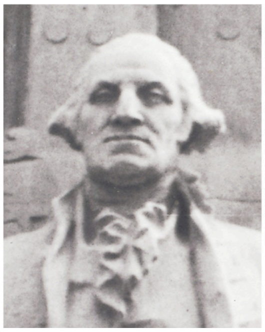
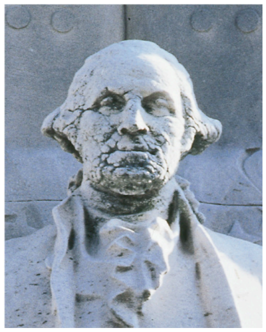
Acids and Bases *Chapter 18*

The effects of acid rain on a statue of George Washington taken in 1935 (left) and 2001 (right) marble.

$$CaCO_3(s) + 2HCl(aq) \Longrightarrow H_2O(l) + CO_2(g) + CaCl_2(aq)$$

Stuff

I need the Exam 1 in my box by Friday. Those who don't turn it in will use the Make-Up Exam for Exam 1.

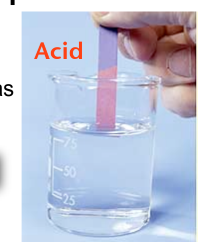
March 10 Exam 3 (Chapter 18/19)

March 17 Make-Up Exam (Comprehensive + 20)

Final Exam (Comprehensive)
March 24
7:30-9:30AM

Acid-Base Equilibria

Acids and bases have distinct properties.



Acids:
- Acrid sour taste
- React with metals (Group I,II) to yield H_2 gas
- Changes plant dye litmus from **blue** to **red**
- React with carbonates and bicarbonates to produce CO_2 gas

200 Million MT H_2SO_4

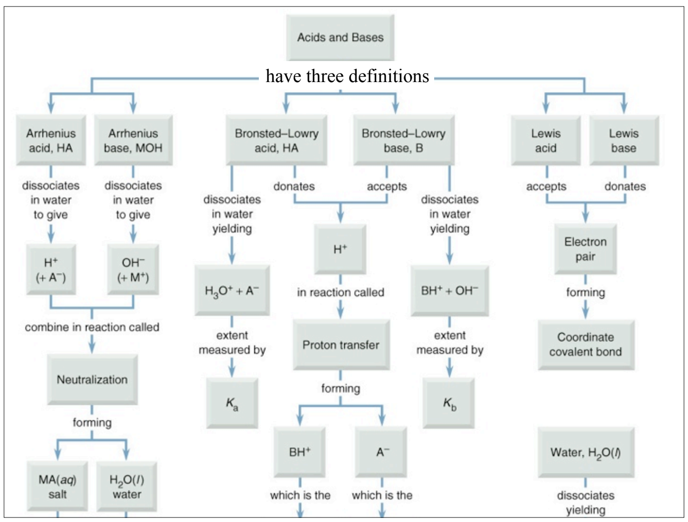
Bases:
- Bitter taste
- Slippery feel
- Changes plant dye litmus from red to blue
- React and neutralizes the effects of acids

50 Million MT NaOH/yr
3 million containers

Acids and bases are everywhere.

Common Acids	
Acetic acid, CH_3COOH	Flavoring, preservative
Citric acid, $H_3C_6H_5O_7$	Flavoring
Phosphoric acid, H_3PO_4	Rust remover, soft drinks
Boric acid, H_3BO_3	Mild antiseptic, insecticide
Aluminum salts, $NaAl(SO_4)_2 \cdot 12H_2O$	Most anti-perspirants, water treatment plants, paper
Hydrochloric acid (muriatic acid), HCl	Brick and ceramic tile cleaner

Common Bases	
Sodium hydroxide (lye), NaOH	Oven cleaner, unblocking plumbing
Ammonia, NH_3	Household cleaner
Sodium carbonate, Na_2CO_3	Water softener, grease remover
Sodium hydrogen carbonate, $NaHCO_3$	Fire extinguisher, rising agent in cake mixes (baking soda), mild antacid
Sodium phosphate, Na_3PO_4	Cleaner for surfaces before painting or wallpapering



Chemistry uses three definitions of acids and bases: 1) Arrehenius 2) Bronsted-Lowry 3) Lewis

Name	Acid Definition	Base Definition
Arrhenius	Substance that increases H^+	Substances that increase OH^-
Brønsted-Lowry	Substances that donate H^+	Substances that accept H^+
Lewis	Electron-pair acceptor	Electron-pair donar

Arrhenius Acid/Base **definitions arise from the reaction with water.**

Acid: a substance that has a covalent H atom in its formula, and releases a proton H^+ when dissolved in water.

$HCl(g)$, $HBr(g)$, $HI(g)$, $HNO_3(l)$, $H_2SO_4(l)$, $HClO_4(l)$

$HCl(aq)$, $HBr(aq)$, $HI(aq)$, $HNO_3(aq)$, $H_2SO_4(aq)$, $HClO_4(aq)$

$$HA(g) \overset{H_2O}{<==>} H^+(aq) + A^-(aq)$$

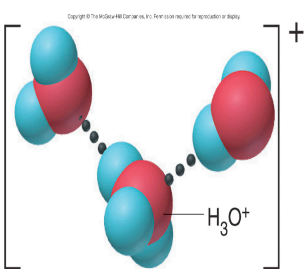
Base: a substance that contains OH in its formula, and releases hydroxide ions (OH^-) when dissolved in water.

$NaOH(s)$, $KOH(s)$, $LiOH(s)$, $Mg(OH)_2(s)$, $Ca(OH)_2(s)$

$NaOH(aq)$, $KOH(aq)$, $LiOH(aq)$, $Mg(OH)_2(aq)$, $Ca(OH)_2(aq)$

$$MOH(s) \overset{H_2O}{<==>} OH^- + M^+$$

H^+ **has never been isolated in the lab, but chemists use it symbolically anyway. *H^+* reacts with water to form the hydronium ion, *H_3O^+***



H^+ and H_3O^+ are equivalent in chemistry.

Acid and base formation is represented symbolically in two ways semi-confusing ways. Learn both & don't let it distract you.

1. $HA(g) \overset{H_2O}{<==>} H^+ + A^-$

   $MOH(s) \overset{H_2O}{<==>} OH^- + M^+$

   The lazy but convenient way. H_2O written over arrow with H^+ as the acid.

2. $HA(g) + H_2O(l) <==> H_3O^+(aq) + A^-(aq)$

   $MOH(s) + H_2O(l) <==> OH^-(aq) + M^+(aq) + H_2O$

   Reacting with H_2O in the equation with H_3O as acid.

An equilibrium constant called "*Acid-Dissociation Constant, K_a*" quantifies the *extent of acid dissociation* (i.e. acid strength).

$$HA(g) \overset{H_2O}{<==>} H^+ + A^- \qquad K_a = \frac{[H^+][A^-]}{[HA]}$$

$$HA(g) + H_2O(l) <==> H_3O^+(aq) + A^-(aq) \qquad K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

stronger acid => higher $[H_3O^+]$ => large K_a

weaker acid => lower $[H_3O^+]$ => small K_a

Chapter 17 & 18 Homework Problems

Problems have been updated for the Principles of Chemistry, Silberberg, 2nd Edition Textbook.

Exam 2

February 12/13/14?

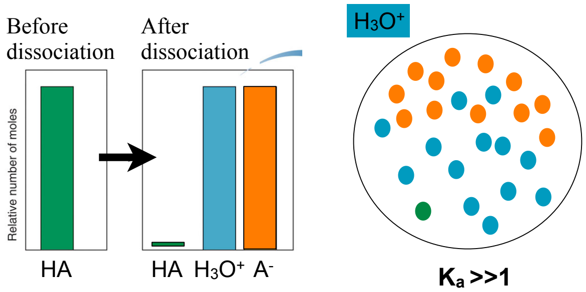
Chapter 17:
1,2,3,9,13,17,19,23,25,28,30,32,35,39,42,44,46,50,51,54,59,64,66,69,72,80,81,86,89,90.

Chapter 18:
5,6,7,9,11,15,16,18,22,26,27,30,32,34,38,44,45,47,49,51,60,64,66,74,81,83,90,92,104,120

Strong acids and **strong** bases completely dissociate or completely ionize in water: $K_a >> 1$.

$HA(g) + H_2O(l) \longrightarrow H_3O^+(aq) + A^-(aq)$ $K_a = \frac{[A^-][H_3O^+]}{[HA]}$

product-favored ⟶



Because of complete dissociation, strong acids and strong bases *conduct electricity* and are *strong electrolytes*.

Uni-directional arrow used to heavily product-favored

$HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)$

$HNO_3(aq) \longrightarrow H^+(aq) + NO_3^-(aq)$

$H_2SO_4(aq) \longrightarrow H^+(aq) + HSO_4^-(aq)$

$NaOH(aq) \longrightarrow Na^+(aq) + OH^-(aq)$

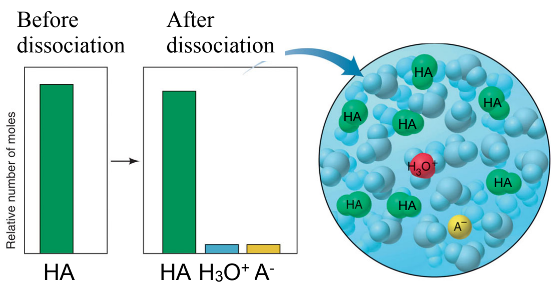
$Ca(OH)_2(aq) \longrightarrow Ca^{2+}(aq) + 2OH^-(aq)$

Strong Acids	Strong Bases
HCl	LiOH
HBr	NaOH
HI	KOH
$HClO_4$	RbOH
HNO_3	CsOH
H_2SO_4[a]	$Mg(OH)_2$
	$Ca(OH)_2$
	$Sr(OH)_2$
	$Ba(OH)_2$

Weak acids and **weak bases** dissociate only to a slight extent in water $K_a << 1$.

$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$ $K_a = \frac{[A^-][H_3O^+]}{[HA]}$

⟵ reactant-favored



Weak acids and **weak bases** do not dissociate or ionize to a large extent in solution, and so are *weak electrolytes* (small value of K_a).

$K_a = \frac{[A^-][H_3O^+]}{[HA]} = << 1$

All not strong is weak!

