

Chemical Equilibria and pH Calculations

Guy Munhoven

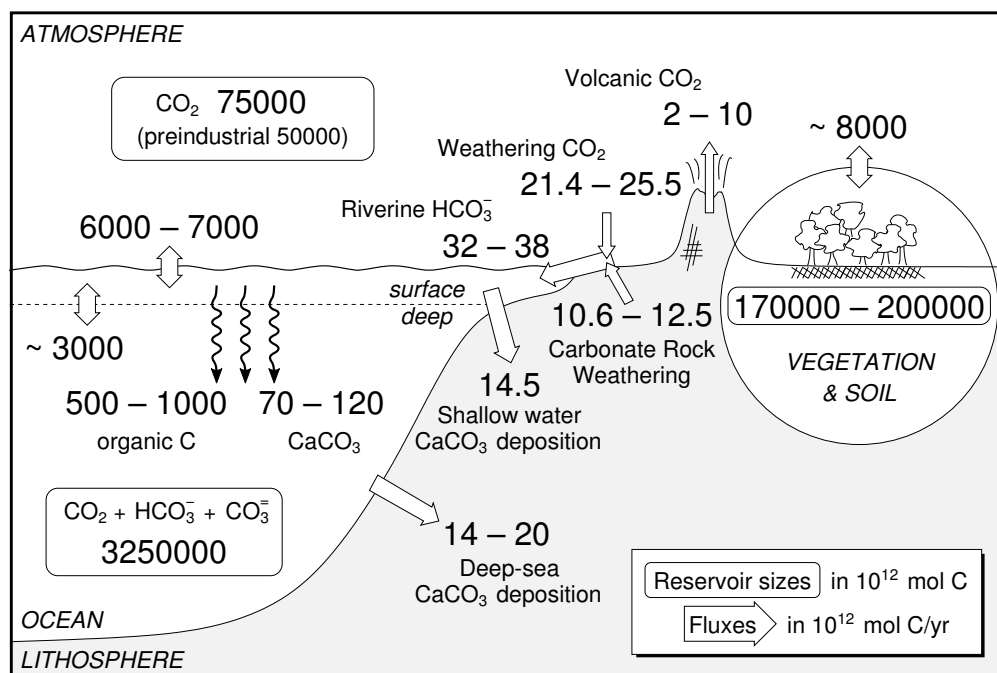
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Plan

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

Processes and Exchange Fluxes

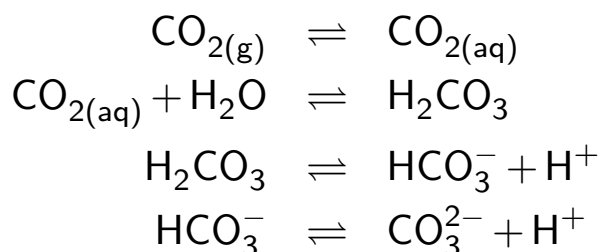


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Chemical Equilibria and pH Calculations

Carbonate Chemistry

Dissolution of atmospheric CO_2 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

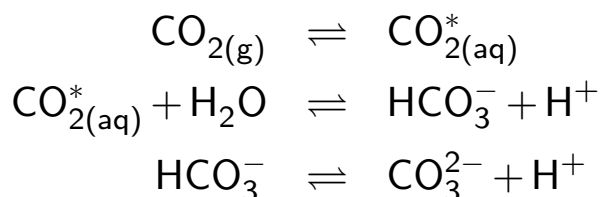
$$\text{CO}_{2(\text{aq})}^* = \text{H}_2\text{CO}_3 + \text{CO}_{2(\text{aq})}$$

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Chemical Equilibria and pH Calculations

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
B(OH)_4^-	0.00008
F^-	0.00007
B(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 $\text{pH} = -\log_{10}[\text{H}^+]$
- 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 $\text{pH} = -\log_{10}\{\text{H}^+\}$
⇒ useless as $\{\text{H}^+\}$ 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*

