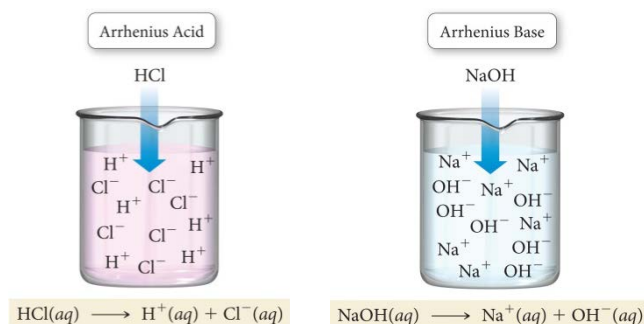# ACIDS AND BASES_____ Z Ch 7.1-7.4, 7.6

"According to this theory strong acids and bases, as well as salts, are in extreme dilution almost completely dissociated into their ions, *i.e.* HCl into H^+ and Cl^-, NaOH into Na^+ and OH^-, and NaCl into Na^+ and Cl^-. On the other hand, water is hardly dissociated at all. The reaction of neutralization of a strong acid with a strong base ... can … be expressed by ... $H^+ + OH^-$. This equation is equivalent to the formation of water from its two ions, H^+ and OH^-, and is evidently independent of the nature of the strong acid and the strong base."   **Svante August Arrhenius, 1903** (Nobel Prize in Chemistry in 1903 "in recognition of the extraordinary services he has rendered to the advancement of chemistry by his electrolytic theory of dissociation".)

7.1 The Nature of Acids and Bases: Acid-Base Theories

Arrhenius

acid – produces $H^+(aq)$ ions (protons) in aqueous solution

Arrhenius Acid
HCl

Arrhenius Base
NaOH

base – produces $OH^-(aq)$ ions in aqueous solution

$HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)$ $NaOH(aq) \longrightarrow Na^+(aq) + OH^-(aq)$
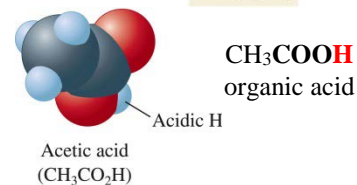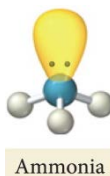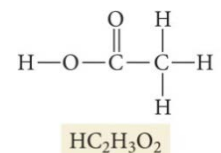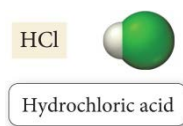
problem – acids only $H^+(aq)$, bases only $OH^-(aq)$, need an aqueous solution

Brønsted-Lowry – focus on hydrogen ion

acid – substance that can **donate** a hydrogen ion (**proton**)

HCl

Hydrochloric acid

$HC_2H_3O_2$

$CH_3COO\mathbf{H}$
organic acid

base – substance that can **accept** a hydrogen ion (**proton**) => must have lone pair of electrons!

Ammonia

Acidic H

Acetic acid
(CH_3CO_2H)

little problem – acids can only donate H^+ => must have H

Lewis (Chapter 19) – focus on electron pair (we will not use in CHEM 116)
acid – species that accepts a pair of electrons
base – species that donates a pair of electrons
advantage – no restriction on acids requiring H atom

Lewis	Brønsted-Lowry	Arrhenius
coordinate covalent bond	conjugate acid-base pairs $A_1 + B_2 \rightarrow A_2 + B_1$	neutralization $H^+ + OH^- \rightarrow H_2O$

7.1 Brønsted-Lowry Acid-Base Theory

Conjugate acids and bases

acids – proton donors => form a species [acid – H^+] called **conjugate base**

bases – proton acceptors => form a species [base + H^+] called **conjugate acid**

