Acid - Base Equilibria 1

Reading: Ch 15 sections 1 – 7	Homework: Chapter 15: 33, 35, 39, 45, 47, 49*, 51, 53, 55, 57, 79*, 81

* = 'important' homework question

Background and Discussion: What is an acid? What is a base? Give some common examples.

There are three models used to describe acid and base behavior: *Arrhenius, Brønsted – Lowery, and Lewis*

Note: Lewis Acids and Bases: will be discussed later in the course

Arrhenius Acids and Bases:

Arrhenius Acid: "*A substance when dissolved in water increases the* $[H^+]$*"* - this is a generic definition, true for all three models

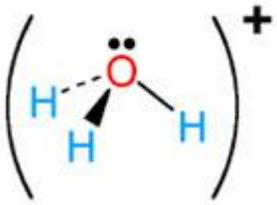
Example:

Arrhenius Base:

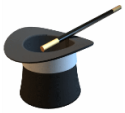
Example:

Brønsted – Lowery Acids and Bases: - ***the proton transfer model***

'Naked' H^+ (aq) ions do not really exist (even though we often write them in chemical equations). H^+ ions 'piggyback' on H_2O molecules – the resulting H_3O^+ (aq) (*hydronium*) ion is what is actually responsible for acidic behavior



Molecular representation of the hydronium ion



Even though we write H^+ (aq) in chemical equations, it is always assumed that this species is actually H_3O^+ (aq)

Aside: Can a completely 'dry' acid cause a chemical burn (like HCl(g)) or just taste acidic (like vinegar)?
Hint: think about sour candies – what is the 'sharp' tasting powdered coating made of?

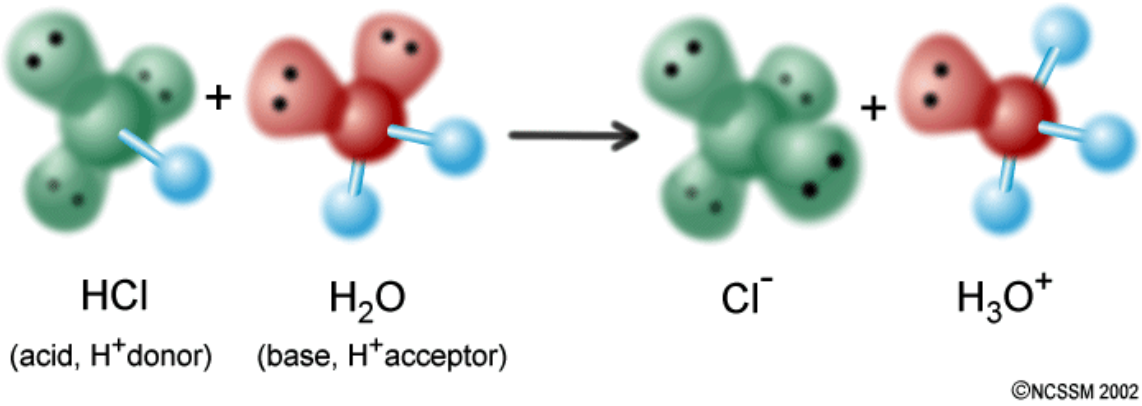
The Brønsted – Lowery Proton Transfer model

Recall: In the Brønsted – Lowery model:

B-L Acids are identified as substances that transfer proton(s) to other substances

B-L Bases are identified as substances that accept proton(s) from other substances

Example: HCl (aq) as a Brønsted – Lowery acid



Task: Identify the B-L acids and B-L bases in the following reactions:

$NH_4^+ (aq) + CN^- (aq) \rightarrow HCN (aq) + NH_3 (aq)$

$HSO_4^- (aq) + HCO_3^- (aq) \rightarrow SO_4^{2-} (aq) + H_2CO_3 (aq)$

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

Conjugate Acid – Base Pairs

In an acid base equilibrium, the reacting acid most protonate (by definition) a base. **The (now) de-protonated acid is now known as a *conjugate base*** and appears on the products side of the equation.

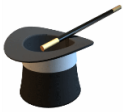
Similarly, **the reactant base that accepts proton(s) becomes a *conjugate acid*** on the reactants side of the equation.

Generic Example:

HX (aq)	+	H_2O (l)	⇔	X^- (aq)	+	H_3O^+ (aq)
Acid		Base		Conjugate base		Conjugate acid

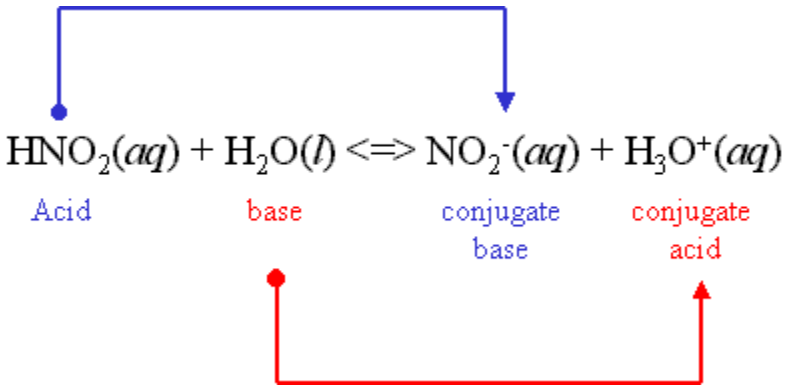
Forward reaction: HX (aq) and X^- (aq) are an acid / conjugate base pair

H_2O (l) and H_3O^+ (aq) are a base / conjugate acid pair



Conjugate acids and bases are so named because they act as acids and bases, respectively, *for the reverse reaction*

Example:



Task: Identify the acid / conjugate base and base / conjugate acid pair for above REVERSE reaction

Workshop: Complete the following assignments:

1. Identify acid / conjugate base and base / conjugate acid pairs for the following forward reactions:

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

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

2. What are the conjugate bases of:

   $H_2PO_4^-$

   H_2S

   H_2SO_3

   HCO_3^-

3. What are the conjugate acids of:

   $H_2PO_4^-$

   SO_4^{2-}

   CN^-

   HCO_3^-

Amphoteric Behavior

Question: Did you notice anything 'interesting' with regarding the behavior of the poly-protic acids in the previous examples?

