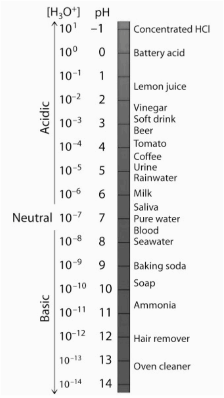
The Chemistry of Acids and Bases *Separately*

Chapter 14 Part I

Chemistry 223
Professor Michael Russell

MAR *Last update: 4/29/24*

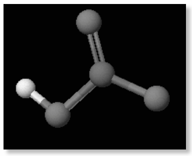


Strong and Weak Acids/Bases

Generally divide acids and bases into STRONG or WEAK categories.

STRONG ACID: $HNO_3(aq) + H_2O(liq) \rightarrow H_3O^+(aq) + NO_3^-(aq)$

HNO_3 is about 100% dissociated in water. Acids create hydronium when they react with water.



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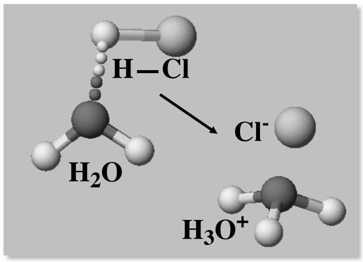
Strong and Weak Acids/Bases

HNO_3, HCl, HBr, HI and $HClO_4$ are among the few known strong *monoprotic* acids.



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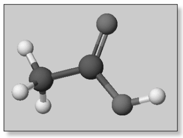
Memorize these five strong acids!

Strong and Weak Acids/Bases

Weak acids are much less than 100% ionized in water.

One of the best known is acetic acid = CH_3CO_2H = HOAc

$HOAc(aq) + H_2O(liq) \rightleftharpoons OAc^-(aq) + H_3O^+(aq)$



OAc^- = $CH_3CO_2^-$ = acetate ion

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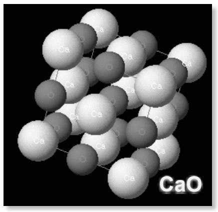
Strong and Weak Acids/Bases

Strong Base: 100% dissociated in water.

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

Other strong *monobasic* bases: KOH, LiOH



$Ca(OH)_2$ is a strong *dibasic* system:

CaO (lime) + H_2O --> $Ca(OH)_2$ (slaked lime)

Memorize the three strong monobasic bases!

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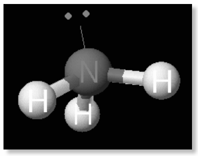
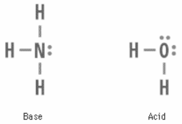
Strong and Weak Acids/Bases

Weak base: less than 100% ionized in water

One of the best known weak bases is ammonia, NH_3

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





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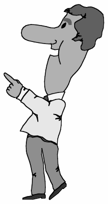
ACID-BASE THEORIES

The most general theory for common aqueous acids and bases is the BRØNSTED - LOWRY theory

ACIDS DONATE H^+ IONS

BASES ACCEPT H^+ IONS



See <u>Brønsted Acids and Bases Handout</u>

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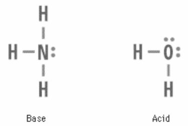
ACID-BASE THEORIES

The Brønsted definition means NH_3 is a BASE in water - and water is itself an ACID

$$\underset{\text{Base}}{NH_3} + \underset{\text{Acid}}{H_2O} \rightleftharpoons \underset{\text{Acid}}{NH_4^+} + \underset{\text{Base}}{OH^-}$$



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ACID-BASE THEORIES

NH_3 is a BASE in water - and water is itself an ACID

$$\underset{\text{Base}}{NH_3(aq)} + H_2O(\ell) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

NH_3 / NH_4^+ is a conjugate pair - related by the gain or loss of H^+

Every acid has a conjugate base - and vice-versa.

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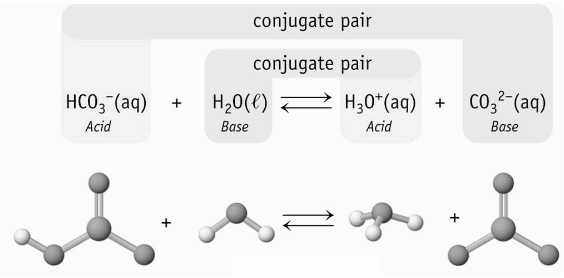
Conjugate Pairs



$$\underset{\text{Acid}}{HCO_3^-(aq)} + \underset{\text{Base}}{H_2O(\ell)} \rightleftharpoons \underset{\text{Acid}}{H_3O^+(aq)} + \underset{\text{Base}}{CO_3^{2-}(aq)}$$

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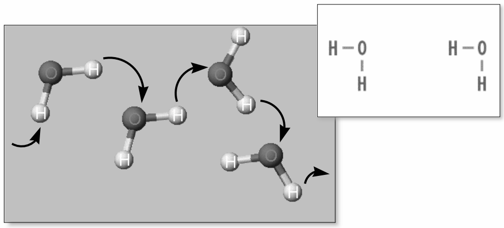
MORE ABOUT WATER

H_2O can function as both an ACID and a BASE.



Pure water undergoes AUTOIONIZATION

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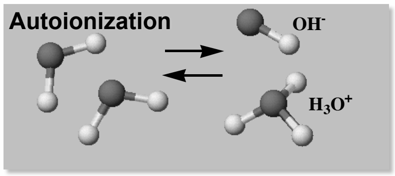
MORE ABOUT WATER



K_w = $[H_3O^+]$ $[OH^-]$ = 1.00×10^{-14} at 25 °C

In a neutral solution $[H_3O^+]$ = $[OH^-]$

so K_w = $[H_3O^+]^2$ = $[OH^-]^2$

and so $[H_3O^+]$ = $[OH^-]$ = $\sqrt{K_w}$ = 1.00×10^{-7} M

Memorize $K_W = 1.00 \times 10^{-14}$!

