ENV-200
Carbonate system and alkalinity

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Learning objectives

You should be able to:

1. Understand the importance of carbonate species on the pH of natural systems.
2. Draw pC – pH diagrams for open and closed carbonate sytems.
3. Determine the equilibrium pH and/or species concentration in pure carbonate systems and systems with additional acids and bases.
4. Calculate the pH of a system based on its alkalinity and total carbon concentration and vice versa.
5. Determine the pH of mixed water sources based on their alkalinity.

Resources

Sigg, Behra, Stumm, Chimie des milieux aquatiques, Chapter 3

And a quick primer on the nomenclature we will use:

C: carbon, an element

CO_2 : carbon dioxide, a gas

H_2CO_3 : carbonic acid (this is dissolved CO_2)

HCO_3^- : bicarbonate

CO_3^{2-} : carbonate

$CaCO_3$: calcite (a solid, mineral)

A little in-class experiment: measuring the pH of pure water

1. Note down the pH at the start of the experiment, immediately after exposing the water to air:

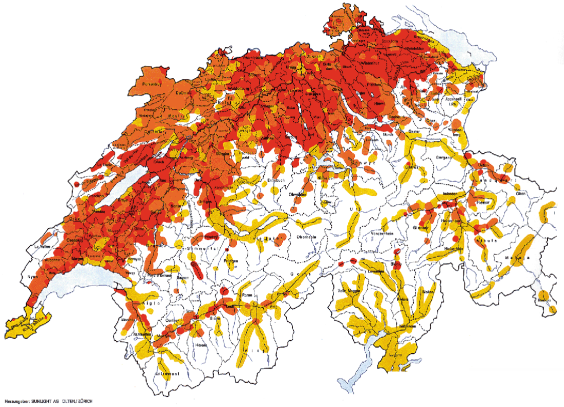
2. What do you think the pH will be at the end of today's lecture?

3. What is the measured pH toward the end of today's lecture?

Engineering example: pipe scaling

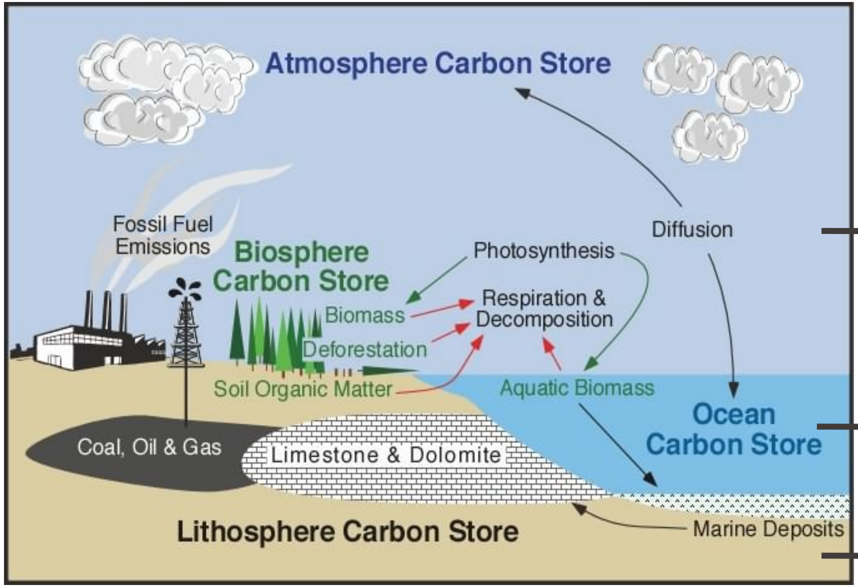
What is pipe scaling?

- Precipitation of carbonate minerals during heating of hard water
- Water hardness arises from divalent and multivalent metal ions: Ca^{2+}, Mg^{2+}, Fe^{2+}, Fe^{3+}, Mn^{2+}, etc., which can precipitate with carbonate to form $CaCO_3(s)$, $MgCO_3$ (s), etc.
- Scaling leads to increase in energy cost:
  - 1 mm scale: + 7.5% energy cost
  - 1.5 mm: +15% energy cost
  - 7 mm: + 70 % energy cost
- To prevent scaling: use of carbonate to precipitate water hardness during water treatment, before entering the pipes.



🟨 0-60 mg/L as $CaCO_3$
🟧 60-100 mg/L as $CaCO_3$
🟥 > 100 mg/L as $CaCO_3$

Global carbon cycle



www.physicalgeography.net

→ CO_2

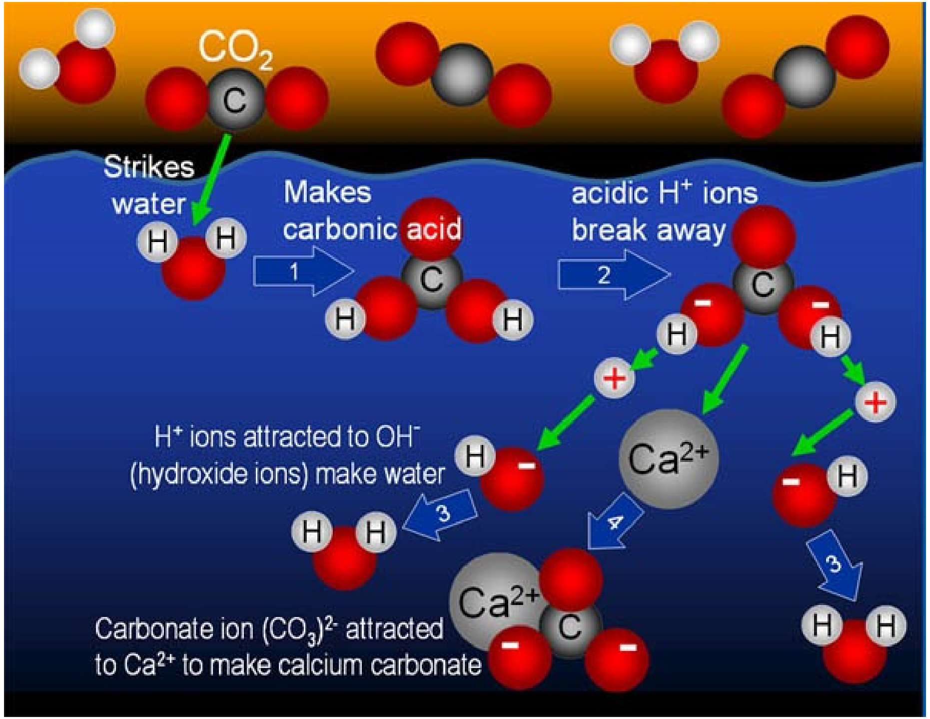
→ $H_2CO_3^*$, HCO_3^- , CO_3^{2-}, Ca^{2+}

→ $CaCO_3$

CO_2 / carbonate is important for:

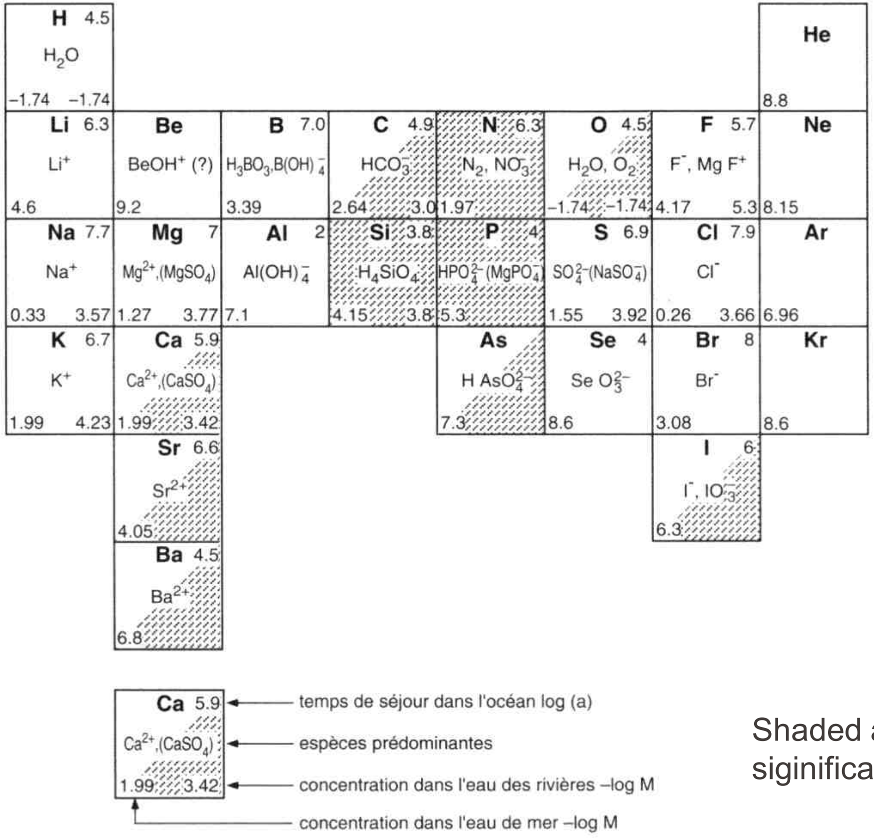
- Climate change
- Photosynthesis
- Precipitation / dissolution of minerals
- Alkalinity (buffering capacity), water hardness

