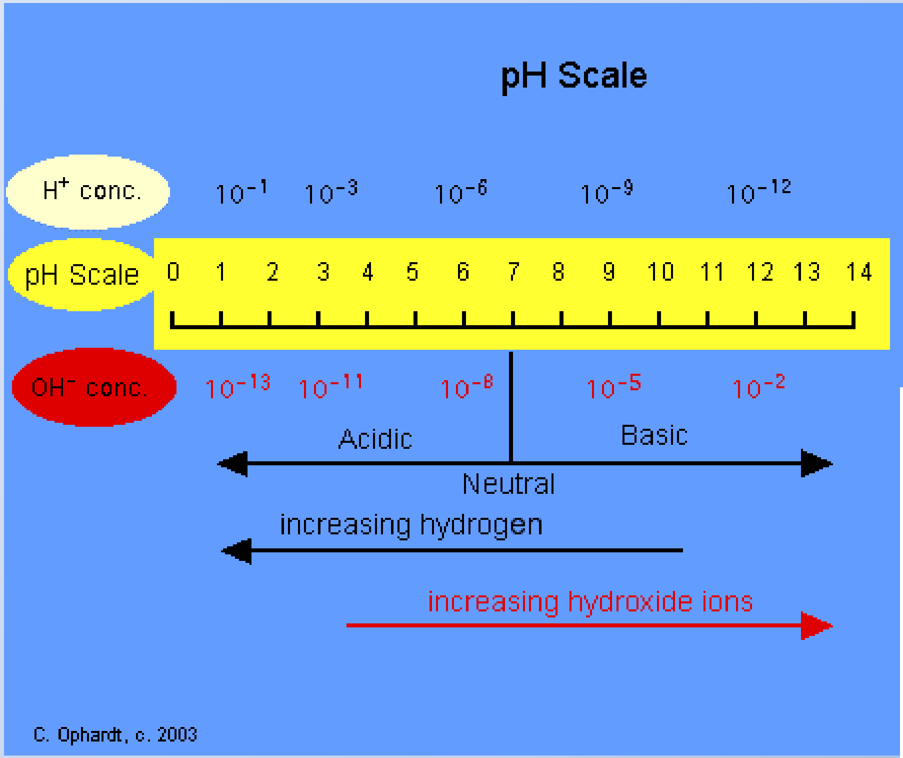
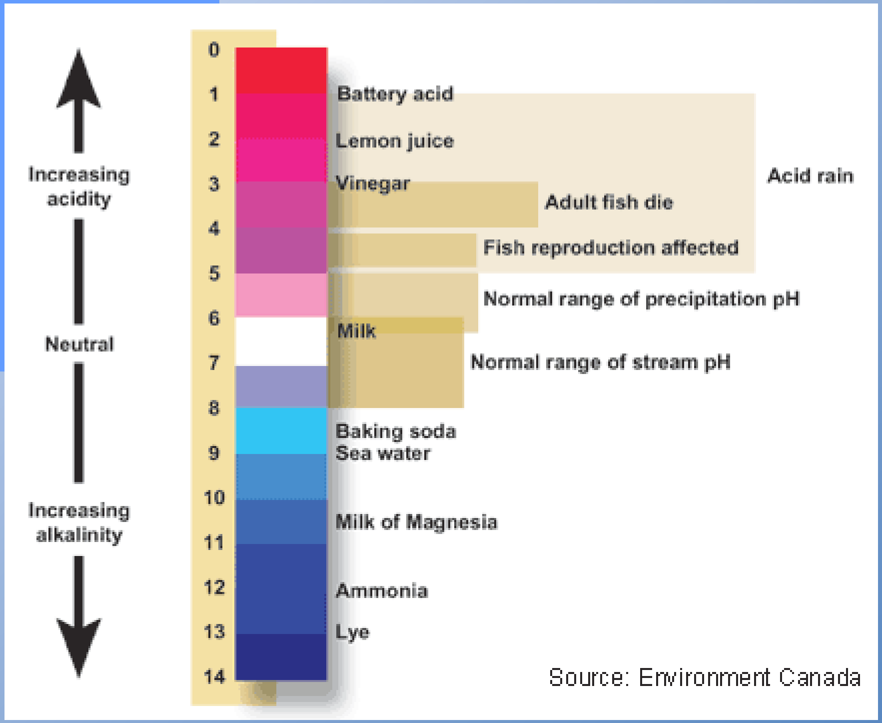
pH and Acid-Base reactions



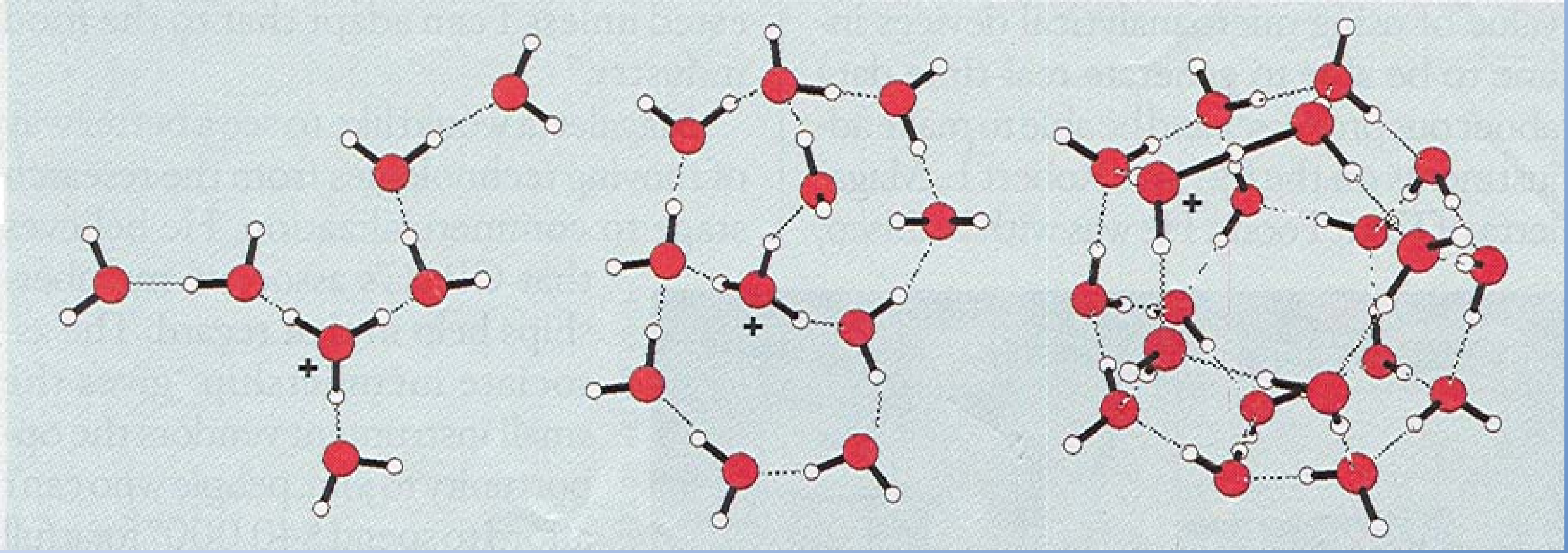


Source: Environment Canada

http://eps.mcgill.ca/~courses/c220/

Interaction of water with H^+ (H_3O^+)

Although it is a minor component of most aqueous solutions, the proton, hydrogen ion or H^+ concentration reflects the balance of acid-base reactions in solution and, consequently, can be used as a master variable to characterize the speciation of protolytic compounds in the solution.



Acid-Base Reactions

At low pH, the following reaction is sufficient to describe the solubility of quartz:

$$SiO_2\ (qz) + 2\ H_2O \leftarrow\rightarrow H_4SiO_4\ (aq)$$

The equilibrium constant for this reaction can be written as:

$$K^o_{eq}(qz) = a(H_4SiO_4)/a(SiO_{2(qz)})\ a^2(H_2O)$$

but at higher pH, the solubility of quartz and amorphous silica are slightly more complicated. Like H_2CO_3, H_4SiO_4 is a weak acid and dissociates at higher pH.

$$H_4SiO_4 \leftarrow \rightarrow H_3SiO_4^- + H^+$$

Arrhenius' definition of acid and base

An acid is any substance that contains an H and releases a proton to the solution:

$$HCl + H_2O \leftrightarrow H_3O^+ + Cl^-$$

and a base is defined as any substance that contains an OH group and releases OH^- to the solution:

$$NaOH \leftrightarrow Na^+ + OH^-$$

but many substances that do not contain an H (e.g., SiO_2, CO_2, SO_2) behave as acids and some substances that do not contain an OH group (e.g., NH_3) behave as bases.

Svante August Arrhenius (1859-1927), Swedish physicist

Bronstead-Lowry definition of acid and base

An acid is simply defined as any substance that can donate a proton to any other substance, such as:

$$HCl + H_2O \leftrightarrow H_3O^+ + Cl^-$$

and a base is defined as any substance that accepts a proton from another substance, such as:

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$$

<u>An acid is a proton donor and a base is a proton acceptor.</u>
<u>An acid-base reaction is a proton exchange reaction.</u>

According to this definition, water is both an acid and a base.

$$H_2O + H_2O \leftrightarrow H_3O^+ + OH^-$$

The H_3O^+- H_2O and H_2O- OH^- pairs are called conjugate acid-base pairs. Similarly, in:

$$NH_3 + H_2S \leftrightarrow NH_4^+ + SH^-$$

NH_4^+-NH_3 and H_2S-HS^- are conjugate acid-base pairs.

Bronstead-Lowry definition of acid and base

Many acids can donate more than one proton, such as H_2SO_4, H_2CO_3, H_3PO_4, and H_4SiO_4. These acids are referred to as **polyprotic acids**. Similarly, some bases can accept more than one proton, such as S^{2-}, OH^-, CO_3^{2-}. These are **polyprotic bases**.

Hydrated metals can also serve as polyprotic acids:
(The acidity of the H_2O molecules in the hydration shell of a metal ion is much greater than that of water because of the repulsion of protons of the water molecules by the positive charge of the central metal ion.)

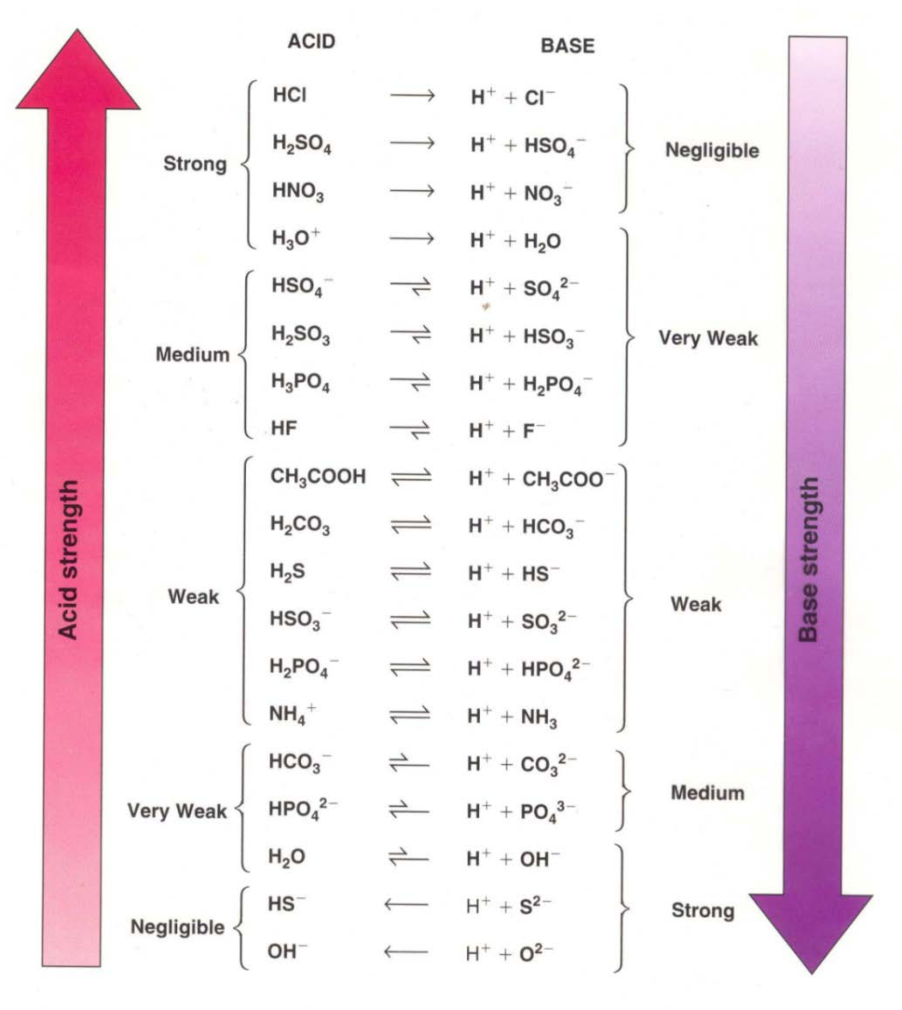
ex: $[Al(H_2O)_6]^{3+} \leftarrow\rightarrow [Al(H_2O)_5OH]^{2+} + H^+$

A more general definition (Lewis Concept) of acids and bases is interpreted in terms of the formation of a coordinate covalent bond. A Lewis acid can accept or share a lone pair of electrons donated by a Lewis base. Because protons readily attach themselves to lone electron pairs, Lewis bases are also Bronstead bases (ex: H_2O). Lewis acids, however, include a large number of substances in addition to proton donors: for example, metal ions, acidic oxides, or even atoms.

$$Fe^{3+} + 3H_2O \leftarrow\rightarrow Fe(OH)_3^{\circ} + 3H^+$$

Acids and their conjugate bases

The strength of an acid or base is measured by its tendency to donate or accept a proton. The relative strengths of acids are measured with respect to a standard base, usually the solvent, water in the case of aqueous solutions.