NH_3 (base) → (Add H^+) → NH_4^+ (conjugate acid) — Conjugate acid–base pair

H_2O (acid) → (Remove H^+) → OH^- (conjugate base) — Conjugate acid–base pair

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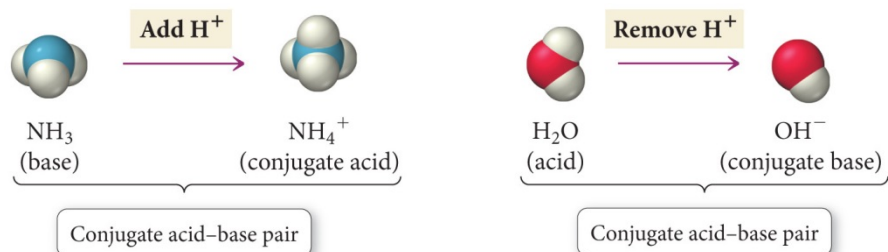
EX 1. For each of the following acids write the formula of its conjugate base and for each of the bases write the formula of its conjugate acid.
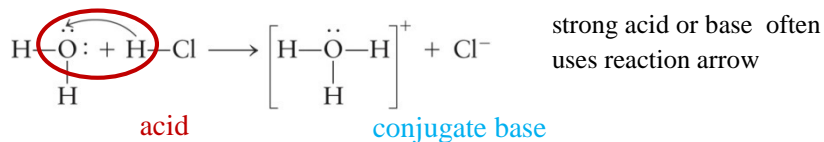
ACIDS - conjugate base	BASES - conjugate acid
HCl	NH_3
H_2O	NaOH
NH_3	H_2S
CH_3COOH	O^{2-}
SH^-	CN^-

Conjugate Acid-Base Pair Chemistry: $A_1 + B_2 \longrightarrow A_2 + B_1$

acid - proton donor

$$H-\overset{..}{O}: + H-Cl \longrightarrow [H-\overset{..}{O}-H]^+ + Cl^-$$

acid   conjugate base

strong acid or base often uses reaction arrow

reaction when acid dissolved in water:

$$H_2SO_4(aq) + H_2O(l) \longrightarrow HSO_4^-(aq) + H_3O^+(aq)$$

Acid   Base   Conjugate base   Conjugate acid
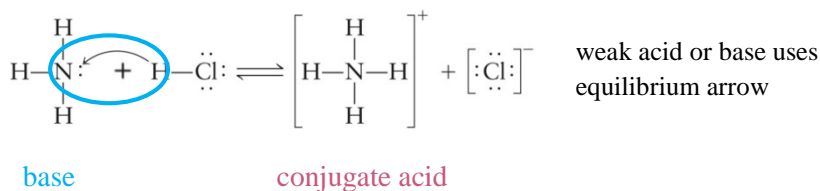
base - proton acceptor

(nonaqueous: reaction in liquid ammonia between hydrogen chloride dissolved in liquid ammonia and liquid ammonia)

$$H-\overset{H}{\underset{H}{N}}: + H-\overset{..}{\underset{..}{Cl}}: \rightleftharpoons [H-\overset{H}{\underset{H}{N}}-H]^+ + [:\overset{..}{\underset{..}{Cl}}:]^-$$

base   conjugate acid

weak acid or base uses equilibrium arrow

reaction when base dissolved in water:

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

Base   Acid   Conjugate acid   Conjugate base

$$H_3PO_4(aq) \quad + \quad CH_3CO_2^-(aq) \quad \rightleftharpoons \quad H_2PO_4^-(aq) \quad + \quad CH_3CO_2H(aq)$$

Brønsted acids

Brønsted bases

| stronger acid than CH_3CO_2H | stronger base than $H_2PO_4^-$ | weaker base than $CH_3CO_2^-$ | weaker acid than H_3PO_4 |