Carbonate in water



Source: www.chemistryland.com

Importance of C in water



H 4.5 H_2O −1.74 −1.74							**He** 8.8
Li 6.3 Li^+ 4.6	**Be** $BeOH^+$ (?) 9.2	**B** 7.0 $H_3BO_3, B(OH)_4^-$ 3.39	**C** 4.9 HCO_3^- 2.64 3.0	**N** 6.3 N_2, NO_3^- 1.97	**O** 4.5 H_2O, O_2 −1.74 −1.74	**F** 5.7 F^-, MgF^+ 4.17 5.3	**Ne** 8.15
Na 7.7 Na^+ 0.33 3.57	**Mg** 7 $Mg^{2+}, (MgSO_4)$ 1.27 3.77	**Al** 2 $Al(OH)_4^-$ 7.1	**Si** 3.8 H_4SiO_4 4.15 3.8	**P** 4 HPO_4^{2-} $(MgPO_4^-)$ 5.3	**S** 6.9 SO_4^{2-} $(NaSO_4^-)$ 1.55 3.92	**Cl** 7.9 Cl^- 0.26 3.66	**Ar** 6.96
K 6.7 K^+ 1.99 4.23	**Ca** 5.9 $Ca^{2+}, (CaSO_4)$ 1.99 3.42			**As** $HAsO_4^{2-}$ 7.3	**Se** 4 SeO_3^{2-} 8.6	**Br** 8 Br^- 3.08	**Kr** 8.6
	Sr 6.6 Sr^{2+} 4.05					**I** 6 I^-, IO_3^- 6.3	
	Ba 4.5 Ba^{2+} 6.8						

Ca 5.9 ← temps de séjour dans l'océan log (a)

$Ca^{2+}, (CaSO_4)$ ← espèces prédominantes

1.99 3.42 ← concentration dans l'eau des rivières −log M

↑ concentration dans l'eau de mer −log M

Sigg, Behra, Stumm, Chimie des milieux aquatiques

- C is highly abundant in natural water
- The predominant species is HCO_3^-
- $[HCO_3^-] \approx 1$ -3 mM

Shaded are elements whose distriubtion is siginificantly affected by biota.

Carbonate equilibrium

$$CO_2\,(g) + H_2O \rightleftharpoons H_2CO_3^*$$

$$H_2CO_3^* \rightleftharpoons H^+ + HCO_3^-$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$$

$H_2CO_3^*$ is the sum of aqueous CO_2 and « true » H_2CO_3. It is a diprotic acid.

Table 1: Some important equilibrium constants for the carbonate system at different temperatures

	Equilbirum constants at ionic strength = 0 M					
Reaction	5 °C	10 °C	15 °C	20 °C	25 °C	40 °C
$CO_2\,(g) + H_2O \rightleftharpoons H_2CO_3^*$	-1.20	-1.27	-1.34	-1.41	-1.47	-1.64
$H_2CO_3^* \rightleftharpoons H^+ + HCO_3^-$	6.52	6.46	6.42	6.38	6.35	6.35
$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$	10.56	10.49	10.43	10.38	10.33	10.22
$H_2O \rightleftharpoons H^+ + OH^-$	14.73	14.53	14.34	14.16	14.0	13.53
$CaCO_3\,(s) \rightleftharpoons Ca^{2+} + CO_3^{2-}$	8.35	8.36	8.37	8.39	8.42	8.53

Reminder from acid-base course: diprotic acids

1. Identify species present at equilibrium:
   H_2A , HA^- , A^{2-}, H^+, OH^-

2. Write out equilibrium equations:

$H_2O \rightleftharpoons H^+ + OH^-$	K_w (always present!)
$H_2A \rightleftharpoons H^+ + HA^-$	K_{a1}
$HA^- \rightleftharpoons H^+ + A^{2-}$	K_{a2}
....	

3. List mass balance equations:
   $C_T = H_2A + HA^- + A^{2-}$

4. List proton balance equation (see next slide):

$[H^+] = [HA^-] + 2[A^{2-}] + [OH^-]$	if added as H_2A
$[H_2A] + [H^+] = [A^{2-}] + [OH^-]$	if added as HA^-
$2[H_2A] + [HA^-] + [H^+] = [OH^-]$	if added as A^{2-}

5. Solve equations (5 unknowns require 5 equations)
   analytically (see Sigg, Behra Stumm, table p. 39)
   graphical approach

Carbonate equilibrium conditions in a pure system

Pure system: composed of carbonate species and water. No additional acids, solids, etc.

Species:
$H_2CO_3^*$, HCO_3^- , CO_3^{2-}, H^+, OH^-

Equilibrium equations (see table 1 for values of K):

$CO_2\,(g) + H_2O$	$\rightleftharpoons$	$H_2CO_3^*$	$p_{CO_2}/[H_2CO_3^*(aq)] = K_H$ (atm/M)
$H_2CO_3^*$	$\rightleftharpoons$	$H^+ + HCO_3^-$	$[HCO_3^-][H^+]/[H_2CO_3^*] = K_1$
HCO_3^-	$\rightleftharpoons$	$H^+ + CO_3^{2-}$	$[CO_3^{2-}][H^+]/[HCO_3^-] = K_2$
H_2O	$\rightleftharpoons$	$H^+ + OH^-$	$[H^+][OH^-] = K_W$

(p_{CO2} is the partial pressure of CO_2. In the atmosphere it is currently, $p_{CO2} \approx 420$ ppm (or $10^{-3.37}$ atm at sea level)

Mass balance equation (total carbon in solution, C_T):
$C_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}]$

Proton balance equations:
$[H^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-]$ (If added as $H_2CO_3^*$)
$[H^+] + [H_2CO_3^*] = [CO_3^{2-}] + [OH^-]$ (if added as $NaHCO_3$)
$[H^+] + [HCO_3^-] + 2[H_2CO_3^*] = [OH^-]$ (if added as Na_2CO_3)

Open and closed systems

Open system

- Exchange of volatile matter between system and environment
- p_{CO2} corresponds to p_{CO2} of the surrounding environment
- C_T is variable, function of p_{CO2}
- E.g., lakes, rivers, rain drops

Closed system

- No exchange of matter between system and environment
- p_{CO2} is system dependent
- C_T remains constant
- E.g., groundwater, bottled water

Carbonate equilibrium in a pure, closed system

Species:

$H_2CO_3^*$, HCO_3^- , CO_3^{2-}, H^+, OH^- → need 5 equations Not known: p_{CO2}

*Equilibrium equations combined with mass balance equation for **graphical solution**:*

i) Express all species as a function of C_T and $[H^+]$ (see Sigg, Behra, Stumm, p. 55)

$$[H_2CO_3^*] = C_T\left(\frac{[H^+]^2}{[H^+]^2 + K_1[H^+] + K_1K_2}\right) = C_T \cdot \alpha_0$$

$$[HCO_3^-] = C_T\left(\frac{K_1[H^+]}{[H^+]^2 + K_1[H^+] + K_1K_2}\right) = C_T \cdot \alpha_1$$

$$[CO_3^{2-}] = C_T\left(\frac{K_1K_2}{[H^+]^2 + K_1[H^+] + K_1K_2}\right) = C_T \cdot \alpha_2$$

ii) Put in « log » form

iii) For each species, simplify equations according to pH regions, e.g. for $[H_2CO_3^*]$:

$pH < pK_1$: $\log[H_2CO_3^*] = \log C_T$

$pK_1 < pH < pK_2$: $\log[H_2CO_3^*] = pK_1 + \log C_T - pH$

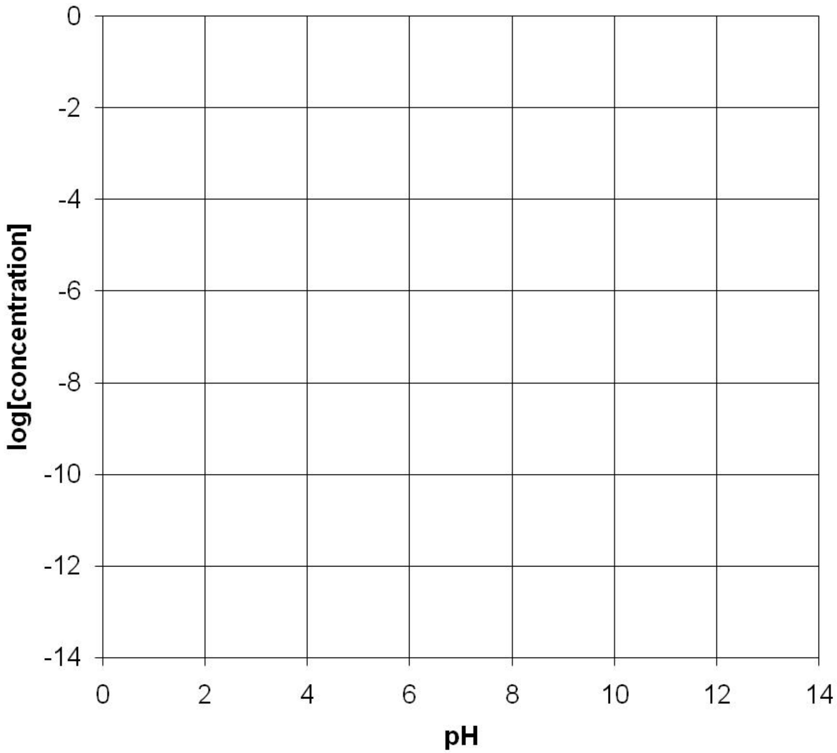
$pH > pK_2$: $\log[H_2CO_3^*] = pK_1 + pK_2 + \log C_T - 2pH$

iv) Put on graph of pH vs. log[concentration]

