CHAPTER 18 ACID-BASE EQUILIBRIA

Section 18.1: Acids and Bases in Water

Water (H_2O) – the most important molecule on earth. Even in pure water, there are small amounts of ions from the equilibrium below ("self-ionization of water" or "auto-ionization of water").

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

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

H_3O^+ (aq) = hydronium ion; often abbreviated as H^+ (aq)
OH^- (aq) = hydroxide ion
$[H_3O^+] = [OH^-]$ in pure water

Definitions of Acids and Bases

1) ACIDS: give $[H_3O^+] > [OH^-]$ in solution (vinegar, lemon juice)
2) BASES: give $[H_3O^+] < [OH^-]$ in solution (bicarb)

Historically, the first definitions of Acids and Bases were the "**Arrhenius Definitions**".

1) **ACID** = a substance with H in its formula, and which dissociates in water to give H_3O^+(aq) (= H^+(aq)) Generic acid = HA (*e.g.*, HCl, HNO_3, H_2SO_4, etc.)

2) **BASE** = a substance with OH in its formula, and dissociates to yield OH^-
Generic base = MOH (*e.g.*, NaOH, $Ca(OH)_2$, etc.)

Neutralization: the reaction between an acid and a base

$$H^+ (aq) + OH^- (aq) \rightarrow H_2O (l);$$

Strengths of Acids and Bases: (i.e., the amount of H^+ or OH^- produced per mole of substance dissolved)

STRONG ACIDS AND BASES DISSOCIATE COMPLETELY (100%) IN WATER - MUST KNOW THEM!!

Strong Acids: HCl, HBr, HI, $HClO_4$, HNO_3, H_2SO_4 - plus a few rare ones (e.g. H_2SeO_4)

Strong Bases: MOH and $M(OH)_2$, where M = Li^+, Na^+, K^+, Rb^+, Cs^+, Ca^{2+}, Sr^{2+}, Ba^{2+}

**** All other acids and bases are "weak" ****

Because strong acids and bases dissociate completely (i.e. ~100%), we do not consider them equilibria, (*i.e.,* $K_c \ggg 1$) and we write them as a one-directional reaction.

Strong Acid: $HA (g \text{ or } l) + H_2O (l) \rightarrow H_3O^+ (aq) + A^- (aq)$

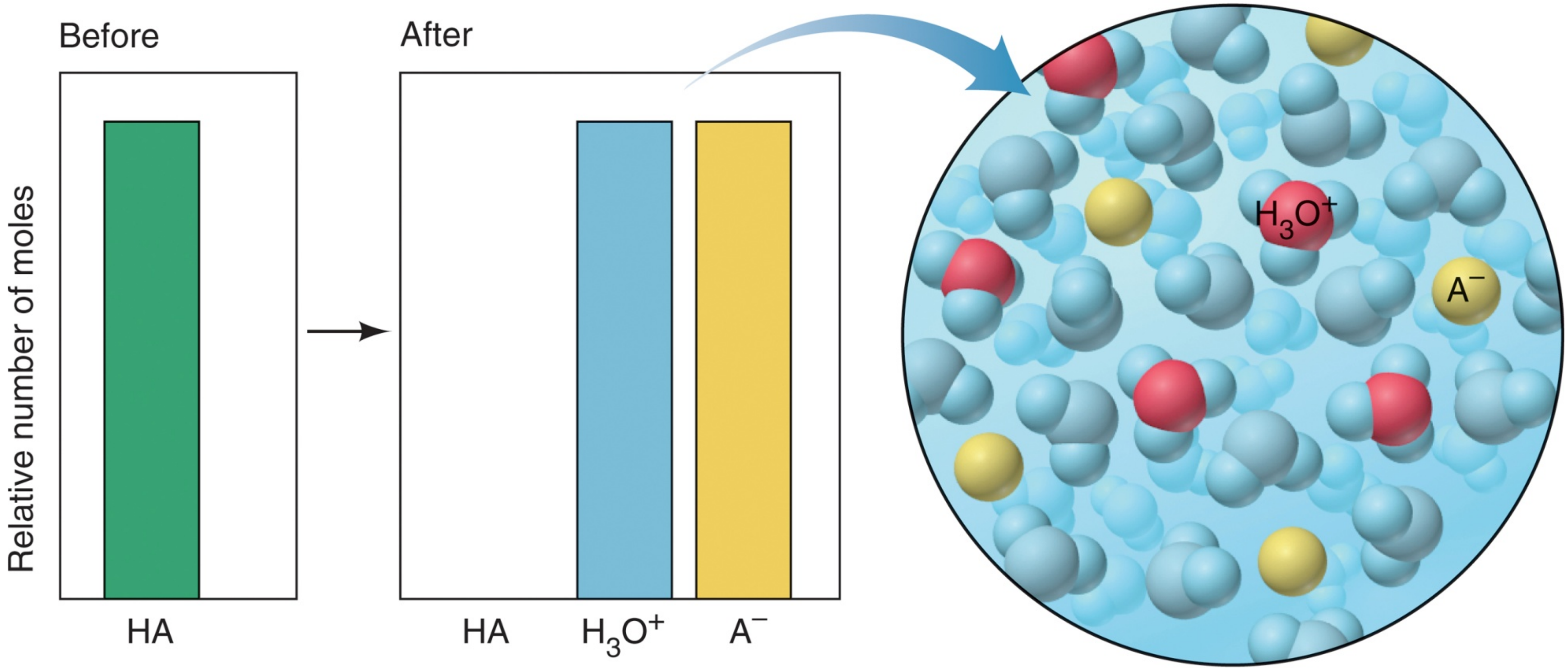
Strong Base: $MOH (s) + H_2O (l) \rightarrow M^+ (aq) + OH^- (aq)$

Weak Acids: dissociate only partially in solution; it is an equilibrium.

