CHEM2100J
Chemistry
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Chapter 11
Acid-Base

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Acids and Bases

Early chemists applied the term acid to substances that had a sharp or sour taste.

Aqueous solutions of bases or alkalis were recognized by their soapy feel.

Acids and bases change the colour of certain dyes known as indicators.

Acids	Bases
Tart/sour	Bitter/soapy
Litmus Red	Litmus Blue
pH < 7	pH > 7

Figure J.1
Atkins, *Chemical Principles: The Quest for Insight*, 7e
Andrew Lambert Photography/Science Source.

Acid and Base: Definitions

The Swedish chemist Svante Arrhenius defined in 1884:

An **acid** is a compound that contains hydrogen and reacts with water to form hydrogen (H^+) ions.

$$HCl(aq) \rightarrow \boldsymbol{H^+(aq)} + Cl^-(aq)$$

Hydrochloric acid, HCl, is an **acid** because it produces an hydrogen ion H^+.

A **base** is a compound that produces hydroxide ions (OH^-) in water.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4{}^+(aq) + OH^-(aq)$$
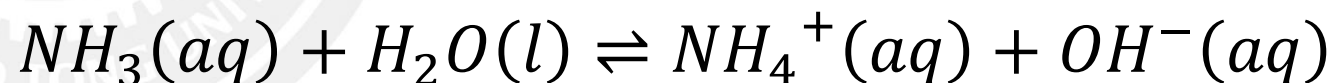
Ammonia, NH_3, is a **base** because it produces an hydroxide ion OH^-.

The Nature of Acids and Bases

An **Arrhenius acid** releases H$^+$ in water and an **Arrhenius base** releases OH$^-$ in water.

A **Brønsted–Lowry acid** is a **proton donor** (hydrogen ion, H$^+$) and a **Brønsted base** is a **proton acceptor**.

$$HCl(aq) + H_2O(l) \rightarrow \boldsymbol{H_3O^+(aq)} + Cl^-(aq)$$

Protonated vs. Deprotonated

The "$\rightarrow$" above means it is not an equilibrium reaction. This type of arrow says HCl is considered as a strong acid.

Hydronium Ion

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

The H_3O^+ ion is called a hydronium ion.

We say that H_2O becomes **strongly protonated** in a solution to form H_3O^+.

A hydrogen ion in water is sometimes represented as $H^+(aq)$, but **H$^+$ does not exist by itself in water**. **H$_3$O$^+$ is a better representation**.
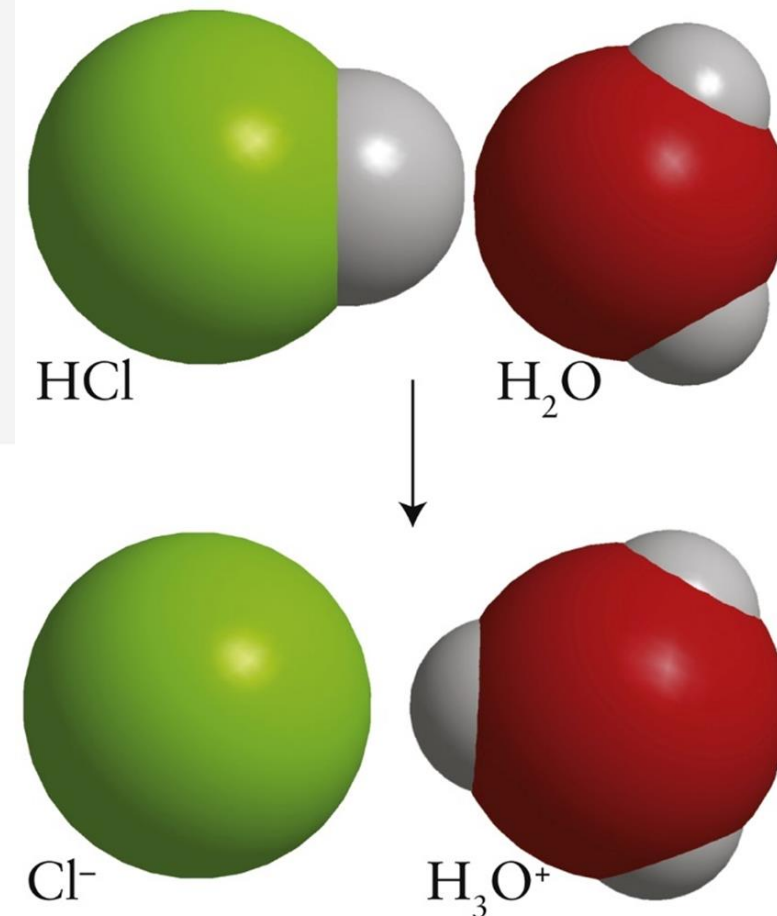

