sup}}}$$

Calculating pH From Alk_T and C_T

$$\frac{K_1^*[\text{H}^+] + 2K_1^*K_2^*}{[\text{H}^+]^2 + K_1^*[\text{H}^+] + K_1^*K_2^*} C_T + \frac{K_B^*}{[\text{H}^+] + K_B^*} B_T + \frac{K_W^*}{[\text{H}^+]} - [\text{H}^+] - \text{Alk}_T = 0$$

- Equation of the form $f([\text{H}^+]) = 0$, where $[\text{H}^+] > 0$ and

- f strictly decreasing with $[\text{H}^+]$
- f unbounded: $\text{sup} = +\infty$, $\text{inf} = -\infty$

\Rightarrow one and only one positive root for any Alk_T .

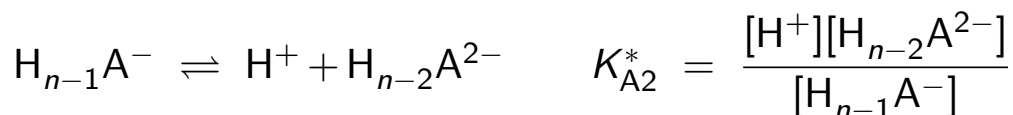
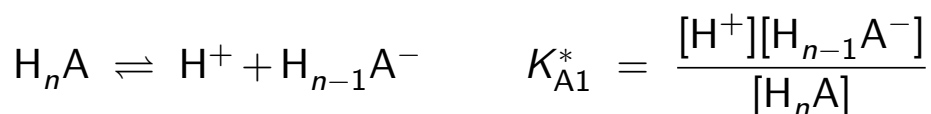
- Root can be intrinsically bracketed
- Equation can be reliably solved for $[\text{H}^+]$ by a hybrid Newton-Raphson–bisection method (convergence guaranteed)

Calculating pH From Alk_T , C_T , and Further Systems

- Add contributions, e. g., from the phosphate system
- $Alk_P = [HPO_4^{2-}] + 2 \times [PO_4^{3-}] - [H_3PO_4]$
- Needs speciation relationships for complex acid-base systems

General Acid-Base System

- Dissociation reactions of a general n -protic acid H_nA



⋮

⋮



- K_{A1}^* , K_{A2}^* , \dots , K_{An}^* (stoichiometric) equilibrium constants

General Acid-Base System

$$\begin{aligned}
 K_{A1}^* &= \frac{[H^+][H_{n-1}A^-]}{[H_nA]} \Rightarrow [H_{n-1}A^-] = \frac{K_{A1}^*}{[H^+]} [H_nA] \\
 K_{A2}^* &= \frac{[H^+][H_{n-2}A^{2-}]}{[H_{n-1}A^-]} \Rightarrow [H_{n-2}A^{2-}] = \frac{K_{A1}^* K_{A2}^*}{[H^+]^2} [H_nA] \\
 K_{A3}^* &= \frac{[H^+][H_{n-3}A^{3-}]}{[H_{n-2}A^{2-}]} \Rightarrow [H_{n-3}A^{3-}] = \frac{K_{A1}^* K_{A2}^* K_{A3}^*}{[H^+]^3} [H_nA] \\
 &\vdots \\
 K_{An}^* &= \frac{[H^+][A^{n-}]}{[HA^{(n-1)-}]} \Rightarrow [A^{n-}] = \frac{K_{A1}^* K_{A2}^* \cdots K_{An}^*}{[H^+]^n} [H_nA]
 \end{aligned}$$

General Acid-Base System: Speciation Relationships

Let $A_T = [H_nA] + \dots + [A^{n-}]$ denote the concentration of total dissolved H_nA . By summing all the previous equations, we get

$$A_T = \left(1 + \frac{K_{A1}^*}{[H^+]} + \frac{K_{A1}^* K_{A2}^*}{[H^+]^2} + \dots + \frac{K_{A1}^* K_{A2}^* \cdots K_{An}^*}{[H^+]^n} \right) [H_nA]$$