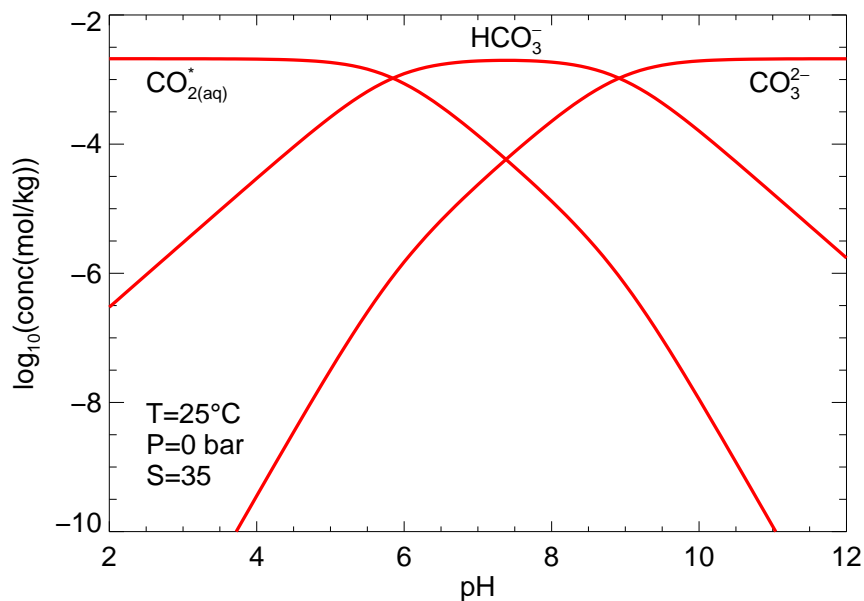
$$\frac{[CO_{2(aq)}^*]}{C_T} = \frac{[H^+]^2}{[H^+]^2 + K_1^*[H^+] + K_1^*K_2^*}$$

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

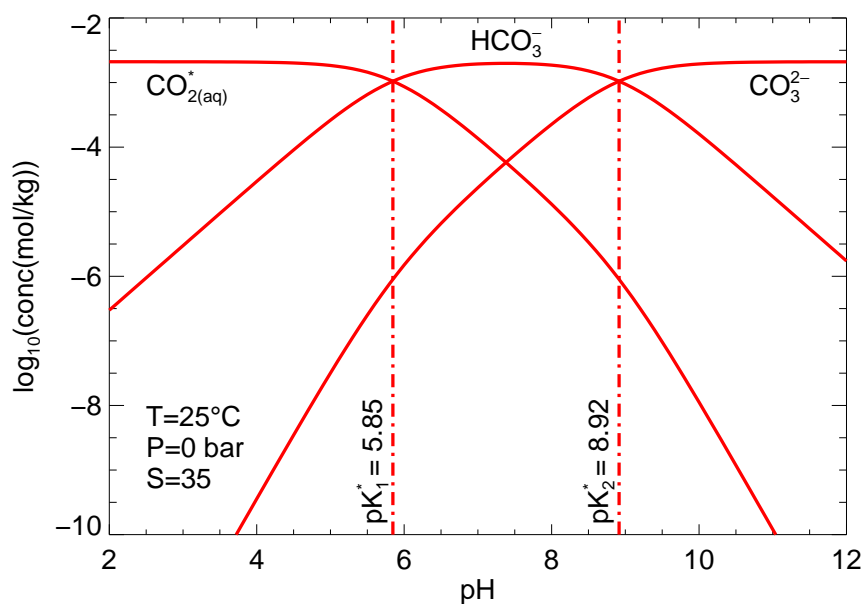
$$\frac{[CO_3^{2-}]}{C_T} = \frac{K_1^*K_2^*}{[H^+]^2 + K_1^*[H^+] + K_1^*K_2^*}$$

