

Chemistry 2404 Forensic & Environmental Chemistry

Lecture 18. Introduction to Aquatic Chemistry

Lecture 19

- Ion Analysis
- Hydrolysis and Solubility

Lecture 20. Solubility equilibria and CO₂

COMMONWEALTH OF AUSTRALIA

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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.

PO_4^{3-} (e.g.; stagnant lake: eutrophication)

NO_3^- (e.g.; groundwater contamination from fertiliser runoff)

F^- (e.g.; municipal water supplies: dental health)

Ion Chromatography

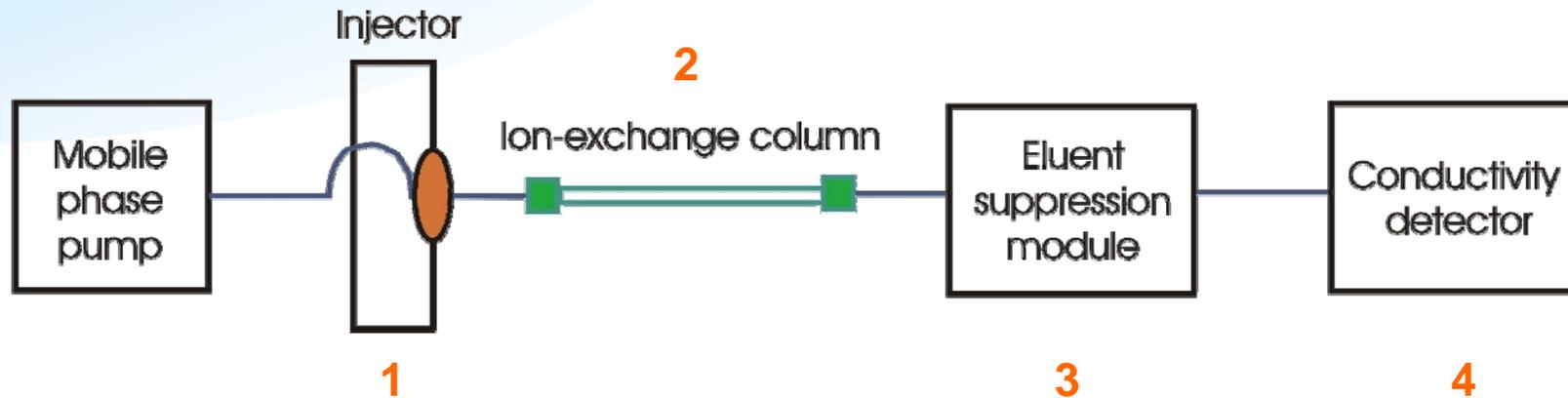
Short column: 10-15 cm packed with ion-exchange resin
styrene/divinylbenzene polymer; or
silica coated with compounds with a charged
functional group:

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

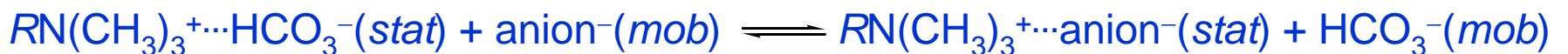
$-\text{SO}_3^-$ (sulfonate): cation-exchange

(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).



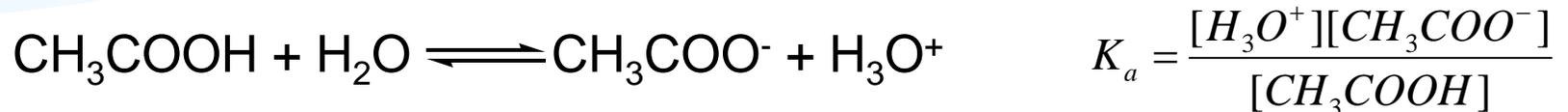
- 3 Mobile phase ions are converted into molecular forms that do not produce significant signals in detector (i.e.; if 1st column is anion-exchange, the eluent suppression module will be a cation-exchange resin).