$HNO_2(aq) \Leftrightarrow NO_2^-(aq) + H^+(aq)$

$CH_3CO_2H(aq) \Leftrightarrow CH_3CO_2^-(aq) + H^+$

$H_2SO_3(aq) \Leftrightarrow HSO_3^-(aq) + H^+(aq)$

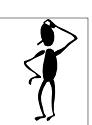
Weak Acids	
CH_3CO_2H	acetic acid
HNO_2	nitrous acid
H_2SO_3	sulfurous acid
HOCl	hypochlorous acid
H_2CO_3	carbonic acid
H_3PO_4	phosphoric acid
HF	hydrofluoric acid

Weak Bases	
$NH_3(aq)$	ammonia

K_a Values For A Few Monoprotic Acids at 25C

Name (Formula)	Lewis Structure*	K_a
Chlorous acid ($HClO_2$)	H—O—Cl=O	1.12×10^{-2}
Nitrous acid (HNO_2)	H—O—N=O	7.1×10^{-4}
Hydrofluoric acid (HF)	H—F	6.8×10^{-4}
Formic acid (HCOOH)	H—C(=O)—O—H	1.8×10^{-4}
Acetic acid (CH_3COOH)	H—CH₂—C(=O)—O—H	1.8×10^{-5}
Propanoic acid (CH_3CH_2COOH)	H—CH₂—CH₂—C(=O)—O—H	1.3×10^{-5}
Hypochlorous acid (HClO)	H—O—Cl	2.9×10^{-8}

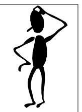
Classify each of the following compounds as a strong acid, weak acid, strong base, or weak base.



(a) H_2SeO_4 **(b)** $(CH_3)_2CHCOOH$ **(c)** KOH **(d)** $(CH_3)_2CHNH_2$

Pay attention to the text definitions of acids and bases. Look at O for acids as well as the -COOH group; watch for amine groups and cations in bases.

Classify each of the following compounds as a strong acid, weak acid, strong base, or weak base.



(a) H_2SeO_4 **(b)** $(CH_3)_2CHCOOH$ **(c)** KOH **(d)** $(CH_3)_2CHNH_2$

Pay attention to the text definitions of acids and bases. Look at O for acids as well as the -COOH group; watch for amine groups and cations in bases.

(a) Strong acid - H_2SeO_4 - the number of O atoms exceeds the number of ionizable protons by 2.

(b) Weak acid - $(CH_3)_2CHCOOH$ is an organic acid having a -COOH group.

(c) Strong base - KOH is a Group 1A(1) hydroxide.

(d) Weak base - $(CH_3)_2CHNH_2$ has a lone pair of electrons on the N and is an amine.

Acids can have one, two or three acidic protons depending on their structure (and K_{a1} K_{a2} K_{a3}).

Monoprotic acids--only one H^+ available

$HCl \longrightarrow H^+ + Cl^-$	Strong electrolyte, strong acid
$HNO_3 \longrightarrow H^+ + NO_3^-$	Strong electrolyte, strong acid
$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$	Weak electrolyte, weak acid

Diprotic acids--two acidic H^+ available for reaction

$H_2SO_4 \longrightarrow H^+ + HSO_4^-$	Strong electrolyte, strong acid
$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$	Weak electrolyte, weak acid

Triprotic acids--three acidic H^+

$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$

$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$ Weak electrolyte, weak acid

$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$

Acid and bases react with one another in a *neutralization reaction forming a salt and water*.

$NaOH(aq) + HCl(aq) \Longleftrightarrow H_2O + Na^+ + Cl^-$

base + acid <==> Water + salt

Net Ionic Equation: $H^+(aq) + OH^-(aq) \Rightarrow H_2O\ (aq)$

$CH_3COOH(aq) + NaOH\ (aq) \Longleftrightarrow H_2O + Na^+ + CH_3COO^-$

Weak acid + strong base <==> Water + salt

The Arrhenius acid-base definition fails to cover all cases..so chemists invented the Bronsted-Lowry definition.

How Arrhenius Defintion Fails

1. NH_3 or amines (like $R\text{-}NH_2$) don't have OH group but are bases.

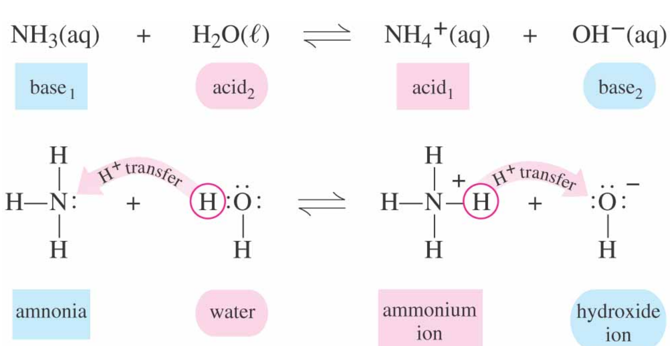
2. Many transition metals Cr, Al, Fe, Cu are acidic but have no H^+.

3. Arrhenius definition requires water...yet some acid base reactions occur *without water* as solvent.

$HCl(g) + NH_3(g) \Rightarrow NH_4Cl(s)$

gaseous without water

The Bronsted-Lowry concept views acids as *proton donars* and bases as *proton acceptors*.



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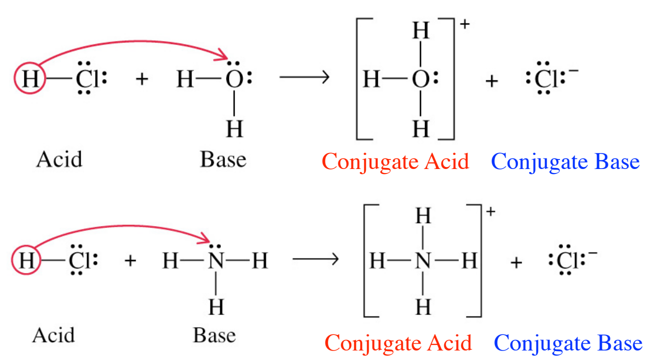
An *Bronsted acid* is a substance that "*donates*" or a proton to a *Bronsted base*. A *Bronsted base* is a substance that "*accepts*" a proton from another a *Bronsted acid*.



- For a molecule or ion to be a ***Bronsted base***, it must ***have at least one unshared pair of electrons*** for ***accepting*** a proton.

All of these have a lone-pair of e^- and are bases!

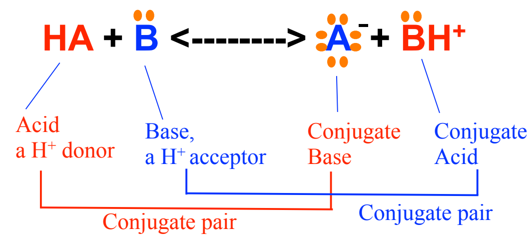
The Lone pairs are there if you draw the Lewis structure!

- H_2O
- F^-
- Cl^-
- NH_3
- OH^-

All can donate H^+ and are acids!

- H_2O
- HF
- HCl
- HNO_3
- HBr
- $HClO_4$

Generalized Bronsted Acid and Base

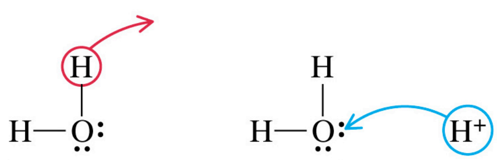


A^- is called the conjugate base of the acid HA. Has a free pair of electrons to "accept a proton".

BH^+ is called the conjugate acid of the base B

Both are called conjugate acid-base pairs!

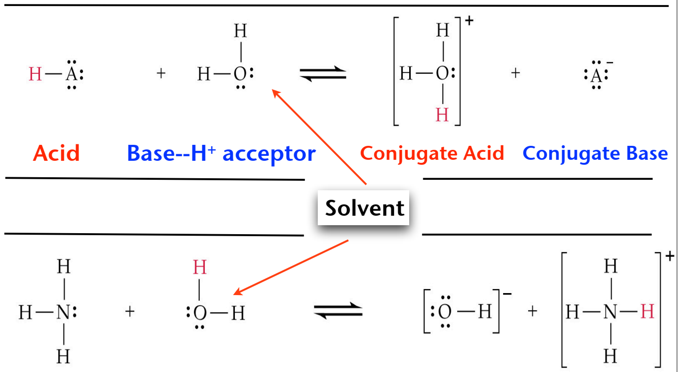
Amphoteric substances **can act an Bronsted acid (proton donar) or a base (a proton acceptor).**



H_2O as an acid H_2O as a base

proton donor **proton acceptor**

Water is *amphoteric,* it can act as a base or acid and depending on what it reacts with.



Identifying the following conjugate acid-base pairs (H^+ donars and H+ acceptors).

conjugate take away H^+

$acid_1$ + $base_2$ ⇌ $base_1$ + $acid_2$

add H^+

reaction 1	HF	+	H_2O	⇌	F^-	+	H_3O^+
reaction 2	HCOOH	+	CN^-	⇌	$HCOO^-$	+	HCN
reaction 3	NH_4^+	+	CO_3^{2-}	⇌	NH_3	+	HCO_3^-
reaction 4	$H_2PO_4^-$	+	OH^-	⇌	HPO_4^{2-}	+	H_2O
reaction 5	H_2SO_4	+	$N_2H_5^+$	⇌	HSO_4^-	+	$N_2H_6^{2+}$
reaction 6	HPO_4^{2-}	+	SO_3^{2-}	⇌	PO_4^{3-}	+	HSO_3^-

Write the equilibrium expression nitrous acid (HNO_2) and explain its acidity in terms of a) the Arrhenius definition, and b) the Brønsted-Lowry acid base theory, c) identify the acid base conjugate pairs.

a) HNO_2 is an Arrhenius acid because it dissociates in water to produce H^+ ions:

$$HNO_2(aq) \Longleftrightarrow H^+(aq) + NO_2^-(aq)$$

- b) Nitrous acid is a Brønsted-Lowry acid because it acts as a proton donor, transferring a proton to water to give hydronium ion

$$\underset{\text{Acid}}{HNO_2(aq)} + \underset{\text{Base}}{H_2O(l)} \rightleftharpoons \underset{\text{Acid}}{H_3O^+(aq)} + \underset{\text{Base}}{NO_2^-(aq)}$$

Conjugate acid–base pairs

- The conjugate base of HNO_2 is NO_2^-, the species that remains after HNO_2 has lost a proton

---

☑ **The stronger the acid (base) is, the weaker is its conjugate base (acid).**

$$HCl(g) + H_2O(aq) \Longleftrightarrow Cl^-(aq) + H_3O^+(aq)$$

very weak base

$$NaOH(s) + H_2O(l) \Longleftrightarrow Na^+ + H_2O + OH^-$$

very weak acid

☑ **Weak acids (bases) give strong conjugate bases (acids).**

$$HCOOH + H_2O \Longleftrightarrow HCOO^- + H_3O^+$$

basic in water

$$NH_3(aq) + H_2O(aq) \Longleftrightarrow NH_4^+(aq) + OH^-(aq)$$

acidic in water

The weaker the acid--the stronger its conjugate base.
The stronger the acid--the weaker its conjugate base.

