

# Chemistry 2404 Forensic & Environmental Chemistry

## Lecture 18. Introduction to Aquatic Chemistry

### Lecture 19

- Ion Analysis
- Hydrolysis and Solubility

## Lecture 20. Solubility equilibria and CO<sub>2</sub>

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## Ion Analysis

In a mixed solution, we may wish to determine the individual concentrations of single cations or anions. E.g.

$\text{PO}_4^{3-}$  (e.g.; stagnant lake: eutrophication)

$\text{NO}_3^-$  (e.g.; groundwater contamination from fertiliser runoff)

$\text{F}^-$  (e.g.; municipal water supplies: dental health)

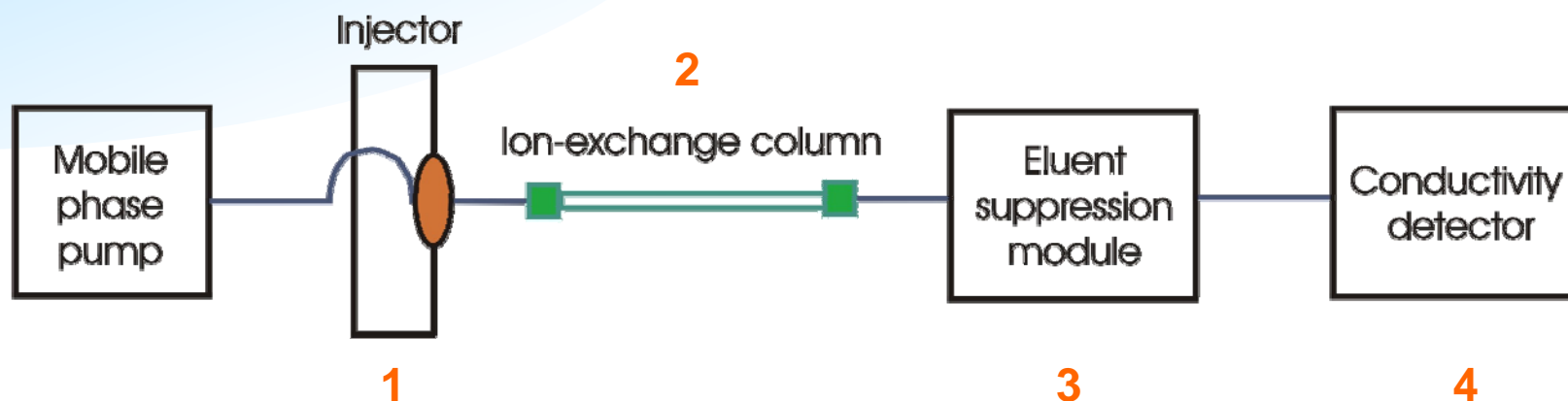
## Ion Chromatography

Short column: 10-15 cm packed with ion-exchange resin  
styrene/divinylbenzene polymer; or  
silica coated with compounds with a charged  
functional group:

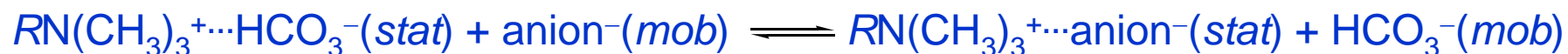
$-\text{N}(\text{CH}_3)_3^+$  (quarternary amine): anion-exchange

$-\text{SO}_3^-$  (sulfonate): cation-exchange  
(exchange of counterion)

# Ion Chromatography



- 1 Sample is introduced.
- 2 The retention time of the analyte is based upon the partition coefficient,  $K$ , defined by the [sample] in the stationary phase ( $C_s$ ) and mobile phase ( $C_m$ ).



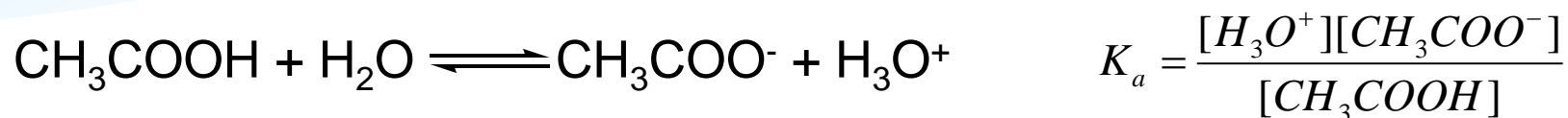
- 3 Mobile phase ions are converted into molecular forms that do not produce significant signals in detector (i.e.; if 1<sup>st</sup> column is anion-exchange, the eluent suppression module will be a cation-exchange resin).



- 4 Analyte ions are detected against a stable background by conductivity.

# Hydrolysis and Speciation

Weak acids and bases can exist in a variety of different chemical forms in solution. Consider the simple, monoprotic acid, acetic acid:-



This is an example of **chemical speciation**. Under different solution conditions (particularly pH in this case), acetic acid is present in its conjugate acid and conjugate base forms in different fractions, or ratios.

