Acid-Base Equilibrium

Chem 108

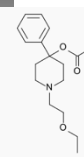
- Acids: taste sour and cause certain dyes to change color.

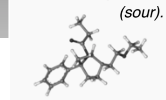
Dr. Ron Rusay

- Bases: taste bitter, feel soapy, and also cause certain dyes to change color.

Taste & Molecules

Prosidol & Capsaicin

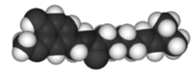




Chemical stimuli and taste:

Generally, sugars are (sweet), amino acids (umami), sodium chloride and other (salty), bases/ alkaloids (bitter) and acids (sour).

Molecules with the same molecular formula can have very different tastes.



Capsaicin: $C_{18}H_{27}NO_3$

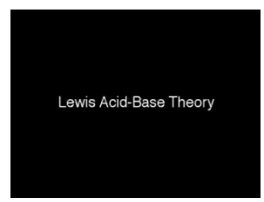
Prosidol: $C_{18}H_{27}NO_3$ bitter alkaloid (opiate analgesic)

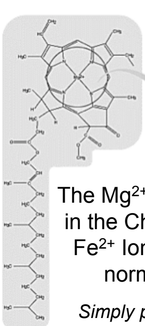
Models of Acids and Bases

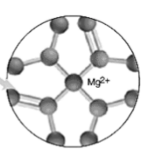
- Arrhenius: Acids produce H^+ & bases produce OH^- ion in aqueous solutions .
- Brønsted-Lowry: Acids are H^+ donors & bases are proton acceptors.
  - $HCl_{(aq)} + H_2O_{(l)} \rightarrow Cl^-_{(aq)} + H_3O^+_{(aq)}$

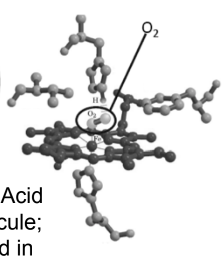
    acid base

Lewis Acids and Bases









The Mg^{2+} Ion is a Lewis Acid in the Chlorophyll Molecule; Fe^{2+} Ion is a Lewis Acid in normal Hemoglobin

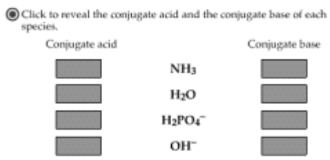
Simply put, Lewis Acids are represented best by cations: eg. H^+, Mg^{2+}, Fe^{2+}; Lewis bases are represented best by anions & free electrons: eg. OH^-, $:NH_3$

Conjugate Acid/Base Pairs

- $HA_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + A^-_{(aq)}$

  acid 1 base 2 conj acid 2 conj base 1

- conjugate acid: formed when the proton is transferred to the base.
- conjugate base: everything that remains of the acid molecule after a proton is lost.



http://chemconnections.org/general/movies/ConjugateAcidBaseActivity.swf

QUESTION

In the following equilibrium reaction, which statement is correct?

$NH_4^+(aq) + H_2O(l) \leftrightarrows NH_3(aq) + H_3O^+(aq)$

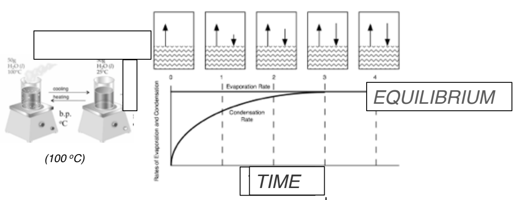
"Conjugate Side"

A. NH_4^+ is an acid and H_2O is its conjugate base.
B. H_2O is a base and NH_3 is its conjugate acid.
C. NH_4^+ is an acid and H_3O^+ is its conjugate base.
D. H_2O is a base and H_3O^+ is its conjugate acid.
E. NH_4^+ is a base and H_2O is its conjugate acid.

What is equilibrium?