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Calculating [H_3O^+] & [OH^-]

You add 0.0010 mol of NaOH to 1.0 L of pure water. Calculate [H_3O^+] and [OH^-].

Solution

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

Le Chatelier predicts equilibrium shifts to the ___________.

[H_3O^+] < 10^{-7} at equilibrium.

Set up an ICE concentration table.

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Calculating [H_3O^+] & [OH^-]

You add 0.0010 mol of NaOH to 1.0 L of pure water. Calculate [H_3O^+] and [OH^-].

Solution

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

initial
change
equilib

K_w = (x)(0.0010 + x)

Because x << 0.0010 M, *assume* [OH^-] = 0.0010 M

K_w = (x)(0.0010 + x) ≈ (x)(0.0010) = [H_3O^+](0.0010)

[H_3O^+] = K_w / 0.0010 = 1.0 x 10^{-11} M

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Calculating [H_3O^+] & [OH^-]

You add 0.0010 mol of NaOH to 1.0 L of pure water. Calculate [H_3O^+] and [OH^-].

Solution

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

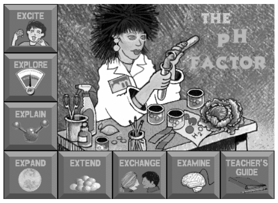
[H_3O^+] = K_w / 0.0010 = 1.0 x 10^{-11} M

[OH^-] = 1.0 x 10^{-3} M

This solution is ___________

because

[OH^-] > [H_3O^+]



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[H_3O^+], [OH^-] and pH

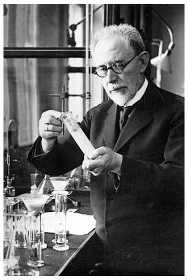
A common way to express acidity and basicity is with pH

pH = - log [H_3O^+]

In a *neutral* solution,
[H_3O^+] = [OH^-] =
1.0 x 10^{-7} at 25 °C

pH = -log (1.00 x 10^{-7})
= - (-7.00) = 7.00

pH = 7.00 for neutral solutions!



***Søren Sørensen**, creator of the pH scale*

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[H_3O^+], [OH^-] and pH

What is the pH of the 0.0010 M NaOH solution?

[H_3O^+] = 1.0 x 10^{-11} M

pH = - log (1.0 x 10^{-11}) = 11.00

General conclusion -

Basic solution	**pH > 7**
Neutral	**pH = 7**
Acidic solution	**pH < 7**

Public Enemy are not scientists!

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[H_3O^+], [OH^-] and pH

If the pH of Diet Coke is 3.12, it is ___________.

Because pH = - log [H_3O^+] then
log [H_3O^+] = - pH

Take antilog and get

[H_3O^+] = 10^{-pH}

[H_3O^+] = $10^{-3.12}$
= 7.6 x 10^{-4} M

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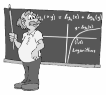
logarithms and sig figs

Logarithms are exponents with special sig figs rules. *General rule:*

log of experimentally measured number with *N* sig figs give numbers with *N* decimal places *after* the decimal (digit before decimal only indicates magnitude)



***Examples*:**

log $3.07*10^{-3}$ = -2.513 (*3 sigs, 3 places after decimal)*

- log $1.1*10^{-8}$ = 7.96 (*2 sigs, 2 places after decimal)*

$10^{-3.12}$ = 7.6 * 10^{-4} *(2 places after decimal, 2 sigs)*

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pH of Common Substances

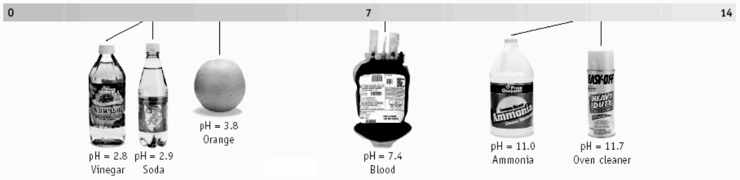

Figure 5.17 pH values of some common substances. Here the "bar" is colored red at one end and blue at the other. These are the colors of litmus paper, commonly used in the laboratory to decide if a solution is acidic (litmus is red) or basic (litmus is blue). *(Charles D. Winters)*

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Other pX Scales

In general **pX = -log X**

and: **pK_a = - log K_a**

and so: **pOH = - log $[OH^-]$**

$K_w = [H_3O^+] [OH^-] = 1.00 \times 10^{-14}$ *at 25 °C*

Take the negative log of both sides

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

14 = pH + pOH

also: **$14 = pK_a + pK_b$**

P.K.A.
KICKBOXING

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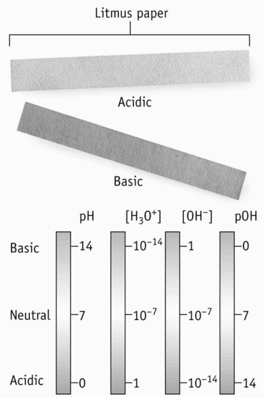

acidic solutions:

pH ↓,

$[H_3O^+]$ ↑,

$[OH^-]$ ↓,

pOH ↑

***basic solutions:* pH ↑,**

$[H_3O^+]$ ↓,

$[OH^-]$ ↑,

pOH ↓

$K_w = [H_3O^+] [OH^-] = 1.00 \times 10^{-14}$ at 25 ˚C

pH + pOH = 14

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Equilibria Considerations Involving Weak Acids and Bases

Acid	Conjugate Base
acetic, CH_3CO_2H	**$CH_3CO_2^-$, acetate**
ammonium, NH_4^+	**NH_3, ammonia**
bicarbonate, HCO_3^-	**CO_3^{2-}, carbonate**

A weak acid (or base) is one that ionizes to a VERY small extent (< 5%).

