

# Air-Water-Soil Interaction

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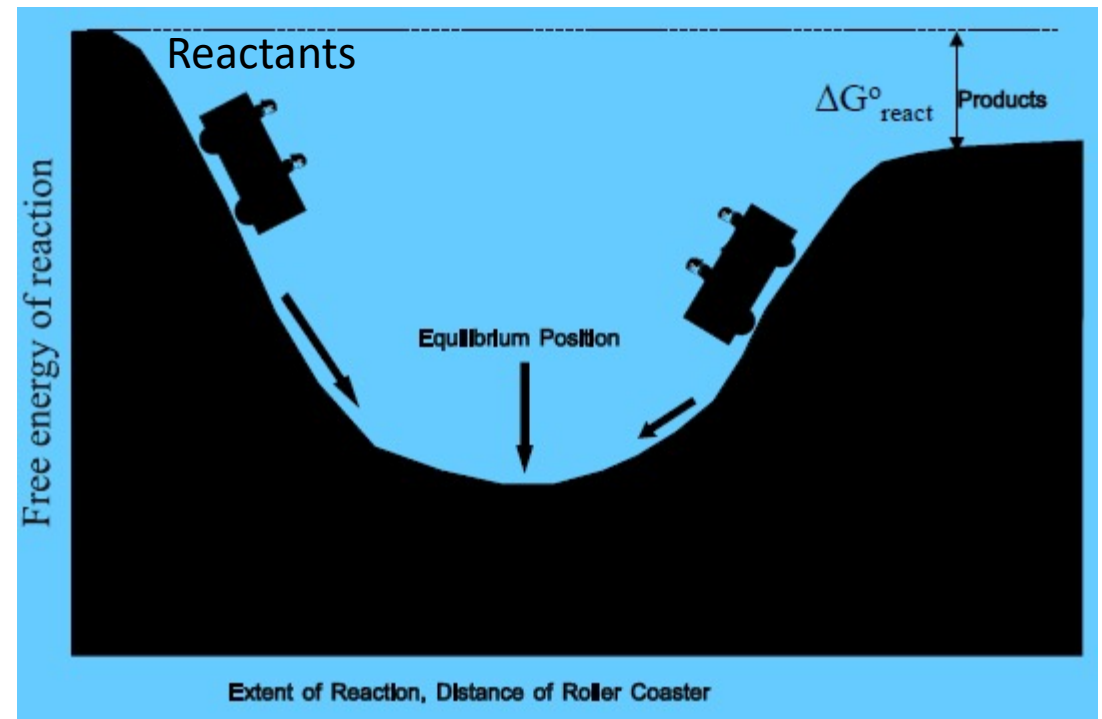
## ➤ Phase Change

### ➤ Gaseous, Aqueous and solid phases

- Change in phase from one to the other
- E.g. Dissolution of oxygen in the atmosphere into the aqueous phase
- System tries to achieve equilibrium

### ➤ Equilibrium: thermodynamics

- Final stopping place
- Best approach for fast reactions
  - Acid/base reaction, complexation, some phase transfer
- **O<sub>2</sub> is central to the sustenance of life of aerobic life-forms.**
- Oxygen enters the surface water in two different pathways:
  - a) Diffusion from atmosphere to water and
  - b) Through photosynthesis by algae in presence of sunlight.



# Equilibrium constant

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For the reaction  $aA + bB \leftrightarrow cC + dD$

Equilibrium constant,  $K$ :

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

$a, b, c, d$  = stoichiometric coefficients of the respective reactants and products

$\{A\}, \{B\}, \{C\}, \{D\}$  = activity of the reactants and products, which can be approximated by concentration of relevant compounds in dilute solutions, at equilibrium

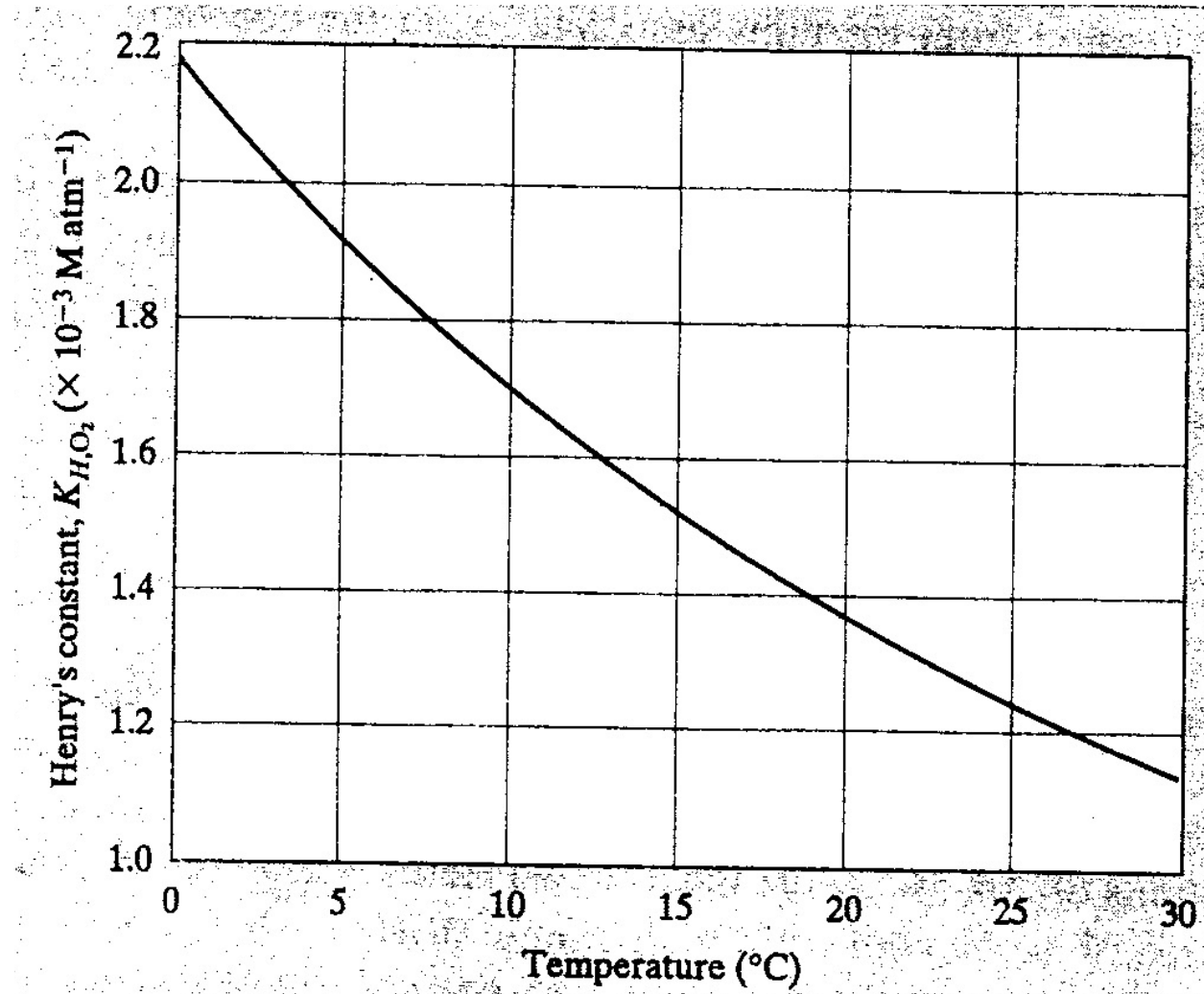
$\{A\}$  stands for activity of A

$[A]$  stands for concentration of A

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- Phase Equilibrium
  - Introduction
    - phase = region with uniform chemical and physical properties (gas, liquid, solid)
    - phase changes can be primarily physical changes (e.g. dissolved in water to gas phase)
  - Gas-liquid
    - Henry's Law
    - applicable to dilute systems, i.e. mole fraction in liquid phase is small
    - Henry's Law states that the amount of a gas that dissolves into a liquid is proportional to the partial pressure that gas exerts on the surface of the liquid.

