

# Chemistry 2404 Forensic & Environmental Chemistry

Lecture 19. Introduction to Aquatic Chemistry

## Lecture 20

- Solubility and Hydrolysis of CO<sub>2</sub>

Lecture 21. CO<sub>2</sub> and calcium carbonate

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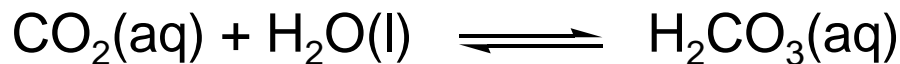
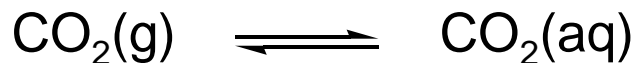
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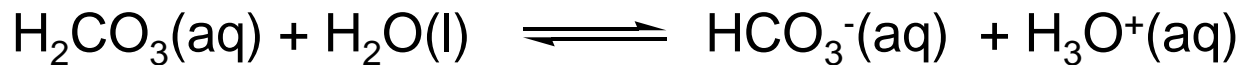
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# Carbon Dioxide in Water

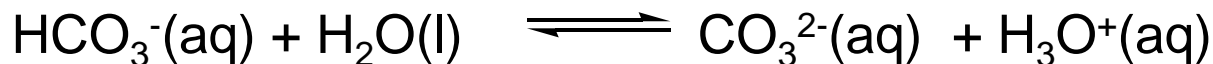
The equations controlling CO<sub>2</sub> gas solubility and hydrolysis equilibria are



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



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



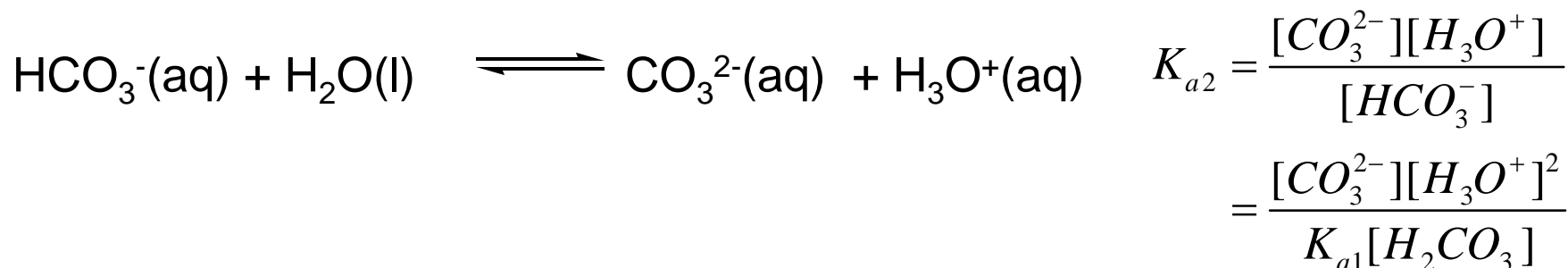
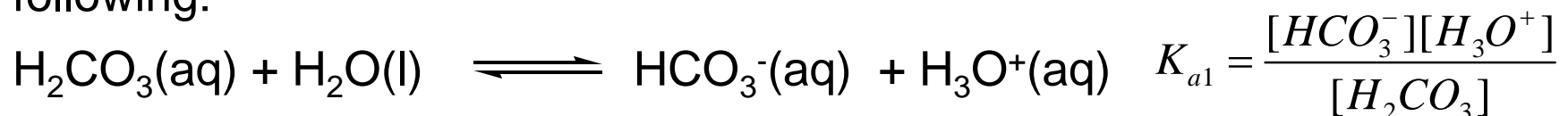
$$K_{a2} = \frac{[\text{CO}_3^{2-}][\text{H}_3\text{O}^+]}{[\text{HCO}_3^-]} = 4.69 \times 10^{-11}$$

First, we examine the (simple) case of pure water in equilibrium with the air – a gas reservoir containing a certain partial pressure of CO<sub>2</sub>, and solve for the equilibrium pH of the resulting solution.

# What is the pH of rainwater?

In order to calculate the solution properties of polyprotic acids like  $\text{H}_2\text{CO}_3$ , we need all the equilibrium expressions, together with the **charge balance** and **mass balance** conditions.

In practice the  $\text{H}_2\text{CO}_3$  concentration is *fixed* by its partial pressure, **so we already know its equilibrium concentration** and need only consider the following:



The **charge balance** condition (total +ve charge = total -ve charge) is:

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

# What is the pH of rainwater?

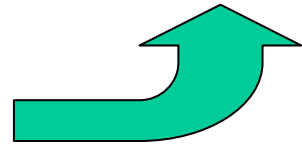
The general solution to such equilibrium problems is to eliminate variables from the charge balance, and solve for one unknown concentration.

