

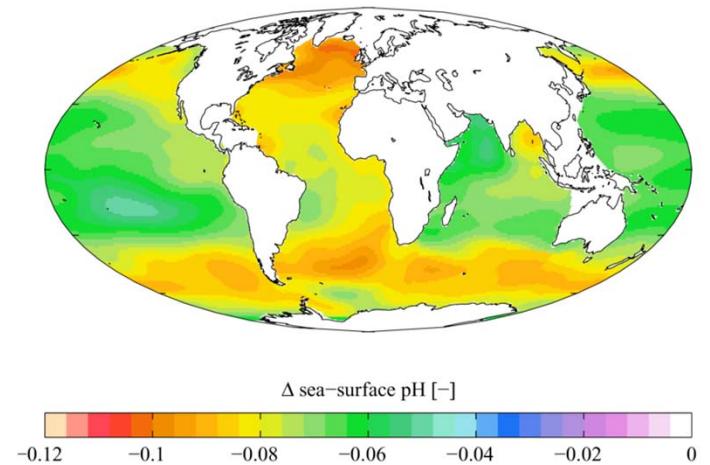
Ch 1b Lecture 17

February 14th, 2013

Next few lectures – OK, let's do some actual chemistry!

Today: Equilibrium & Acid:Base Chemistry

Reading: OGC Chapter 15, esp. through Section 15.7



Equilibrium and ΔG°

Explicit Example

This implies that:

$$-\Delta G^\circ = RT \ln \left(\frac{\left(\frac{P_{H_2O}}{P_{ref}} \right)^2}{\left(\frac{P_{H_2}}{P_{ref}} \right)^2 \left(\frac{P_{O_2}}{P_{ref}} \right)} \right)$$

Note that this looks a lot like the expression for K_P

$$K_P = \frac{[P_C]_eq^c [P_D]_eq^d}{[P_A]_eq^a [P_B]_eq^b}$$

Except this expression is unit-less

Acid-base reactions are widely important commercially and in nature, and are best understood using modest extensions of the equilibrium theory we have gone over in the past two lectures. A particular example we'll cover at the end of today is the pH of the Earth's oceans and how it is responding to the growth of atmospheric CO₂.

Equilibrium and ΔG°

Explicit Example

When we are away from equilibrium

$$\Delta G = \Delta G^\circ + RT \ln \left(\frac{\left(\frac{P_{H_2O}}{P_{ref}} \right)^2}{\left(\frac{P_{H_2}}{P_{ref}} \right)^2 \left(\frac{P_{O_2}}{P_{ref}} \right)} \right)$$


From standard states

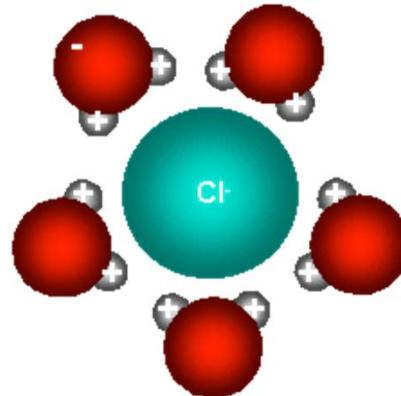
Accounts for the actual conditions on the reaction (for gases), with $P_{ref} = 1 \text{ atm}$

If $\Delta G < 0$ reaction proceeds spontaneously

If $\Delta G > 0$ reaction proceeds in reverse spontaneously

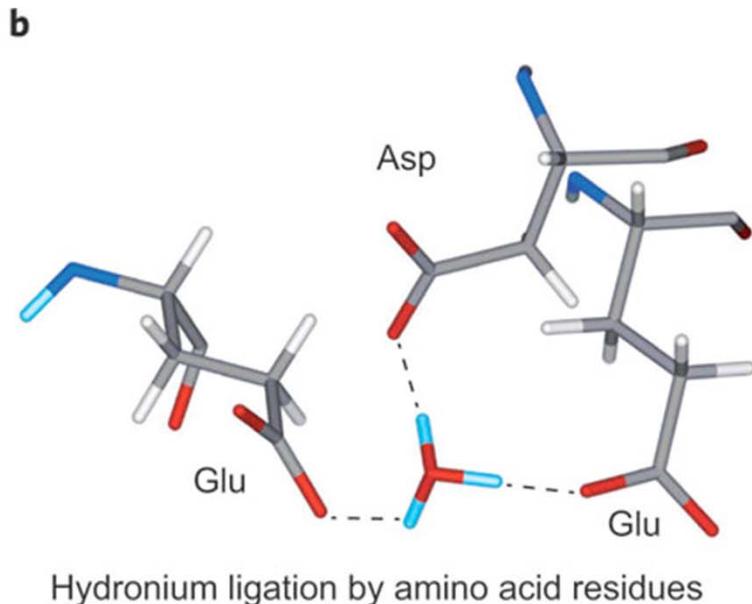
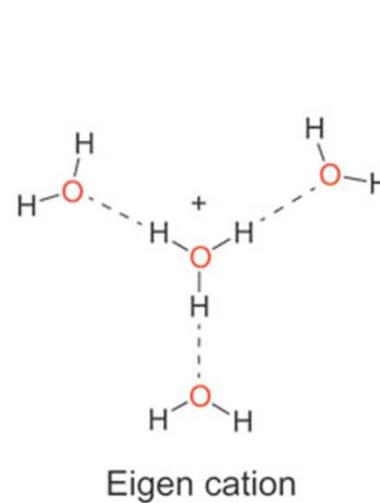
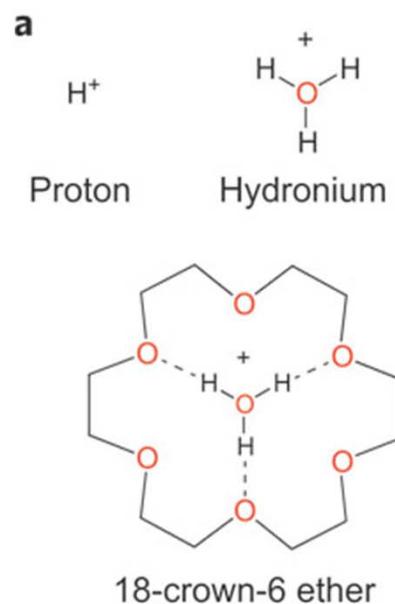
If $\Delta G = 0$ reactants and products are at equilibrium

Acids & Bases: An Extension of Chemical Equilibria

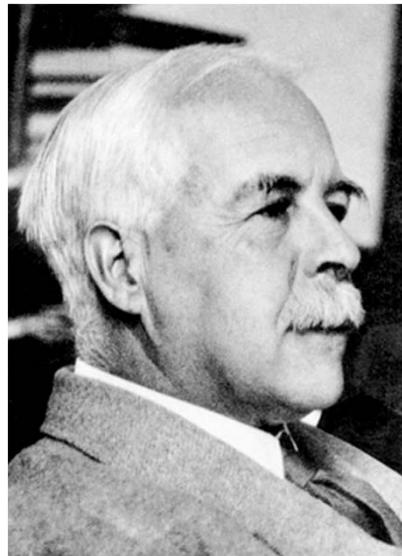


Here, gas phase approaches are woefully inadequate – think about HCl in the gas phase ($\text{H}^+ + \text{Cl}^-$) versus solution!

Thus, we'll need thermodynamic data under the appropriate conditions...



Acids & Bases: An Extension of Chemical Equilibria



G.N. Lewis 1875-1946

You should think in terms of electron donors & acceptors!

Protons!! Think in terms of proton donors & acceptors!

I think this Brønsted fellow is on to something...