Relative Strengths of Conjugate Acid-Base Pairs

	Acid (HA)		Conjugate Base, A⁻		
Stronger acid	$HClO_4$	Strong acids. 100% dissociated in aqueous solution.	ClO_4^-	Very weak bases. Negligible tendency to be protonated in aqueous solution.	Weaker base
	HCl		Cl^-		
	H_2SO_4		HSO_4^-		
	HNO_3		NO_3^-		
	H_3O^+		H_2O		
	HSO_4^-	Weak acids. Exist in solution as a mixture of HA, A⁻, and H_3O^+.	SO_4^{2-}	Weak bases. Moderate tendency to be protonated in aqueous solution.	
	H_3PO_4		$H_2PO_4^-$		
	HNO_2		NO_2^-		
	HF		F^-		
	CH_3CO_2H		$CH_3CO_2^-$		
	H_2CO_3		HCO_3^-		
	H_2S		HS^-		
	NH_4^+		NH_3		
	HCN		CN^-		
	HCO_3^-		CO_3^{2-}		
	H_2O		OH^-		
Weaker acid	NH_3	Very weak acids. Negligible tendency to dissociate.	NH_2^-	Strong bases. 100% protonated in aqueous solution.	
	OH^-		O^{2-}		
	H_2		H^-		Stronger base

An *acid-base reaction* will go in that direction that *forms the weaker acid-base pair*.

Given that K_a for HF $= 6.8 \times 10^{-4}$ and K_a for $H_2S = 9.0 \times 10^{-8}$

In which direction will this reaction proceed?

$$HS^-(aq) + HF(aq) \rightleftharpoons F^-(aq) + H_2S(aq)$$

In which direction will these reactions proceed?

$$H_2SO_4(aq) + NH_3(aq) \rightleftharpoons NH_4^+(aq) + HSO_4^-(aq)$$

$$HCO_3^-(aq) + SO_4^{2-}(aq) \rightleftharpoons HSO_4^-(aq) + CO_3^{2-}(aq)$$

Name	Formula	K_{a1}	K_{a2}	K_{a3}
Ascorbic	$H_2C_6H_6O_6$	8.0×10^{-5}	1.6×10^{-12}	
Carbonic	H_2CO_3	4.3×10^{-7}	5.6×10^{-11}	
Citric	$H_3C_6H_5O_7$	7.4×10^{-4}	1.7×10^{-5}	4.0×10^{-7}
Oxalic	$H_2C_2O_4$	5.9×10^{-2}	6.4×10^{-5}	
Phosphoric	H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.2×10^{-13}
Sulfurous	H_2SO_3	1.7×10^{-2}	6.4×10^{-8}	
Sulfuric	H_2SO_4	Large	1.2×10^{-2}	
Tartaric	$H_2C_4H_4O_6$	1.0×10^{-3}	4.6×10^{-5}	

In which direction will these reactions proceed?

$$H_2SO_4(aq) + NH_3(aq) \rightleftharpoons NH_4^+(aq) + HSO_4^-(aq)$$

$$\longrightarrow$$

$$HCO_3^-(aq) + SO_4^{2-}(aq) \rightleftharpoons HSO_4^-(aq) + CO_3^{2-}(aq)$$

$$\longleftarrow$$

Name	Formula	K_{a1}	K_{a2}	K_{a3}
Ascorbic	$H_2C_6H_6O_6$	8.0×10^{-5}	1.6×10^{-12}	
Carbonic	H_2CO_3	4.3×10^{-7}	5.6×10^{-11}	
Citric	$H_3C_6H_5O_7$	7.4×10^{-4}	1.7×10^{-5}	4.0×10^{-7}
Oxalic	$H_2C_2O_4$	5.9×10^{-2}	6.4×10^{-5}	
Phosphoric	H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.2×10^{-13}
Sulfurous	H_2SO_3	1.7×10^{-2}	6.4×10^{-8}	
Sulfuric	H_2SO_4	Large	1.2×10^{-2}	
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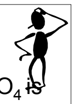
In which direction will these reactions proceed?



H_2SO_4 and NH_4^+ are acids, NH_3 and HSO_4^- are bases. H_2SO_4 is stronger acid than NH_4^+, and NH_3 stronger base than HSO_4^-, therefore NH_3 gets the proton

$$H_2SO_4(aq) + NH_3(aq) \rightarrow NH_4^+(aq) + HSO_4^-(aq)$$

stronger acid   stronger base   weaker acid   weaker base

HCO_3^- and HSO_4^- are acids, SO_4^{2-} and CO_3^{2-} are bases. HSO_4^- is the stronger acid, and CO_3^{2-} is the stronger base. Therefore, CO_3^{2-} gets the proton

$$HCO_3^-(aq) + SO_4^{2-}(aq) \leftarrow HSO_4^-(aq) + CO_3^{2-}(aq)$$

weaker acid   weaker base   stronger acid   stronger bas

Water is usually a "reactive-solvent" with all acids and bases.

$$HClO_4(l) + H_2O(l) <==> H_3O^+(aq) + ClO_4^-(aq)$$

$$NaOH(s) + H_2O(l) <==> OH^-(aq) + Na^+(aq) + H_2O(l)$$

Water's reaction can be viewed as acid-base reaction.

$$HClO_4(l) + H_2O(l) <==> H_3O^+(aq) + ClO_4^-(aq)$$

acid + base <==> conjugate acid + base

Net Ionic Equation: $H^+(aq) + OH^-(aq) => H_2O\ (aq)$

The hydronium ion, H_3O^+, and the OH^- are the ***strongest acid and base*** that can exist ***in the presence of water.***

$$H_2O(l) + HCl(aq) ==> H_3O^+ + Cl^-$$

$$H_2O(l) + HNO_3(aq) ==> H_3O^+ + Cl^-$$

$$H_2O(l) + H_2SO_4(aq) ==> H_3O^+ + HSO_4^-$$

Strong acid ===> produce H_3O^+

We can not distinguish H_3O^+ in these cases. All proton acceptors give OH^- in aqueous solutions.

$$O_2^-(l) + H_2O(l) <==> 2OH^-$$

$$NH_2^-(aq) + H_2O(l) <==> NH_3(aq) + OH^-$$

We can not distinguish OH^- in these cases. All proton acceptors give OH^- in aqueous solutions.

Acid Strength Is Summarized in Tables of K_a and pK_a

Acid	Ionization Equilibrium	K_a	pK_a
Hydroiodic Acid	$HI + H_2O <==> H_3O^+ + I^-$	$3 X 10^9$	-9
Hydrochloric Acid	$HCl + H_2O <==> H_3O^+ + Cl^-$	$1.3 X 10^6$	-6
Sulfuric Acid	$H_2SO_4 + H_2O <==> H_3O^+ + HSO_4^-$	1000	-3
Hydronium Ion	$H_3O + H_2O <==> H_3O^+ + IO_3^-$	55	-1.7
Nitric Acid	$HNO_3 + H_2O <==> H_3O^+ + NO_3^-$	28	-1.4
Iodic acid	$HIO_3 + H_2O <==> H_3O^+ + IO_3^-$	$1.61 X 10^{-1}$	0.80
Chlorous Acid	$HClO_2 + H_2O <==> H_3O^+ + ClO_2^-$	$1.1 X 10^{-2}$	1.96
Phosphoric Acid	$H_3PO_4 + H_2O <==> H_3O^+ + H_2PO_4^-$	$7.6 X 10^{-3}$	2.12
Nitrous Acid	$HNO_2 + H_2O <==> H_3O^+ + NO_2^-$	$7.2 X 10^{-4}$	3.14
Hydrofluoric Acid	$HF + H_2O <==> H_3O^+ + F^-$	$6.61 X 10^{-4}$	3.18
Formic Acid	$HCOOH + H_2O <==> H_3O^+ + HCO_2^-$	$1.8 X 10^{-4}$	3.74
Acetic Acid	$CH_3CO_2H + H_2O <==> H_3O^+ + CH_3CO_2^-$	$1.8 X 10^{-5}$	4.74
Hydrosulfuric Acid	$H_2S + H_2O <==> H_3O^+ + HS^-$	$1.32 X 10^{-7}$	6.88
Hypochlorous Acid	$HClO + H_2O <==> H_3O^+ + ClO^-$	$2.88 X 10^{-8}$	7.54
Hydrocyanic Acid	$HCN + H_2O <==> H_3O^+ + CN^-$	$6.2 X 10^{-10}$	9.21

K_w is the *equilibrium constant* that describes the auto or self-ionization of water.

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \qquad K_w = [H^+][OH^-]$$

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \qquad K_w = [H_3O^+][OH^-]$$

Base   Acid   Acid   Base

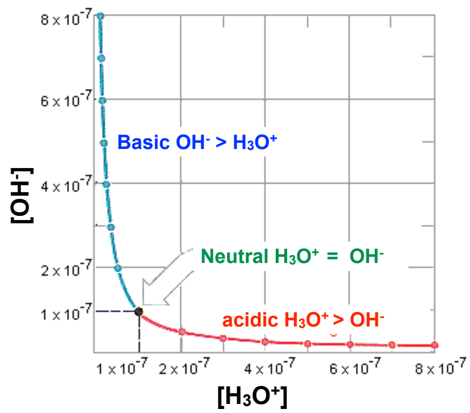
$$K_w = [H_3O^+][OH^-] = 1 X 10^{-14}$$

This equilibrium constant for water is called the "Ion-Product of Water". Memorize the value.

The product of $[H_3O^+][OH^-] = 1 X 10^{-14}$ a constant. Once we know one......we know the other!