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- $A_{(aq)} \leftrightarrow A_{(g)}$ 
    - E.g.:  $O_{2(aq)} \leftrightarrow O_{2(g)}$
    - at equilibrium,  $K = \{A_{(g)}\} / \{A_{(aq)}\}$
    - equilibrium constant called the Henry's law constant, and activity coefficients normally considered as equal to 1.0
  - $H = [A_{(g)}] / [A_{(aq)}]$ 
    - note that assumption about activity coefficients gives H units, many different types of H are used. E.g.:
      - $H = \text{partial pressure} / (\text{mole/liter})$  (atm-L/mole, etc)
      - $H = \text{partial pressure} / \text{mole fraction}$  (bar or atm or psi)
      - $H = \text{mole/liter} / (\text{mole liter})$  (dimensionless)
    - Higher H means more volatile compound
    - Effect of temperature: increases H
  - Sometimes define reaction in other direction
    - $A_{(g)} \leftrightarrow A_{(aq)}$
    - $K_H = [A_{(aq)}] / [A_{(g)}] = 1/H$

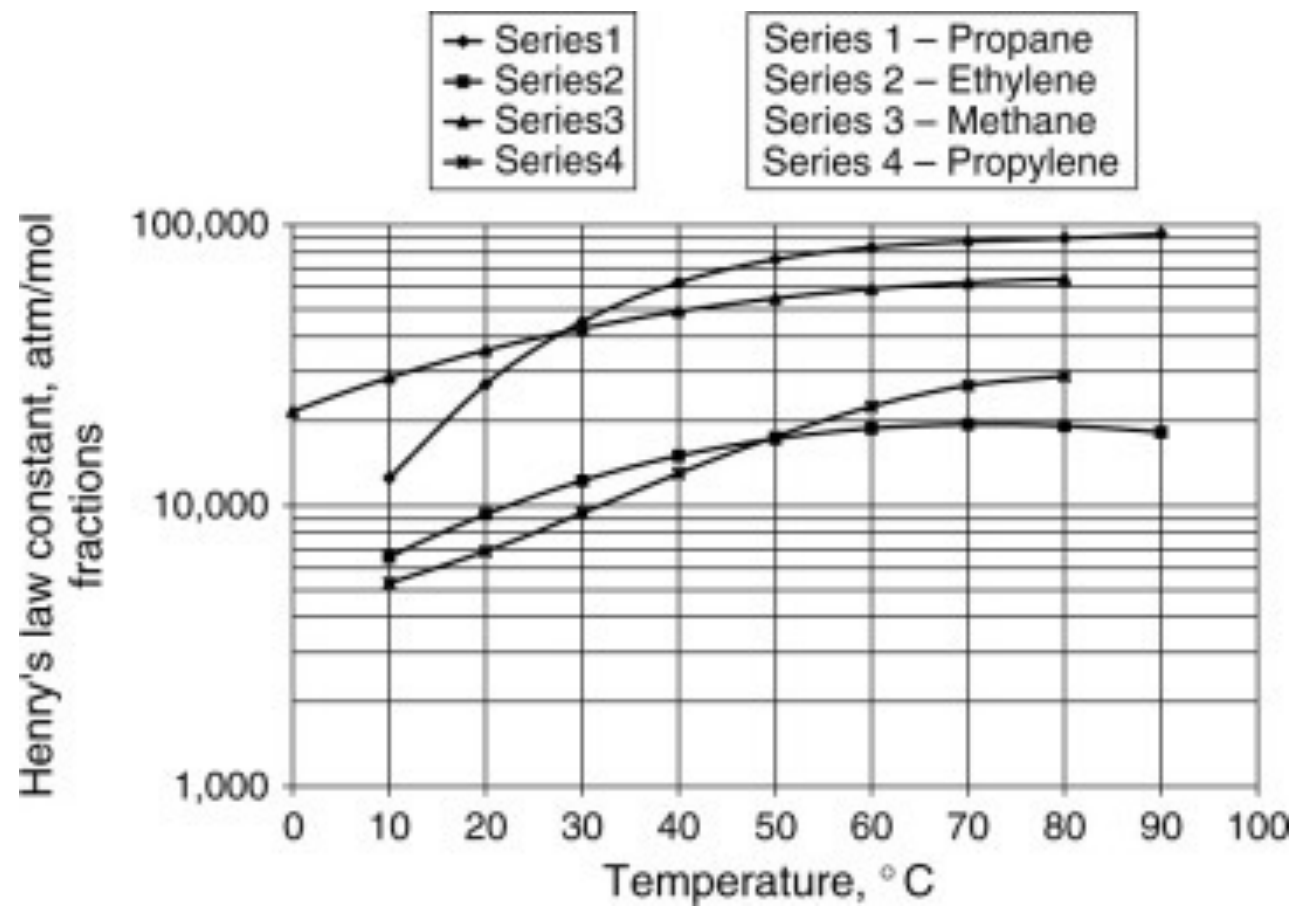
$$K_H = 1/H$$



**Implication:** In the summer, the rivers and lakes shall have less dissolved oxygen as compared to the dissolved oxygen concentration in winter

Reaction	Name	$K_h$ , mol/L-atm	$pK_h = -\log K_h$
$\text{CO}_2(\text{g}) \rightleftharpoons \text{CO}_2(\text{aq})$	Carbon dioxide	$3.41 \times 10^{-2}$	1.47
$\text{NH}_3(\text{g}) \rightleftharpoons \text{NH}_3(\text{aq})$	Ammonia	57.6	-1.76
$\text{H}_2\text{S}(\text{g}) \rightleftharpoons \text{H}_2\text{S}(\text{aq})$	Hydrogen sulfide	$1.02 \times 10^{-1}$	0.99
$\text{CH}_4(\text{g}) \rightleftharpoons \text{CH}_4(\text{aq})$	Methane	$1.50 \times 10^{-3}$	2.82
$\text{O}_2(\text{g}) \rightleftharpoons \text{O}_2(\text{aq})$	Oxygen	$1.26 \times 10^{-3}$	2.90

## Henry's constant-H





# Ideal Gas Law and Dalton's law of partial pressure

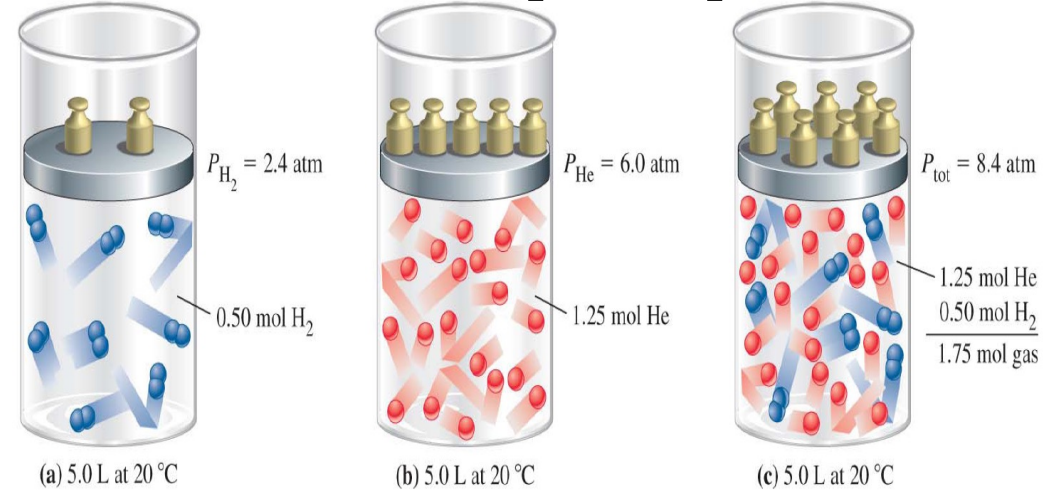
Ideal Gas Law:  $pV = nRT$   $R = 0.0820578 \text{ L.atm}/(\text{K.mol})$

Molar concentration:  $C = \frac{n}{V} = \frac{P}{RT}$

- Partial pressure of each gas in a gas mixture, such as the atmosphere, is the portion of the total pressure that a particular gas would exert

Dalton's Law: Dalton's Law of partial pressures states that the total pressure of a mixture of several gases is the sum of the partial pressures of the individual gases

$$\begin{aligned}P_{\text{tot}} &= p_A + p_B + \dots \\&= (n_A + n_B + \dots)RT/V \\&= (n_{\text{tot}})RT/V\end{aligned}$$



Partial pressure of CO<sub>2</sub> =  $p_{\text{CO}_2} = 0.000400 \times 1 \text{ atm}$

# Example

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Find out the DO in aerated water at 25 deg C in a treatment plant.

$K_H$  of  $O_2$  at 25 C =  $1.26 \times 10^{-3}$  M/atm

[1M  $O_2$  = 32 g/L]

Partial pressure of oxygen in the atmosphere = 0.21 atm.

$K_H = [O_2] / p_{O_2}$

Aqueous concentration of oxygen =  $K_H * p_{O_2}$

=  $1.26 \times 10^{-3}$  M/atm \* 0.21 atm.

