

## Gases in Water

Environmental Chemistry, vanLoon & Duffy – Chapter 11

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August 1, 2011

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Henry's Law constant  
(pure water, 25°C,  
vanLoon & Duffy, p. 237)

Gas	$K_H$ $\text{mol L}^{-1} \text{Pa}^{-1}$
$\text{O}_2$	$1.3 \times 10^{-8}$
$\text{N}_2$	$6.4 \times 10^{-9}$
$\text{CH}_4$	$1.3 \times 10^{-8}$
$\text{CO}_2$	$3.3 \times 10^{-7}$
$\text{SO}_2$	$1.2 \times 10^{-5}$
$\text{NH}_3$	$5.7 \times 10^{-4}$
Hg	$8.6 \times 10^{-7}$
$\text{CCl}_4$	$3.7 \times 10^{-7}$
$\text{CH}_3\text{COCH}_3$	$3.9 \times 10^{-3}$

According to *Henry's Law* gases are soluble in liquids to a certain degree. The solubility is proportional to the partial pressure of the particular gas

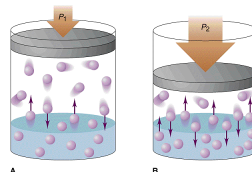
$$C = K_H P$$

Limitation: The **gas must not react** with the solvent

Example  $\text{O}_2$ :

$$C_{\text{O}_2} = 1.3 \times 10^{-8} * 0.21 * 101325 \text{ mol L}^{-1}$$

$$C_{\text{O}_2} = 2.766 \times 10^{-4} \text{ mol L}^{-1} = 8.85 \text{ mg L}^{-1}$$





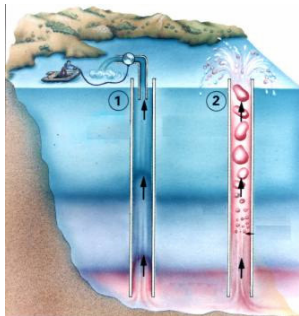
**The disaster of Lake Nyos - Cameroon**

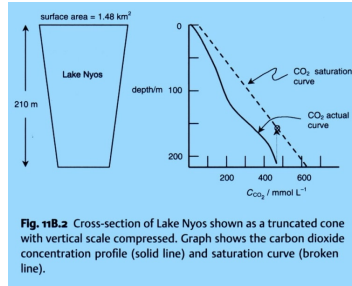
An eruption of toxic gases killed about 1700 people on Aug. 21<sup>st</sup>, 1986.

An investigation of this disaster showed that the lake is supplied with a steady flux of CO<sub>2</sub> at the bottom in a depth of about 200m.

Normally the sea is stratified with a thermocline that separates surface water and the water in the depth.

Once the water at the bottom of the sea was saturated with CO<sub>2</sub> it needed the smallest disturbance to release the disaster.



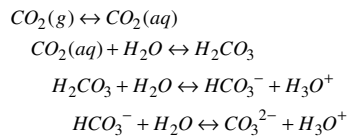


**The disaster of Lake Nyos - Cameroon**

CO<sub>2</sub> is toxic for man and animals  
 CO<sub>2</sub> solubility increases with pressure  
 CO<sub>2</sub> reacts with water  
 CO<sub>2</sub> enters the stratified body of the sea from the bottom due to volcanic activity CO<sub>2</sub> as a gas has a much lower density than water.

Once the water at the bottom of the sea was saturated with CO<sub>2</sub> it needed the smallest disturbance to release the disaster.

Henry's Law constant (pure water, 25 °C, vanLoon & Duffy, p. 225)	
Gas	K <sub>H</sub> mol L <sup>-1</sup> Pa <sup>-1</sup>
CO <sub>2</sub>	3.3 × 10 <sup>-7</sup>



**Divers fear the so called divers sickness**

When diving with scuba equipment "self-contained underwater breathing apparatus" the diver respire from a gas-phase which has the same pressure as the surroundings. An accumulation of N<sub>2</sub>-gas in the blood causes this accident when the diver rises too fast.

Apply Henry's law to calculate the solubility of N<sub>2</sub>-gas in the blood at sea-level and at a depth of 40m.