$[H_3O^+]$	$[OH^-]$	K_w
$1 X 10^{-14}$	$1 X 10^{-0}$	$1 X 10^{-14}$
$1 X 10^{-13}$	$1 X 10^{-1}$	$1 X 10^{-14}$
$1 X 10^{-12}$	$1 X 10^{-2}$	$1 X 10^{-14}$
$1 X 10^{-11}$	$1 X 10^{-3}$	$1 X 10^{-14}$
$1 X 10^{-10}$	$1 X 10^{-4}$	$1 X 10^{-14}$
$1 X 10^{-9}$	$1 X 10^{-5}$	$1 X 10^{-14}$
$1 X 10^{-8}$	$1 X 10^{-6}$	$1 X 10^{-14}$
$1 X 10^{-7}$	$1 X 10^{-7}$	$1 X 10^{-14}$
$1 X 10^{-6}$	$1 X 10^{-8}$	$1 X 10^{-14}$
$1 X 10^{-5}$	$1 X 10^{-9}$	$1 X 10^{-14}$
$1 X 10^{-4}$	$1 X 10^{-10}$	$1 X 10^{-14}$

$[OH^-]$ and $[H^+]$ can vary over 14 orders of magnitude



If we plot a few points of $[OH^-]$ vs $[H^+]$ then we see that we can not plot all the various powers of 10 that can exist in solution.

In 1909, Sorenson suggests using a logarithmic plot and this makes things easy to see and to plot. It defines pH!

pH is a defined logarithmic scale for measuring acidity. It is directly related to $[H^+]$ concentration in solution.

$$pH = -\log_{10} [H^+] = -\log_{10} [H_3O^+]$$ logarithmic form

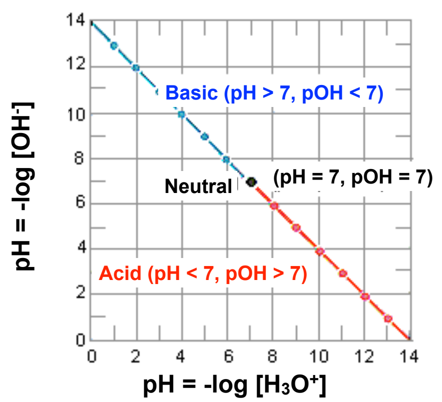
↑

$p = -\log_{10}$

$$[H^+] = 10^{-pH}$$ exponential form

1 pH unit represents a power of 10X in concentration (or an order of magnitude as it is called).

We can compress all 14 orders of magnitude using a logarithmic scale--called the pH scale!



14 orders of magnitude can be seen in a single graph!

Acidic, basic and neutral solutions are identified by their pH values

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

connect these dots

$$K_w = [H_3O^+][OH^-] = 10^{-14}$$

The ion-product of water is a constant!

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

A solution with a pH of 4 is 10X lower in $[H^+]$ than one with pH=3, 100X lower than pH=2 and 1000X lower than pH = 1.

$[H^+]$	$-\log[H^+]$ = pH
0.5M	0.301
0.05M	1.301
0.005M	2.301
0.0005M	3.301

When concentration changes by factor of 10, pH changes by +/- 1

The amounts of H_3O^+ and OH^- in aqueous solution determines whether a solution is acidic, neutral or basic.

WHEN

$[H_3O^+] > [OH^-]$	$[H_3O^+] = [OH^-]$	$[H_3O^+] < [OH^-]$
acidic solution pH < 7	neutral solution pH = 7	basic solution pH > 7

Litmus Paper Color

A Logarithm of a number is an Exponent

Let y be any number. Let b also be a number and let's call it "the base", b. Lastly let's call the power we raise the base to an "exponent" and label it as "x". In equation form:

$y = b^x$ — **b = base, x = exponent and y = a number**

$100 = 10^x$ — **b = 10 and y =100 and x = exponent**

The logarithm of 100 = log (100) is the value of the exponent, x, needed to raise 10 to in order to obtain 100.

$\log_{10}(100) = x = 2$ ← **The logarithm of 100 is the value of the exponent in the equation: $10^x = 100$**

Logs are easy if you see the riff.

What is the $\log_{10}$ of the following numbers?

1000, 100, 10, 1, 0, 0.1, 0.01, 0.001

$\log_{10} 1000 = \log 1000 = x$ —means→ $10^X = 1000$

$\log_{10} 100 = \log 100 = x$ —means→ $10^X = 100$

$\log 10 = x$ —means→ $10^X = 10$

$\log 1 = x$ → $10^X = 1$

$\log 0 = x$ — $10^X = 0$

$\log 0.1 = x$ — $10^X = 0.1$

$\log 0.01 = x$ — $10^X = 0.01$

Two very common logarithm functions are log to the base 10 and the natural log base e (2.7183).

$\log = \log_{10}$ — "log to the base 10"

$\log_e = \log_{2.7183} = \ln$ — the "natural log"

Just as there are distributive, associative properties with equations there are "properties of logs that should be memorized.

Properties of Logs

$$\log(A \times B) = \log A + \log B$$

$$\log\left(\frac{A}{B}\right) = \log A - \log B$$

$$\log A^n = n \log A$$

$$\text{antilog}(\log x) = 10^{\log x} = x$$

Antilog of a number means use the number as an exponent.

Sometimes we know the base and the exponent, but we need to compute the number. We can write it like this:

$$\log(?) = 2$$

In words we would say: "The $\log_{10}$ of what number is equal to 2"?

Finding this number is called taking the ***"antilogarithm"***

$$\text{Antilog}[\log(?)] = \text{Antilog}(2)$$

$$? = 10^2 = 100$$

The antilog$_{10}$ is the same as the base 10 operator!

Knowing the math can help you go fast

Logarithmic Form	Exponential Form
$pH = -\log[H_3O^+]$	$10^{-pH} = [H_3O^+]$
$pOH = -\log[OH^-]$	$10^{-pOH} = [OH^-]$
$pK_a = -\log K_a$	$10^{-pK_a} = pK_a$

When H_3O^+, OH^-, K_a are large values----the pK's are small values. Strong acids have large H_3O and K_a therefore small pH and small pK_a

K_w is related to pH via logarithm.

$$K_W = [H_3O^+][OH^-] = 1.0 \text{ X } 10^{-14}$$

take -log of both sides

$$-\log K_w = -\log([H_3O^+][OH^-]) = -\log(1.0 \text{ X } 10^{-14})$$

$$-\log K_W = -\log[H_3O^+] + -\log[OH^-] = -\log(10^{-14})$$

$$pK_W = \quad pH \quad + \quad pOH \quad = -(-14)$$

$$pK_W = pH + pOH = 14$$

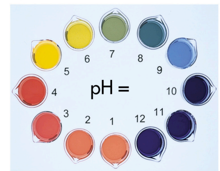
$$K_W = [H_3O^+][OH^-] = 10^{-14}$$

pH is measured with dyed paper or with a commercial instrument.

pH (indicator) paper

pH meter

(a)



(b)

What is the concentration of OH^- ions in a HCl solution whose hydrogen ion concentration is 1.3 *M*?

What is the concentration of OH^- ions in a HCl solution whose hydrogen ion concentration is 1.3 *M*?

Key: Strong acids dissociate completely--stoichiometry dictates $[H^+]$. Memorize all strong acids (HCl, HBr, HI, HNO_3, H_2SO_4, $HClO_4$)

$$[H^+] = 1.3\ M$$

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

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{1 \times 10^{-14}}{1.3} = 7.7 \times 10^{-15}\ M$$

A research chemist adds a measured amount of HCl gas to pure water at 25ºC and obtains a solution with $[H_3O^+] = 3.0 \times 10^{-4}$ *M*. Calculate $[OH^-]$. Is the solution neutral, acidic or basic?

A research chemist adds a measured amount of HCl gas to pure water at 25 ºC and obtains a solution with $[H_3O^+] = 3.0 \times 10^{-4}$ *M*. Calculate $[OH^-]$. Is the solution neutral, acidic or basic?

Again, strong acids dissociate completely--stoichiometry dictates $[H^+]$

SOLUTION: $K_w = 1.0 \times 10^{-14} = [H_3O^+][OH^-]$

$$[OH^-] = K_w / [H_3O^+] = 1.0 \times 10^{-14} / 3.0 \times 10^{-4} = 3.3 \times 10^{-11}\ M$$

$[H_3O^+] > [OH^-]$; the solution is acidic.

Significant figures in logarithm calculations follow different rules than we are used to.

1. When taking the log of a ***measured number***, retain in the mantissa (the numbers to the right of the decimal point in the answer) the same number of significant figures as there are in the number whose logarithm you are taking.

$\log(3.000 \times 10^4) = ? = 4.4771$

4 SF's — 4 SF's after decimal pt

$\log(3. \times 10^4) = ? = 4.5$

1 SF's — 1 SF's after decimal pt

2. When taking an antilog, the number of SF's in the answer is the same as the number of digits after the decimal point.

$\text{antilog}(4.4711) = 10^{4.4711} = 3.000 \times 10^4$

4 SF's after decimal pt — 4 SF's

The pH of rainwater collected in a certain region of the northeastern United States on a particular day was 4.82. What is the H^+ ion concentration of the rainwater?

The OH^- ion concentration of a blood sample is 2.5×10^{-7} *M*. What is the pH of the blood?

The pH of rainwater collected in a certain region of the northeastern United States on a particular day was 4.82. What is the H^+ ion concentration of the rainwater?

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

$$\text{antilog}(-pH) = \text{antilog}(\log [H^+])$$

$$[H^+] = 10^{-pH} = 10^{-4.82} = 1.5 \times 10^{-5}\ M$$

The OH^- ion concentration of a blood sample is 2.5×10^{-7} *M*. What is the pH of the blood?

$$pH + pOH = 14.00$$

$$pOH = -\log [OH^-] = -\log (2.5 \times 10^{-7}) = 6.60$$

$$pH = 14.00 - pOH = 14.00 - 6.60 = 7.40$$

Problem: Calculating $[H_3O^+]$, pH, $[OH^-]$, and pOH

In a restoration project, a conservator prepares copper-plate etching solutions by diluting concentrated nitric acid, HNO_3, to 2.0 *M*, 0.30 *M*, and 0.0063 *M* HNO_3. Calculate $[H_3O^+]$, pH, $[OH^-]$, and pOH of the three solutions at 25 °C.

PLAN: HNO_3 is a strong acid so $[H_3O^+] = [HNO_3]$. Use K_w to find the $[OH^-]$ and then convert to pH and pOH.