Observation:

Answer: Dihydrogen phosphate is *amphoteric*:

Amphoteric: "capable as behaving as *either* an acid *or* a base"

Tasks:

a. Write and equation for the reaction of $H_2PO_4^-$ with water in which it acts as an acid

b. Write and equation for the reaction of $H_2PO_4^-$ with water in which it acts as a base

c. Write a single equilibrium equation that represents what happens when dihydrogen phosphate is dissolved in water

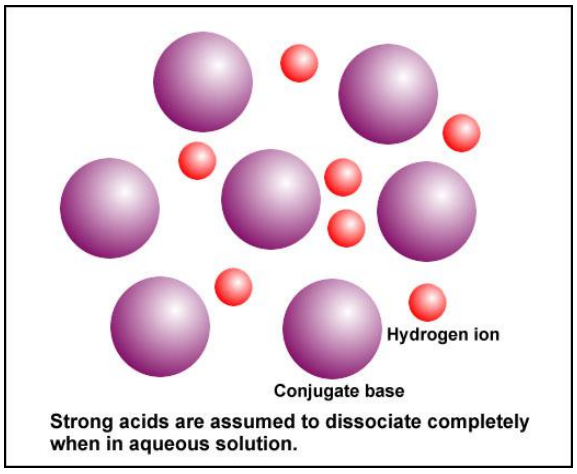
The Relative Strengths of Acids and Bases

Back to the fish ‘n chips: Why can 0.1 M acetic acid (vinegar) be sprinkled on fish ‘n chips, while it is *unadvised* to sprinkle 0.1 M HCl on this Scottish staple?

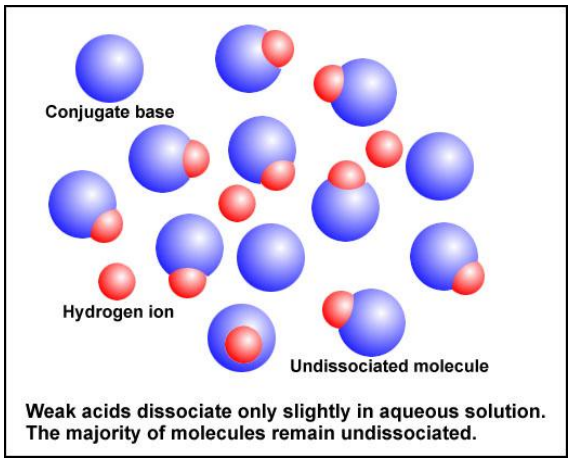
Strong (mineral) acids, such as HCl, *dissociate completely* in water:

Weak (organic) acids undergo *partial dissociation* in water (much more on this later):

Microscopic View



HCl (aq) – 100% dissociation



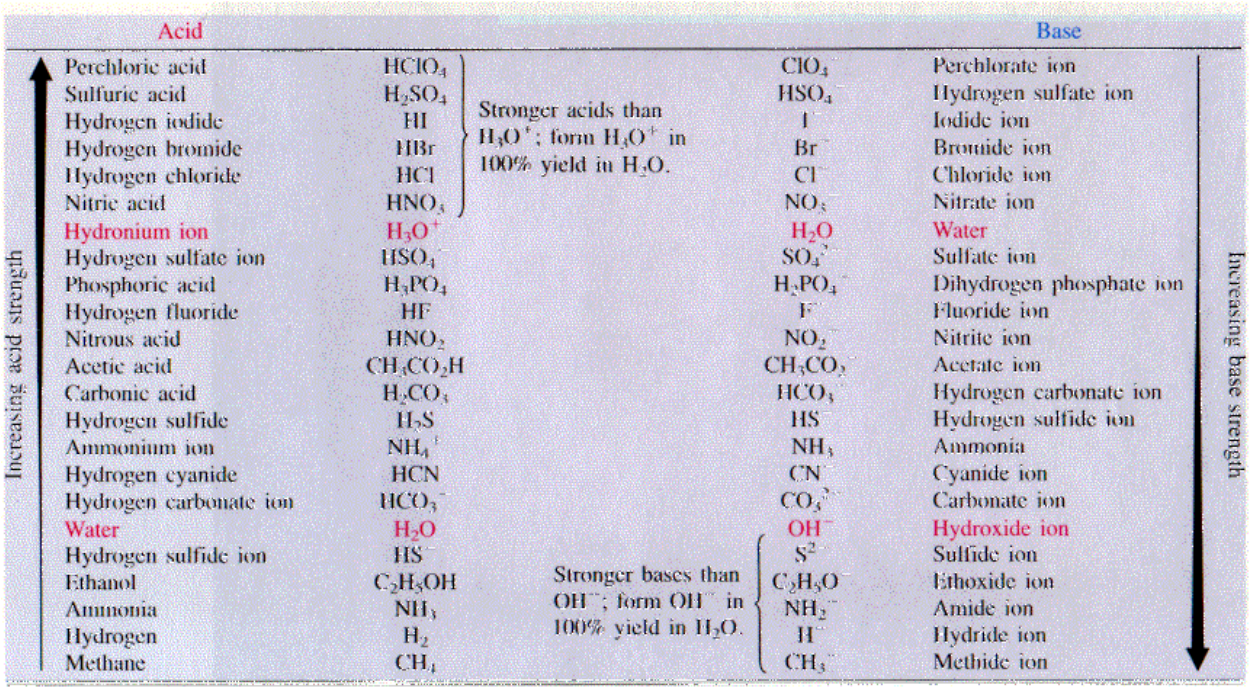
HA (weak acid) ~ 10% dissociation

Observations from the slide – *Conjugate Acid and Base Pairs*

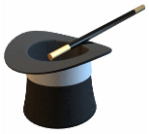
1.