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

Speciation: Bjerrum Plot

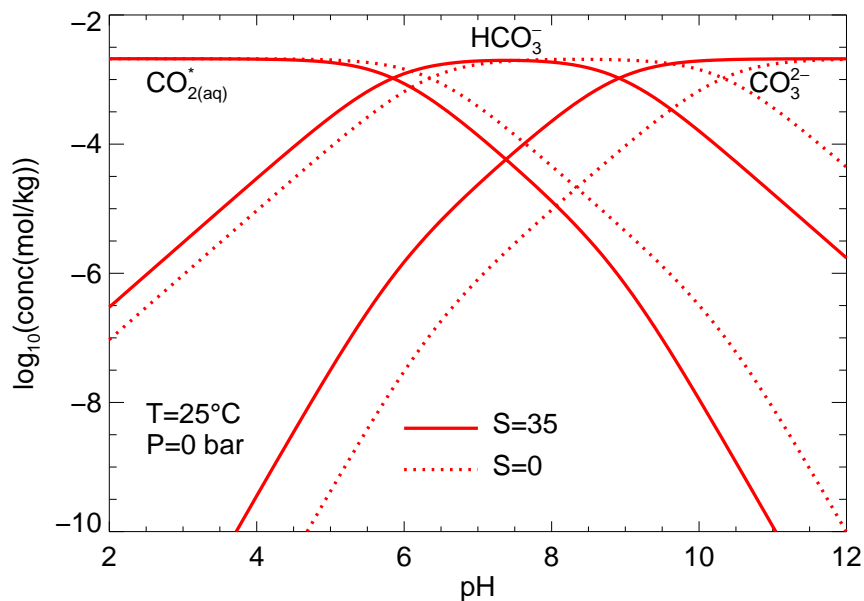


Speciation: Bjerrum Plot



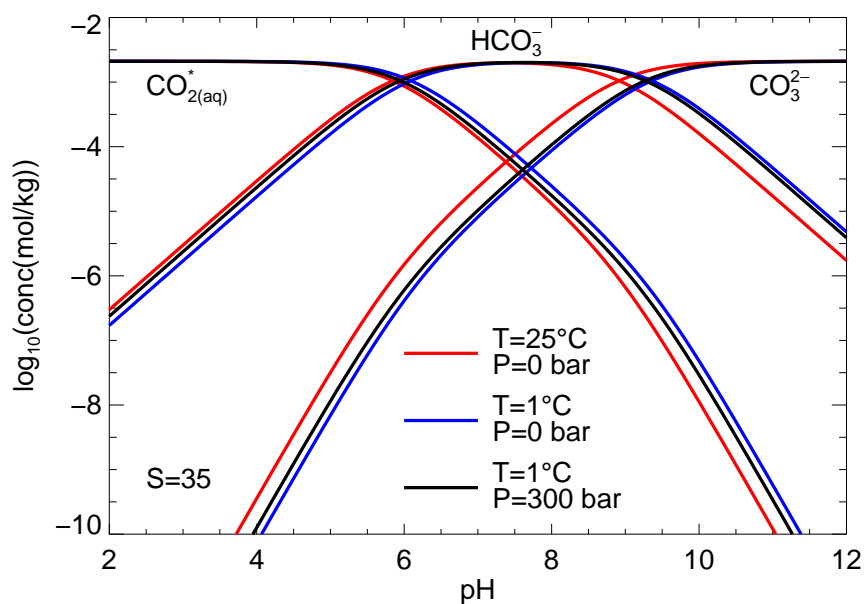
Points d'équivalence

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, ...

\Rightarrow 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
⇒ 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.”

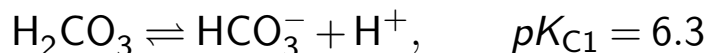
$$\text{Alk}_T := \sum_i [\text{proton acceptor}_i] - \sum_j [\text{proton donor}_j]$$

Notice that

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

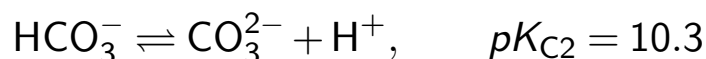
Alkalinity Contributions: Carbonic Acid Example

- Carbonic Acid H_2CO_3



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

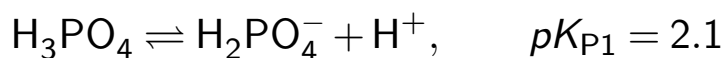
- Bicarbonate ion HCO_3^-



$pK_{\text{C2}} \geq 4.5 \Rightarrow$ 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.