Hence

$$A_T = \frac{[H^+]^n + K_{A1}^* [H^+]^{n-1} + K_{A1}^* K_{A2}^* [H^+]^{n-2} + \dots + K_{A1}^* K_{A2}^* \cdots K_{An}^*}{[H^+]^n} [H_nA]$$

and thus finally

$$[H_nA] = \frac{[H^+]^n}{[H^+]^n + K_{A1}^* [H^+]^{n-1} + K_{A1}^* K_{A2}^* [H^+]^{n-2} + \dots + K_{A1}^* K_{A2}^* \cdots K_{An}^*} A_T$$

General Acid-Base System

The fractions of undissociated acid and of the dissociated forms $H_{n-1}A^-$, $H_{n-2}A^{2-}$, ..., A^{n-} then alternately write

$$\begin{aligned} \frac{[H_nA]}{A_T} &= \frac{[H^+]^n}{[H^+]^n + K_{A1}^*[H^+]^{n-1} + K_{A1}^*K_{A2}^*[H^+]^{n-2} + \dots + K_{A1}^*K_{A2}^*\dots K_{An}^*} \\ &\vdots \\ \frac{[H_{n-j}A^{j-}]}{A_T} &= \frac{K_{A1}^*\dots K_{Aj}^*[H^+]^{n-j}}{[H^+]^n + K_{A1}^*[H^+]^{n-1} + K_{A1}^*K_{A2}^*[H^+]^{n-2} + \dots + K_{A1}^*K_{A2}^*\dots K_{An}^*} \\ &\vdots \\ \frac{[A^{n-}]}{A_T} &= \frac{K_{A1}^*K_{A2}^*\dots K_{An}^*}{[H^+]^n + K_{A1}^*[H^+]^{n-1} + K_{A1}^*K_{A2}^*[H^+]^{n-2} + \dots + K_{A1}^*K_{A2}^*\dots K_{An}^*} \end{aligned}$$

Phosphate System Speciation ...

Application to the phosphate system: $n = 3$

$$\begin{aligned} P_T &= [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}] \\ [H_3PO_4] &= \frac{[H^+]^3}{[H^+]^3 + K_{P1}^*[H^+]^2 + K_{P1}^*K_{P2}^*[H^+] + K_{P1}^*K_{P2}^*K_{P3}^*} P_T \\ [H_2PO_4^-] &= \frac{K_{P1}^*[H^+]^2}{[H^+]^3 + K_{P1}^*[H^+]^2 + K_{P1}^*K_{P2}^*[H^+] + K_{P1}^*K_{P2}^*K_{P3}^*} P_T \\ [HPO_4^{2-}] &= \frac{K_{P1}^*K_{P2}^*[H^+]}{[H^+]^3 + K_{P1}^*[H^+]^2 + K_{P1}^*K_{P2}^*[H^+] + K_{P1}^*K_{P2}^*K_{P3}^*} P_T \\ [PO_4^{3-}] &= \frac{K_{P1}^*K_{P2}^*K_{P3}^*}{[H^+]^3 + K_{P1}^*[H^+]^2 + K_{P1}^*K_{P2}^*[H^+] + K_{P1}^*K_{P2}^*K_{P3}^*} P_T \end{aligned}$$

... and Phosphate Alkalinity

$$\begin{aligned}
 \text{Alk}_P &= -[\text{H}_3\text{PO}_4] + [\text{HPO}_4^{2-}] + 2[\text{PO}_4^{3-}] \\
 &= \frac{-[\text{H}^+]^3 + K_{P1}^* K_{P2}^* [\text{H}^+] + 2K_{P1}^* K_{P2}^* K_{P3}^*}{[\text{H}^+]^3 + K_{P1}^* [\text{H}^+]^2 + K_{P1}^* K_{P2}^* [\text{H}^+] + K_{P1}^* K_{P2}^* K_{P3}^*} P_T \\
 &= \left(\frac{K_{P1}^* [\text{H}^+]^2 + 2K_{P1}^* K_{P2}^* [\text{H}^+] + 3K_{P1}^* K_{P2}^* K_{P3}^*}{[\text{H}^+]^3 + K_{P1}^* [\text{H}^+]^2 + K_{P1}^* K_{P2}^* [\text{H}^+] + K_{P1}^* K_{P2}^* K_{P3}^*} - 1 \right) P_T
 \end{aligned}$$