two bases competing for the acidic proton – the stronger base "wins"
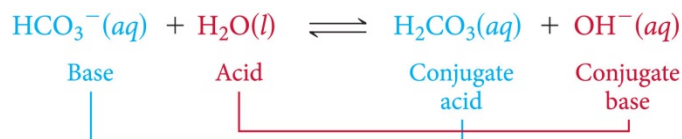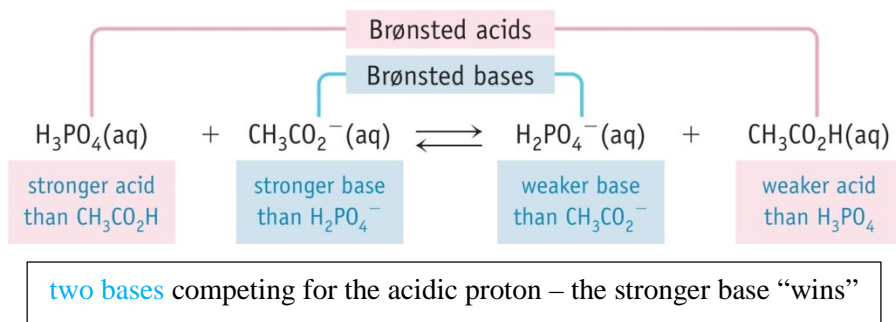
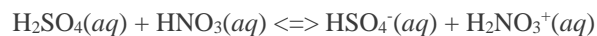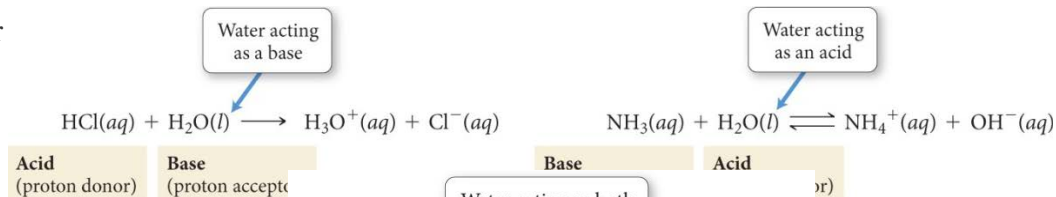**EX 2.** Show how the reaction of aqueous potassium hydroxide with aqueous ammonium sulfate can be viewed as a Brønsted-Lowry acid-base reaction.

EX 3. From the Brønsted-Lowry point of view, which is the stronger acid in the following reaction:

$$H_2SO_4(aq) + HNO_3(aq) <=> HSO_4^-(aq) + H_2NO_3^+(aq)$$

---

amphoteric nature
of water

Water acting as a base

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

| **Acid** (proton donor) | **Base** (proton accept |

Water acting as an acid

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

| **Base** | **Acid** |

autoionization

Water acting as both an acid and a base

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

of water:

| **Acid** (proton donor) | **Base** (proton acceptor) |
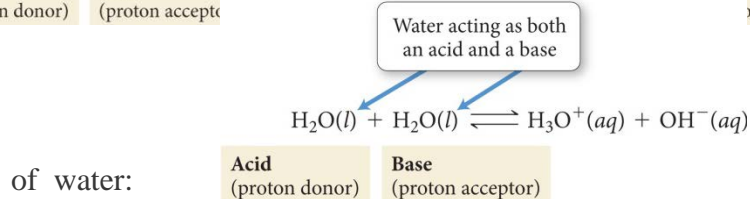
of ammonia: $NH_3(l) + NH_3(l) <=> NH_4^+(aq) + NH_2^-(aq)$

base   acid   conjugate acid   conjugate base
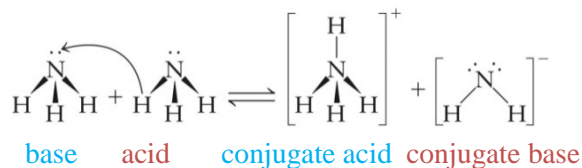
7.2 Acid Strength

strong/weak electrolytes

Perchloric acid
($HClO_4$)

Sulfuric acid
(H_2SO_4)
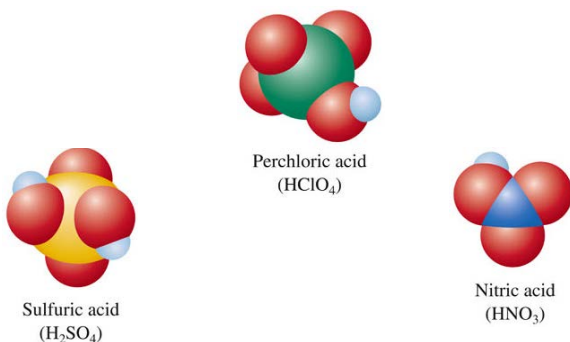
Nitric acid
(HNO_3)

seven strong acids to know	
hydrochloric acid	HCl
hydrobromic acid	HBr
hydroiodic acid	HI
perchloric acid	$HClO_4$
chloric acid	$HClO_3$
sulfuric acid	H_2SO_4
nitric acid	HNO_3

acid strength – determined by extent of reaction of acid with water to form $H_3O^+(aq)$, or the extent of its ionization or dissociation, as shown by the magnitude of its equilibrium constant, K_a
– then for any hydrogen-containing compound, HA