Use proton balances to find equilibrium pH

Equilibrium concentrations in a pure, closed system

Conditions: 25° C, C_T = 10^{-3} M; pK_1= 6.35, pK_2= 10.33



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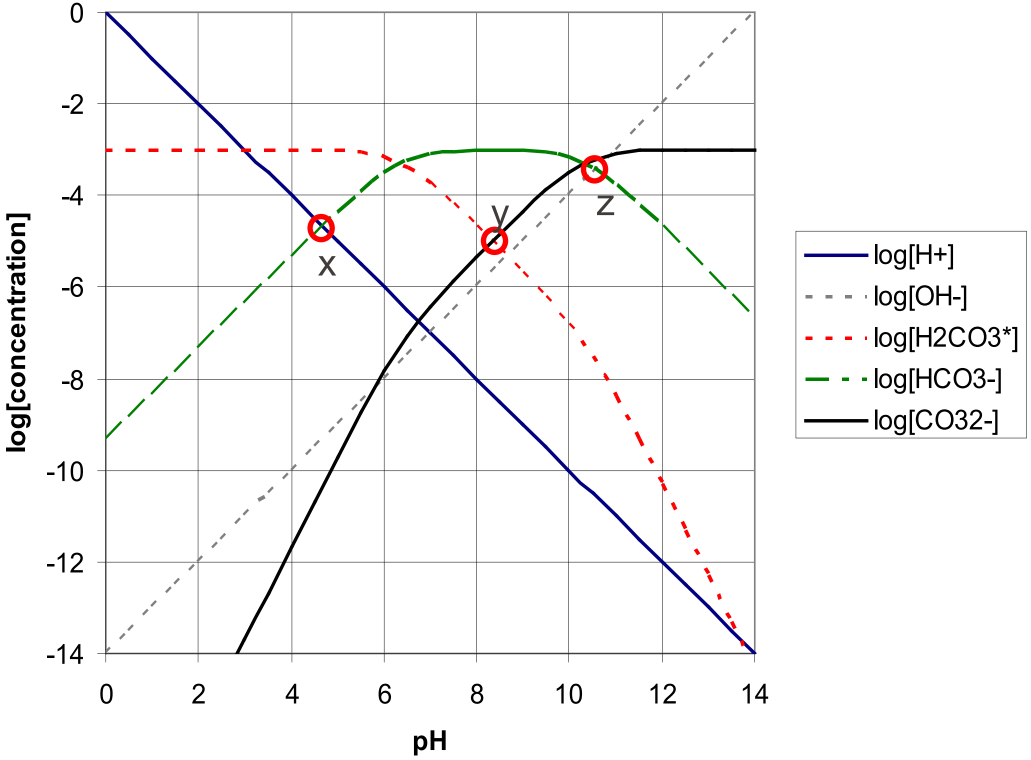


x: $[H^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-]$
y: $[H^+] + [H_2CO_3^*] = [CO_3^{2-}] + [OH^-]$
z: $[H^+] + 2[H_2CO_3^*] + [HCO_3^-] = [OH^-]$

Exercise 1

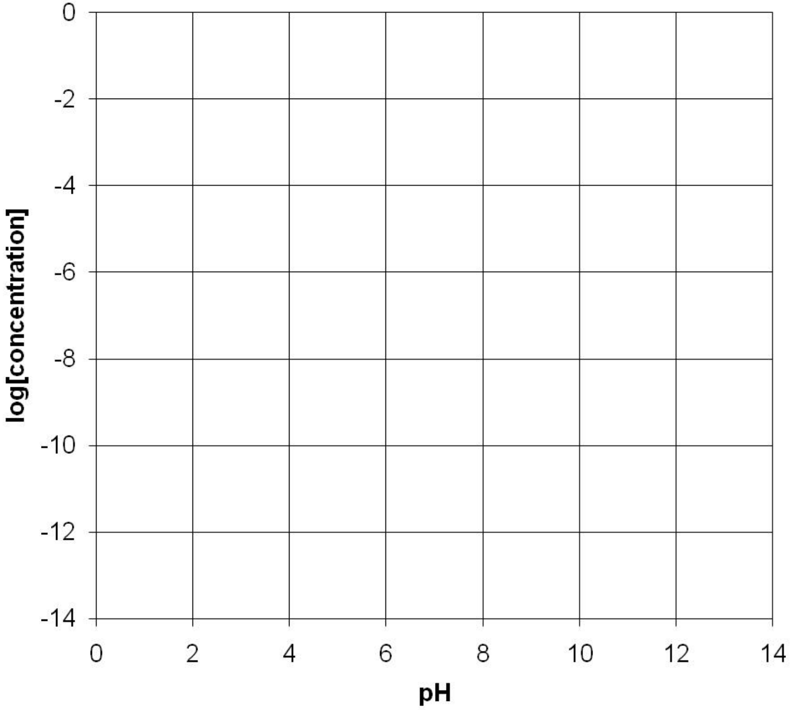
Addition of other acids

How does the equilibrium pH values change compared to the previous example ($C_T = 10^{-3}$ M, T = 25 ºC) if 4.1 * 10^{-4} M boric acid (as $B(OH)_3$) are added ?

Boric acid:

$B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+$; $pK_a = 9.2$

C_T (boric acid / borate) = $B(OH)_3 + B(OH)_4^-$



Equilibrium concentrations in a pure, open system

Species:
$H_2CO_3^*$, HCO_3^- , CO_3^{2-}, H^+, OH^- → need 5 equations

Not known: C_T

Equilibrium equations:

i) Express all species as a function of pH and p_{CO2}
ii) put in « log » form:

$$\log[H_2CO_3^*] = \log[p_{CO_2}] + pK_H$$

$$\log[HCO_3^-] = -pK_1 + pH + \log[H_2CO_3^*] = -pK_1 + pH + \log[p_{CO2}] + pK_H$$

$$\log[CO_3^{2-}] = -pK_2 + pH + \log[HCO_3^-] = -pK_2 - pK_1 + 2pH + \log[p_{CO2}] + pK_H$$

iii) No need to define different pH regions and simplify equations!

iv) Put on graph of pH vs. log[concentration]

Use proton balance to find equilibrium pH

Can determine C_T using the mass balance

Recall:

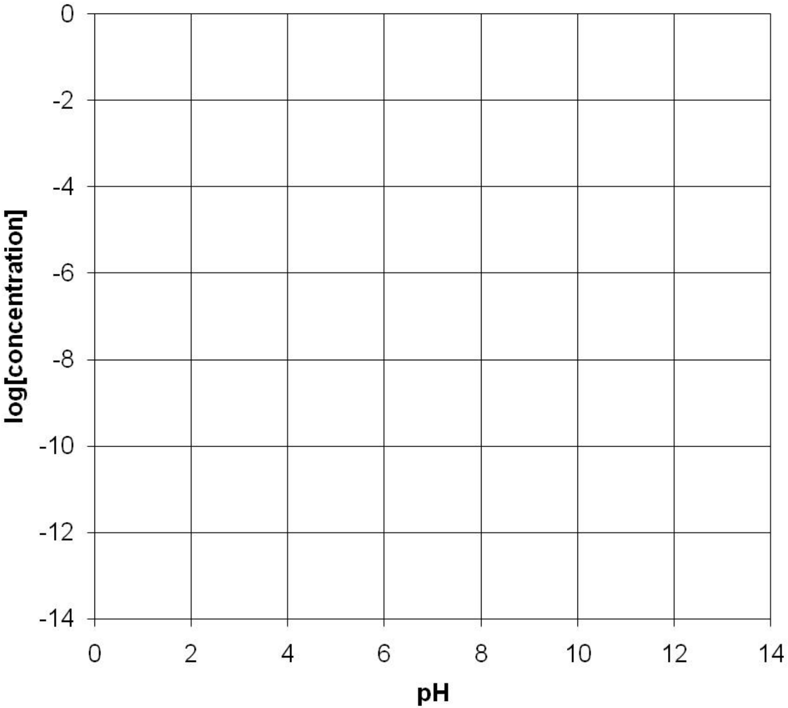
$$p_{CO_2}/[H_2CO_3^*(aq)] = K_H$$

$$[HCO_3^-][H^+]/[H_2CO_3^*] = K_1$$

$$[CO_3^{2-}][H^+]/[HCO_3^-] = K_2$$

Equilibrium concentrations in a pure, open system

Conditions: 25° C, p_{CO2} = $10^{-3.37}$ atm; 25° C; pK_1= 6.35; pK_2= 10.33; pK_H = -1.47