2.

3.



Task: Use the slide/handout to predict if the following equilibria lie to the left or to the right:

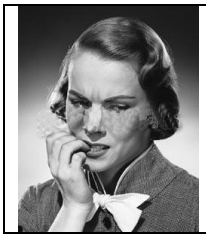


Recall that protonation favors transfer from stronger acid (or weaker base) to stronger base (or weaker acid)

1. $PO_4^{3-} + H_2O\ (l) \Leftrightarrow HPO_4^{2-} + {}^{-}OH\ (aq)$

2. $NH_4^{+}\ (aq) + OH^{-}\ (aq) \Leftrightarrow NH_3\ (aq) + H_2O\ (l)$

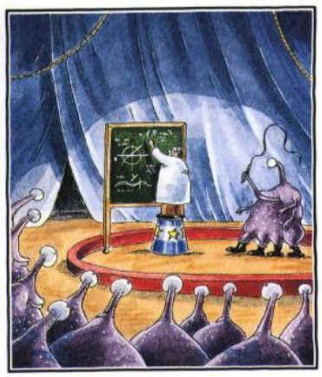
The Autoionization of Water



Water is 'special' – it dissociates to simultaneously give both H_3O^+ (aq) and ^-OH (aq) ions (*autoionization*):

$2\ H_2O\ (l) \Leftrightarrow H_3O^+\ (aq) + {}^-OH\ (aq)$

Task: Write an equilibrium (K) expression for the autoionization of water



Abducted by an alien circus company, Professor Doyle is forced to write calculus equations in center ring.

Derivation of K_w and Other Useful Math

The value of K_w is constant for **ANY** aqueous solution, regardless of how much acid or base is added from external sources. I.E., for any aqueous solution:

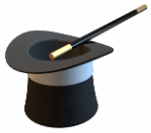
$K_w = 1.0 \times 10^{-14} = [H^+][^-OH]$ @ 25^oC

Applications of K_w - pH, pOH and pK_w

Discussion Questions:

1. If $1.0 \times 10^{-14} = [H^+][^-OH]$, what is the concentration of both H^+ (aq) and OH^- (aq) in *any* neutral solution. Hint: What must always true in terms of the concentrations of $[H^+]$ and $[^-OH]$ for any neutral solution?

2. What is pH, what is it a measure of? What is the relationship between pH and $[H^+]$ for a neutral solution?



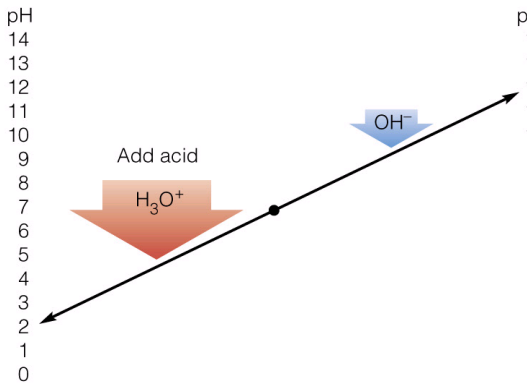
p* is simply a mathematical function that means: *"take the $-\log_{10}$ of the quantity of interest (such as $[H^+]$)"

Further expressions:

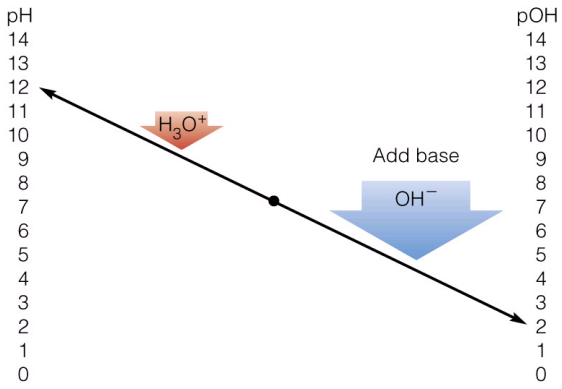
pOH =

pK_w =

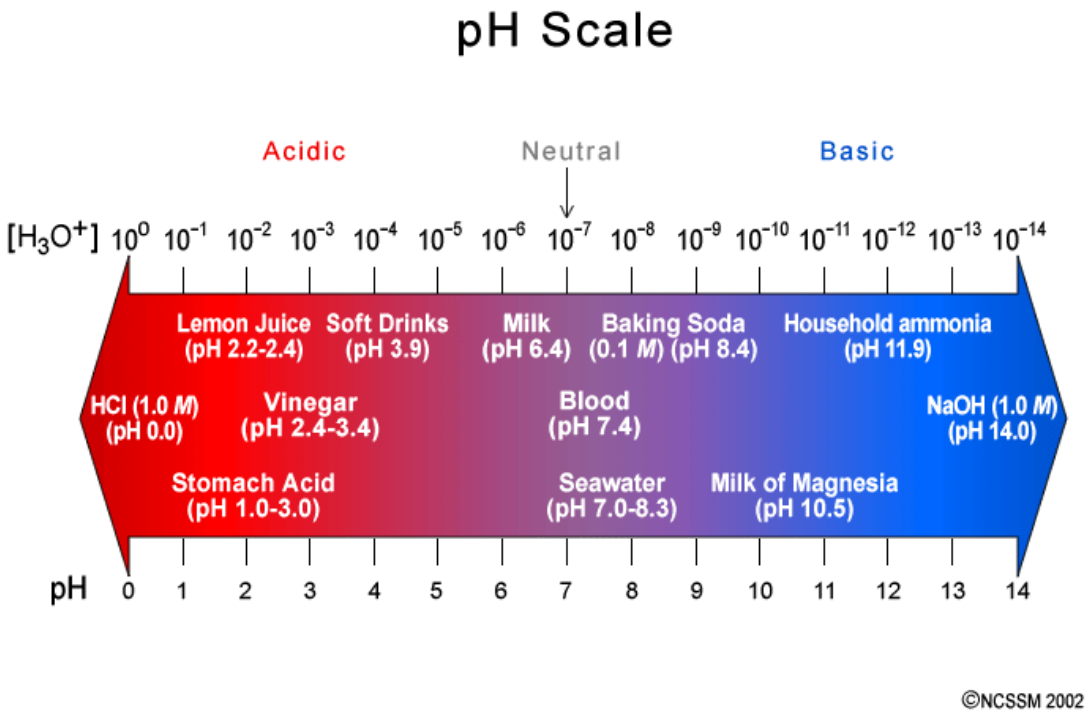
There is a *synergic* relationship between pH and pOH (or $[H^+]$ and $[^-OH]$) for any solution. I.E., as one rises ↑, one falls ↓:



(a) When excess acid is added, pH decreases, and pOH increases.