The charge balance condition is:

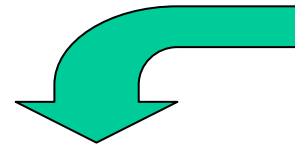
$$[H_3O^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-]$$

$$= K_{a1}[H_2CO_3]/[H_3O^+] + 2[CO_3^{2-}] + [OH^-]$$

$$K_{a1} = \frac{[HCO_3^-][H_3O^+]}{[H_2CO_3]}$$

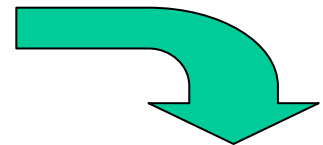


$$K_{a1}K_{a2} = \frac{[CO_3^{2-}][H_3O^+]^2}{[H_2CO_3]}$$



$$= K_{a1}[H_2CO_3]/[H_3O^+] + 2K_{a1}K_{a2}[H_2CO_3]/[H_3O^+]^2 + [OH^-]$$

$$K_w = [OH^-][H_3O^+]$$

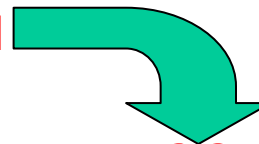


$$= K_{a1}[H_2CO_3]/[H_3O^+] + 2K_{a1}K_{a2}[H_2CO_3]/[H_3O^+]^2 + K_w/[H_3O^+]$$

Or



$$1.29 \times 10^{-5} \text{ M}$$



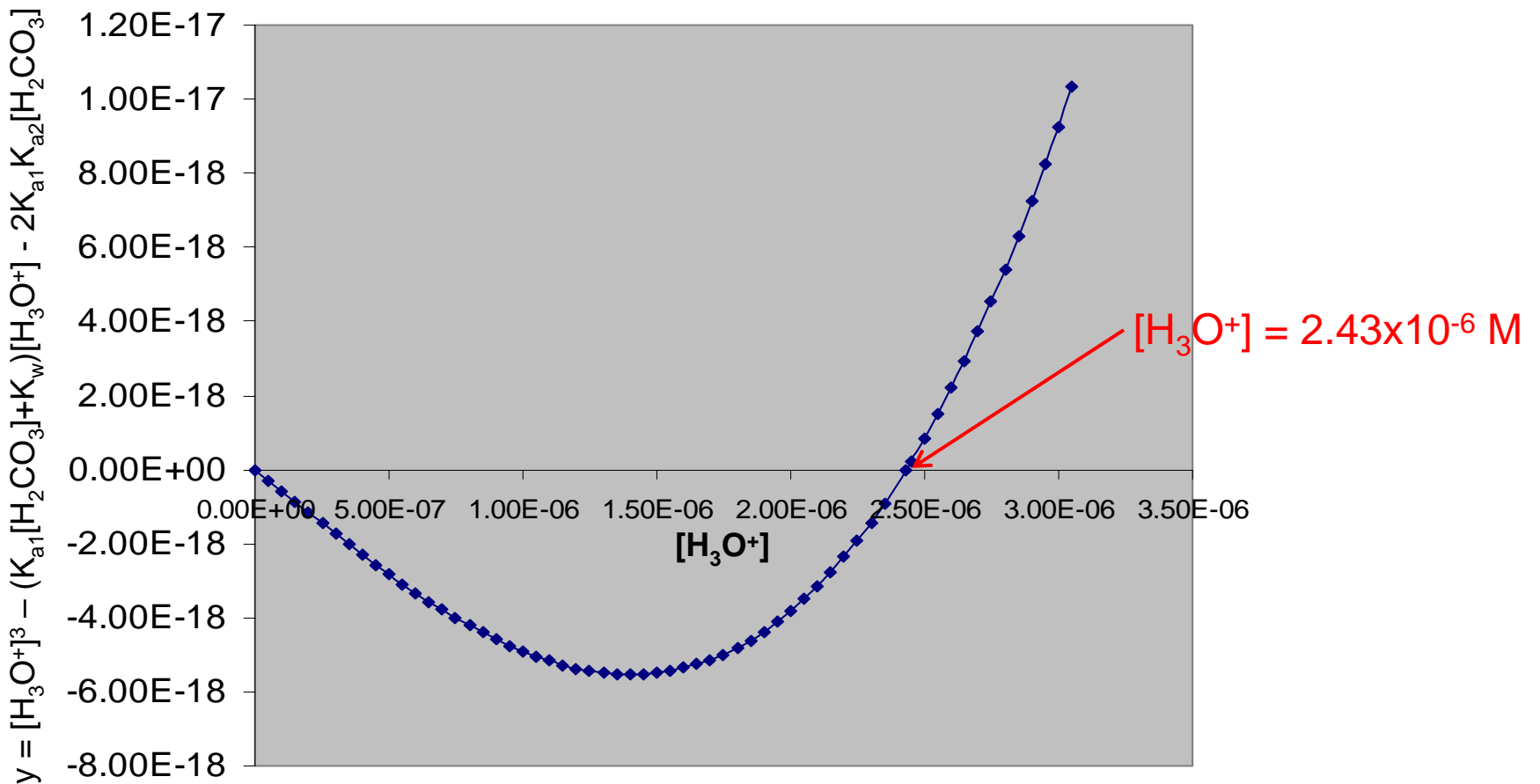
$$[H_3O^+]^3 - (K_{a1}[H_2CO_3] + K_w)[H_3O^+] - 2K_{a1}K_{a2}[H_2CO_3] = 0$$

