

# Water Chemistry 3

## Controls on Water Chemistry

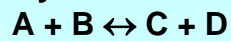
Chemical Equilibrium

Activity

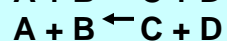
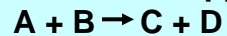
Saturation Index

Carbonate Equilibrium and Alkalinity

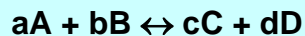
Recall: LAW OF MASS ACTION  
indicates that a system strives to equilibrium



At equilibrium both reactions happen simultaneously



A chemical reaction can be written as



a b c d are molar proportions of compounds A B C D  
(i.e. stoichiometric coefficients in a balanced chemical equation)

## EQUILIBRIUM CONSTANT

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b} = \text{constant}$$

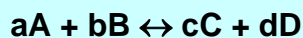
[A] [B] [C] [D] represent equilibrium molal or molar concentration  
a b c d are molar amounts of compounds A B C D

K is the equilibrium constant (tabulated in aqueous chem books)  
If one compound changes concentration others adjust to maintain K

For equilibrium evaluations the [ ] of a pure liquid or solid is defined as 1

Depending on the type of reaction, K may be called  
*acidity or dissociation constant* for acid/base reactions  
*complexation constant* for complexation reactions  
*solubility product* for dissolution reaction  
*adsorption constant* for surface reactions

### Given



Reactants                      Products

and

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

If a reactant, say A, increases  
then to maintain equilibrium:  
the reaction must shift to the right  
activities of reactants decrease  
activities of products increase  
keeping K constant

## ACTIVITY

In concentrated solutions, ions interact electrostatically with each other (surrounded by a cloud of opposite charge) so the stoichiometric coefficients do not reflect reactive availability

Activity coefficients  $\gamma$  adjust molal/molar concentrations  $M$  to **effective concentrations called activities,  $a$**

$$a = \gamma(M)$$

Activity is proportional to concentration, and the proportionality constant is the **activity coefficient,  $\gamma$**

Activity Coef. depends on temperature, pressure & total composition

In dilute solutions, the dissolved components are spread far apart, so interactions among them are very weak then

$$\gamma_i \approx 1, \text{ so } a_i \approx M_i$$

In concentrated solutions  $a$  &  $M$  may be far from equal

## Estimating activity coefficient $\gamma_i$

Activity depends on **ionic strength  $I$**  of a solution:

$$I \cong \frac{1}{2} \sum m_i z_i^2$$

where  $m$  = molar concentration

$$I \cong (2.5 \times 10^{-5}) \times \text{TDS}(\text{mg/L}) \text{ by Langelier}$$

**Debye-Hückel method (accurate up to  $I \sim 0.01\text{M}$ )**

$$\log \gamma_i = -A z_i^2 \sqrt{I}$$

where  $A$  = a constant depending on solvent,  $P$  &  $T$

$z_i$  = the charge on the particular ion

**Güntelberg method (accurate up to  $I \sim 0.1 \text{ M}$ )**

$$\log \gamma_i = -\frac{0.5(z_i)^2 I^{1/2}}{1 + I^{1/2}}$$

### A bit of elaboration on the source of the Güntelberg method

#### Debye-Hückel method (accurate up to $I \sim 0.01M$ )

$$\log \gamma_i = -Az_i^2 \sqrt{I} \quad A = \text{constant depending on P \& T, } z_i = \text{charge}$$

#### For higher ionic strengths Debye-Hückel developed:

$$\log \gamma_i = \frac{-Az_i^2 \sqrt{I}}{1 + Ba_o \sqrt{I}}$$

$B$  = constant depending on P & T,  $a_o$  = hydrated radius of ion

Typically  $Ba_o \approx 1.0$

At  $15^\circ C$ ,  $A = 0.5$  @  $0^\circ C$   $A = 0.49$  and @  $60^\circ C$   $A = 0.54$

#### Thus we simplify to: Güntelberg method

$$\log \gamma_i = -\frac{0.5(z_i)^2 I^{1/2}}{1 + I^{1/2}}$$



### Determine the ionic strength and Ca and $HCO_3^-$ activity for Denver water

Constituent	Conc. (mg/L)	Conc. (mol/L)
TDS	179	-
$Ca^{+2}$	42	$1.05 \times 10^{-3}$
$HCO_3^-$	115	$1.89 \times 10^{-3}$
pH = 7.9, Temp = 20°C		

Determine the ionic strength in solution based on TDS

Determine activity coefficients for  $HCO_3^-$  using Güntelberg method

Determine activity coefficients for  $Ca^{+2}$  using Güntelberg method

## CHEMICAL EQUILIBRIUM

- **Thermodynamics vs. Kinetics**

Thermodynamics tells us where the system should go at equilibrium, and kinetics tells us how fast.