The fraction of acid is simply  $\alpha_{\text{CH}_3\text{COOH}} = \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COOH}] + [\text{CH}_3\text{COO}^-]} = \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COOH}]_T}$

The  $K_a$  expression allows us to write this as

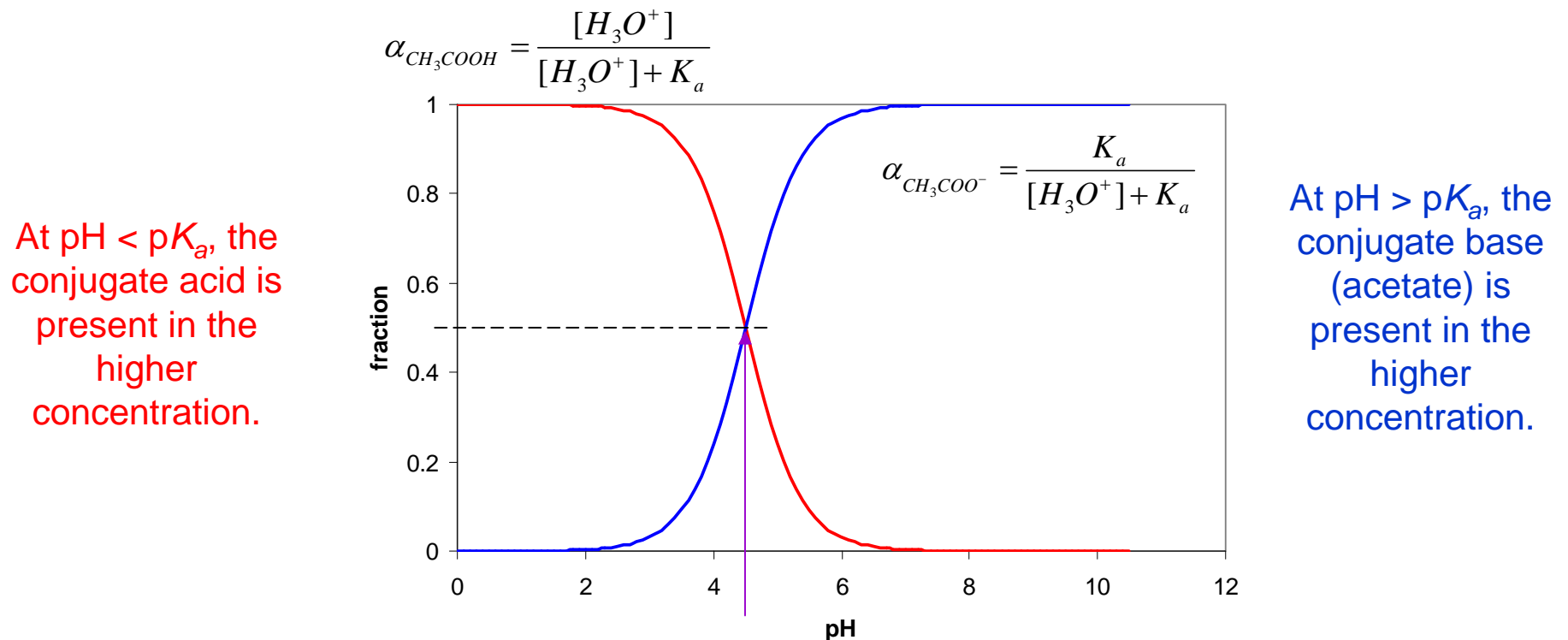
$$\alpha_{\text{CH}_3\text{COOH}} = \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COOH}] + \frac{K_a[\text{CH}_3\text{COOH}]}{[\text{H}_3\text{O}^+]}} = \frac{1}{1 + \frac{K_a}{[\text{H}_3\text{O}^+]}} = \frac{[\text{H}_3\text{O}^+]}{[\text{H}_3\text{O}^+] + K_a}$$

$$\text{and } \alpha_{\text{CH}_3\text{COO}^-} = 1 - \alpha_{\text{CH}_3\text{COOH}} = 1 - \frac{[\text{H}_3\text{O}^+]}{[\text{H}_3\text{O}^+] + K_a} = \frac{K_a}{[\text{H}_3\text{O}^+] + K_a}$$

Forget the specific equations. **The fractions of conjugate acid and conjugate base only depend on pH.**

# Hydrolysis and Speciation

We can plot this as a speciation diagram, showing fractions of the two species. Speciation diagrams clearly identify which of the various chemical species formed will be present at the highest concentration under given conditions (here, pH), and therefore which are most important in determining the observed chemistry.



Note that when  $[H_3O^+] = K_a$ , or pH = pK<sub>a</sub>, the fractions of both species are equal, and equal to 0.5.