(b) When excess base is added, pH increases, and pOH decreases.



See the additional slide also

Questions: Determine the pH and pOH of the following strong acid and strong base solutions (assume 100% dissociation in each case):

0.055 M HCl (aq)

0.008 M NaOH (aq)

0.055 M H_2SO_4 (aq)

0.008 M $Ca(OH)_2$ (aq)

Workshop: Work in small groups to solve the following problems:

Calculate pH, pOH and [$^{-}$OH] for each of the following solutions. State if each solution is acidic, basic or neutral:

1. $[H^{+}] = 0.0041$ M

2. $[H^{+}] = 3.5 \times 10^{-9}$ M

3. A solution where $[H^{+}]$ is 10 times greater than [$^{-}$OH]

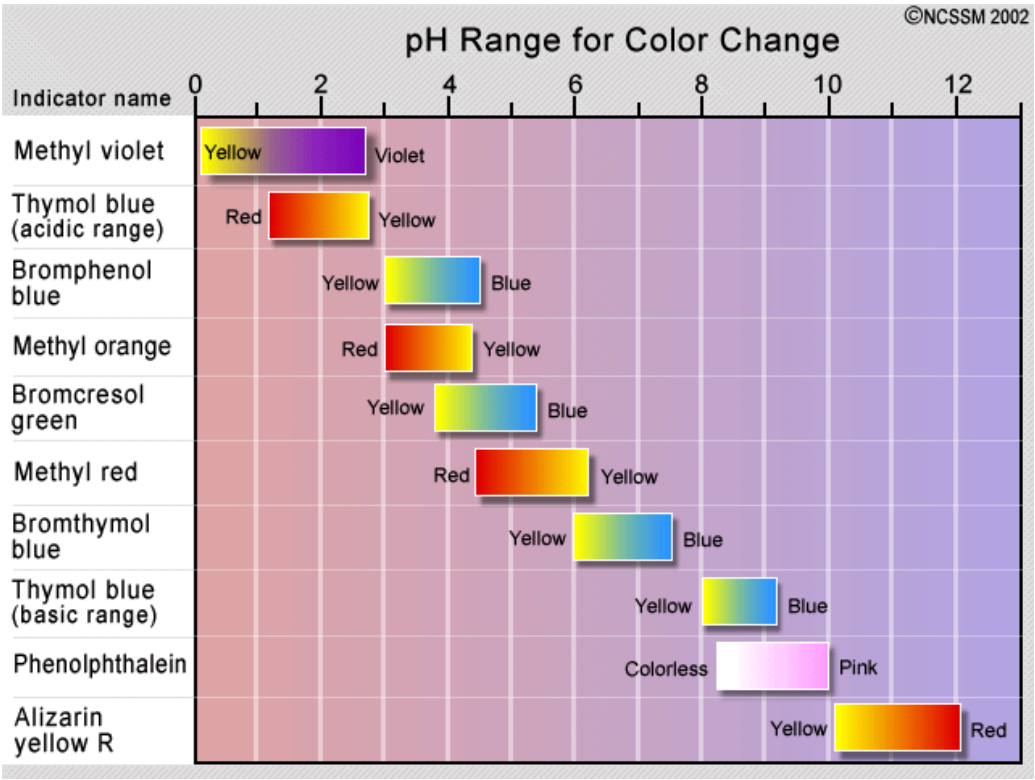
4. If you finish the above, try some homework problems

Acid – Base Indicators

Recall your Lab: Acid base indicators are simply chemicals that undergo a color change when exposed to a specific [H^+] or [^-OH].

Thus, acid-base indicators work over a specific pH range. Indicators are selected based on their observed colors over specific / desired pH ranges

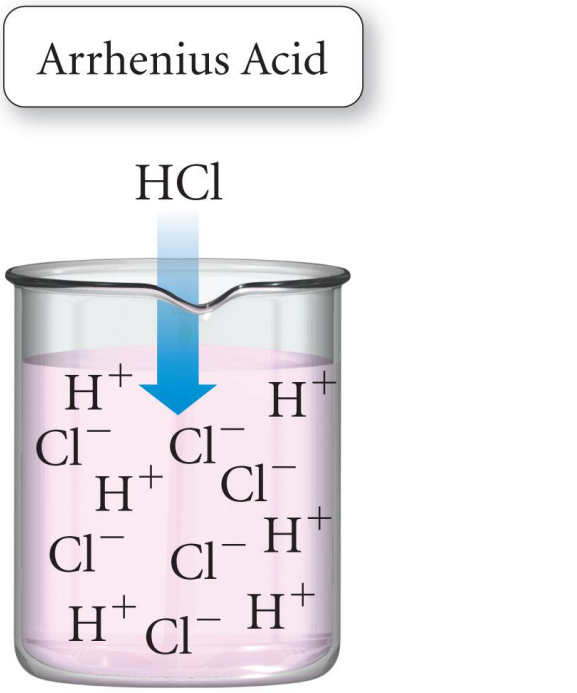
Table of common Indicators



Questions: Which indicator would be best for detecting a titration endpoint that occurs at pH 4.0? What color change would be observed if the acidic sample was titrated with NaOH (aq)?