Henry's Law constant (pure water, 25 °C, vanLoon & Duffy, p. 237)	
Gas	K <sub>H</sub> mol L <sup>-1</sup> Pa <sup>-1</sup>
N <sub>2</sub>	6.4 × 10 <sup>-9</sup>



Henry's Law constant  
(pure water, 25 °C,  
vanLoon & Duffy, p. 237)

Gas	$K_H$ $\text{mol L}^{-1} \text{Pa}^{-1}$
$\text{N}_2$	$6.4 \times 10^{-9}$



Divers sickness - the answer:

$$\begin{aligned}
 P(\text{sea-level}) &= 101325 \text{ Pa} \\
 P_{\text{N}_2}(\text{sea-level}) &= 0.78 \times 101325 \text{ Pa} \\
 &= 79034 \text{ Pa} \\
 [\text{N}_2] &= 6.4 \times 10^{-9} \times 79034 \\
 &= 5.058 \times 10^{-4} \text{ mol L}^{-1} \\
 &= 12.9 \text{ mL L}^{-1} (37^\circ\text{C}, 0\text{m})
 \end{aligned}$$

$$\begin{aligned}
 P(-40 \text{ m}) &\cong 101325 + 406130 \text{ Pa} \\
 P_{\text{N}_2}(-40 \text{ m}) &= 0.78 \times 507455 \text{ Pa} \\
 [\text{N}_2] &= 6.4 \times 10^{-9} \times 395815 \\
 &= 2.533 \times 10^{-3} \text{ mol L}^{-1} \\
 &= 64.5 \text{ mL L}^{-1} (37^\circ\text{C}, 0\text{m})
 \end{aligned}$$

The sudden release of about 50 mL gas per L of blood and cell fluid may kill the diver instantly.

The mass of acetate ( $m_{\text{Ac}}$ ) put into solution must still be present even though it is now present as HAc and  $\text{Ac}^-$ .

The mass balance equation could be written:

$$m_{\text{Ac}} = m_{\text{HAc}} + m_{\text{Ac}^-}$$

As the volume of water (V) is fixed - divide by V to convert the equation to its concentration form:

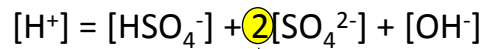
$$C_{\text{Ac}} = [\text{CH}_3\text{COOH}] + [\text{CH}_3\text{COO}^-]$$

$C_{\text{Ac}}$  represents the "analytical" concentration, i.e. the concentration of the material made up in the laboratory

The total number of positive charges must equal the number of negative charges.

This leads us to the charge balance equation:

For sulfuric acid in solution:

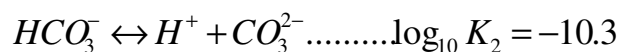
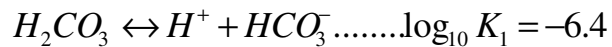
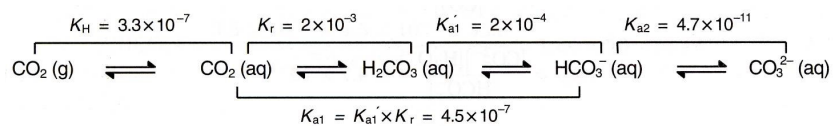


NB 2- ion

Carbonic acid - crucial element in controlling the pH of natural waters and for plant photosynthesis. Dissolution product of limestone and chalk, sink for atmospheric CO<sub>2</sub> (greenhouse gas) etc. ...