“-1” → 1 is the order of the acid dissociation step that defined the last (i. e., the weakest) proton donor

Alkalinity Contribution of a General Acid-Base System

For a general acid-base system $\text{H}_n\text{A} - \text{H}_{n-1}\text{A}^- - \dots - \text{A}^{n-}$ with dissociation constant pK values pK_1, \dots, pK_n , we have:

$$\begin{aligned}
 \text{Alk}_A &= -m[\text{H}_n\text{A}] \dots - (m-1)[\text{H}_{n-1}\text{A}^-] \dots - [\text{H}_{n-m-1}\text{A}^{(m-1)-}] \\
 &\quad + [\text{H}_{n-m+1}\text{A}^{(m+1)-}] + \dots + (n-m)[\text{A}^{n-}]
 \end{aligned}$$

where m is an integer such that

- $pK_m < 4.5 \leq pK_{m+1}$ if $pK_1 < 4.5$ and $pK_n \geq 4.5$
- $m = 0$ if $pK_1 \geq 4.5$
- $m = n$ if $pK_n < 4.5$

Alkalinity Contribution of a General Acid-Base System

- Then

$$\text{Alk}_A = \sum_{j=0}^n (j - m) [\text{H}_{n-j} \text{A}^{j-}]$$

- It was previously established that

$$\frac{[\text{H}_{n-j} \text{A}^{j-}]}{A_T} = \frac{K_{A1}^* \cdots K_{Aj}^* [\text{H}^+]^{n-j}}{[\text{H}^+]^n + K_{A1}^* [\text{H}^+]^{n-1} + K_{A1}^* K_{A2}^* [\text{H}^+]^{n-2} + \dots + K_{A1}^* K_{A2}^* \cdots K_{An}^*}$$

- With $\Pi_j = \prod_{i=0}^j K_{Ai}^*$ and $\Pi_0 = 1$ this can be rewritten

$$[\text{H}_{n-j} \text{A}^{j-}] = \frac{\Pi_j [\text{H}^+]^{n-j}}{\sum_{i=0}^n \Pi_i [\text{H}^+]^{n-i}} A_T$$

Alkalinity Contribution of a General Acid-Base System

Hence

$$\begin{aligned} \text{Alk}_A &= \sum_{j=0}^n (j - m) \frac{\Pi_j [\text{H}^+]^{n-j}}{\sum_{i=0}^n \Pi_i [\text{H}^+]^{n-i}} A_T \\ &= \left(\frac{\sum_{j=0}^n j \Pi_j [\text{H}^+]^{n-j}}{\sum_{j=0}^n \Pi_j [\text{H}^+]^{n-j}} - m \right) A_T \end{aligned}$$

For $A_T > 0$ this expression

- is strictly decreasing for $[\text{H}^+] > 0$;
- has the supremum $\lim_{[\text{H}^+] \rightarrow 0} = (n - m) A_T$;
- has the infimum $\lim_{[\text{H}^+] \rightarrow +\infty} = -m A_T$.

(Munhoven, GMD 2013)

pH From Alk_T and Arbitrary Acid-Base Systems

General Alkalinity-pH equation

$$\text{Alk}_C([\text{H}^+]; C_T) + \dots + \text{Alk}_A([\text{H}^+]; A_T) + \dots + \frac{K_W^*}{[\text{H}^+]} - [\text{H}^+] - \text{Alk}_T = 0$$

- Equation of the form $f([\text{H}^+]) = 0$, where $[\text{H}^+] > 0$ and
 - f strictly decreasing with $[\text{H}^+]$
 - f unbounded: $\sup = +\infty$, $\inf = -\infty$ \Rightarrow one and only one positive root for any Alk_T .
- Root has intrinsic brackets that can be calculated from the non-water-alkalinity infimum and supremum
- Equation can be reliably solved for $[\text{H}^+]$ by a hybrid Newton-Raphson-bisection method (convergence guaranteed)