HA(*aq*)   + H_2O(*l*)   <=> H_3O^+(*aq*)   + A^-(*aq*)

acid   **conjugate base**
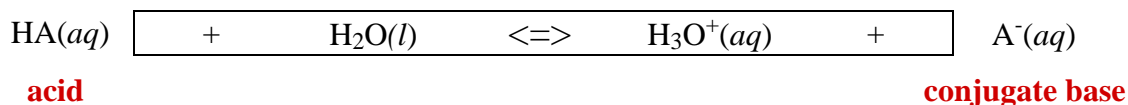
equilibrium constant, $K_a = \dfrac{[H_3O^+][A^-]}{[HA]}$

Various Ways to Describe Acid Strength

Property	Strong Acid	Weak Acid
K_a value	K_a is large	K_a is small
Position of the dissociation equilibrium	Far to the right	Far to the left
Equilibrium concentration of H^+ compared with original concentration of HA	$[H^+] \approx [HA]_0$	$[H^+] \ll [HA]_0$
Strength of conjugate base compared with that of water	A^- much weaker base than H_2O	A^- much stronger base than H_2O

Acidity Constants in Water at 25°C

Acid	Formula	Conjugate Base	K_a	pK_a
Hydriodic	HI	I$^-$	$\approx 10^{11}$	≈ -11
Hydrobromic	HBr	Br$^-$	$\approx 10^9$	≈ -9
Perchloric	HClO$_4$	ClO$_4^-$	$\approx 10^7$	≈ -7
Hydrochloric	HCl	Cl$^-$	$\approx 10^7$	≈ -7
Chloric	HClO$_3$	ClO$_3^-$	$\approx 10^3$	≈ -3
Sulfuric (1)	H$_2$SO$_4$	HSO$_4^-$	$\approx 10^2$	≈ -2
Nitric	HNO$_3$	NO$_3^-$	≈ 20	≈ -1.3
Hydronium ion	H$_3$O$^+$	H$_2$O	1	0.0
Urea acidium ion	(NH$_2$)CONH$_3^+$	(NH$_2$)$_2$CO (urea)	6.6×10^{-1}	0.18
Iodic	HIO$_3$	IO$_3^-$	1.6×10^{-1}	0.80
Oxalic (1)	H$_2$C$_2$O$_4$	HC$_2$O$_4^-$	5.9×10^{-2}	1.23
Sulfurous (1)	H$_2$SO$_3$	HSO$_3^-$	1.5×10^{-2}	1.82
Sulfuric (2)	HSO$_4^-$	SO$_4^{2-}$	1.2×10^{-2}	1.92
Chlorous	HClO$_2$	ClO$_2^-$	1.1×10^{-2}	1.96
Phosphoric (1)	H$_3$PO$_4$	H$_2$PO$_4^-$	7.5×10^{-3}	2.12
Arsenic (1)	H$_3$AsO$_4$	H$_2$AsO$_4^-$	5.0×10^{-3}	2.30