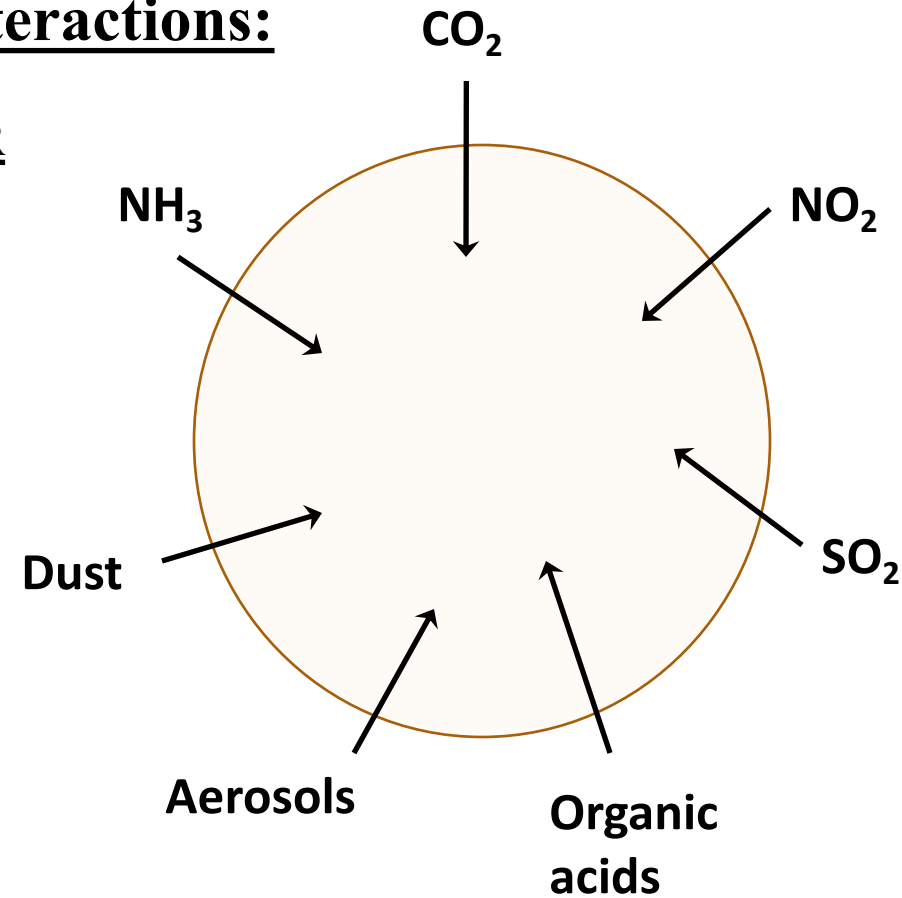
= 0.0002646 M

= 8.467 mg/L

## Atmosphere-Surface Water Interactions:

### RAINWATER DROPLET IN THE AIR

As the droplet passes through the atmosphere to fall on the earth surface, various gases, liquid and solids that are either part of the atmosphere or are suspended in air, tend to get inside the water droplet.



Many of the species establish a quick equilibrium, thus imbibing impurities even before the rain water reaches the earth surface.

## Other Applications/ Phenomena Linked with Gas –Water Interaction



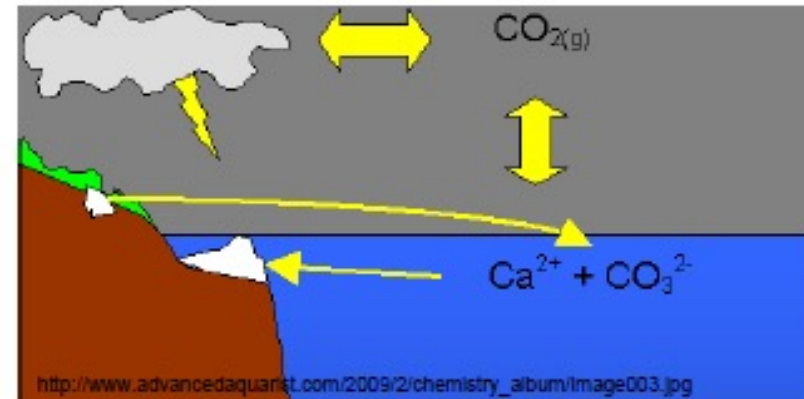
Dissolution of gases



Stripping ammonia



Aeration in activated sludge system



Carbonate system

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After change in phase from gaseous to aqueous, if acids or bases are formed, they can undergo further reactions, effecting the pH.

# Acids and Bases

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- pH of most mineral-bearing waters is 6 to 9. (fairly constant)
- pH and composition of natural waters is regulated by reactions of acids & bases
  - chemical reactions; mostly with minerals
    - carbonate rocks: react with  $\text{CO}_2$  (an acid)
      - $\text{CaCO}_3 (\text{s}) + \text{CO}_2 \rightarrow \text{Ca}^{+2} + 2\text{HCO}_3^-$
    - acids from volcanic activity:  $\text{HCl}$ ,  $\text{SO}_2$
  - Biological reactions: photosynthesis & resp.

➤ Equilibrium is rapidly established

➤ Acid/base reactions are very fast

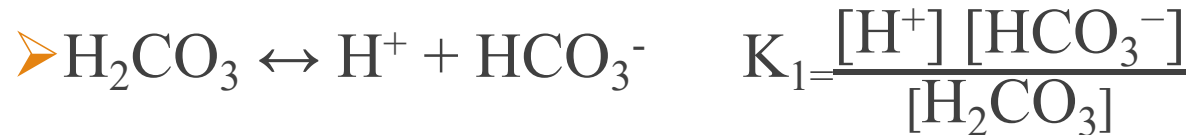
➤  $[H^+]$  is the Master Variable

➤ because Protons react with so many chemical species, affect equilibria and rates

➤ Strength of acids & bases

➤ strong acids have a substantial tendency to donate a proton. This depends on the nature of the acid as well as the base accepting the proton (often water).