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

**** Amount of dissociation varies depending on the acid ****

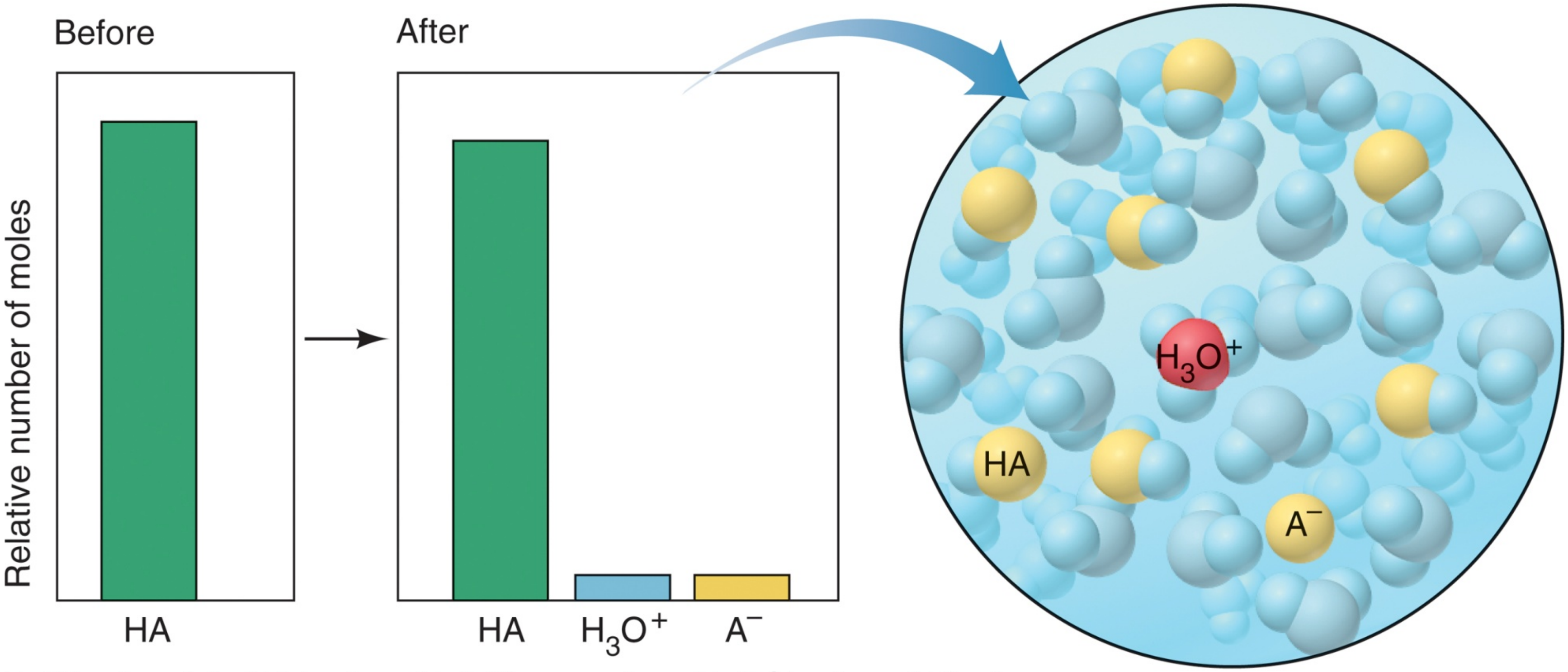
Figure 18.1A The extent of dissociation for strong acids.



Strong acid: HA(*g* or *l*) + H_2O(*l*) → H_3O^+(*aq*) + A^-(*aq*)

There are ~zero HA molecules in solution.

Figure 18.1B The extent of dissociation for weak acids.



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

** Most HA molecules are undissociated **

Figure 18.2 **Reaction of zinc with a strong acid (*left*) and a weak acid (*right*).**

1 *M* HCl(*aq*) **1 *M* CH_3COOH(*aq*)**

Zinc reacts rapidly with the strong acid, since $[H_3O^+]$ is much higher.

Acid Dissociation Constant (K_a)

= a way to measure "strength" of a weak acid.

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

Equilibrium constant $$K_c = \frac{[A^-\ (aq)][H_3O^-\ (aq)]}{[H_2O\ (l)][HA\ (aq)]}$$

$[H_2O] \gg [HA]$, so it changes negligibly when HA dissociates

$\therefore$ we put it with K_c and we have

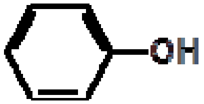
$$K_c\ [H_2O] = K_a = \frac{[H_3O^-][A^-]}{[HA]}$$ (omitting (aq) for convenience)

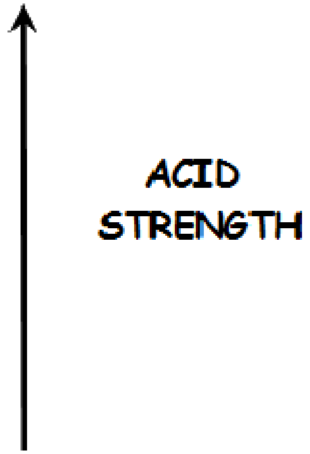
$$\therefore\ \boxed{K_a = \frac{[H_3O^-][A^-]}{[HA]}}$$

The bigger is K_a, the stronger the acid HA

$\therefore$ the bigger is K_a, the greater the % dissociation.