Why is indicator choice less important for a strong acid / strong base titration??

Appendix



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

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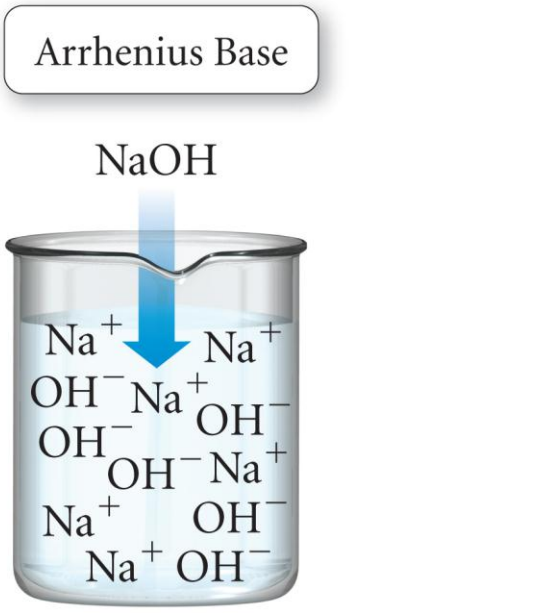

$$NaOH(aq) \longrightarrow Na^+(aq) + OH^-(aq)$$

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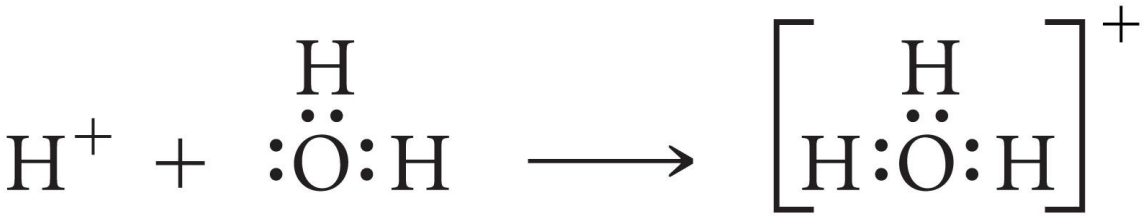

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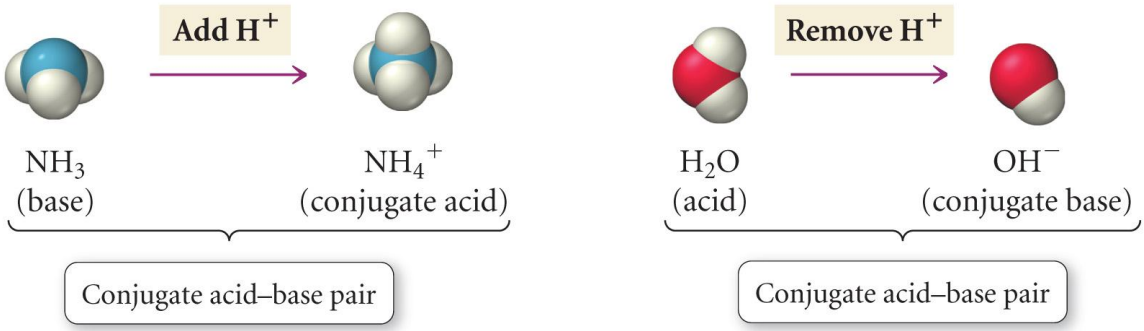

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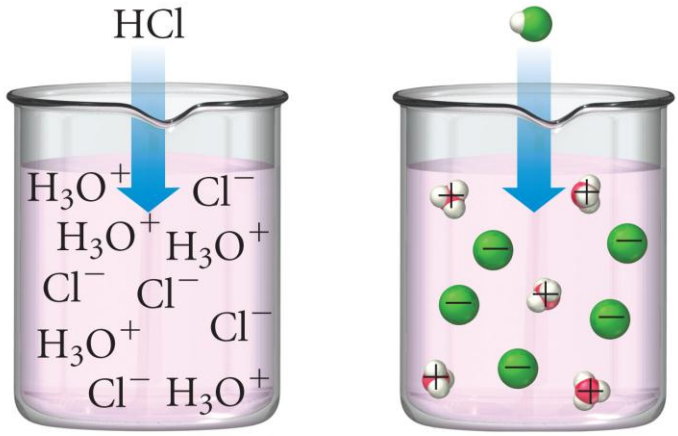
A Strong Acid

When HCl dissolves in water, it ionizes completely.



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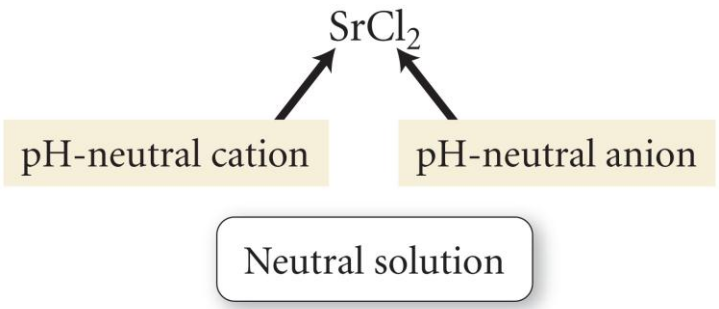

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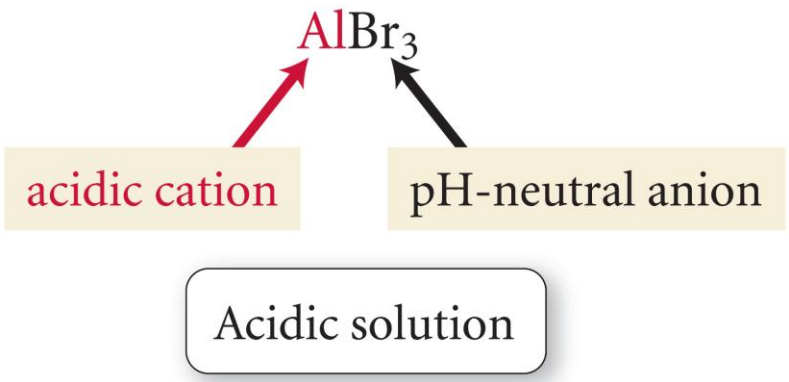