➤ Equilibrium constant and pka



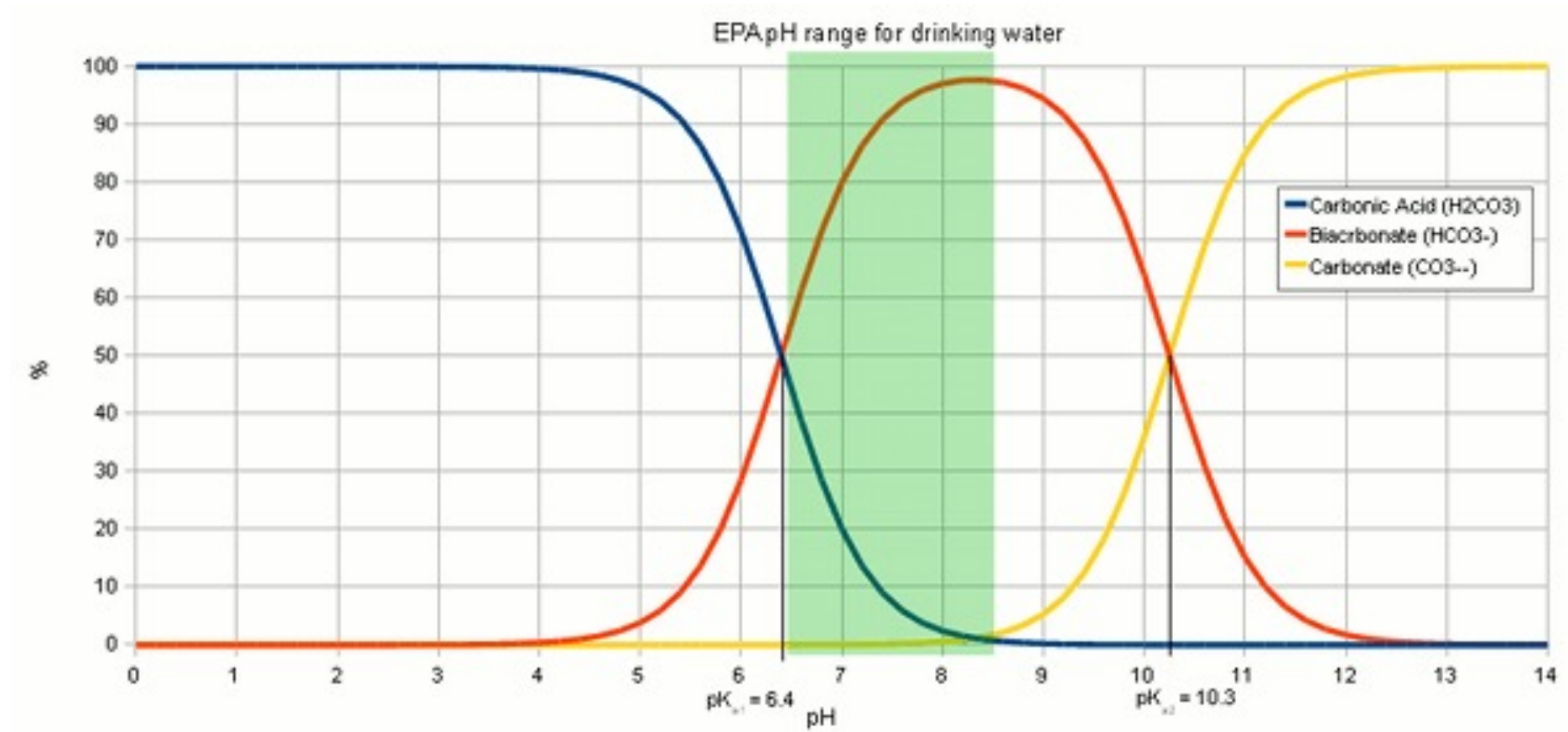
➤  $pK_1 = -\log K_1 = 6.3$

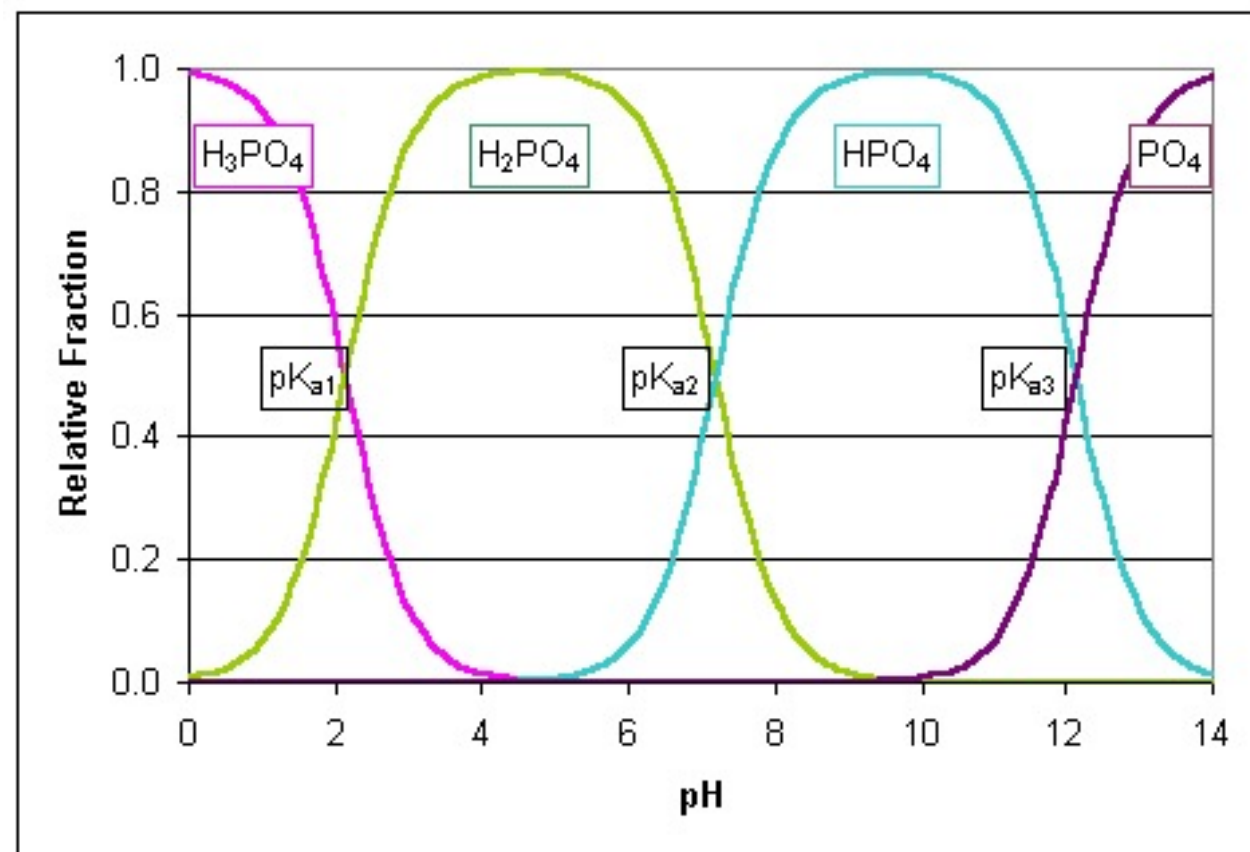
# Acidity Constants

Reaction	Name	K <sub>a</sub>	pK <sub>a</sub> = -log K <sub>a</sub>
$\text{HCl} = \text{H}^+ + \text{Cl}^-$	Hydrochloric	1000	-3
$\text{H}_2\text{SO}_4 = \text{H}^+ + \text{HSO}_4^-$	Sulfuric, H1	1000	-3
$\text{HNO}_3 = \text{H}^+ + \text{NO}_3^-$	Nitric	~1	~0
$\text{HSO}_4^- = \text{H}^+ + \text{SO}_4^{2-}$	Sulfuric, H2	$1 \times 10^{-2}$	2
$\text{H}_3\text{PO}_4 = \text{H}^+ + \text{H}_2\text{PO}_4^-$	Phosphoric, H1	$7.94 \times 10^{-3}$	2.1
$\text{HAc} = \text{H}^+ + \text{Ac}^-$	Acetic	$2.00 \times 10^{-5}$	4.7
$\text{H}_2\text{CO}_3 = \text{H}^+ + \text{HCO}_3^-$	Carbonic, H1	$5.01 \times 10^{-7}$	6.3
$\text{H}_2\text{S} = \text{H}^+ + \text{HS}^-$	Hydrosulfuric, H1	$7.94 \times 10^{-8}$	7.1
$\text{H}_2\text{PO}_4^- = \text{H}^+ + \text{HPO}_4^{2-}$	Phosphoric, H2	$6.31 \times 10^{-8}$	7.2
$\text{HOCl} = \text{H}^+ + \text{OCl}^-$	Hypochlorous	$3.16 \times 10^{-8}$	7.5
$\text{NH}_4^+ = \text{H}^+ + \text{NH}_3$	Ammonium	$5.01 \times 10^{-10}$	9.3
$\text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{2-}$	Carbonic, H2	$5.01 \times 10^{-11}$	10.3
$\text{HPO}_4^{2-} = \text{H}^+ + \text{PO}_4^{3-}$	Phosphoric, H3	$5.01 \times 10^{-13}$	12.3



## Speciation with pH

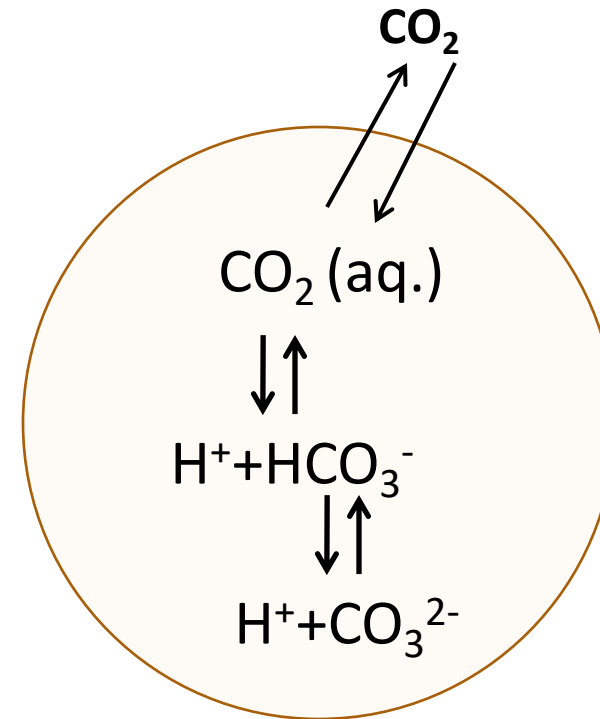




# Carbon dioxide -Water Interaction

The acidity imposed by carbon dioxide is referred as natural acidity.

Depending upon the solution pH, the carbonic acid (dissolved  $\text{CO}_2$ ) further dissociates into hydrogen ion and bicarbonate ion.



Bicarbonate ion can get further dissociated into hydrogen ion and carbonate ions.

# Steps in Solving chemical equilibria

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1. List all chemical species or elemental groupings that are likely to exist
  1. Cations:  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{+2}$ ,  $\text{NH}_4^+$ ,  $\text{H}^+$ , etc.
  2. Anions:  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{-2}$ ,  $\text{OH}^-$ ,  $\text{PO}_4^{-3}$ ,  $\text{HPO}_4^{-2}$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{Ac}^-$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{-2}$ , etc.
  3. Neutral species:  $\text{NH}_3$ ,  $\text{HAc}$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{CO}_3$ , etc.
  4. In this class we will typically deal with acids and bases reactions and some precipitation/dissolution reactions
  5. note that ionic salts (e.g.,  $\text{NaCl}$ ,  $\text{KCl}$ ) completely dissociate in water and thus should not be listed.
2. List all independent chemical equations that involve the species present, including:
  1. Chemical Equilibria
    - E.g., acid base equilibria
    - $\text{H}_2\text{CO}_3 \leftrightarrow \text{H}^+ + \text{HCO}_3^- \quad K_1 = \frac{[\text{H}^+] + [\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$
    - $\text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{2-} \quad K_2 = \frac{[\text{H}^+] + [\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$

# Steps in Solving chemical equilibria (contd.)

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2. List all independent chemical equations that involve the species present, including:
  1. Chemical Equilibria
  2. Mass Balance equations/component balance equations
    1. Total amount of each element is conserved
    2. E.g:  $C_{\text{carbonates}} = C_{\text{CO}_3\text{t}} = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$
3. Electro neutrality or charge balance
  1. All water solutions must be neutrally charged
  2. sum of positive charges = sum of negative charges
    1. In a solution with carbonates in waters and NaCl
    2.  $[\text{Na}^+] + [\text{H}^+] = [\text{OH}^-] + [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}] + [\text{Cl}^-]$

# Steps in Solving chemical equilibria (contd.)

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4. Solve the equations
  1. You need as many independent equations as chemical species
  2. Often it is easiest to solve for  $H^+$  and then use that concentration to calculate all other species

# Example

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Calculate the pH of a water droplet in equilibrium with the atmospheric carbon di oxide. Assume that there are no other species other than the carbonate species in the water. Assume carbon di oxide concentration in the atmosphere is 370 ppm, by mole basis.

➤ Relevant species are:

➤  $\text{H}^+$ ,  $\text{OH}^-$ ,  $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$  and  $\text{CO}_2(\text{g})$

➤ To solve quickly, you can neglect  $\text{CO}_3^{2-}$  if you can estimate the probable pH of the solution and compare it with  $\text{pK}_{\text{a}2}$  (10.3). Since  $\text{CO}_2$  ( $\text{H}_2\text{CO}_3$ ) is coming into contact with the solution, and there are no other species other than the carbonate species, the pH of the final solution will be slightly less than  $\text{pK}_{\text{a}1}$  (6.3).