Some Details Skipped

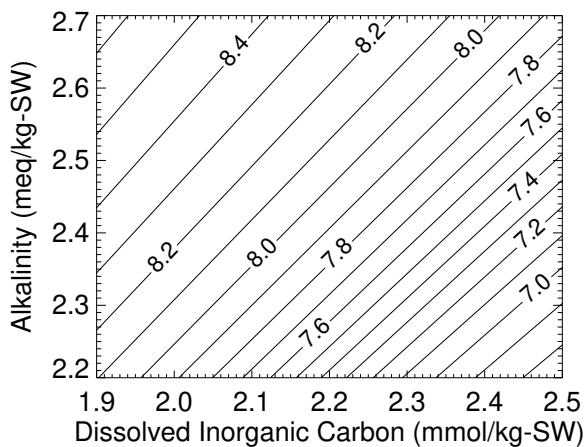
- All dissociation constants must be given on the same pH scale
 - $\Rightarrow [\text{H}^+]$ root on that scale
- $\frac{K_W^*}{[\text{H}^+]} - [\text{H}^+]$ should actually read $\frac{K_W^*}{[\text{H}^+]} - [\text{H}^+]_f$
- $[\text{H}^+]_f = [\text{H}^+]/s$, where $s = O(1)$ ($s \geq 1$) is a scale conversion factor from the free to the working scale (total or seawater)
- Other background acids (HSO_4^- , HF) to be added as part of their respective acid-base systems
- Initial iterations in pH-Alk space, switching to $[\text{H}^+]$ -Alk space when sufficiently close to the root

Calculating pH From Alk_T and C_T

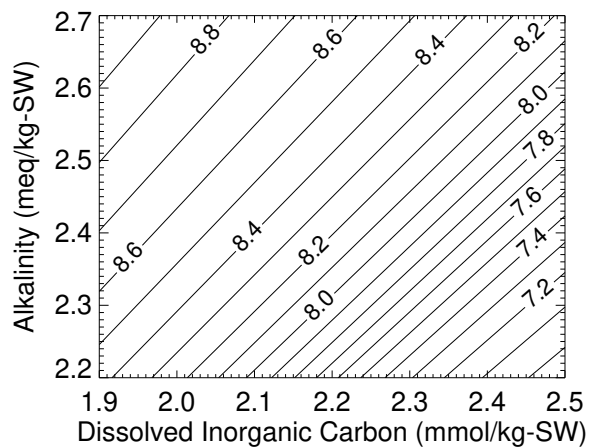
- Concentrations $[CO_{2(aq)}^*]$, $[HCO_3^-]$, $[CO_3^{2-}]$ can now be calculated from the speciation relationships and $[H^+]$
- pCO_2 is calculated from Henry's Law