Problem: Calculating $[H_3O^+]$, pH, $[OH^-]$, and pOH

In a restoration project, a conservator prepares copper-plate etching solutions by diluting concentrated nitric acid, HNO_3, to 2.0 *M*, 0.30 *M*, and 0.0063 *M* HNO_3. Calculate $[H_3O^+]$, pH, $[OH^-]$, and pOH of the three solutions at 25 °C.

For 2.0 *M*

HNO_3, $[H_3O^+] = 2.0\ M$, and $pH = -\log [H_3O^+] = -0.30 = pH$

$[OH^-] = K_w / [H_3O^+] = 1.0 \times 10^{-14}/2.0 = 5.0 \times 10^{-15}\ M$; $pOH = 14.30$

For 0.3 *M* HNO_3,

$[H_3O^+] = 0.30\ M$ and $-\log [H_3O^+] = 0.52 = pH$

$[OH^-] = K_w/[H_3O^+] = 1.0 \times 10^{-14}/0.30 = 3.3 \times 10^{-14}\ M$; $pOH = 13.48$

For 0.0063 *M* HNO_3,

$[H_3O^+] = 0.0063\ M$ and $-\log [H_3O^+] = 2.20 = pH$

$[OH^-] = K_w/ [H_3O^+] = 1.0 \times 10^{-14}/6.3 \times 10^{-3} = 1.6 \times 10^{-12}\ M$; $pOH = 11.80$

Acid-Base Equilibrium Problems

1 → **Strong Acids/Bases**
- 100% dissociation
- No need for ICE table. $[H_3O^+] = [HA]$.

2 → **Weak Acid** / **Weak Bases**
- 1. Find K_a /K_b given equilibrium values
- 2. Find equilibrium values given K_a
- Identify and write the correct equation
- 1. Simplify: If $100 \times K_{a/b} < [A]_0$ then $[HA] - x = [HA]$
- 2. Look for perfect square
- 3. Quadratic equation

Strong acids and bases dissociate completely while weak acids (bases) are equilibrium dependent.

$$HCl(aq) + H_2O \longrightarrow H_3O^+(aq) + Cl^-(aq)$$

0.004% at equilibrium — 99.996% at equilibrium

STRONG ACID

1.0M HCl ⟶ 1.0M H_3O^+

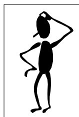
$$CH_3CO_2H(aq) + H_2O \longleftrightarrow H_3O^+(aq) + CH_3CO_2^-(aq)$$

98.7% at equilibrium — 1.3% at equilibrium

WEAK ACID

Know all strong acids and bases and you will recognize be able to recognize all weak acids/bases.

	Acids	Bases	
hydrohalic acids	HCl	LiOH	Group I hydroxides
	HBr	NaOH	
	HI	KOH	
perchloric	$HClO_4$	RbOH	
nitric	HNO_3	CsOH	
sulfuric	H_2SO_4[a]	$Mg(OH)_2$	Group II hydroxides
		$Ca(OH)_2$	
		$Sr(OH)_2$	
		$Ba(OH)_2$	



What is the pH of a 1.8×10^{-2} *M* $Ba(OH)_2$ solution?

$Ba(OH)_2$ is a strong base – 100% dissociation.

1 mol $Ba(OH)_2$ = 2 mol OH^-

	$Ba(OH)_2$ *(s)* ⟶	Ba^{2+} *(aq)* +	$2OH^-$ *(aq)*
Initial	0.018 *M*	0.0 *M*	0.0 *M*
Change	-0.018 *M*	0.018 *M*	0.036 *M*
Equilibrium	0.0 *M*	0.018 *M*	0.036 *M*

pK_w = pH + pOH = 14.00

pH = 14.00 – pOH

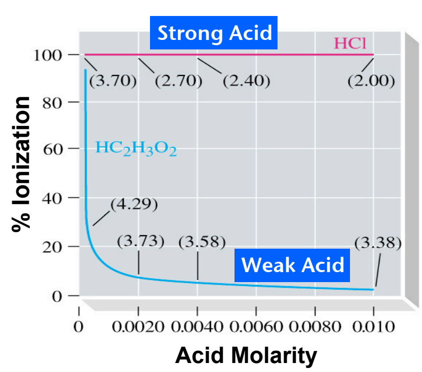
pH = 14.00 - (- log(0.036)) = 12.56

% ionization of an acid is the ratio of $[H^+]$ at equilibrium to $[HA]_{initial}$ X 100.

$$\% \text{ ionization} = \frac{[H^+]_{equilibrium}}{[HA]_{inital}} \times 100\%$$

$$\% \text{ ionization}_b = \frac{[OH^-]_{equilbrium}}{[OH^-]_{inital}} \times 100\%$$

As the concentration of a weak acid (base) decreases, the % ionization of the acid (base) increases!

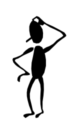


Rationale: larger solution volume accommodates more ions (analogous to pressure effects on gas equilibria when Δn_{gas} is non-zero)

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

$$K_a = \frac{n_{H_3O^+} n_{A^-}}{n_{HA}} \frac{1}{V}$$

Strong Acid Equilibrium Sample Problem



What is the pH of a 2.00×10^{-3} *M* HNO_3 solution?

1. What does the problem ask--write it down make a picture?
2. Is the acid or base--strong or weak?
3. Can we make an ICE table?

What is the pH of a 2×10^{-3} *M* HNO_3 solution?

HNO_3 is a strong acid it is100% dissociated.

$$HNO_3\,(aq) + H_2O\,(l) \longrightarrow H_3O^+\,(aq) + NO_3^-\,(aq)$$

	HNO_3		H_3O^+	NO_3^-
Initial	0.002 *M*		0.0 *M*	0.0 *M*
Change	-0.002 *M*		+0.002 *M*	0.002 *M*
Equilibrium	0.0 *M*		+0.002 *M*	+0.002 *M*

$$pH = -\log [H_3O^+] = -\log(0.002) = 2.7$$

There are 2 key simplifications that can help us solve equilibrium problems rapidly.

1. $[H_3O^+]$ from the auto-ionization of water is negligible in comparison to H^+ from an acid, HA in solution.

2. If $100 \times K_a < [HA]_{initial}$ then $[HA]_{initial} - x = [HA]$

Why Does it Work?
Because K_a values are known to about ± 5% accuracy.

Check using the 5% Rule $\quad \dfrac{[H^+]_{equilbrium}}{[HA]_{inital}} \times 100 < 5\%$

3. If #2 fails then you must use the quadratic equation

Find the K_a of a weak acid from the pH of its solution

Phenylacetic acid ($C_6H_5CH_2COOH$, denoted as HPAc) builds up in the blood of people afflicted with phenylketonuria, an inherited genetic disorder that, if left untreated, causes mental retardation and death. A study of the acid shows that the pH of a 0.12 *M* solution of HPAc is 2.60. What is the K_a of phenylacetic acid?

PLAN: Same as last chapter

1. Write a balanced equation for acid in water.
2. Write the equation for K_a.
3. Set-up and fill in the ICE Table
4. Use pH, initial solution concentration and ICE table to find K_a.

Find the K_a of a weak acid from the pH of its solution

What is the K_a of phenylacetic acid (HPAc)?

	$HPAc(aq)$ +	$H_2O(l)$ ⇌	$H_3O^+(aq)$ +	$PAc^-(aq)$
initial	0.12	-	1×10^{-7}	0
change	-x	-	+x	+x
equilibrium	0.12 - x	-	$x + (1 \times 10^{-7})$	x

$$K_a = \frac{[H_3O^+][PAc^-]}{[HPAc]} = \frac{[x + (10^{-7})][x]}{[0.12 - x]} = \frac{[x]^2}{[0.12 - x]}$$

Solution pH = 2.6 = $-\log[H_3O^+]$

$[H_3O^+] = 10^{-pH} = 10^{-2.6} = 2.5 \times 10^{-3}$ *M*

>> 10^{-7} (the $[H_3O^+]$ contribution from water)

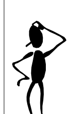
$[H_3O^+] \approx [PAc^-] = x = 2.5 \times 10^{-3}$ *M*

$[HPAc]_{eq} = 0.12 - x = 0.12 - 2.5 \times 10^{-3} \approx 0.117$ *M*

$$K_a = \frac{[H_3O^+][PAc^-]}{[HPAc]} = \frac{[x]^2}{[0.12 - x]}$$

$$K_a = \frac{(2.5 \times 10^{-3})^2}{0.117} = 5.2 \times 10^{-5}$$

Determining concentrations and pH from K_a and initial [HA]



The pH of a solution containing 0.250 M HF solution is 2.036. What is the value of K_a for HF at equilibrium?

Determining concentrations and pH from K_a and initial [HA]

The pH of a solution originally containing 0.250 M HF solution is 2.036. What is the value of K_a for HF at equilibrium?

	HF	+	H_2O	⇌	H_3O^+	+	F^-
Initial	.250 *M*				? *M*		? *M*
Change	-x *M*				+x *M*		+x *M*
Equilibrium	0.250-x				x		x

pH = 2.036 = -log $[H_3O^+]$

$$K_a = \frac{[H_3O^+][F^-]}{[HF]}$$

$10^{-pH} = [H_3O^+] = 10^{-2.036} = 9.20 \times 10^{-3}$ M

[HF] = 0.25 – 0.00920 = 0.241 M

$K_a = (9.2 \times 10^{-3})^2/0.241 = 3.52 \times 10^{-4}$

Determining concentrations from K_a and initial [HA]

Propanoic acid (CH_3CH_2COOH, simplified as HPr) is an organic acid whose salts are used to retard mold growth in foods. What is the $[H_3O^+]$ of a 0.10 *M* aqueous solution of HPr (K_a of HPr = 1.3×10^{-5})?

PLAN:
1. Write a balanced equation for acid in water.
2. Write the equation for K_a.
3. Set-up and fill in the ICE Table
4. Use pH, initial solution concentration and ICE table to find K_a.

	$HPr(aq)$ + $H_2O(l)$		⇌	$H_3O^+(aq)$	+ $Pr^-(aq)$
initial	0.10	-		0	0
change	-x	-		+x	+x
equilibrium	0.10 - x	-		x	x

$$K_a = \frac{[H_3O^+][Pr^-]}{[HPr]} = 1.3 \times 10^{-5} = \frac{x^2}{0.10 - x}$$

Can We Simplify?