HCl   H$_2$O

Cl$^-$ H$_3$O$^+$

Figure 6A.1
Atkins, *Chemical Principles: The Quest for Insight*, 7e
W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

Hydronium Ion

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

When HCl is placed in water, it transfers a proton to a water molecule, forming H_3O^+ and Cl^-.

This is a **one-way reaction**. While the reverse reaction **could take place**, as soon as Cl^- is protonated by H_3O^+ to HCl, the **HCl "immedately" loses the proton again**.

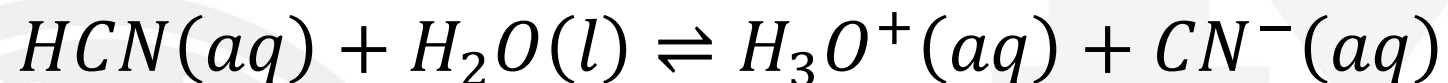In other words, given an atomic microscope, we would never see HCl.

What does this mean for the equilibrium constant *K*?

$HCN(aq)$ transfers only a small fraction of its protons to water, so we classify HCN as a **weak acid** in water; note the equilibrium half-arrow:

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

We <u>envision protons ceaselessly exchanging</u> between HCN and H$_2$O molecules, constantly producing low concentrations of H$_3$O$^+$ and CN$^-$ ions—a dynamic equilibrium.

The equilibrium so **strongly favours reactants** that we see little products.
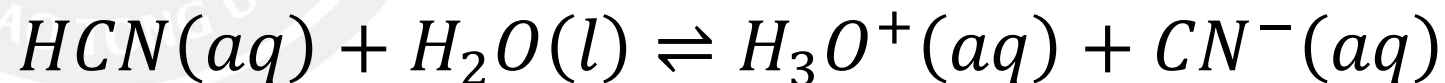
What does this mean for the equilibrium constant *K*?

Summary of Brønsted–Lowry acid theory:

A strong acid is fully deprotonated in a solution ($\rightarrow$).

$$HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$$
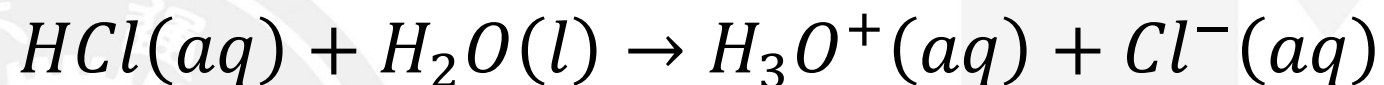
A weak acid is only partly deprotonated in a solution ($\rightleftharpoons$).