This cubic equation can easily be solved numerically, to yield  $[H_3O^+]$ , hence pH.

# What is the pH of rainwater?

To find the solution of this equation numerically, we treat it as a function,  $y$ , and then simply plot it against  $[\text{H}_3\text{O}^+]$  (on the x axis), and find where  $y = 0$

$$y = [\text{H}_3\text{O}^+]^3 - (K_{a1}[\text{H}_2\text{CO}_3] + K_w)[\text{H}_3\text{O}^+] - 2K_{a1}K_{a2}[\text{H}_2\text{CO}_3]$$



# What are all the solute concentrations in rainwater?

From the pH and  $pK_a$ 's, we can calculate the concentrations of **all** dissolved species.

$$[\text{H}_2\text{CO}_3] = 1.29 \times 10^{-5} \text{ M (we already knew this – Henry's Law)}$$

$$[\text{H}_3\text{O}^+] = 2.43 \times 10^{-6} \text{ M (and this – just solved)}$$

$$\begin{aligned} [\text{HCO}_3^-] &= K_{a1}[\text{H}_2\text{CO}_3]/[\text{H}_3\text{O}^+] \\ &= 4.45 \times 10^{-7} \times 1.29 \times 10^{-5} / 2.43 \times 10^{-6} = 2.36 \times 10^{-6} \text{ M} \end{aligned}$$

$$\begin{aligned} [\text{CO}_3^{2-}] &= K_{a2}[\text{HCO}_3^-]/[\text{H}_3\text{O}^+] \\ &= 4.69 \times 10^{-11} \times 2.36 \times 10^{-6} / 2.43 \times 10^{-6} = 4.55 \times 10^{-11} \text{ M} \end{aligned}$$

$$[\text{OH}^-] = K_w / [\text{H}_3\text{O}^+] = 1.0 \times 10^{-14} / 2.43 \times 10^{-6} \text{ M} = 4.12 \times 10^{-9} \text{ M}$$

We can also identify which species' concentrations are most or least important.

$$[\text{H}_2\text{CO}_3] = 1.29 \times 10^{-5} \text{ M is present in the highest concentration}$$

$$[\text{H}_3\text{O}^+] = 2.43 \times 10^{-6} \text{ M and } [\text{HCO}_3^-] = 2.36 \times 10^{-6} \text{ M are roughly equal in concentration}$$

$$[\text{CO}_3^{2-}] = 4.55 \times 10^{-11} \text{ M and } [\text{OH}^-] = 4.12 \times 10^{-9} \text{ M are negligible in charge or material balance considerations compared to the other species.}$$

# What is the pH of rainwater? Simplifying Assumptions

1. The dissociation reactions all *produce*  $\text{H}_3\text{O}^+$ , so we expect the final pH will be  $< 7$ . Therefore  $[\text{OH}^-]$  will be very low (as it is), and can be ignored in the *charge balance*

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

This modestly simplifies the equilibria, but still leaves a cubic equation to solve.

2. We can also ignore  $[\text{CO}_3^{2-}]$ , because it only forms to a significant extent at high pH. We expect this from inspecting the values of the acid-dissociation constants:  $K_{a1} = 4.45 \times 10^{-7}$ ;  $K_{a2} = 4.69 \times 10^{-11}$ .