100 x K_a < $[HA]_{initial}$ then $[HA]_{initial}$ - x = [HA]

100 x 1.3×10^{-5} < [.10]?

Yes, it is: .10 - x = 0.10

If No

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$K_a = \frac{[H_3O^+][Pr^-]}{[HPr]} = 1.3 \times 10^{-5} = \frac{x^2}{0.10}$$

$$K_a = \frac{[H_3O^+][Pr^-]}{[HPr]} = 1.3 \times 10^{-5} = \frac{x^2}{0.10}$$

$$x = \sqrt{(0.10)(1.3 \times 10^{-5})}$$ solving for x

$= 1.1 \times 10^{-3}$ *M* = $[H_3O^+]$

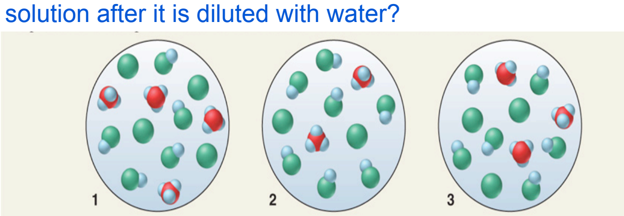
Checking assumption with 5% Rule: If $[H^+]_{equilibrium}$ divided by $[HA]_{initial}$ (x 100) is < 5% then assumption is valid.

$$\%[HPr]_{diss} = \frac{1.1 \times 10^{-3} M}{0.10 M} = 1.1\% \ll 5\%$$

our assumption is valid

Using Molecular Scenes to Determine the Extent of HA Dissociation

A 0.15 *M* solution of acid HA (blue and green) is 33% dissociated. Which scene best represents a sample of the solution after it is diluted with water?

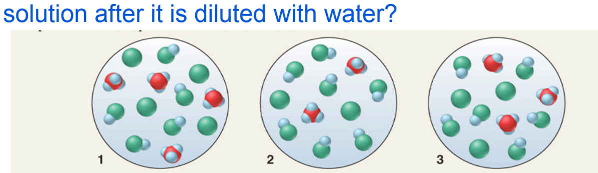


Percent dissociation increase as solution is diluted. Calculate the percent dissociation of each sample.

$$\% \text{ dissociation} = \frac{[H_3O^+]}{[HA] + [H_3O^+]} \times 100\%$$

Using Molecular Scenes to Determine the Extent of HA Dissociation

A 0.15 *M* solution of acid HA (blue and green) is 33% dissociated. Which scene best represents a sample of the solution after it is diluted with water?



$$\% \text{ dissociation} = \frac{[H_3O^+]}{[HA] + [H_3O^+]} \times 100\%$$

SOLUTION:

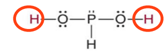
Solution 1. % dissociated = 4/(5 + 4) x 100 = 44%
Solution 2. % dissociated = 2/(7 + 2) x 100 = 22%
Solution 3. % dissociated = 3/(6 + 3) x 100 = 33%

Scene 1 represents the diluted solution.

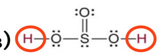
Polyprotic Acids

Polyprotic acids are acids that have more than one ionizable H^+ when reacted with water

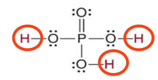
Phosphorous Acid (H_3PO_3)



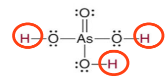
Sulfurous Acid (H_2SO_3)



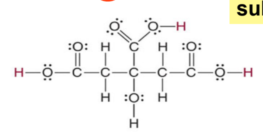
Phosphoric Acid



Arsenic Acid (H_3AsO_4)



Citric Acid ($H_3C_6H_5O_7$)



Each H has its own K_a

The electronegativity of the bonded atoms influence the ionizability of an acidic hydrogen in a substance.

Phosphoric acid, H_3PO_4

$$H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_2PO_4^-(aq) + H_3O^+(aq) \quad K_{a1} = \frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4]} = 7.2 \times 10^{-3}$$

$$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons HPO_4^{2-}(aq) + H_3O^+(aq) \quad K_{a2} = \frac{[H_3O^+][HPO_4^{2-}]}{[H_2PO_4^-]} = 6.3 \times 10^{-8}$$

$$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons PO_4^{3-}(aq) + H_3O^+(aq) \quad K_{a3} = \frac{[H_3O^+][PO_4^{3-}]}{[HPO_4^{2-}]} = 4.2 \times 10^{-13}$$

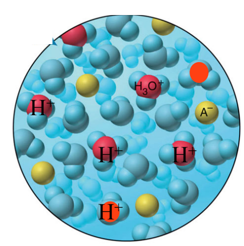
$$K_{a1} > K_{a2} > K_{a3}$$

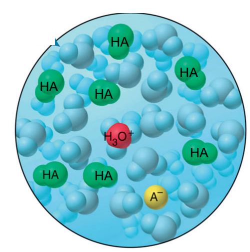
K_a quantifies and communicates the degree of acid dissociation = an acids strength

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq) \qquad K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

strong acid = K_a is large, pK_a is small

weak acid = K_a is small, pK_a is large





K_b is the equilbrium constant that quantifies a degree OH dissociation, a base's strength.

$$\ddot{B} + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq) \qquad K_b = \frac{[BH^+][OH^-]}{[B]}$$

---Strong bases dissociate completely

$Ca(OH)_2(s) + H_2O(l) \Longrightarrow Ca^{2+}(aq) + 2OH^-(aq) + H_2O(l)$

$NaOH(s) \overset{H_2O}{====>} Na^+(aq) + Cl^-(aq)$

---Weak bases dissociate partially

$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad K_b = 1.76 \times 10^{-5}$

$(CH_3)_2NH_2(aq) + H_2O(l) \rightleftharpoons (CH_3)_2NH^+(aq) + OH^-(aq) \qquad K_b = 5.4 \times 10^{-4}$

KEY DOT CONNECTION: The K_a of an acid and the K_b of the acid's conjugate base are related through the ion-product constant of water.

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq) \qquad K_a = \frac{[H^+][A^-]}{[HA]}$$

$$A^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + HA(aq) \qquad K_b = \frac{[OH^-][HA]}{[A^-]}$$

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \qquad K_a K_b = [OH^-][H^+]$$

If you know K_a for an acid you can determine K_b for its conjugate base!

$$K_w = K_a K_b = 10^{-14}$$

$$pK_w = pK_a + pK_b = 14$$

A table of bases and their conjugate acids, BH^+.

Notice! $K_b \times K_a = K_w = 1 \times 10^{14}$

TABLE 15.4 K_b Values for Some Weak Bases and K_a Values for Their Conjugate Acids

Base	Formula, B	K_b	Conjugate Acid, BH^+	K_a
Ammonia	NH_3	1.8×10^{-5}	NH_4^+	5.6×10^{-10}
Aniline	$C_6H_5NH_2$	4.3×10^{-10}	$C_6H_5NH_3^+$	2.3×10^{-5}
Dimethylamine	$(CH_3)_2NH$	5.4×10^{-4}	$(CH_3)_2NH_2^+$	1.9×10^{-11}
Hydrazine	N_2H_4	8.9×10^{-7}	$N_2H_5^+$	1.1×10^{-8}
Hydroxylamine	NH_2OH	9.1×10^{-9}	NH_3OH^+	1.1×10^{-6}
Methylamine	CH_3NH_2	3.7×10^{-4}	$CH_3NH_3^+$	2.7×10^{-11}

K_a and K_b of Some Common Weak Acids and Base

Acid	Formula	K_a	Conjugate	K_b
Iodic acid	HI	1.61 X 10^{-1}	I^-	6.1 X 10^{-14}
Chlorous Acid	$HClO_2$	1.1 X 10^{-2}	ClO_2^-	9.1 X 10^{-13}
Phosphoric Acid	H_3PO_4	7.6 X 10^{-3}	$H_2PO_4^-$	1.3 X 10^{-12}
Nitrous Acid	HNO_2	7.2 X 10^{-4}	NO_2^-	1.4 X 10^{-11}
Hydrofluoric Acid	HF	6.6 X 10^{-4}	F^-	1.5 X 10^{-11}
Formic Acid	HCOOH	1.8 X 10^{-4}	HCO_2^-	5.6 X 10^{-11}
Acetic Acid	CH_3CO_2H	1.8 X 10^{-5}	$CH_3CO_2^-$	5.6 X 10^{-10}
Hydrosulfuric Acid	H_2S	1.32 X 10^{-7}	HS^-	7.6 X 10^{-8}
Hypochlorous Acid	HClO	3.5 X 10^{-8}	ClO^-	2.9 X 10^{-7}
Hydrazine	N_2H_4	1.1 X 10^{-8}	OH^-	8.9 X 10^{-7}
Water	H_2O	1.0 X 10^{-7}	OH^-	1.0 X 10^{-7}
Ammonia	NH3	5.6 X 10^{-10}	NH_4^+	1.8 X 10^{-5}
Hydrocyanic Acid	HCN	4.0 X 10^{-10}	CN^-	2.5 X 10^{-5}
Dimethyl Amine	$(CH_3)_2NH$	1.9 X 10^{-11}	$(CH_3)_2NH_2^+$	5.4 X 10^{-4}

We solve weak base problems just like weak acid ones, except we solve for [OH-] instead of [H+].

$$NH_3\,(aq) + H_2O\,(l) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq) \quad K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

For ammonia, K_b = 1.76 x 10^{-5} what is the conjugate acid and what is it's pK_a? How would you write the reaction of NH_4^+ with water?

Generalized Base Equilibria

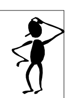
$$A^- + H_2O(l) \rightleftharpoons AH^+\,(aq) + OH^-\,(aq) \qquad K_b = \frac{[AH^+][OH^-]}{[A^-]}$$

Perhaps the hardest part for students is writing the base reaction in water...just think proton donar and acceptor.

Determining pH from K_b and initial [B]

Dimethylamine, $(CH_3)_2NH$, a key intermediate in detergent manufacture, has a K_b = 5.9 x 10^{-4}. What is the pH of a 1.5 M aqueous solution of $(CH_3)_2NH$?