- **Definition of Equilibrium**

- 1) A system at equilibrium has none of its properties changing with time, no matter how long it is observed
- 2) A system at equilibrium will return to that state after being disturbed
- 3) Thermodynamically speaking, a system is at equilibrium when  $\Delta_r G$  (the change in Gibbs Free Energy) = 0

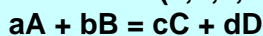
**Gibbs Free Energy** is a thermodynamic quantity which can be used to determine if a reaction is spontaneous or not.

Gibbs free energy is  $G = H(\text{enthalpy}) - T(\text{temp}) * S(\text{entropy})$

Enthalpy (useful work you can get from a closed system) InternalE+SurroundingP\*Volume  
Entropy (a quantitative measure of a system's disorder) when ice melts entropy increases

## CHEMICAL EQUILIBRIUM

A and B react to produce C and D (a,b,c,d are number of moles)



Reactants                      Products

The Gibbs free energy change of reaction is calculated:

$$\Delta_r G = \sum_{\text{products}} \Delta_f G - \sum_{\text{reactants}} \Delta_f G$$

Multiply Gibbs free energies of formation ( $\Delta_f G$ ) by stoichiometric coefficients and subtract sum of reactants from sum of products

$$\Delta_r G = c\Delta_f G_C + d\Delta_f G_D - a\Delta_f G_A - b\Delta_f G_B$$

- If  $\Delta_r G = 0$ , the reaction is at equilibrium
- if  $\Delta_r G < 0$ , the reaction will proceed to the right
- if  $\Delta_r G > 0$ , the reaction will proceed to the left

Gibb's free energies of formation are determined by experiment

For Some Gibb's Free Energy Values  
[http://inside.mines.edu/~epoeter/\\_GW19WaterChem3/GibbsFreeEnergyValues.xls](http://inside.mines.edu/~epoeter/_GW19WaterChem3/GibbsFreeEnergyValues.xls)

### K and Gibb's Free Energy are Related:

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$\Delta_r G = \sum_{\text{products}} \Delta_f G - \sum_{\text{reactants}} \Delta_f G$$

$$\log K = \frac{-\Delta_r G^\circ}{2.303 RT}$$

$G^\circ$  - Gibbs free energy change of reaction at standard state

$R$  - gas constant

energy per degree Kelvin per mole

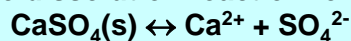
$T$  - Temperature Degrees Kelvin  $^\circ K = ^\circ C + 273.15$

2.303 converts ln to log

Values of R	Units (V·P·T <sup>-1</sup> ·n <sup>-1</sup> )
8.314472	J·K <sup>-1</sup> ·mol <sup>-1</sup>
0.0820574587	L·atm·K <sup>-1</sup> ·mol <sup>-1</sup>
83.14472	cm <sup>3</sup> ·bar·mol <sup>-1</sup> ·K <sup>-1</sup>
8.20574587 × 10 <sup>-5</sup>	m <sup>3</sup> ·atm·K <sup>-1</sup> ·mol <sup>-1</sup>
8.314472	cm <sup>3</sup> ·MPa·K <sup>-1</sup> ·mol <sup>-1</sup>
8.314472	L·kPa·K <sup>-1</sup> ·mol <sup>-1</sup>
8.314472	m <sup>3</sup> ·Pa·K <sup>-1</sup> ·mol <sup>-1</sup>
62.36367	L·mmHg·K <sup>-1</sup> ·mol <sup>-1</sup>
62.36367	L·Torr·K <sup>-1</sup> ·mol <sup>-1</sup>
83.14472	L·mbar·K <sup>-1</sup> ·mol <sup>-1</sup>
0.08314472	L·bar·K <sup>-1</sup> ·mol <sup>-1</sup>
1.987	cal·K <sup>-1</sup> ·mol <sup>-1</sup>
6.132440	lbf·ft·K <sup>-1</sup> ·g·mol <sup>-1</sup>
10.73159	ft <sup>3</sup> ·psi·°R <sup>-1</sup> ·lb·mol <sup>-1</sup>
0.7302413	ft <sup>3</sup> ·atm·°R <sup>-1</sup> ·lb·mol <sup>-1</sup>
998.9701	ft <sup>3</sup> ·mmHg·K <sup>-1</sup> ·lb·mol <sup>-1</sup>
8.314472 × 10 <sup>7</sup>	erg·K <sup>-1</sup> ·mol <sup>-1</sup>