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Equilibria Involving Weak Acids and Bases

Consider acetic acid, CH_3CO_2H (HOAc)

$$\underset{\text{Acid}}{HOAc} + H_2O \rightleftharpoons H_3O^+ + \underset{\text{Conj. base}}{OAc^-}$$

$$K_a = \frac{[H_3O^+][OAc^-]}{[HOAc]} = 1.8 \times 10^{-5}$$

(K is designated K_a for ACID)

Because $[H_3O^+]$ and $[OAc^-]$ are SMALL, K_a << 1.

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Equilibrium Constants for Weak Acids (K_a)

$$HA(aq) + H_2O(\ell) \rightleftarrows H_3O^+(aq) + A^-(aq)$$

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

Weak acids have $K_a < 1$
Leads to small $[H_3O^+]$ and a pH of 2 - 7

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Equilibrium Constants for Weak Bases (K_b)

$$B(aq) + H_2O(\ell) \rightleftarrows BH^+(aq) + OH^-(aq)$$

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

Weak bases have $K_b < 1$
Leads to small $[OH^-]$ and a pH of 12 - 7

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Equilibrium Constants for Weak Acids and Bases

$\cancel{HA} + H_2O \rightleftharpoons H_3O^+ + \cancel{A^-}$ K_a

$\cancel{A^-} + H_2O \rightleftharpoons \cancel{HA} + OH^-$ K_b

----

$2\ H_2O \rightleftharpoons H_3O^+ + OH^-$ $K_a{*}K_b = K_w$

Important relations: $K_a{*}K_b = K_w$ and $pK_a + pK_b = 14$

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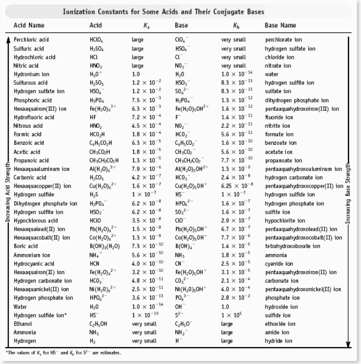
Ionization Constants for Acids/Bases

Acids

Increase strength



Ionization Constants for Some Acids and Their Conjugate Bases

Acid Name	Acid	K_a	Base	K_b	Base Name
Perchloric acid	$HClO_4$	large	ClO_4^-	very small	perchlorate ion
Sulfuric acid	H_2SO_4	large	HSO_4^-	very small	hydrogen sulfate ion
Hydrochloric acid	HCl	large	Cl^-	very small	chloride ion
Nitric acid	HNO_3	large	NO_3^-	very small	nitrate ion
Hydronium ion	H_3O^+	1.0	H_2O	1.0×10^{-14}	water
Sulfurous acid	H_2SO_3	1.2×10^{-2}	HSO_3^-	8.3×10^{-13}	hydrogen sulfite ion
Hydrogen sulfate ion	HSO_4^-	1.2×10^{-2}	SO_4^{2-}	8.3×10^{-13}	sulfate ion
Phosphoric acid	H_3PO_4	7.5×10^{-3}	$H_2PO_4^-$	1.3×10^{-12}	dihydrogen phosphate ion
Hexaaquairon(III) ion	$Fe(H_2O)_6^{3+}$	6.3×10^{-3}	$Fe(H_2O)_5OH^{2+}$	1.6×10^{-12}	pentaaquahydroxoiron(III) ion
Hydrofluoric acid	HF	7.2×10^{-4}	F^-	1.4×10^{-11}	fluoride ion
Nitrous acid	HNO_2	4.5×10^{-4}	NO_2^-	2.2×10^{-11}	nitrite ion
Formic acid	HCO_2H	1.8×10^{-4}	HCO_2^-	5.6×10^{-11}	formate ion
Benzoic acid	$C_6H_5CO_2H$	6.3×10^{-5}	$C_6H_5CO_2^-$	1.6×10^{-10}	benzoate ion
Acetic acid	CH_3CO_2H	1.8×10^{-5}	$CH_3CO_2^-$	5.6×10^{-10}	acetate ion
Propanoic acid	$CH_3CH_2CO_2H$	1.3×10^{-5}	$CH_3CH_2CO_2^-$	7.7×10^{-10}	propanoate ion
Hexaaqualuminum ion	$Al(H_2O)_6^{3+}$	7.9×10^{-6}	$Al(H_2O)_5OH^{2+}$	1.3×10^{-9}	pentaaquahydroxoaluminum ion
Carbonic acid	H_2CO_3	4.2×10^{-7}	HCO_3^-	2.4×10^{-8}	hydrogen carbonate ion
Hexaaquacopper(II) ion	$Cu(H_2O)_6^{2+}$	1.6×10^{-7}	$Cu(H_2O)_5OH^+$	6.25×10^{-8}	pentaaquahydroxocopper(II) ion
Hydrogen sulfide	H_2S	1×10^{-7}	HS^-	1×10^{-7}	hydrogen sulfide ion
Dihydrogen phosphate ion	$H_2PO_4^-$	6.2×10^{-8}	HPO_4^{2-}	1.6×10^{-7}	hydrogen phosphate ion
Hydrogen sulfite ion	HSO_3^-	6.2×10^{-8}	SO_3^{2-}	1.6×10^{-7}	sulfite ion
Hypochlorous acid	$HClO$	3.5×10^{-8}	ClO^-	2.9×10^{-7}	hypochlorite ion
Hexaaqualead(II) ion	$Pb(H_2O)_6^{2+}$	1.5×10^{-8}	$Pb(H_2O)_5OH^+$	6.7×10^{-7}	pentaaquahydroxolead(II) ion
Hexaaquacobalt(II) ion	$Co(H_2O)_6^{2+}$	1.3×10^{-9}	$Co(H_2O)_5OH^+$	7.7×10^{-6}	pentaaquahydroxocobalt(II) ion
Boric acid	$B(OH)_3(H_2O)$	7.3×10^{-10}	$B(OH)_4^-$	1.4×10^{-5}	tetrahydroxoborate ion
Ammonium ion	NH_4^+	5.6×10^{-10}	NH_3	1.8×10^{-5}	ammonia
Hydrocyanic acid	HCN	4.0×10^{-10}	CN^-	2.5×10^{-5}	cyanide ion
Hexaaquairon(II) ion	$Fe(H_2O)_6^{2+}$	3.2×10^{-10}	$Fe(H_2O)_5OH^+$	3.1×10^{-5}	pentaaquahydroxoiron(II) ion
Hydrogen carbonate ion	HCO_3^-	4.8×10^{-11}	CO_3^{2-}	2.1×10^{-4}	carbonate ion
Hexaaquanickel(II) ion	$Ni(H_2O)_6^{2+}$	2.5×10^{-11}	$Ni(H_2O)_5OH^+$	4.0×10^{-4}	pentaaquahydroxonickel(II) ion
Hydrogen phosphate ion	HPO_4^{2-}	3.6×10^{-13}	PO_4^{3-}	2.8×10^{-2}	phosphate ion
Water	H_2O	1.0×10^{-14}	OH^-	1.0	hydroxide ion
Hydrogen sulfide ion*	HS^-	1×10^{-19}	S^{2-}	1×10^5	sulfide ion
Ethanol	C_2H_5OH	very small	$C_2H_5O^-$	large	ethoxide ion
Ammonia	NH_3	very small	NH_2^-	large	amide ion
Hydrogen	H_2	very small	H^-	large	hydride ion