Determining pH from K_b and initial [B]



Dimethylamine, $(CH_3)_2NH$, a key intermediate in detergent manufacture, has a K_b = 5.9 x 10^{-4}. What is the pH of a 1.5 M aqueous solution of $(CH_3)_2NH$?

concentration	$(CH_3)_2NH(aq)$ +	$H_2O(l)$ ⇌	$(CH_3)_2NH_2^+(aq)$ +	$OH^-(aq)$
initial	1.50	-	0	0
change	- x	-	+ x	+ x
equilibrium	1.50 - x	-	x	x

$$K_b = 5.9 \times 10^{-4} = \frac{[(CH_3)_2NH_2^+][OH^-]}{[(CH_3)_2NH]} = \frac{x^2}{1.5 - x}$$

Simplify? $\frac{[B_{initial}]}{K_b} > 100 \qquad K_b = \frac{[1.5]}{5.9 \times 10^{-4}} = 2542 > 100$

$$K_b = 5.9 \times 10^{-4} = \frac{x^2}{1.5}$$

$x = 3.0 \times 10^{-2}\ M = [OH^-]$

Check assumption: $[3.0 \times 10^{-2}\ M / 1.5\ M] \times 100 = 2\%$ (error is < 5%; thus, assumption is justified)

$$[H_3O^+] = K_w/[OH^-] = 1.0 \times 10^{-14}/3.0 \times 10^{-2} = 3.3 \times 10^{-13}\ M$$

$pH = -\log(3.3 \times 10^{-13}) = 12.5$

Determining the pH of a solution of A^-

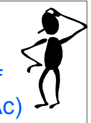
Sodium acetate (CH_3COONa, abbreviated NaAc) has applications in photographic development and textile dyeing. What is the pH of a 0.25 M aqueous solution of NaAc? The K_a of acetic acid (HAc) (conjugate acid of Ac) is 1.8 x 10^{-5}.

1. Write balanced equation knowing that sodium salts are completely soluble in water and acetate will be basic $[Ac^-] = 0.25\ M$.

2. Write the equilibrium expression--looking for pH.

3. Be organized set up ICE table and fill in the unknowns

4. Use K_a to find K_b and recall pH + pOH = 14.



Sodium acetate (CH_3COONa, abbreviated NaAc) has applications in photographic development and textile dyeing. What is the pH of a 0.25 M aqueous solution of NaAc? The K_a of acetic acid (HAc) (conjugate acid of Ac) is 1.8 x 10^{-5}.

concentration	$Ac^-(aq)$ +	$H_2O(l)$ ⇌	$HAc(aq)$ +	$OH^-(aq)$
initial	0.25	-	0	0
change	-x	-	+x	+x
equilibrium	0.25 - x	-	x	x

$$K_b = \frac{[HAc][OH^-]}{[Ac^-]} = \frac{K_w}{K_a}$$

$$\frac{K_w}{K_a} = K_b = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

$[Ac^-] = 0.25\ M - x \approx 0.25\ M$ (since K_b is small)

Check assumption: $[Ac^-]_{in} / K_b > 100 = .25/ 5.6 \times 10^{-10} > 100$

$$K_b = \frac{[HAc][OH^-]}{[Ac^-]}$$

$$5.6 \times 10^{-10} \approx x^2/0.25\ M$$

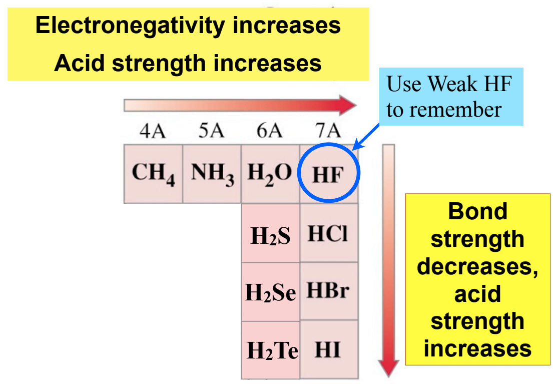
$$[OH^-] = x \approx 1.2 \times 10^{-5}\ M$$

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

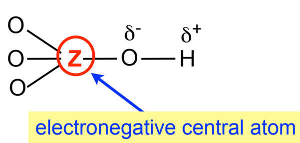
$$[H_3O^+] = K_w/[OH^-] = 1.0 \times 10^{-14}/1.2 \times 10^{-5} = 8.3 \times 10^{-10}\ M$$

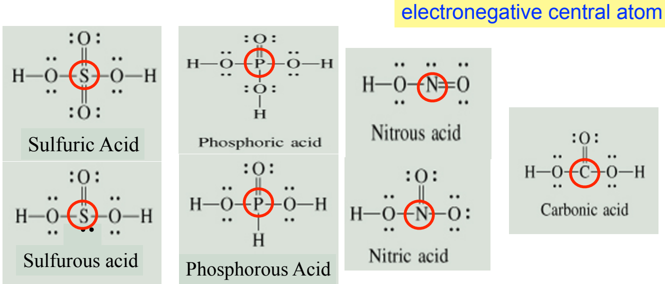
$$pH = -\log (8.3 \times 10^{-10}\ M) = 9.1$$

The acid strength of *non-metal hydrides* increase across a period and down a group.

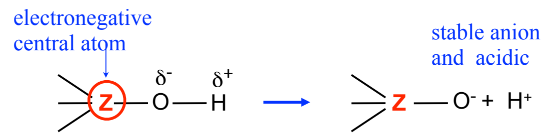


Oxo-acids **are compounds with one or more acidic hydrogens bonded to oxygen atom which is further bound to another central atom, Z.**





OXO-ACIDS: The greater electronegativity and number of internal atoms the more acidic the compound.



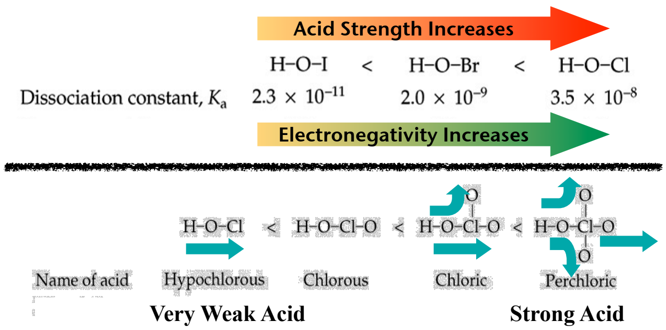
Less acidic → **More acidic**

IIA	IVA	VA	VIA	VIIA
H_3BO_3	H_2CO_3	HNO_3		
	H_2SiO_4	H_3PO_4	H_2SO_4	$HClO_3$
		H_3AsO_4	H_2SeO	$HBrO_3$
			H_6TeO_6	HIO_3

Electro-negativity increases acidity increases

More acidic ↑ **Less acidic**

The acidity of oxo-acids is determined by electronegativity (electron withdrawing effects).



$HClO < HClO_2 < HClO_3 < HClO_4$

More oxygens, more electron-withdrawing, increase polarity and acidity

Indicate whether each is a strong or weak acid, name each acid and its sodium salt, and predict the relative strengths of the following groups of oxoacids:

a) $HClO_2$, $HBrO_2$, and HIO_2.

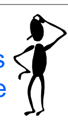
b) HIO HIO_2, HIO_3

c) HNO_3 and HNO_2.

d) H_3PO_3 and H_3PO_4.

e) H_2SO_4 and H_2SO_3

Indicate whether each is a strong or weak acid, predict the relative strengths of the following groups of oxoacids and the strengths of the conjugate base salts.



a) $HClO_2$, $HBrO_2$, and HIO_2. $HClO_2 > HBrO_2, > HIO_2$.

b) HIO HIO_2, HIO_3 $HIO < HIO_2 < HIO_3$

c) HNO_3 and HNO_2. $HNO_3 > HNO_2$.

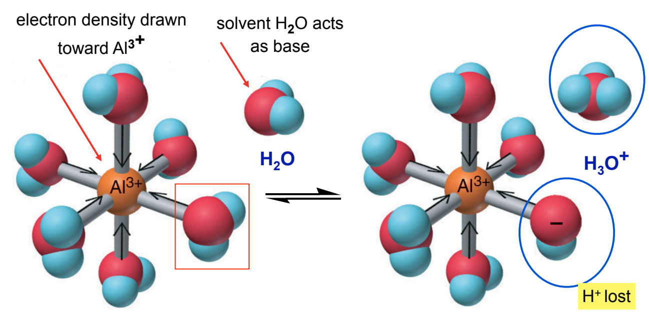
d) H_3PO_3 and H_3PO_4. $H_3PO_3 < H_3PO_4$.

e) H_2SO_4 and H_2SO_3 $H_2SO_4 > H_2SO_3$

Transition metal ions (Al^{3+}, Fe^{3+}, Cr^{3+}) react with water and are acids in aqueous solution.

$$Al(H_2O)_6^{3+}(aq) \rightleftharpoons Al(OH)(H_2O)_5^{2+}(aq) + H^+(aq)$$

Acid Hydrolysis of Al^{3+}



Aqueous solutions of many metal ions are acidic because the hydrated metal ions transfers an H^+ ion to water.

$$M(NO_3)_n(s) + xH_2O(l) \longrightarrow M(H_2O)_x^{n+}(aq) + nNO_3^-(aq)$$

$$M(H_2O)_x^{n+}(aq) + H_2O(l) \longrightarrow M(H_2O)_{x-1}OH^{(n-1)+}(aq) + H_3O^+(aq)$$

Free Ion	Hydrated Ion	K_a
Fe^{3+}	$Fe(H_2O)_6^{3+}(aq)$	6×10^{-3}
Sn^{2+}	$Sn(H_2O)_6^{2+}(aq)$	4×10^{-4}
Cr^{3+}	$Cr(H_2O)_6^{3+}(aq)$	1×10^{-4}
Al^{3+}	$Al(H_2O)_6^{3+}(aq)$	1×10^{-5}
Be^{2+}	$Be(H_2O)_4^{2+}(aq)$	4×10^{-6}
Cu^{2+}	$Cu(H_2O)_6^{2+}(aq)$	3×10^{-8}
Pb^{2+}	$Pb(H_2O)_6^{2+}(aq)$	3×10^{-8}
Zn^{2+}	$Zn(H_2O)_6^{2+}(aq)$	1×10^{-9}

high charge and small size enhance acidity

Hydrolysis of Ionic Salts

Ionic Salt + Water ==> ? pH

Acid and bases react with one another in a *neutralization reaction*.

$NaOH(aq) + HCl(aq) \Longleftrightarrow H_2O + Na^+ + Cl^-$

base + acid <==> Water + salt

Most salts can be viewed as coming from a "parent acid and parent base". If the parents are "strong" the cation or anion will not react with water, if the parents are "weak" the ion will react with water in a process called hydrolysis.

