

Acid-Base Equilibrium

Dr. Ron Rusay

<https://www.youtube.com/watch?v=l5fk7HPmo5g>

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Introduction to Aqueous Acids

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

Introduction to
Aqueous Acids

<http://chemconnections.org/general/movies/acid-intro.mov>

Introduction to Aqueous Bases

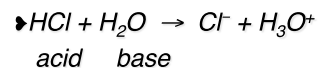
- ▶ Bases: taste bitter, feel soapy and cause certain dyes to turn color.

Introduction to
Aqueous Bases

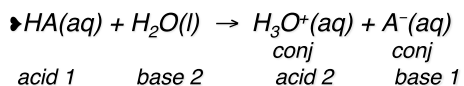
<http://chemconnections.org/general/movies/Bases-intro.mov>

Models of Acids and Bases

- ▶ Acids are H^+ donors & bases include all proton acceptors and are not limited to hydroxide ion (OH^-)

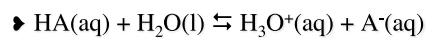


Conjugate Acid/Base Pairs

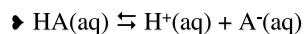


- ▶ conjugate acid: formed when the proton is transferred to the base.
- ▶ conjugate base: everything that remains of the acid molecule after a proton is lost.

Equilibrium Constant (K_a)



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$



Acid Strength

Strong Acid:

⇒ Equilibrium position lies far to the right.
(HNO_3); $K_a \gg 1$

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); $K_a < 1$

ACID		BASE	
Strong	HCl	Cl ⁻	Negligible
	H_2SO_4	HSO_4^-	
	HNO_3	NO_3^-	
	$\text{H}_3\text{O}^+(\text{aq})$	H_2O	
	HSO_4^-	SO_4^{2-}	
	H_3PO_4	H_2PO_4^-	
	HF	F^-	
	$\text{HC}_2\text{H}_3\text{O}_2$	$\text{C}_2\text{H}_3\text{O}_2^-$	
	H_2CO_3	HCO_3^-	
	H_2S	HS^-	
	H_2PO_4^-	HPO_4^{2-}	
	NH_4^+	NH_3	
	HCO_3^-	CO_3^{2-}	
	HPO_4^{2-}	PO_4^{3-}	
	H_2O	OH^-	
Negligible	OH^-	O^{2-}	Strong
	H_2	H^-	
	CH_4	CH_3^-	

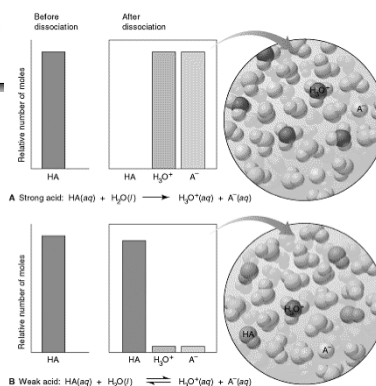
100% ionized in H_2O

Acid strength increases ↑

Base strength increases ↓

100% protonated in H_2O

The Extent of Dissociation for Strong and Weak Acids



QUESTION

Nitric acid, HNO_3 , is considered to be a strong acid whereas nitrous acid, HNO_2 , is considered to be a weak acid. Which of the statements here is fully correct?

- Nitric acid has an aqueous equilibrium that lies far to the right and NO_3^- is considered a weak conjugate base.
- Nitric acid has a stronger conjugate base than nitrous acid.
- The dissociation of nitrous acid compared to an equal concentration of nitric acid produces more H^+ .
- The equilibrium of nitrous acid lies far to the left and the conjugate base is weaker than the conjugate base of nitric acid.

ANSWER

- A) correctly compares equilibrium and conjugate base characteristics. The conjugate base of a strong acid is considered to be weak. The stronger the acid, the more reaction in water. Therefore, a weak acid's equilibrium is favored to the left.