T.M. Lowry 1874-1936

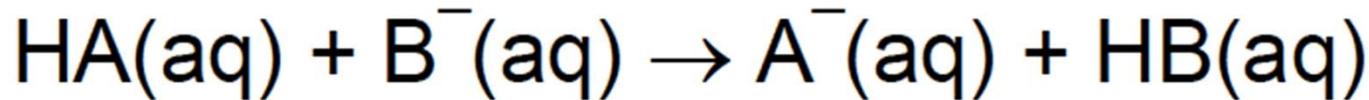


J.N. Brønsted 1879-1947

Acids & Bases: An Extension of Chemical Equilibria

Bronsted-Lowry Model for Acids and Bases

- An acid is a proton (H^+) donor
- A base is a proton (H^+) acceptor



- A^- is the conjugate base of the acid HA
- HB is the conjugate acid of the base B^-

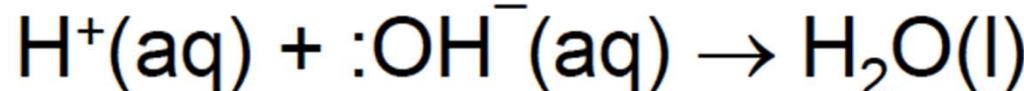
Acids & Bases: An Extension of Chemical Equilibria

Lewis Model for Acids and Bases

- An acid is an electron pair acceptor
- A base is an electron pair donor

This definition is *more general* than the Bronsted-Lowry definition.

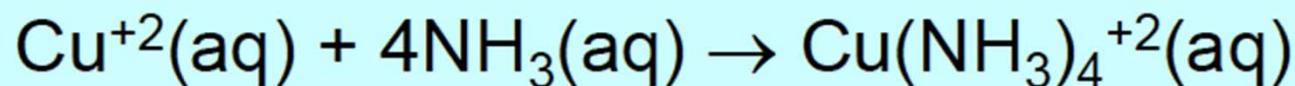
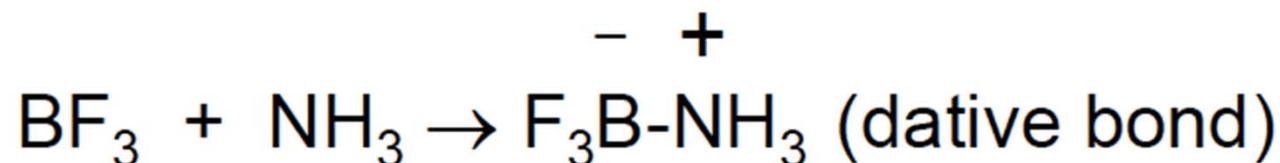
H^+ = acid and OH^- = base either way:



Acids & Bases: An Extension of Chemical Equilibria

Lewis Model for Acids and Bases

BF_3 (a Lewis acid) with NH_3 (a Lewis Base):



Cu^{+2} accepts 4 pairs of e's from the NH_3 molecules,

Cu_{+2} = acid; $:\text{NH}_3$ = base.

Acids & Bases: An Extension of Chemical Equilibria

Increasing acidity →						
I	II	III	IV	V	VI	VII
Li ₂ O	BeO	B ₂ O ₃	CO ₂	N ₂ O ₅	(O ₂)	OF ₂
Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₄ O ₁₀	SO ₃	Cl ₂ O ₇
K ₂ O	CaO	Ga ₂ O ₃	GeO ₂	As ₂ O ₅	SeO ₃	Br ₂ O ₇
Rb ₂ O	SrO	In ₂ O ₃	SnO ₂	Sb ₂ O ₅	TeO ₃	I ₂ O ₇
Cs ₂ O	BaO	Tl ₂ O ₃	PbO ₂	Bi ₂ O ₅	PoO ₃	At ₂ O ₇

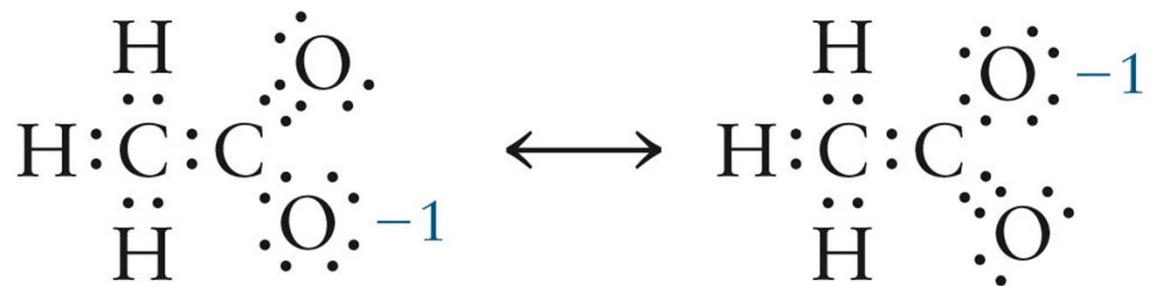
→ Increasing basicity

↑ Increasing acidity

These pictures help make sense of trends observed across the periodic table (esp. w.r.t. electronegativities).

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And for the wide variety of organic acids that are used commercially or found in nature (resonance, steric effects that we saw in the first two weeks of class).

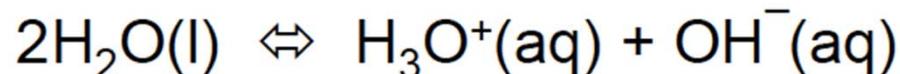


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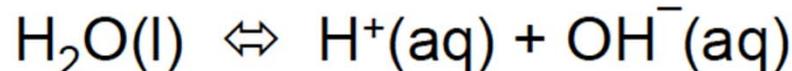
Acids & Bases: An Extension of Chemical Equilibria

Water Autoionization

Water = acid or base:



or, more simply,



$$K_{\text{eq}} = K_w = [\text{H}^+][\text{OH}^-]$$

25°C, K_w is 1.0×10^{-14} .

What drives the temperature dependence?

T A B L E 15.1 Temperature Dependence of K_w

$T(\text{°C})$	K_w	pH of Water
0	0.114×10^{-14}	7.47
10	0.292×10^{-14}	7.27
20	0.681×10^{-14}	7.08
25	1.01×10^{-14}	7.00
30	1.47×10^{-14}	6.92
40	2.92×10^{-14}	6.77
50	5.47×10^{-14}	6.63
60	9.61×10^{-14}	6.51

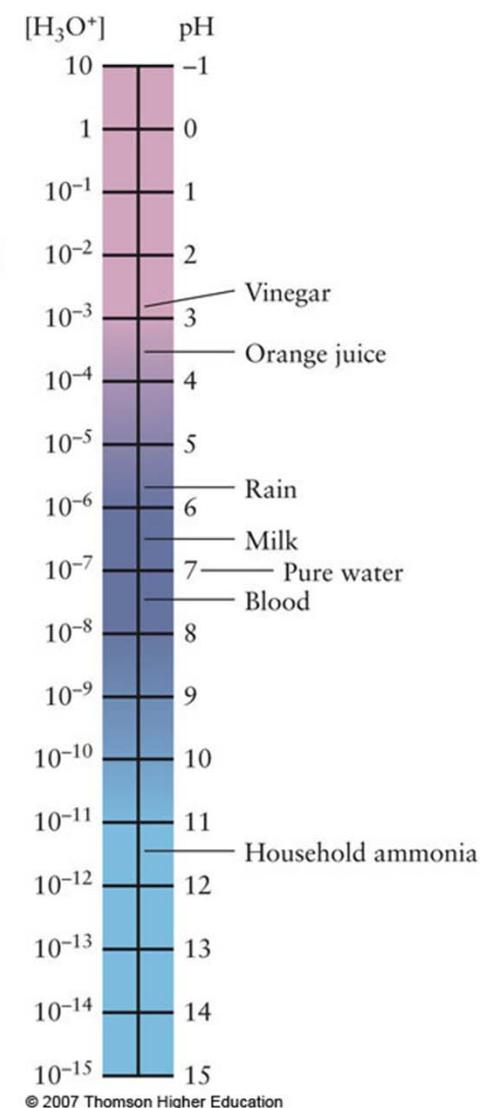
Acids & Bases: An Extension of Chemical Equilibria