Therefore the charge balance is simplified to the approximate relationship

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

described by a single hydrolysis equilibrium  $K_{a1} = [\text{H}_3\text{O}^+][\text{HCO}_3^-]/[\text{H}_2\text{CO}_3]$

$$\begin{aligned} [\text{H}_3\text{O}^+] = [\text{HCO}_3^-] &= \{K_{a1}[\text{H}_2\text{CO}_3]\}^{1/2} = \{4.45 \times 10^{-7} \times 1.29 \times 10^{-5}\}^{1/2} \\ &= 2.43 \times 10^{-6} \text{ M... (same as exact calc.)} \end{aligned}$$

$$\text{pH} = 5.615$$

# What is the effect of atmospheric CO<sub>2</sub> levels?

This approximate result is useful as it allows us to easily see the effect of changes in atmospheric CO<sub>2</sub> levels on the pH of fresh (rain) water without resorting to numerical analysis every time.

$$\begin{aligned} [\text{H}_3\text{O}^+] &= [\text{HCO}_3^-] = \{K_{a1}k_H P(\text{CO}_2)\}^{1/2} \\ &= \{4.45 \times 10^{-7} \times 3.4 \times 10^{-2} \times 0.000390\}^{1/2} \quad (2010 \text{ level}) \\ &= 2.43 \times 10^{-6} \text{ M} \quad \text{or pH} = 5.615 \end{aligned}$$

Compare this with the result for pre-industrial revolution rainwater, when  $P(\text{CO}_2) = 0.00028 \text{ atm}$

$$\Rightarrow [\text{H}_3\text{O}^+] = 2.06 \times 10^{-6} \text{ M} \quad \text{or pH} = 5.687$$

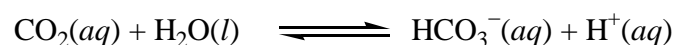
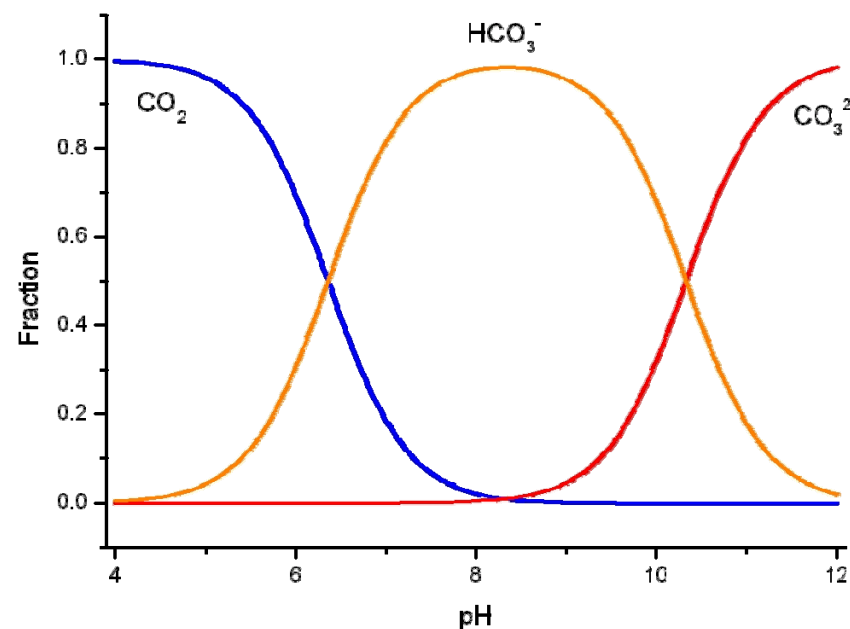
or with the predicted  $P(\text{CO}_2)$  for 2100, from 730-1020 ppm. Conservatively,

$$\begin{aligned} \Rightarrow [\text{H}_3\text{O}^+] &= \{4.45 \times 10^{-7} \times 3.4 \times 10^{-2} \times 0.000730\}^{1/2} = 3.32 \times 10^{-6} \text{ M} \\ &\quad \text{or pH} = 5.478 \end{aligned}$$



# Speciation of dissolved CO<sub>2</sub>

The *fraction* of total dissolved CO<sub>2</sub> present in the form of each hydrolysis product is determined in the same way as for a monoprotic acid. Once again, they can be expressed as a function of only solution pH.