	ACID	BASE
100% ionized in H ₂ O	Strong HCl H ₂ SO ₄ HNO ₃	Negligible Cl ⁻ HSO ₄ ⁻ NO ₃ ⁻
	H ₃ O ⁺ (aq)	H ₂ O
	HSO ₄ ⁻	SO ₄ ²⁻
	H ₃ PO ₄	H ₂ PO ₄ ⁻
	HF	F ⁻
	HC ₃ H ₅ O ₂	C ₃ H ₅ O ₂ ⁻
	H ₂ CO ₃	HCO ₃ ⁻
	H ₂ S	HS ⁻
	H ₂ PO ₄ ⁻	HPO ₄ ²⁻
	NH ₄ ⁺	NH ₃
	HCO ₃ ⁻	CO ₃ ²⁻
	HPO ₄ ²⁻	PO ₄ ³⁻
	H ₂ O	OH ⁻
	OH ⁻	O ²⁻
	H ₂	H ⁻
	CH ₄	CH ₃ ⁻
	Negligible	Strong 100% protonated in H ₂ O
Acid strength increases ↑	Weak	Weak ↓
		Base strength increases ↓

Bases

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

$$\text{NaOH(s)} \rightarrow \text{Na}^{\text{+}}(\text{aq}) + \text{OH}^{\text{-}}(\text{aq})$$
- ▶ $\text{NaOH(s)} + \text{H}_2\text{O(l)} \rightarrow \text{Na}^{\text{+}}(\text{aq}) + \text{OH}^{\text{-}}(\text{aq})$

Bases

(continued)

- ▶ Weak bases have very little dissociation, $K_b < 1$ (little ionization with water)
- ▶ $\text{CH}_3\text{NH}_2(\text{aq}) + \text{H}_2\text{O(l)} \rightleftharpoons \text{CH}_3\text{NH}_3^+(\text{aq}) + \text{OH}^-(\text{aq})$
- ▶ How conductive is NaOH(aq) vs morphine, C₁₇H₁₉NO₃(aq)?

Acid-Base Strengths

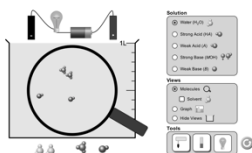
http://phet.colorado.edu/sims/html/acid-base-solutions/latest/acid-base-solutions_en.html

Strong Acid:

Strong Base:

Weak Acid:

Weak Base:



Water as an Acid and a Base Self-ionization

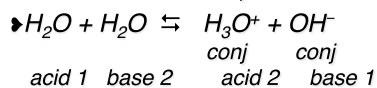


<http://chemconnections.org/general/movies/H2O-ionz.MOV>

Water as an Acid and a Base

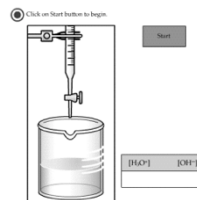


► Water is amphoteric (it can behave either as an acid or a base).



$$K_w = 1 \times 10^{-14} \text{ at } 25^\circ\text{C}$$

Water as an Acid and a Base Self-ionization



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

The pH Scale

$$\text{pH} \approx -\log[\text{H}^+] \approx -\log[\text{H}_3\text{O}^+]$$

► pH in water ranges from 0 to 14.

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

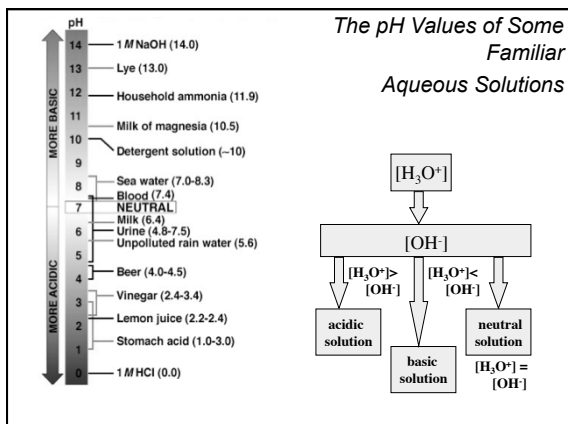
$$\text{p}K_w = 14.00 = \text{pH} + \text{pOH}$$

► 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)

The
Relations
Among
[H₃O⁺],
pH,
[OH⁻],
and pOH

	[H ₃ O ⁺]	pH	[OH ⁻]	pOH
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
NEUTRAL	1.0×10^{-8}	8.00	1.0×10^{-6}	6.00
	1.0×10^{-7}	7.00	1.0×10^{-7}	7.00
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



QUESTION

In an aqueous solution at a particular temperature the [H⁺] was measured as 1×10^{-6} M. What is the [OH⁻] in the same solution? Is the solution acidic, basic, or neutral?

- A. 1×10^{-20} M; acidic
- B. 1×10^{-8} M; acidic
- C. 1×10^{-6} M; basic
- D. 1×10^{-8} M; basic
- E. 1×10^{-7} M; neutral

Answer

In an aqueous solution at a particular temperature the $[H^+]$ was measured as $1 \times 10^{-6} M$. What is the $[OH^-]$ in the same solution? Is the solution acidic, basic, or neutral?