Chloroacetic	ClCH$_2$COOH	ClCH$_2$COO$^-$	1.4×10^{-3}	2.85
Hydrofluoric	HF	F$^-$	6.6×10^{-4}	3.18
Nitrous	HNO$_2$	NO$_2^-$	4.6×10^{-4}	3.34
Formic	HCOOH	HCOO$^-$	1.8×10^{-4}	3.74
Benzoic	C$_6$H$_5$COOH	C$_6$H$_5$COO$^-$	6.5×10^{-5}	4.19
Oxalic (2)	HC$_2$O$_4^-$	C$_2$O$_4^{2-}$	6.4×10^{-5}	4.19
Hydrazoic	HN$_3$	N$_3^-$	1.9×10^{-5}	4.72
Acetic	CH$_3$COOH	CH$_3$COO$^-$	1.8×10^{-5}	4.74
Propionic	CH$_3$CH$_2$COOH	CH$_3$CH$_2$COO$^-$	1.3×10^{-5}	4.89
Pyridinium ion	HC$_5$H$_5$N$^+$	C$_5$H$_5$N (pyridine)	5.6×10^{-6}	5.25
Carbonic (1)	H$_2$CO$_3$	HCO$_3^-$	4.3×10^{-7}	6.37
Sulfurous (2)	HSO$_3^-$	SO$_3^{2-}$	1.0×10^{-7}	7.00
Arsenic (2)	H$_2$AsO$_4^-$	HAsO$_4^{2-}$	9.3×10^{-8}	7.03
Hydrosulfuric	H$_2$S	HS$^-$	9.1×10^{-8}	7.04
Phosphoric (2)	H$_2$PO$_4^-$	HPO$_4^{2-}$	6.2×10^{-8}	7.21
Hypochlorous	HClO	ClO$^-$	3.0×10^{-8}	7.52
Hydrocyanic	HCN	CN$^-$	6.2×10^{-10}	9.21
Ammonium ion	NH$_4^+$	NH$_3$	5.6×10^{-10}	9.25
Carbonic (2)	HCO$_3^-$	CO$_3^{2-}$	4.8×10^{-11}	10.32
Methylammonium ion	CH$_3$NH$_3^+$	CH$_3$NH$_2$	2.3×10^{-11}	10.64
Arsenic (3)	HAsO$_4^{2-}$	AsO$_4^{3-}$	3.0×10^{-12}	11.52
Hydrogen peroxide	H$_2$O$_2$	HO$_2^-$	2.4×10^{-12}	11.62
Phosphoric (3)	HPO$_4^{2-}$	PO$_4^{3-}$	2.2×10^{-13}	12.66
Water	H$_2$O	OH$^-$	1.0×10^{-14}	14.00
Hydrogen sulfide ion	HS$^-$	S^{2-}	1.0×10^{-19}	19.00
Hydrogen	H$_2$	H$^-$	1.0×10^{-33}	33.00
Ammonia	NH$_3$	NH$_2^-$	1.0×10^{-38}	38.00
Hydroxide ion	OH$^-$	O^{2-}		