### How much of a substance will dissolve in water? SOLUBILITY PRODUCT

Suppose we have the dissolution reaction for anhydrite:



in this case K equilibrium constant is a **solubility product ( $K_{\text{SP}}$ )**

$$K = K_{\text{sp}} = \frac{a_{\text{Ca}^{2+}} a_{\text{SO}_4^{2-}}}{a_{\text{CaSO}_4(\text{s})}} = a_{\text{Ca}^{2+}} a_{\text{SO}_4^{2-}}$$

*activity of most pure solids can be taken equal to unity (so  $a_{\text{CaSO}_4(\text{s})} = 1$ )*

Calculate  $K_{\text{SP}}$  by finding the Gibbs free energy change of reaction:

$$\Delta_r G^\circ = \Delta_f G^\circ_{\text{Ca}^{2+}} + \Delta_f G^\circ_{\text{SO}_4^{2-}} - \Delta_f G^\circ_{\text{CaSO}_4(\text{s})}$$

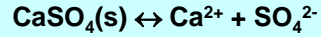
and calculating

$$\log K_{\text{SP}} = \frac{-\Delta_r G^\circ}{2.303RT}$$



## SOLUBILITY PRODUCT

Calculate the solubility product of anhydrite at 25°C



Look up:

[http://inside.mines.edu/~epoeter/\\_GW19WaterChem3/GibbsFreeEnergyValues.xls](http://inside.mines.edu/~epoeter/_GW19WaterChem3/GibbsFreeEnergyValues.xls)

$$\Delta_f G^\circ_{\text{Ca}^{2+}} = -553.6 \text{ kJ mol}^{-1}$$

$$\Delta_f G^\circ_{\text{SO}_4^{2-}} = -744.0 \text{ kJ mol}^{-1}$$

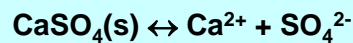
$$\Delta_f G^\circ_{\text{CaSO}_4(\text{s})} = -1321.8 \text{ kJ mol}^{-1}$$

$$R \text{ (gas constant)} = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

assume Kelvin for thermodynamic expressions, unless noted otherwise

## Will a substance dissolve or precipitate? ION ACTIVITY PRODUCT (IAP)

Consider again:



Equilibrium constant in terms of activities of reactants & products *at equilibrium*

$$K = \left( a_{\text{Ca}^{2+}} \right)_{\text{equil}} \left( a_{\text{SO}_4^{2-}} \right)_{\text{equil}}$$

However, a real solution may or may not be in equilibrium. The *ion activity product (IAP)* has the same form as the equilibrium constant, but involves the *actual(measured)* activities:

$$\text{IAP} = \left( a_{\text{Ca}^{2+}} \right)_{\text{actual}} \left( a_{\text{SO}_4^{2-}} \right)_{\text{actual}}$$

**if IAP = K, the solution is in equilibrium with anhydrite**

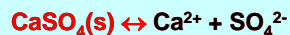
**if IAP < K, the reaction will proceed to the right (dissolution)**

**if IAP > K, the reaction will proceed to the left (precipitation)**

## Will a substance dissolve or precipitate? THE SATURATION INDEX

The saturation index (SI) is defined as:

$$SI = \log\left(\frac{IAP}{K_{SP}}\right)$$



$IAP = K_{SP}$   $SI = 0$  ( $-0.2 < SI < 0.2$ ) water is **saturated** with the mineral