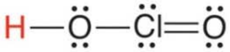
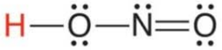
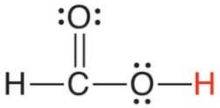
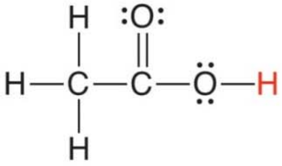
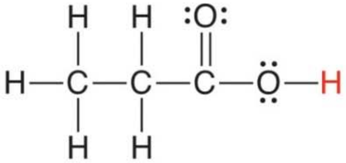
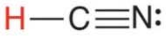
Table 18.2

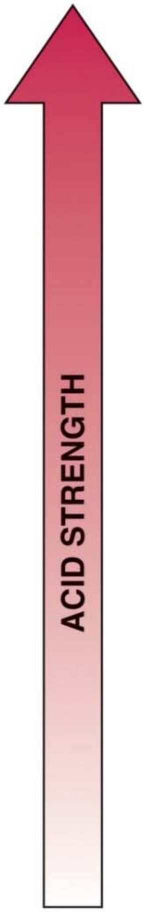
Acid HA	Name	K_a
HF	hydrofluoric acid	6.8×10^{-4}
PhCOOH	benzoic acid	6.3×10^{-5}
MeCOOH	acetic acid	1.8×10^{-5}
HCN	hydrocyanic acid	6.2×10^{-10}
PhOH 	phenol	1.0×10^{-10}



ACID STRENGTH

Table 18.2 K_a Values for some Monoprotic Acids at 25°C

Name (Formula)	**Lewis Structure***	**K_a**
Chlorous acid ($HClO_2$)		1.1×10^{-2}
Nitrous acid (HNO_2)		7.1×10^{-4}
Hydrofluoric acid (HF)		6.8×10^{-4}
Formic acid (HCOOH)		1.8×10^{-4}
Acetic acid (CH_3COOH)		1.8×10^{-5}
Propanoic acid (CH_3CH_2COOH)		1.3×10^{-5}
Hypochlorous acid (HClO)		2.9×10^{-8}
Hydrocyanic acid (HCN)		6.2×10^{-10}



* Red type indicates the ionizable proton; all atoms have zero formal charge.

Weak Bases: none are Arrhenius bases, because they do not have OH in formula.
Most have a N atom with a lone pair (e.g. $:NH_3$, $R_2HN:$, etc)
They react with H_2O to give OH^- – that's why they are bases!

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

Section 18.2. The pH Scale

Remember that even pure water contains H^+ and OH^- ions from self-ionization.

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

$$K_c = \frac{[H_3O^+][OH^-]}{[H_2O]^2} \qquad \therefore\ K_c\,[H_2O]^2 = [H_3O^+]\,[OH^-]$$

Putting $K_w = K_c\,[H_2O]^2$ gives $\boxed{K_w = [H_3O^+]\,[OH^-]}$

K_w = ion-product constant for water
$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$ (at 25 °C)

$\therefore$ in pure water, $[H_3O^+] = [OH^-] = 1.0 \times 10^{-7}$ M

The K_w equation tells us that the product $[H_3O^+][OH^-]$ is a constant (= 1.0×10^{-14} at 25 °C)

$\therefore$ if $[H_3O^+]$ increases, $[OH^-]$ decreases
if $[H_3O^+]$ decreases, $[OH^-]$ increases.

We can thus define "acidic" and "basic" in terms of $[H_3O^+]$ and $[OH^-]$.

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

Note: If you know $[H_3O^+]$, easy to calculate $[OH^-]$

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{[H_3O^+]}$$ (at 25 °C), and vice-versa

Question: What are $[H_3O^+]$ and $[OH^-]$ in 0.0012 M NaOH soln at 25 °C?

Answer: NaOH is a strong base $\therefore$ 100 % dissociated in water.

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

$\therefore$ 0.0012 M NaOH gives 0.0012 M OH^- (aq) $\therefore$ $[OH^-] = 0.0012$ M

Since $K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$ (at 25 °C)

$$\therefore [H_3O^+] = \frac{(1.0 \times 10^{-14})}{[OH^-]} = \frac{(1.0 \times 10^{-14})}{(0.0012)} = 8.3 \times 10^{-12} \text{ M}$$

The pH Scale

- is a more convenient way to describe how acidic or basic a solution is.

$$\boxed{pH = -\log_{10} [H_3O^+]}$$

In an acidic solution: $pH < 7.00$
In a neutral solution: $pH = 7.00$
In basic solution: $pH > 7.00$

Example 1: What is the pH of a $[H_3O^+] = 10^{-3}$ M solution?