Equilibrium concentrations in a pure, open system

Conditions: 25° C, $p_{CO2} = 10^{-3.37}$ atm; $pK_1 = 6.35$, $pK_2 = 10.33$, $pK_H = -1.47$

$$\log[H_2CO_3^*] = \log[p_{CO_2}] + pK_H \quad = -3.37 - 1.47 = -4.84$$

$$\log[HCO_3^-] = -pK_1 + pH + \log[H_2CO_3^*] = -pK_1 + pH + \log[p_{CO2}] + pK_H$$

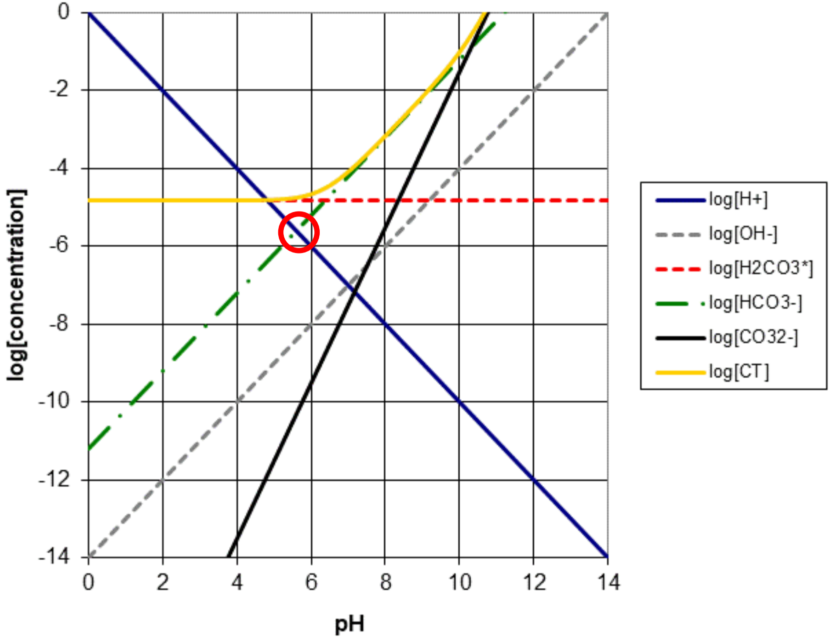
$$= -6.35 - 3.37 - 1.47 + pH = -11.19 + pH$$

$$\log[CO_3^{2-}] = -pK_2 + pH + \log[HCO_3^-] = -pK_2 - pK_1 + 2pH + \log[p_{CO2}] + pK_H$$

$$= -10.33 - 6.35 - 3.37 - 1.47 + 2pH = -21.52 + 2pH$$

Equilibrium concentrations in a pure, open system

Conditions: 25° C, $p_{CO2} = 10^{-3.37}$ atm; $pK_1 = 6.35$, $pK_2 = 10.33$, $pK_H = -1.47$



Only considering point x, because we assume that the source of carbonate in the system is CO_2

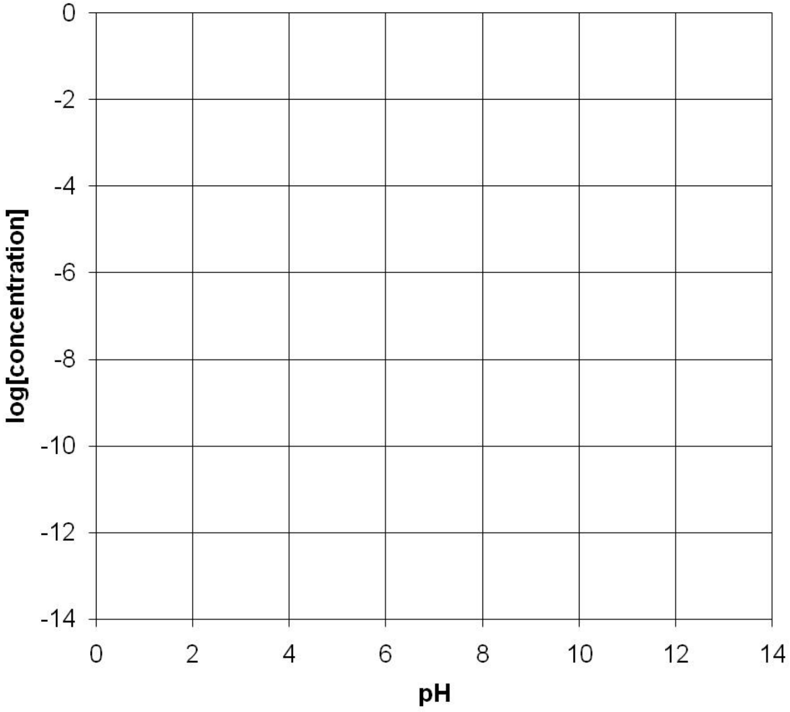
Proton balance: $[H^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-]$ → Equilibrium pH = 5.6

pH = 5.6: $[H_2CO_3^*] = 10^{-4.84}$ M; $[HCO_3^-] = 2.6 \cdot 10^{-6}$ M; $[CO_3^{2-}] = 4.7 \cdot 10^{-11}$ M; $[OH^-] = 10^{-8.4}$ M

This conditions are true for any open, pristine system in equilibrium with the atmosphere

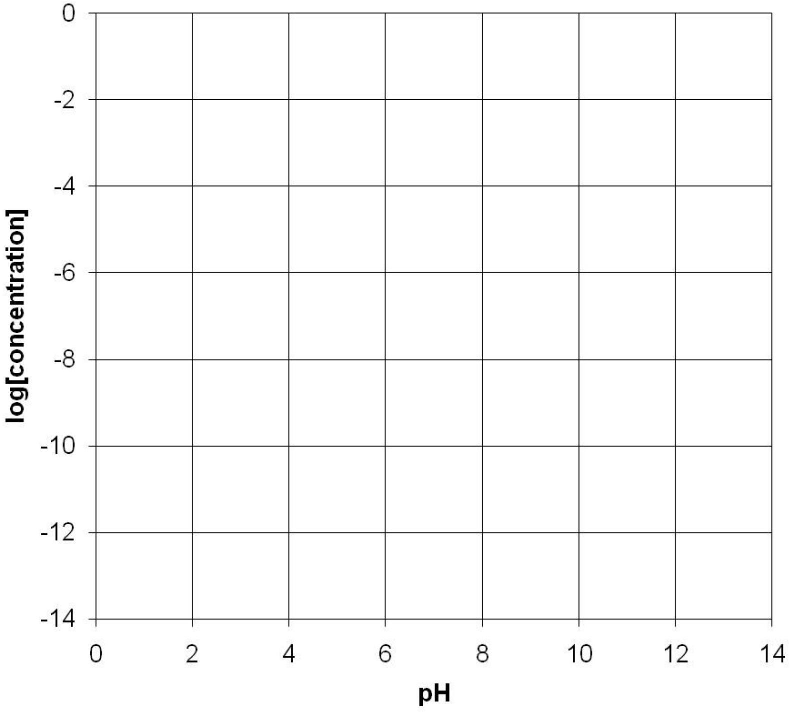
Exercise 2

What is the equilibrium pH of rainwater (T= 25 ºC) if p_{CO2} increases 10x (up to $10^{-2.37}$) due to fossil fuel burning?