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



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

$$\alpha_{\text{CO}_2} = \frac{[\text{CO}_2]}{[\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]}$$

$$\alpha_{\text{HCO}_3^-} = \frac{[\text{HCO}_3^-]}{[\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]}$$

$$\alpha_{\text{CO}_3^{2-}} = \frac{[\text{CO}_3^{2-}]}{[\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]}$$

$$\alpha_{\text{CO}_2} = \frac{[\text{H}^+]^2}{[\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1}K_{a2}}$$

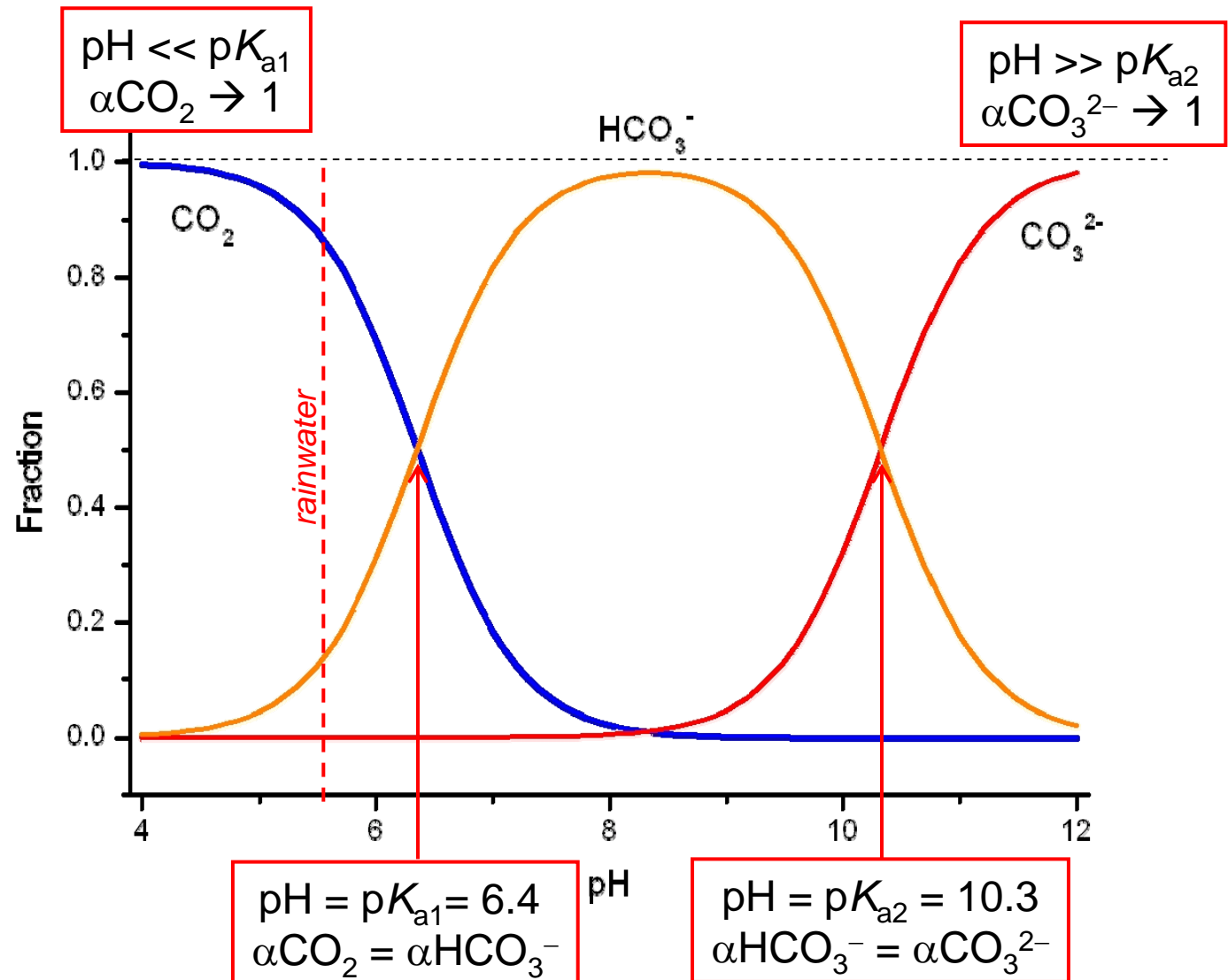
$$\alpha_{\text{HCO}_3^-} = \frac{K_{a1}[\text{H}^+]}{[\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1}K_{a2}}$$

$$\alpha_{\text{CO}_3^{2-}} = \frac{K_{a1}K_{a2}}{[\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1}K_{a2}}$$

# Speciation of dissolved CO<sub>2</sub>

The speciation diagram defines pH regions in which the dominant species are CO<sub>2</sub>(H<sub>2</sub>CO<sub>3</sub>), HCO<sub>3</sub><sup>-</sup>, or CO<sub>3</sub><sup>2-</sup>.