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

** Note: the number of sig. figs. in the concentration = the number of digits after the decimal point in the logarithm **

Number of sig figs in the conc = number of digits after decimal point in the log

$[H_3O^+]$	pH
10^{-3}	3
1×10^{-3}	3.0
1.0×10^{-3}	3.00

e.g. $[H_3O^+] = 5.4 \times 10^{-4}$ M
pH = 3.27

Note: pH is a $\log_{10}$ scale ∴ difference of one pH unit means a factor of 10 difference
A solution with pH = 1.0 has ten times higher $[H_3O^+]$ than a solution with pH = 2.0.

Example 2: What is the pH of pure water at 25 °C?
In pure water, $[H_3O^+] = 1.0 \times 10^{-7}$ M ∴ pH = $-\log[H_3O^+] = -\log[1.0 \times 10^{-7}] =$ **7.00**

Note $[H_3O^+] = 10^{-pH}$ ∴ to go from pH to $[H_3O^+]$, **change sign, and antilog**

Other uses of the p-scale

(i) The pOH scale

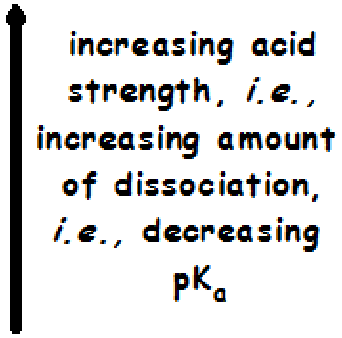
$pOH = -\log_{10} [OH^-]$

(ii) The pK scale

$pK = -\log_{10} K$

Particularly useful for acid dissociation constants (K_a) of weak acids (see Table 18.3)

acid	K_a	pK_a
HSO_4^-	1.02×10^{-2}	1.991
HNO_2	7.1×10^{-4}	3.15
CH_3COOH	1.8×10^{-5}	4.74
HBrO	2.3×10^{-9}	8.64
Phenol	1.0×10^{-10}	10.00



increasing acid strength, *i.e.*, increasing amount of dissociation, *i.e.*, decreasing pK_a

Figure 18.6 Methods for measuring the pH of an aqueous solution.

pH paper

pH meter

Relationship between pH, pOH and pK_w

Since $K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$ (at 25 °C)

taking logs: $-\log K_w = (-\log[H_3O^+] + (-\log[OH^-] = -\log (1.0 \times 10^{-14})$

$\therefore$ $\boxed{pK_w = pH + pOH = 14.00}$ (at 25 °C)

$\therefore$ if you know pH, can calculate pOH

$$pOH = 14.00 - pH$$

if you know pOH, can calculate pH

$$pH = 14.0 - pOH$$

See Fig. 18.5

Example. Calculate pH and pOH of a solution with $[H_3O^+] = 1.5 \times 10^{-4}$ M.

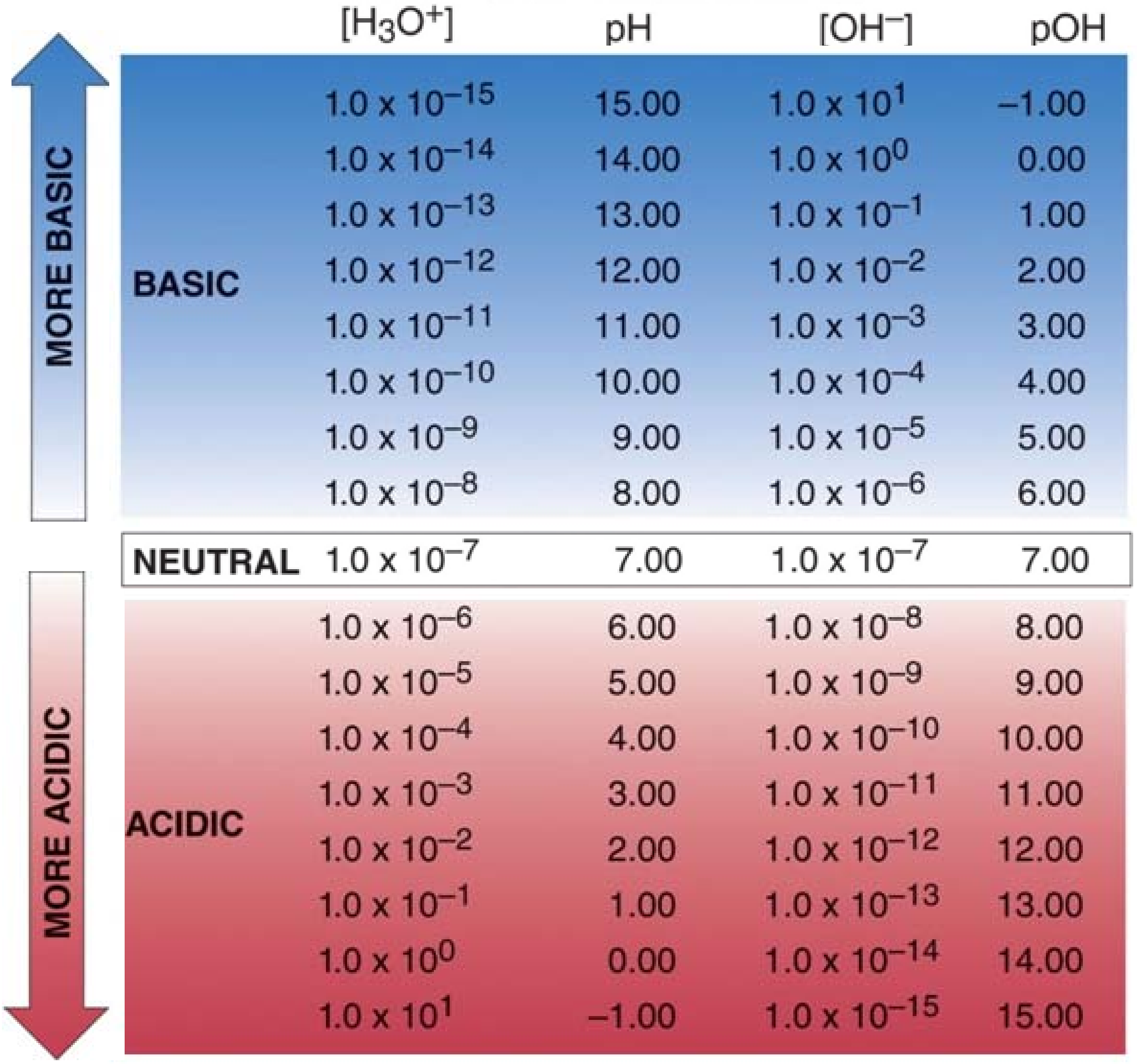
$pH = -\log[H_3O^+] = -\log (1.5 \times 10^{-4}) = \mathbf{3.82}$