	ACID		BASE	
Strong	HCl	$\longrightarrow$	$H^+ + Cl^-$	Negligible
	H_2SO_4	$\longrightarrow$	$H^+ + HSO_4^-$	
	HNO_3	$\longrightarrow$	$H^+ + NO_3^-$	
	H_3O^+	$\longrightarrow$	$H^+ + H_2O$	Very Weak
Medium	HSO_4^-	$\rightleftharpoons$	$H^+ + SO_4^{2-}$	
	H_2SO_3	$\rightleftharpoons$	$H^+ + HSO_3^-$	
	H_3PO_4	$\rightleftharpoons$	$H^+ + H_2PO_4^-$	
	HF	$\rightleftharpoons$	$H^+ + F^-$	
Weak	CH_3COOH	$\rightleftharpoons$	$H^+ + CH_3COO^-$	Weak
	H_2CO_3	$\rightleftharpoons$	$H^+ + HCO_3^-$	
	H_2S	$\rightleftharpoons$	$H^+ + HS^-$	
	HSO_3^-	$\rightleftharpoons$	$H^+ + SO_3^{2-}$	
	$H_2PO_4^-$	$\rightleftharpoons$	$H^+ + HPO_4^{2-}$	
	NH_4^+	$\rightleftharpoons$	$H^+ + NH_3$	
Very Weak	HCO_3^-	$\rightleftharpoons$	$H^+ + CO_3^{2-}$	Medium
	HPO_4^{2-}	$\rightleftharpoons$	$H^+ + PO_4^{3-}$	
	H_2O	$\rightleftharpoons$	$H^+ + OH^-$	Strong
Negligible	HS^-	$\longleftarrow$	$H^+ + S^{2-}$	
	OH^-	$\longleftarrow$	$H^+ + O^{2-}$	

pH and the self-dissociation of water

The pH is the negative logarithm of the (H^+) or (H_3O^+).

$$pH = - \log (H^+) = - \log (H_3O^+)$$

A 5.4 x 10^{-4} M H_3O^+ solution has a pH of 3.27 (significant figures!).

Note that this nomenclature is also applied to express the K^o_a or K^o_b.
In which case $pK^o_a = -\log K^o_a$ and $pK^o_b = -\log K^o_b$.

The pH of pure water is equal to 7 and is determined by the self-ionization or auto-ionization of the water molecule described by the following reaction:

$$H_2O(l) + H_2O(l) \leftarrow \rightarrow H_3O^+ + OH^-$$

$$K^o_{eq} = K^o_W = (H_3O^+)\,(OH^-)/(H_2O)(H_2O) = (H_3O^+)(OH^-)$$
$$= 1.008 \times 10^{-14} \text{ at } 25^oC \quad \text{or} \quad pK_W = 14$$

Since the dissociation of pure water will yield one H_3O^+ and one OH^-, (H_3O^+) = (OH^-) and therefore:

$$(H_3O^+) = (OH^-) = \sqrt{K^o_W} \quad \text{or} \quad pH = pOH = 7$$

Because K^o_W changes with temperature (and pressure), the pH of neutrality also changes with temperature.

Strong acids

Acids are generally classified as either strong or weak, on the basis of their reaction with a standard base (water) or the extent of their dissociation into ions in water. Strong acids are completely dissociated in water. For example,

$$HCl_{(aq)} + H_2O \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$$

Virtually none of the $HCl_{(aq)}$ remains after it is dissolved in water, so that $[H_3O^+] \sim [Cl^-]$ or $[HCl_{(aq)}] \sim 0$. Hence, the equilibrium constant for the reaction is extremely large:

$$K^o_{eq} = \frac{(H_3O^+)\ (Cl^-)}{(HCl)\ (H_2O)} \quad >> 1$$

Consequently, it is not very practical to express the strength of a strong acid (e.g., HCl, HNO_3, H_2SO_4, $HClO_4$) in this manner nor the reaction as an equilibrium process since the reaction is essentially complete. Hence, **the strongest acid possible in water is H_3O^+**. In order to rank the strong acids in terms of relative strength, they must be dissolved in a solvent that is a weaker base than water (e.g., acetic acid).

Weak acids

In contrast, weak acids are only partly dissociated or mostly undissociated in water. For example,

$$H_4SiO_4 + H_2O \leftarrow \rightarrow H_3SiO_4^- + H_3O^+$$

For which the equilibrium constant is equal to:

$$K^o_{eq} = K^o_a = (H_3O^+)(H_3SiO_4^-)/(H_2O)(H_4SiO_4) = 10^{-9.46}$$

Like any equilibrium constant, K^o_a varies with T and P and reflects how far the reaction will proceed to the right. Hence, for any weak acid, the higher the K_a, the larger is $[H_3O^+]$ at equilibrium, and the stronger the acid. The larger the K_a, the more dissociated will the acid be.

For the general reaction: $HA + H_2O \leftarrow \rightarrow A^- + H_3O^+$

$$K_{HA} = ([H^+]\ [A^-])/[HA]$$
$$\log K_{HA} = \log [H^+] + \log ([A^-]/[HA])$$
$$-pK_{HA} = -pH + \log ([A^-]/[HA])$$
$$pH = pK_{HA} + + \log ([A^-]/[HA])$$

Strong and weak bases

Similarly, the strength of a base is determined by the amount of OH^- produced per mole of base dissolved. Like strong acids, the reaction describing the dissociation of a strong base is essentially complete. For example,

$$NaOH \rightarrow Na^+ + OH^-$$

$$K^o_{eq} = K^o_b = (Na^+)(OH^-)/(NaOH) >> 1$$

The value of the equilibrium constant describing this reaction is extremely large because $[NaOH^o] \sim 0$ and $[OH^-] \sim [Na^+]$. Hence, **the strongest base in water is OH^-**. The dissolution of weak bases, on the other hand, does not proceed to completion and can be appropriately described by an equilibrium constant. For example, consider the dissolution of ammonia in water:

$$NH_3 + H_2O \leftarrow \rightarrow OH^- + NH_4^+$$

The equilibrium constant for this reaction is equal to:

$$K^o_{eq} = K^o_b = (OH^-)(NH_4^+)/(NH_3)(H_2O) = 10^{-4.75}$$

Strong/weak acids and bases

The self-ionization or auto-ionization of the water molecule is described by :

$$H_2O(l) + H_2O(l) \leftarrow \rightarrow H_3O^+ + OH^-$$

$$K^o_{eq} = K^o_W = (H_3O^+)\ (OH^-)/(H_2O)(H_2O) = (H_3O^+)(OH^-)$$
$$= 1.008 \times 10^{-14} \text{ at } 25^oC \quad \text{or} \quad pK_W = 14$$

This constant allows us to interrelate the acidity constant of an acid with the basicity constant of its conjugate base. For example, for the acid-base pair HB^+-B, the basicity constant for the reaction:

$B + H_2O = OH^- + BH^+$ is $K_B = (HB^+)(OH^-)/(B)$

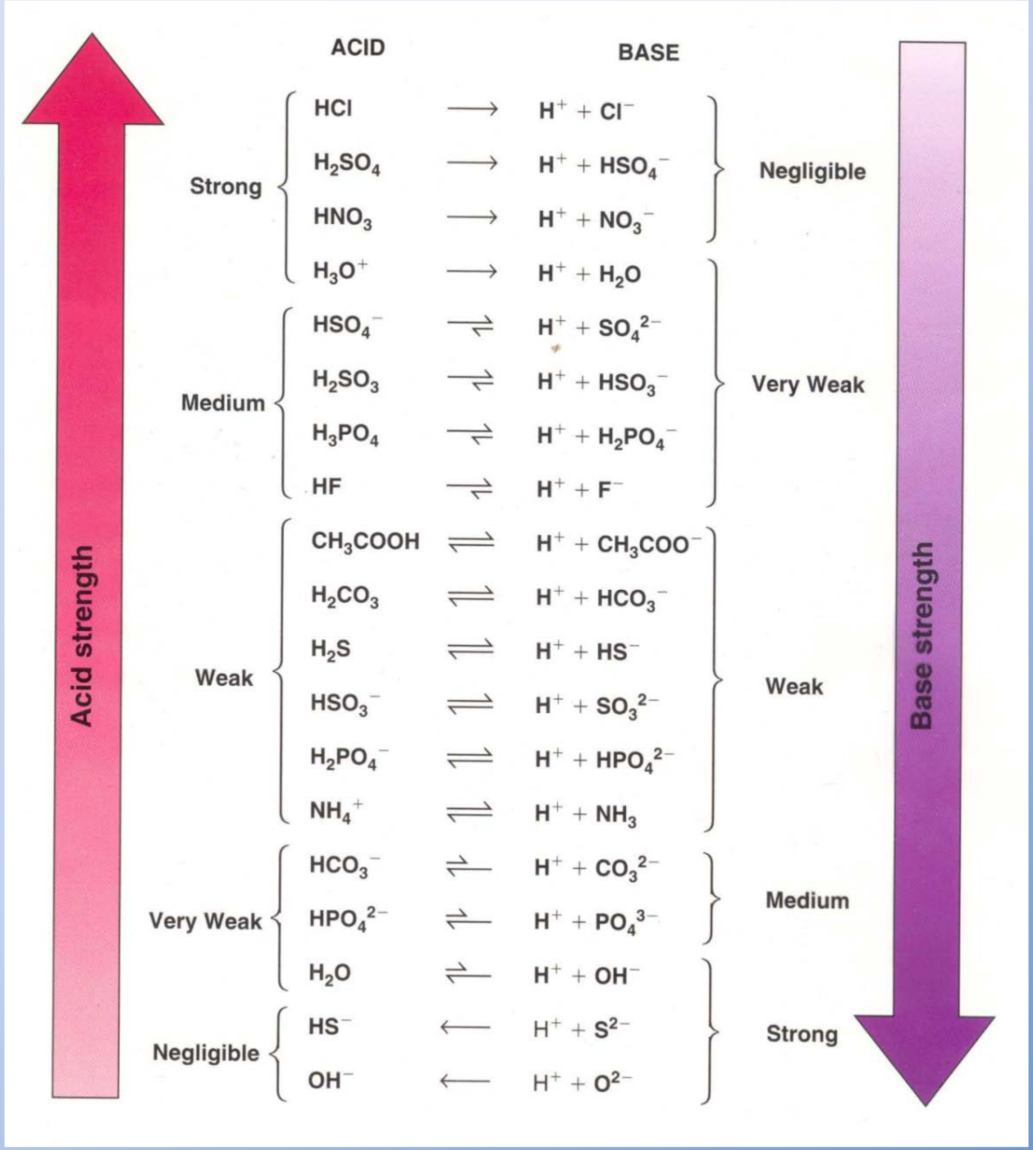
Whereas the acidity constant for:

$HB^+ + H_2O = H_3O^+ + B$ is $K_{HB+} = (H^+)(B)/(HB^+)$

Thus, $K_{HB+} = (H^+)(B)/(HB^+) = (H^+)(OH^-)/K_B = K_W / K_B$

Thus, either the acidity or basicity constant describes fully the protolysis (proton transfer) properties of an acid-base pair in water. The stronger the acidity of an acid, the weaker the basicity of its conjugate base, and vice versa. The product of the $K_a \cdot K_b$ of a conjugate pair is equal to K_W.