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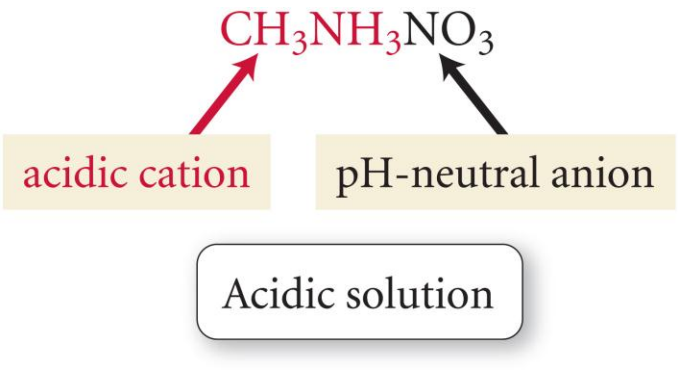

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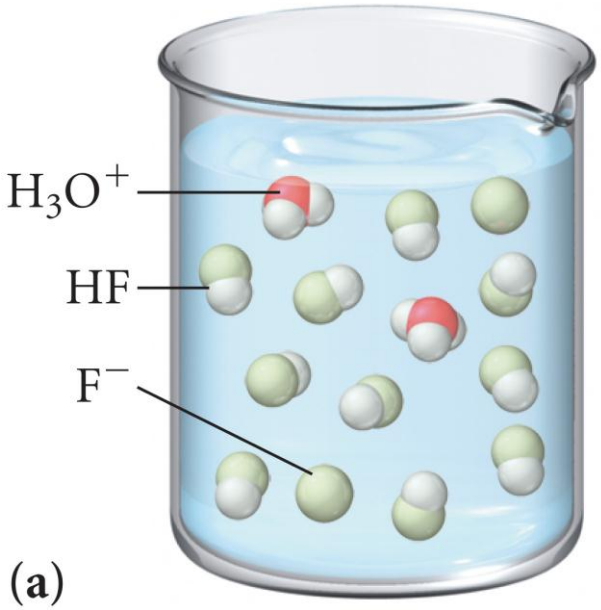

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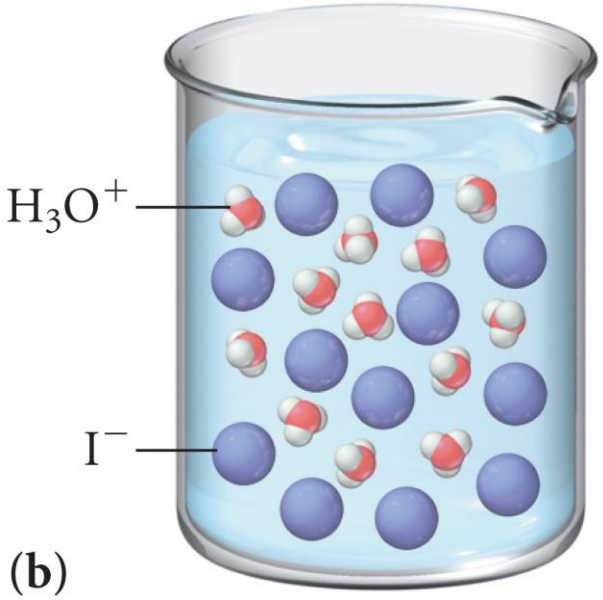

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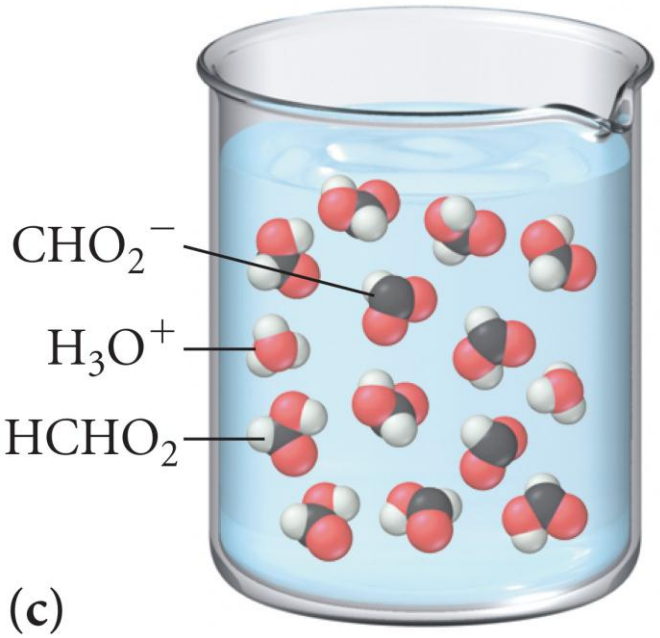

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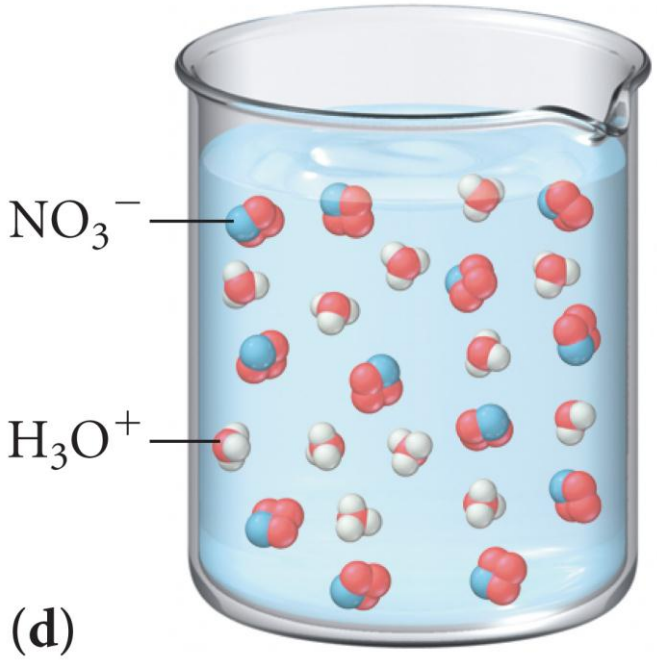