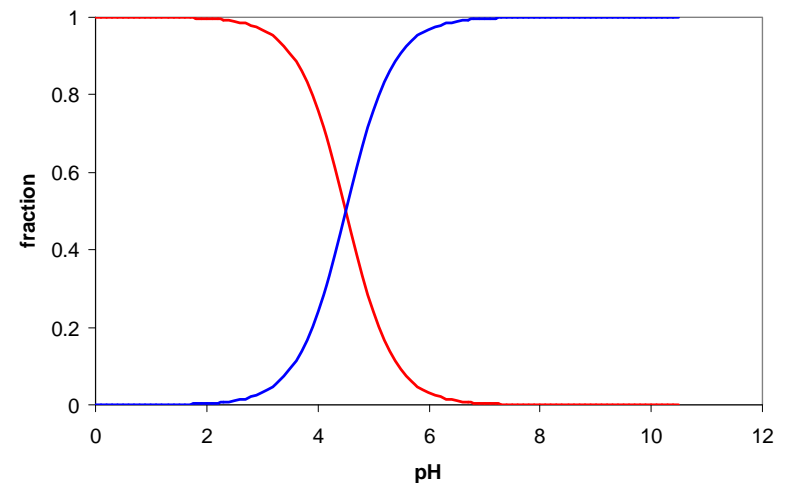
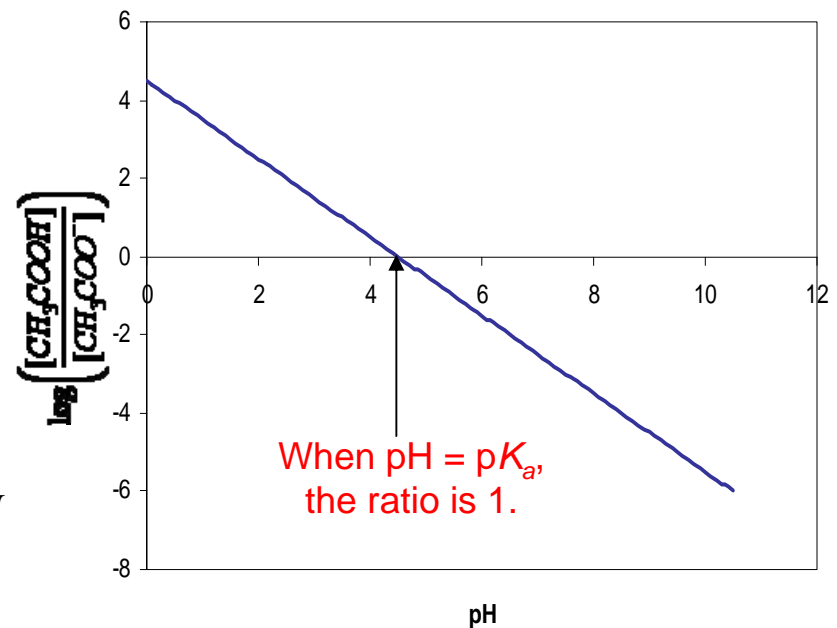
# Hydrolysis and Speciation

The **ratio** of conjugate acid to conjugate base can be derived simply from the  $K_a$  expression:

$$\frac{[CH_3COOH]}{[CH_3COO^-]} = \frac{[H_3O^+]}{K_a}$$

or  $\log\left(\frac{[CH_3COOH]}{[CH_3COO^-]}\right) = pK_a - pH$

A feature common to hydrolysis speciation is that the concentration **ratios** of two different species are **straight lines** as a function of pH on a logarithmic plot.



# Hydrolysis and Speciation

We will see this behaviour numerous times in aquatic systems, usually with polyprotic acids. The general properties are the same, but the algebra is more complex as it involves multiple hydrolysis equilibria. E.g.

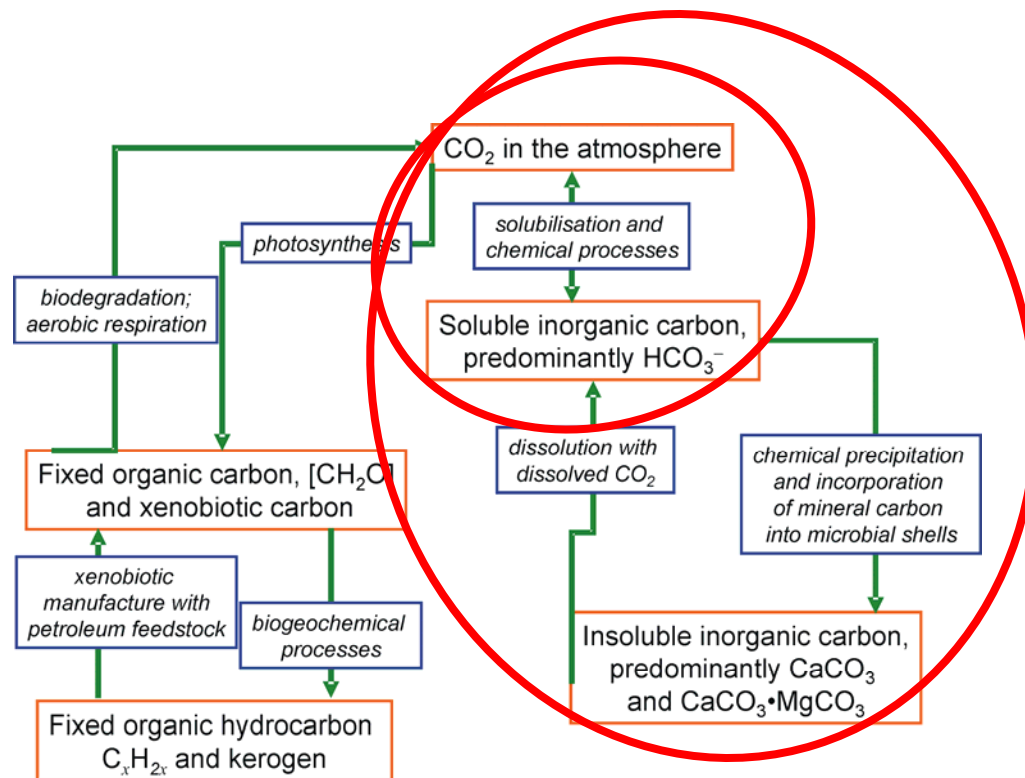
- Hydrolysable metal ions:  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Zn}^{2+}$ ...
- Acidic gases:  $\text{H}_2\text{S}$ ,  $\text{CO}_2$ ,  $\text{HNO}_2$ , ...
- Organic acids and chelating agents:  $\text{H}_4\text{EDTA}$ ,  $\text{H}_3\text{NTA}$ , citric acid...
- Phosphates and silicates:  $\text{H}_3\text{PO}_4$ ,  $\text{H}_4\text{SiO}_4$