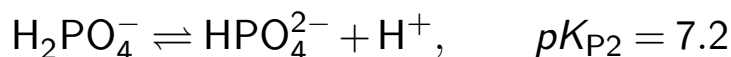
Alkalinity Contributions: Phosphoric Acid Example

- Orthophosphoric Acid H_3PO_4



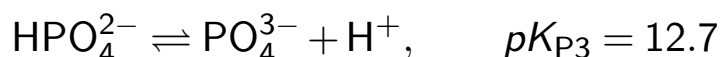
$pK_{\text{P1}} < 4.5 \Rightarrow$ acid is a donor and contributes $-\text{[H}_3\text{PO}_4]$

- Dihydrogen phosphate H_2PO_4^-



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

- Hydrogen phosphate HPO_4^{2-}



$pK_{\text{P3}} \geq 4.5 \Rightarrow$ 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

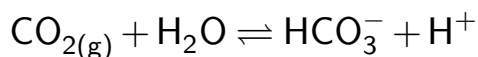
- Alkalinity is a complex concept, with an opaque definition
- In the literature, there are alternative definitions based upon electroneutrality, that define alkalinity as being equal to the charge difference between conservative cations and anions
- Alkalinity defined this way
 - is also conservative (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



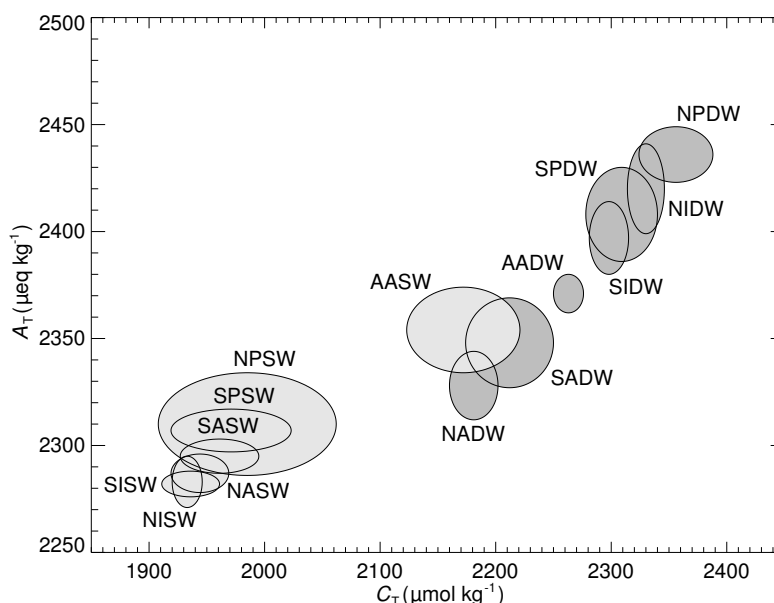
- not affected by the dissolution of gaseous CO_2 in water