Strong Acids and Bases

Strong acids are completely ionized in aqueous solution: HCl, HBr, HI, H_2SO_4 , HNO_3 , and HClO_4

Strong bases react completely to give OH^- in aqueous solution: examples - NH_2^- and H^-

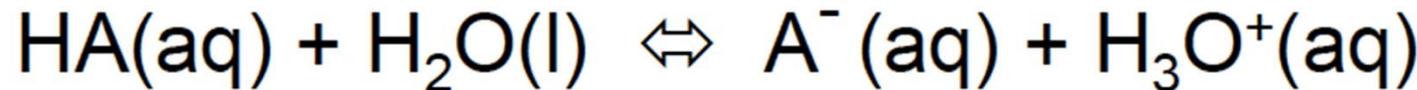
Water has a **leveling effect** on strong acids and bases. For example, the concentration of H^+ is 0.1 molar in solutions containing any strong acid at a concentration of 0.1 molar.



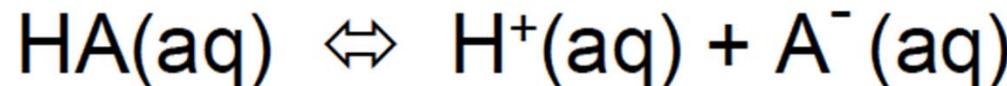
Acids & Bases: An Extension of Chemical Equilibria

Equilibrium Constants for Weak Acids

When a weak acid is added to water, an equilibrium is quickly reached:



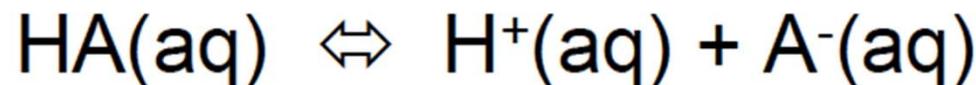
More simply, this can be expressed as



Weak bases are similar

Acids & Bases: An Extension of Chemical Equilibria

Equilibrium Constants for Weak Acids



The equilibrium constant for a weak acid is thus

$$K_a = [\text{H}^+][\text{A}^-]/[\text{HA}]$$

A common way to express the strength of an acid is the pK_a , which is similar in form to the pH:

$$\text{pK}_a = -\log_{10} K_a$$

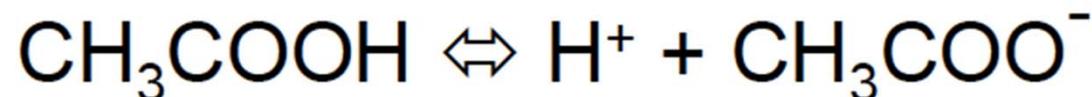
The lower the pK_a value for an acid, the stronger the acid.

Acids & Bases: An Extension of Chemical Equilibria

Sample Problem: pH of a Weak Acid

Acetic acid has a K_a value of 1.8×10^{-5} . What is the pH of a 0.100 M solution of acetic acid?

First, write down the reaction, then write the equilibrium constant expression for the reaction:



$$K_a = [\text{H}^+][\text{CH}_3\text{COO}^-]/[\text{CH}_3\text{COOH}]$$

Sample Problem: pH of Acetic Acid (Weak Acid)

Make up a table of initial concentrations and their change when a reaction occurs. For every molecule of acetic acid that dissociates, we form one H^+ ion and one CH_3COO^- ion. Represent the amount of acetic acid used up as x :

	$[\text{CH}_3\text{COOH}] (\text{M})$	$[\text{H}^+] (\text{M})$	$[\text{CH}_3\text{COO}^-] (\text{M})$
Initial	0.100	0.000	0.000
Change	$-x$	$+x$	$+x$
Equilibrium	$0.100-x$	x	x

Write out the equilibrium expression and solve for x :

$$K_a = [\text{H}^+][\text{CH}_3\text{COO}^-]/[\text{CH}_3\text{COOH}]$$

$$1.8 \times 10^{-5} = (x)(x)/(0.100-x)$$

$$x = 0.00134 = [\text{H}^+] \quad \text{Answer: } \text{pH} = -\log_{10}([\text{H}^+]) = 2.87$$

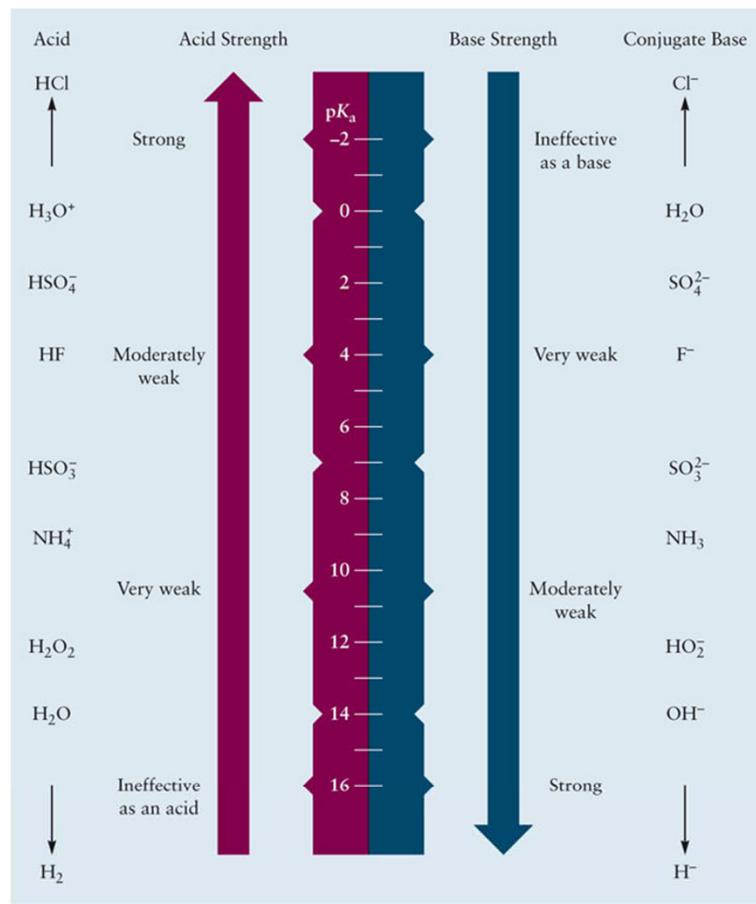
Some representative pK_a 's:

$$pK_a = -\log_{10} K_a$$

TABLE 15.2 Ionization Constants of Acids at 25°C

Acid	HA	A^-	K_a	pK_a
Hydroiodic	HI	I^-	$\sim 10^{11}$	~ -11
Hydrobromic	HBr	Br^-	$\sim 10^9$	~ -9
Perchloric	$HClO_4$	ClO_4^-	$\sim 10^7$	~ -7
Hydrochloric	HCl	Cl^-	$\sim 10^7$	~ -7
Chloric	$HClO_3$	ClO_3^-	$\sim 10^3$	~ -3
Sulfuric (1)	H_2SO_4	HSO_4^-	$\sim 10^2$	~ -2
Nitric	HNO_3	NO_3^-	~ 20	~ -1.3
Hydronium ion	H_3O^+	H_2O	1	0.0
Iodic	HIO_3	IO_3^-	1.6×10^{-1}	0.80
Oxalic (1)	$H_2C_2O_4$	$HC_2O_4^-$	5.9×10^{-2}	1.23
Sulfurous (1)	H_2SO_3	HSO_3^-	1.54×10^{-2}	1.81
Sulfuric (2)	HSO_4^-	SO_4^{2-}	1.2×10^{-2}	1.92
Chlorous	$HClO_2$	ClO_2^-	1.1×10^{-2}	1.96
Phosphoric (1)	H_3PO_4	$H_2PO_4^-$	7.52×10^{-3}	2.12
Arsenic (1)	H_3AsO_4	$H_2AsO_4^-$	5.0×10^{-3}	2.30
Chloroacetic	$CH_2ClCOOH$	CH_2ClCOO^-	1.4×10^{-3}	2.85
Hydrofluoric	HF	F^-	6.6×10^{-4}	3.18
Nitrous	HNO_2	NO_2^-	4.6×10^{-4}	3.34
Formic	$HCOOH$	$HCOO^-$	1.77×10^{-4}	3.75
Benzoic	C_6H_5COOH	$C_6H_5COO^-$	6.46×10^{-5}	4.19
Oxalic (2)	$HC_2O_4^-$	$C_2O_4^{2-}$	6.4×10^{-5}	4.19
Hydrazoic	HN_3	N_3^-	1.9×10^{-5}	4.72
Acetic	CH_3COOH	CH_3COO^-	1.76×10^{-5}	4.75
Propionic	CH_3CH_2COOH	$CH_3CH_2COO^-$	1.34×10^{-5}	4.87
Pyridinium ion	$HC_5H_5N^+$	C_5H_5N	5.6×10^{-6}	5.25
Carbonic (1)	H_2CO_3	HCO_3^-	4.3×10^{-7}	6.37
Sulfurous (2)	HSO_3^-	SO_3^{2-}	1.02×10^{-7}	6.91
Arsenic (2)	$H_2AsO_4^-$	$HAsO_4^{2-}$	9.3×10^{-8}	7.03
Hydrosulfuric	H_2S	HS^-	9.1×10^{-8}	7.04
Phosphoric (2)	$H_2PO_4^-$	HPO_4^{2-}	6.23×10^{-8}	7.21
Hypochlorous	$HClO$	ClO^-	3.0×10^{-8}	7.53
Hydrocyanic	HCN	CN^-	6.17×10^{-10}	9.21
Ammonium ion	NH_4^+	NH_3	5.6×10^{-10}	9.25
Carbonic (2)	HCO_3^-	CO_3^{2-}	4.8×10^{-11}	10.32
Arsenic (3)	$HAsO_4^{2-}$	AsO_4^{3-}	3.0×10^{-12}	11.53
Hydrogen peroxide	H_2O_2	HO_2^-	2.4×10^{-12}	11.62
Phosphoric (3)	HPO_4^{2-}	PO_4^{3-}	2.2×10^{-13}	12.67
Water	H_2O	OH^-	1.0×10^{-14}	14.00

$$K_a = \frac{[A^+][B^-]}{[AB]}$$



Similarly

$$K_b = [HB][OH^-]/[B^-]$$

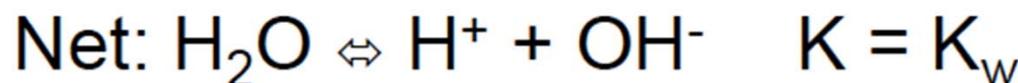
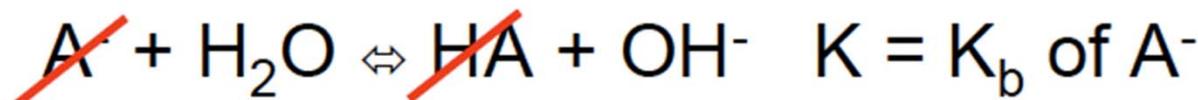
Relationship between K_a and K_b

There is a simple relationship between K_a and K_b . Consider two reactions involving an acid and its conjugate base:



Relationship between K_a and K_b

There is a simple relationship between K_a and K_b . Consider two reactions involving an acid and its conjugate base:



$$K_w = (K_a \text{ of HA}) \times (K_b \text{ of A}^-)$$

Taking the log of both sides gives the useful relation:

$$\text{p}K_a + \text{p}K_b = 14$$

Acids & Bases: An Extension of Chemical Equilibria

Example (Part I)

Prepare solutions with pH=3 from nitric acid and then from acetic acid

For nitric acid (HNO_3) $\text{pK}_a = -1.44$

$$K_a = \frac{[A^+][B^-]}{[AB]} = 27.5 = \frac{[H^+][NO_3^-]}{[HNO_3]} = \frac{[10^{-3}][10^{-3}]}{[M] - 10^{-3}}$$

Solve for M; $M = 1.003 \times 10^{-3} \text{ M}$

This is the sign of a strong acid; the concentration of $[\text{H}^+] \approx [\text{HA}]$ added

Acids & Bases: An Extension of Chemical Equilibria

Example (Part I)

Prepare solutions with pH=3 from nitric acid and then from acetic acid

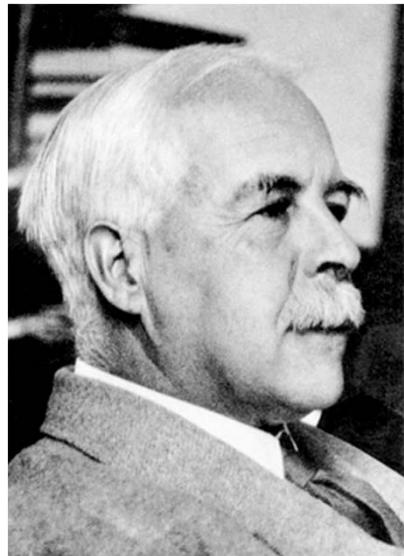
For acetic acid ($\text{H}_3\text{CCO}_2\text{H}$) $\text{pK}_a = 4.756$

$$K_a = \frac{[A^+][B^-]}{[AB]} = 1.75 \times 10^{-5} = \frac{[H^+][\text{H}_3\text{CO}_2^-]}{[\text{H}_3\text{CO}_2\text{H}]} = \frac{[10^{-3}][10^{-3}]}{[M] - 10^{-3}}$$

Solve for M; $M = 5.8 \times 10^{-2} \text{ M}$

This is the sign of a weak acid; the concentration of $[\text{H}^+] \ll [\text{HA}]$ added

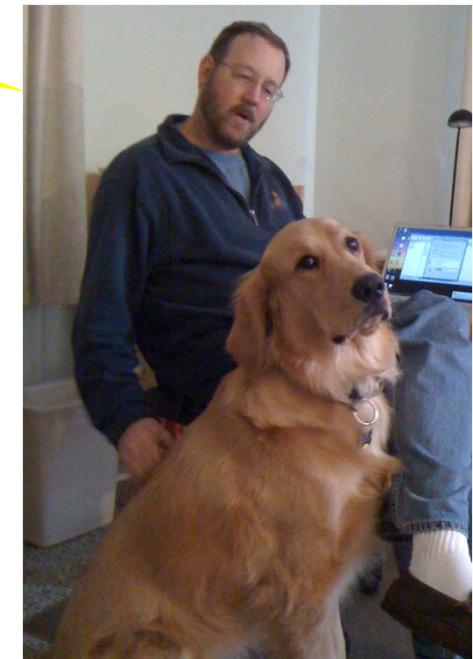
Acids & Bases: An Extension of Chemical Equilibria



G.N. Lewis 1875-1946

Buffers! You should tell them about buffers!

Good idea Gilbert!
What do you think
Ranger?



Acids & Bases: An Extension of Chemical Equilibria

Acids and Bases: Buffers

A **buffer** contains both a weak acid and its conjugate base. Example: for an acetic acid/acetate buffer you would add acetic acid and sodium acetate to water.