Exercise 3

What is the equilibrium pH of rainwater in winter? (T= 5 ºC)? Assume that the p_{CO2} remains $10^{-3.37}$ atm



Exercise 4

In class, we discussed that pure rain has a pH of 5.6 at 25 C, as a result of the exposure of rain to CO_2 in the atmosphere. In addition to CO_2, the air in agricultural areas can contain up to 10^{-5} atm of ammonia (NH_3). NH_3 is a volatile base that can evaporate from fertilizer applied to land. When gaseous NH_3 dissolves into water, it is present as aqueous NH_3 in equilibrium with its conjugated acid NH_4^+:

$$NH_3\,(g) + H_2O \rightleftharpoons NH_3\,(aq) + H_2O \qquad pK_H = 1.79$$

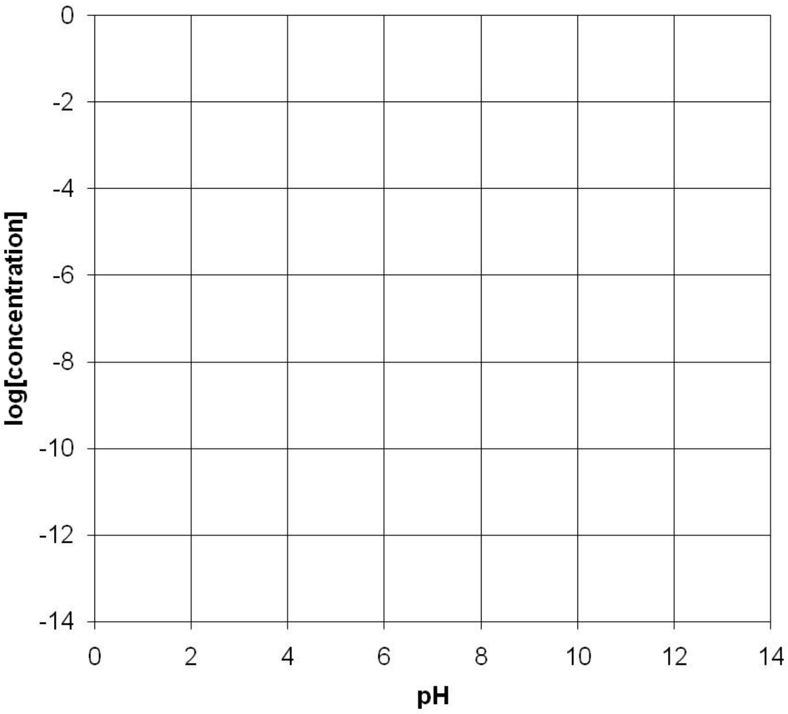
$$NH_3\,(aq) + H^+ \rightleftharpoons NH_4^+ \qquad pK_a = 9.4$$

Use the grid on the next slide to answer the following questions.

a) What is the concentration of NH_3 in rain?

b) If the air contains both CO_2 and $NH_{3,}$ what is the pH of this rain?

Exercise 4



Dissolution of $CaCO_3$ in an open system

As before, we have three carbonate species and water in an open system:

CO_2 (g) + H_2O ⇌ $H_2CO_3^*$

$H_2CO_3^*$ ⇌ $H^+ + HCO_3^-$

HCO_3^- ⇌ $H^+ + CO_3^{2-}$

H_2O ⇌ $H^+ + OH^-$

Now the system is in equlibrium with solid $CaCO_3$, which equilibrates with the solution and yields Ca^{2+} and CO_3^{2-} according to the followig dissolution reaction:

$CaCO_3 + H_2O$ ⇌ $Ca^{2+} + CO_3^{2-}$

We have one more species (Ca^{2+}) in the system, so we, need one additional equilibrium equation:

$[Ca^{2+}]*[CO_3^{2-}] = K_{s0}$

Add line for $[Ca^{2+}]$ to the graph:

$\log [Ca^{2+}] = -pK_{s0} - \log[CO_3^{2-}] = -pK_{s0} + pK_2 + pK_1 – 2pH - \log [p_{CO2}] - pK_H = 13.1 – 2pH$

New charge (not only proton!) balance:

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

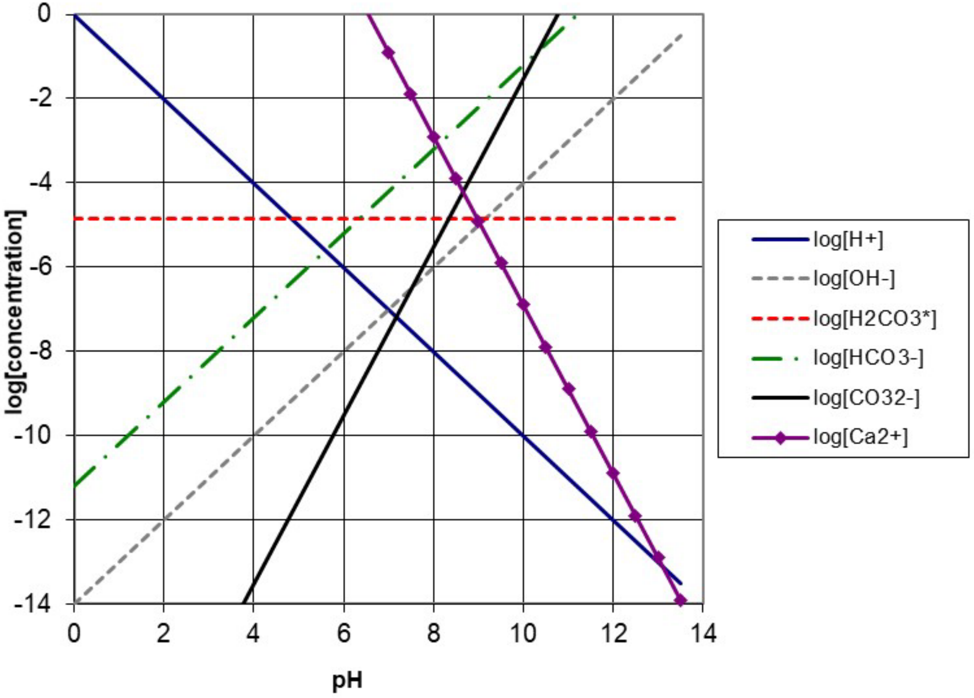
Can simplify the proton balance in the pH and $[Ca^{2+}]$ range of natural systems:

$2 [Ca^{2+}] \approx [HCO_3^-]$ or

$\log [Ca^{2+}] + 0.3 \approx \log [HCO_3^-]$

Dissolution of $CaCO_3$ in an open system

Conditions: $p_{CO2}=10^{-3.37}$ atm, T = 25 ºC



Dissolution of $CaCO_3$ in an open system

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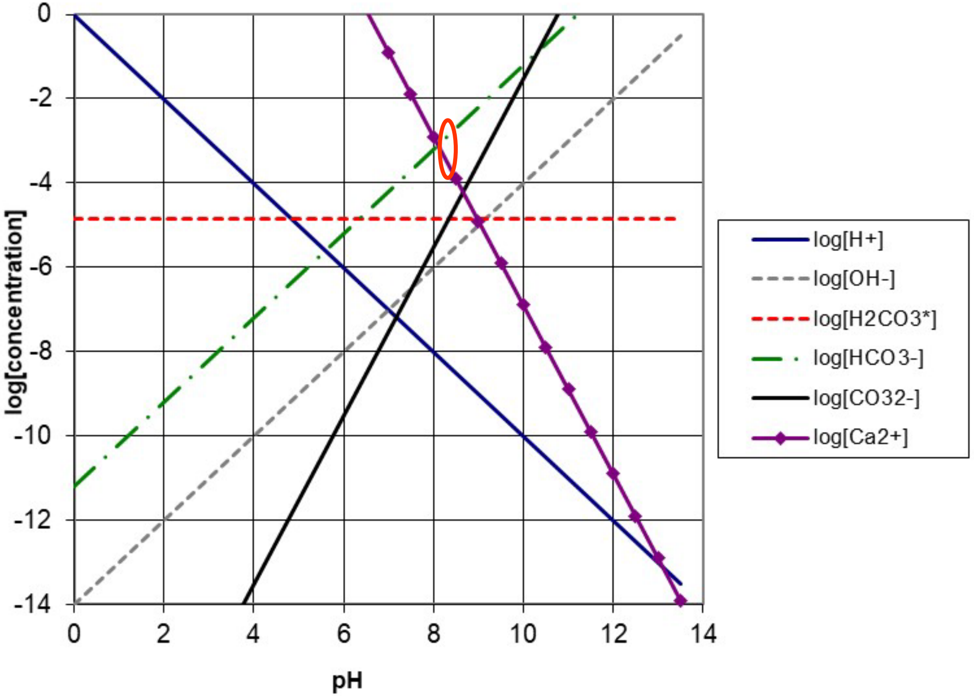
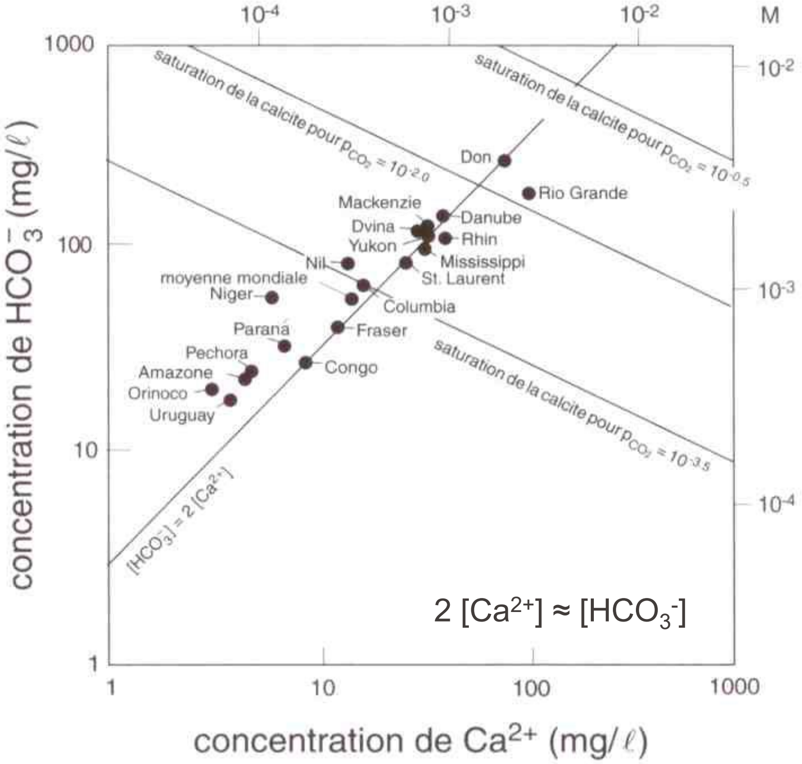