- 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*

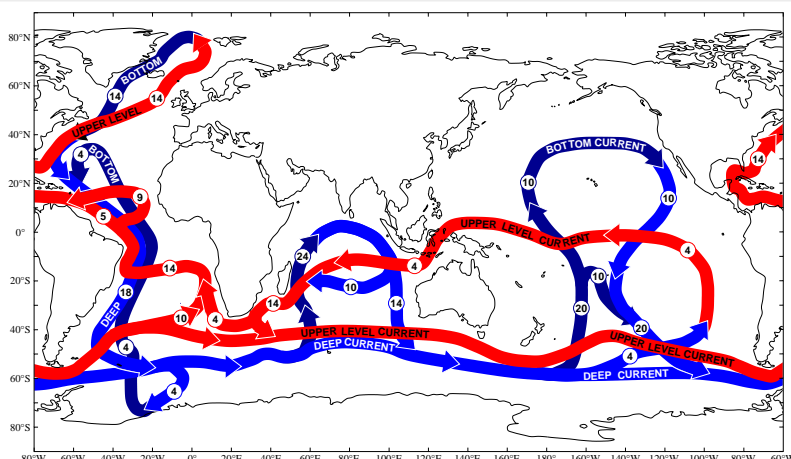
$$\text{Alk}_C = [\text{HCO}_3^-] + 2 \times [\text{CO}_3^{2-}]$$

C_T and Alk_T in the Ocean

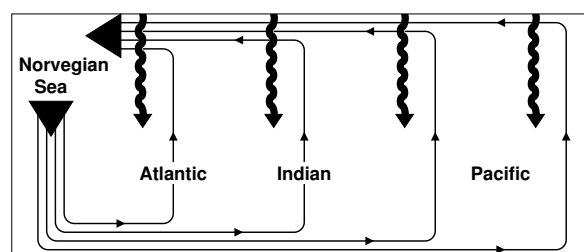


DIC: Dissolved Inorganic Carbon

C_T and Alk_T in the Ocean: Origin of Gradients



Vertical
gradients



Inter-basin
gradients

Following Broecker and Peng (1982)

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Chemical Equilibria and pH Calculations

Calculating pH and Speciation From Alk_T and C_T

Posing the problem

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

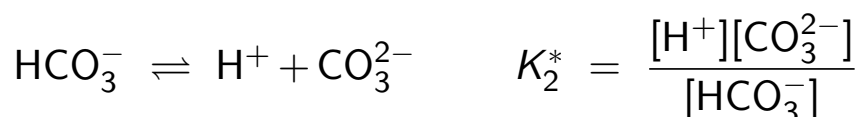
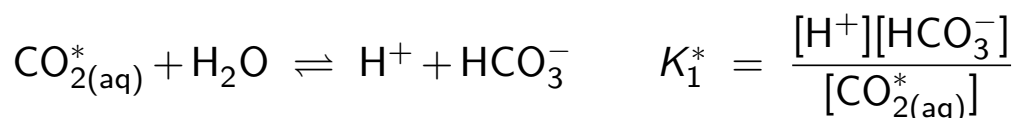
$$Alk_T \simeq [HCO_3^-] + 2 \times [CO_3^{2-}] + [B(OH)_4^-] + [OH^-] - [H^+]$$

- 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)

\Rightarrow 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

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

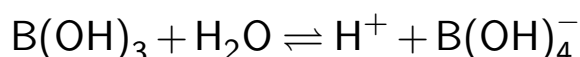
$$[\text{CO}_3^{2-}] = \frac{K_1^*K_2^*}{[\text{H}^+]^2 + K_1^*[\text{H}^+] + K_1^*K_2^*} C_T$$

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

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

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

Hence

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

Calculating pH From Alk_T and C_T

Processing of the Alk_T terms related to the carbonate system

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

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

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

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

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: $A_{\text{nWinf}} = 0$
- let H_{inf} be the positive root of $A_{\text{nWinf}} + \frac{K_W^*}{H_{\text{inf}}} - H_{\text{inf}} - \text{Alk}_T = 0$
- $f(H_{\text{inf}}) > A_{\text{nWinf}} + \frac{K_W^*}{H_{\text{inf}}} - H_{\text{inf}} - \text{Alk}_T = 0$
- 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: $\sup = +\infty$, $\inf = -\infty$