Water evaporates and condenses in equilibrium
And, water is an acid & a base in equilibrium

$H_2O_{(l)} + energy \leftrightarrows H_2O_{(g)}$



$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$

Acid-Base Strengths

Conductivity & pH [indicator paper & pH meter]

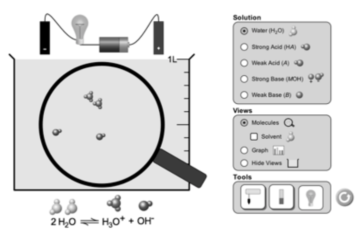
https://phet.colorado.edu/en/simulation/acid-base-solutions

Strong Acid:

Strong Base:

Weak Acid:

Weak Base:



Water itself is neutral
It is both an Acid and a Base

What is equilibrium?
*Equilibrium Constant (**K**)*

- *K is a proportional measure of concentrations in equilibria mixtures*
  [Products] ÷ [Reactants]

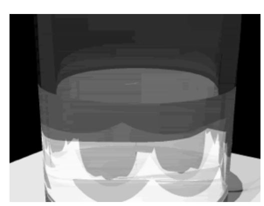
$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$

$$K = \frac{[H_3O^+][OH^-]}{[H_2O]\,[H_2O]}$$

Water itself is neutral having very very low concentrations of ions @ equilibrium
It is both an Acid and a Base: $[H_3O^+] = [OH^-]$

Water as an Acid and a Base

Self-ionization



Pure Water: an Acid and a Base

It is amphoteric. (It can behave either as an acid or a base).

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

What is equilibrium?

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

acid 1 base 2 conj acid 2 conj base 1

$$K = \frac{[H_3O^+][OH^-]}{[H_2O]\,[H_2O]}$$

- $K_w = 1 \times 10^{-14}$ at 25°C
- $K_w = [H_3O^+][OH^-] = [1 \times 10^{-7} M][1 \times 10^{-7} M]$

NOTE: **only concentrations [mol/L] are used in the calculation;** liquids (l) and solids (s) are not included

Strong & Weak Acids:
Dissociation Constant (K_a)

A proportional measure of the concentration of ions in solution:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \quad \text{or} \quad K_a = \frac{[H^+][A^-]}{[HA]}$$

- K_a is the "acid" dissociation constant, it does not have a unit although it is calculated with concentration, mol/L, (M)

What is equilibrium?

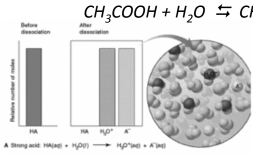
Water is neutral

until something is added

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

$HCl + H_2O \rightarrow Cl^- + H_3O^+$

$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$

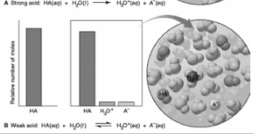


HCl ("Strong Acid")

1.0 M $_{HCl}$ solution

K = [Products][Reactants]

K = 1.0 ÷ 0 = ∞ (100% reacts)



CH_3COOH ("Weak Acid")

1.0 M $_{HOAc}$ (vinegar) solution

K = [Products][Reactants]

K ≈ 10^{-5} (<<< 100% reacts)

Water is neutral
It is an Acid and a Base

What is equilibrium?

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

until something is added

("Equilibrium Constant") K = [Products]/[Reactants]

Reactants ⇆ Products

For example weak acids

EXPERIMENT #1

TIME	Amount Reactant	Amount Product
1	100	0
2	**75**	**25**
3	59	41
4	48	42
5	41	59
6	37	63
7	34	64
8	32	68
9	31	69
10	30	70
11	29	71
12	29	71
13	29	71

K = [71][29]

K = 2.4

Water is neutral
It is an Acid and a Base

What is equilibrium?

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

until something is added

("Equilibrium Constant") K = [Products]/[Reactants]

Reactants ⇆ Products

For example weak acids

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TIME	Amount Reactant	Amount Product
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6	37	63
7	34	64
8	32	68
9	31	69
10	30	70
11	29	71
12	29	71
13	29	71

K = [71][29]

K = 2.4

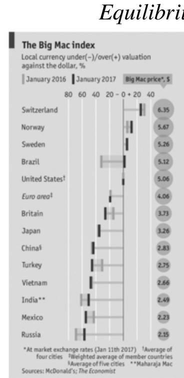
EXPERIMENT #2

TIME	Amount Reactant	Amount Product
1	0	100
2	10	**90**
3	16	84
4	20	80
5	22	78
6	24	76
7	25	75
8	26	74
9	27	73
10	28	72
11	29	71
12	29	71
13	29	71