For example, at the natural pH of rain, the most common species is CO<sub>2</sub>, which is much more abundant than HCO<sub>3</sub><sup>-</sup> or CO<sub>3</sub><sup>2-</sup>.



# Speciation of Polyprotic Acids

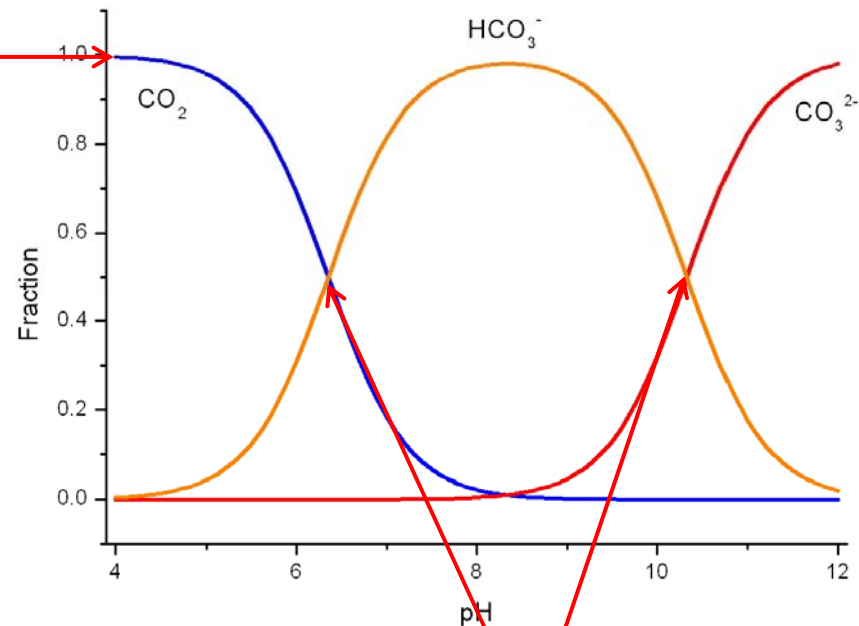
When  $\text{pH} \ll \text{p}K_{a1}$ ,  $[\text{H}^+] \gg K_{a1}$ .  
Therefore the equilibrium constant tells us  
 $[\text{HA}] = [\text{H}^+][\text{A}^-]/K_a$ , or  $[\text{HA}] \gg [\text{A}^-]$ .  
*The converse argument works at  $\text{pH} \gg \text{p}K_a$ .*

These features are common to *all polyprotic acids*.

The conjugate acid and base are present at equal concentrations when  $\text{pH} = \text{p}K_a$ .

At sufficiently low pH, only the most acidic species (greatest number of protons) is present to any significant degree ( $\alpha = 1$ ).

At sufficiently high pH, only the most basic species is present ( $\alpha = 1$ ).



For any acid-dissociation reaction,  
$$\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$$

Whenever  $\text{pH} = \text{p}K_a$ ,  $[\text{H}^+] = K_a$ . Therefore the equilibrium constant tells us