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

Brønsted Base
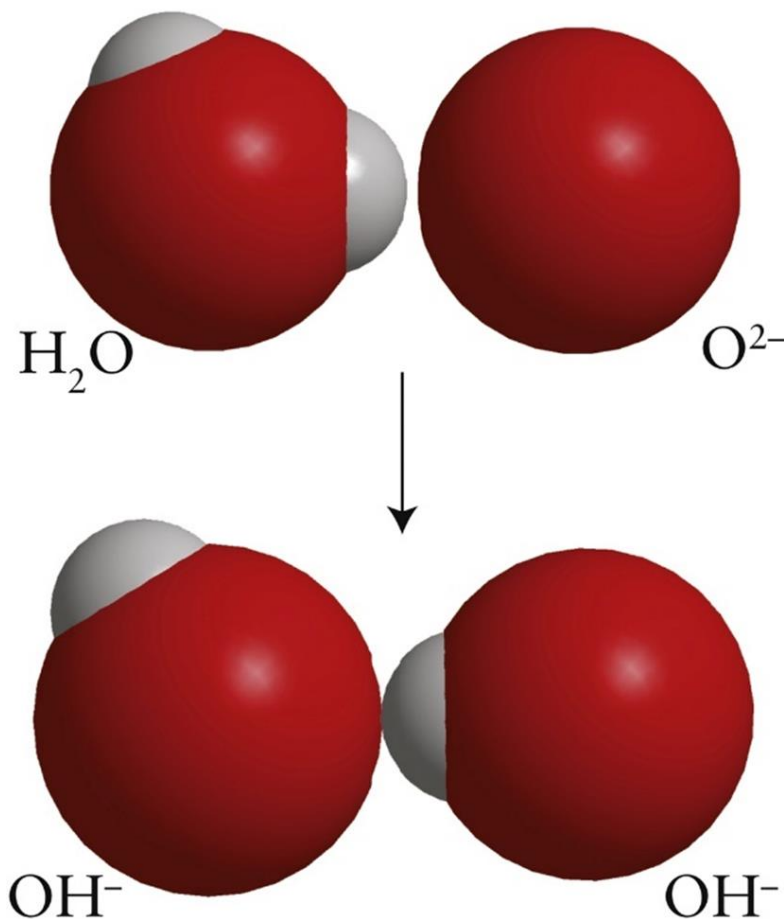
H$_2$O

O^{2-}

OH$^-$

OH$^-$

Figure 6A.3
Atkins, *Chemical Principles: The Quest for Insight*, 7e
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A Brønsted base is a **proton acceptor**, which means that it possesses a **lone pair of electrons** to which a proton can bind.

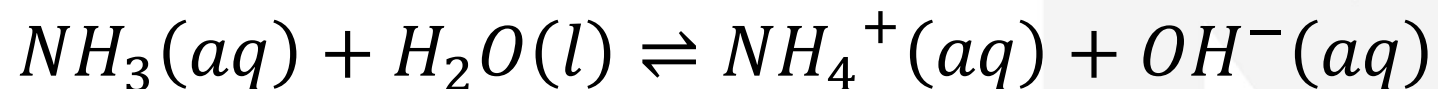Oxide ions, are **highly charged O^{2-} ions**.

O^{2-} is a proton acceptor, so O^{2-} is an example of a **strong base** in water:

$$O^{2-}(aq) + H_2)(l) \rightarrow OH^-(aq) + OH^-(aq)$$
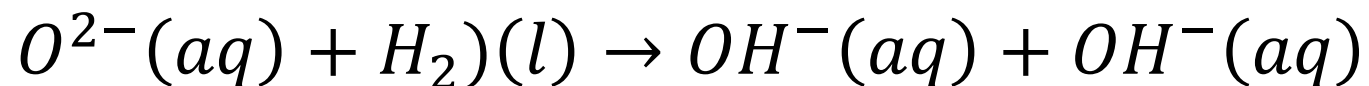
Brønsted Weak Base

The **lone pair** on N can accept a proton from H_2O:

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

The NH_3 molecule is **electrically neutral**. Therefore, it has **less proton-pulling power** than the oxide ion.

As a result, only a very **small proportion** of the NH_3 molecules are converted into $NH_4{}^+$ ions. Ammonia is therefore an example of a **weak base**. All amines, organic derivatives of ammonia, such as methylamine, CH_3NH_2, are weak bases in water.

Brønsted Weak Base

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4{}^+(aq) + OH^-(aq)$$
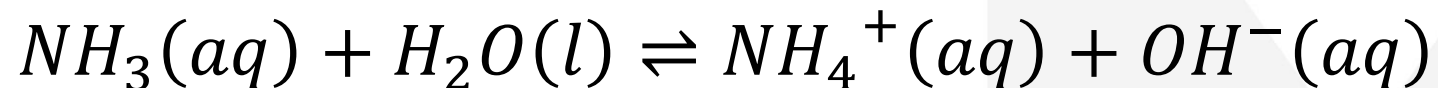
The proton transfer is a **dynamic equilibrium**.