Buffers resist change in pH. The weak acid and its conjugate base react with either acid or base

- $\text{HA(aq)} + \text{OH}^-(\text{aq}) \rightarrow \text{A}^-(\text{aq}) + \text{H}_2\text{O(l)}$
- $\text{A}^-(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow \text{HA(aq)}$

Both of these reactions have large equilibrium constants.

Acids & Bases: An Extension of Chemical Equilibria

Example, Part II

Make a buffer solution that remains at approximately pH=5 from acetic acid & sodium acetate, and show that it remains close to pH=5 upon addition of 20 mM HNO₃

Start with [1M] CH₃CO₂H and, with Na⁺CH₃CO₂⁻, make the buffer

$$K_a = \frac{[A^+][B^-]}{[AB]} = 1.75 \times 10^{-5} = \frac{[H^+][H_3CO_2^-]}{[H_3CO_2H]} = \frac{[10^{-5}][x + 10^{-5}]}{[1]}$$

Acetic acid is only weakly ionized (at pH=5) and so we assume its concentration stays at [1M]

Solving for x yields x=1.75M CH₃CO₂⁻ Na⁺

Acids & Bases: An Extension of Chemical Equilibria

Example, Part II

Make a buffer solution that remains at approximately pH=5 from acetic acid & sodium acetate, and show that it remains close to pH=5 upon addition of 20 mM HNO₃

Start with [1M] CH₃CO₂H and, with Na⁺CH₃CO₂⁻, make the buffer

$$K_a = \frac{[A^+][B^-]}{[AB]} = 1.75 \times 10^{-5} = \frac{[H^+][H_3CO_2^-]}{[H_3CO_2H]} = \frac{[10^{-5}][x + 10^{-5}]}{[1]}$$

Now we add 20 mM HNO₃ = [0.02M]

Assume that all HNO₃ ionizes (it is a strong acid)
 [0.02M] H⁺ is taken up by H₃CO₂⁻, thereby reducing the concentration of acetate from 1.75 M to 1.73 M

Acids & Bases: An Extension of Chemical Equilibria

Example, Part II

Make a buffer solution that remains at approximately pH=5 from acetic acid & sodium acetate, and show that it remains close to pH=5 upon addition of 20 mM HNO₃

Assume that all HNO₃ ionizes (it is a strong acid)

[0.02M] H⁺ is taken up by H₃CO₂⁻; thereby reducing the concentration of acetate from 1.75 M to 1.73 M

Then set up the K_a equation, allowing for the concentration of [H⁺] to vary

$$K_a = \frac{[A^+][B^-]}{[AB]} = 1.75 \times 10^{-5} = \frac{x[1.73 + x]}{[1.02 - x]}$$

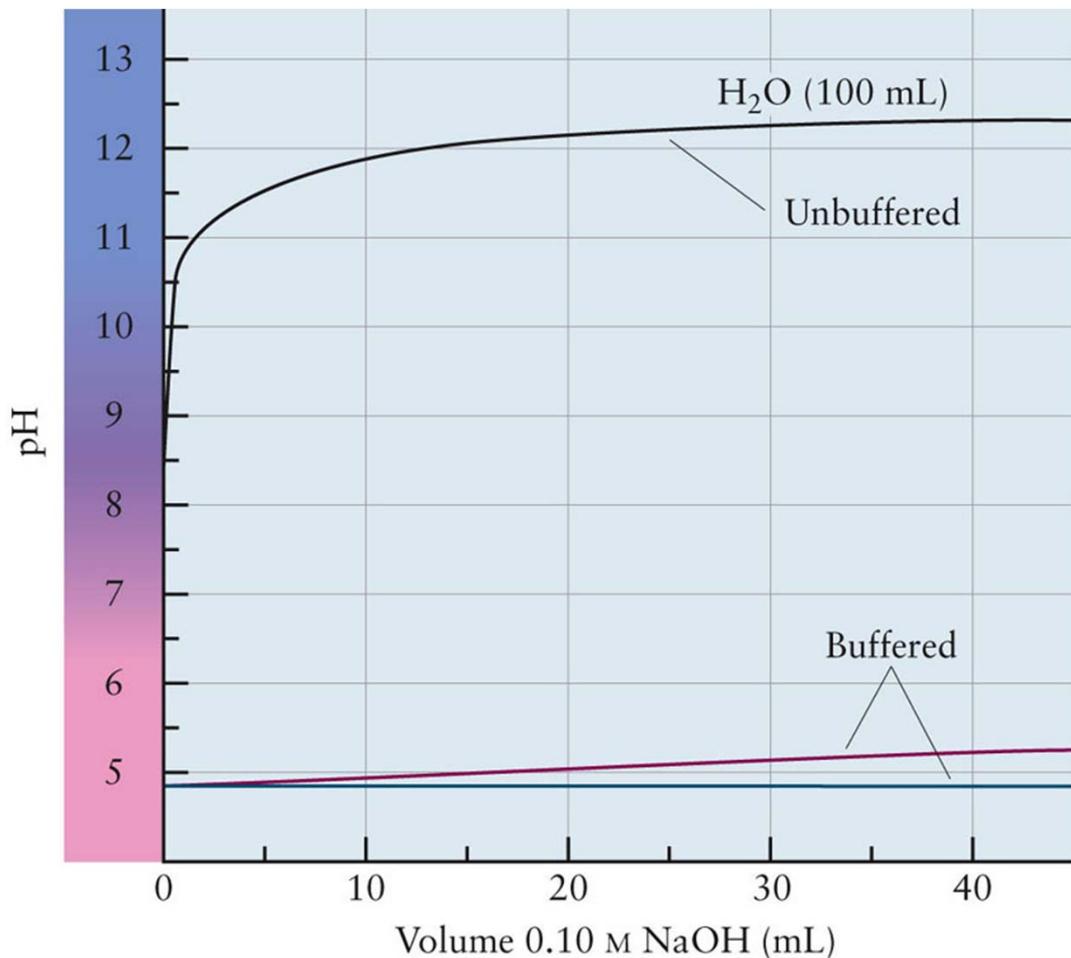
Solve for x; **[x] = 1.032x10⁻⁵; pH = 4.98**

The pH has hardly changed, even though we added a strong acid!
This is the point of a buffer!!

Acids & Bases: An Extension of Chemical Equilibria

Here's a graphical example of buffering from OGC:

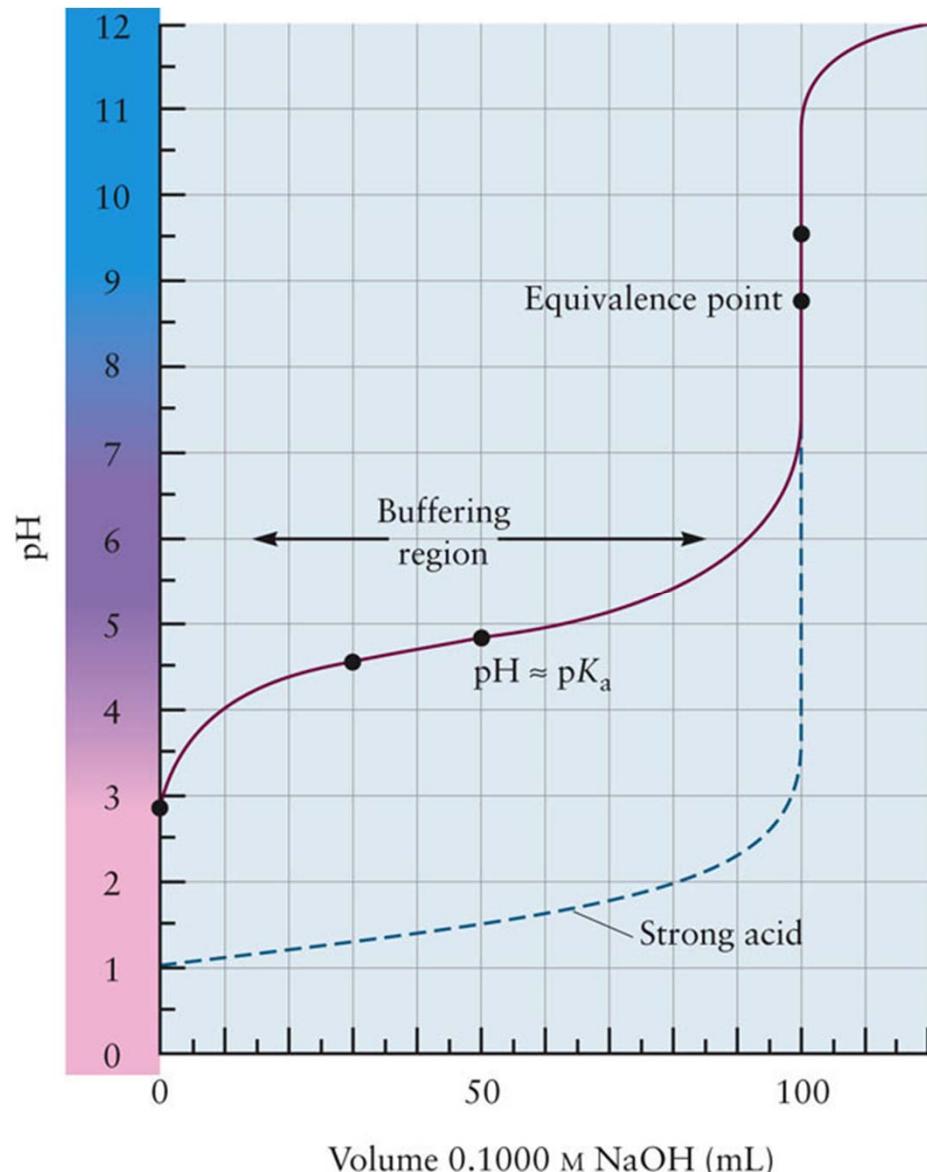
Note the very small change in pH for a significant addition, in this case, of base. Such behavior can be very useful, especially for living systems!



Acids & Bases: An Extension of Chemical Equilibria

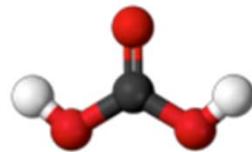
The titration curves discussed in OGC also involve buffering, for weak acids, where the buffering region is tied to the pK_a :

Blood and the ocean are two examples of buffered systems, both involving the *diprotic* acid H_2CO_3 . How should we try to analyze such systems?



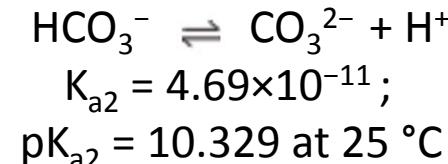
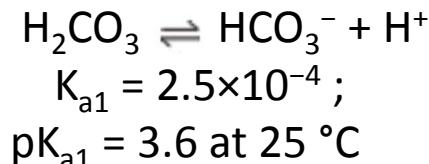
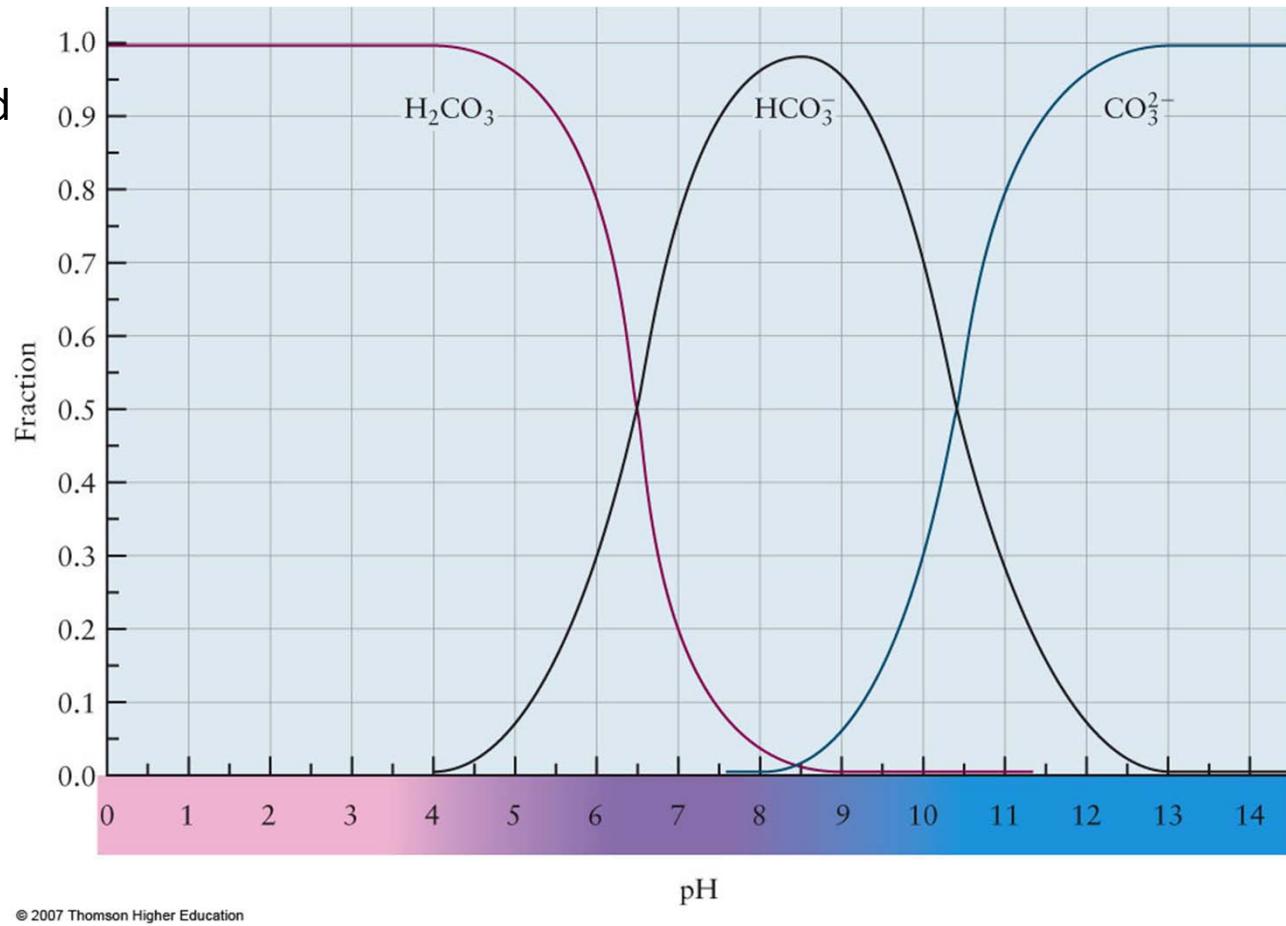
Acids & Bases: An Extension of Chemical Equilibria

CO_2 is somewhat soluble in water, and the solvated CO_2 can react with the water to form carbonic acid (H_2CO_3):