- 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 $\alpha_{\text{CH}_3\text{COOH}} = \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COOH}] + [\text{CH}_3\text{COO}^-]} = \frac{[\text{CH}_3\text{COOH}]_T}{[\text{CH}_3\text{COOH}]_T}$

The K_a expression allows us to write this as

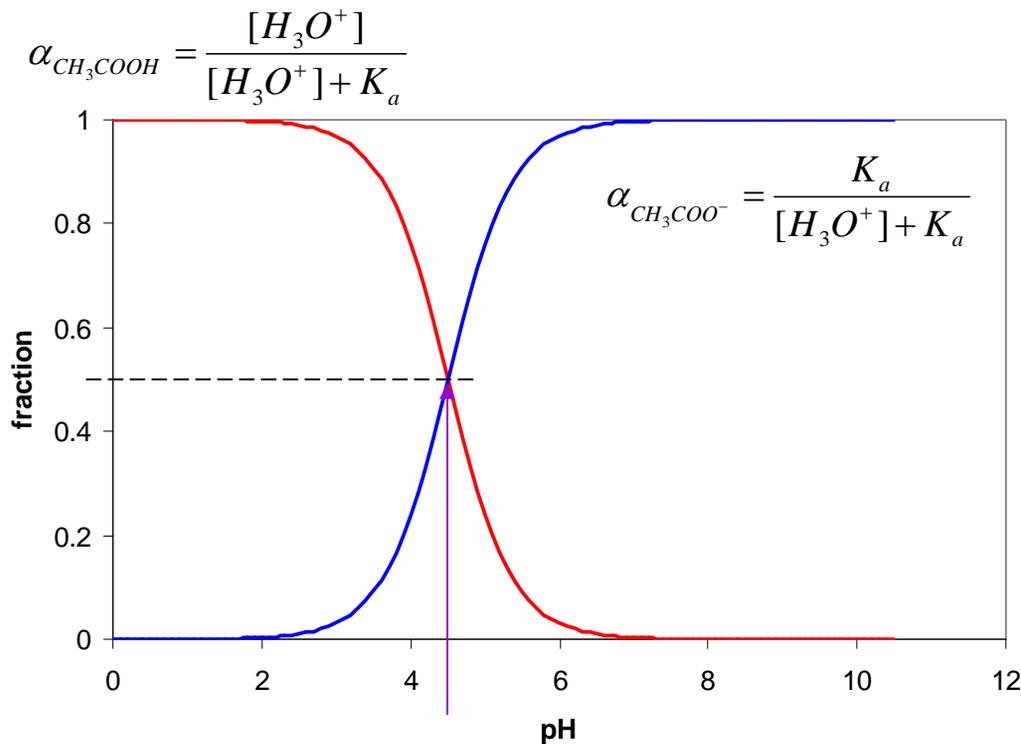
$$\alpha_{\text{CH}_3\text{COOH}} = \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COOH}] + \frac{K_a[\text{CH}_3\text{COOH}]}{[\text{H}_3\text{O}^+]}} = \frac{1}{1 + \frac{K_a}{[\text{H}_3\text{O}^+]}} = \frac{[\text{H}_3\text{O}^+]}{[\text{H}_3\text{O}^+] + K_a}$$

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.



At $pH < pK_a$, the conjugate acid is present in the higher concentration.

At $pH > pK_a$, the conjugate base (acetate) is present in the higher concentration.

Note that when $[H_3O^+] = K_a$, or $pH = pK_a$, the fractions of both species are equal, and equal to 0.5.