Speciation in these systems will be explored on a case-by-case basis, beginning with  $\text{CO}_2$ .

# Carbon Dioxide in Water

Phenomena of carbonate system:

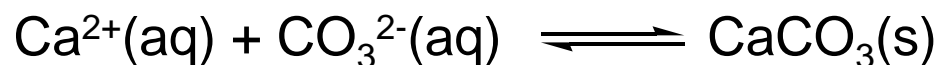
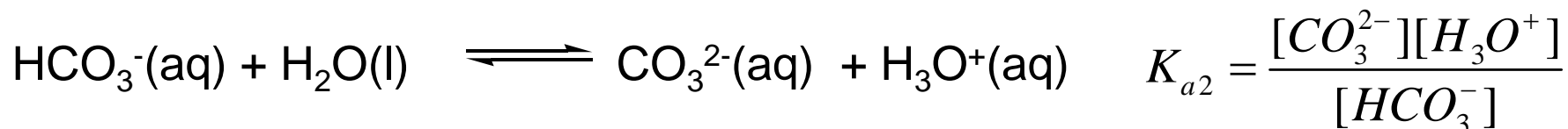
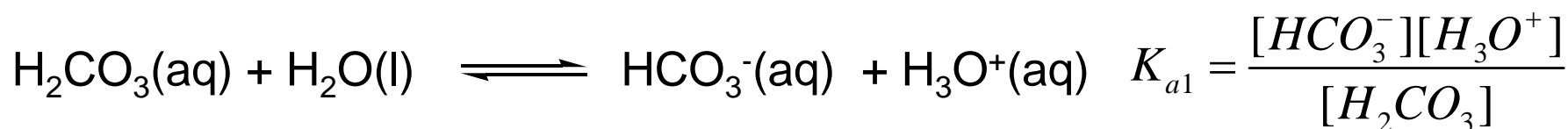
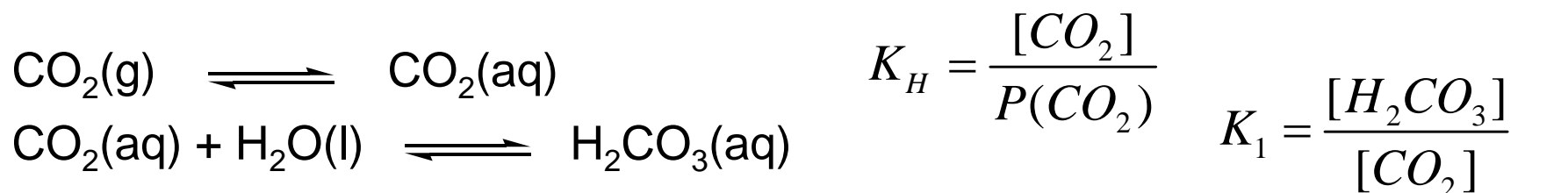
- Dissolution of  $\text{CO}_2(g)$  in water to give  $\text{CO}_2(aq)$  (Henry's Law)
- Acid-Base reactions of  $\text{CO}_2(aq)$
- Solubility and precipitation of  $\text{CaCO}_3(s)$





# Carbon Dioxide in Water

We can express these processes as a series of chemical reactions and their associated equilibria

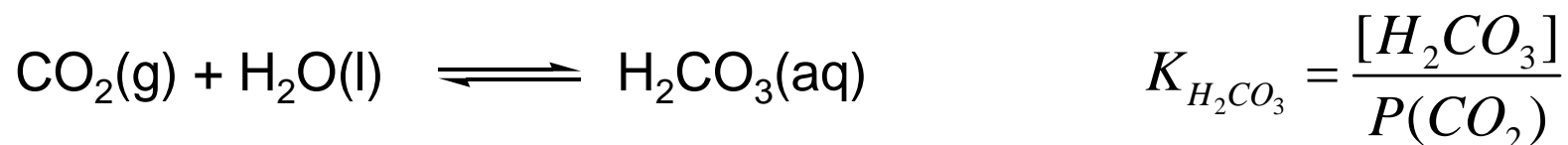


We'll assume there is *no*  $\text{Ca}^{2+}$  to start with, and ignore this equilibrium... for now.