$\log [Ca^{2+}] + \mathbf{0.3} \approx \log [HCO_3^-]$

At equilibrium: pH = 8.2; $[HCO_3^-] \approx 10^{-3}$ M; $[Ca^{2+}] = 10^{-3.3}$ M

Relationship between HCO^{3-} and Ca^{2+} in rivers



$2\,[Ca^{2+}] \approx [HCO_3^-]$

Source: Sigg, Behra, Stumm

Exercise 5

Assume a clean lake that is in equilibrium with the atmosphere at 25° C. The lake is located in a region where $MnCO_3$ dominates the subsurface, so the water is also in equilibrium with $MnCO_3$ (but not $CaCO_3$). The K_s of $MnCO_3$ is $10^{-10.65}$.

a) What is the pH of this lake?

b) What is the pH of this lake after the spill of an acid HA? Assume that the total acid concentration (HA + A-) after the spill is1 mM, the pK_a of the acid is 2, and the acid is not volatile.

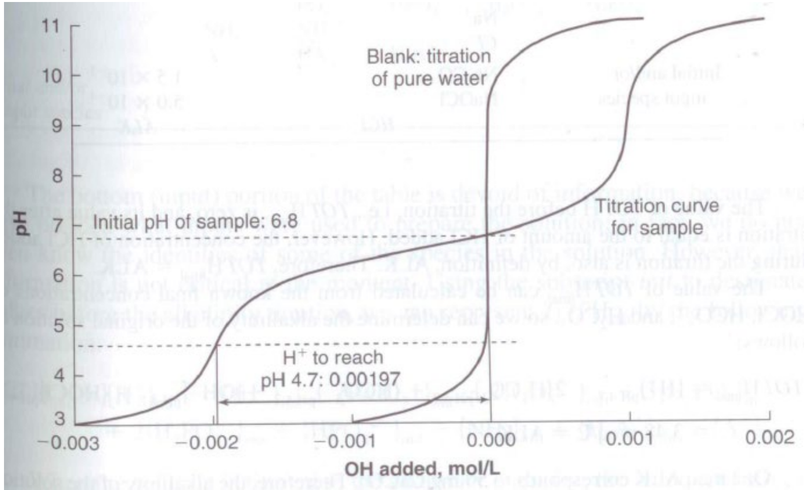
Alkalinity

Many anthropogenic inputs to water bodies are acidic (acid rain, acid mine drainage, etc.). How will the pH of a water body change in response to such an input?

To answer this question, we use the concept of alkalinity [Alk]. Alk is a measure of the amount of protons the solution can buffer (= acid neutralization capacity). It is an indicator of the stability of a system (whereas pH is an indicator of the specific state of acidity of a solution).

Alk is operationally and historically defined as the amount of acid that we need to add to a solution to shift its pH down to 4.7 (or 4.5). 4.7 is often chosen as the endpoint because it is the pH below which a significant loss of biodiversity starts to occur.

Alk is measurable by titration:
How much acid do we have to add to reach pH 4.7?



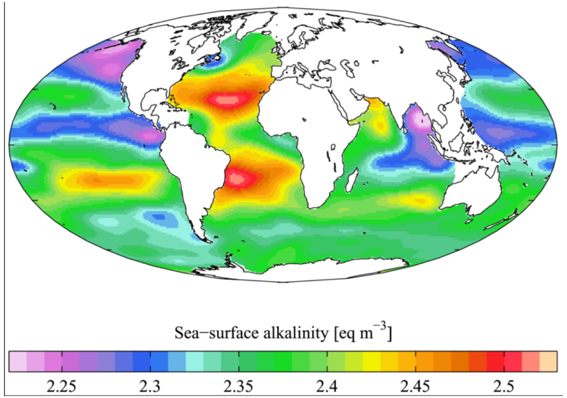
Source: Benjamin: Water Chemistry

Alkalinity with (bi)carbonate as the only contributor

The main contributors to alkalinity are HCO_3^- , CO_3^{2-} and OH^-. Note that some of the (bi)carbonate in solution comes from $CaCO_3$, $CaHCO_3^+$, $MgCO_3$, etc. The (bi)carbonate-based Alk reflects the proton deficiency with respect to $H_2CO_3^*$ and H_2O.

To neutralize all (bi)carbonate and OH^-, need:

1 mol H^+ per mol of HCO_3^-
2 mol H^+ per mol of CO_3^{2-}
1 mol H^+ per mol of OH^-
– 1 mol H^+ for each H^+ already present in solution.



www.wikipedia.org

Overall: **$[Alk] = [HCO_3^-] + 2\,[CO_3^{2-}] + [OH^-] - [H^+]$**

In natural water, can often use simplification: **$[Alk] \approx [HCO_3^-] \approx 2\,[Ca^{2+}]$**

Typical Alk values:	0.1 – 2.5 mM in surface water
	1 – 10 mM in groundwater

Extended definitions of alkalinity

Other definitions of Alk exist that include not only carbonate, but other acids and bases. E.g., silicic acid, boric acid or other organic acids can contribute to the total alkalinity, as they can also buffer acid.

$$[Alk] = [HCO_3^-] + 2\,[CO_3^{2-}] + [OH^-] - [H^+] + [B(OH)_4^-] + [H_3SiO_4^-] + \ldots$$

All these definitions use the same concept of relating the proton condition to a reference level of protons.

The presence of additional acids is often neglected, because:

1) $[CO_3^{2-}]+[HCO_3^-] >>$ other acids

2) Typically, by the time all carbonate is protonated to H_2CO_3, all other acids are also protonated ($pK_a(H_2CO_3) < pK_a$ (other acids)). Exceptions are phosphoric acid and some organic acids.

Alkalinity in open and closed systems

General expression:

$$[\mathrm{Alk}] = [\mathrm{HCO_3^-}] + 2\,[\mathrm{CO_3^{2-}}] + [\mathrm{OH^-}] - [\mathrm{H^+}]$$

In a closed system, can re-write as a function of C_T:

$$[\mathrm{Alk}] = C_T(\alpha_1 + 2\alpha_2) + [\mathrm{OH^-}] - [\mathrm{H^+}]$$

In an open system, can re-write as a function of p_{CO2}:

$$[\mathrm{Alk}] = \frac{p_{CO2}}{K_H\alpha_0}\left(\alpha_1 + 2\alpha_2\right) + [\mathrm{OH^-}] - [\mathrm{H^+}]$$

Recall: $C_T=[H_2CO_3^*]/\alpha_0=p_{CO2}\,/(K_{H*}\alpha_0)$

Units of alkalinity

While chemists typcially use mol/L (M) as the units of alkalinity, engineers like to use units of $CaCO_3$, either in mg/L as $CaCO_3$ or meq/L. (An « equivalent » is typically a mole of charge/L. In the context of alkalinity, 1 eq/L corresponds to 1 mol H^+/L.)

The unit «mg/L as $CaCO_3$» indicates what amount of $CaCO_3$ would have to be dissolved in pure water to create the same alkalinity as your sample.

Relation between mM and meq/L or mg/L $CaCO_3$:

1 mM $CaCO_3$ = 100 mg/L $CaCO_3$
1 mM (or 100 mg/L) $CaCO_3$ provide 1 mM Ca^{2+} and 1 mM CO_3^{2-}
1 mM CO_3^{2-} + 2 mM $H^+ \rightarrow$ 1 mM H_2CO_3, so 2 mM (or 2 meq/L) H^+ are needed to titrate 1 mM (or 100 mg/L) $CaCO_3$ to H_2CO_3

Recall: [Alk] = [H^+] added to titrate all (bi)carbonate to H_2CO_3. So:
1 mM Alk = 1 meq/L = 50 mg/L as $CaCO_3$

Acidity

Definition: Proton excess with respect to $H_2CO_3^*$ and H_2O.

In the acidic pH range, [Alk] can be negative, because protons are in overall excess compared to the reference state. We then talk about Acidity [Acy]:

$$[Acy] = -[Alk] = [H^+] - [HCO_3^-] - 2\,[CO_3^{2-}] - [OH^-] \qquad (M)$$

Acy is measurable by titration (see Sigg, Behra, Stumm for details)

Often waters are characterized by two out of the three following parameters:

i) C_T (closed system) or p_{CO2} (open system)
ii) Alk or Acy
iii) pH.

If one knows two, the third and the carbon speciation can be determined.

Exercise 6

What is the alkalinity of a solution containing:

a) 10^{-4} M NaOH, pH 10

b) 10^{-4} M NaOH in 3×10^{-4} M C_T, pH 6.26

Typical water composition (from introduction lecture)

Which water has the highest and which one the lowest carbonate alkalinity?