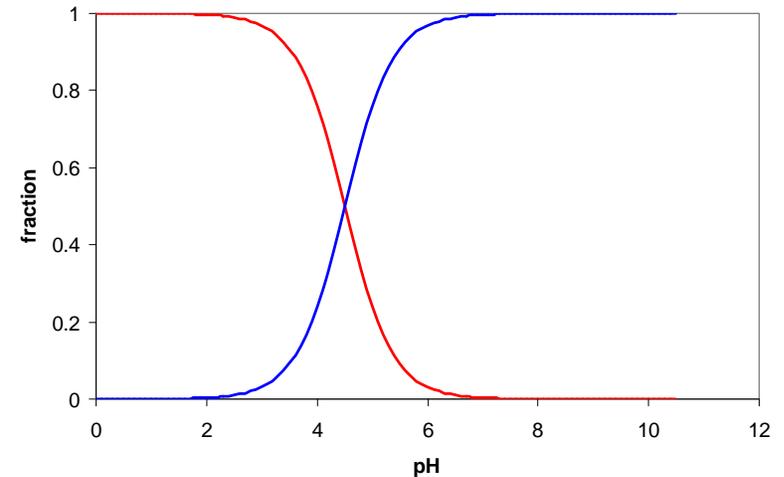
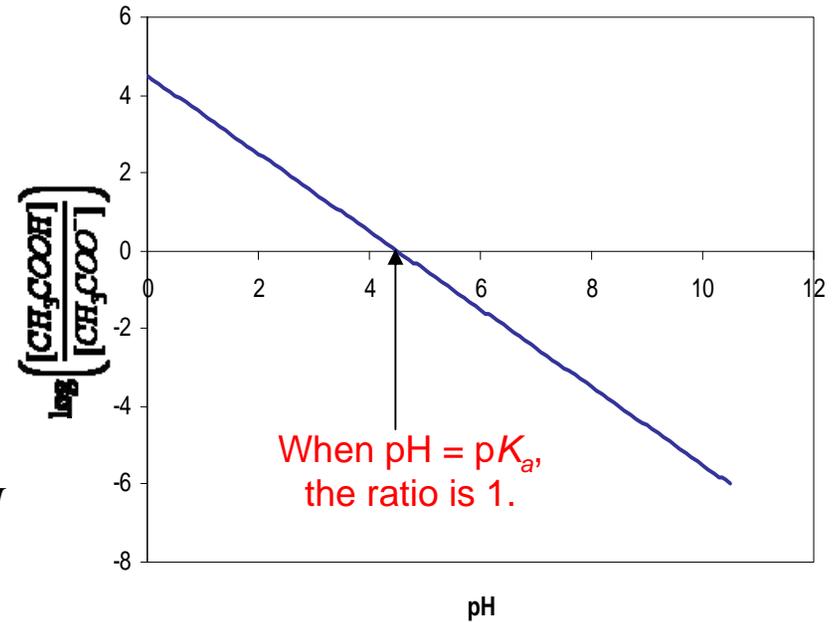
Hydrolysis and Speciation

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.

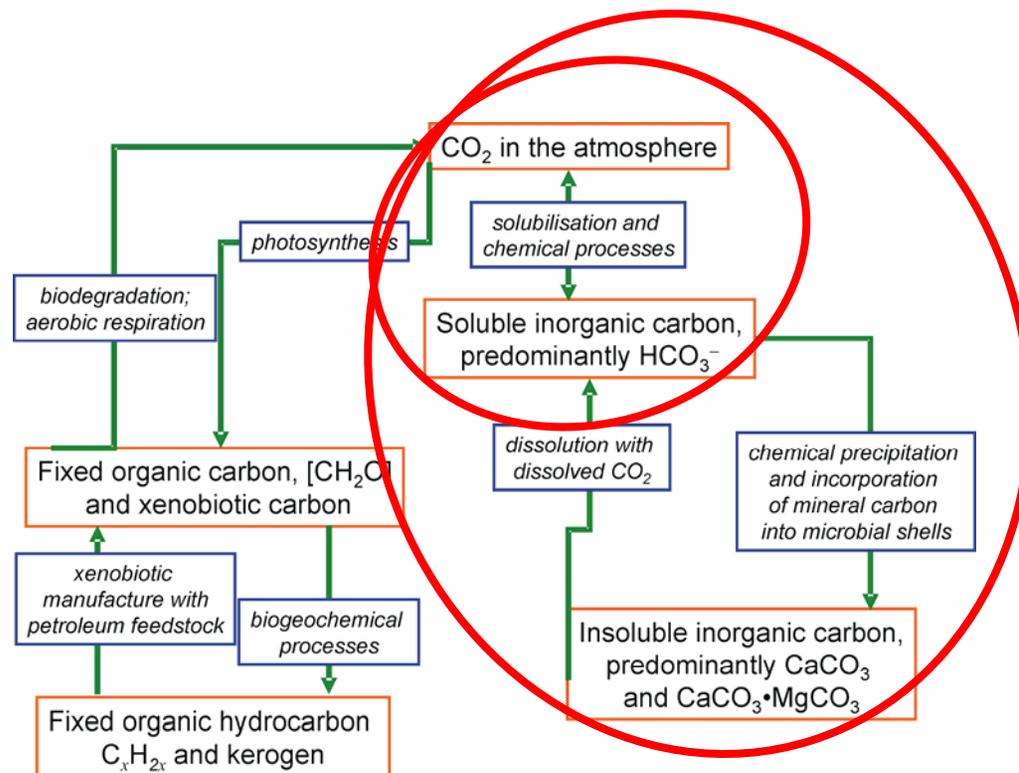
- Hydrolysable metal ions: Al^{3+} , Fe^{3+} , Fe^{2+} , Zn^{2+} ...
- Acidic gases: H_2S , CO_2 , HNO_2 , ...
- Organic acids and chelating agents: H_4EDTA , H_3NTA , citric acid...
- Phosphates and silicates: H_3PO_4 , H_4SiO_4