Qualitative and quantitative understanding of aquatic systems requires us to handle multiple equilibria.

# Carbon Dioxide Dissolution in Water

It's conventional to combine the dissolution of gaseous  $\text{CO}_2$  with its reaction with water as a single equilibrium expression, viz,



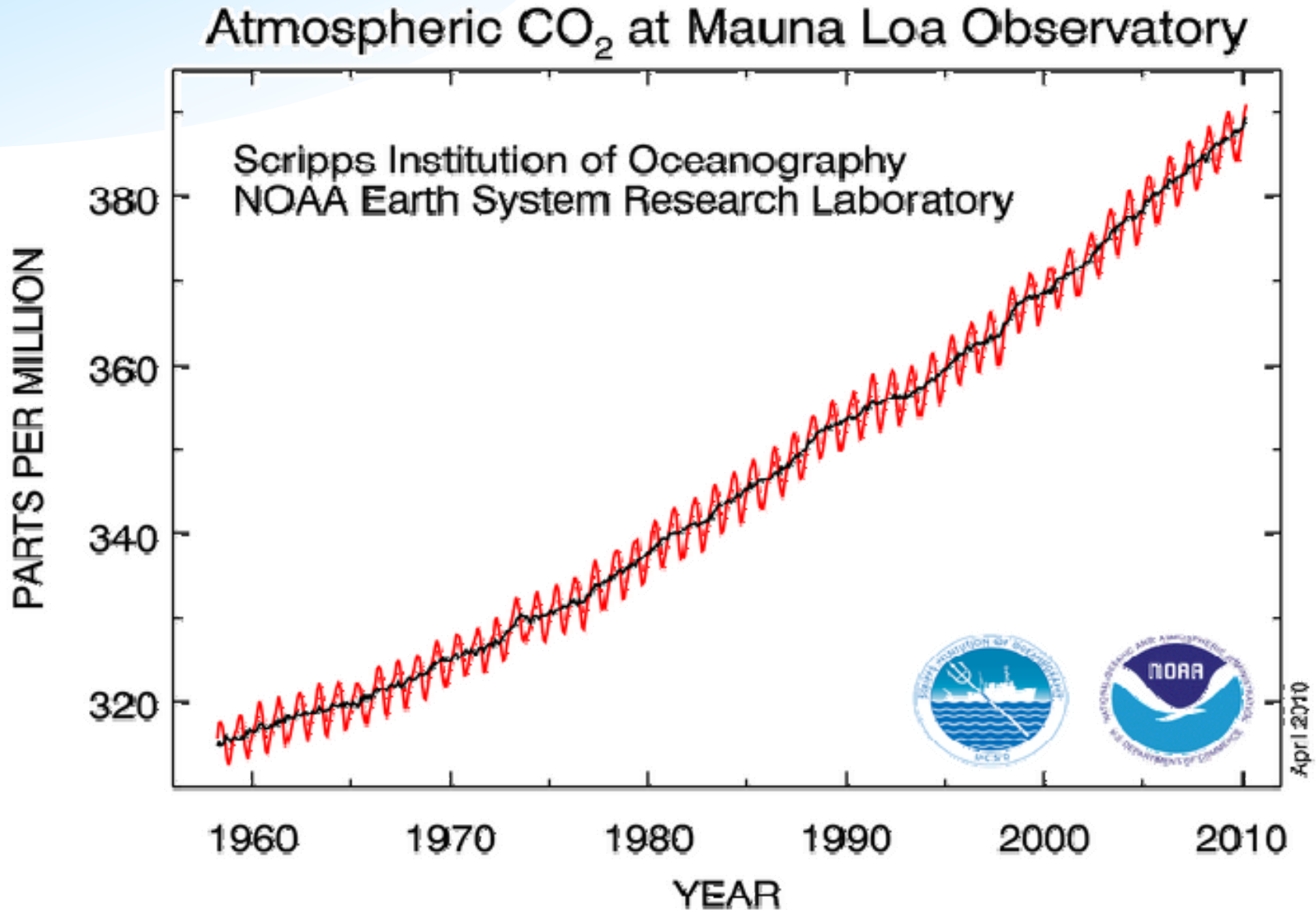
$\text{H}_2\text{CO}_3$  can just be regarded as hydrated  $\text{CO}_2$ . Both equilibria are forms of Henry's Law, relating the total amount of  $\text{CO}_2$  in the gas phase and in solution,

$$[\text{X}](\text{aq}) = k_{\text{H}} \times P(\text{X})$$

The Henry's law constant for  $\text{CO}_2$  dissolved in water is  $k_{\text{H}} = 3.3 \times 10^{-2} \text{ mol L}^{-1} \text{ atm}^{-1}$  at 25 °C – and we won't worry about whether we call it  $\text{CO}_2$  or  $\text{H}_2\text{CO}_3$ .