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

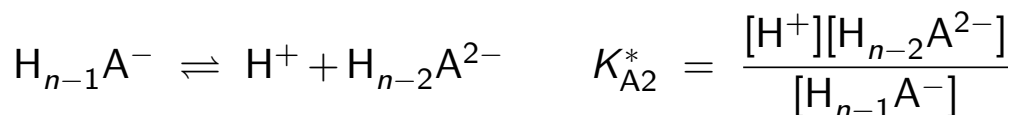
- Root can be intrinsically bracketed
- Equation can be reliably solved for $[\text{H}^+]$ by a hybrid Newton-Raphson-bisection method (convergence guaranteed)

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



\vdots

\vdots



- 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

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

- 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

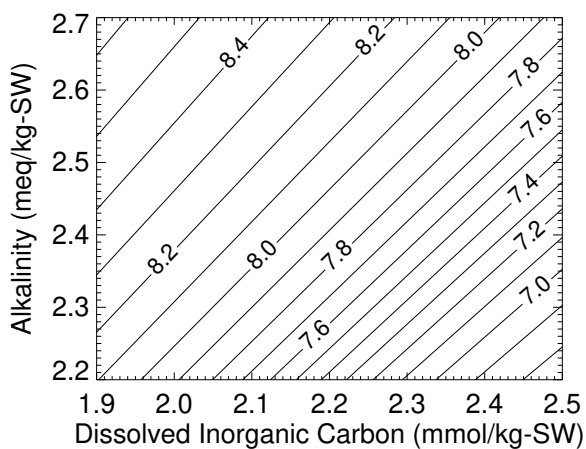
- All dissociation constants must be given on the same pH scale
 $\Rightarrow [\text{H}^+]$ root on that scale
- $\frac{K_W^*}{[\text{H}^+]} - [\text{H}^+]$ should actually read $\frac{K_W^*}{[\text{H}^+]_f} - [\text{H}^+]_f$
- $[\text{H}^+]_f = [\text{H}^+]/s$, where $s = O(1)$ ($s \geq 1$) is a scale 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

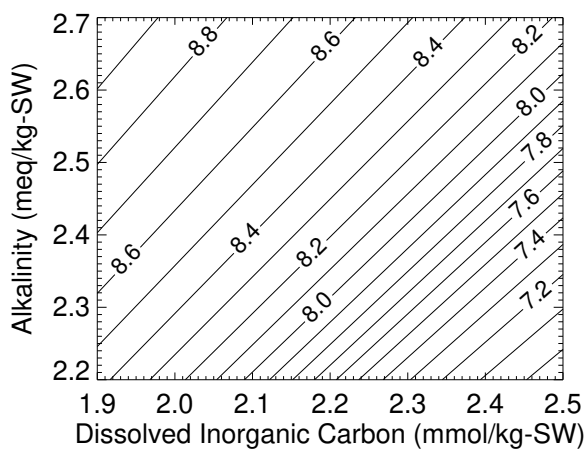
- Concentrations $[\text{CO}_{2(\text{aq})}^*]$, $[\text{HCO}_3^-]$, $[\text{CO}_3^{2-}]$ can now be calculated from the speciation relationships and $[\text{H}^+]$
- pCO_2 is calculated from Henry's Law

$$\text{pCO}_2 \simeq f_{\text{CO}_2} = \frac{[\text{CO}_{2(\text{aq})}^*]}{K_H^*}$$