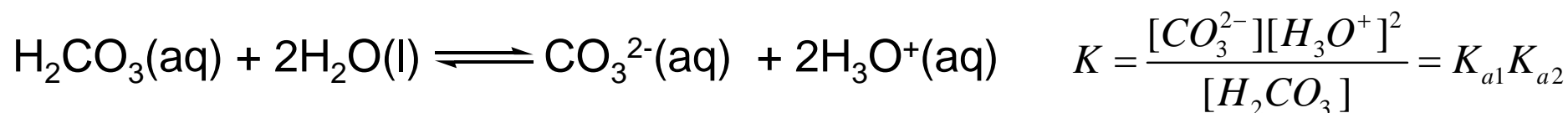
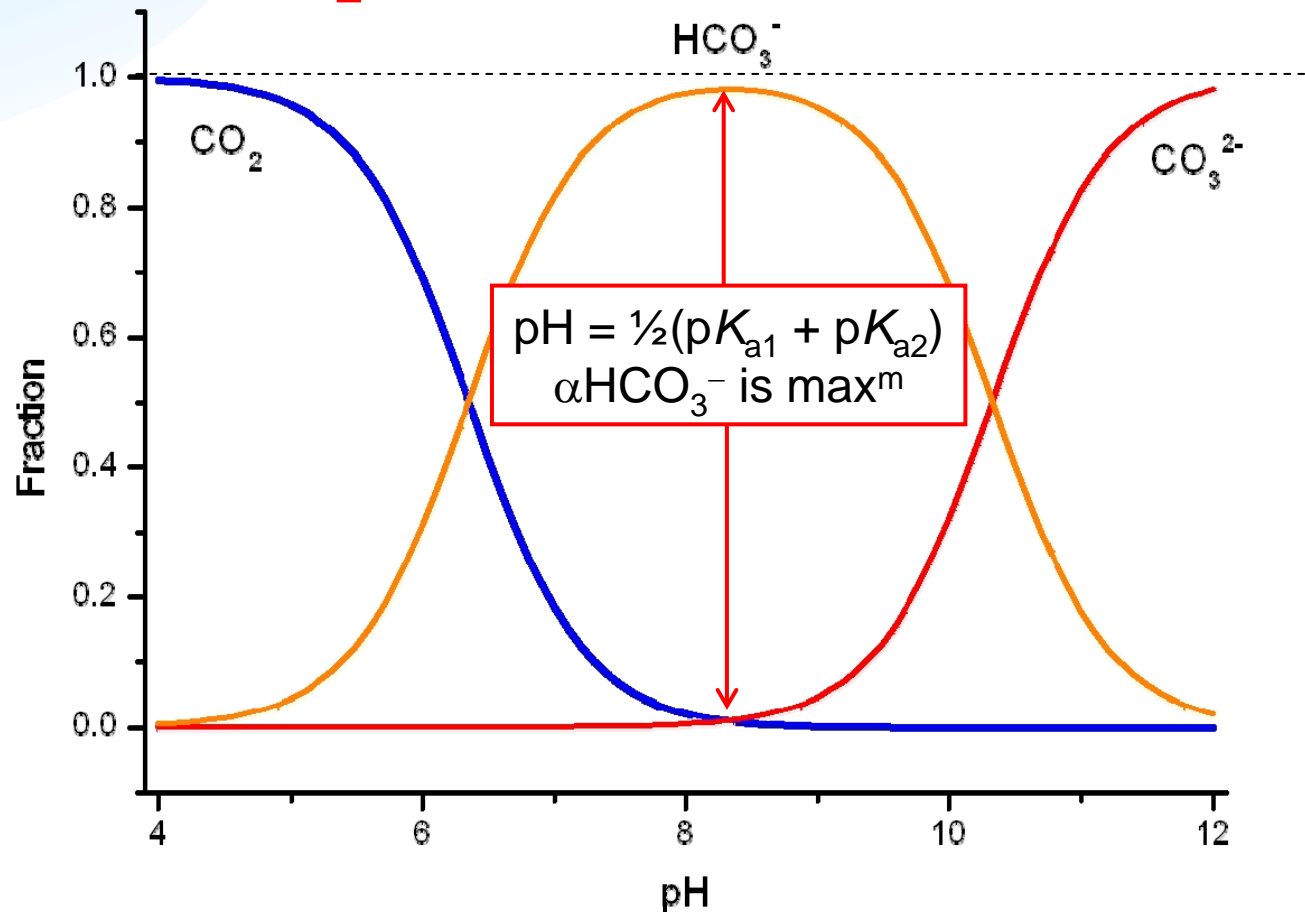
$$K_a = [\text{H}^+][\text{A}^-]/[\text{HA}], \text{ or } [\text{A}^-] = [\text{HA}]$$
  
*independent of all other equilibria.*

# Speciation of dissolved CO<sub>2</sub>

We can define a few other features of the speciation diagram of polyprotic acids, using CO<sub>2</sub> as an example.

When does  $\alpha\text{CO}_2 = \alpha\text{CO}_3^{2-}$ ?

The equilibrium between H<sub>2</sub>CO<sub>3</sub> and CO<sub>3</sub><sup>2-</sup> is



If  $\alpha\text{CO}_2 = \alpha\text{CO}_3^{2-}$ , then  $[\text{H}_2\text{CO}_3] = [\text{CO}_3^{2-}]$ , and  $[\text{H}_3\text{O}^+]^2 = K_{a1}K_{a2}$ ,  
or  $\text{pH} = \frac{1}{2}(\text{p}K_{a1} + \text{p}K_{a2})$