H<sub>2</sub>CO<sub>3</sub> is a diprotic acid

The dissociation constants for this acid are:



$$K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = 10^{-6.4} \Rightarrow$$

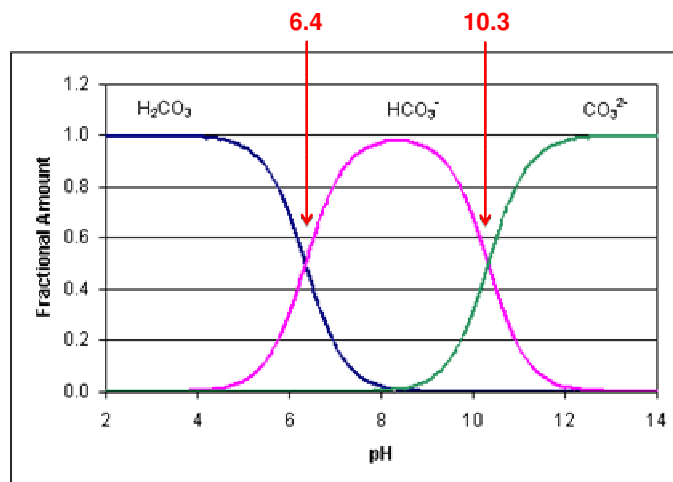
$$K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = 10^{-6.4} \Rightarrow$$

$$\log_{10} K_1 = \log_{10} \frac{[HCO_3^-]}{[H_2CO_3]} + \log_{10} [H^+]$$

$$pK_1 = -\log_{10} \frac{[HCO_3^-]}{[H_2CO_3]} + pH \Rightarrow$$

This is a variant of the Henderson- Hasselbach equation:

$$pH = pK_1 - \log_{10} \frac{[H_2CO_3]}{[HCO_3^-]}$$



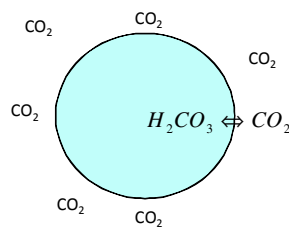
The common belief that the pH of rain should be 7.0 is erroneous as precipitation has to travel through an atmosphere containing  $\text{CO}_2$ , an acid gas.

Unpolluted rain is actually acidic and discussions of acid rain must bear this in mind.

To predict the how acidic rain should be we need to cover 2 stages:

1. Estimate how much  $\text{CO}_2$  dissolves in the rain to give a solution of  $\text{H}_2\text{CO}_3$
2. Explore the dissociation of the  $\text{H}_2\text{CO}_3$  to release  $\text{H}_3\text{O}^+$

Rain droplets as they fall through the atmosphere:



The concentration of dissolved  $\text{CO}_2$  within the droplet reaches an equilibrium with the concentration of  $\text{CO}_2$  in the atmosphere (its partial pressure  $P_{\text{CO}_2}$ ).

Numerically this is described by Henry's Law:

$$[\text{CO}_2] = K_H P_{\text{CO}_2}$$

Henry's law constants at 25°C

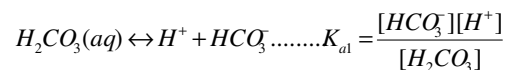
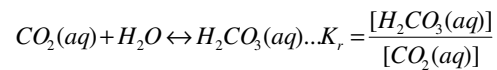
	(mol.dm <sup>-3</sup> .atm <sup>-1</sup> )
O <sub>2</sub>	1.28 x 10 <sup>-3</sup>
CO <sub>2</sub>	3.38 x 10 <sup>-2</sup>
CH <sub>4</sub>	1.34 x 10 <sup>-3</sup>
N <sub>2</sub>	6.48 x 10 <sup>-4</sup>

$$P_{\text{CO}_2} = 3.6 \times 10^{-4} \text{ atm and } K_{\text{H}} = 0.034 \text{ (mol.L}^{-1}\text{.atm}^{-1}\text{)}$$

What is the equilibrium concentration of CO<sub>2</sub> in water at 25°C?

From Henry's Law:

$$[\text{CO}_{2\text{aq}}] = K_{\text{H}} \cdot P_{\text{CO}_2} = 0.034 \times 3.6 \times 10^{-4} = 1.224 \times 10^{-5} \text{ mol.dm}^{-3}$$



For every H<sup>+</sup> produced one HCO<sub>3</sub><sup>-</sup> is generated, therefore:

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

via the charge balance equation:

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

For an acidic solution [OH<sup>-</sup>] will be negligible:

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

$$K_{a1} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = \frac{[\text{H}^+]^2}{[\text{H}_2\text{CO}_3]} \Rightarrow$$

$$[\text{H}^+] = \sqrt{K_{a1}[\text{H}_2\text{CO}_3]}$$



We have already calculated  
 $[CO_2(aq)] = 1.224 \times 10^{-5} \text{ mol. L}^{-1}$

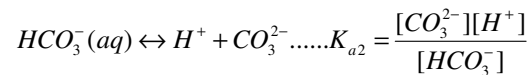
$$K_r \times K_{a1} = 4.5 \times 10^{-7}$$

$$[H^+] = \sqrt{K_{a1} \times K_r \times [CO_2(aq)]}$$

$$[H^+] = \sqrt{(4.5 \times 10^{-7})(1.224 \times 10^{-5})}$$

$$\text{pH} = 5.6$$

Rather more acidic than the expected value of pH of 7



$$[CO_3^{2-}] = K_{a2} \frac{[HCO_3^-]}{[H^+]}$$

$$K_{a1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = \frac{[H^+]^2[HCO_3^-]}{[H^+][H_2CO_3]}$$

$$\Rightarrow \frac{[HCO_3^-]}{[H^+]} = K_{a1} \frac{[H_2CO_3]}{[H^+]^2} \Rightarrow$$

$$\therefore [CO_3^{2-}] = K_{a2} K_{a1} \frac{[H_2CO_3]}{[H^+]^2}$$

$$= K_{a2} K_{a1} K_r \frac{[CO_2(aq)]}{[H^+]^2} = 5.0 \times 10^{-11} M$$

**Identify the relationships:**

1. Atmospheric CO<sub>2</sub> dissolves in the water:

$$K_H = \frac{[CO_2]}{p_{CO_2}} = 3.3 \times 10^{-7} \dots\dots(1) \{ p_{CO_2} = 35.8 Pa \}$$

2. we have CaCO<sub>3</sub> dissolving (solubility product):

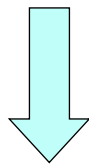
$$K_{sp} = [Ca^{2+}][CO_3^{2-}] = 5 \times 10^{-9} \dots\dots(2)$$

3. The carbonate and dissolved CO<sub>2</sub> all end up as H<sub>2</sub>CO<sub>3</sub>, HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>, linked by the acid dissociation constants K<sub>a1</sub> and K<sub>a2</sub>:

$$K_{a1} = \frac{[HCO_3^-][H_3O^+]}{[H_2CO_3]} = 4.5 \times 10^{-7} \dots\dots(3)$$

$$K_{a2} = \frac{[CO_3^{2-}][H_3O^+]}{[HCO_3^-]} = 4.7 \times 10^{-11} \dots\dots(4)$$

The Charge Balance:  $2[Ca^{2+}] + [H_3O^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-]$



Simplify as between pH 6 and 9:

- [H<sub>3</sub>O<sup>+</sup>] << [Ca<sup>2+</sup>]
- [CO<sub>3</sub><sup>2-</sup>] and [OH<sup>-</sup>] << [HCO<sub>3</sub><sup>-</sup>]

$$2[Ca^{2+}] = [HCO_3^-] \dots\dots(5)$$

Combining equations 1 to 5 gives:  $[H_3O^+] = \sqrt[3]{\frac{K_H^2 K_{a1}^2 K_{a2} p_{CO_2}^2}{2K_{sp}}} = 5.1 \times 10^{-9} \text{ mol.L}^{-1}$   
pH = 8.3

Remember the calculated pH of rainwater? **pH = 5.6**

We have now shown how dissolving some calcium carbonate significantly shifts the pH to alkaline values giving a good estimate of the pH of seawater or lakes in chalky areas.

$$\therefore [CO_3^{2-}] = K_{a2}K_{a1} \frac{[H_2CO_3]}{[H^+]^2}$$

$$= K_{a2}K_{a1}K_rK_H \frac{P_{CO_2}}{[H^+]^2}$$

$$[Ca^{+2}] = \frac{K_{sp}}{[CO_3^{2-}]} = \frac{K_{sp}[H^+]^2}{K_{a2}K_{a1}K_rK_H P_{CO_2}}$$

$$[HCO_3^-] = 2[Ca^{+2}] = \frac{2K_{sp}[H^+]^2}{K_{a2}K_{a1}K_rK_H P_{CO_2}}$$

**Alkalinity** - a measure of the ability of a water body to neutralize acids:

$$alkalinity = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] - [H_3O^+]$$

Proton acceptors

Proton donor

Alkalinity is easily measured by titration of the water with acid.