K = [71][29]

K = 2.4

Equilibrium & Currency Exchange Rates



The US $ is the current common global currency

The cost of a McDonald's Big Mac in US $, country by country, provides a basis for the relative global market equilibrium value of the local currency

The "Big Mac Index" was introduced by the Economist magazine in September 1986 by Pam Woodall and is published annually

Currently, US $20 would only buy 3 Big Macs in Geneva, Switzerland, but 9 in Moscow, Russia

Normalized to 1 Big Mac in US $

Geneva ⇆ US ⇆ Moscow

Dynamic Equilibrium

"The Big Mac Index"

http://www.economist.com/content/big-mac-index

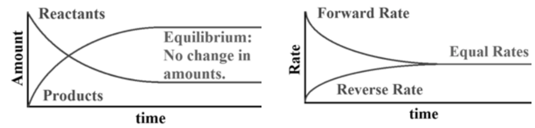
How fast does water ionize?

How do the rate(s) affect concentration?

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

What is equilibrium?

Reactants ⇆ Products



("Equilibrium Constant") K = [Products]/[Reactants]

Reaching Equilibrium (TIME)

*("Equilibrium **Constant**") K = [Products]/[Reactants]*

Reactants ⇆ Products

For example weak acids

$CH_3COOH + H_2O \leftrightarrows CH_3COO^- + H_3O^+$

EXPERIMENT #1

TIME	Amount Reactant	Amount Product
1	100	0
2	**75**	**25**
3	59	41
4	48	42
5	41	59
6	37	63
7	34	64
8	32	68
9	31	69
10	30	70
11	29	71
12	29	71
13	29	71

K = [71][29]
K = 2.4

EXPERIMENT #2

TIME	Amount Reactant	Amount Product
1	0	100
2	10	**90**
3	16	84
4	20	80
5	22	78
6	24	76
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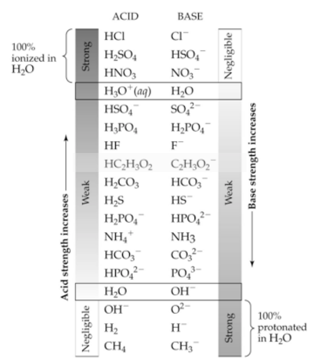
13	29	71

K = [71][29]
K = 2.4



$CH_3COOH + H_2O \leftrightarrows CH_3COO^- + H_3O^+$

Acid Strength

Strong Acid:

- *Equilibrium position lies far to the right. (HNO_3); Ka >>> 1*
- *Produces a conjugate base. (NO_3^-) and a conjugate acid which are weaker than the starting acid and base (H_2O).*

Acid Strength

Strong Acids:

Strong Acid	Formula
Hydrochloric	HCl
Hydrobromic	HBr
Hydroiodic	HI
Nitric	HNO_3
Chloric	$HClO_3$
Perchloric	$HClO_4$
Sulfuric *	H_2SO_4

Acid Strength
(continued)

Weak Acid:

- Equilibrium lies far to the left. (CH_3COOH); Ka < 1
- Yields a stronger (relatively strong) conjugate base than water. (CH_3COO^-)

Bases

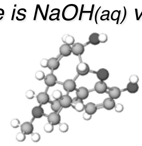
- "Strong" and "weak" are used in the same sense for bases as for acids.
- Strong = complete dissociation, $K_b >> 1$ (concentration of hydroxide ion in solution)

$$NaOH_{(s)} \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$$

- $NaOH_{(s)} + H_2O_{(l)} \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$

Bases
(continued)

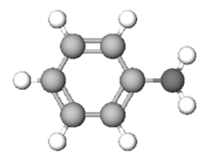
- Weak bases have very little dissociation, $K_b < 1$ (little ionization with water)
- $CH_3NH_{2(aq)} + H_2O_{(l)} \leftrightarrows CH_3NH_3^+{}_{(aq)} + OH^-{}_{(aq)}$
- How conductive is $NaOH_{(aq)}$ vs morphine, $C_{17}H_{19}NO_3$?