Acids and their conjugate bases



	ACID		BASE	
Strong	HCl	$\longrightarrow$	$H^+ + Cl^-$	Negligible
	H_2SO_4	$\longrightarrow$	$H^+ + HSO_4^-$	
	HNO_3	$\longrightarrow$	$H^+ + NO_3^-$	
	H_3O^+	$\longrightarrow$	$H^+ + H_2O$	Very Weak
Medium	HSO_4^-	$\stackrel{\longrightarrow}{\leftarrow}$	$H^+ + SO_4^{2-}$	
	H_2SO_3	$\stackrel{\longrightarrow}{\leftarrow}$	$H^+ + HSO_3^-$	
	H_3PO_4	$\stackrel{\longrightarrow}{\leftarrow}$	$H^+ + H_2PO_4^-$	
	HF	$\stackrel{\longrightarrow}{\leftarrow}$	$H^+ + F^-$	
Weak	CH_3COOH	$\rightleftharpoons$	$H^+ + CH_3COO^-$	Weak
	H_2CO_3	$\rightleftharpoons$	$H^+ + HCO_3^-$	
	H_2S	$\rightleftharpoons$	$H^+ + HS^-$	
	HSO_3^-	$\rightleftharpoons$	$H^+ + SO_3^{2-}$	
	$H_2PO_4^-$	$\rightleftharpoons$	$H^+ + HPO_4^{2-}$	
	NH_4^+	$\rightleftharpoons$	$H^+ + NH_3$	
Very Weak	HCO_3^-	$\stackrel{\rightarrow}{\longleftarrow}$	$H^+ + CO_3^{2-}$	Medium
	HPO_4^{2-}	$\stackrel{\rightarrow}{\longleftarrow}$	$H^+ + PO_4^{3-}$	
	H_2O	$\stackrel{\rightarrow}{\longleftarrow}$	$H^+ + OH^-$	Strong
Negligible	HS^-	$\longleftarrow$	$H^+ + S^{2-}$	
	OH^-	$\longleftarrow$	$H^+ + O^{2-}$	

Composite Acidity Constants

It is not always possible to describe a protolysis reaction unambiguously in terms of the actual acid and base species. In this case more than one reaction, usually the hydration of the acid is included in the constant. Furthermore, in many cases, it may be difficult to analytically distinguish between species in solution. For example, CO_2(aq) and H_2CO_3 in solution (CO_2(aq):H_2CO_3 = 670) can only be distinguished by infrared spectroscopy but it is certainly not practical to do so on a routine basis. To circumvent this problem the hydration and first dissociation reactions are combined:

$H_2CO_3 \leftrightarrow CO_2(aq) + H_2O$ $\quad K = (CO_{2(aq)})/(H_2CO_3)$

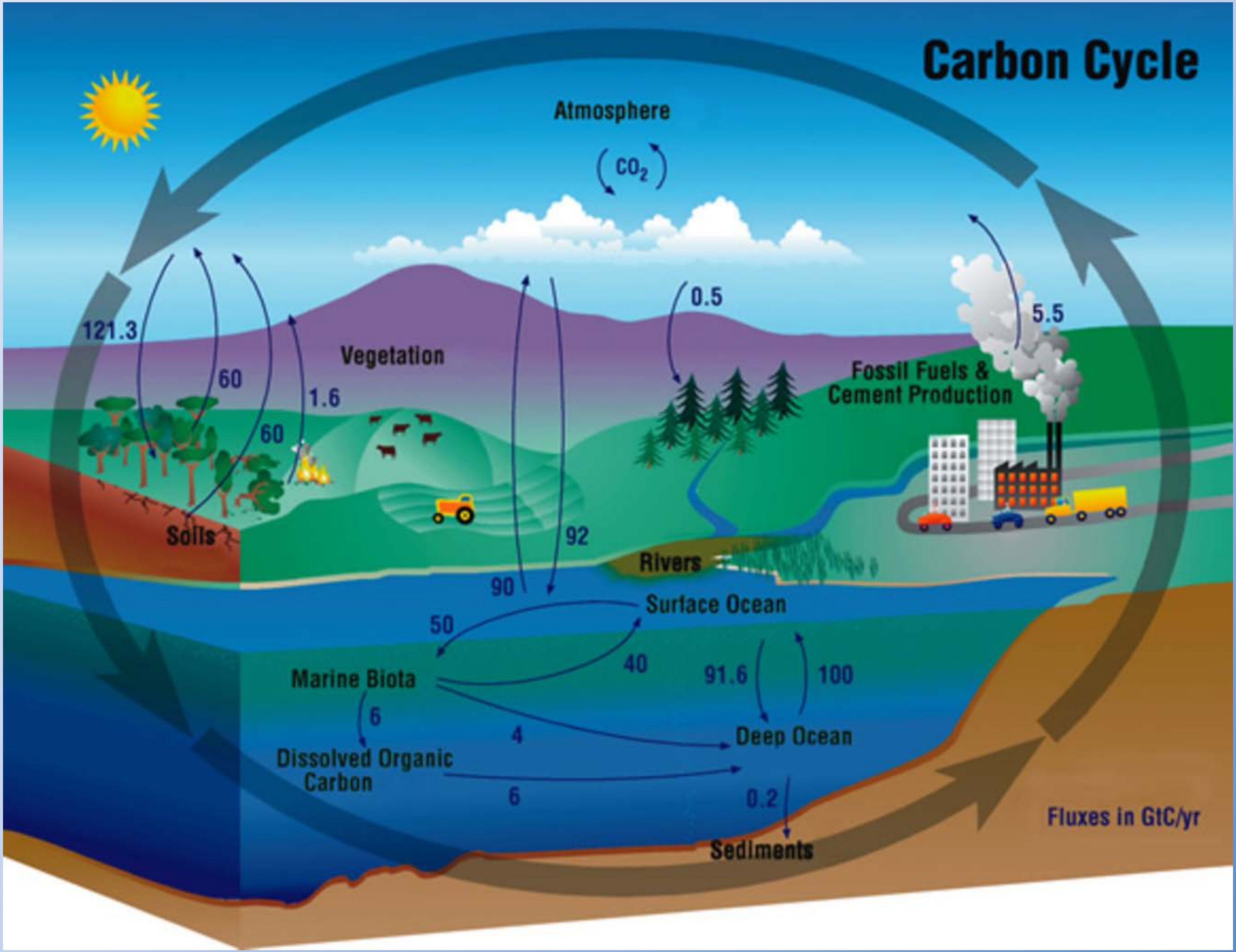
$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$ $\quad K_{(H2CO3)} = (H^+)(HCO_3^-)/(H_2CO_3) = 10^{-3.8}$

A combination of the two gives:

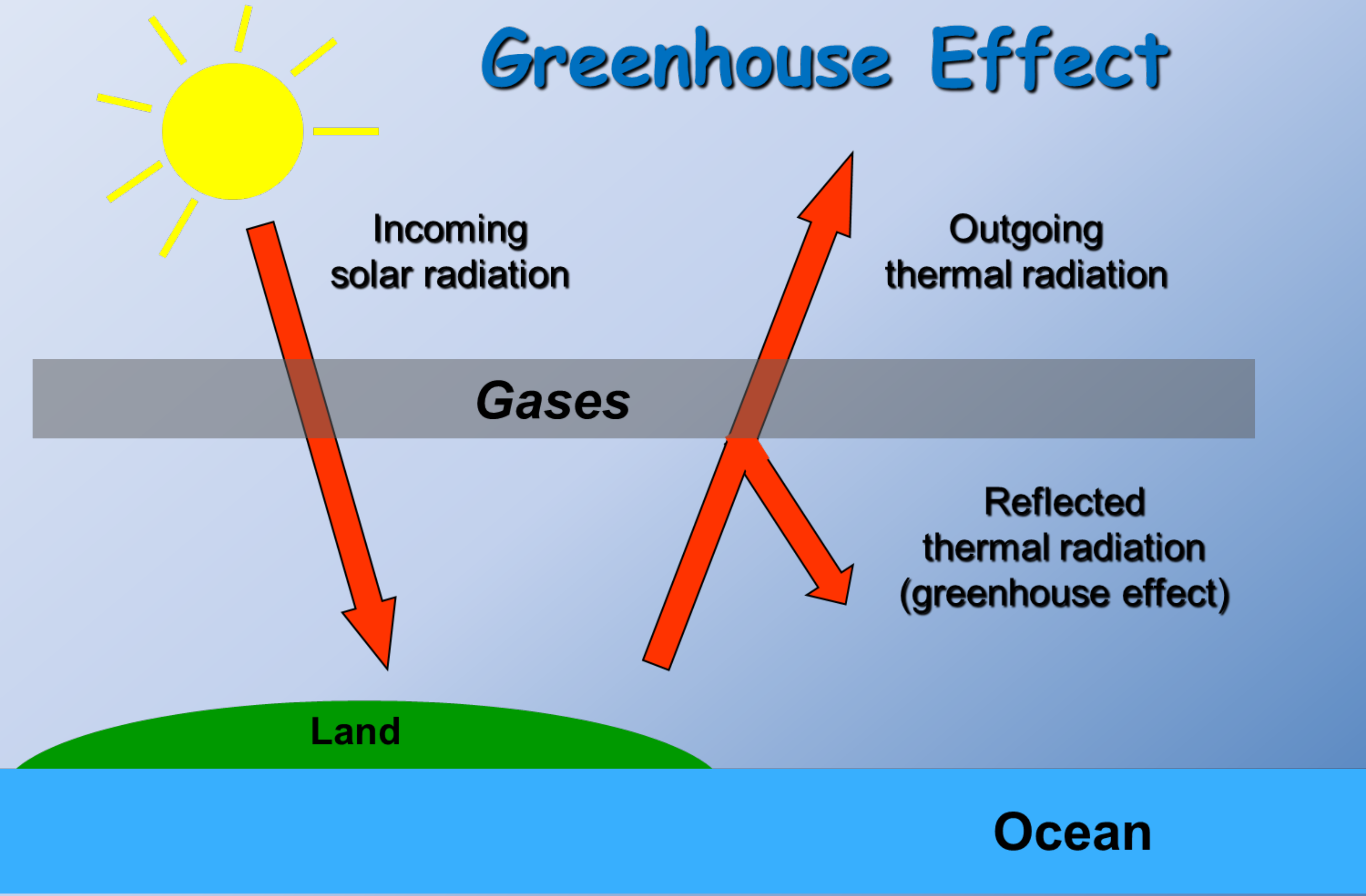
$(H^+)(HCO_3^-)/((H_2CO_3)+(CO_{2(aq)})) = K_{(H2CO3)}/(1+K) = K_{(H2CO3*)} = 10^{-6.35}$

where $K_{(H2CO3*)}$ is the composite acidity constant. Under conditions in which activities can be considered equal to concentration,
the sum $(H_2CO_3)+(CO_{2(aq)}) \sim [H_2CO_3]+[CO_{2(aq)}] = [H_2CO_3^*]$.

The true H_2CO_3 is a much stronger acid ($pK_{(H2CO3)} = 3.8$) than the composite $H_2CO_3^*$ ($pK_{(H2CO3*)} = 6.3$) because less than 0.3% of the CO_2 is hydrated at 25°C.