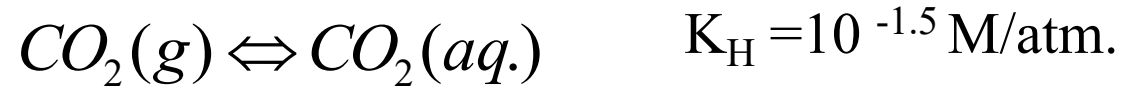
➤ Relevant equations are:

➤ Phase equilibrium (Henry's law)

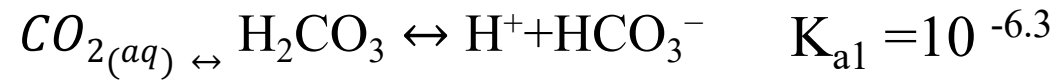
➤ Equilibrium constant for the acid base reactions

➤ Charge balance

## Carbon dioxide : Natural Acidity (cont'd)

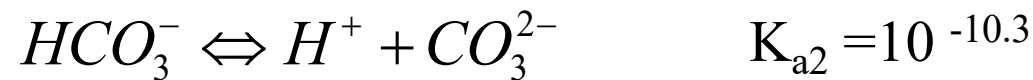


According to Henry's Law:  $[CO_2]_{aq} = K_H p_{CO_2} = 10^{-1.5} p_{CO_2}$



$$K_{a1} = \frac{[H^+][HCO_3^-]}{[CO_2]_{(aq.)}} = 10^{-6.3}$$

$$[HCO_3^-] = \frac{K_{a1}[CO_2]_{(aq.)}}{[H^+]} = \frac{10^{-6.3} * K_H p_{CO_2}}{[H^+]} = \frac{10^{-7.8} p_{CO_2}}{[H^+]}$$



$$K_{a2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 10^{-10.3}$$

$$[CO_3^{2-}] = \frac{K_{a2}[HCO_3^-]}{[H^+]} = \frac{10^{-10.3} * 10^{-7.8} p_{CO_2}}{[H^+]^2} = \frac{10^{-18.1} p_{CO_2}}{[H^+]^2}$$



## Carbon dioxide : Natural Acidity (cont'd)

**Charge Balance:** The sum of the equivalent concentration of cations is equal to the sum of equivalent concentration of anions.

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

Because for divalent ions,  
equivalent conc. = 2 X molar conc.

$$[H^+] = \frac{10^{-7.8} p_{CO_2}}{[H^+]} + 2 * \frac{10^{-18.1} p_{CO_2}}{[H^+]^2} + \frac{10^{-14}}{[H^+]}$$

In atmosphere, there is 370 ppm of carbon dioxide on mole basis.

$$p_{CO_2} = 370 * 10^{-6} \text{ atm.}$$

$$[H^+] = \frac{10^{-11.2}}{[H^+]} + 2 * \frac{10^{-21.5}}{[H^+]^2} + \frac{10^{-14}}{[H^+]}$$

Comparing 1<sup>st</sup> and 3<sup>rd</sup> term on the right hand side, 3<sup>rd</sup> term is at least 600 times smaller than 1<sup>st</sup> term. So, it can be neglected

$$[H^+] = \frac{10^{-11.2}}{[H^+]} + 2 * \frac{10^{-21.5}}{[H^+]^2}$$

For trial, if the pH is 6 or  $[H^+] = 10^{-6}$ , then left hand side and first term in the right hand side are dimensionally similar, whereas the last term is about 2000 times smaller than the other two terms. Hence, the last term can be neglected.

$$[H^+] = \frac{10^{-11.2}}{[H^+]} \quad [H^+]^2 = 10^{-11.2} \quad [H^+] = 10^{-5.6}$$

$$pH = -\log[H^+] = 5.6$$

In general, for rainwater containing only  $CO_2$  approximately,

$$[H^+]^2 \approx 10^{-6.3} * 10^{-1.5} * p_{CO_2}$$

**Find out the pH if the atmospheric CO<sub>2</sub> concentration is doubled.**

$$p_{\text{CO}_2} = 2 * 370 * 10^{-6} \text{ atm.} = 10^{-3.13}$$

$$[H^+] = \sqrt{10^{-6.3} * 10^{-1.5} * 10^{-3.13}}$$

$$pH = -\log[H^+] = 5.47$$

**This means that rise in atmospheric CO<sub>2</sub> concentration does not change the acidity of rain water by a significant amount**

pH?

For a can of carbonated drink,

$$p_{\text{CO}_2} = 5 \text{ atm.}$$

$$[H^+] = \sqrt{10^{-6.3} * 10^{-1.5} * 5}$$

$$pH = -\log[H^+] = 3.56$$



- If CO<sub>2</sub> is the only species that affects the rainwater's acidity, its natural pH is 5.6

- When additional acidic species are present at appreciable levels due to man-made activities, pH of rainwater becomes lower than 5.7 →

### **ACID RAIN**

- Major contributors to acid rain : H<sub>2</sub>SO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>



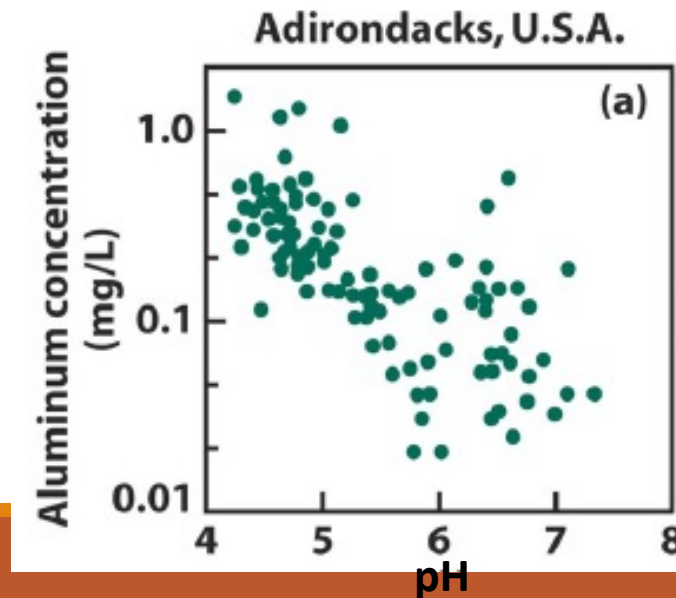
- Both substances are formed in the air
  - Precursor to H<sub>2</sub>SO<sub>4</sub>: SO<sub>2</sub>
  - Precursor to HNO<sub>3</sub>: NO<sub>2</sub>
- Concentrations of the precursors SO<sub>2</sub> and NO<sub>2</sub> are greatly increased by fossil fuel combustion.

# Effects of acid rain

- Acidification of surface water (lakes, rivers, etc), and subsequent damage to aquatic ecosystems.
  - kills aquatic plants, fish and microorganisms in lakes and streams by releasing ions of Al, Pb, Hg and Cd from soils and sediments.
- Damage to forests and vegetation
  - Weakens or kills trees, especially conifers at high elevations;
  - Makes trees more susceptible to diseases, insects, drought, and fungi and mosses that thrive under acidic conditions;
  - Stunts growth of crops such as tomatoes, soybeans, spinach, carrots, broccoli and cotton



60 years....