Predicting the effects of lake acidification.

[strictly the Acid Neutralizing Capacity of a water should be used that includes borate, silicate, phosphate etc species. For most natural waters however the acid neutralizing capacity equals the alkalinity].

Typical alkalinities range from 50 to >2000 μmol L<sup>-1</sup>

$$ANC = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] +$$

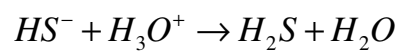
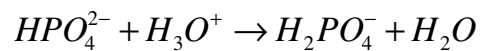
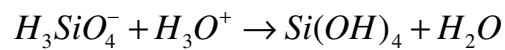
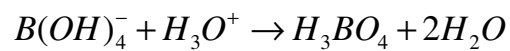
$$[H_3SiO_4^-] + [HPO_4^{2-}] + [HS^-] + [NOM^-] + \dots$$

$$-[H_3O^+] - 3[Al^{3+}] - \dots$$

Proton donating species

Natural Organic Matter (NOM)

Taken as 10 mmol/g



A lake containing 10 micrograms/mL NOM and no other proton donors or acceptors would have an ANC of:

$$10 \text{ micrograms/mL} \times 10 \text{ mmol/g} = 100 \text{ micromol/L}$$

A water of pH= 9, but no carbonate species present would have the following ANC:

$$[H_3O^+] = 10^{-9}$$

$$[OH^-] = 10^{-5}$$

$$[CO_3^{2-}] = [HCO_3^-] = 0$$

$$ANC = 10^{-5} - 10^{-9} = 10^{-5} \text{ mol/L} = 10 \mu\text{mol/L}$$

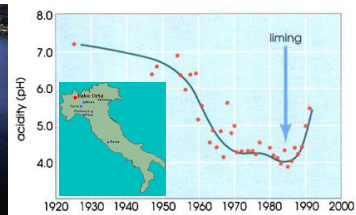
A water of pH= 8.3 and contains 0.01 mol/L of sodium bicarbonate would have the following ANC:

$$[H_3O^+] = 10^{-8.3}; [OH^-] = 10^{-5.7}; [HCO_3^-] = 0.01$$

$$[CO_3^{2-}] = \frac{K_{a2}[HCO_3^-]}{[H_3O^+]} = \frac{4.7 \times 10^{-11} \times 0.01}{10^{-8.3}} = 9.4 \times 10^{-5}$$

$$ANC = 10^{-5.7} + 0.01 + 2 \times 9.4 \times 10^{-5} - 10^{-8.3} \\ = 0.01 \text{ mol/L} = 10000 \mu\text{mol/L}$$

Acid contamination in a lake with poor buffering capacity (drains watershed with gneiss, mica schists, granitic geologies).



Pollution started at the end of 1926 with construction of rayon (artificial silk) factory using the cupro-ammoniacal method taking water from lake and returning it adulterated with ammonium sulphate and copper.

- During the first few years biota suffered from algicidal effects of copper.
- Subsequently pH dropped due to oxidation of ammonia to nitrate.

Original rayon factory reduced copper inputs in 1958 and 1980 but additional heavy metals (Cu, Zn, Cr, Ni) have been introduced since the mid-70's from small bathroom-accessory factories sited on a small tributary river.

Pollution still prevents effective use of an activated sludge plant intended to treat domestic sewage.

Large scale liming was started in 1982.

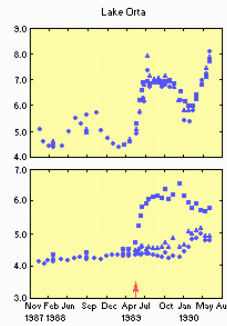


Fig. EUR-46-10 Epilimnetic (upper) and hypolimnetic (lower) mean pH at the three sampling stations (A, B, C) after the liming operation (7).