Carbon Cycle
Atmosphere
CO_2
121.3
60
60
1.6
Vegetation
Soils
90
92
0.5
5.5
Fossil Fuels & Cement Production
Rivers
Surface Ocean
50
40
Marine Biota
6
Dissolved Organic Carbon
4
6
91.6
100
Deep Ocean
0.2
Sediments
Fluxes in GtC/yr

Greenhouse Effect



Incoming
solar radiation

Outgoing
thermal radiation

Gases

Reflected
thermal radiation
(greenhouse effect)

Land

Ocean

Chemical Weathering
Congruent Dissolution

(all mineral constituents pass into solution but the amount is determined by the solubility of the parent mineral)

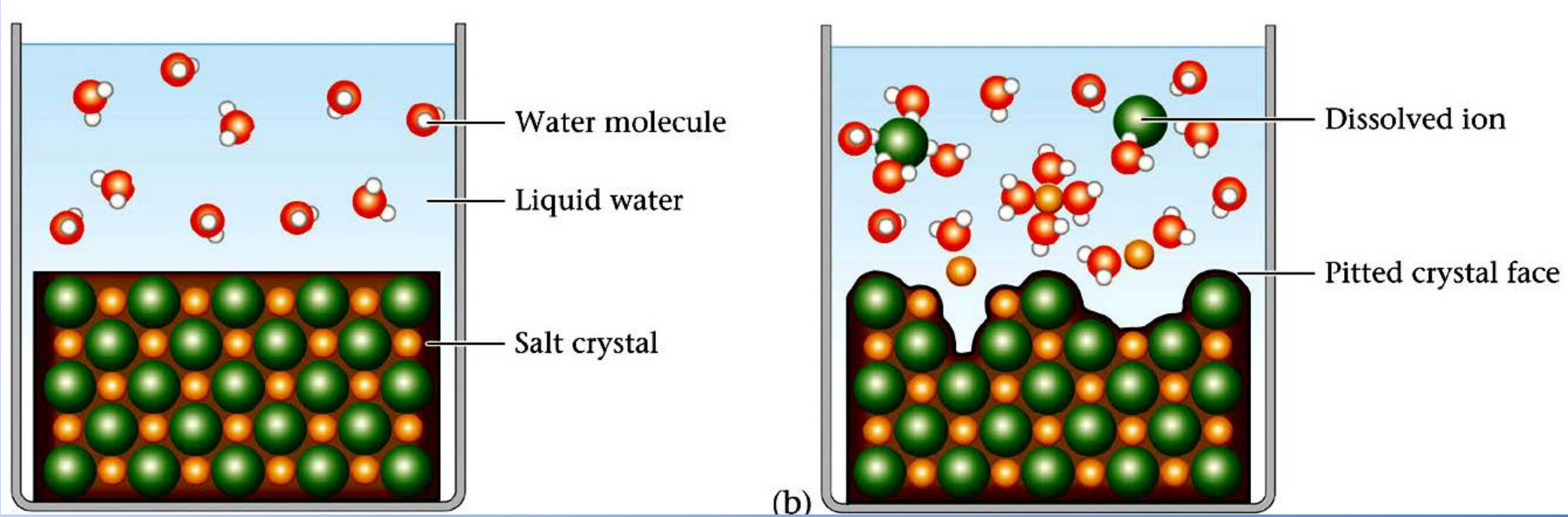
$$CaCO_3 + \underbrace{CO_2 + H_2O} \leftarrow\rightarrow Ca^{2+} + 2HCO_3^-$$

Calcite

H_2CO_3 – carbonic acid

$$CaMg(CO_3)_2 + \overbrace{2CO_2 + 2H_2O} \leftarrow\rightarrow Ca^{2+} + Mg^{2+} + 4HCO_3^-$$

Dolomite



Chemical Weathering

Incongruent dissolution or Hydrolysis

(H^+ or OH^-, the constituents of water, replace other ions of a mineral)

Weathering of granite

$$2KAlSi_3O_8 + 2CO_2 + 3H_2O \rightarrow 2K^+ + Al_2Si_2O_5(OH)_4 + + 2HCO_3^- + 4SiO_2$$

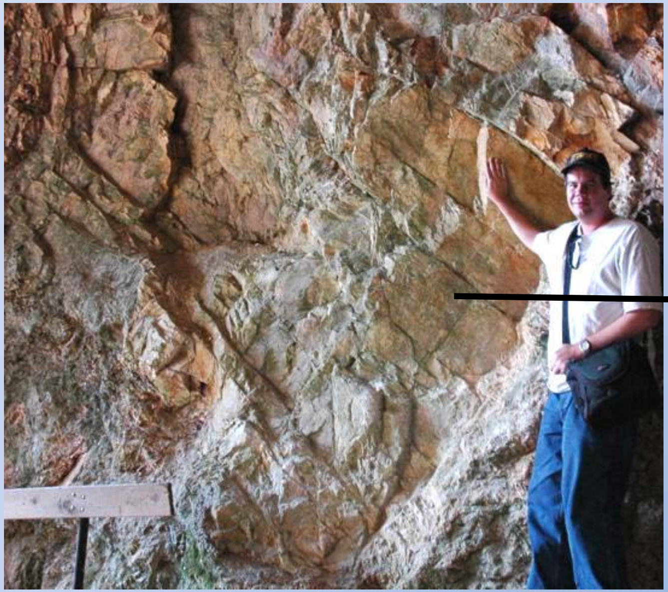
K-feldspar

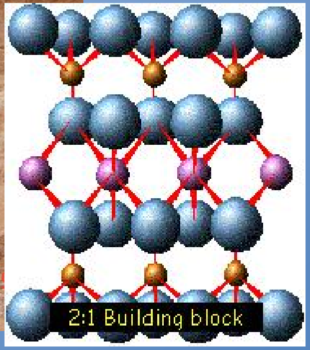
Kaolinite

(a secondary mineral)

Quartz

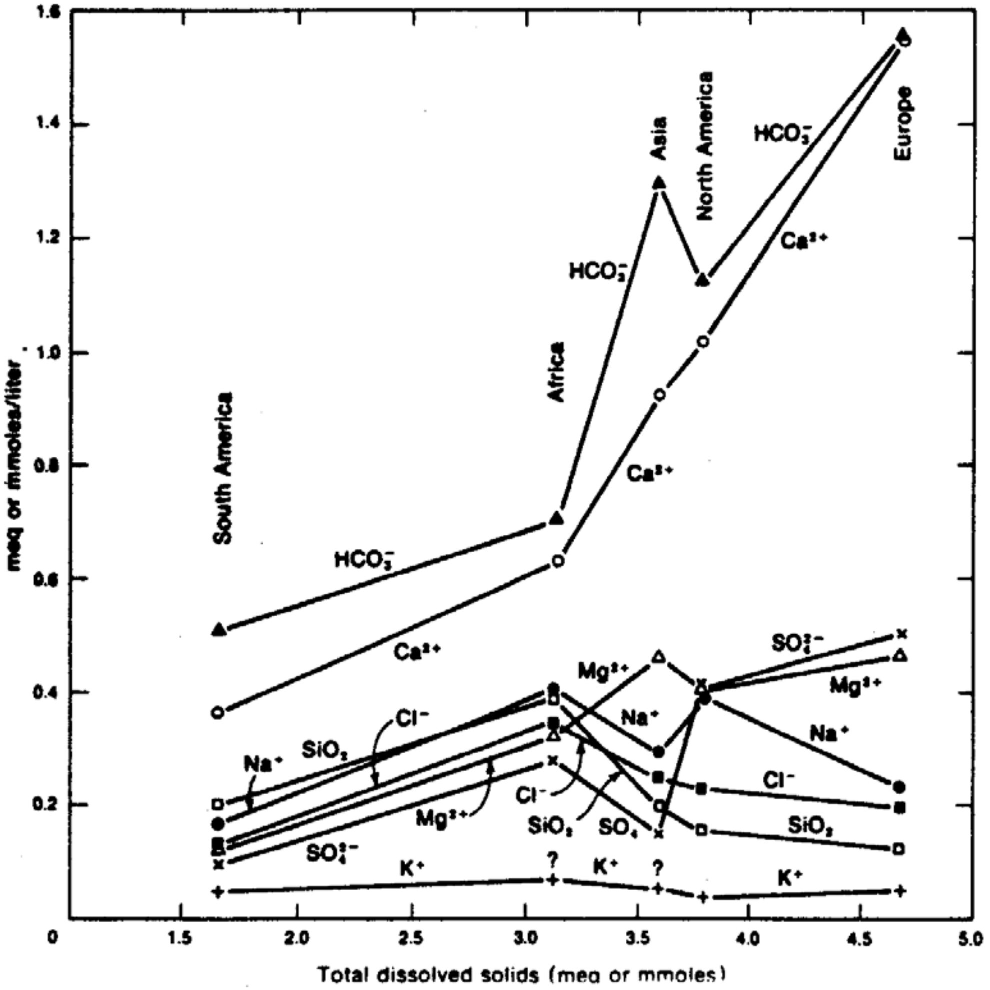

Clay mineral
Sheet silicate





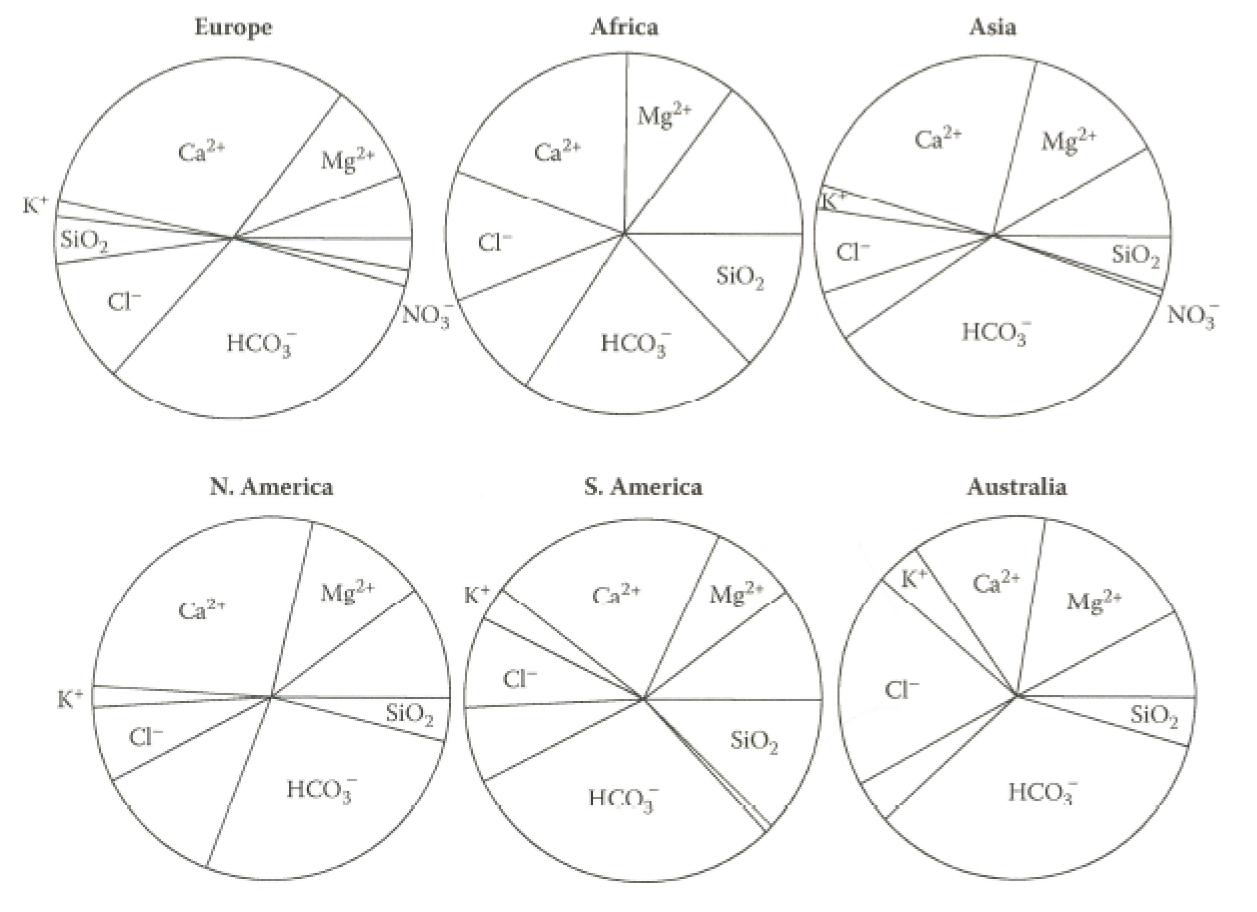
Composition of world rivers

Figure 5.3 Concentrations of dissolved species in continental drainage. The major differences from continent to continent are in the contents of Ca^{2+} and HCO_3^- (data from Livingstone, 1963).



From: Garrels and Mackenzie (1971)
Evolution of Sedimentary Rocks

Major components of various rivers of the continents of the world



Composite Acidity Constants

Carbon dioxide dissolved in water produces carbonic acid which, in turn, dissociates into bicarbonate and carbonate ions, releasing H^+ to the solution.