We visualize *protons ceaselessly exchanging* between NH$_3$ and H$_2$O molecules, producing a low concentration of NH$_4{}^+$ and OH$^-$ ions.
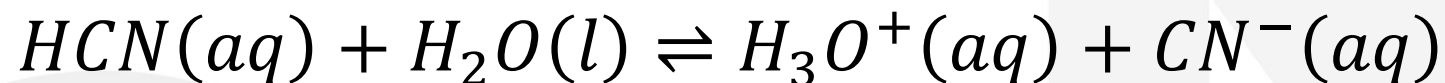
We can **summarize**:

A strong base is completely protonated in a solution ($\rightarrow$).

A weak base is only partially protonated in a solution ($\rightleftharpoons$).
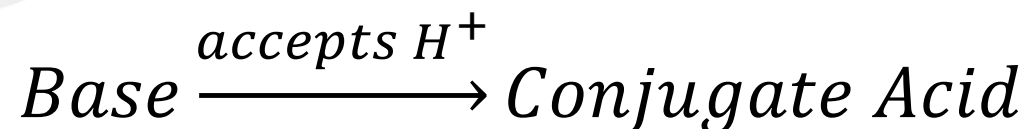
Conjugate Acids and Bases

In weak acid reactions, a new term called **conjugate base** describes what happens to the acid after it donates a proton.

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

The acid HCN forms the conjugate base CN⁻.

Likewise, the base $H_2O(l)$ forms the conjugate acid $H_3O^+(aq)$.

Summary:

$$Acid \xrightarrow{donates\ H^+} Conjugate\ Base$$

$$Base \xrightarrow{accepts\ H^+} Conjugate\ Acid$$
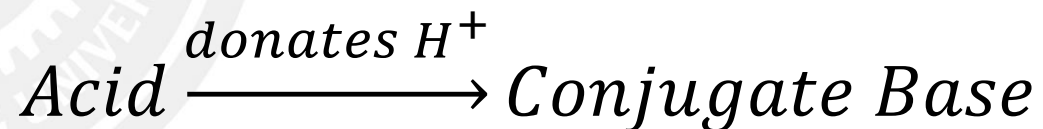
Identify the acids, bases, and conjugates for the following reactions.

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

base   acid   Conjugate acid   Conjugate base

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

acid   base   Conjugate acid   Conjugate base
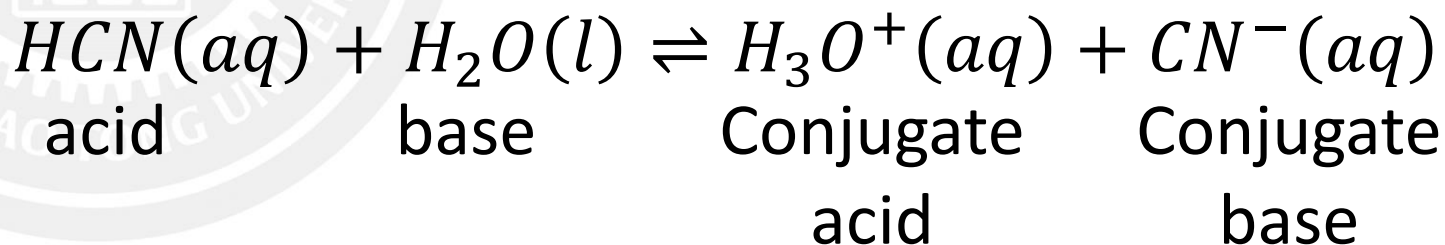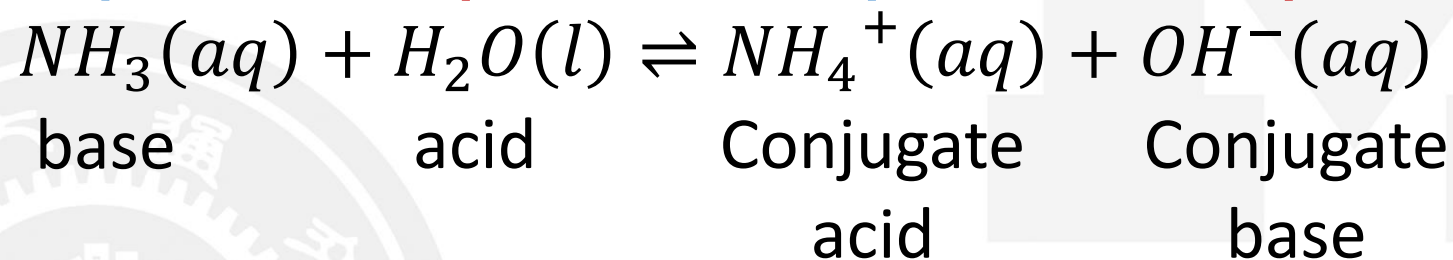
Example

Write the formulas of the conjugate base of HCO_3^-.