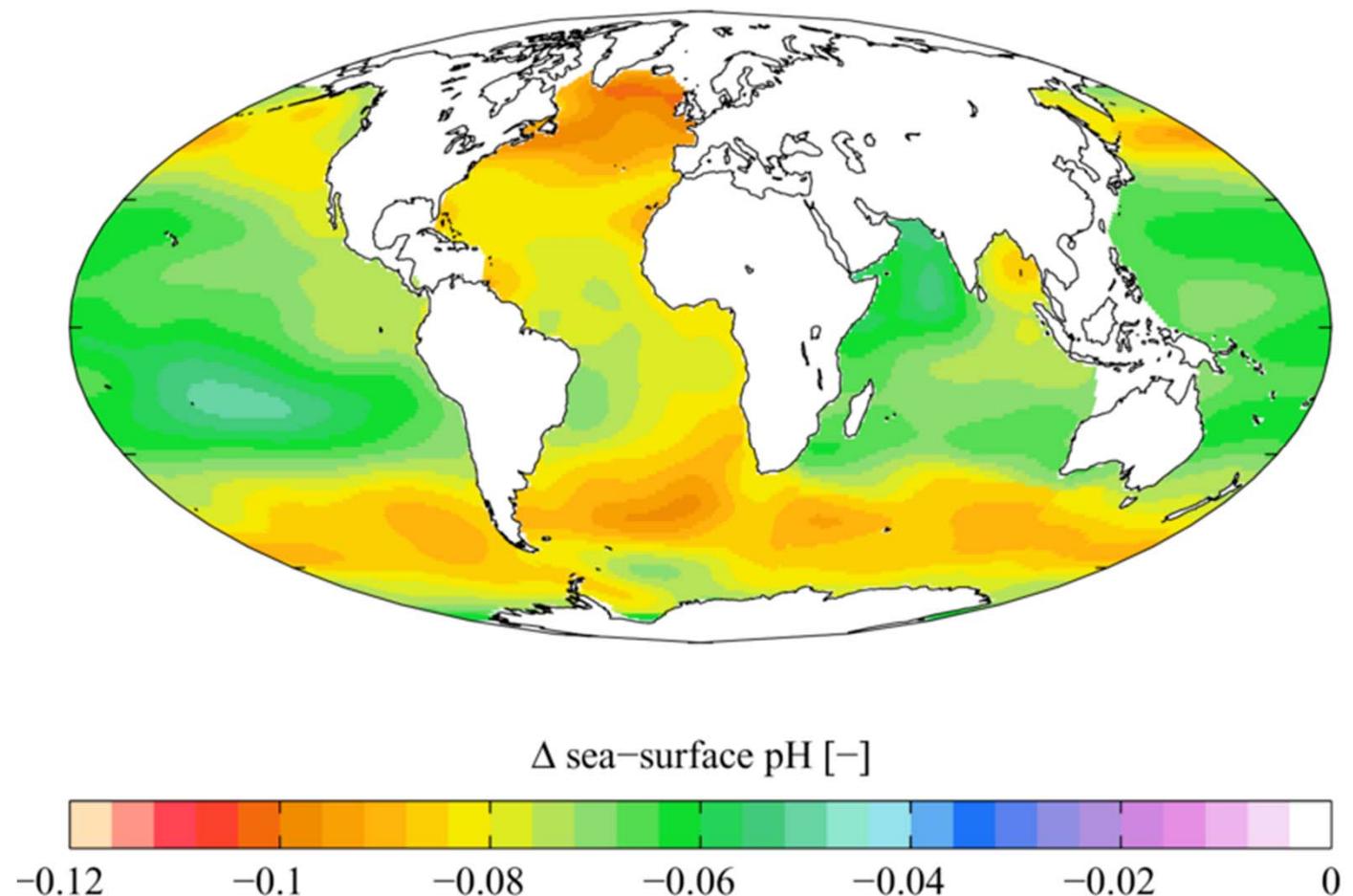
Only a small part of the gas dissolves to form $\text{CO}_2(aq)$ and reacts to create H_2CO_3 . There are two dissociation constants to consider ($K_{a1} \gg K_{a2}$, this is typically true).

Why?



Ocean Acidification:

Here is a map of the change in the pH at the surface of the ocean from the 1700s to ~today (combination of data & models).



What is driving this change?

Ocean Acidification:

First, a bit about the ocean...

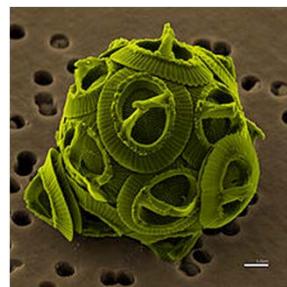
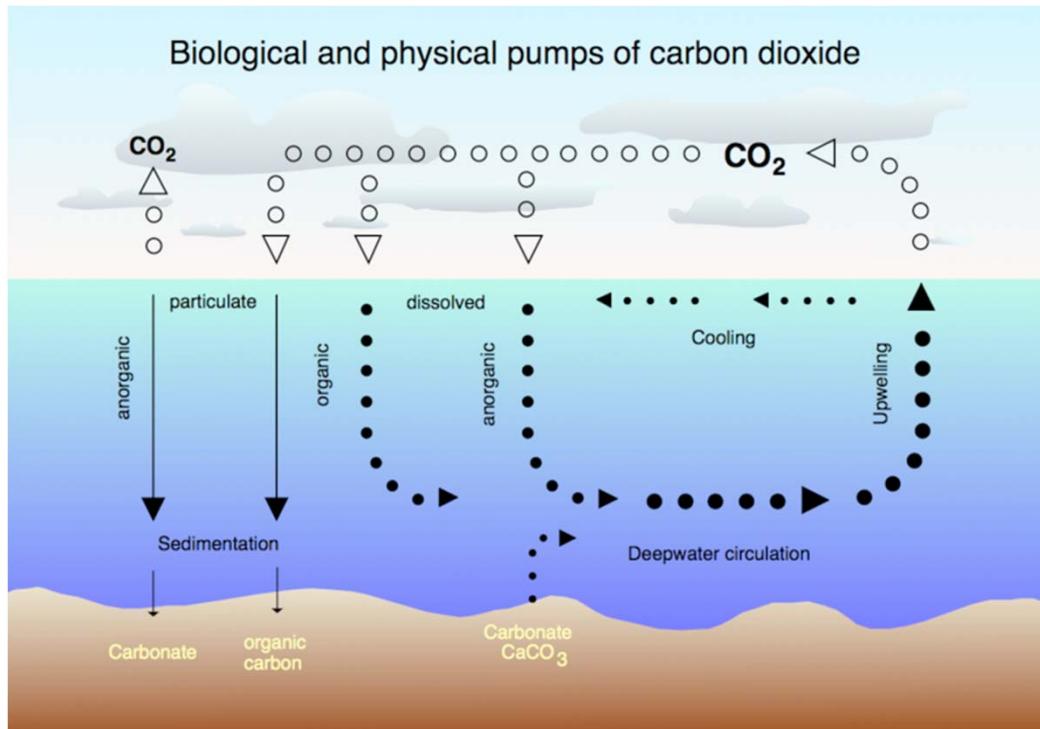
- The salinity (grams salt/kilogram of water) is typically 30-35.

So, decent ionic strength and we can't use the simple model from page 28 to get the pH. Fortunately, example 15.15 from OGC calculates the pH for 0.1 M NaHCO₃. The pH is found to be 8.34 (page 660), and so the oceans are *slightly basic*.

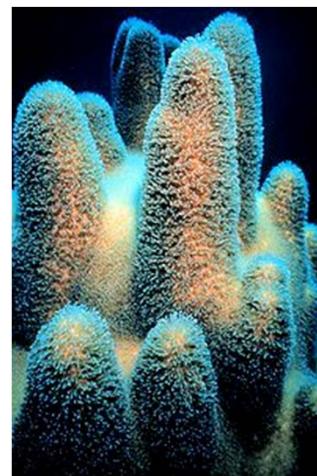
- The surface and deep oceans have greatly different masses and transport processes.

Thus, the actual atmosphere-ocean system will respond in a complex way on multiple time scales. Here, we will just worry about the simplest model & chemistry.