# Acid Rain: Cross-boundary Pollution

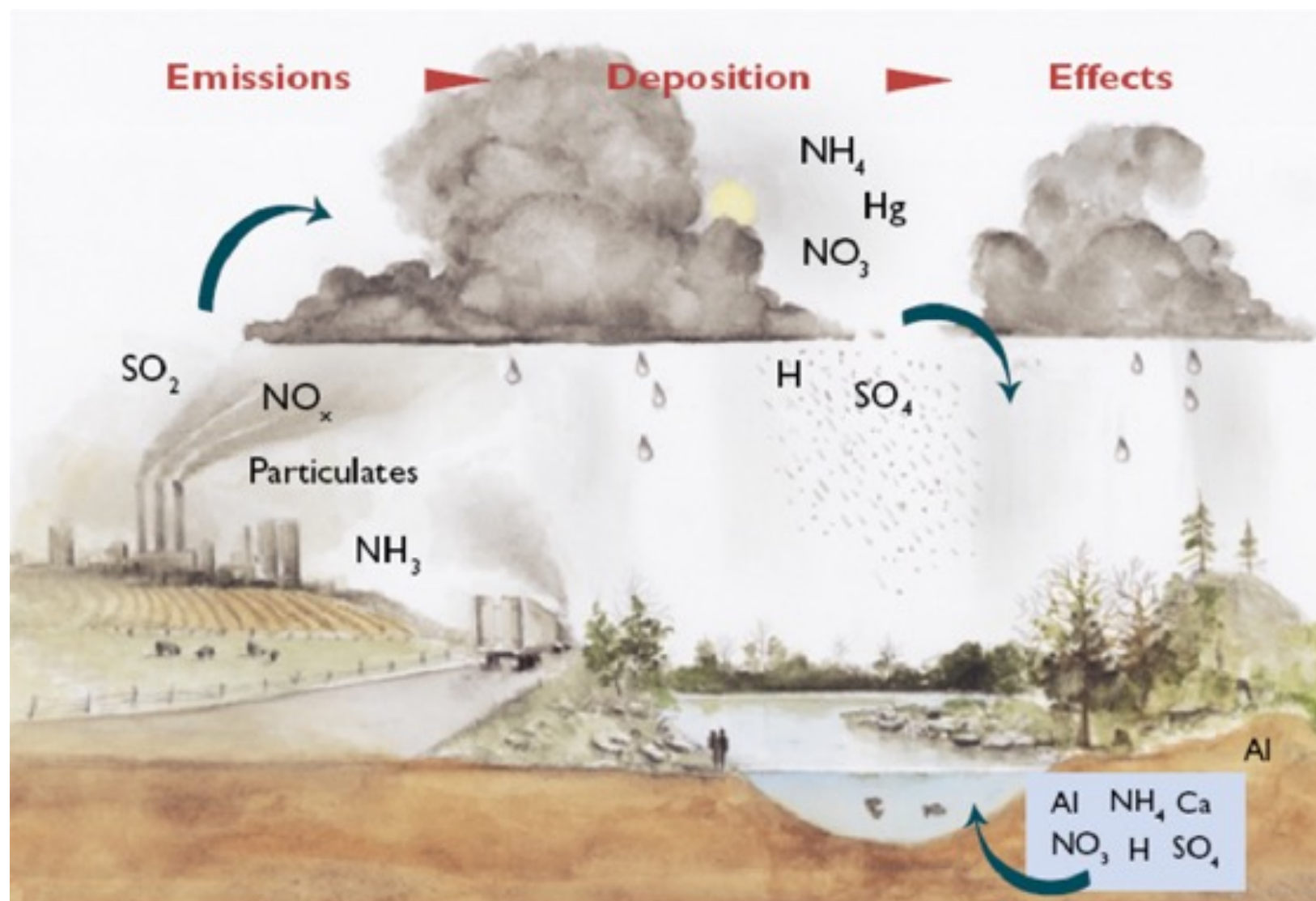
<http://nadp.sws.uiuc.edu/>

A large portion of  $\text{SO}_2$  and  $\text{NO}_2$  produced in one country is exported to others by prevailing surface winds.

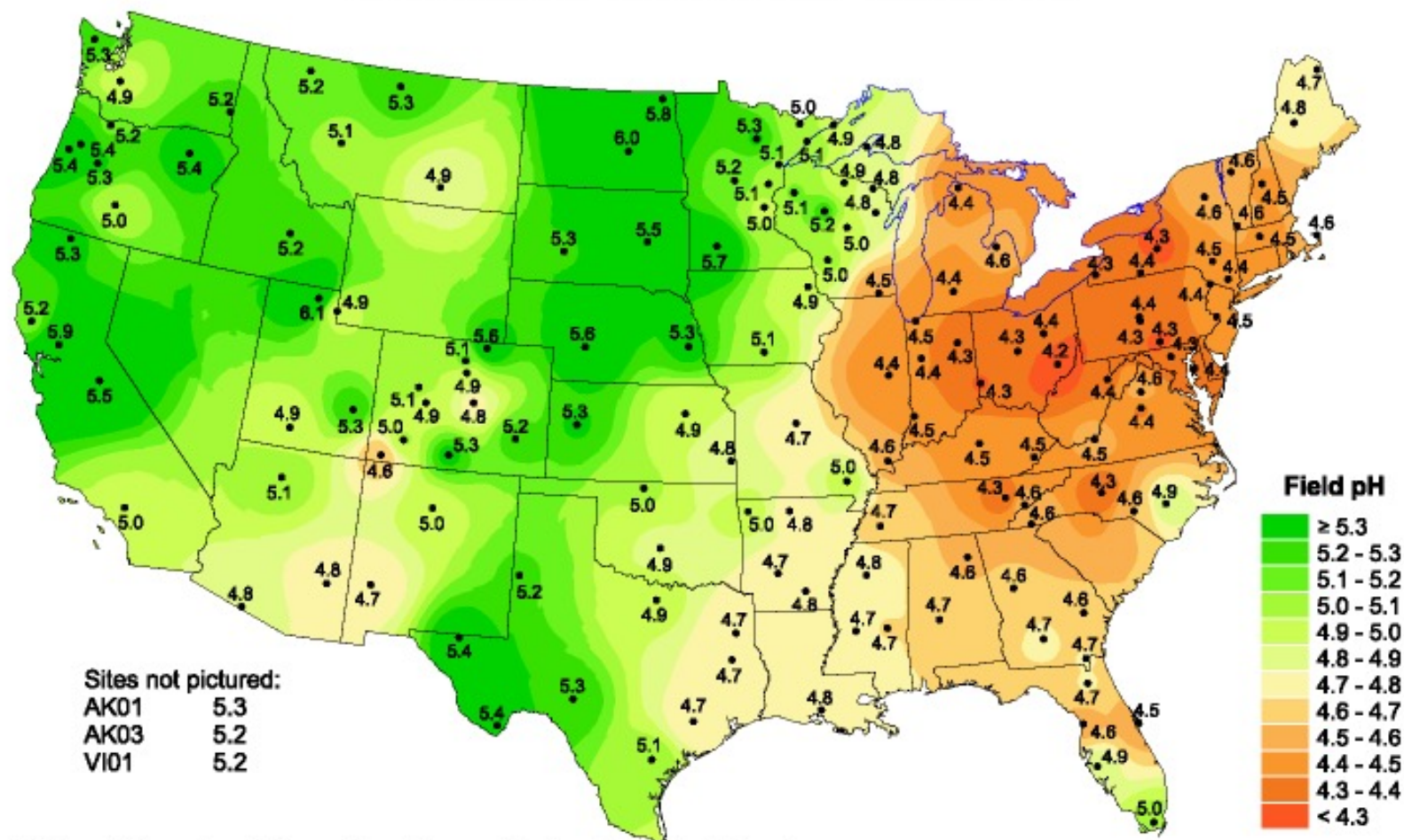
More than half the acid deposition in heavily populated southern Canada originates from seven central and upper midwestern states-Ohio, Indiana, PA, IL, Missouri, WV, and TN, where coal and oil-burning power and industrial plants are concentrated.



Regions of North America with low soil alkalinity



## Hydrogen ion concentration as pH from measurements made at the field laboratories, 1999



National Atmospheric Deposition Program/National Trends Network  
<http://nadp.sws.uiuc.edu>

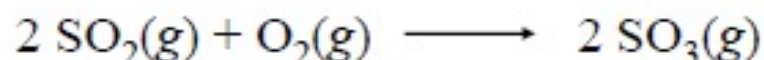


## The source and the cause of acid rain

Example:

The burning of coal.

Coal contains 1-3% sulfur



# Example

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Find out the pH of acid rain when the atmosphere has 5 ppb of  $\text{SO}_2$  along with 370 ppm of  $\text{CO}_2$  as discussed earlier.  $K_{\text{H}}$  for  $\text{SO}_2$  is  $10^{0.096}$  M/atm,  $K_{\text{a1}}=10^{-1.77}$ ;  $K_{\text{a2}}=10^{-7.21}$ . Assume that  $\text{SO}_{3(\text{g})}$  is not formed. Assume that there are no other species other than those that can be formed from  $\text{CO}_2$  and  $\text{SO}_3$ .

➤ Relevant species are:

➤  $\text{H}^+$ ,  $\text{OH}^-$ ,  $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{H}_2\text{SO}_3$ ,  $\text{HSO}_3^-$ ,  $\text{SO}_3^{2-}$  and  $\text{SO}_{2(\text{g})}$

➤ To solve quickly, you can neglect  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  if you can estimate the probable pH of the solution and compare it with  $\text{pK}_{\text{a1}}$  (6.3) and  $\text{pK}_{\text{a2}}$  (10.3) of the carbonate system. Since the  $\text{pK}_{\text{a1}}$  of  $\text{H}_2\text{SO}_3$  is -1.77, and  $\text{pK}_{\text{a1}}$  of  $\text{H}_2\text{CO}_3$  is 6.3, at the relevant concentrations considered here, the pH of the solution at equilibrium will be certainly less than 6.3. It should be slightly lesser than the pH of the earlier problem with only the carbonates. At this pH,  $\text{H}_2\text{SO}_3$  and  $\text{SO}_3^{2-}$  will be negligible ( $\text{pK}_{\text{a1}}$  of  $\text{H}_2\text{SO}_3 = 1.77$  and  $\text{pK}_{\text{a2}} = 7.21$ ).