1) The conjugate base of HCO_3^- means that HCO_3^- is an acid or proton donor.

2) Therefore, we remove a proton (H^+, note the "+" charge) and write CO_3^{2-}.

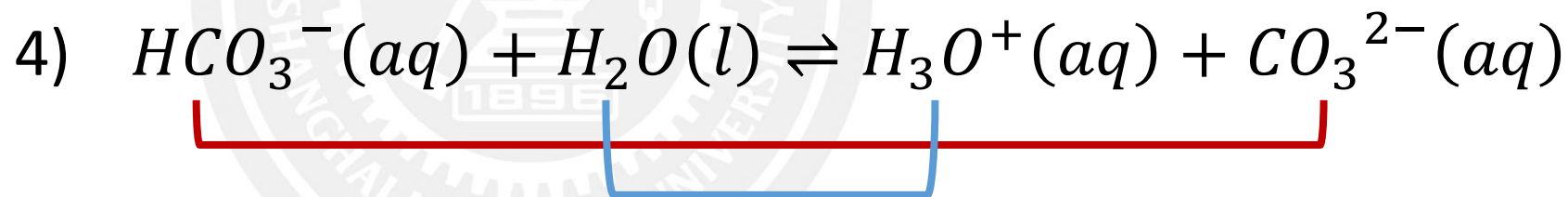3) A more formal method is to write the reaction in water, an important skill for the later stages in this chapter, and noting the conjugate to HCO_3^- is CO_3^{2-} (deprotonated).

4) $$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$$

5) The conjugate acid to the water (H_2O) is the hydronium ion (H_3O^+).

Brønsted vs Arrhenius

The **Brønsted** definition of acids and bases is <u>more general</u> than the **Arrhenius** definition.

Here are some **nonaqueous solvents** and **gas phase** reactions.

$$CH_3COOH(l) + NH_3(l) \rightleftharpoons CH_3COO^-(am) + NH_4{}^+(am)$$

(The label "am" indicates a species dissolved in liquid ammonia.)

An example of **proton transfer in the gas phase** is the reaction of hydrogen chloride and ammonia gases.

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

Brønstedt

Arrhenius

Lewis Acids and Bases
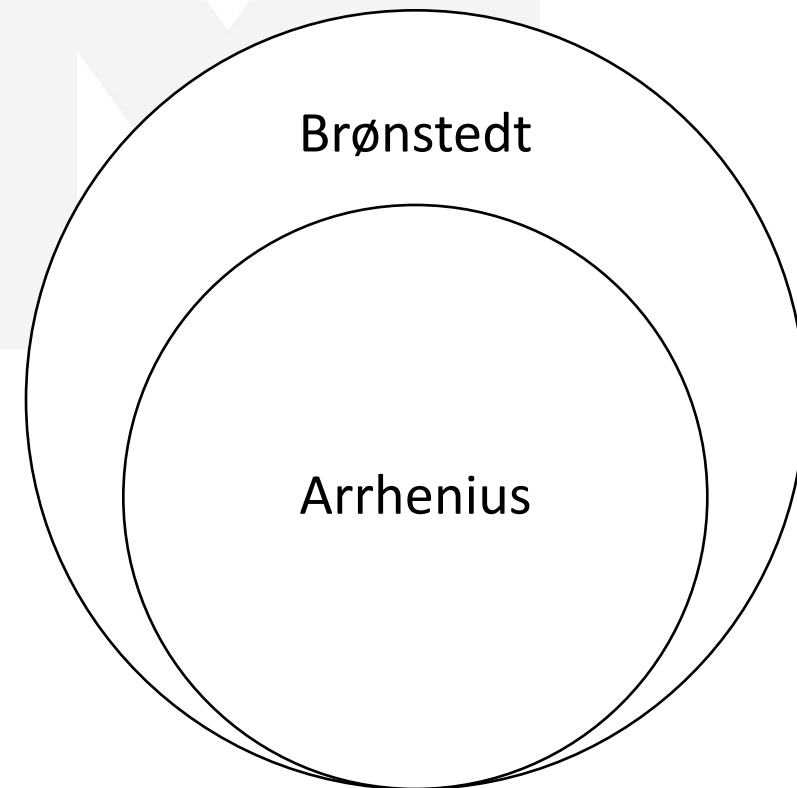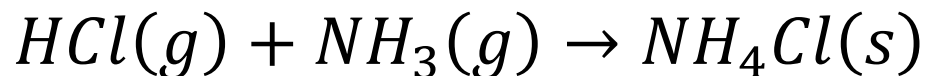
The third and final type of acid base theory is **Lewis theory**.