$pOH = pK_w - pH = 14.00 - 3.82 = \mathbf{10.18}$

Remember:

$$\begin{tikzcd}
H_3O^+ \arrow[r, leftrightarrow, "K_w = {[H^+][OH^-]}"] \arrow[d, leftrightarrow, "pH = -\log{[H_3O^+]}"'] & OH^- \arrow[d, leftrightarrow, "pOH = -\log{[OH^-]}"] \\
pH \arrow[r, leftrightarrow, "pH + pOH = 14.00"'] & pOH
\end{tikzcd}$$

Figure 18.5 The relations among [H_3O^+], pH, [OH^-], and pOH.



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

Section 18.3 The Brønsted-Lowry Definition

Arrhenius definition of acids and bases doesn't cover all possibilities, *e.g.,* some bases do not contain OH in their formula. **Brønsted-Lowry definition** is much better

Acid = an H^+ donor. Must contain H^+ in its formula (all Brønsted-Lowry acids are also Arrhenius acids).

Base = an H^+ acceptor. Must contain a lone-pair capable of binding an H^+ (*e.g.,* NH_3, F^-, OH^-, etc.). Brønsted-Lowry bases are not Arrhenius bases, but Arrhenius bases contain the Brønsted-Lowry base, OH^-.

This gives acid/base reactions: something can only act as a Brønsted-Lowry acid if there is a Brønsted-Lowry base to pick up H^+.

**** The acid is the H^+ donor; the base is the H^+ acceptor ****

e.g.

$HCl\ (g) + H_2O\ (l) \rightarrow Cl^-\ (aq) + H_3O^+\ (aq)$
(acid) (base)

$NH_3\ (g) + H_2O\ (l) \rightarrow NH_4^+\ (aq) + OH^-\ (aq)$
(base) (acid)

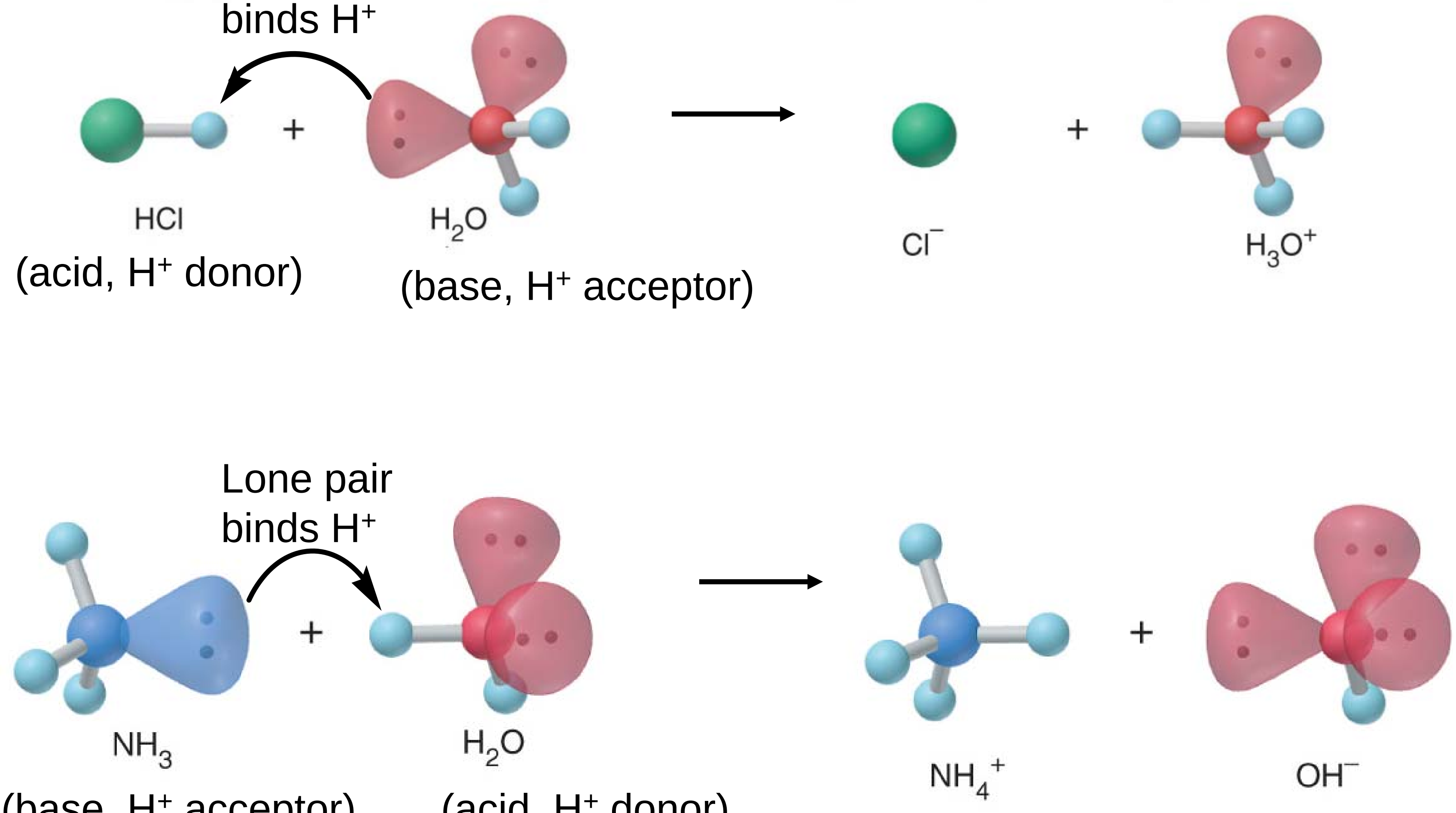
$HCl\ (g) + NH_3\ (g) \rightarrow NH_4Cl\ (s)$
(acid) (base)