*The values of K_a for HS^- and K_b for S^{2-} are estimates.

Conjugate Bases

Increase strength

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K and Acid-Base Reactions

ACIDS	CONJUGATE BASES
STRONG	weak
↑	↓
weak	STRONG

In general, **Reactions always go from the** stronger A-B pair (larger K) **to the** weaker A-B pair (smaller K).

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K and Acid-Base Reactions

A strong acid is 100% dissociated.

Therefore, a STRONG ACID **- a good H^+ donor- must have a** WEAK CONJUGATE BASE **- a poor H^+ acceptor.**

$HNO_3(aq) + H_2O(liq) \rightleftharpoons H_3O^+(aq) + NO_3^-(aq)$

STRONG A	base	acid	weak B

Every **A-B reaction has** two acids **and** two bases**.**
Equilibrium always lies *toward the weaker pair.*
Here K is *very* large... should write:

$HNO_3(aq) + H_2O(liq) \rightarrow H_3O^+(aq) + NO_3^-(aq)$

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K and Acid-Base Reactions

Acetic acid is only 0.42% ionized when [HOAc] = 1.0 M. It is a WEAK ACID

$HOAc + H_2O \rightleftharpoons H_3O^+ + OAc^-$

WEAK A base acid STRONG B

Because $[H_3O^+]$ is small, this must mean

1. **H_3O^+ is a stronger acid than HOAc**
2. **OAc^- is a stronger base than H_2O**
3. **K for this reaction is small**

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Types of Acid/Base Reactions

1. Strong acid + Strong base (SA + SB) reactions:

$HCl(aq) + NaOH(aq) \rightleftharpoons H_2O(l) + NaCl(aq)$

$H^+ + Cl^- + Na^+ + OH^- \rightleftharpoons H_2O + Na^+ + Cl^-$

Net ionic equation:

$H^+(aq) + OH^-(aq) \rightleftharpoons H_2O(liq)$

$K = 1/K_w = 1 \times 10^{14}$ *very product favored K!*

Mixing equal molar quantities of a strong acid and strong base produces a neutral solution.

should write:

$HCl(aq) + NaOH(aq) \rightarrow H_2O(l) + NaCl(aq)$

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Types of Acid/Base Reactions

2. Weak acid + Strong base (WA + SB) reactions:

$CH_3CO_2H + OH^- \rightleftharpoons H_2O + CH_3CO_2^-$

This is the reverse of the reaction of $CH_3CO_2^-$ (conjugate base) with H_2O.

OH^- stronger base than $CH_3CO_2^-$

$K = 1/K_b = 1.8 \times 10^9$ *very product favored K!*

Mixing equal molar quantities of a weak acid and strong base produces the acid's conjugate base. The solution is basic.

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Types of Acid/Base Reactions

3. Weak base + Strong acid (WB + SA) reactions:

$H_3O^+ + NH_3 \rightleftharpoons H_2O + NH_4^+$

This is the reverse of the reaction of NH_4^+ (conjugate acid of NH_3) with H_2O.

H_3O^+ stronger acid than NH_4^+

$K = 1/K_a = 1.8 \times 10^9$ *very product favored K!*

Mixing equal molar quantities of a strong acid and weak base produces the base's conjugate acid. The solution is acidic.

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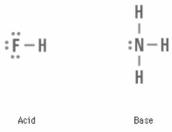
Types of Acid/Base Reactions

4. Weak acid + weak base (WA + WB) reactions:



Product cation = conjugate acid of weak base.
Product anion = conjugate base of weak acid.
pH of solution depends on relative strengths of cation and anion (larger K → smaller K).