$$pCO_2 \simeq f_{CO_2} = \frac{[CO_{2(aq)}^*]}{K_H^*}$$

pH as a Function of C_T and Alk_T

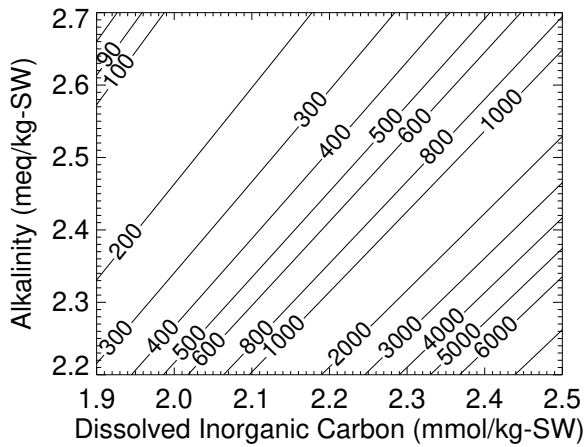


$t = 20^\circ C$, $P = 0$ bar, $S = 35$



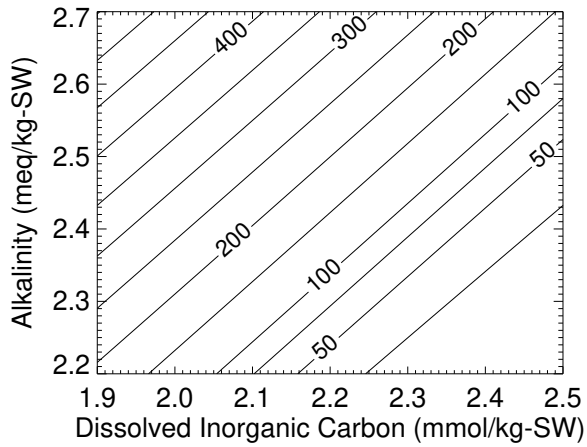
$t = 1^\circ C$, $P = 0$ bar, $S = 35$

$p\text{CO}_2$ and $[\text{CO}_3^{2-}]$ as a Function of C_T and Alk_T



$t = 20^\circ\text{C}$, $P = 0$ bar, $S = 35$

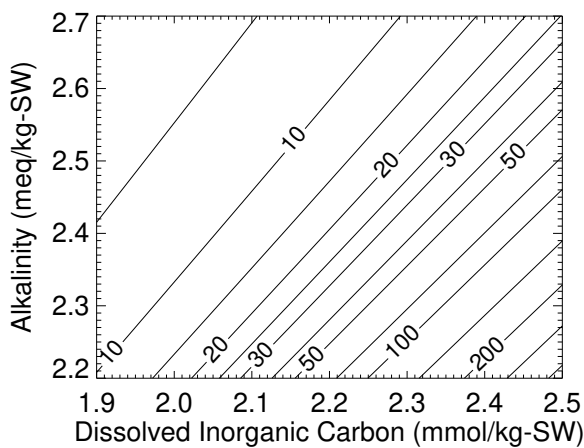
$p\text{CO}_2$ (μatm)



$t = 1^\circ\text{C}$, $P = 300$ bar, $S = 35$

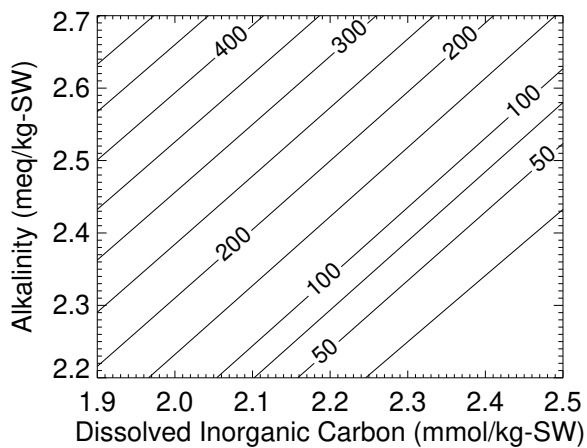
$[\text{CO}_3^{2-}]$ ($\mu\text{mol/kg-SW}$)

$[\text{CO}_2^*]$ and $[\text{CO}_3^{2-}]$ as a Function of C_T and Alk_T



$t = 20^\circ\text{C}$, $P = 0$ bar, $S = 35$

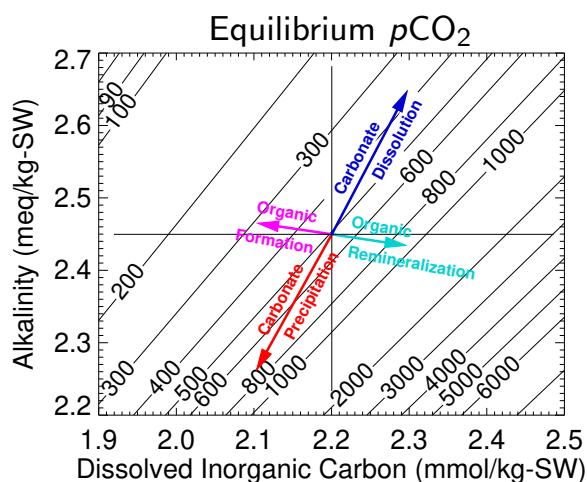
$[\text{CO}_2^*]$ ($\mu\text{mol/kg-SW}$)