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

$[Fe(H_2O)_6]^{3+}\ (aq) + H_2O\ (l) \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+}\ (aq) + H_3O^+\ (aq)$
(acid) (base)

Note: H_2O is **amphiprotic** – it can be a Bronsted acid or base (Fig. 18.7)

Figure 18.7 Dissolving of an acid or base in water as a Brønsted-Lowry acid-base reaction.



Lone pair binds H^+

(acid, H^+ donor)

(base, H^+ acceptor)

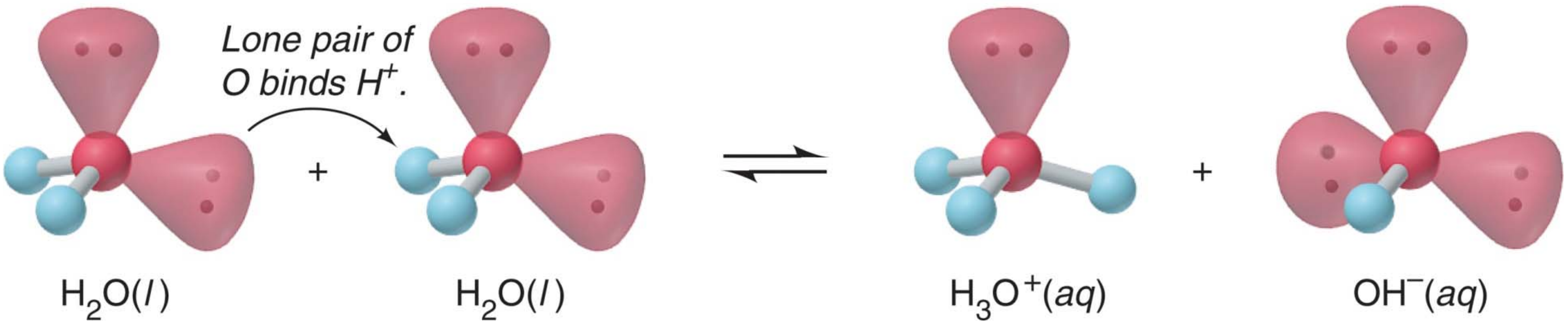
Lone pair binds H^+

(base, H^+ acceptor)

(acid, H^+ donor)

H_2O can even be both and acid and a base in the same reaction!

Consider the self-ionization of water



base

acid

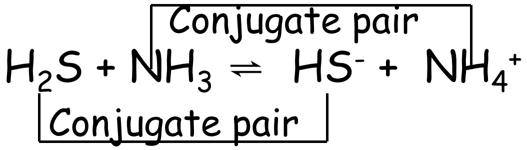
Conjugate Acid/Base Pairs

The B-L definition introduces the idea of conjugate acids and bases. Consider NH_3/NH_4^+.

$$\underset{\text{(acid)}}{H_2S} \quad + \quad \underset{\text{(base)}}{NH_3} \quad \rightleftharpoons \quad \underset{\text{(base)}}{HS^-} \quad + \quad \underset{\text{(acid)}}{NH_4^+}$$

Forward rxn: NH_3 is the base/H_2S is the acid.
Reverse rxn: NH_4^+ is the acid/HS^- is the base.

∴ we say NH_4^+/NH_3 are a conjugate acid/base pair. Also H_2S/HS^-.