Henry's Law thus tells us that the solubility of  $\text{CO}_2$  (and concentration of  $\text{H}_2\text{CO}_3$ ) depends linearly on its partial pressure.

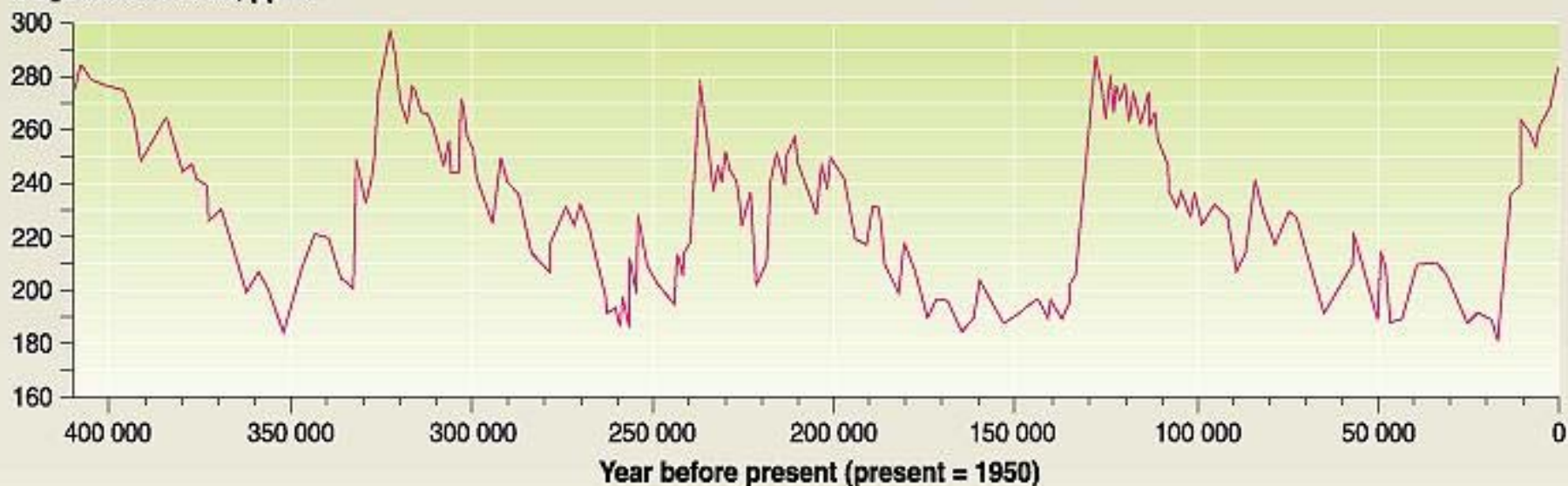
# CO<sub>2</sub> Atmospheric Levels



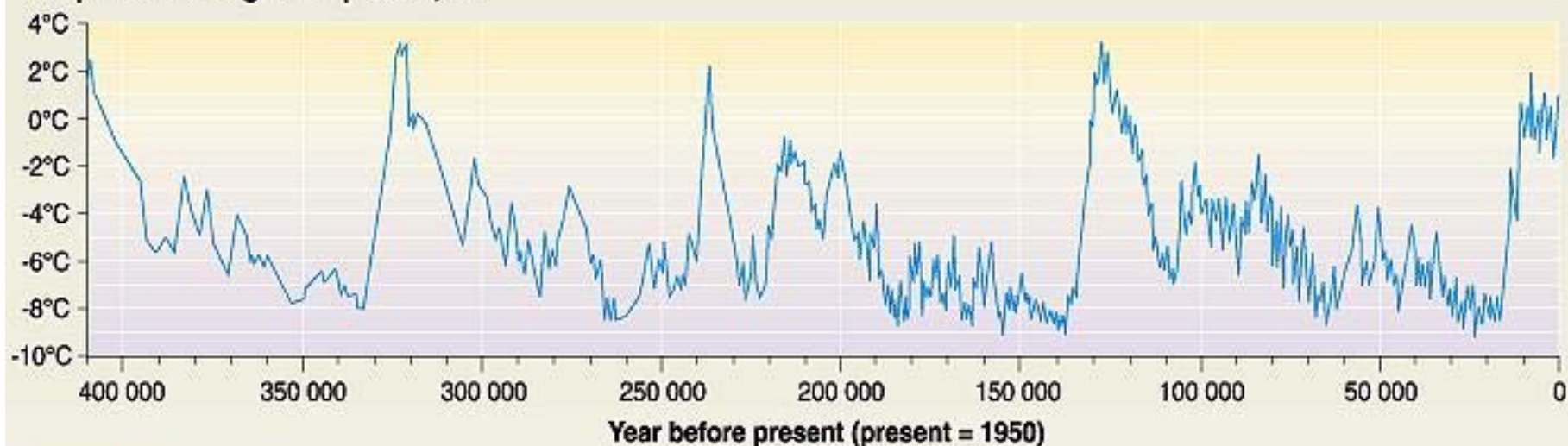
Keeling, C.D. and T.P. Whorf. 2005. Atmospheric CO<sub>2</sub> records from sites in the SIO air sampling network. In *Trends: A Compendium of Data on Global Change*. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tenn., U.S.A. [http://www.esrl.noaa.gov/gmd/ccgg/trends/#mlo\\_full](http://www.esrl.noaa.gov/gmd/ccgg/trends/#mlo_full)