The <u>focus here is away from protons</u> and instead focuses on those with and without **lone pairs** of electrons.

This theory developed by G. N. Lewis, is <u>more general</u> than Brønsted's acid–base theory.

A Lewis acid is an electron pair acceptor.

A Lewis base is an electron pair donor.

<u>These definitions is used frequently</u> in both **organic** and **inorganic** chemistry. For instance, it explains how metal atoms can form molecules referred to as **complex ions** like $Ni(CO)_4{}^{4+}$, which neither Brønsted nor Arrhenius theory can explain.

Lewis Acids and Bases

A Lewis **acid** is an electron pair **acceptor.**

A Lewis **base** is an electron pair **donor**.

Lewis base   Lewis acid
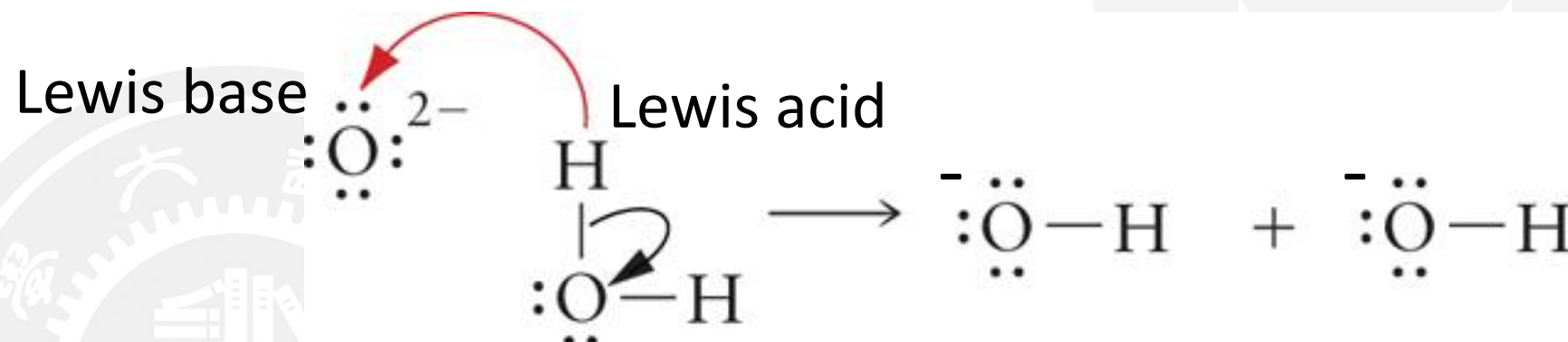
A *covalent bond forms* between the oxide ion (Lewis base) and the proton (Lewis acid) on water.

The **curved arrows** (black) show the **direction** in which the electrons can be thought to move. The **red arrow** shows where the atom will migrate.

Lewis vs. Brønsted vs Arrhenius

Lewis theory is more general than Brønsted or Arrhenius acid–base theory.

> A Lewis **acid** is an electron pair **acceptor.**
>
> A Lewis **base** is an electron pair **donor**.