Conjugate pair

$H_2S + NH_3 \rightleftharpoons HS^- + NH_4^+$

Conjugate pair

See Table 18.4

**** The acid has <u>one</u> extra H^+ and one unit greater positive charge (or one less negative charge) ****

Language:

" NH_4^+ is the conjugate acid of NH_3 "   " NH_3 is the conjugate base of NH_4^+ "

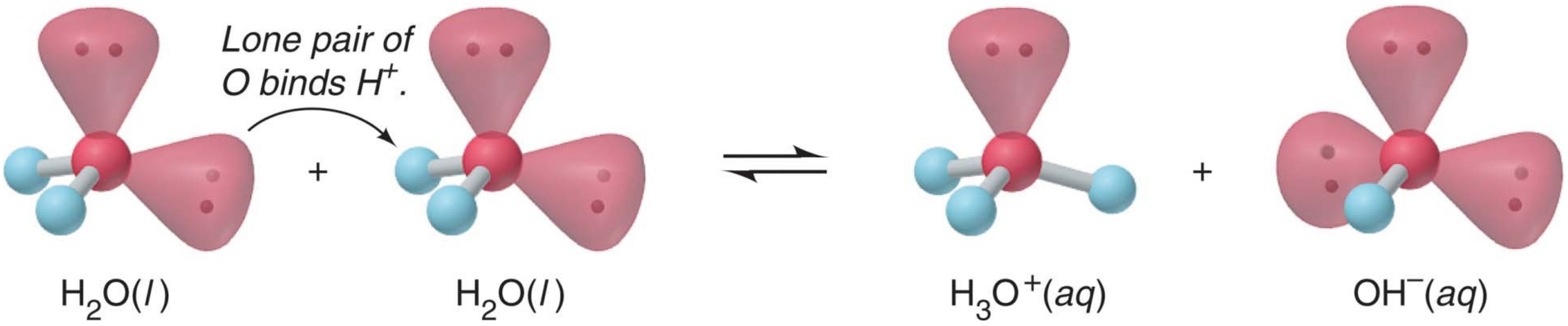
" HCl is the conjugate acid of Cl^-"   " Cl^- is the conjugate base of HCl "

" MeCOOH is the conjugate acid of $MeCOO^-$ "
(acetic acid)   (acetate ion)

"$MeCOO^-$ is the conjugate base of MeCOOH"

H_2O can even be both and acid <u>and</u> a base in the <u>same</u> reaction!

Consider the self-ionization of water



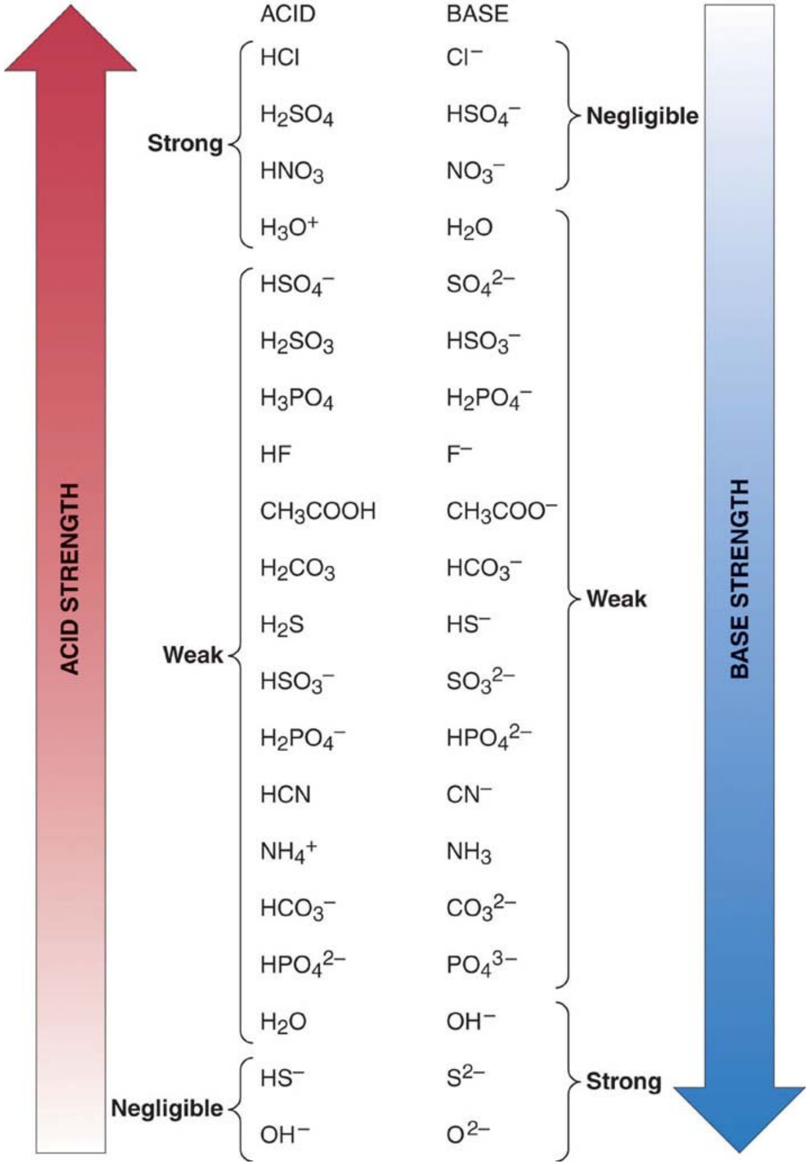
base

acid

conjugate acid

conjugate base

Figure 18.8 Strengths of conjugate acid-base pairs.