$CO_{2(g)} \leftrightarrow CO_{2(aq)}$ (1)

$H_2O + CO_{2(aq)} \leftrightarrow H_2CO_3$ (2) slow reaction

$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$ (3) fast reaction

$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$ (4) fast reaction

Carbonic acid reactions

The equilibrium constants for each of these reactions can be defined in terms of the ratio of the activity of the products to the reactants such as:

$K^o_0 = a(H_2CO_3^*)/ a(H_2O)\, fCO_2$ (Henry's constant or Bunsen coefficient)
$= [H_2CO_3^*]\, \gamma(H_2CO_3^*)/ pCO_2 = 10^{-1.47}$ at 25°C (0.03406)

From the latter equation, you can easily appreciate how an increase in pCO_2 in the atmosphere due to fossil fuel burning will lead to an uptake by the oceans …

$K^o_1 = a(HCO_3^-)\, a(H^+)/ a(H_2CO_3^*)$
$= [HCO_3^-]\, \gamma(HCO_3^-)\, a(H^+)/ [H_2CO_3^*]\, \gamma(H_2CO_3^*)$
$= 10^{-6.35}$ at 25°C (4.45 x 10^{-7})

The two constants defined above are called **composite constants** because they are defined in terms of the activity of the sum of $H_2CO_3 + CO_2$(sol'n) = $H_2CO_3^*$. Finally,

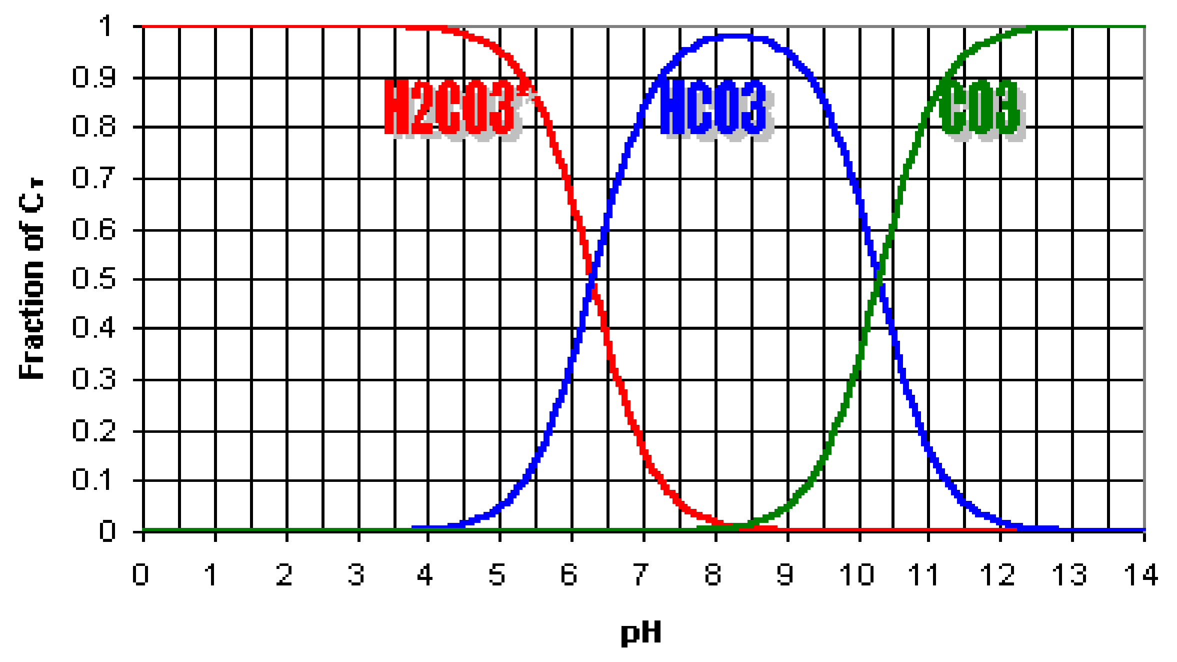
$K^o_2 = a(CO_3^{2-})\, a(H^+)/ a(HCO_3^-)$
$= [CO_3^{2-}]\, \gamma(CO_3^{2-})\, a(H^+)/ [HCO_3^-]\, \gamma(HCO_3^-)$
$= 10^{-10.33}$ at 25°C (4.68 x 10^{-11})

Carbonic acid reaction equilibria

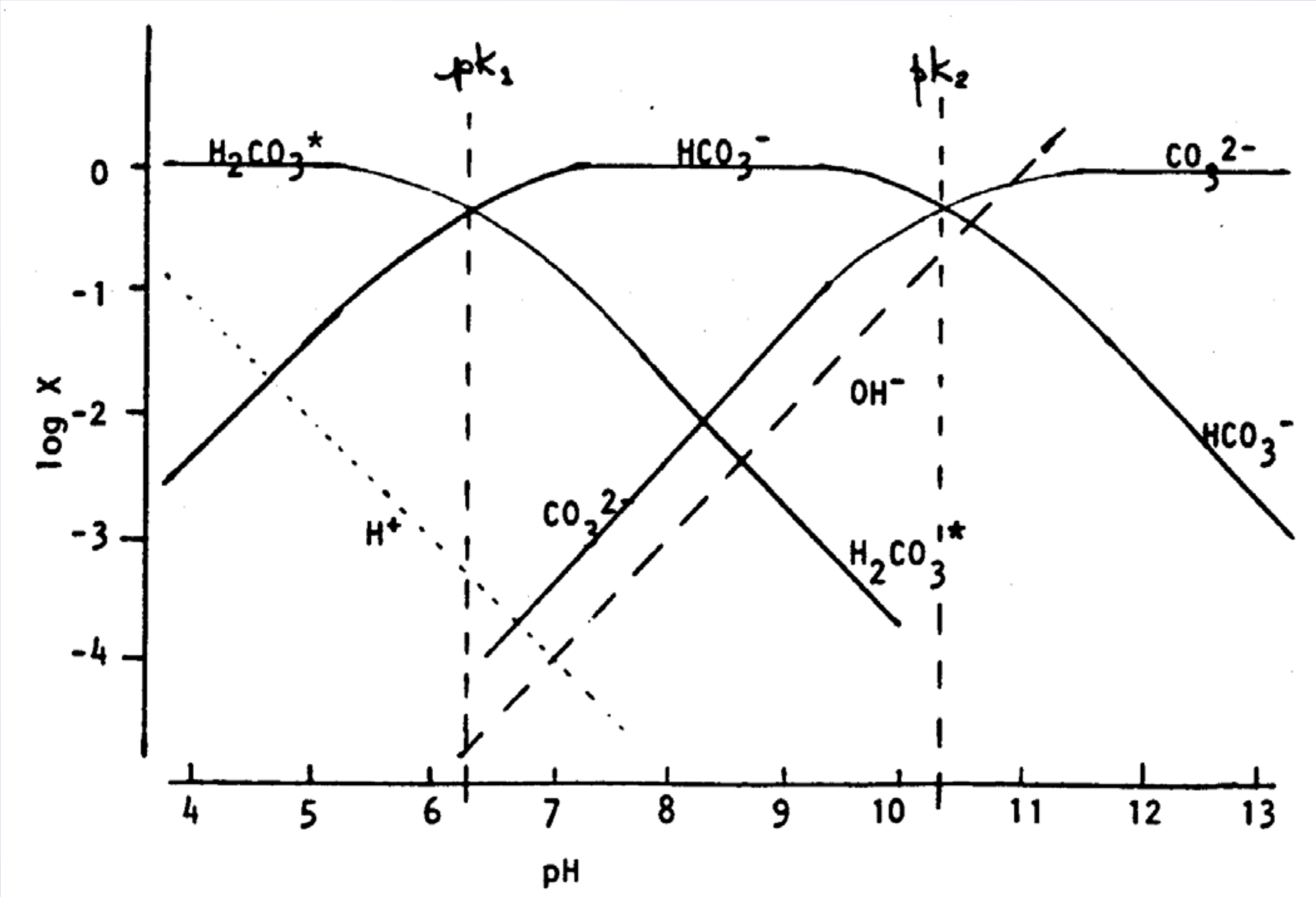
$K^o_2 = a(H^+)\,a(CO_3^{2-}) / a(HCO_3^-)$

$= [CO_3^{2-}]\,\gamma(CO_3^{2-})\,a(H^+) / [HCO_3^-]\,\gamma(HCO_3^-)$

$= 10^{-10.33}$ at 25°C (4.68 x 10^{-11})

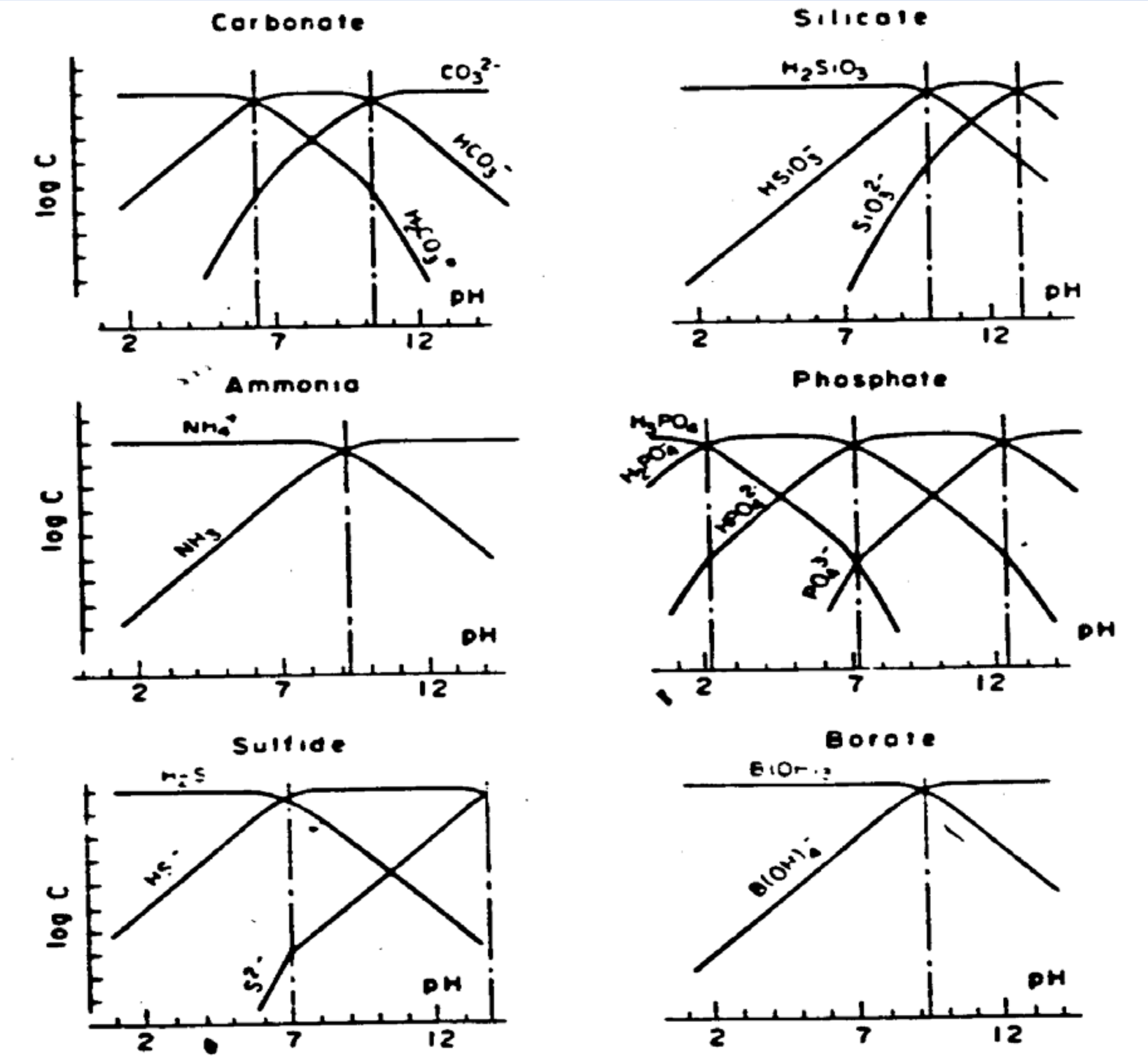


Carbonic acid species as a function of pH



$(H^+)(OH^-)/(H_2O) = 10^{-14}$

Bjerrum or speciation diagrams for weak acids and bases



Carbonic acid species as a function of pH

$$C_T \text{ or } \Sigma CO_2 = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}]$$

Using the equilibrium constants defined previously, we can describe each species in terms of pH and C_T, so that:

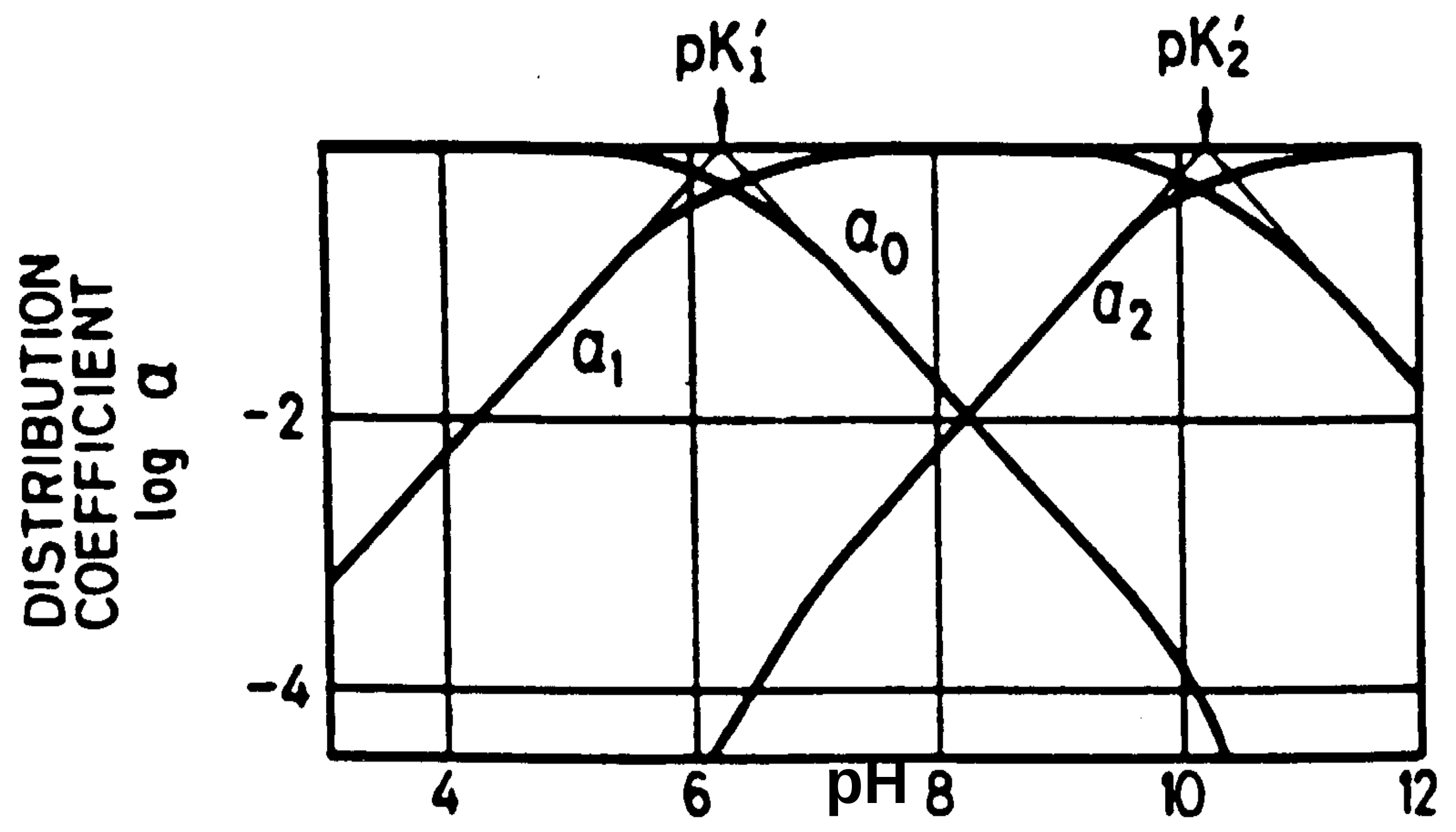
$$\begin{aligned} C_T &= \alpha_0\, C_T + \alpha_1\, C_T + \alpha_2\, C_T \\ &= [H_2CO_3^*] + K_1\, [H_2CO_3^*]\, /[H^+] + K_1K_2\, [H_2CO_3^*]\, /[H^+]^2 \\ &= [H_2CO_3^*]\, (1 + K_1/[H^+] + K_1K_2/[H^+]^2) \end{aligned}$$

$$[H_2CO_3^*] = C_T/(1 + K_1/[H^+] + K_1K_2/[H^+]^2) = \alpha_0\, C_T$$

where α_I is the relative fraction of each species in solution or the ionization factor or degree of protolysis, and $\alpha_0 + \alpha_1 + \alpha_2 = 1$. The subscript refers to the number of protons lost from the most protonated species.

$$\begin{aligned} \alpha_0 &= 1/(1 + K_1/[H^+] + K_1K_2/[H^+]^2) \\ \alpha_1 &= 1/([H^+]/K_1 + 1 + K_2/[H^+]) \\ \alpha_2 &= 1/([H^+]^2/K_1K_2 + [H^+]/K_2 + 1) \end{aligned}$$

Carbonic acid species as a function of pH



Solubility and saturation state of $CaCO_3$

The reaction describing the solubility of calcium carbonate is:

$$CaCO_3 \leftrightarrow Ca^{2+} + CO_3^{2-}$$

the equilibrium constant for this reaction, or the solubility constant is given by:

$$K° = \frac{(Ca^{2+})\,(CO_3^{2-})}{(CaCO_3)} = \frac{(Ca^{2+})\,(CO_3^{2-})}{1}$$

$K°_C = 10^{-8.48}$ @ 25°C, 1 atm

$K°_A = 10^{-8.31}$ @ 25°C, 1 atm

$$K° = [Ca^{2+}]\,[CO_3^{2-}]\,\gamma(Ca^{2+})\,\gamma(CO_3^{2-}) = K^*\,\gamma(Ca^{2+})\,\gamma(CO_3^{2-})$$

$pK^* = pK° + 0.5\,(Z^2_{HB} - Z^2_{B})\,I^{1/2}/(1 + I^{1/2})$ (Stumm and Morgan, p. 102-105)

Saturation state of a solution with respect to calcite or aragonite is defined as:

$$\Omega_{C\text{ or }A} = \frac{(Ca^{2+})\,(CO_3^{2-})}{K°_{C\text{ or }A}} = \frac{[Ca^{2+}]\,[CO_3^{2-}]}{K^*_{C\text{ or }A}}$$

$\Omega > 1$, the solution is supersaturated

$\Omega = 1$, the solution is at equilibrium

$\Omega < 1$, the solution is undersaturated

Characterization of the carbonate system

Measurable parameters:

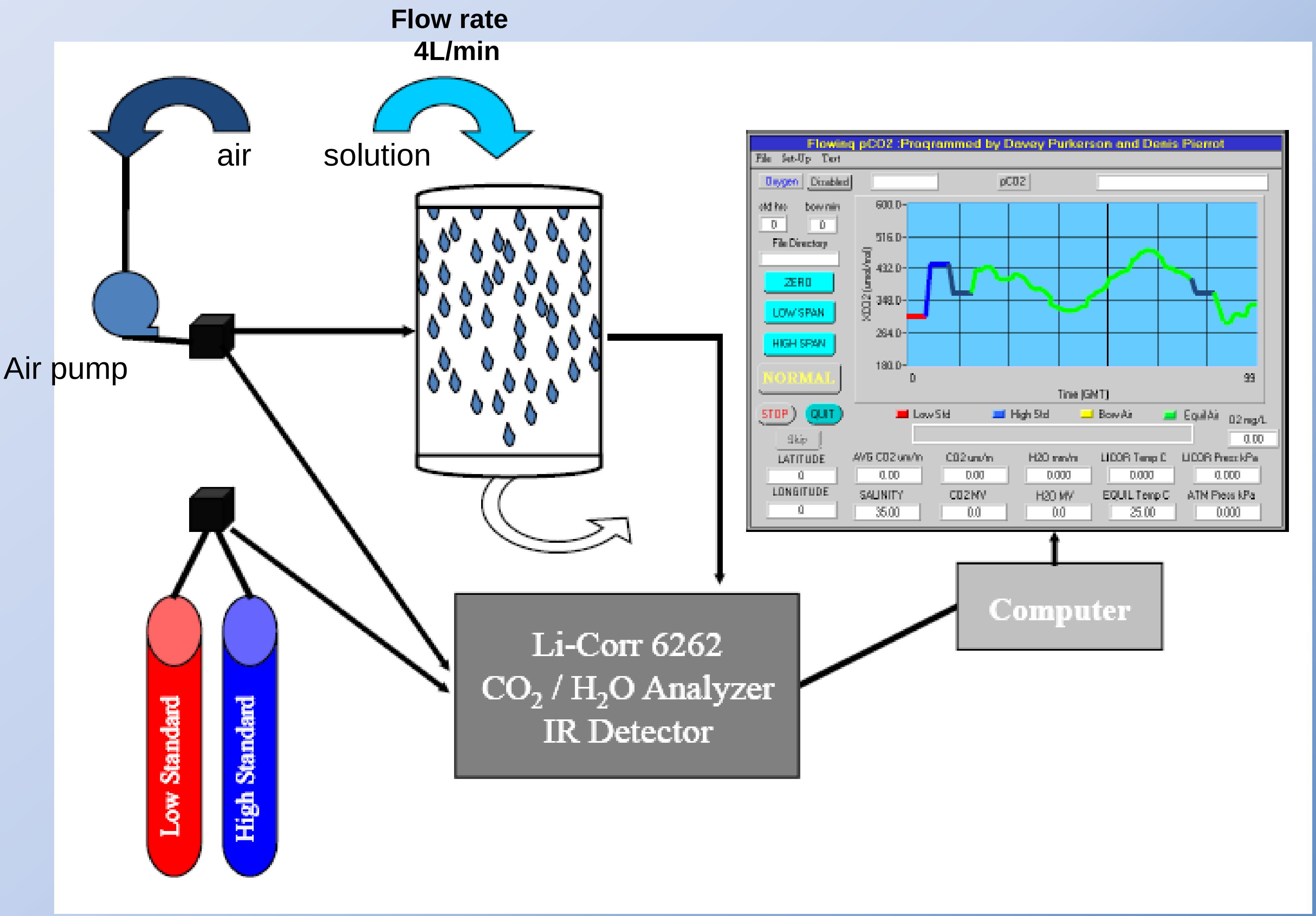
- pCO_2 = CO_2 partial pressure in equilibrium with the solution.
- pH = - log (H^+) ~ -log [H^+]
- ΣCO_2 or DIC or C_T = $[H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}]$
total dissolved inorganic carbon concentration
- $A_c = [HCO_3^-] + 2\,[CO_3^{2-}]$ = carbonate alkalinity
The carbonate alkalinity is derived from the titration alkalinity.

For a simple CO_2-H_2O system: $A_t = [HCO_3^-] + 2\,[CO_3^{2-}] + [OH^-] - [H^+]$

For a more complex electrolyte solutions:
$A_t = [HCO_3^-] + 2\,[CO_3^{2-}] + [OH^-] + [B(OH)_4^-] + [H_3SiO_4^-] + [HS^-] + [HPO_4^{2-}] + 2[PO_4^{3-}] - [H^+]$

A_t = equivalent sum of the bases that are titratable with a strong acid

pCO_2 shower head equilibrator chamber

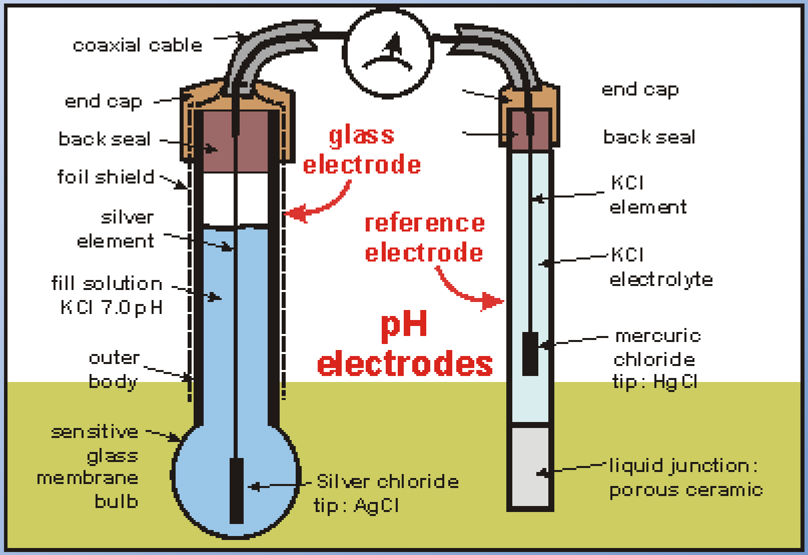


Flowing pCO2 :Programmed by Davey Purkerson and Denis Pierrot

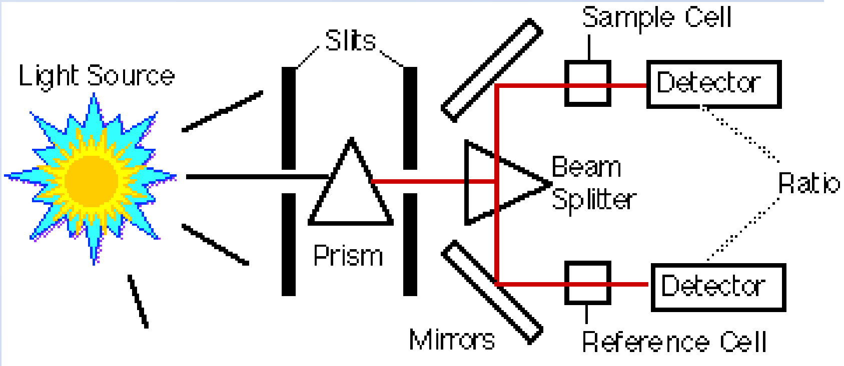
std hrs: 0
bow min: 0
File Directory:
O2 mg/L: 0.00
LATITUDE: 0
LONGITUDE: 0
AVG CO2 um/m: 0.00
CO2 um/m: 0.00
H2O mm/m: 0.000
LICOR Temp C: 0.000
LICOR Press kPa: 0.000
SALINITY: 35.00
CO2 MV: 0.0
H2O MV: 0.0
EQUIL Temp C: 25.00
ATM Press kPa: 0.000