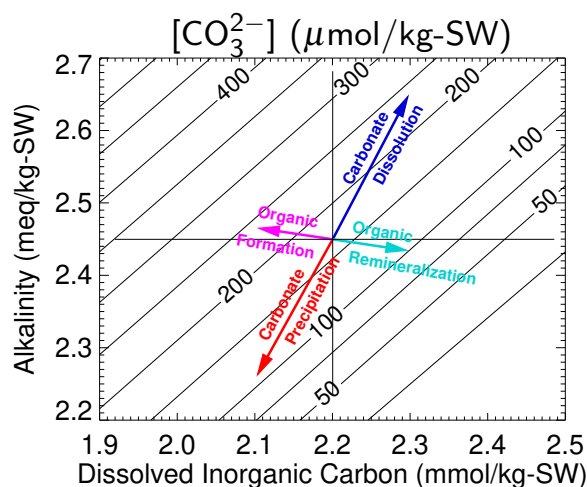
$t = 1^\circ\text{C}$, $P = 300$ bar, $S = 35$

$[\text{CO}_3^{2-}]$ ($\mu\text{mol/kg-SW}$)

Atmospheric CO₂ and Deep-Sea CO₃²⁻



Surface temperate



Deep Ocean (3000 m)

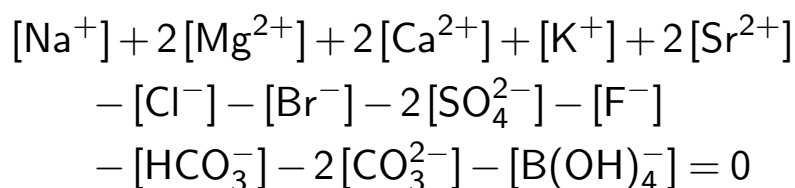
In Summary

Calculating pH and Chemical Speciation in General

- Determine the total concentrations of all the acid-base systems present
- Chose an adequate approximation for Total Alkalinity
- Use the speciation relationships to convert the expression for Alk_T to an equation in $[H^+]$
- Solve that equation (robust and efficient methods available)
- Calculate the speciation of all the systems present from the speciation relationships

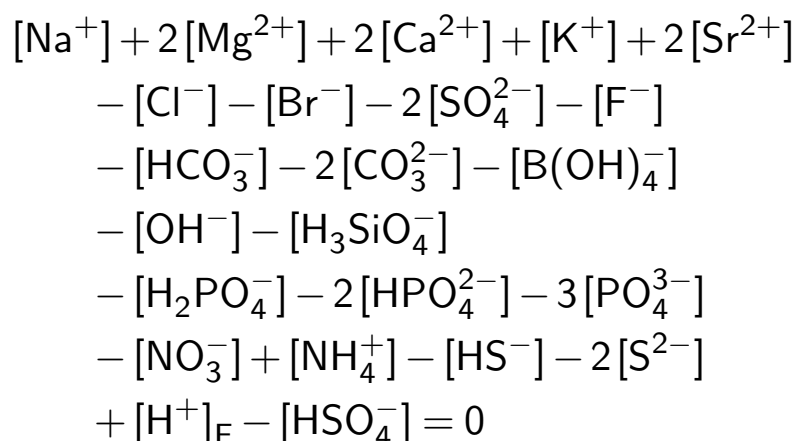
Alkalinity, a Conservative Variable? A Detour via Electroneutrality...

Electroneutrality equation for the major (plus a few minor) ions in average seawater:



From Electroneutrality...

Electroneutrality equation for the major ions in average seawater, completed by the missing ion concentrations from alkalinity and nutrients:



... to Alkalinity

Collect the alkalinity components at the right-hand side and complete by the missing chargeless contributions :

$$\begin{aligned}
 & [\text{Na}^+] + 2[\text{Mg}^{2+}] + 2[\text{Ca}^{2+}] + [\text{K}^+] + 2[\text{Sr}^{2+}] \\
 & - [\text{Cl}^-] - [\text{Br}^-] - 2[\text{SO}_4^{2-}] - [\text{F}^-] - [\text{HF}] \\
 & - [\text{H}_2\text{PO}_4^-] - [\text{HPO}_4^{2-}] - [\text{PO}_4^{3-}] - [\text{H}_3\text{PO}_4] \\
 & - 2[\text{HSO}_4^-] - [\text{NO}_3^-] + [\text{NH}_4^+] + [\text{NH}_3] - [\text{HNO}_3] \\
 = & \left. \begin{aligned}
 & [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] + [\text{OH}^-] \\
 & + [\text{HPO}_4^{2-}] + 2[\text{PO}_4^{3-}] + [\text{H}_3\text{SiO}_4^-] \\
 & + [\text{HS}^-] + 2[\text{S}^{2-}] + [\text{NH}_3] \\
 & - [\text{H}^+]_{\text{F}} - [\text{HSO}_4^-] - [\text{HF}] - [\text{H}_3\text{PO}_4] - [\text{HNO}_3]
 \end{aligned} \right\} = A_{\text{T}}
 \end{aligned}$$