QUESTION

Aniline, $C_6H_5NH_2$, was isolated in the 1800s and began immediate use in the dye industry. What is the formula of the conjugate acid of this base?

A. $C_6H_5NH_2^+$
B. $C_6H_5NH_3^+$
C. $C_6H_5NH^-$
D. $C_6H_5NH^+$



Water as an Acid and a Base

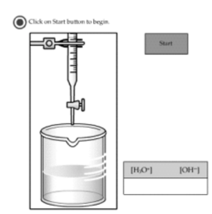
$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

- Remember: Water is amphoteric (it can behave either as an acid or a base).
- $H_2O + H_2O \leftrightarrows H_3O^+ + OH^-$

H_2O	H_2O	H_3O^+	OH^-
		conj	conj
acid 1	base 2	acid 2	base 1

- $K_w = 1 \times 10^{-14}$ at 25°C

Water as an Acid and a Base
Self-ionization



http://chemconnections.org/general/movies/KwActivity.swf

The pH Scale

- $pH \approx -log[H^+] \approx -log[H_3O^+]$
- pH in water ranges from 0 to 14.
  $K_w = 1.00 \times 10^{-14} = [H^+] [OH^-]$
  $pK_w = 14.00 = pH + pOH$
- As pH rises, pOH falls (sum = 14.00).
- There are no theoretical limits on the values of pH or pOH. (e.g. pH of 2.0 M HCl is -0.301)

https://phet.colorado.edu/en/simulation/ph-scale-basics

Acid-Base Strengths

pH [indicator paper & pH meter]

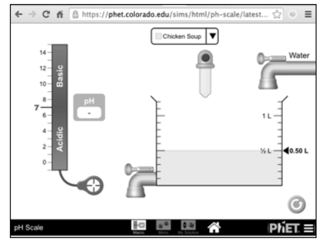
https://phet.colorado.edu/en/simulation/ph-scale

Strong Acid:

Strong Base:

Weak Acid:

Weak Base:

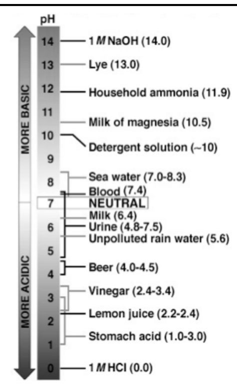


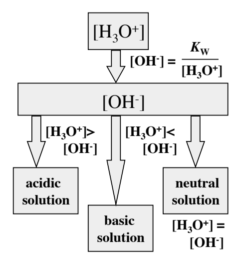
http://www.chemconnections.org/general/chem108/Acids-Bases%20Guide.html

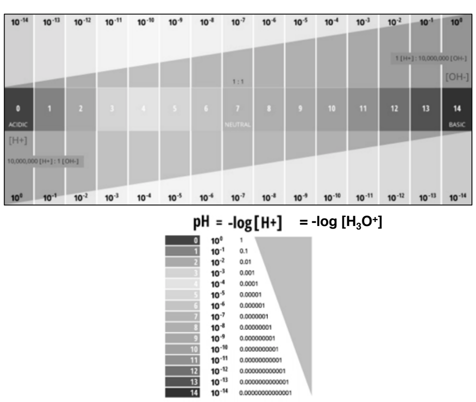
The Relations Among $[H_3O^+]$, pH, $[OH^-]$, and pOH