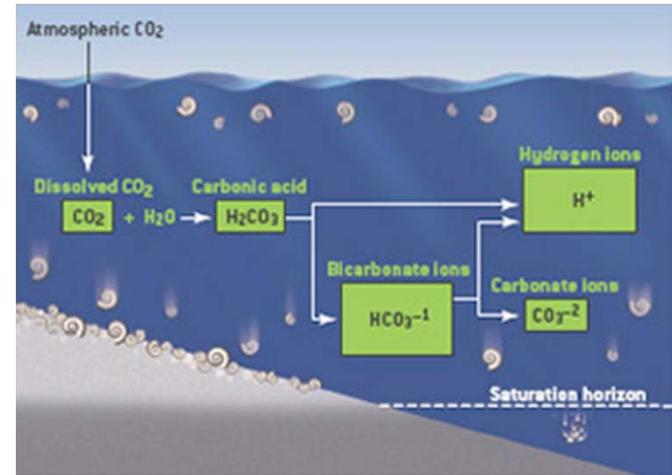
Ocean Acidification:



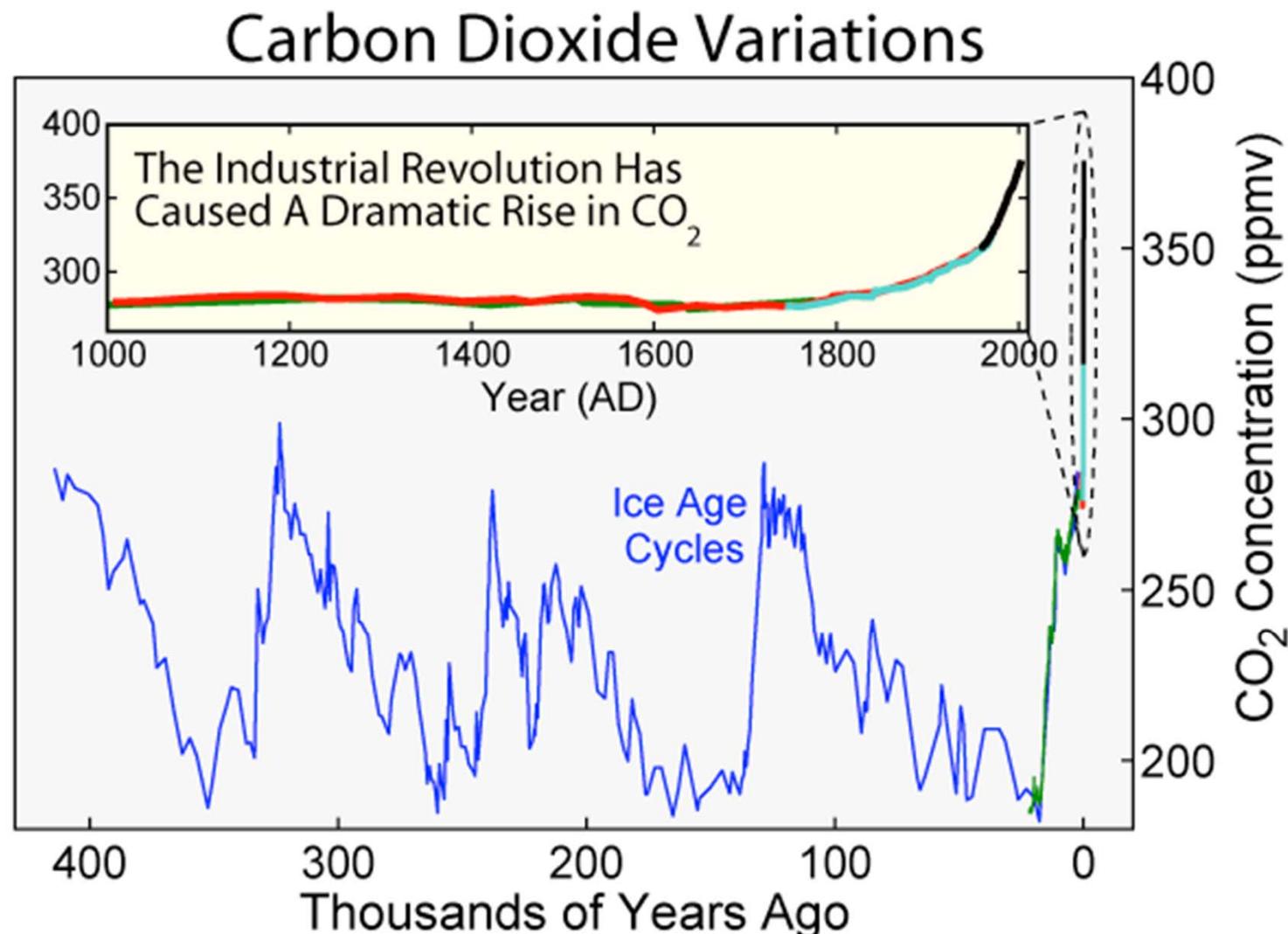
The carbonate is generated by phytoplankton, corals, etc.



On very long time scales, there is a competition/balance between dissolution of carbon dioxide into seawater and the deposition of carbonate into marine sediments (if sufficiently shallow).



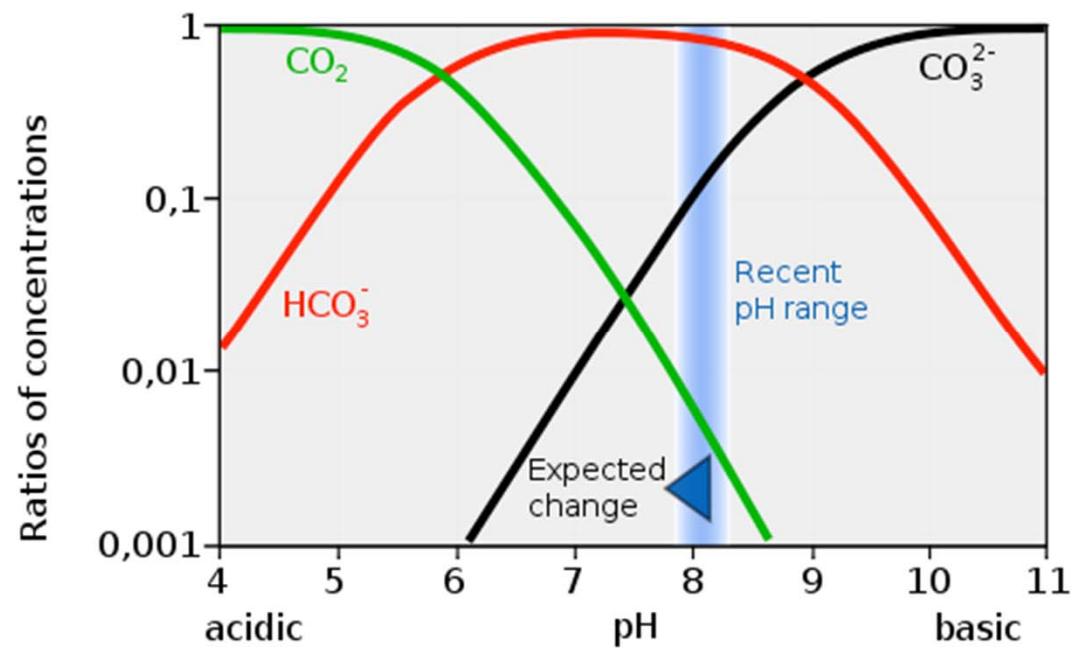
Ocean Acidification: Enter the industrial revolution...



Ocean Acidification:

What effect does the increased CO_2 have on the oceans?

$p\text{CO}_2$ (atm)	pH
10^{-8}	7.00
10^{-7}	6.94
10^{-6}	6.81
10^{-5}	6.42
10^{-4}	5.92
3.5×10^{-4}	5.65
10^{-3}	5.42
10^{-2}	4.92
10^{-1}	4.42
10^0	3.92
2.5×10^0	3.72
10^1	3.42



From Le Chatlier's principle, etc. an increasing CO_2 concentration drives the pH to lower values.