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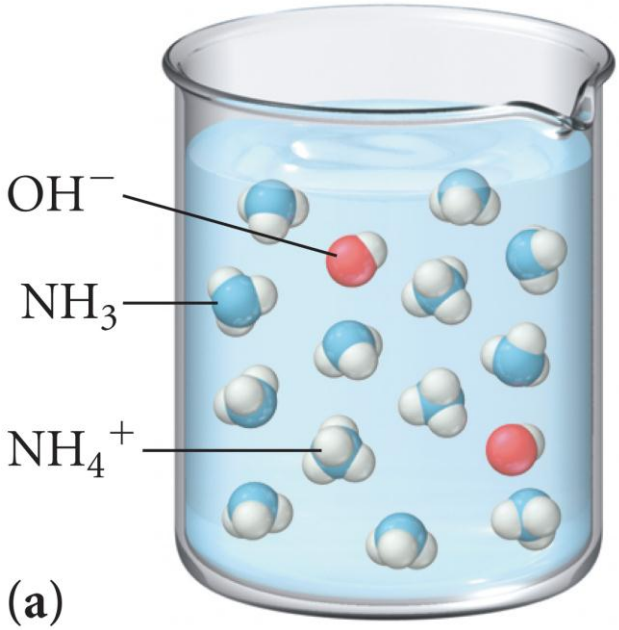

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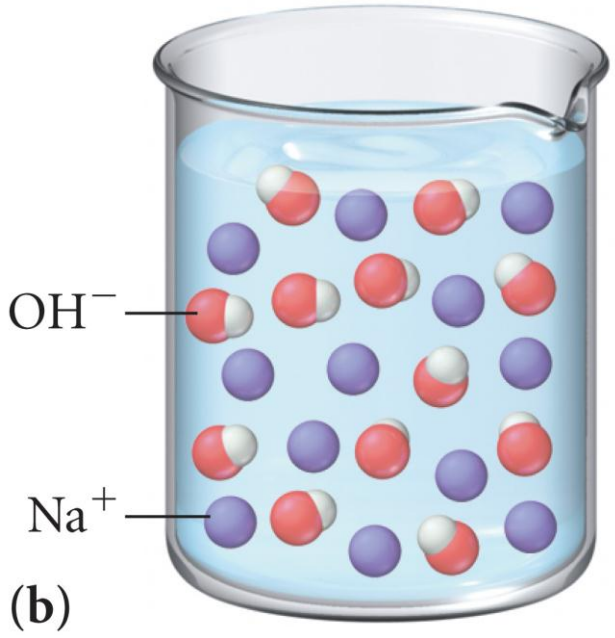

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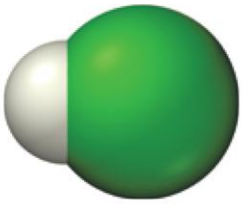
HCl



Hydrochloric acid

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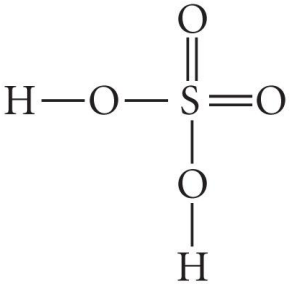
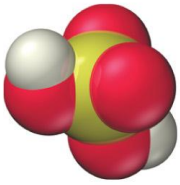
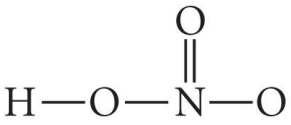
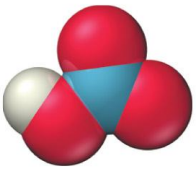




H_2SO_4

Sulfuric Acid





HNO_3

Nitric Acid

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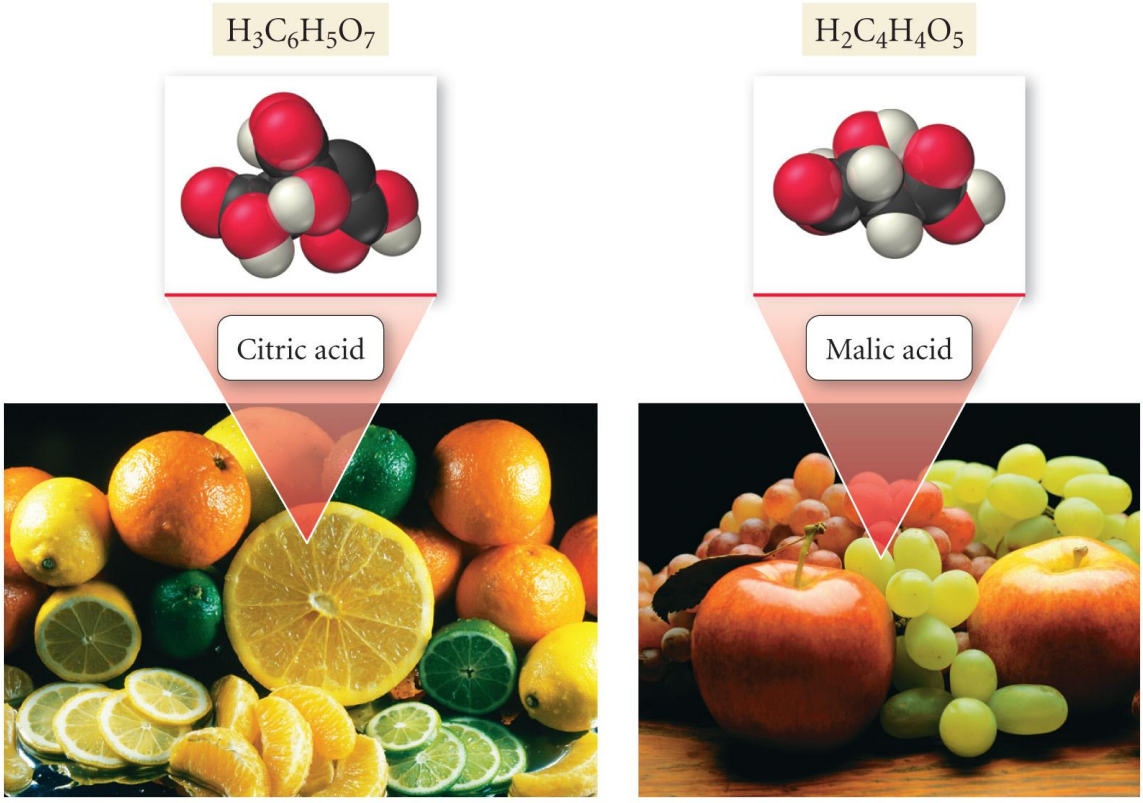