		$[H_3O^+]$	pH	$[OH^-]$	pOH
MORE BASIC	BASIC	1.0×10^{-15}	15.00	1.0×10^{1}	−1.00
		1.0×10^{-14}	14.00	1.0×10^{0}	0.00
		1.0×10^{-13}	13.00	1.0×10^{-1}	1.00
		1.0×10^{-12}	12.00	1.0×10^{-2}	2.00
		1.0×10^{-11}	11.00	1.0×10^{-3}	3.00
		1.0×10^{-10}	10.00	1.0×10^{-4}	4.00
		1.0×10^{-9}	9.00	1.0×10^{-5}	5.00
		1.0×10^{-8}	8.00	1.0×10^{-6}	6.00
	NEUTRAL	1.0×10^{-7}	7.00	1.0×10^{-7}	7.00
MORE ACIDIC	ACIDIC	1.0×10^{-6}	6.00	1.0×10^{-8}	8.00
		1.0×10^{-5}	5.00	1.0×10^{-9}	9.00
		1.0×10^{-4}	4.00	1.0×10^{-10}	10.00
		1.0×10^{-3}	3.00	1.0×10^{-11}	11.00
		1.0×10^{-2}	2.00	1.0×10^{-12}	12.00
		1.0×10^{-1}	1.00	1.0×10^{-13}	13.00
		1.0×10^{0}	0.00	1.0×10^{-14}	14.00
		1.0×10^{1}	−1.00	1.0×10^{-15}	15.00

The pH Values of Some Familiar Aqueous Solutions







QUESTION

In a solution of water at a particular temperature the $[H^+]$ may be 1.2×10^{-6} M. What is the $[OH^-]$ in the same solution? Is the solution acidic, basic, or neutral?

A. 1.2×10^{-20} *M*; acidic
B. 1.2×10^{-20} *M*; basic
C. 8.3×10^{-9} *M*; basic
D. 8.3×10^{-9} *M*; acidic

$K_w = 1.00 \times 10^{-14} = [H^+] [OH^-] = [H_3O^+] [OH^-]$

http://chemconnections.org/general/movies/pHEstimation.swf

pH Estimation

pH = -log $[H_3O^+]$

Using the pH benchmarks, estimate the pH of solutions with each of the following hydronium ion concentrations. Click on the boxes to see the estimate and the calculated value of each solution's pH.

pH Benchmarks

$[H_3O^+]$	pH
1.0 M	0.00
0.10	1.00
0.010	2.00
0.0010	3.00
1.0×10^{-4}	4.00
1.0×10^{-5}	5.00
1.0×10^{-6}	6.00
1.0×10^{-7}	7.00

	$[H_3O^+]$	Estimated pH	Calculated pH
1.5×10^{-2}	0.015 M	2	
5.8×10^{-2}	0.058 M	2	
_._ $\times 10^{-5}$	4.5×10^{-5} M	5	
_._ $\times 10^{-7}$	3.9×10^{-7} M	7	

http://chemconnections.org/general/movies/pHEstimation.swf

pH = -log $[H_3O^+]$

	$[H_3O^+]$	Estimated pH	Calculated pH
1.5×10^{-2}	0.015 M	2 (<2)	1.82
5.8×10^{-2}	0.058 M	2 (<2)	1.24
_._ $\times 10^{-5}$	4.5×10^{-5} M	5 (<5)	4.35
_._ $\times 10^{-7}$	3.9×10^{-7} M	7 (<7)	6.41

QUESTION

An environmental chemist obtains a sample of rainwater near a large industrial city. The $[H^+]$ was determined to be 3.5×10^{-6} *M*. What is the pH, pOH, and $[OH^-]$ of the solution?

A. pH = 5.46 ; pOH = 8.54; $[OH^-] = 7.0 \times 10^{-6}$ *M*
B. pH = 5.46 ; pOH = 8.54; $[OH^-] = 2.9 \times 10^{-9}$ *M*
C. pH = 12.56 ; pOH =1.44 ; $[OH^-] = 3.6 \times 10^{-2}$ *M*
D. pH = 8.54; pOH = 5.46; $[OH^-] = 2.9 \times 10^{-9}$ *M*

$K_w = 1.00 \times 10^{-14} = [H^+][OH^-] = [H_3O^+][OH^-]$
$pK_w = 14.00 = pH + pOH$

pH = -log $[H_3O^+]$ = -log $[H^+]$

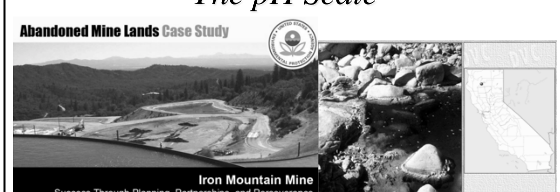
The pH Scale

$[H^+]$	$[OH^-]$	pH	pOH	acidic or basic?
7.5×10^{-3} *M*				
	3.6×10^{-10} *M*			
		8.25		
			5.70	