# Speciation of dissolved CO<sub>2</sub>

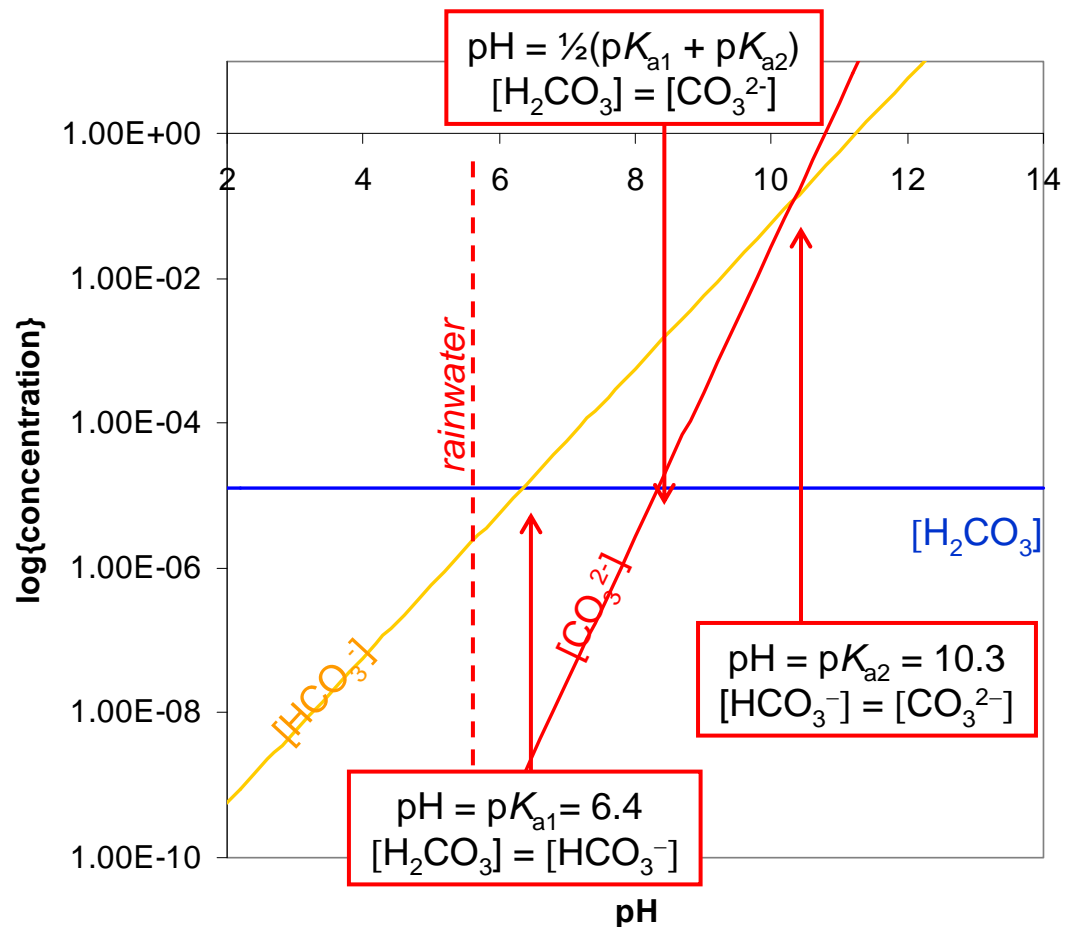
The alternative representation of a speciation diagram is as a graph of log{concentration} versus pH for all species

$$K_{a1} = \frac{[HCO_3^-][H_3O^+]}{[H_2CO_3]} \Rightarrow \log[HCO_3^-] = \log[H_2CO_3] - pK_{a1} + pH$$

$$K_{a2}K_{a1} = \frac{[CO_3^{2-}][H_3O^+]^2}{[H_2CO_3]} \Rightarrow \log[CO_3^{2-}] = \log[H_2CO_3] + 2pH - pK_{a1} - pK_{a2}$$

Here we see again

- (i) the linear variation of concentrations with pH for hydrolysis products
- (ii) That [H<sub>2</sub>CO<sub>3</sub>] is independent of pH
- (iii) Concentration lines *cross* at pH = pK<sub>a</sub>.



## Summary

You should now be able to

- Calculate the speciation of  $\text{CO}_2$  (or any other acidic gas) as a function of pH and plot it in species fraction or  $\log\{\text{concentration}\}$  form.
- Calculate the equilibrium pH of  $\text{CO}_2$ -saturated water under various conditions.
- Read and interpret both forms of speciation diagrams.

## Next Lecture

Calcium carbonate and speciation diagrams.

## Practice/Review problems

1. If the pH of a solution decreases by 0.3, by what *factor* has  $[\text{H}_3\text{O}^+]$  increased?
2. Calculate the approximate pH of rainwater at the worst-case prediction for atmospheric  $\text{CO}_2$  levels by the year 2100.
3. At what pH is the concentration of  $\text{H}_2\text{CO}_3$  half that of  $\text{HCO}_3^-$ ?