acids stronger than H_3O^+

Leveling effect: Acids stronger than the hydronium ion or bases stronger than the hydroxide ion have the same effective strength in water, that of a strong acid or a strong base, since the equilibrium lies so far to the right that it cannot be accurately measured. In general all acids (or bases) stronger than the conjugate acid (or base) of the solvent have the same effective strength in that solvent and the solvent is said to have a leveling effect on those acids and bases.
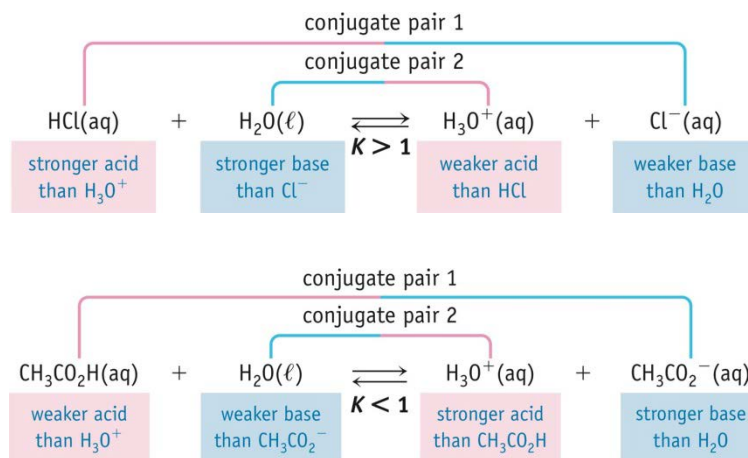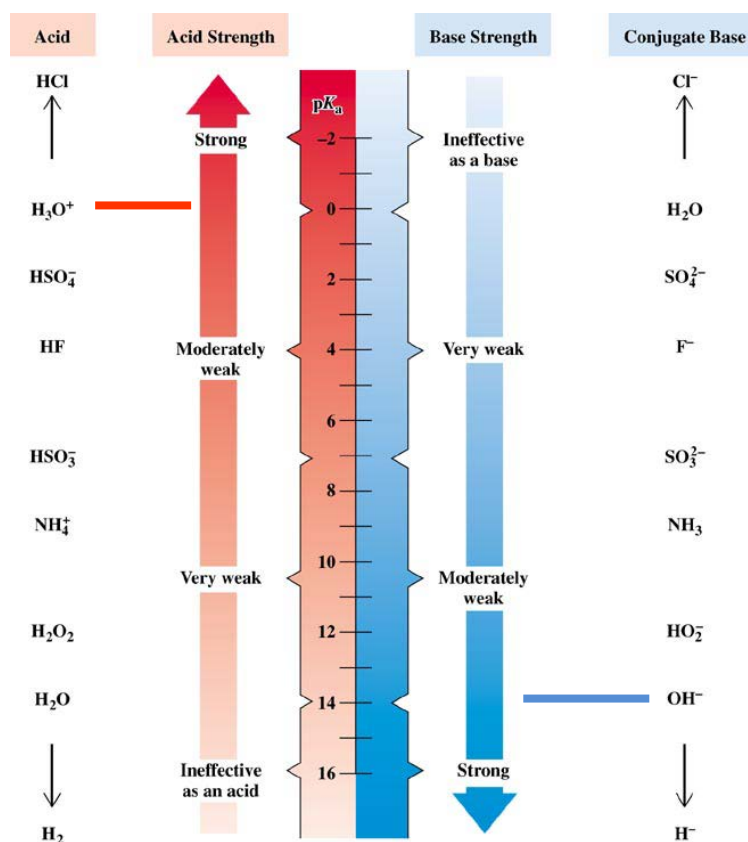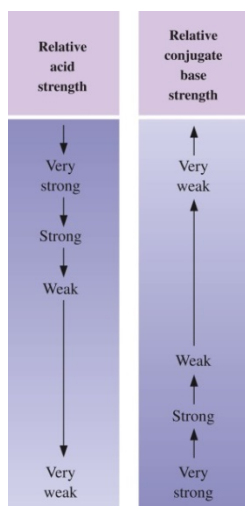
conjugate bases stronger than OH$^-$

Conjugate Acid-Base Pairs

the stronger the acid
the weaker is its conjugate base

the stronger the base the weaker
is its conjugate acid

$$K_a \times K_b = K_w$$

conjugate pair 1
conjugate pair 2

$HCl(aq)$ + $H_2O(\ell)$ $\rightleftharpoons$ $H_3O^+(aq)$ + $Cl^-(aq)$
$K > 1$

| stronger acid than H_3O^+ | stronger base than Cl^- | weaker acid than HCl | weaker base than H_2O |

conjugate pair 1
conjugate pair 2

$CH_3CO_2H(aq)$ + $H_2O(\ell)$ $\rightleftharpoons$ $H_3O^+(aq)$ + $CH_3CO_2^-(aq)$
$K < 1$

| weaker acid than H_3O^+ | weaker base than $CH_3CO_2^-$ | stronger acid than CH_3CO_2H | stronger base than H_2O |

EX 4. K_a for hydrosulfuric acid is 9.1×10^{-8} at 25°C.

a) What is its conjugate base?

b) What is the basicity constant (K_b) for its conjugate base?

EX 5. For the reaction

$$HNO_2(aq) + CH_3COO^-(aq) <=> NO_2^-(aq) + CH_3COOH(aq)$$

a) From the Brønsted-Lowry point of view, identify each acid and its conjugate base and each base and its conjugate acid.

b) If $K_a(HNO_2) = 4.6 \times 10^{-4}$ and $K_a(CH_3COOH) = 1.8 \times 10^{-5}$ what is K for the reaction?