Lewis

Brønstedt

Arrhenius

Acidic, Basic, and Amphoteric Oxides
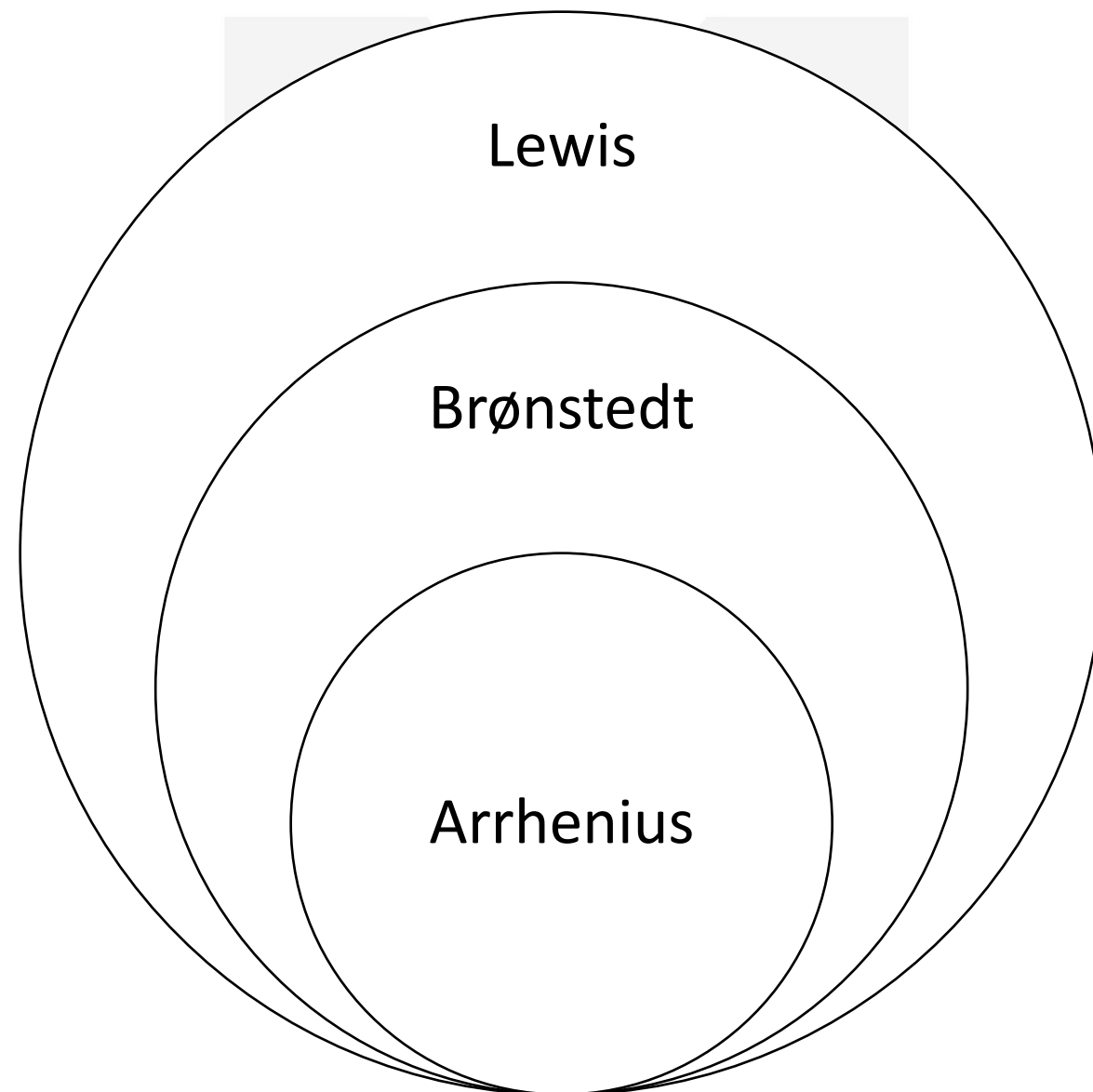
Acidic oxides like CO_2, react with Brønsted bases.