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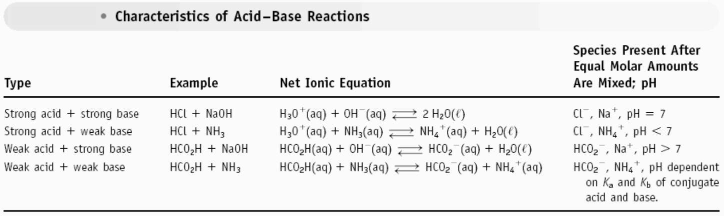
We will not be studying WA + WB reactions in CH 223

Types of Acid/Base Reactions: Summary



Characteristics of Acid–Base Reactions

Type	Example	Net Ionic Equation	Species Present After Equal Molar Amounts Are Mixed; pH
Strong acid + strong base	$HCl + NaOH$	$H_3O^+(aq) + OH^-(aq) \rightleftharpoons 2\,H_2O(\ell)$	Cl^-, Na^+, pH = 7
Strong acid + weak base	$HCl + NH_3$	$H_3O^+(aq) + NH_3(aq) \rightleftharpoons NH_4^+(aq) + H_2O(\ell)$	Cl^-, NH_4^+, pH < 7
Weak acid + strong base	$HCO_2H + NaOH$	$HCO_2H(aq) + OH^-(aq) \rightleftharpoons HCO_2^-(aq) + H_2O(\ell)$	HCO_2^-, Na^+, pH > 7
Weak acid + weak base	$HCO_2H + NH_3$	$HCO_2H(aq) + NH_3(aq) \rightleftharpoons HCO_2^-(aq) + NH_4^+(aq)$	HCO_2^-, NH_4^+, pH dependent on K_a and K_b of conjugate acid and base.

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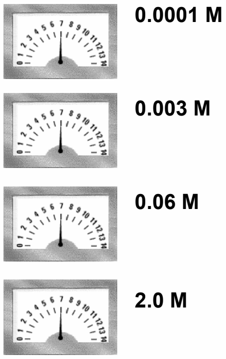


a pH meter

Equilibria Involving A Weak Acid

Determining the pH of an acetic acid solution

MAR

Equilibria Involving A Weak Acid

You have 1.00 M HOAc. Calc. the equilibrium concs. of HOAc, H_3O^+, OAc^-, and the pH.

Step 1. **Define ICE equilibrium using K_a.**

	HOAc + H_2O $\rightleftharpoons$	H_3O^+ +	OAc^-
	[HOAc]	**[H_3O^+]**	**[OAc^-]**
initial			
change			
equilib			

Note that we neglect [H_3O^+] from H_2O.
HOAc = acetic acid, OAc^- = acetate ion

MAR

Equilibria Involving A Weak Acid

You have 1.00 M HOAc. Calc. the equilibrium concs. of HOAc, H_3O^+, OAc^-, and the pH.

$$\text{HOAc} + H_2O \rightleftharpoons H_3O^+ + OAc^-$$

Step 2. **Write K_a expression**

$$K_a = 1.8 \text{ x } 10^{-5} = \frac{[H_3O^+][OAc^-]}{[HOAc]} = \frac{x^2}{1.00 - x}$$

This is a quadratic equation; solve using the quadratic formula.

MAR

Equilibria Involving A Weak Acid

You have 1.00 M HOAc. Calc. the equilibrium concs. of HOAc, H_3O^+, OAc^-, and the pH.

Step 3. **Solve K_a expression**

$$K_a = 1.8 \text{ x } 10^{-5} = \frac{[H_3O^+][OAc^-]}{[HOAc]} = \frac{x^2}{1.00 - x}$$

First assume x is *very small* because K_a is so small. If so:

$$K_a = 1.8 \text{ x } 10^{-5} = \frac{x^2}{1.00}$$

Therefore,

x = [H_3O^+] = [OAc^-] = [$1.8 \text{x} 10^{-5} \cdot 1.00]^{1/2}$ = [$K_a \cdot C_a]^{1/2}$

C_a = concentration (M) of acid

MAR

Equilibria Involving A Weak Acid

You have 1.00 M HOAc. Calc. the equilibrium concs. of HOAc, H_3O^+, OAc^-, and the pH.

Step 3. **Solve K_a *approximate* expression:**

$$K_a = 1.8 \text{ x } 10^{-5} = \frac{x^2}{1.00}$$

x = [H_3O^+] = [OAc^-] = [$1.8 \text{x} 10^{-5} \cdot 1.00]^{1/2}$

x = [H_3O^+] = [OAc^-] = $4.2 \text{ x } 10^{-3}$ M

pH = - log [H_3O^+] = -log ($4.2 \text{ x } 10^{-3}$) = 2.37

MAR

Exact solution with quadratic: x = 0.0042, x = -0.0043

Equilibria Involving A Weak Acid

Consider the approximate expression:

$$K_a = 1.8 \text{ x } 10^{-5} = \frac{x^2}{1.00} \qquad x = [H_3O^+] = [K_a \bullet 1.00]^{1/2}$$

For many weak acids

$[H_3O^+] = [\text{conj. base}] = [K_a \cdot C_a]^{1/2}$

where C_a = initial conc. of acid

Useful Rule of Thumb:

If $100 \cdot K_a < C_a$, then $[H_3O^+] = [K_a \cdot C_a]^{1/2}$

or pH = $- \log [K_a \cdot C_a]^{1/2}$

MAR

Equilibria Involving A Weak Acid

Calculate the pH of a 0.0010 M solution of formic acid, HCO_2H.

$HCO_2H + H_2O \rightleftharpoons HCO_2^- + H_3O^+$

$K_a = 1.8 \times 10^{-4}$

$100 * K_a$ is not less than C_a!