Speciation in these systems will be explored on a case-by-case basis, beginning with CO_2 .

Carbon Dioxide in Water

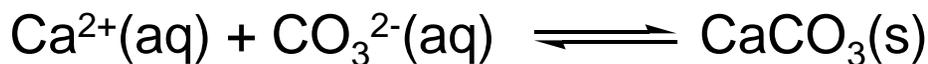
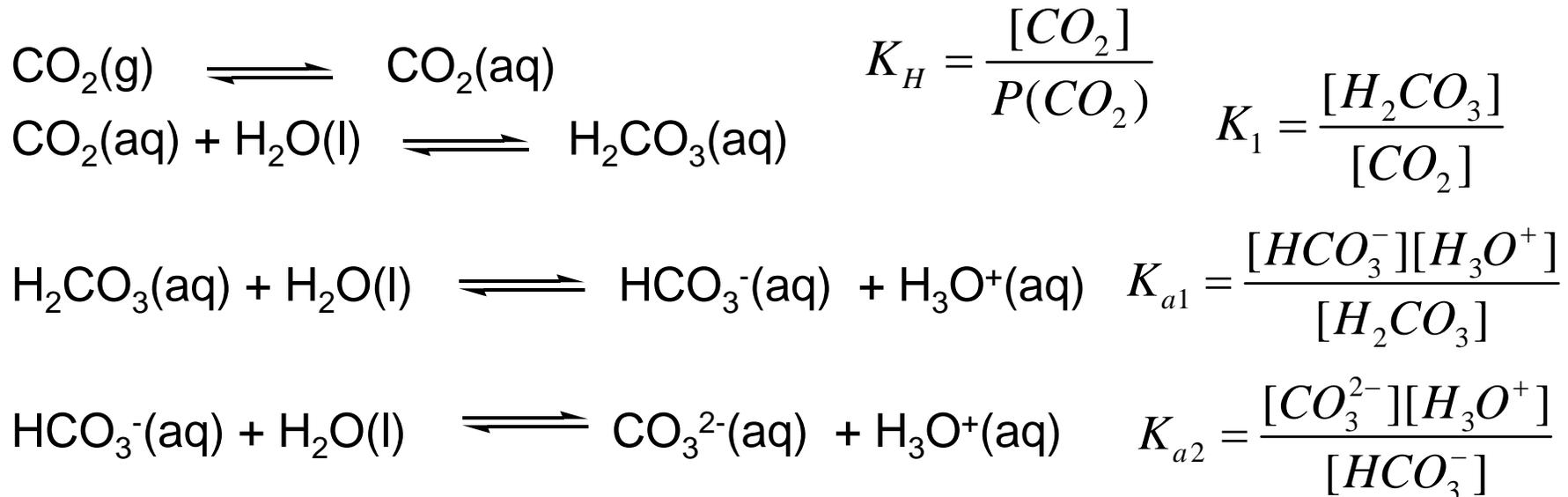
Phenomena of carbonate system:

- 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

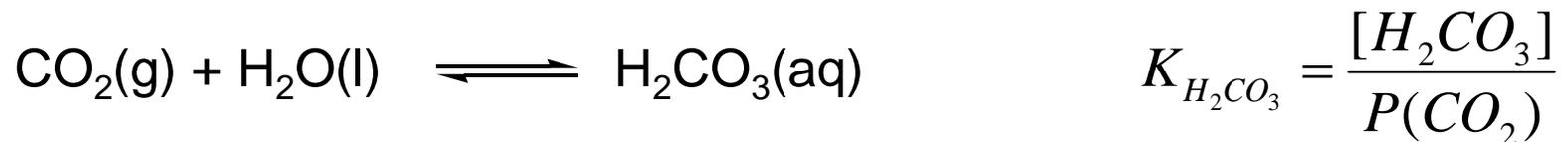


We'll assume there is *no* Ca^{2+} to start with, and ignore this equilibrium... for now.