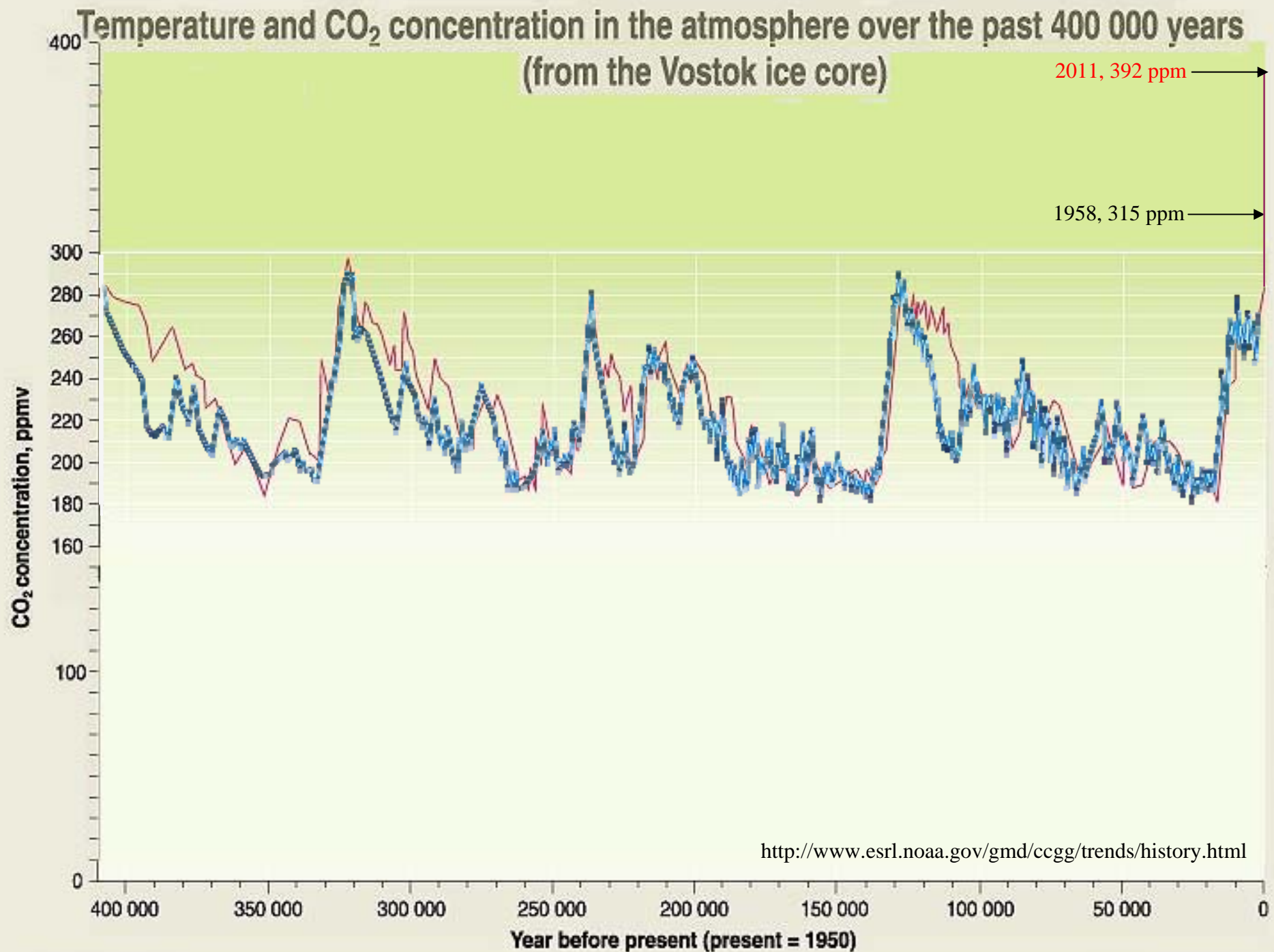
## Temperature and CO<sub>2</sub> concentration in the atmosphere over the past 400 000 years (from the Vostok ice core)

CO<sub>2</sub> concentration, ppmv



Temperature change from present, °C





Source: J.R. Petit, J. Jouzel, et al. Climate and atmospheric history of the past 420 000 years from the Vostok ice core in Antarctica, Nature 399 (3June), pp 429-436, 1999.