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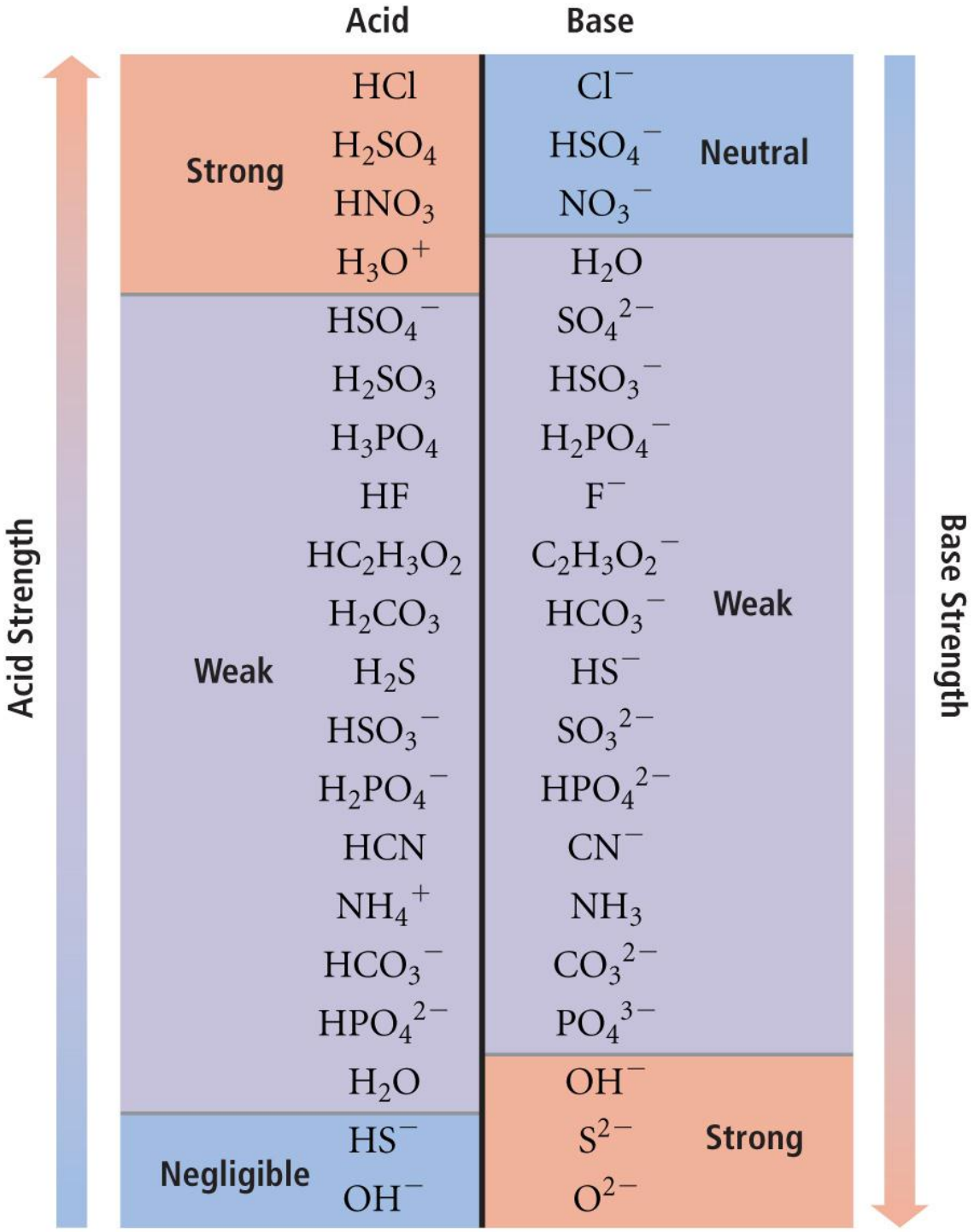
Acid
Base
Acid Strength
Base Strength
Strong
HCl
H_2SO_4
HNO_3
H_3O^+
Cl^-
HSO_4^-
NO_3^-
Neutral
Weak
HSO_4^-
H_2SO_3
H_3PO_4
HF
$HC_2H_3O_2$
H_2CO_3
H_2S
HSO_3^-
$H_2PO_4^-$
HCN
NH_4^+
HCO_3^-
HPO_4^{2-}
H_2O
SO_4^{2-}
HSO_3^-
$H_2PO_4^-$
F^-
$C_2H_3O_2^-$
HCO_3^-
HS^-
SO_3^{2-}
HPO_4^{2-}
CN^-
NH_3
CO_3^{2-}
PO_4^{3-}
Weak
Negligible
HS^-
OH^-
OH^-
S^{2-}
O^{2-}
Strong