$NaCl(s)$

$Ca(NO_3)(s)$

$NH_4Br(s)$

$CH_3COOK(s)$

Salts are the product of an acid-base reaction. Salts that have either an anion or cation derived from a weak acid (anion) or weak base (cation) will react with water (hydrolysis) in an acid base reaction called hydrolysis.

1. look at the cation and anion and ask is it strong or weak parent acid/base?

2. If its from a weak parent...it will hydrolyze

Hydrolysis yields opposite pH as the parent.

NH_4Cl

CH_3CO_2K

$Ca(NO_3)_2$

There are 4 acid-base neutralization reactions yielding salts that can react with water.

1. **Strong acid + Strong base ==> Ionic salt + H_2O**
   $HCl\ (aq) + NaOH\ (aq) \Longrightarrow Na^+ + Cl^- + H_2O$ **Neutral salt**

2. **Strong acid + Weak base ==> Ionic salt + H_2O**
   $HBr\ (aq) + NH_3\ (aq) \Longrightarrow NH_4^+ + Br^- + H_2O$ **Acidic salt**

3. **Weak acid + Strong base ==> Ionic salt + H_2O**
   $2HCOOH\ (aq) + Ca(OH)_2\ (aq) \Longrightarrow Ca^{+2} + 2HCOO^- + 2H_2O$
   Basic Salt

4. **Weak acid + Weak base ==> Ionic salt + H_2O**
   $CH_3COOH\ (aq) + NH_3\ (aq) \Longrightarrow NH_4^+ + CH_3COO^- + H_2O$
   Depends on pK_a vs pk_b

---

1. Salts formed from a *strong acid* and a *strong base* are *neutral* when dissolved in H_2O.

parent is NaOH a strong base

parent is HCl a strong acid

neither Na^+ or Cl^- react with water. Neutral!

$NaCl(s) + H_2O(l) \Longleftrightarrow Na^+\ (aq) + Cl^-\ (aq) + H_2O$ pH = 7

parent is KOH a strong base

parent is H_2SO_4 a strong acid

neither K^+ or SO_4^- react with water. Neutral!

$K_2SO_4(s) + H_2O(l) \Longleftrightarrow K^+\ (aq) + SO_4^-\ (aq) + H_2O$ pH = 7

Why? The anion of a strong acid (Cl^-, I^-, Br^-, NO_3^-) is a much weaker base than water, and the cation of from the strong acid is a much weaker acid than water!

---

2. Solutions of salts formed from a strong acid and a weak base are acidic when dissolved in H_2O.

parent is NH_4OH = weak base

parent is HBr = strong acid

cation will hydrolyze or react with water

anion is from a strong acid and does not hydrolyze.

$$NH_4Br(s) \longrightarrow NH_4^+\ (aq) + Br^-(aq)$$

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

hydrolysis gives acidic solution

---

3. Solutions of salts formed from a weak acid and a strong base are basic when dissolved in H_2O.

parent acid of the anion is CH_3CO_2H = weak acid

parent of cation is KOH = strong base

anion hydrolyzible

$$CH_3COOK\ (s) \xrightarrow{H_2O} K^+\ (aq) + CH_3COO^-\ (aq)$$

$$CH_3COO^-\ (aq) + H_2O\ (l) \rightleftharpoons CH_3COOH\ (aq) + OH^-\ (aq)$$

hydrolysis of salt of weak acid gives a basic solution

$$NaH_2PO_4(s) \longrightarrow Na^+(aq) + H_2PO_4^-\ (aq)$$

$$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons HPO_4^{2-}(aq) + H_3O^+(aq)$$

4. Solutions of salts formed from a weak acid and a weak base depend on the K_a and K_b of the salt.

Both are weak and thus cation and anion will hydrolyze. Which one wins depends on strength (K_a vs K_b) or the ions.

Example: NH_4HS

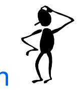
$$NH_4^+(aq) + H_2O \longleftrightarrow NH_3(aq) + H_3O^+(aq)$$

$$HS^-(aq) + H_2O \longleftrightarrow H_2S(aq) + OH^-(aq)$$

$K_a(NH_4^+) = 5.7 \times 10^{-10}$ vs $K_b(HS^-) = 1.0 \times 10^{-7}$

Since $K_b > K_a$, the solution is basic.

Predict whether aqueous solutions of the following compounds are acidic, basic, or neutral (write an equation for the reaction of the appropriate ion with water to explain pH effect).



(a) $KClO_4$ **(b)** sodium benzoate, C_6H_5COONa

(c) $CrCl_3$ **(d)** $NaHSO_4$

PLAN: Consider the acid-base nature of the anions and cations. Strong acid-strong base combinations produce a neutral solution; strong acid-weak base, acidic; weak acid-strong base, basic.

(a) $KClO_4$ **(b)** sodium benzoate, C_6H_5COONa

(c) $CrCl_3$ **(d)** $NaHSO_4$

(a) The ions are K^+ and ClO_4^-, which come from a strong base (KOH) and a strong acid ($HClO_4$). The solution will be neutral.

(b) Na^+ comes from the strong base NaOH while $C_6H_5COO^-$ is the anion of a weak organic acid. The salt solution will be basic.

(c) Cr^{3+} is a small cation with a large + charge, so its hydrated form will react with water to produce H_3O^+. Cl^- comes from the strong acid HCl. The salt solution will be acidic.

(d) Na^+ comes from a strong base. HSO_4^- can react with water to form H_3O^+. The salt solution will be acidic.

You are given 0.1M solutions of the following. What is the nature of the solutions acid/ base/ neutral or amphoteric?

- $KClO_2$
- CsI
- $NaHSO_4$
- HCO2K
- $Al(H_2O)_6$
- $NaNO_3$
- Na_3PO_4
- Na_2HPO_4
- $FeCl_3$
- $KClO_4$
- CH_3COONH_4

You are given 0.1M solutions of the following. What is the nature of the solutions acid/ base/ neutral or amphoteric?

$KClO_2$	Basic
CsI	Neutral
$NaHSO_4$	Acidic
HCO_2K	Basic
$Al(H_2O)_6$	Acidic
$NaNO_3$	Neutral
Na_3PO_4	Basic
CH_3COONH_4	Depends on Ka vs Kb
$FeCl_3$	Acidic

Predicting the relative acidity of weak-weak salt solutions

Determine whether an aqueous solution of zinc formate, $Zn(HCOO)_2$, is acidic, basic, or neutral. The K_a for $Zn(H_2O)_6^{2+} = 10^{-9}$ and K_a for formic acid is 1.8×10^{-4}.

Both Zn^{2+} and $HCOO^-$ come from weak conjugates. In order to find the relatively acidity, write the dissociation reactions and use the information in Tables 18.2 and 18.7.

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SOLUTION:

$$Zn(H_2O)_6^{2+}(aq) + H_2O(l) \rightleftharpoons Zn(H_2O)_5OH^+(aq) + H_3O^+(aq)$$

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

K_a $Zn(H_2O)_6^{2+}$ = 1×10^{-9}

K_a HCOOH = 1.8×10^{-4} ; $K_b = K_w/K_a = 1.0 \times 10^{-14}/1.8 \times 10^{-4} = 5.6 \times 10^{-11}$

K_a for $Zn(H_2O)_6^{2+}$ > K_b $HCOO^-$; the solution is acidic.

A *Lewis Acid* is any substance that is an *electron-pair acceptor.*

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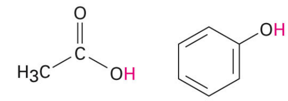
Neutral Proton Donors **H^+** **BF_3**

H_2O HCl HBr HNO_3 H_2SO_4



CH_3CH_2OH

A carboxylic acid **A phenol** **An alcohol**

Lewis acids lack electrons and have an orbital.

Cations

Li^+ Mg^{2+}

Transition Metal Cations

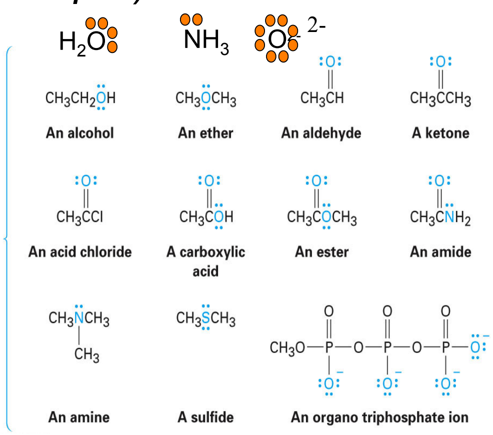
$AlCl_3$ $TiCl_4$ $FeCl_3$ $ZnCl_2$

Al^{3+}, Ti^{4+}, Fe^{3+}, Zn^{2+},

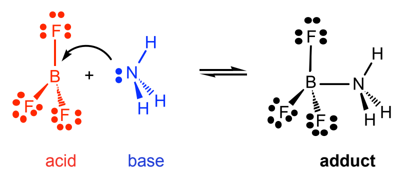
A Lewis Base is any substance that is an *electron-pair donor (nucleophile).*

Atoms having lone pairs of electrons is the distinguishing feature

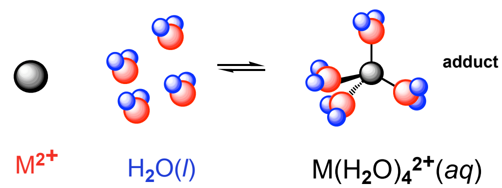
Some Lewis bases



***Neutralization* (in the Lewis acid context) occurs when a Lewis acid reacts and forms a covalent bond with a Lewis base. The bond is called a *coordinate bond*.**



The adduct contains a new covalent bond.



Identify the Lewis acids and Lewis bases in the following reactions:

(a) $H^+ + OH^- \rightleftharpoons H_2O$
(b) $Cl^- + BCl_3 \rightleftharpoons BCl_4^-$
(c) $K^+ + 6H_2O \rightleftharpoons K(H_2O)_6^+$

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Look for electron pair acceptors (acids) and donors (bases).

(a) H^+ (acceptor) + OH^- (donor) $\rightleftharpoons H_2O$

(b) Cl^- (donor) + BCl_3 (acceptor) $\rightleftharpoons BCl_4^-$

(c) K^+ (acceptor) + $6H_2O$ (donor) $\rightleftharpoons K(H_2O)_6^+$