	ACID	BASE	
Strong	HCl	Cl^-	Negligible
	H_2SO_4	HSO_4^-	
	HNO_3	NO_3^-	
	H_3O^+	H_2O	Weak
Weak	HSO_4^-	SO_4^{2-}	
	H_2SO_3	HSO_3^-	
	H_3PO_4	$H_2PO_4^-$	
	HF	F^-	
	CH_3COOH	CH_3COO^-	
	H_2CO_3	HCO_3^-	
	H_2S	HS^-	
	HSO_3^-	SO_3^{2-}	
	$H_2PO_4^-$	HPO_4^{2-}	
	HCN	CN^-	
	NH_4^+	NH_3	
	HCO_3^-	CO_3^{2-}	
	HPO_4^{2-}	PO_4^{3-}	
	H_2O	OH^-	Strong
Negligible	HS^-	S^{2-}	
	OH^-	O^{2-}	

**** The stronger the acid is, the weaker its conjugate base ****

When an acid reacts with a base that is farther down the list, the reaction proceeds to the ***right*** ($K_c > 1$).

Prediction of Direction of Reactions:

Think of the reaction as a competition between the bases for the H^+ - the stronger base will win!!

∴stronger acid/base pair → weaker acid/base pair is the direction the reaction will favor

FIG. 18.8

$$HNO_3 + H_2O \xrightarrow{K_c >>> 1} NO_3^- + H_3O^+$$

(stronger acid) (stronger base) (weaker base) (weaker acid)

$$HCN + F^- \overset{K_c < 1}{\rightleftharpoons} CN^- + HF$$

(weaker acid) (weaker base) (stronger base) (stronger acid)

$$H_2SO_3 + PO_4^{3-} \overset{K_c > 1}{\rightleftharpoons} HSO_3^- + HPO_4^{2-}$$

(stronger acid) (stronger base) (weaker base) (weaker acid)

Note: (i) the acid with the bigger K_a (lower pK_a) is the stronger acid.
(ii) the stronger is the acid, the weaker is its conjugate base

Section 18.4. Problems Involving Weak Acid Equilibria

Two types: (a) given conc's, find K_a ; (b) given K_a, find conc's.

Method: Write balanced equation and set up reaction table - let x be the unknown conc. Solve. Use quadratic equation if necessary.

Remember: If we are told the pH, we will know $[H^+]$ (i.e. $[H_3O^+]$)

	HA (aq)	$\rightleftharpoons$	H^+ (aq)	+	A^- (aq)
[Initial]	1.0 M		0		0
[Change]	-x		+x		+x
[Equil]	(1.0–x)		x		x

** Ignore H^+ from self-ionization of water unless [HA] is very small **

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{x^2}{(1.0 - x)}$$

Given x (e.g. from pH), can calculate K_a
Given K_a, can calculate x, and then pH

Example 1: K_a for HNO_2 is 7.1 x 10^{-4}. What are $[H_3O^+]$, $[NO_2^-]$, and $[OH^-]$ in 0.50 M HNO_2? What is the pH?

	HNO_2 (aq)	$\rightleftharpoons$	H^+ (aq)	+	NO_2^- (aq)
[Initial]	0.50 M		0		0
Change	-x		+x		+x
[Equil]	(0.50 –x)		x		x

$$K_a = 7.1x10^{-4} = \frac{x^2}{0.50 - x} \approx \frac{x^2}{0.50}$$

(Assume x << 0.50)

~3.8% of 0.50
∴ good assumption)

∴ $x^2 = (0.50)(7.1 \times 10^{-4}) = 3.55 \times 10^{-4}$ ∴ $x = 1.88 \times 10^{-2} = 1.9 \times 10^{-2}$ M (sig. figs!)

∴ $[H_3O^+] = [NO_2^-] = 1.9 \times 10^{-2}$ M

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0x10^{-14}}{1.9x10^{-2}} = 5.3x10^{-13} M$$

∴ pH = -log(1.9 x 10^{-2}) = **1.72**

Example 2: The pH of a 0.010 M solution of formic acid is 2.92. What are K_a and percent ionization?

	$HCOOH$ (aq)	$\rightleftharpoons$	H^+ (aq)	+	$HCOO^-$ (aq)
[Initial]	0.010 M		0		0
[Change]	-x		+x		+x
[Equil]	(0.010-x)		x		x

$$K_a = \frac{x^2}{(0.010 - x)}$$

pH = -log [H^+] = -log (x) = 2.92 x = 0.00120

$$K_a = \frac{(0.00120)^2}{(0.010 - 0.00120)} = \frac{(0.00120)^2}{0.0088} = 1.636\text{x}10^{-4} = \boxed{1.6 \times 10^{-4}}$$

$$\text{ionization of an acid} = \left(\frac{[HA]_{diss}}{[HA]_{init}}\right) \times 100\% = \left(\frac{[H^+]}{[HA]_{init}}\right) \times 100\%$$

Note: $[HA]_{diss} = x = [H^+]$

$$= \frac{0.0012}{0.010} \times 100\% = \mathbf{12\%}$$

NOTE: % ionization increases with decreasing $[HA]_{init}$. *General Rule*: If % ionization is > 5%, must solve quadratic equation for x if calculating conc's to 2 sig. figs. If % ionization < 5 %, can assume [HA]-x ≈ [HA]. This applies to problems like the first one above, where K_a is given and we have to calculate [x].

Remember: if $[HA]_{init}/K_a > 400$, approximation is valid
if $[HA]_{init}/K_a < 400$, use the quadratic equation