7.3, 7.4 Water and the pH Scale

autoionization of water (at 25°C):

$$2 H_2O(l) <=> H_3O^+(aq) + OH^-(aq) \qquad K_w = [H_3O^+][OH^-] = 1.01 \times 10^{-14} =>$$

Temperature Dependence of K_w

Temperature (°C)	K_w
0	0.114×10^{-14}
10	0.292×10^{-14}
20	0.681×10^{-14}
25	1.01×10^{-14}
30	1.47×10^{-14}
40	2.92×10^{-14}
50	5.47×10^{-14}
60	9.61×10^{-14}

EX 6. $K_w = 2.4 \times 10^{-14}$ at body temperature (98.6°C = 37.0°C).

a) What is the hydrogen ion concentration?

b) What is the pH?

condition	concentrations	pH (**only** at 25°C)
acidic	$[H_3O^+] > [OH^-]$	pH < 7
neutral	$[H_3O^+] = [OH^-]$	pH = 7
basic	$[H_3O^+] < [OH^-]$	pH > 7

significant figures for logarithms:

3 significant digits   3 decimal places

$$\log 1.00 \times 10^{-3} = 3.000$$

some "p" functions

$pH = - \log_{10}[H_3O^+]$
$pOH = - \log_{10}[OH^-]$
$pK_w = - \log_{10}K_w$
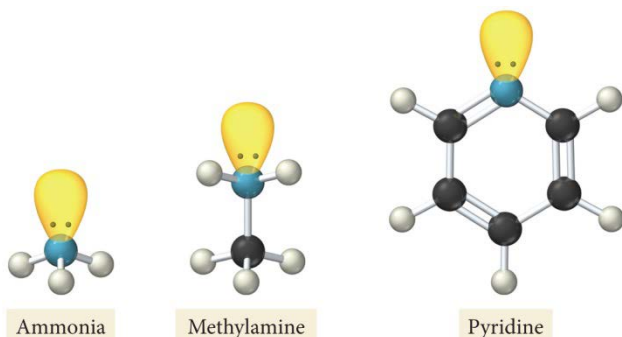$pK_a = - \log_{10}K_a$
$pK_b = - \log_{10}K_b$
$pK_{sp} = - \log_{10}K_{sp}$

in general

$$pX = - \log_{10}X$$

EX 7. Answer each of the following

a) $[H_3O^+] = 2.5 \times 10^{-14}$, pH = ?

b) pH = 9.3, $[H_3O^+]$ = ?

c) 0.40 moles of Ba(OH)$_2$ is dissolved in a liter of water, pOH?

d) pH = 9.3, $[OH^-]$ = ?

7.6 Base Strength

strong/weak electrolytes

soluble strong bases to know	
lithium hydroxide	LiOH
sodium hydroxide	NaOH
potassium hydroxide	KOH
rubidium hydroxide	RbOH
cesium hydroxide	CsOH
barium hydroxide	$Ba(OH)_2$

strong bases - all Group I and
Group II hydroxides except Be

Ammonia   Methylamine   Pyridine

base strength – (aside from Group I and II hydroxides) determined by extent of reaction of base with water to form $OH^-(aq)$, or extent of its ionization, as shown by the magnitude of its equilibrium constant, K_b – then for any base B:

$B:(aq)$	+	$H_2O(l)$	<=>	$OH^-(aq)$	+	$BH^+(aq)$
base						conjugate acid
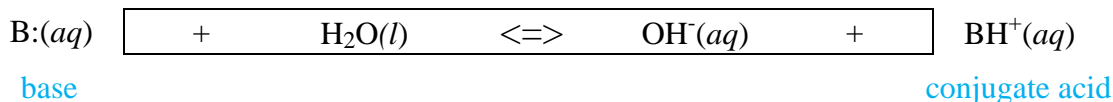
equilibrium constant, $K_b = \dfrac{[OH^-][BH^+]}{[B:]}$

Various Ways to Describe Base Strength

Property	Strong Base	Weak Base
K_b value	completely, either	K_b is small
	1) dissociates to	
Position of the dissociation equilibrium	give OH^- ions to the solution or	Far to the left
Equilibrium concentration of OH^- compared with original concentration of B:	2) reacts with water	$[OH^-] \ll [B:]_0$
	in either case:	
Strength of conjugate acid compared with that of water		BH^+ much stronger acid than water
	$[OH^-] = [B:]_0$	