➤ Relevant equations are:

➤ Phase equilibrium (Henry's law)

➤ Equilibrium constant for the acid base reactions

➤ Charge balance



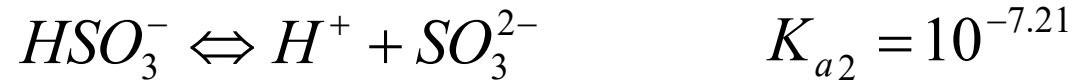
According to Henry's Law:  $[SO_2]_{aq} = K_H p_{SO_2} = 10^{0.096} p_{SO_2}$



$$K_{a1} = \frac{[H^+][HSO_3^-]}{[SO_2]_{(aq.)}} = 10^{-1.77}$$

$$[HSO_3^-] = \frac{K_{a1}[SO_2]_{(aq.)}}{[H^+]} = \frac{10^{-1.77} * K_H p_{SO_2}}{[H^+]} = \frac{10^{-1.674} p_{SO_2}}{[H^+]}$$

$$p_{SO_2} = 5 * 10^{-9} \text{ atm.} \quad [HSO_3^-] = \frac{10^{-1.674} p_{SO_2}}{[H^+]} = \frac{10^{-9.97}}{[H^+]}$$



$$K_{a2} = \frac{[H^+][SO_3^{2-}]}{[HSO_3^-]} = 10^{-7.21}$$

$$[SO_3^{2-}] = \frac{K_{a2}[HSO_3^-]}{[H^+]} = \frac{10^{-7.21} * 10^{-9.97}}{[H^+]^2} = \frac{10^{-17.18}}{[H^+]^2}$$

Applying charge balance:

$$[H^+] = [HCO_3^-] + [HSO_3^-] + 2[CO_3^{2-}] + 2[SO_3^{2-}] + [OH^-]$$

$$[H^+] = \frac{10^{-11.2}}{[H^+]} + \frac{10^{-9.97}}{[H^+]} + 2 * \frac{10^{-21.5}}{[H^+]^2} + 2 * \frac{10^{-17.18}}{[H^+]^2} + \frac{10^{-14}}{[H^+]}$$

With an initial guess of pH = 5, third, fourth and fifth terms on the RHS are found to be negligible compared to the other terms in the equation.

Therefore, considering only significant terms, the previous equation can be approximated as,

$$[H^+] = \frac{10^{-11.2}}{[H^+]} + \frac{10^{-9.97}}{[H^+]}$$

$$[H^+]^2 = 10^{-11.2} + 10^{-9.97} = 10^{-9.96}$$

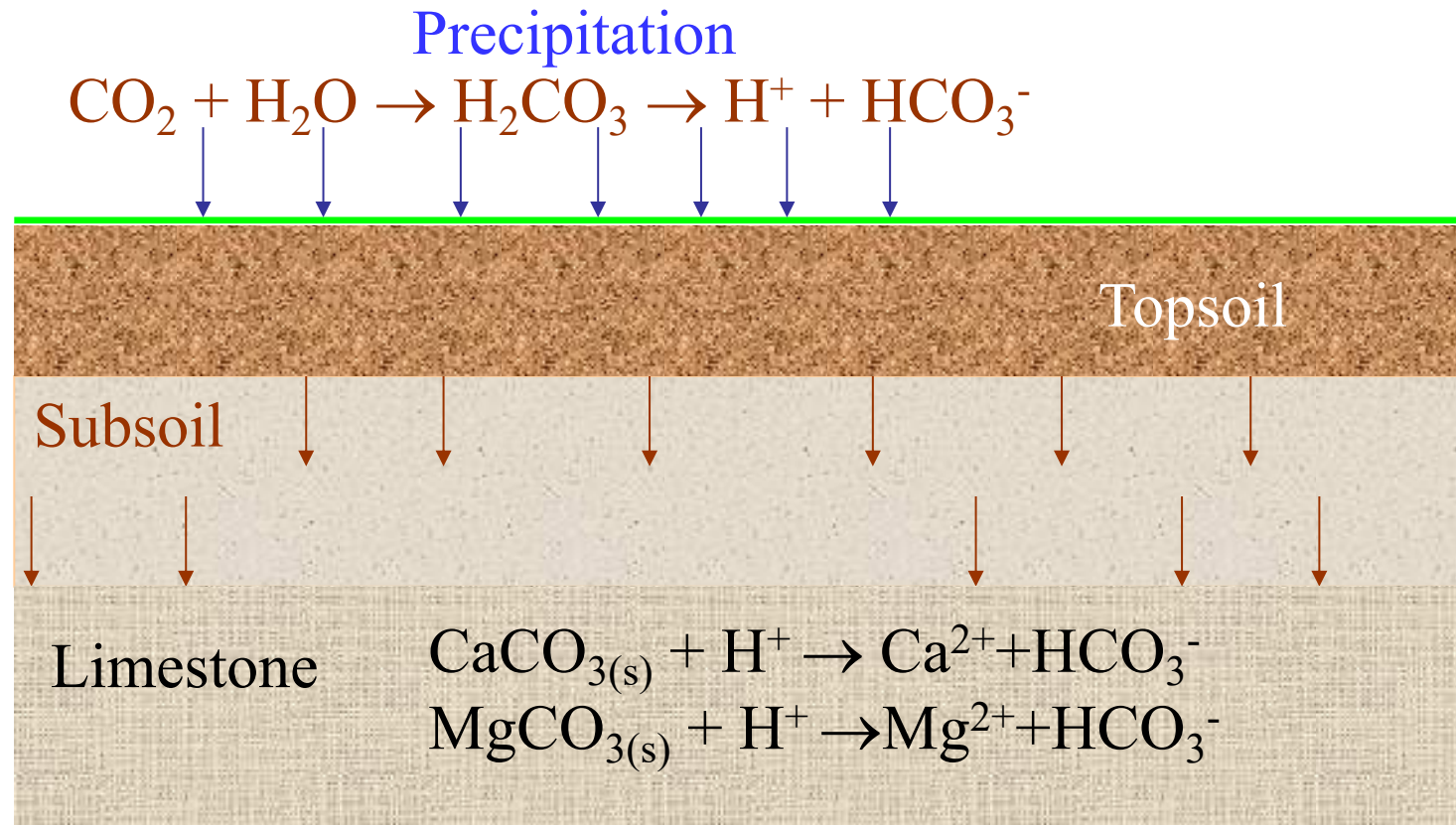
$$[H^+] = 10^{-4.98}$$

$$pH = -\log[H^+] = 4.98$$

We observe that the presence of trace amount  $SO_2$  can significantly alter the pH of the rainwater, the acid causing potential being more than carbon dioxide.

This is because  $pK_{a1}$  of  $H_2SO_3 \ll pK_{a1}$  of  $H_2CO_3$ .  $NO_x$  have the same effect as  $SO_x$  for imparting acidity to rainwater.

# SOIL-WATER INTERACTION



**Result: Mobilization of different ions in the groundwater from the minerals constituting the topsoil and subsoil**

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➤ Additional reactions here are the dissolution of  $\text{CaCO}_{3(s)}$  and  $\text{MgCO}_{3(s)}$

➤ **Dissolution = process of forming dissolved compounds from solid compounds (reverse of precipitation)**

➤ Example:

➤ For  $\text{CaCO}_{3(s)} \leftrightarrow \text{Ca}^{2+} + \text{CO}_3^{2-}$

➤ The relevant equilibrium constant for the above equation, also called the solubility product,  $K_{sp}$

➤ 
$$K_{sp, \text{caco3}} = \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{[\text{CaCO}_{3(s)}]}$$

➤ Concentration or activity of the solid, considering solid to be pure, is 1.