Approximate solution

$[H_3O^+] = [K_a \bullet C_a]^{1/2} = 4.2 \times 10^{-4}$ M, pH = 3.37

Exact Solution

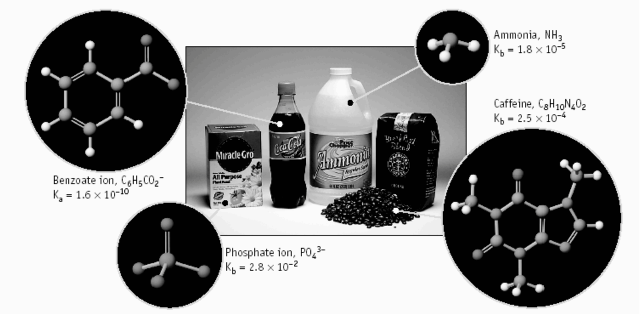
$[H_3O^+] = [HCO_2^-] = 3.4 \times 10^{-4}$ M

$[HCO_2H] = 0.0010 - 3.4 \times 10^{-4} = 0.0007$ M

pH = 3.47

MAR

Weak Bases



MAR

Equilibria Involving A Weak Base

You have 0.010 M NH_3. Calculate the pH.

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

$K_b = 1.8 \times 10^{-5}$

Step 1. **Define equilibrium concs.**

	$[NH_3]$	$[NH_4^+]$	$[OH^-]$
initial			
change			
equilib			

MAR

Equilibria Involving A Weak Base

You have 0.010 M NH_3. Calculate the pH.

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

$K_b = 1.8 \times 10^{-5}$

Step 2. **Solve the equilibrium expression**

$$K_b = 1.8 \times 10^{-5} = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{x^2}{0.010 - x}$$

Assume **x is small ($100 \bullet K_b < C_b$)**, *so*

x = $[OH^-]$ = $[NH_4^+]$ = $[K_b \bullet C_b]^{1/2}$ = 4.2×10^{-4} M

check: **$[NH_3] = 0.010 - 4.2 \times 10^{-4} \approx 0.010$ M**

Valid approximation!

Exact solution with quadratic: x = 0.00042, x = -0.00043

MAR

Equilibria Involving A Weak Base

You have 0.010 M NH_3. Calculate the pH.

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

$K_b = 1.8 \times 10^{-5}$

Step 3. **Calculate pH**

$[OH^-] = 4.2 \times 10^{-4}$ M

so pOH = - log $[OH^-]$ = 3.37

Because pH + pOH = 14,

pH = 10.63

***or* pH = 14 + log $[K_b \bullet C_b]^{1/2}$ = 10.63**

MAR

Overview: Calculating pH of Acids & Bases

Strong acid: **pH = - log C_a = - log $[H_3O^+]$**

Strong base:

pH = 14 + log C_b = 14 + log $[OH^{-1}]$

Weak acid:

pH = - log $[K_a \bullet C_a]^{1/2}$ *($100 * K_a < C_a$)*

Weak base:

pH = 14 + log $[K_b \bullet C_b]^{1/2}$ *($100 * K_b < C_b$)*

Memorize!

MAR

Acid-Base Properties of Salts

MX + H_2O ----> acidic or basic solution?

Consider NH_4Cl

$NH_4Cl(aq)$ ----> $NH_4^+(aq)$ + $Cl^-(aq)$

(a) Reaction of Cl^- with H_2O

Cl^- + H_2O ----> HCl + OH^-

base acid acid base

Cl^- ion is a VERY weak base because its conjugate acid is strong.

Therefore, Cl^- ----> neutral solution

MAR

Acid-Base Properties of Salts

MX + H_2O ----> acidic or basic solution?

$NH_4Cl(aq)$ ----> $NH_4^+(aq)$ + $Cl^-(aq)$

(b) Reaction of NH_4^+ with H_2O

NH_4^+ + H_2O ----> NH_3 + H_3O^+

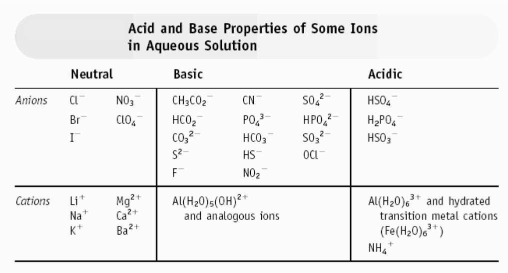
acid base base acid

NH_4^+ ion is a moderate acid ($K_a = 5.6 \times 10^{-10}$) because its conjugate base is weak.

Therefore, NH_4^+ ----> acidic solution

MAR

Acid-Base Properties of Salts



Acid and Base Properties of Some Ions in Aqueous Solution

	Neutral		Basic			Acidic
Anions	Cl^- Br^- I^-	NO_3^- ClO_4^-	$CH_3CO_2^-$ HCO_2^- CO_3^{2-} S^{2-} F^-	CN^- PO_4^{3-} HCO_3^- HS^- NO_2^-	SO_4^{2-} HPO_4^{2-} SO_3^{2-} OCl^-	HSO_4^- $H_2PO_4^-$ HSO_3^-
Cations	Li^+ Na^+ K^+	Mg^{2+} Ca^{2+} Ba^{2+}	$Al(H_2O)_5(OH)^{2+}$ and analogous ions			$Al(H_2O)_6^{3+}$ and hydrated transition metal cations ($Fe(H_2O)_6^{3+}$) NH_4^+

MAR

Acid-Base Properties of Salts

Calculate the pH of a 0.10 M solution of Na_2CO_3.

Na^+ + H_2O ---> neutral

CO_3^{2-} + $H_2O \rightleftharpoons HCO_3^-$ + OH^-

base acid acid base

$K_b = 2.1 \times 10^{-4}$

Step 1. Set up ICE concentration table

	$[CO_3^{2-}]$	$[HCO_3^-]$	$[OH^-]$
initial			
change			
equilib			

MAR

Acid-Base Properties of Salts

Calculate the pH of a 0.10 M solution of Na_2CO_3.