The pH Scale

$[H^+]$	$[OH^-]$	pH	pOH	acidic or basic?
7.5×10^{-3} *M*	1.3×10^{-12}	2.1	11.9	Acid
2.8×10^{-5}	3.6×10^{-10} *M*	4.6	9.4	Acid
5.62×10^{-9}	1.78×10^{-6}	8.25	5.75	Base
5.00×10^{-9}	2.00×10^{-6}	8.30	5.70	Base

The pH Scale

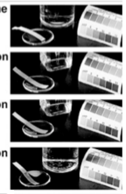


The drainage water from the Iron Mountain Mine is the most acidic water on Earth; some samples collected in 1990 and 1991 have been measured to have a pH value of -3.6, which is the lowest pH observed globally in a natural environment.

Behavior of Salts in Water

The Behavior of Salts in Water

Salt Solution (Examples)	pH	Nature of Ions	Ion That Reacts with Water
Neutral [NaCl, KBr, $Ba(NO_3)_2$]	7.0	Cation of strong base; Anion of strong acid	None
Acidic [NH_4Cl, NH_4NO_3, CH_3NH_3Br]	<7.0	Cation of weak base; Anion of strong acid	Cation
Acidic [$Al(NO_3)_3$, $CrCl_3$, $FeBr_3$]	<7.0	Small, highly charged cation; Anion of strong acid	Cation
Basic [CH_3COONa, KF, Na_2CO_3]	>7.0	Cation of strong base; Anion of weak acid	Anion



$LiNO_2$ NH_4Cl $Ca(NO_3)_2$

http://chemconnections.org/general/movies/pHofSaltSolutions.swf

$MgSO_4$ $AgClO_3$ CsCN

QUESTION

The following salts were dissolved to form separate 0.10M solutions at the same temperature so that their concentrations were all equal. Arrange them in order from lowest pH to highest pH.

NaCl; NH_4NO_3; $Na(C_2H_3O_2)$

A. NaCl; NH_4NO_3; $Na(C_2H_3O_2)$
B. $Na(C_2H_3O_2)$; NaCl; NH_4NO_3
C. NH_4NO_3; NaCl; $Na(C_2H_3O_2)$
D. NH_4NO_3; $Na(C_2H_3O_2)$; NaCl

$Na(C_2H_3O_2) = CH_3COONa$

Acid-Base Equilibrium

BUFFERS

Dr. Ron Rusay

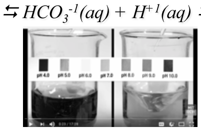
BUFFERS

Weak Acid-Weak Base Systems

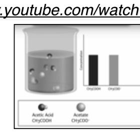
Example:

$H_2CO_3(aq)$ / $HCO_3^{-1}(aq)$ / $CO_3^{-2}(aq)$

$CO_2(g) + H_2O(l) \leftrightarrows HCO_3^{-1}(aq) + H^{+1}(aq) \leftrightarrows CO_3^{-2}(aq) + H^{+1}(aq)$



https://www.youtube.com/watch?v=XR_0k8JlawY



https://www.youtube.com/watch?v=ZLKEjXbCU30

QUESTION

In the following equilibrium:

$HCO_3^-(aq) + H_2O(l) \leftrightarrows H_2CO_3(aq) + OH^-(aq)$

A) HCO_3^- is an acid and H_2CO_3 is its conjugate base.
B) H_2O is an acid and OH^- is its conjugate base.
C) HCO_3^- is an acid and OH^- is its conjugate base.
D) H_2O is an acid and H_2CO_3 is its conjugate base.
E) H_2O is an acid and HCO_3^- is its conjugate base.