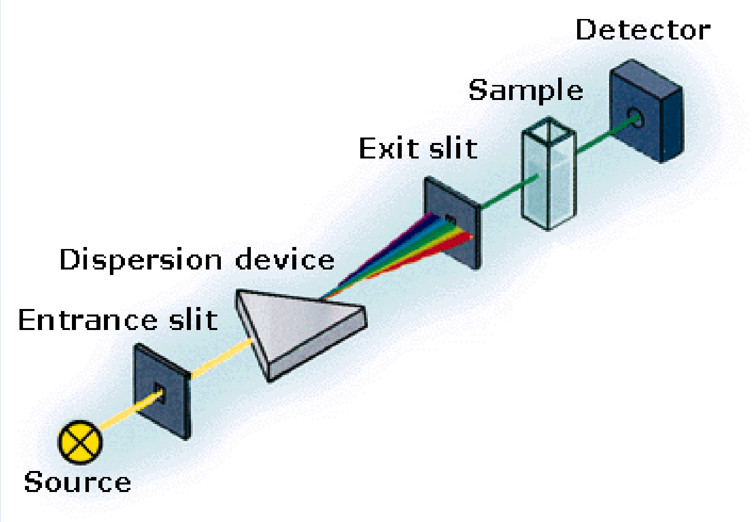
Semi-permeable membrane pCO_2 probe

Potentiometric pH measurements



Spectrophotometric pH measurements





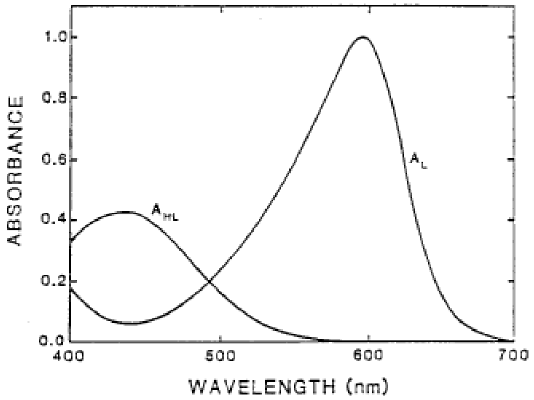


Figure 1. Relative molar absorbances of L^{2-} and HL^- are shown for the pH indicator thymol blue at 25.0 °C. A_L and A_{HL} were obtained at pH $\simeq$ 12 and pH $\simeq$ 4 at a constant total indicator concentration.

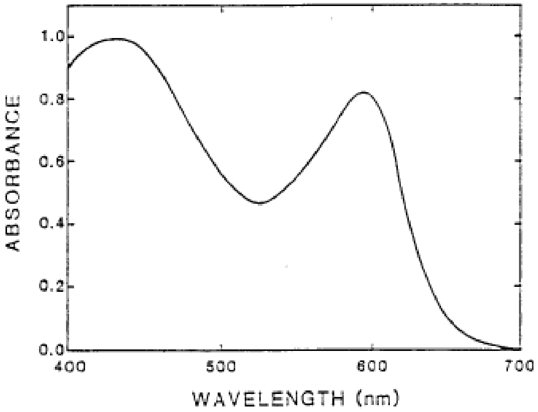
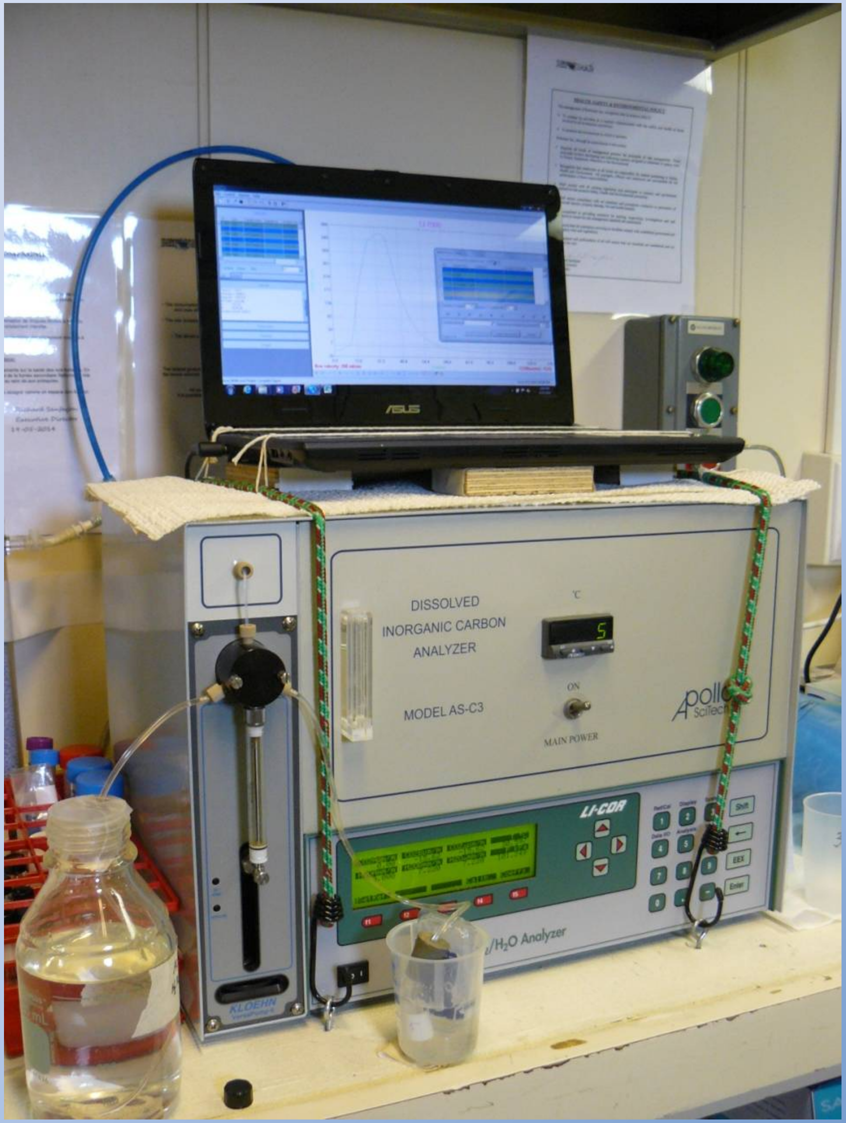
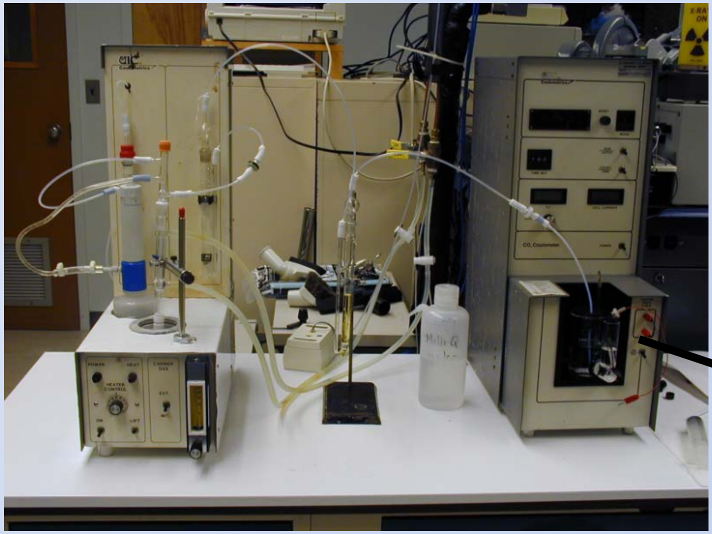


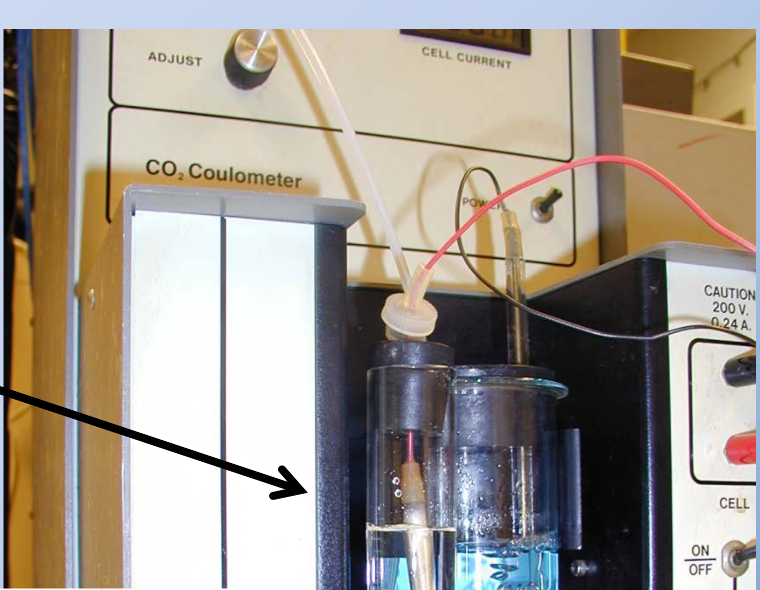
Figure 2. Absorbance of thymol blue is shown in Tris seawater buffer at pH 8.201 (35‰, 25 °C).

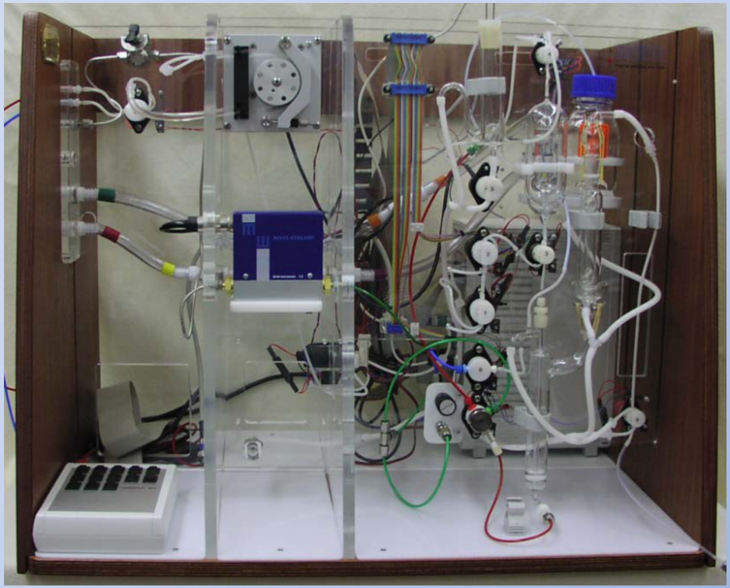
DIC infra-red analyzer

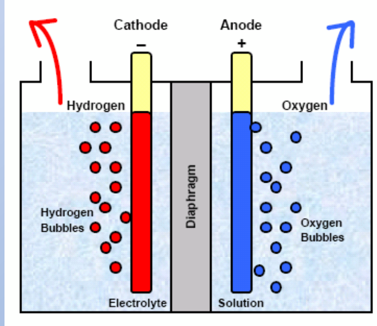


Coulometric determination of DIC (TCO_2, ΣCO_2)