Na^+ + H_2O ---> neutral

CO_3^{2-} + $H_2O \rightleftharpoons HCO_3^-$ + OH^-

base acid acid base

$K_b = 2.1 \times 10^{-4}$

Step 2. Solve the equilibrium expression

$$K_b = 2.1 \text{ x } 10^{-4} = \frac{[HCO_3^-][OH^-]}{[CO_3^{2-}]} = \frac{x^2}{0.10 - x}$$

Assume **0.10 - x ≈ 0.10,** *because* **100•K_b < C_b**

x = $[HCO_3^-]$ = $[OH^-]$ = $[K_b \cdot C_b]^{1/2}$ = 0.0046 M

MAR

Exact solution with quadratic: x = 0.0045, x = -0.0047

Acid-Base Properties of Salts

Calculate the pH of a 0.10 M solution of Na_2CO_3.

Na^+ + H_2O ---> neutral

CO_3^{2-} + $H_2O \rightleftharpoons HCO_3^-$ + OH^-

base acid acid base

$K_b = 2.1 \times 10^{-4}$

Step 3. Calculate the pH

$[OH^-]$ = 0.0046 M

pOH = - log $[OH^-]$ = 2.34

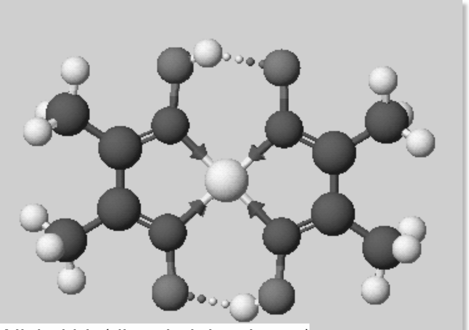
pH + pOH = 14,

so pH = 11.66, and the solution is ________.

***or* pH = 14 + log $[K_b \cdot C_b]^{1/2}$ = 11.66**

MAR

Lewis Acids & Bases

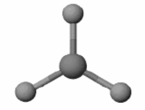


Nickel bis(dimethylglyoximate)

Clifford and Aiden with red Nickel bis(dimethylglyoximate) solution (April 2023)

Lewis Acids & Bases

Lewis acid = electron pair acceptor (BF_3)

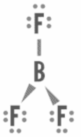


BF_3, the boron atom is surrounded by only three electron pairs.

Lewis base = electron pair donor (NH_3)

MAR

Lewis Acids & Bases



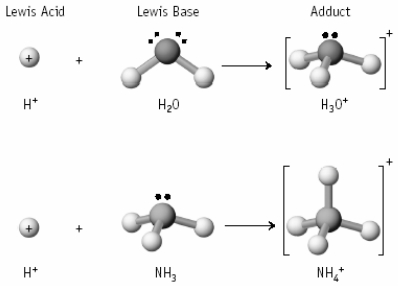
New bond formed using electron pair from the Lewis base.

Coordinate covalent bond

Notice geometry change on reaction.

MAR

Lewis Acids & Bases



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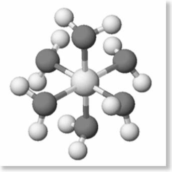
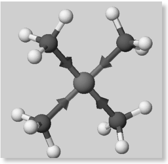
Lewis Acids & Bases

The combination of metal ions (Lewis acids) with Lewis bases such as H_2O and NH_3 ------> COMPLEX IONS

***All* metal ions form complex ions with water and are of the type $[M(H_2O)_x]^{n+}$ where x = 4 and 6.**



$[Co(H_2O)_6]^{3+}$



$[Cu(NH_3)_4]^{2+}$

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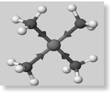
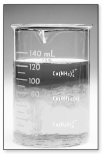
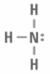
Lewis Acids & Bases

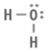
Add NH_3 to light blue $[Cu(H_2O)_4]^{2+}$ ------> light blue $Cu(OH)_2$ and then deep blue $[Cu(NH_3)_4]^{2+}$







Ammonia



Water

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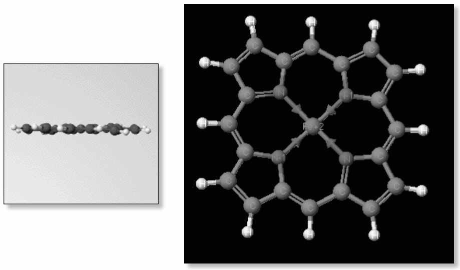
Lewis Acids & Bases

The Fe^{2+} in heme can interact with O_2 or CO in a Lewis acid-base reaction.



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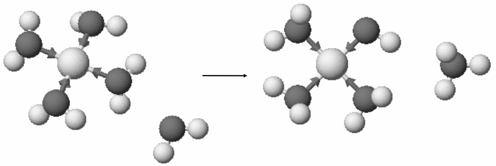
Lewis Acids & Bases

Many complex ions containing water undergo HYDROLYSIS to give acidic solutions.

$[Cu(H_2O)_4]^{2+} + H_2O \text{ ---> } [Cu(H_2O)_3(OH)]^+ + H_3O^+$

This is a K_a expression



This explains why water solutions of transition metals are acidic.

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Lewis Acids & Bases

Lewis acid & base theory explains AMPHOTERIC nature of some metal hydroxides.

$Al(OH)_3(s) + 3\ H^+ \text{ --> } Al^{3+} + 3\ H_2O$

Here $Al(OH)_3$ is a Brønsted base.

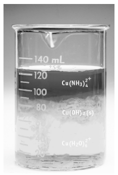
$Al(OH)_3(s) + OH^- \text{ --> } Al(OH)_4^-$

Here $Al(OH)_3$ is a Lewis acid.

$$Al^{3+} \leftarrow :\ddot{\underset{\cdot\cdot}{O}}-H^-$$

MAR

Lewis Acids & Bases



Many complex ions are very stable.