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 CO_2 with its reaction with water as a single equilibrium expression, viz,



H_2CO_3 can just be regarded as hydrated CO_2 . Both equilibria are forms of Henry's Law, relating the total amount of CO_2 in the gas phase and in solution,

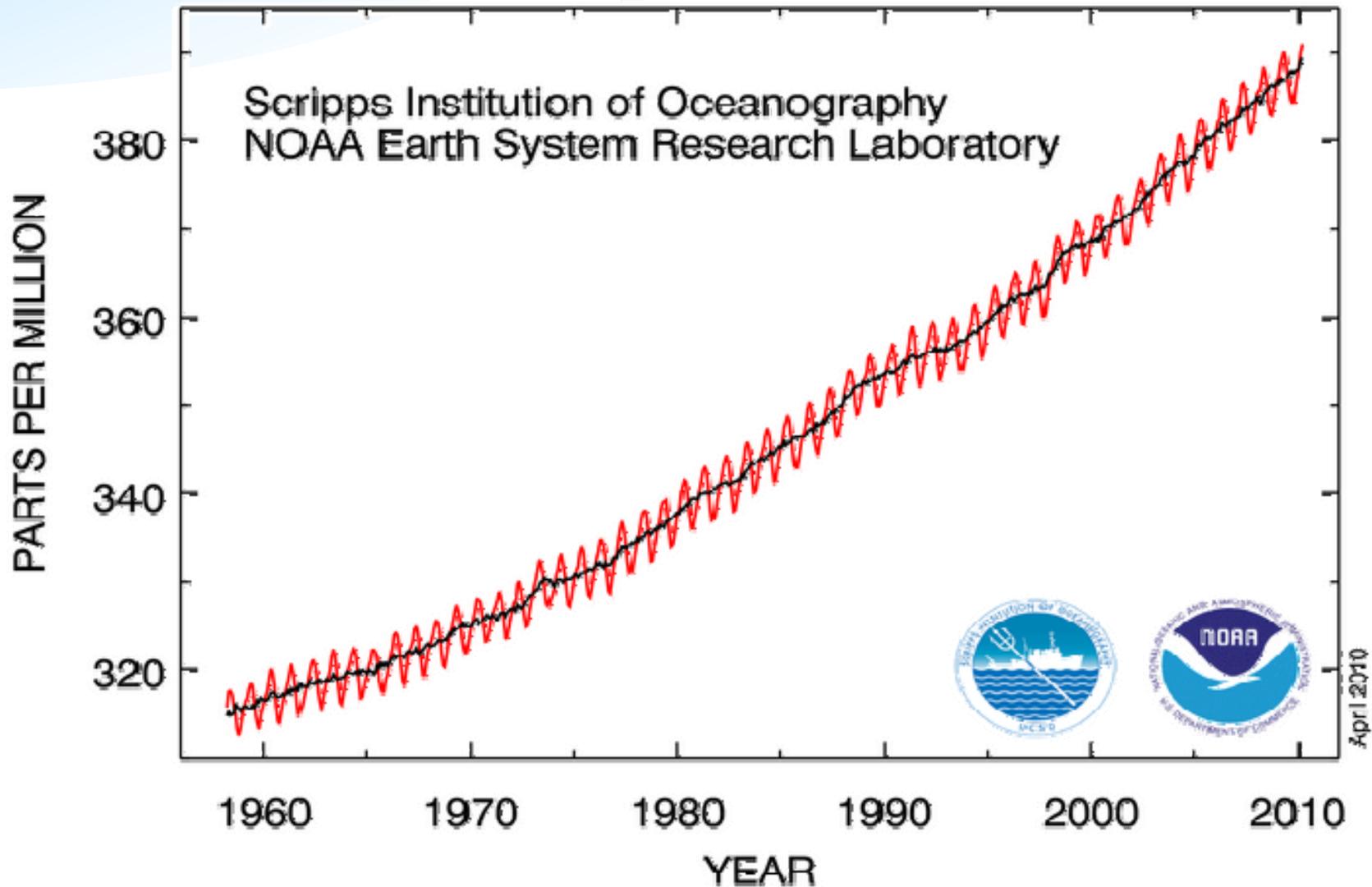
$$[\text{X}](\text{aq}) = k_{\text{H}} \times P(\text{X})$$

The Henry's law constant for 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 CO_2 or H_2CO_3 .