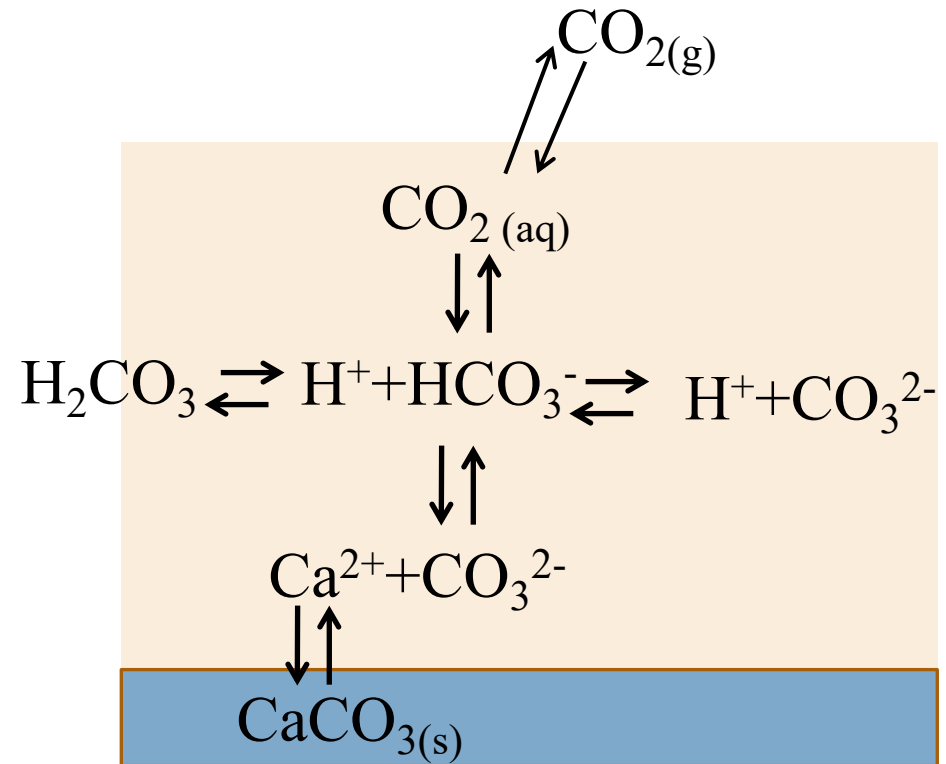
# Example

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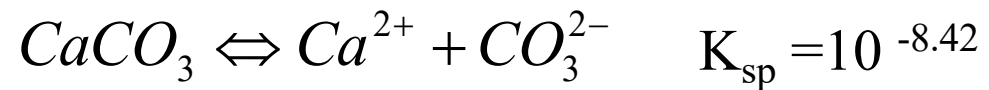
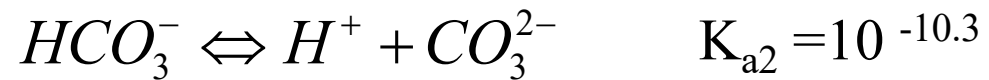
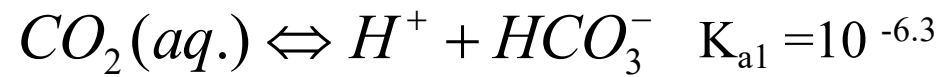
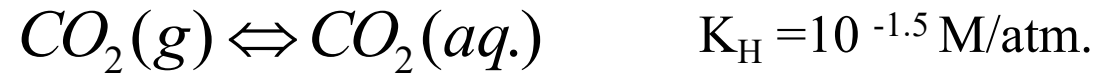
Rainwater falls on a soil surface and is under open atmosphere in contact with soil containing abundant amount of limestone (calcium carbonate). What will be the pH in this case?  $K_{sp}$  of calcium carbonate is  $10^{-8.42}$ . Assume instantaneous equilibrium for the dissolution, phase change and acid/base reactions. Assume there is infinite calcium carbonate. Assume that there are no other species other than those from the carbonate system and dissolution of limestone.



Three phases, gaseous, aqueous, and solid, are in equilibrium.



The relevant reactions, 1,2,3,4 are:



Applying charge balance on the species in the aqueous phase:

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

From equilibrium reactions relevant to reactions 1, 2 and 3

$$[\text{CO}_3^{2-}] = \frac{K_{a2}[\text{HCO}_3^-]}{[\text{H}^+]} = \frac{10^{-10.3} * 10^{-7.8} p_{\text{CO}_2}}{[\text{H}^+]^2} = \frac{10^{-18.1} p_{\text{CO}_2}}{[\text{H}^+]^2}$$

From solubility of calcium carbonate,

$$[\text{Ca}^{2+}] = \frac{K_{sp}}{[\text{CO}_3^{2-}]} = \frac{K_{sp}[\text{H}^+]^2}{10^{-18.1} p_{\text{CO}_2}} = \frac{10^{-8.42}[\text{H}^+]^2}{10^{-18.1} p_{\text{CO}_2}} = \frac{10^{9.68}[\text{H}^+]^2}{p_{\text{CO}_2}}$$

Hence,

$$2 * \frac{10^{9.68}[\text{H}^+]^2}{p_{\text{CO}_2}} + [\text{H}^+] = \frac{10^{-14}}{[\text{H}^+]} + \frac{10^{-7.8} p_{\text{CO}_2}}{[\text{H}^+]} + 2 * \frac{10^{-18.1} p_{\text{CO}_2}}{[\text{H}^+]^2}$$

$p_{\text{CO}_2}$  = pressure exerted by 370 ppm (by volume) gas =  $370 * 10^{-6}$  atm

$$2 * \frac{10^{9.68} [H^+]^2}{370 * 10^{-6}} + [H^+] = \frac{10^{-14}}{[H^+]} + \frac{10^{-7.8} * 370 * 10^{-6}}{[H^+]} + 2 * \frac{10^{-18.1} * 370 * 10^{-6}}{[H^+]^2}$$

$$10^{13.41} [H^+]^2 + [H^+] = \frac{10^{-14}}{[H^+]} + \frac{10^{-11.23}}{[H^+]} + \frac{10^{-21.23}}{[H^+]^2}$$

For a test case, let's consider that  $[H^+] = 10^{-7}$

$$10^{-0.59} + 10^{-7} = 10^{-7} + 10^{-4.23} + 10^{-7.23}$$

This means that only first term and second term in the equation is significant for obtaining an approximate solution.

$$10^{13.41} [H^+]^2 = \frac{10^{-11.23}}{[H^+]}$$

$$[H^+]^3 = 10^{-24.64}$$

$$[H^+] = 10^{-8.21}$$

$$\text{pH} = 8.21$$

$$[Ca^{2+}] = \frac{10^{9.68} [H^+]^2}{p_{CO_2}}$$

$$[H^+] = 10^{-8.21}$$

$$p_{CO_2} = 360 * 10^{-6} atm$$

$$[Ca^{2+}] = \frac{10^{9.68} [10^{-8.21}]^2}{360 * 10^{-6}} = 5.05 * 10^{-4} M \quad \Rightarrow \quad [Ca^{2+}] = 20 mg / L$$

This means that the rainwater which has a pH of 5.6, when it comes in contact with a limestone deposit on the surface, the water turns alkaline with pH of 8.2. The chemistry changes because of the dissolution of limestone into the water, releasing calcium and carbonate into the water. Carbonate adds to the alkalinity or the acid buffering capacity of water, increasing the pH.

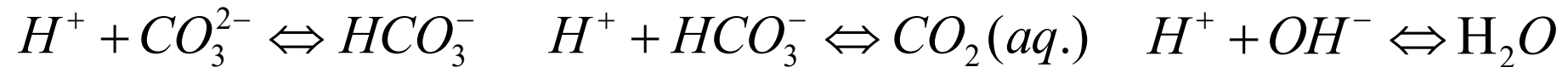
# Alkalinity

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Alkalinity is a measure of the acid neutralizing capacity of water. In other words, it measures the water's capability to neutralize the hydrogen ion, thus resisting decrease in the pH of the system.

What happens then to  $H^+$  ions added to the system?

The  $H^+$  ions would react with the components in water mainly,  $HCO_3^-$ ,  $CO_3^{2-}$  and  $OH^-$  according to the following reactions and would get consumed and will be unavailable for lowering the pH.



Typically, the summation of all those ions which can neutralize  $H^+$  is called alkalinity .

$$Alkalinity(meq / L) = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$$

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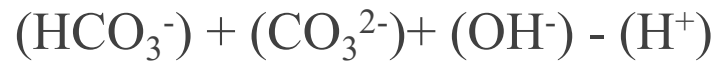
Alkalinity is essential to the aquatic eco system. Without it, the pH of the oceans will be more acidic, especially with the increasing CO<sub>2</sub> levels in the atmosphere.

# Alkalinity

In freshwaters, alkalinity is primarily due to the presence of bicarbonate salts

Alkalinity is always measured in units of equivalents/L or normality:

Total Alkalinity (in eq/L) =



where concentrations of the ions are given in units of eq/L.



# Alkalinity

Often we would rather use molar concentrations:

Total Alkalinity (in eq/L) =

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

where concentrations of the ions are given in units of mol/L or M.

Implicit in this is a conversion factor:

(1 equivalents/mol) for  $\text{HCO}_3^-$ ,  $\text{OH}^-$ ,  $\text{H}^+$

(2 equivalents/mol) for  $\text{CO}_3^{2-}$

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Alkalinity of a solution does not change when  $\text{CO}_2$  is bubbled through the solution. To understand this phenomena, the relevant equation of alkalinity can be analysed along with the relevant acid dissociation.

# Estimating Alkalinity

At pH values between 6 and 8

$(\text{H}^+) \approx (\text{OH}^-) \rightarrow$  terms cancel

Then: Alkalinity (meq/L)  $\approx (\text{HCO}_3^-) + (\text{CO}_3^{2-})$



$$\frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = 10^{-10.33}$$

$$\text{If pH} < 8 \text{ then } \frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} < 10^{-2.33}$$

Alkalinity (meq/L)  $\approx (\text{HCO}_3^-)$

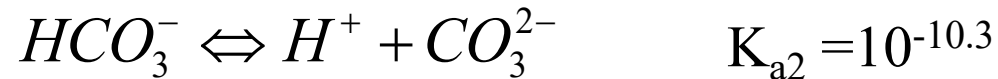
Note: this is true for pH between 6 and 8

# Example

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At equilibrium, a sample of water at pH 10 has 32 mg/L of  $\text{CO}_3^{2-}$ . Find the alkalinity of the water in the following units: eq/L as well as mg/L as  $\text{CaCO}_3$ .

$$32 \text{ mg/L of } \text{CO}_3^{2-} = \frac{32 * 10^{-3} \text{ g / L}}{60 \text{ g / mole}} = 0.53 * 10^{-3} \text{ M} = 10^{-3.27} \text{ M}$$



$$K_{a2} = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = 10^{-10.3}$$

$$[\text{HCO}_3^-] = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{K_{a2}} = \frac{10^{-10} * 10^{-3.27}}{10^{-10.3}} = 10^{-2.97}$$

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$$\text{Total Alkalinity (in eq/L)} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+]$$

$$= 10^{-2.97} + 2 \cdot 10^{-3.27} + 10^{-4} + 10^{-10}$$

$$= 2.246 \cdot 10^{-3}$$

$$= 2.2 \cdot 10^{-3} \text{ eq/L}$$

MW of  $\text{CaCO}_3$  = 100 g, and is divalent (Z=2). Thus its equivalent weight is 50 g.

$$\text{Alkalinity} = 2.246 \cdot 10^{-3} \text{ eq/L} \cdot 50 \text{ g of CaCO}_3/\text{eq} = 112.3 \text{ mg/L as CaCO}_3$$