$IAP < K_{SP}$   $SI < 0$  water is **undersaturated** with the mineral

Reaction is proceeding from left to right (**dissolution**)

$IAP > K_{SP}$   $SI > 0$  water is **supersaturated** with the mineral

Reaction is proceeding from right to left (**precipitation**)



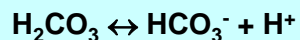
Suppose a groundwater analysis indicates

$5 \times 10^{-2}$  mol/L  $\text{Ca}^{2+}$  and  $7 \times 10^{-3}$  mol/L  $\text{SO}_4^{2-}$  (ignore activity coefficients)

Is this water saturated with respect to anhydrite?



Consider the acid-base reaction



$$K = 10^{-6.35}$$

Which way should the reaction go if

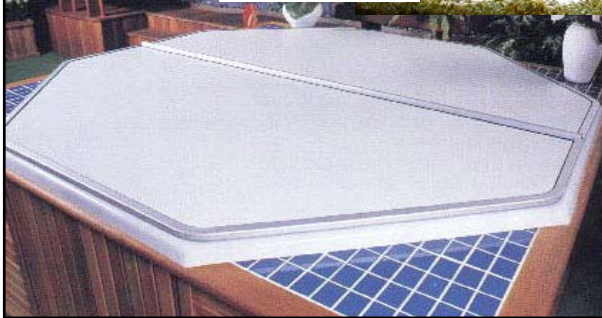
$$\text{pH} = 7 \quad a_{\text{H}_2\text{CO}_3} = 10^{-4} \quad a_{\text{HCO}_3^-} = 10^{-3}?$$



Whether your concern is domestic water, spa water, or a fish tank, you will want to know about carbonate equilibrium.



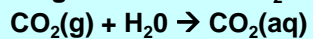
Picture by Anthony Miralles



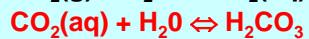
## CARBONATE EQUILIBRIUM

Most important acid-base system in water, controls the pH of most waters

Water exposed to the atmosphere dissolves carbon dioxide  $\text{CO}_2(\text{g})$  creating carbonic acid  $\text{H}_2\text{CO}_3$



Gas dissolution



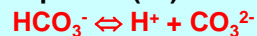
Carbonic acid formation

Carbonic acid dissociates in two steps

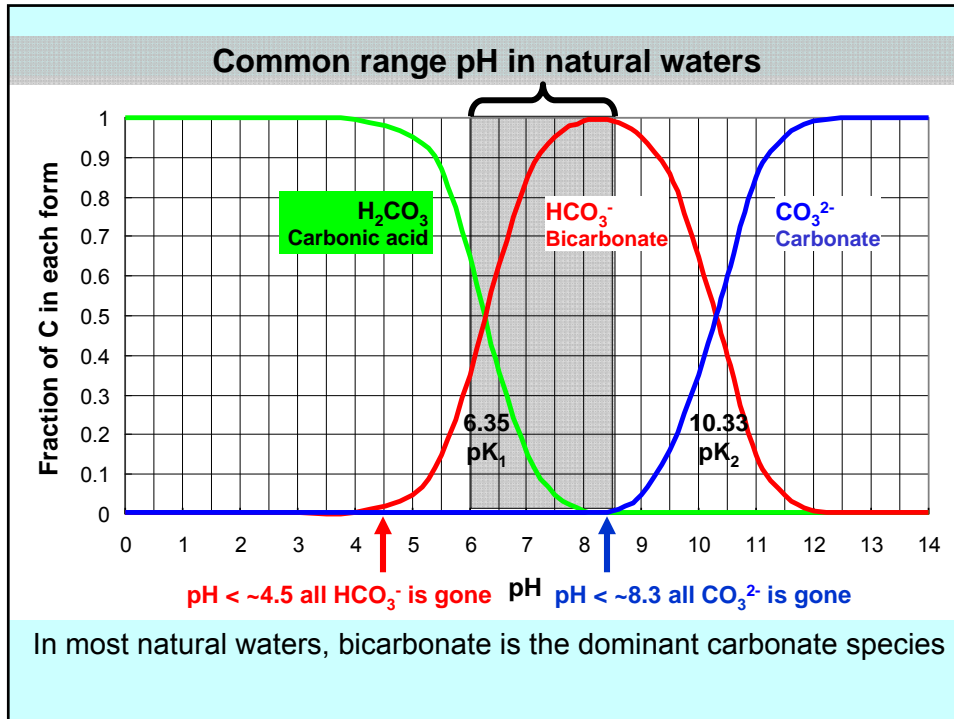
1) Carbonic acid donates one proton ( $\text{H}^+$ ) to create bicarbonate  $\text{HCO}_3^-$