Henry's Law thus tells us that the solubility of CO_2 (and concentration of H_2CO_3) depends linearly on its partial pressure.

CO₂ Atmospheric Levels

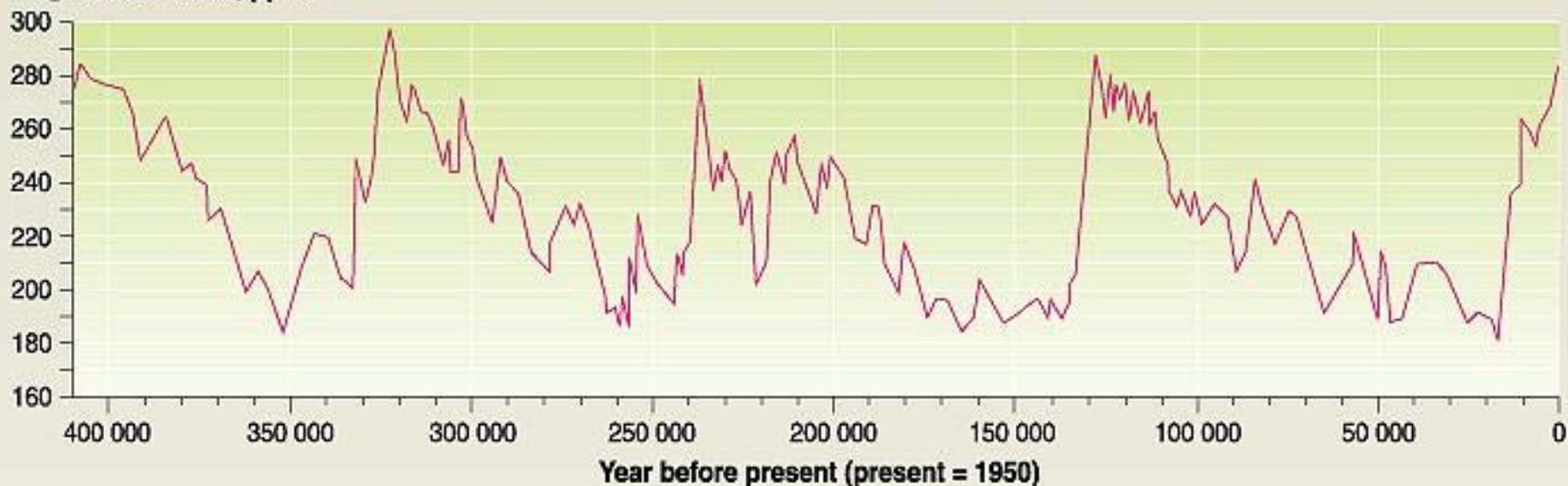
Atmospheric CO₂ at Mauna Loa Observatory