Type of water Rock Location	Wet deposition (Rain) Dübendorf	River water Limestones kleine Emme	**River water** **Molasses** **Rhine (Basel)**	Spring water Silicates Verzasca	Groundwater Molasses Glattfelden	**Lake water** **Molasses** **Lake Zürich**	Ocean
Parameter /Unit	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/kg
Calcium	0,39	56	53	5,2	80	45,6	410
Magnesium	0,055	4,2	6,6	0,85	18	6,0	1300
Sodium	0,14	3,3	6,2	0,40	22		11 000
Potassium	0,060	1,3	1,4	0,16	4,0		400
Bicarbonat		172	129	15,4	284	126	140
Sulfate	1,5	12	27	7,9	27	15	2700
Chloride	0,71	4,3	8,6	0,53	36	2.5	19 300
Silicic acid	<0,2	5,6	3,6	18,8	10		7,6
Ammonium	0,71	0,06	0,09	0,005	0,01	< 0,1	0,07
Nitrate	2,3	5,7	1,3	2,1	22	0.77	2,6
Phosphate	0,003	0,15	0,09	0,030	1,8	0.08	0,2
Unit	µg/l	µg/l		µg/l	µg/l		µg/kg
Lead	7,6	2,2		<1	0,2		0,2
Cadmium	0,13			<0,1	0,05		0,07
Zinc	18	24		<5	1,8		0,1
Copper	1,6	3,8		<1	3,6		0,3

Alkalinity and acidity are conservative parameters

Alk is a conservative parameters, i.e., independent of:

- temperature
- pressure
- changes in C_T due to the removal/addition of the reference compound CO_2 / $H_2CO_3^*$

  (Note: C_T changes due to the addition of other sources of carbonate do change Alk!)
- pH changes due to the removal/addition of the reference compound CO_2 / $H_2CO_3^*$

  (Note: pH changes due to the addition of a strong acid or base do change Alk!)

Alk has a linear mixing behavior.

E.g., mix solution A with $[Alk]_A$ and solution B with $[Alk]_B$ at a 1:1 ratio:

$[Alk]_{mix} = 0.5*([Alk]_A + [Alk]_B)$

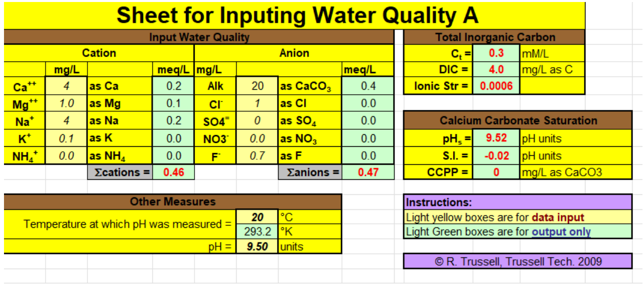
Whereas $pH_{mix} \neq 0.5*(pH_A + pH_B)$

Exercise 7

The effluent of an acidic lake (pH 5, [Acy] = 10^{-5} M) is mixed at a 1:1 ratio with a river (pH 7.5, [Alk]=$2*10^{-4}$ M). The mixed water (10 ºC) remains in equilibrium with the atmosphere (p_{CO2} = $10^{-3.37}$ atm). What is the pH of the mixed water?

Alkalinity of mixed solutions

Of course there automated ways to determine the Alk of mixtures, in particular for water treatment applications. Example from Trussell Technologies (*https://trusselltech.com/downloads/*):



Sheet for Inputing Water Quality A

Input Water Quality

Cation				Anion			
	mg/L		meq/L	mg/L			meq/L
Ca^{++}	4	as Ca	0.2	Alk	20	as $CaCO_3$	0.4
Mg^{++}	1.0	as Mg	0.1	Cl^-	1	as Cl	0.0
Na^+	4	as Na	0.2	$SO4^=$	0	as SO_4	0.0
K^+	0.1	as K	0.0	$NO3^-$	0.0	as NO_3	0.0
NH_4^+	0.0	as NH_4	0.0	F^-	0.7	as F	0.0
		Σcations =	0.46			Σanions =	0.47

Total Inorganic Carbon

C_t =	0.3	mM/L
DIC =	4.0	mg/L as C
Ionic Str =	0.0006	

Calcium Carbonate Saturation

pH_s =	9.52	pH units
S.I. =	-0.02	pH units
CCPP =	0	mg/L as CaCO3

Other Measures

Temperature at which pH was measured =	20	°C
	293.2	°K
pH =	9.50	units

Instructions:

Light yellow boxes are for **data input**

Light Green boxes are for **output only**

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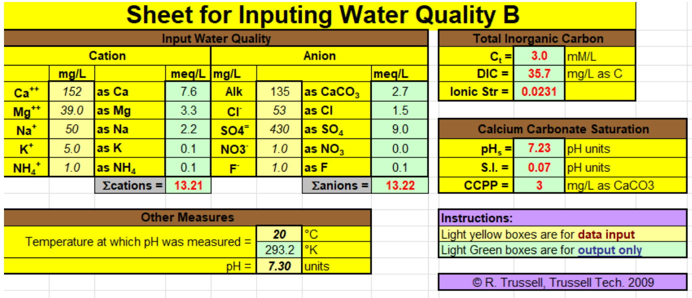

Sheet for Inputing Water Quality B

Input Water Quality

Cation				Anion			
	mg/L		meq/L	mg/L			meq/L
Ca^{++}	152	as Ca	7.6	Alk	135	as $CaCO_3$	2.7
Mg^{++}	39.0	as Mg	3.3	Cl^-	53	as Cl	1.5
Na^+	50	as Na	2.2	$SO4^=$	430	as SO_4	9.0
K^+	5.0	as K	0.1	$NO3^-$	1.0	as NO_3	0.0
NH_4^+	1.0	as NH_4	0.1	F^-	1.0	as F	0.1
		Σcations =	13.21			Σanions =	13.22

Total Inorganic Carbon

C_t =	3.0	mM/L
DIC =	35.7	mg/L as C
Ionic Str =	0.0231	

Calcium Carbonate Saturation

pH_s =	7.23	pH units
S.I. =	0.07	pH units
CCPP =	3	mg/L as CaCO3

Other Measures

Temperature at which pH was measured =	20	°C
	293.2	°K
pH =	7.30	units

Instructions:

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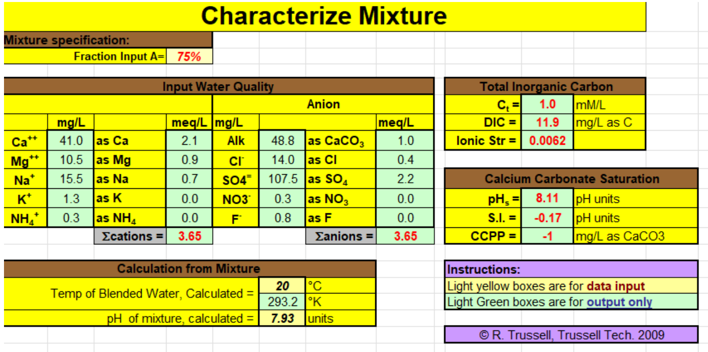

Characterize Mixture

Mixture specification:

Fraction Input A= 75%

Input Water Quality

				Anion			
	mg/L		meq/L	mg/L			meq/L
Ca^{++}	41.0	as Ca	2.1	Alk	48.8	as $CaCO_3$	1.0
Mg^{++}	10.5	as Mg	0.9	Cl^-	14.0	as Cl	0.4
Na^+	15.5	as Na	0.7	$SO4^=$	107.5	as SO_4	2.2
K^+	1.3	as K	0.0	$NO3^-$	0.3	as NO_3	0.0
NH_4^+	0.3	as NH_4	0.0	F^-	0.8	as F	0.0
		Σcations =	3.65			Σanions =	3.65

Total Inorganic Carbon

C_t =	1.0	mM/L
DIC =	11.9	mg/L as C
Ionic Str =	0.0062	

Calcium Carbonate Saturation

pH_s =	8.11	pH units
S.I. =	-0.17	pH units
CCPP =	-1	mg/L as CaCO3

Calculation from Mixture

Temp of Blended Water, Calculated =	20	°C
	293.2	°K
pH of mixture, calculated =	7.93	units

Instructions:

Light yellow boxes are for **data input**

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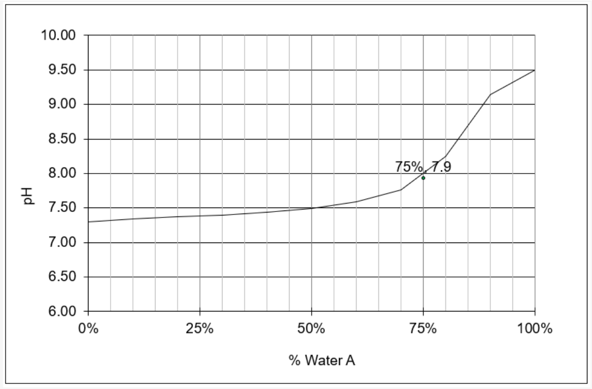


Alkalinity: changes

Alkalinity is affected by:

- Processes that produce or consume H^+ or OH^-

  E.g., reduction of MnO_2 (s) by CH_2O:

  $2\ MnO_2 + CH_2O + 4\ H^+ = CO_2 + 3H_2O + 2\ Mn^{2+}$ → Alk increases due to H^+ consumption

- Processes that yield or consume HCO_3^- or CO_3^{2-}

  E.g., mineral weathering typically increases Alk:

  e.g., $CaCO_3 \rightarrow Ca^{2+} + CO_3^{2-}$ → Alk increases due to release of CO_3^{2-}

- Biological activity:

  Simple expression of photosynthesis / respiration:

  $nCO_2 + nH_2O \leftrightarrow (CH_2O)n + nO_2$ → no change!