2) Bicarbonate donates a proton ( $\text{H}^+$ ) to form carbonate  $\text{CO}_3^{2-}$



Reaction	Equilibrium constant (25°C)
$\text{CO}_2(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$	$\text{pK}_\text{H} = 1.46$
$\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$	$\text{pK}_1 = 6.35$
$\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$	$\text{pK}_2 = 10.33$



## CARBONATE SYSTEM

In aqueous solutions, positive & negative charges must balance

At  $\text{pH}=7$ ,  $[\text{H}^+] = [\text{OH}^-]$

At  $\text{pH}>7$ ,  $[\text{H}^+] < [\text{OH}^-]$

For a pure  $\text{CO}_2 - \text{H}_2\text{O}$  system,

possible species are  $\text{H}^+$   $\text{OH}^-$   $\text{H}_2\text{CO}_3$   $\text{HCO}_3^-$   $\text{CO}_3^{2-}$

the charge-balance equation is:

$$[\text{H}^+] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-]$$

*Each mole of  $\text{CO}_3^{2-}$  provides two equivalents of negative charge in solution, so carbonate concentration must be multiplied by 2*

## CARBONATE SYSTEM

If we increase partial pressure of CO<sub>2</sub>  $[H^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-]$

pH decreases (due to increased H<sup>+</sup> activity in solution)

What is **partial pressure**?

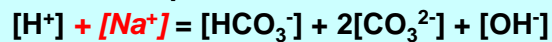
Air is a mixture of gases

Each gas exerts a pressure depending on its proportion

This is the partial pressure of that gas

Air pressure is the sum of all these partial pressures

If we add sodium to the system,  
the charge-balance equation is:



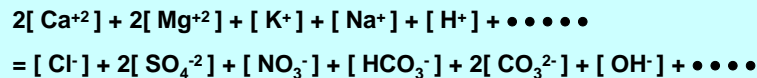
Then, if we add a strong acid. What would change?

The concentration of H<sup>+</sup>, OH<sup>-</sup>, and all the carbonate species would change, but the concentration of Na<sup>+</sup> would not change.

Thus, Na<sup>+</sup> is a **conservative** ion, and HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, H<sup>+</sup> and OH<sup>-</sup> are **non-conservative** and this concept is the basis for the definition of alkalinity

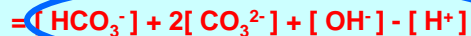
## ALKALINITY

For all dissolved species, the charge balance equation can be extended:



Put conservative ions on left & non-conservative ions on right

In equivalents:  $\Sigma$  conservative cations -  $\Sigma$  conservative anions



If the left-hand side of the equation is conservative then the right-hand side of the equation must also be conservative

Although none of the individual species on the right is conservative, their mathematical combination as shown is conservative

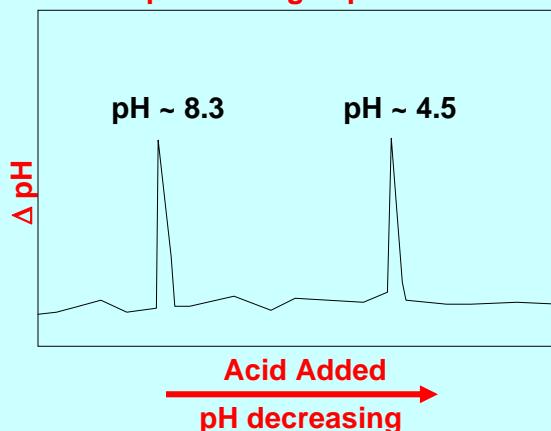
Therefore, the quantity on the right-hand side of the equation is a special combination, and we call this quantity the **total alkalinity**