- A. $1 \times 10^{-20} M$; acidic
 B. $1 \times 10^{-8} M$; acidic
 C. $1 \times 10^{-6} M$; basic
 D. $1 \times 10^{-8} M$; basic
 E. $1 \times 10^{-7} M$; neutral

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$$

QUESTION

An environmental chemist obtains a sample of rainwater near a large industrial city. The $[H^+]$ was determined to be $3.5 \times 10^{-6} M$. 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; $[OH^-] = 2.9 \times 10^{-9} M$

Refer to:

<http://chemconnections.org/general/chem106/Acids%20and%20Bases-WKS-2016.pdf>
https://phet.colorado.edu/sims/html/ph-scale/latest/ph-scale_en.html

Answer

$pH = -\log[H^+]$ can be used to find the pH then: $14.00 = pH + pOH$ can be used to obtain the pOH. Finally, $[OH^-] = 10^{-pOH}$

- A. pH = 5.46 ; pOH = 8.54; $[OH^-] = 7.0 \times 10^{-6} M$
 B. pH = 5.46 ; pOH = 8.54; $[OH^-] = 2.9 \times 10^{-9} M$
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Indicators

Natural Indicators

http://chemconnections.org/public_html/general/movies/indicators.MOV

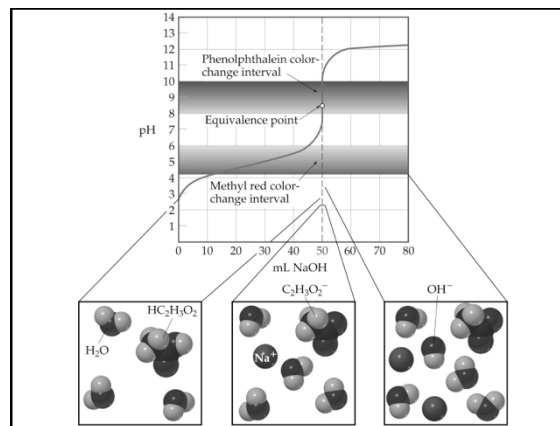
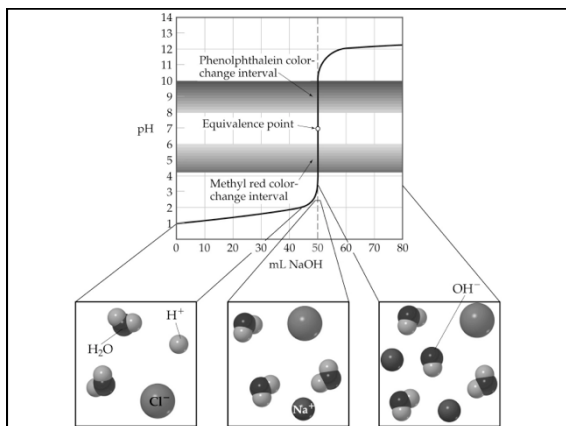
Acid-Base Indicators

	pH range for color change													
	0	2	4	6	8	10	12	14						
Methyl violet	Yellow													
Thymol blue		Red		Yellow		Yellow		Blue						
Methyl orange			Red		Yellow									
Methyl red				Red		Yellow								
Bromthymol blue					Yellow		Blue							
Phenolphthalein						Colorless		Pink						
Alizarin yellow R							Yellow		Red					

Titrations: Indicators & (pH) Curves

► **pH Curve** is a plot of pH of the solution being analyzed as a function of the amount of titrant added.

► **Equivalence (stoichiometric) point:** Enough titrant has been added to react exactly with the solution being analyzed. An indicator provides a visible color change to determine an (end point) volume of titrant.



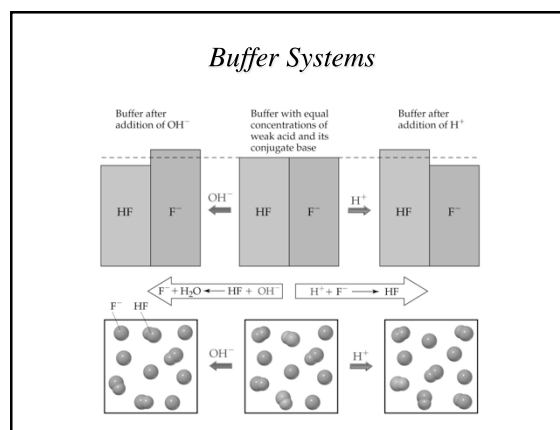
Behavior of Salts in Water

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 ₄ Cl, NH ₄ NO ₃ , CH ₃ NH ₃ Br]	<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 ₃ COONa, KF, Na ₂ CO ₃]	>7.0	Cation of strong base Anion of weak acid	Anion