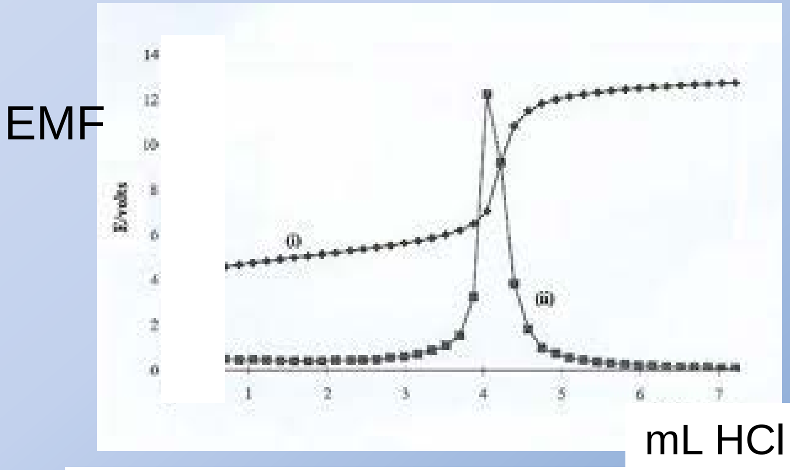
Standard Electrolysis

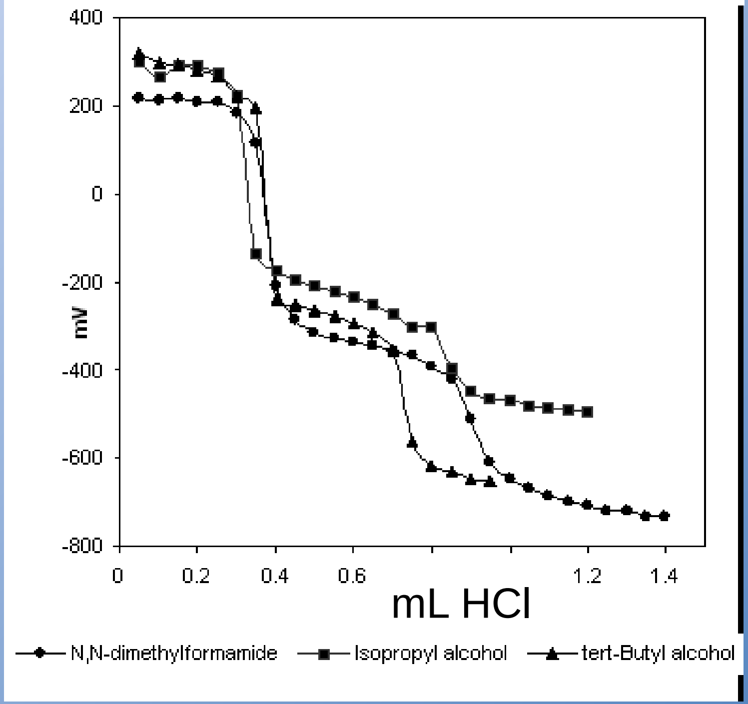
$CO_2 + HO(CH_2)_2NH_2 \rightarrow O(CH_2)_2NHCOO^-$ (blue)+ H^+

At the cathode: $4\ H_2O + 4é \rightarrow 2H_2(g) + 4OH^-$

At the anode: $4Ag^0 + 4Cl^- \rightarrow 4AgCl + 4é$

Potentiometric titrations of alkalinity





Organic and humic acids

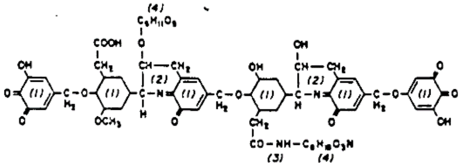


Fig. 3.6. The structure of the humic acid molecule (according to Dragunov, 1948). (1) Aromatic ring of the di- and trihydroxyphenol type, part of which has the double linkage of a quinone groupings; (2) Nitrogen in cyclic forms; (3) Nitrogen of peripheral chains; (4) Carbohydrate residues. (From Kononova, 1966.)

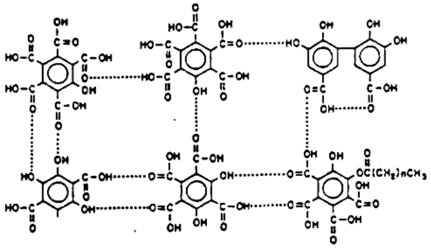


Fig. 3.7. Partial chemical structure of fulvic acid. (From Schnitzer, 1978.)

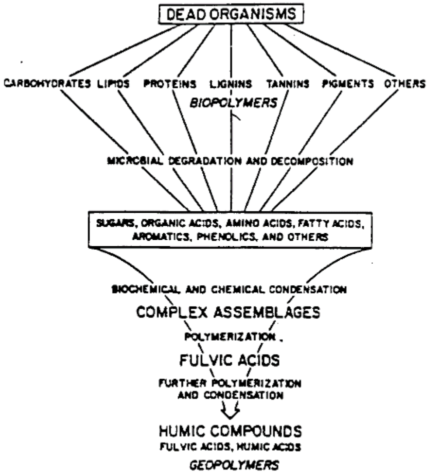


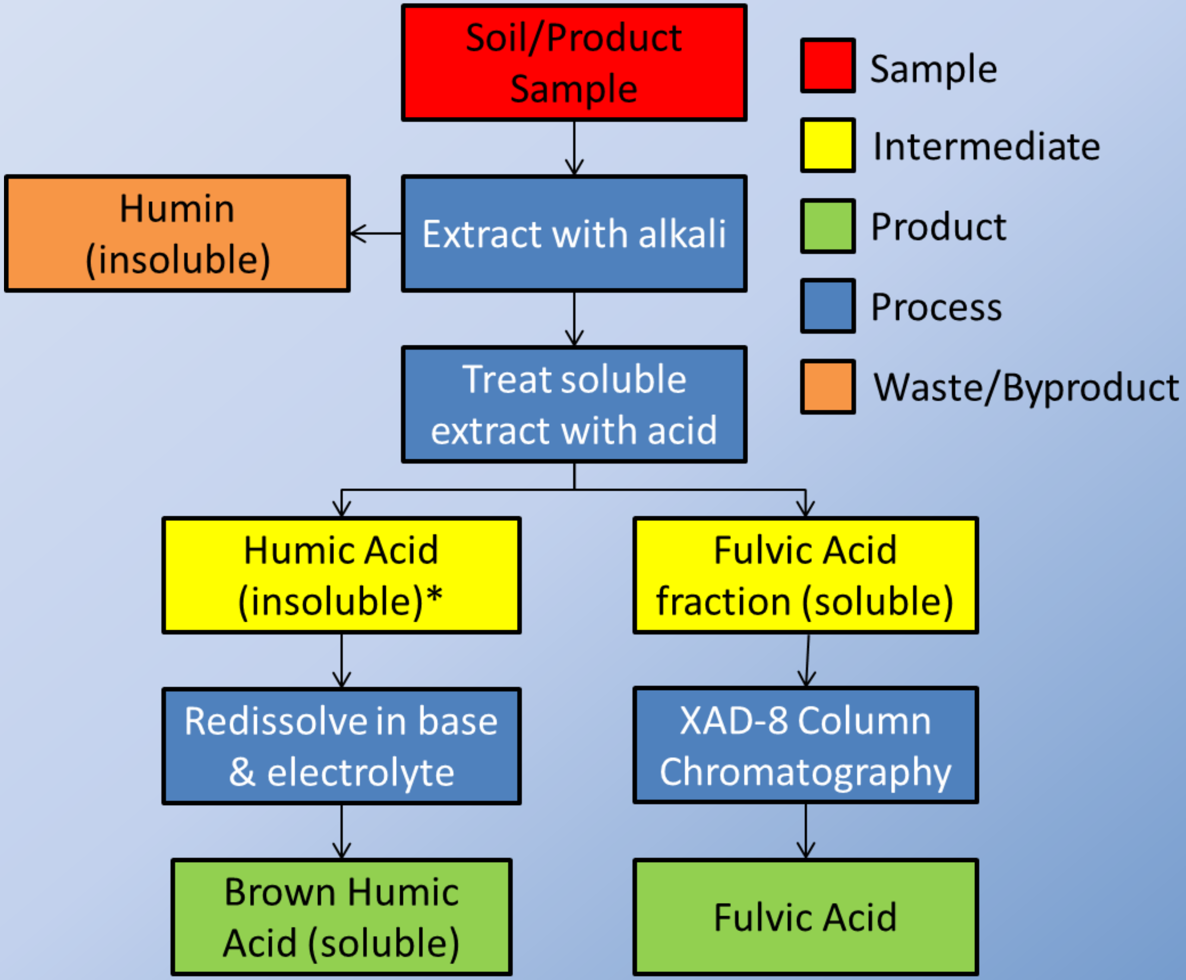
Fig. 2.23. A simplified scheme of the process of humification.

From: M.A. Rashid
Geochemistry of Marine Humic Compouncs

They are formed through a series of enzymatic reactions mediated by micro-organisms in soils and sediments from carbohydrates, proteins, peptides, amino acids, lipids and waxes.

These polyelectric acids, unlike their more easily identifiable monomeric components are biologically refractory. They have a high surface charge and cation exchange capacity.

Isolating and separating humic and fulvic acids



Soil/Product Sample

Extract with alkali

Humin (insoluble)

Treat soluble extract with acid

Humic Acid (insoluble)*

Fulvic Acid fraction (soluble)

Redissolve in base & electrolyte

XAD-8 Column Chromatography

Brown Humic Acid (soluble)

Fulvic Acid

🟥 Sample
🟨 Intermediate
🟩 Product
🟦 Process
🟧 Waste/Byproduct

Organic and humic acids

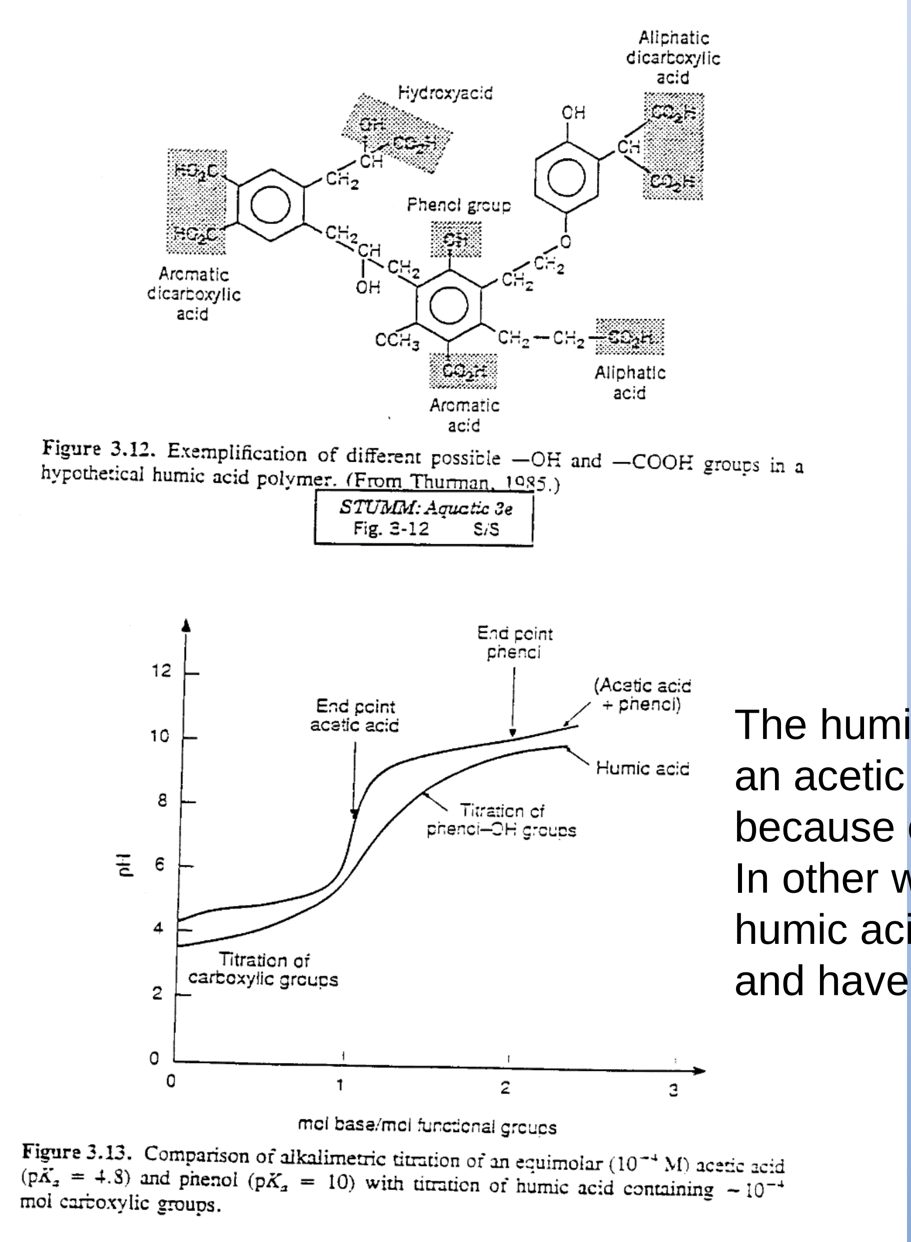


Figure 3.12. Exemplification of different possible —OH and —COOH groups in a hypothetical humic acid polymer. (From Thurman, 1985.)

STUMM: Aquatic 3e
Fig. 3-12 S/S

Figure 3.13. Comparison of alkalimetric titration of an equimolar (10^{-4} M) acetic acid ($p\bar{K}_a = 4.8$) and phenol ($p\bar{K}_a = 10$) with titration of humic acid containing ~ 10^{-4} mol carboxylic groups.

The humic acid titration curve is flatter than that of an acetic acid (pK=4.8)-phenol (pK~10) mixture because of the polyfunctionality of the humic acid. In other words, the –COOH and –OH groups in humic acid are present in different configurations and have somewhat different pK_a values.