# Carbon Dioxide Dissolution in Water

Assume that the concentration of atmospheric CO<sub>2</sub> is 390 ppm. Its partial pressure is thus  $390 \times 10^{-6}$  atm or 0.000390 atm. (ppm for gas is v/10<sup>6</sup> v)

$$\begin{aligned}\text{Therefore, } [\text{CO}_2(\text{aq})] \text{ at } 25^\circ\text{C} &= k_{\text{H}} \times P(\text{CO}_2) \\ &= 3.4 \times 10^{-2} \text{ mol L}^{-1} \text{ atm}^{-1} \times 0.000390 \text{ atm} \\ &= 1.29 \times 10^{-5} \text{ mol L}^{-1}.\end{aligned}$$

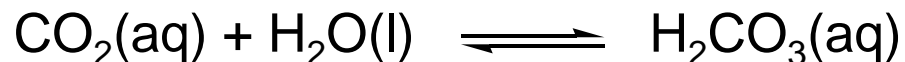
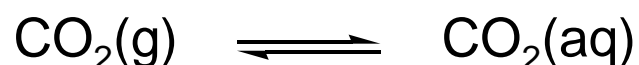
That is, the concentration of H<sub>2</sub>CO<sub>3</sub>(aq) is *fixed* by the partial pressure of atmospheric CO<sub>2</sub>.

The dissolved H<sub>2</sub>CO<sub>3</sub> can then undergo one or more acid-dissociation reactions, forming HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>, and this affects

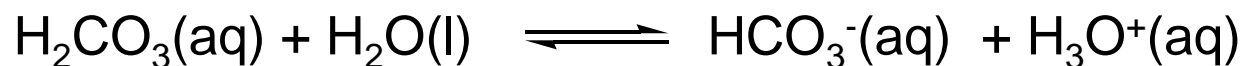
- the pH of aquatic solutions
- the total amount of dissolved CO<sub>2</sub> in all its forms,
- but the concentration of H<sub>2</sub>CO<sub>3</sub> is a constant at all pHs.

# Carbon Dioxide in Water

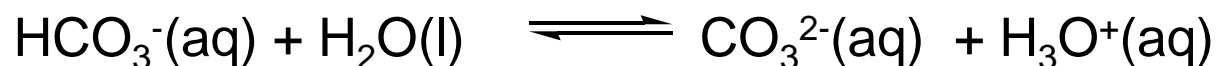
The equations controlling CO<sub>2</sub> gas solubility and hydrolysis equilibria are



$$K_H = \frac{[\text{H}_2\text{CO}_3]}{P(\text{CO}_2)} = 3.3 \times 10^{-2}$$



$$K_{a1} = \frac{[\text{HCO}_3^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{CO}_3]} = 4.45 \times 10^{-7}$$



$$K_{a2} = \frac{[\text{CO}_3^{2-}][\text{H}_3\text{O}^+]}{[\text{HCO}_3^-]} = 4.69 \times 10^{-11}$$

Most dissolved CO<sub>2</sub> exists as CO<sub>2</sub>(aq), not H<sub>2</sub>CO<sub>3</sub>. Accounts for low acidity: pK<sub>a1</sub> = 6.35, not pK 2-3 as predicted by Pauling's Rule

# Pauling's Rules for Oxo Acids

- For oxoacid  $\text{O}_x\text{E}(\text{OH})_y$ ,  $\text{pK}_a = 7 - 5x$ , and successive  $\text{pK}_a$ 's differ by 5
- $\text{H}_3\text{PO}_4$  ( $x = 1$ ,  $y = 3$ )  $\text{pK}_a$  (pred) = 2, obs = 2, then  $\text{pK}_{a2} = 7$  and  $\text{pK}_{a3} = 12$
- $\text{H}_2\text{SO}_4$  ( $x = 2$ ,  $y = 2$ )  $\text{pK}_a$  (pred) = -3, obs = <0,  $\text{pK}_{a2} = 2$ , as observed for  $\text{HSO}_4^-$
- $\text{HOCl}$  ( $x = 0$ )  $\text{pK}_a$  (pred) = 7, obs = 7.5
- doesn't work for  $\text{H}_2\text{CO}_3$   $\text{pK}_a$  (pred) = 2, obs = 6.5; evidence for  $\text{CO}_2(\text{aq})$ , not  $\text{H}_2\text{CO}_3$



## Summary

You should now be able to

- Describe the operation of Ion Chromatography
- Calculate the fractions of various chemical species present in a solution from appropriate data, and plot a speciation diagram.
- Determine which is the dominant species from a speciation diagram or other suitable data.
- Use Henry's Law to calculate the concentration of a dissolved gas such as  $\text{N}_2$ ,  $\text{O}_2$  or  $\text{CO}_2$ .

## Next Lecture

Carbon dioxide and carbonate speciation.

# Practice/Review problems

1. In what pH range would you expect the benzoate ion to be the dominant chemical species of an aqueous solution of benzoic acid? ( $\text{pK}_a = 4.2$ )
2. Calculate (a) the fraction of benzoic acid present in its acidic form, and (b) ratio of benzoic acid to benzoate ion at  $\text{pH} = 7$ .
3. Calculate the concentration of dissolved  $\text{CO}_2$  that would have existed about 10,000 years ago, when the atmospheric concentration was 270 ppm. (The ice age was over – assume a modern temperature for your calculation.)