pH as a Function of C_T and Alk_T

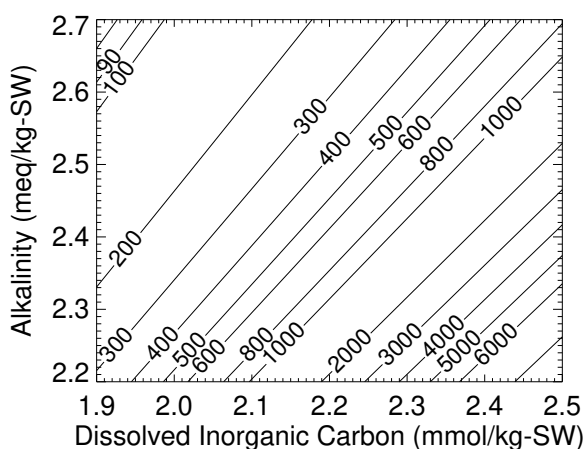


$t = 20^\circ\text{C}$, $P = 0$ bar, $S = 35$



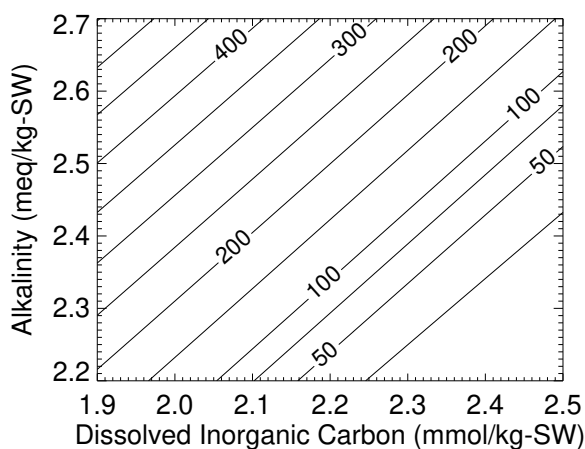
$t = 1^\circ\text{C}$, $P = 0$ bar, $S = 35$

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



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

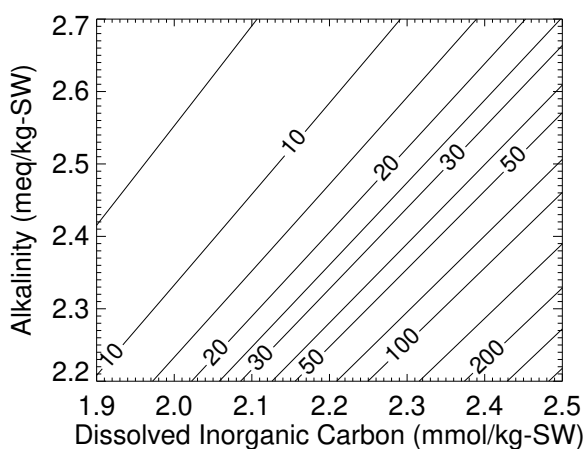
$p\text{CO}_2$ (μatm)



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

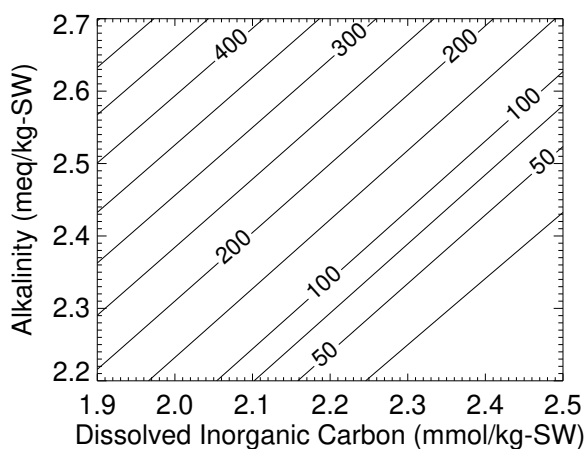
$[\text{CO}_3^{2-}]$ ($\mu\text{mol/kg-SW}$)

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



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

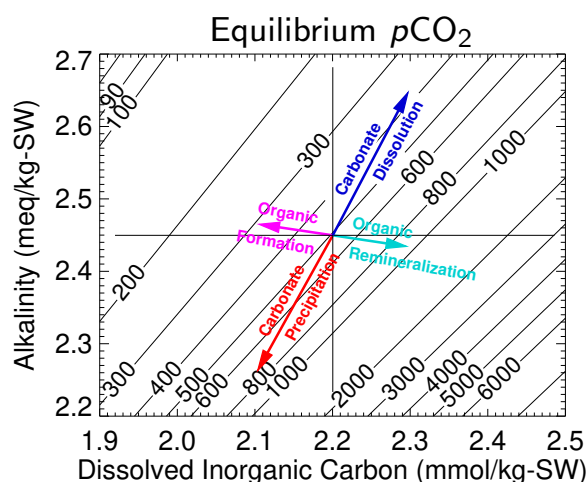
$[\text{CO}_2^*]$ ($\mu\text{mol/kg-SW}$)