LiNO₃
NH₄Cl
Ca(NO₃)₂

MgSO₄
AgClO₄
CsCN

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



$H_2CO_3(aq) / HCO_3^{-1}(aq) / CO_3^{-2}(aq)$
Two VERY IMPORTANT Complex Bicarbonate Buffer Systems

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

- Blood:** a human's blood serum volume is relatively small, 4-6 Liters. pH = 7.35 – 7.45 (homeostasis)
 ▶ Ever had respiratory alkalosis?
- Oceans:** an extraordinarily large volume "salt water" solution. pH = 8.1 and falling
http://www.tos.org/oceanography/issues/issue_archive/22_4.html
 ▶ Increasing CO₂, decreasing ocean pH, long term effects? Coral reefs?
http://sos.noaa.gov/datasets/Ocean/ocean_acidification.html

Human & Oceanic Bicarbonate Buffer Systems

Acid-Base Disorders

Stephen W. Smith, M.D.
 Department of Emergency Medicine
 Hennepin County Medical Center

Cartoons Courtesy of Dr. Rock

Resource: www.acid-base.com, Tintinalli

http://chemconnections.org/general/chem121/Buffer/Buffer_Med-Press.htm

Overview of Marine Carbon System

Christopher L. Sabine (NOAA/PMEL)

The carbon dioxide system in sea water: equilibrium chemistry and measurements

Andrew G. Dickson

Scripps Institution of Oceanography, University of California, San Diego
 9500 Gilman Drive, La Jolla, CA 92093-0204, USA adickson@ucsd.edu

http://chemconnections.org/general/chem121/Buffer/Buffer_CO2-Oceans-2011.htm

OCEAN CARBON STORAGE

CO₂ absorbed from the atmosphere
 CO₂ + H₂O → H₂CO₃ → H⁺ + HCO₃⁻
 CO₂ + water makes bicarbonate
 Bicarbonate stored in the ocean interior

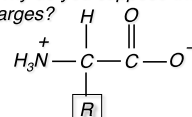
Buffers



<http://chemconnections.org/general/movies/buffer.MOV>

Amino Acids

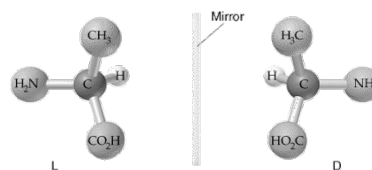
- ▶ More than 700 amino acids occur naturally, but 20 (22?) of them are especially important.
- ▶ These 20 amino acids are the building blocks of proteins in humans and developed organisms
- ▶ They differ in respect to the group attached to the α carbon. Why do you suppose they are written with + and - charges?



Amino Acids

- Our bodies can synthesize about 10 amino acids.
- Essential amino acids are the other 10 amino acids, which have to be ingested.
- The α -carbon in all amino acids except glycine is chiral (has 4 different groups attached to it).
- Chiral molecules exist as two non-superimposable mirror images called enantiomers.
- L-amino acids are the common natural enantiomers.

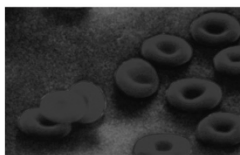
Amino Acids



- L-amino acids are the common natural enantiomers, eg. Alanine above.

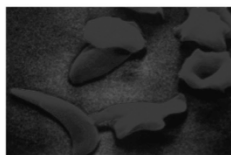
Sickle Cell Anemia

Normal hemoglobin vs sickle cell hemoglobin



1 Val 2 His 3 Leu 4 Thr 5 Pro 6 Glu 7 Glu ...

(a) Normal red blood cells and the primary structure of normal hemoglobin

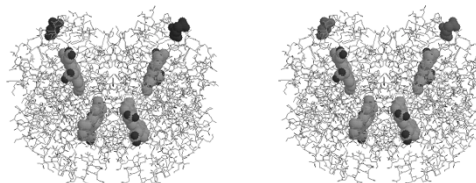


1 Val 2 His 3 Leu 4 Thr 5 Pro 6 Val 7 Glu ...

(b) Sickled red blood cells and the primary structure of sickle-cell hemoglobin

Sickle Cell Anemia

Normal hemoglobin vs sickle cell hemoglobin



Valine replaces Glutamate

<http://chemconnections.org/Presentations/Columbia/slide9-3.html>