$\text{HNO}_3:$
 $\text{p}K_{\text{A}} = -1.55$

The Explicit Conservative Expression of Alkalinity

The *explicit conservative* expression of alkalinity, Alk_{EC} , then follows from the left-hand side of the previous equation:

$$\begin{aligned}
 \text{Alk}_{\text{EC}} = & [\text{Na}^+] + 2[\text{Mg}^{2+}] + 2[\text{Ca}^{2+}] + [\text{K}^+] + 2[\text{Sr}^{2+}] \\
 & - [\text{Cl}^-] - [\text{Br}^-] \\
 & - 2\text{T}_{\text{SO}_4} - \text{T}_{\text{HF}} - \text{T}_{\text{PO}_4} - \text{T}_{\text{NO}_3} + \text{T}_{\text{NH}_3}
 \end{aligned}$$

where

$$\text{T}_{\text{SO}_4} = [\text{HSO}_4^-] + [\text{SO}_4^{2-}] \quad (= S_{\text{T}})$$

$$\text{T}_{\text{HF}} = [\text{HF}] + [\text{F}^-] \quad (= F_{\text{T}})$$

$$\text{T}_{\text{PO}_4} = [\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}] \quad (= P_{\text{T}})$$

$$\text{T}_{\text{NO}_3} = [\text{HNO}_3] + [\text{NO}_3^-]$$

$$\text{T}_{\text{NH}_3} = [\text{NH}_4^+] + [\text{NH}_3]$$

(Wolf-Gladrow et al., 2007)

Explicit Conservative Expression of Alkalinity: Corollaries

- Alk_{EC} shows that Alk_{T} does not simply reduce to the charge difference between conservative cations and anions
 - “conservative ion” sometimes ambiguous (e. g., Sr^{2+} , Ca^{2+})
 - surface-to-deep-sea alkalinity gradients would have to be proportional to salinity
 - important role of nutrients
- Alk_{EC} allows to quantify the effect of biogeochemical processes on alkalinity more easily
- Alk_{EC} clearly shows the conservative nature of Alk_{T}
 - each single term unaffected by pH, pressure and temperature changes

References Cited and Recommended

- Broecker W. S. and Peng T.-H. (1982) *Tracers in the Sea*, Eldigio Press, Palisades, NY. 690 pp.
- Dickson A. G. et al. (2007) *Guide to Best Practices for Ocean CO₂ Measurements*, PICES Special Publication 3, 191 pp.
- Dickson A. G. (1981) An exact definition of total alkalinity and a procedure for the estimation of alkalinity and total inorganic carbon from titration data. *Deep-Sea Res.*, 28A(6):609–623.
- Dickson A. G. (1984) pH scales and proton-transfer reactions in saline media such as sea water. *Geochim. Cosmochim. Acta* 48:2299–2308.
- Gruber N. and J. Sarmiento (2006) *Ocean Biogeochemical Dynamics*. Princeton University Press, Princeton, NJ. 503 pp.
- Munhoven G. (2013) Mathematics of the total alkalinity-pH equation – pathway to robust and universal solution algorithms: the SolveSAPHE package v1.0.1. *Geoscientif. Model Dev.* 6, 1367–1388.
- Wolf-Gladrow D. A. et al. (2007) Total alkalinity: The explicit conservative expression and its application to biogeochemical processes. *Mar. Chem.* 106, 287–300.
- Zeebe R. and D. Wolf-Gladrow (2003) *CO₂ in Seawater: Equilibrium, Kinetics, Isotopes*. Elsevier, Amsterdam. 346 pp.