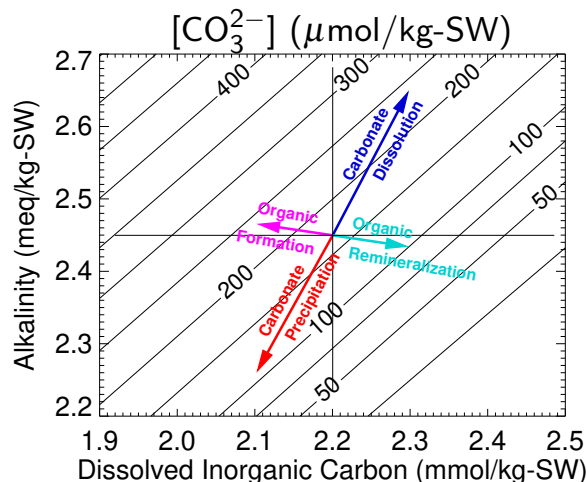
$t = 1^\circ\text{C}$, $P = 300$ bar, $S = 35$

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

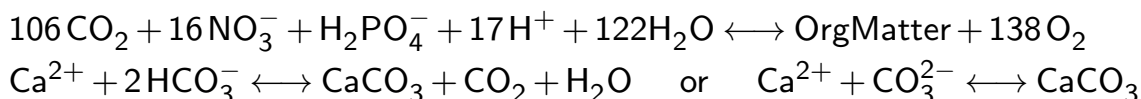
Atmospheric CO₂ and Deep-Sea CO₃²⁻



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:

$$\begin{aligned}
 & [\text{Na}^+] + 2[\text{Mg}^{2+}] + 2[\text{Ca}^{2+}] + [\text{K}^+] + 2[\text{Sr}^{2+}] \\
 & - [\text{Cl}^-] - [\text{Br}^-] - 2[\text{SO}_4^{2-}] - [\text{F}^-] \\
 & - [\text{HCO}_3^-] - 2[\text{CO}_3^{2-}] - [\text{B(OH)}_4^-] = 0
 \end{aligned}$$

From Electroneutrality...

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

$$\begin{aligned}
 & [\text{Na}^+] + 2[\text{Mg}^{2+}] + 2[\text{Ca}^{2+}] + [\text{K}^+] + 2[\text{Sr}^{2+}] \\
 & - [\text{Cl}^-] - [\text{Br}^-] - 2[\text{SO}_4^{2-}] - [\text{F}^-] \\
 & - [\text{HCO}_3^-] - 2[\text{CO}_3^{2-}] - [\text{B(OH)}_4^-] \\
 & - [\text{OH}^-] - [\text{H}_3\text{SiO}_4^-] \\
 & - [\text{H}_2\text{PO}_4^-] - 2[\text{HPO}_4^{2-}] - 3[\text{PO}_4^{3-}] \\
 & - [\text{NO}_3^-] + [\text{NH}_4^+] - [\text{HS}^-] - 2[\text{S}^{2-}] \\
 & + [\text{H}^+]_{\text{F}} - [\text{HSO}_4^-] = 0
 \end{aligned}$$

... to Alkalinity

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

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

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:

$$\begin{aligned}
 \text{Alk}_{\text{EC}} = & [\text{Na}^+] + 2[\text{Mg}^{2+}] + 2[\text{Ca}^{2+}] + [\text{K}^+] + 2[\text{Sr}^{2+}] \\
 & - [\text{Cl}^-] - [\text{Br}^-] \\
 & - 2\text{TSO}_4 - \text{THF} - \text{TPO}_4 - \text{TNO}_3 + \text{TNH}_3
 \end{aligned}$$

where

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

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

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

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

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

(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

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