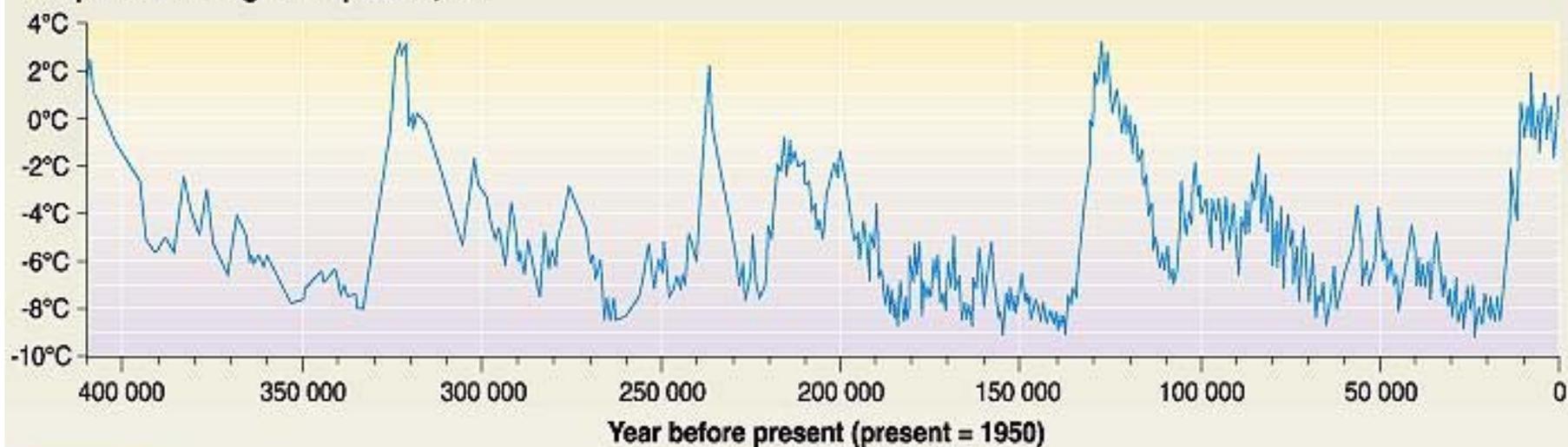
Keeling, C.D. and T.P. Whorf. 2005. Atmospheric CO₂ records from sites in the SIO air sampling network. In *Trends: A Compendium of Data on Global Change*. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tenn., U.S.A. http://www.esrl.noaa.gov/gmd/ccgg/trends/#mlo_full

Temperature and CO₂ concentration in the atmosphere over the past 400 000 years (from the Vostok ice core)

CO₂ concentration, ppmv



Temperature change from present, °C



Temperature and CO₂ concentration in the atmosphere over the past 400 000 years (from the Vostok ice core)



<http://www.esrl.noaa.gov/gmd/ccgg/trends/history.html>

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 CO₂ is 390 ppm. Its partial pressure is thus 390×10^{-6} atm or 0.000390 atm. (ppm for gas is v/10⁶ v)

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

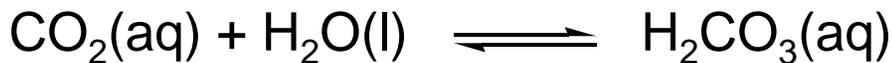
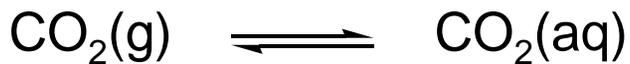
That is, the concentration of H₂CO₃(aq) is *fixed* by the partial pressure of atmospheric CO₂.

The dissolved H₂CO₃ can then undergo one or more acid-dissociation reactions, forming HCO₃⁻ and CO₃²⁻, and this affects

- the pH of aquatic solutions
- the total amount of dissolved CO₂ in all its forms,
- but the concentration of H₂CO₃ is a constant at all pHs.

Carbon Dioxide in Water

The equations controlling CO₂ 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 CO₂ exists as CO₂(aq), not H₂CO₃. Accounts for low acidity: pK_{a1} = 6.35, not pK 2-3 as predicted by Pauling's Rule

Pauling's Rules for Oxo Acids

- For oxoacid $O_xE(OH)_y$, $pK_a = 7 - 5x$, and successive pK_a 's differ by 5
- H_3PO_4 ($x = 1$, $y = 3$) pK_a (pred) = 2, obs = 2, then $pK_{a2} = 7$ and $pK_{a3} = 12$
- H_2SO_4 ($x = 2$, $y = 2$) pK_a (pred) = -3, obs = <0, $pK_{a2} = 2$, as observed for HSO_4^-
- $HOCl$ ($x = 0$) pK_a (pred) = 7, obs = 7.5
- doesn't work for H_2CO_3 pK_a (pred) = 2, obs = 6.5; evidence for $CO_2(aq)$, not H_2CO_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 N_2 , O_2 or 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? ($pK_a = 4.2$)
2. Calculate (a) the fraction of benzoic acid present in its acidic form, and (b) ratio of benzoic acid to benzoate ion at $pH = 7$.
3. Calculate the concentration of dissolved 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.)