  But: photosynthesis / respiration according to Redfield stoichiometry:

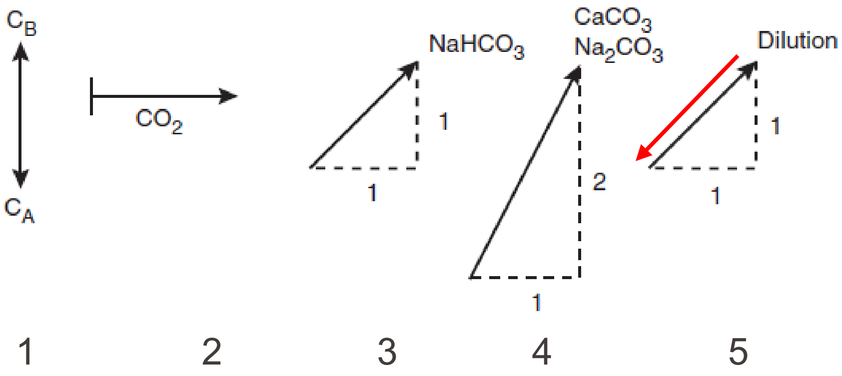
  $106\ CO_2 + 16\ NO_3^- + HPO_4^{2-} + 122\ H_2O + 18\ H^+ \leftrightarrow \{C_{106}H_{263}O_{110}N_{16}P_1\} + 138\ O_2$

  → Alk increases due to photosynthesis

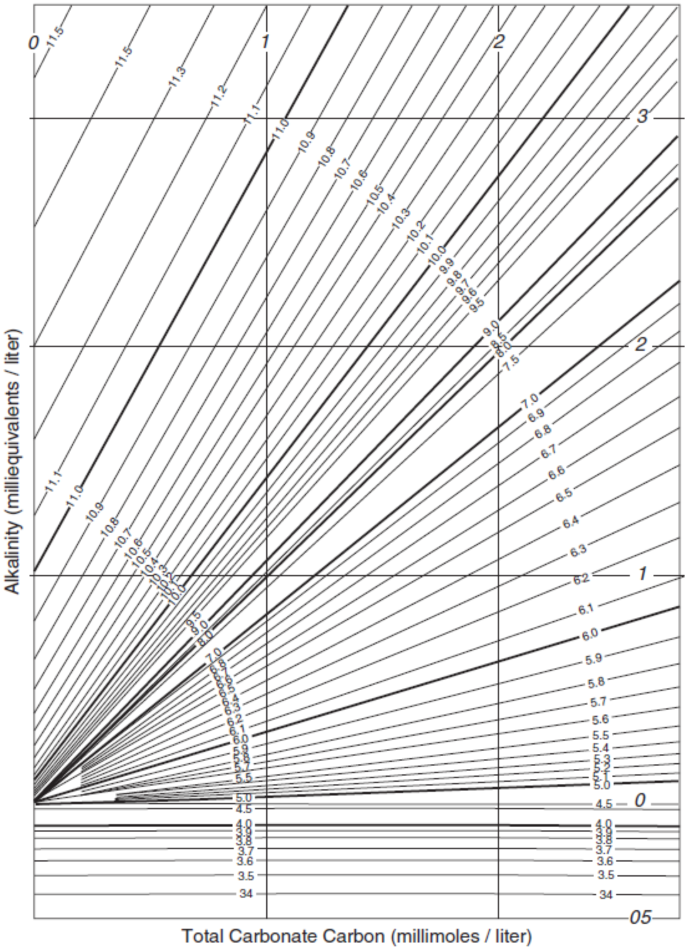
  → Alk decreases due to respiration

Deffeyes Diagram

Representation of the interdependece of $C_{T,}$ Alk and pH (at 25°C, I=0). It is a plot of the relationship $[Alk] = C_T(\alpha_1 + 2\alpha_2) + [OH^-] - [H^+]$



1) $C_A - C_B$: addition of strong acid or base, without changing C_T
2) CO_2 addition
3) HCO_3^- addition
4) CO_3^{2-} addition
5) Dilution by C-free water



Excercise 8

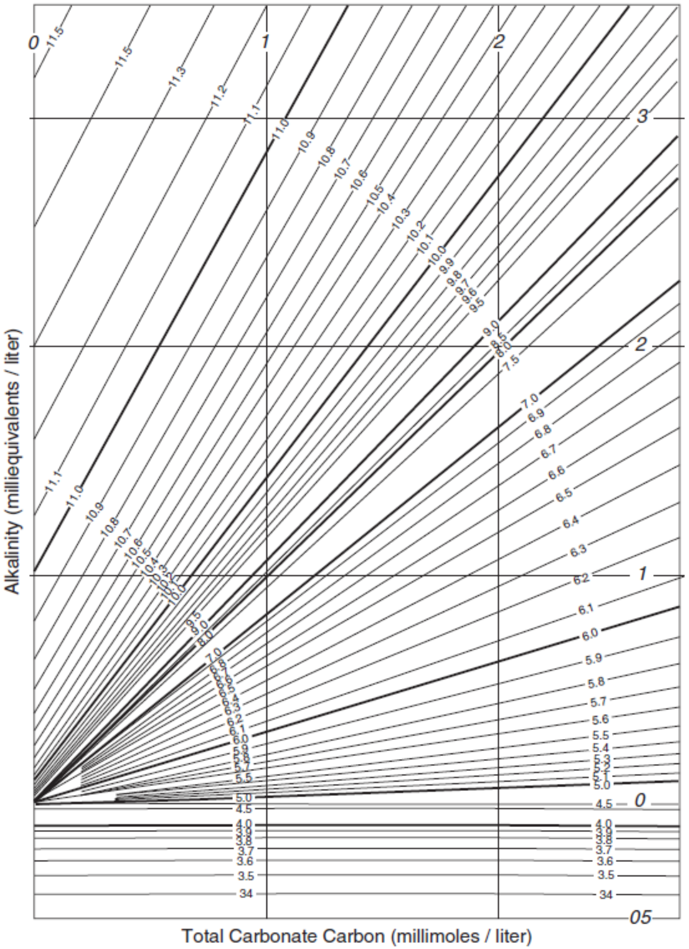
A 25 °C solution has an Alk of 0.4 meq/L and a pH of 6.0. Use the Deffeyes Diagram to determine:

a) C_T of the solution

b) The pH after removal of 0.5 mM of CO_2

c) The pH of the original solution after addition of 1 mM NaOH

d) The pH of the original solution after addition of 0.2 mM $NaHCO_3$



Excercise 9

The source water entering a treatment plant has pH 5.8 and an alkalinity of 0.2 meq/L. Assume that this is a closed system at 25°C.

a) What are the new alkalinity and pH if 0.5 mM $NaHCO_3$ is added to the water?

b) What are the new alkalinity and pH if 0.3 mM $Ca(OH)_2$ (lime) is added to the initial water?

c) Propose a strategy to adjust the source water to pH 6.2 and an alkalinity = 2.5 meq/L

Summary

- Carbonate/bicarbonate are the most important and abundant constituents in natural water.
- Carbonate buffers most natural systems in the pH range 5 – 10.5.
- In closed systems, the total carbon content (C_T) is constant.
- In open systems, the CO_2 pressure is constant (currently $10^{-3.37}$ atm).
- Mineral dissolution (mostly $CaCO_3$) is an important contributor of C to the system.
- In most natural systems, the relationship $2\,[Ca^{2+}] \approx [HCO_3^-]$ applies.
- We can use graphical methods to determine pH, carbonate/bicarbonate concentration and speciation, total C and calcium solubility under equilibrium conditions.
- The carbonate content and equilibrium determines alkalinity.
- Alkalinity denotes the ability to buffer acids. It is defined as $[Alk]=[HCO_3^-]+2[CO_3^{2-}]+[OH^-]-[H^+]$
- Acidity denotes the ability to buffer base. It is defined as $[Acy]= -[Alk]=[H^+]-[HCO_3^-]-2[CO_3^{2-}]-[OH^-]$
- Alkalinity and acidity are conservative parameters with linear mixing behavior. They are useful for calculating equilibrium conditions in mixed waters.