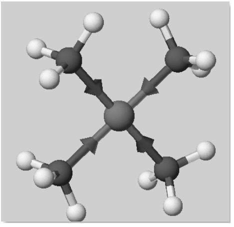
$Cu^{2+} + 4\ NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$

K for the reaction is called $K_{formation}$

or a "formation constant"

Here $K_f = 6.8 \times 10^{12}$. Reaction is strongly product-favored.

$$K_f = \frac{[Cu(NH_3)_4]^{2+}}{[Cu^{2+}][NH_3]^4}$$



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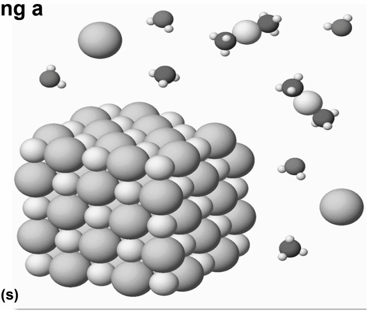
Lewis Acids & Bases

Formation of complex ions explains why you can dissolve a precipitate by forming a complex ion.

$AgCl(s) + 2\ NH_3 \rightleftharpoons Ag(NH_3)_2^+ + Cl^-$



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Lewis Acids & Bases

Formation of complex ions explains why you can dissolve a precipitate by forming a complex ion.

$AgCl(s) \rightleftharpoons Ag^+ + Cl^-$ $\quad K_{sp} = 1.8 \times 10^{-10}$

$Ag^+ + 2\ NH_3 \rightleftharpoons Ag(NH_3)_2^+$ $\quad K_{form} = 1.6 \times 10^7$

$AgCl(s) + 2\ NH_3 \rightleftharpoons Ag(NH_3)_2^+ + Cl^-$

$K_{net} = K_{sp} \bullet K_{form} = 2.9 \times 10^{-3}$

MAR

Hints for This Chapter

$pH_{(strong\ acid)} = -\log C_a$

$pH_{(strong\ base)} = 14 + \log C_b$

$pH_{(weak\ acid)} = -\log [K_a * C_a]^{1/2}$

$pH_{(weak\ base)} = 14 + \log [K_b * C_b]^{1/2}$

$14 = pH + pOH = pK_a + pK_b$

$K_w = 1.00 * 10^{-14} = [H_3O^+][OH^-] = K_a * K_b$ **(25 °C)**

***Know* equivalence point pH values for different titrations**

***Know* how to use formation constants**

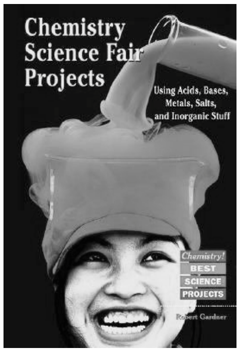
***Understand* Lewis acid/base theory**

MAR

End of Chapter 14 Part I

See:

- *Chapter Fourteen Part I Study Guide*
- *Chapter Fourteen Part I Concept Guide*
- *Types of Equilibrium Constants*
- *Important Equations (following this slide)*
- *End of Chapter Problems (following this slide)*



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Important Equations, Constants, and Handouts from this Chapter:

$pH_{(strong\ acid)} = -\log C_a$

$pH_{(strong\ base)} = 14 + \log C_b$

$pH_{(weak\ acid)} = -\log [K_a * C_a]^{1/2}$

$pH_{(weak\ base)} = 14 + \log [K_b * C_b]^{1/2}$

$14 = pH + pOH = pK_a + pK_b$

$K_w = 1.00 * 10^{-14} = [H_3O^+][OH^-] = K_a * K_b$ (25 °C)

$HOAc + H_2O \rightleftharpoons H_3O^+ + OAc^-$

$$K_a = \frac{[H_3O^+][OAc^-]}{[HOAc]};$$

$$B(aq) + H_2O(\ell) \rightleftharpoons BH^+(aq) + OH^-(aq)$$

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

Acid-Base Theory: **Brønsted theory, conjugate acid** *and* **base, strong** *and* **weak acids** *and* **bases,** *know the* **8 strong acids** *and* **bases!, autoionization, Lewis theory, electron pair acceptor** *and* **donator, salt acidity/basicity, formation constants (K_f)**

Handouts:

- *Manipulating Equilibrium Constant Expressions*
- *Types of Equilibrium Constants*
- *Table of K_a and K_b values in Problem Set #2*

MAR

End of Chapter Problems: *Test Yourself*

1. An aqueous solution has a pH of 3.75. What is the hydronium ion concentration of the solution? What is the hydroxide ion concentration of the solution? Is it acidic or basic?
2. What is the pH of a 0.0015 M solution of $Ba(OH)_2$?
3. Epinephrine hydrochloride has a pK_a value of 9.53. What is the value of K_a?
4. A weak base has $K_b = 4.7 \times 10^{-11}$. What is the value of K_a for the conjugate acid?
5. A 0.015 M solution of hydrogen cyanate, HOCN, has a pH of 2.67. What is the hydronium ion concentration in the solution? What is the ionization constant, K_a, for the acid?
6. A 0.015 M solution of a base has a pH of 10.09. What are the hydronium and hydroxide ion concentrations of this solution? What is the value of K_b for this base?
7. Which of the following substances should be classified as a Lewis acid and a Lewis base: $Fe^{2+}(aq)$, CH_3NH_2

MAR

End of Chapter Problems: *Answers*

1. $[H_3O^+] = 1.8 \times 10^{-4}$ M, $[OH^-] = 5.6 \times 10^{-11}$ M, acidic
2. 11.48
3. 3.0×10^{-10}
4. 2.1×10^{-4}
5. 0.0021 M, 3.6×10^{-4} ($K_a = 3.0 \times 10^{-4}$ using short method)
6. $[H_3O^+] = 8.1 \times 10^{-11}$ M, $[OH^-] = 1.2 \times 10^{-4}$ M, $K_b = 9.7 \times 10^{-7}$
7. $Fe^{2+}(aq)$ would be a Lewis acid, CH_3NH_2 would be a Lewis base

MAR