$H_2CO_3(aq)$ / $HCO_3^{-1}(aq)$ / $CO_3^{-2}(aq)$

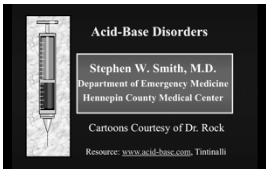
Two VERY IMPORTANT Buffer Systems

"Bicarbonate"

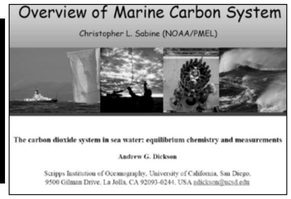
$CO_2(g) + H_2O(l) \leftrightarrows HCO_3^{-1}(aq) + H^{+1}(aq) \leftrightarrows CO_3^{-2}(aq) + H^{+1}(aq)$

1. ***Blood:*** *a human's blood serum volume is relatively small, 4-6 Liters with a narrow pH range, pH = 7.35 – 7.45; pH is maintained through buffering (homeostasis)*
   Have you ever had respiratory alkalosis during an exam?
2. ***Oceans:*** *an extraordinarily large volume of a "salt water" solution with a pH ~ 8.1; maintained through buffering*

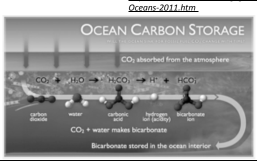
Human & Oceanic Bicarbonate Buffer Systems



http://chemconnections.org/general/chem121/Buffers/Buffers-Med-Pres.htm

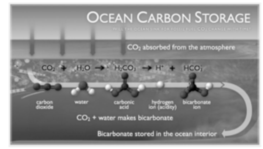


http://chemconnections.org/general/chem121/Buffers/Buffers-CO2-Oceans-2011.htm



EQUILIBRIUM

CO_2 & Oceanic Bicarbonate Buffering



$CO_2(g) + H_2O\ (l) \leftrightarrows HCO_3^{-1}(aq) + H^{+1}(aq) \leftrightarrows CO_3^{-2}(aq) + H^{+1}(aq)$

Oceans: *pH ~ 8.1 and falling*

http://www.tos.org/oceanography/issues/issue_archive/22_4.html

Increasing CO_2 is decreasing ocean pH; long term effects?

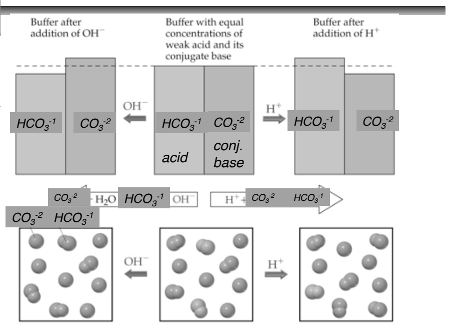
http://sos.noaa.gov/datasets/Ocean/ocean_acidification.html

Bicarbonate Buffer Systems

Which is the buffer?

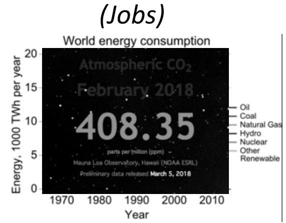
One is bicarbonate buffer to pH ≈ 8 - 9.
One is water plus sodium hydroxide, pH ≈ 8 - 9.

Volunteers to experiment and find out which is which?



Energy —(Carbon) (CO_2)→ *Global Warming*

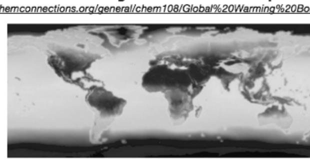
Economy (Jobs) —(Carbon) (CO_2)→



Your Future?

Global Warming & Your Carbon Footprint

http://chemconnections.org/general/chem108/Global%20Warming%20Bonus.html



The United Nations' Nobel Prize winning International Panel on Climate Change (IPCC: http://www.ipcc.ch/) of more than 1,000 scientists have concluded that "Human influence on the climate system is clear, and recent anthropogenic (man made) emissions of greenhouse gases are the highest in history, The atmospheric concentration of key greenhouse gases — carbon dioxide, methane, and nitrous oxide — is unprecedented in at least the last 800,000 years, and our fossil-fuel driven economies and (mankind's) ever-increasing population are to blame."