## Titration for Carbonate System Compents

Add strong acid  
e.g. 0.0200N  $\text{H}_2\text{SO}_4$



For a sample starting at pH ~9.9



Determine the volume of acid solution required to reach the 8.3 and 4.5 endpoints

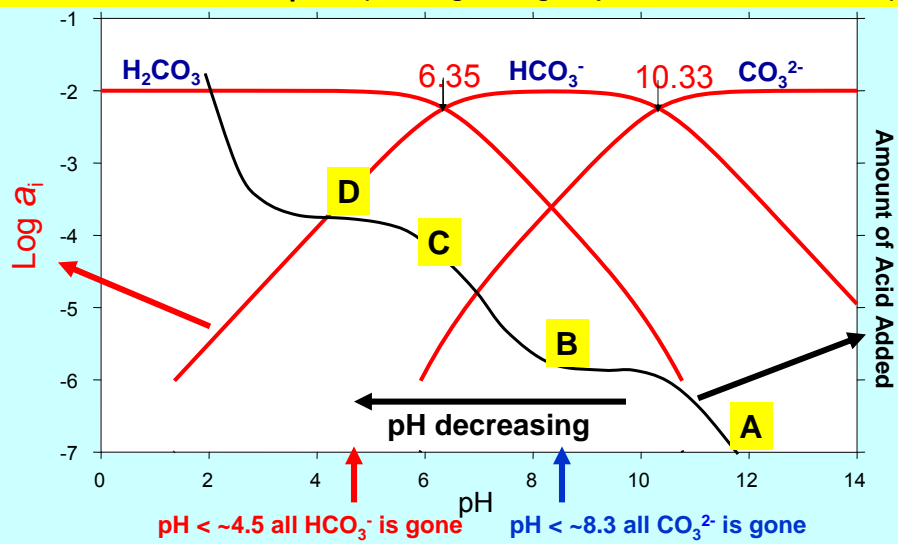
Titration curve for a  $\text{Na}_2\text{CO}_3$  solution, with a Bjerrum plot

A is the beginning of the titration

B is the carbonate endpoint (note large change in pH for little addition of acid)

C is the region of strong carbonate buffering

D is the bicarbonate endpoint (note large change in pH for little addition of acid)



## ALKALINITY

Alkalinity is normally reported by the laboratory  
in **units of mg/L as CaCO<sub>3</sub> (calcium carbonate)**

**Alkalinity (eq/L) = Alkalinity (mg/L as CaCO<sub>3</sub>) x 2 eq/mole**

*This does not mean that CaCO<sub>3</sub> is necessarily present in the solution. What it means is that the solution has numerically the same alkalinity as a solution in which the same weight of CaCO<sub>3</sub> per liter has been dissolved.*

Calculation of alkalinity from a titration to a pH of 4.5:

$$\text{Alk}_T = \frac{\text{mL}_{\text{acid}} \times N_{\text{acid}} \times \text{eq. wt. CaCO}_3}{\text{mL}_{\text{sample}}}$$

The **equivalent weight of CaCO<sub>3</sub>**:

$$\text{molar mass of CaCO}_3 \frac{100\text{g}}{\text{mole}} \times \frac{1\text{mole}}{2\text{eq}} = 50 \frac{\text{g}}{\text{eq}}$$

*recall that an equivalent is essentially a mole of charge*

*\* CaCO<sub>3</sub> does not carry a charge, but we calculate equivalent weight of a salt as its molecular weight divided by the valence of the metal ion in the compound*



## ALKALINITY

**A 100 mL sample with a pH of 8 is titrated to the methyl-orange-end-point (which goes from yellow at pH 4.4 to red at pH 3.1) with 2 mL of 0.5 N H<sub>2</sub>SO<sub>4</sub>**

**What is the total alkalinity in mg L<sup>-1</sup> as CaCO<sub>3</sub> and what is the concentration of HCO<sub>3</sub><sup>-</sup> in mg L<sup>-1</sup>?**