$$2\,NaOH(aq) + CO_2(g) \rightarrow Na_2CO_3(aq) + H_2O(l)$$
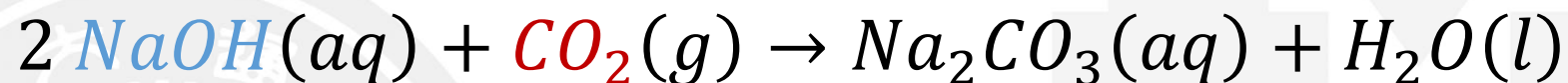
Basic oxides like MgO, react with Brønsted acids.

$$2\,HCl(aq) + MgO(s) \rightarrow MgCl_2(aq) + H_2O(l)$$
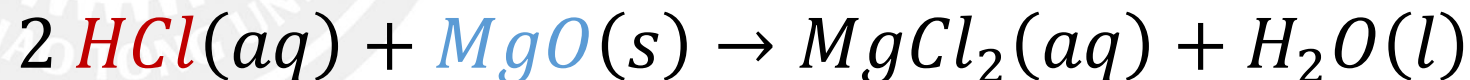
Acidic, Basic, and Amphoteric Oxides

An interesting feature of **frontier elements** is that their metal oxides can act as <u>either an acid or base</u>, meaning they are **Amphoteric Oxides**.

$$Al_2O_3\,(s) + 6\,HCl\,(aq) \rightarrow 2\,AlCl_3\,(aq) + 3\,H_2O\,(l)$$

$$Al_2O_3\,(s) + 2\,NaOH\,(aq) + H_2O\,(l) \rightarrow 2\,Na[Al[OH]_4]\,(aq)$$
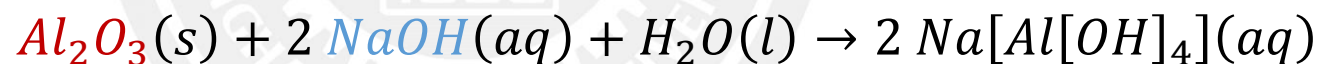
2	13	14	15	16
BeO	B			
	Al_2O_3	Si		
	Ga_2O_3	GeO_2	As_2O_3	
	In_2O_3	SnO / SnO_2	Sb_2O_3	Te
		PbO / PbO_2	Bi_2O_3	Po

Figure 6A.7
Atkins, *Chemical Principles: The Quest for Insight*, 7e
W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

Water is **amphiprotic**

$HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$, water is a Brønstedt base

$NH_3(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + NH_4^+(aq)$, water is a Brønstedt acid

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$
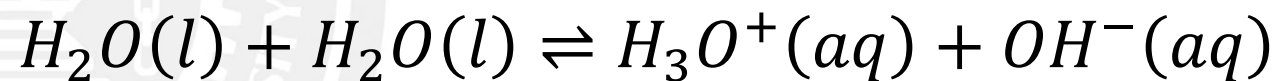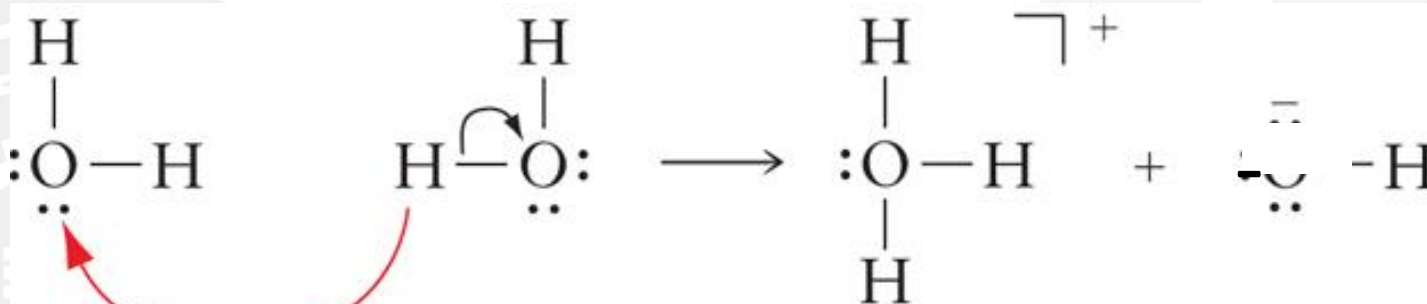
Distinguishing between **amphoteric** and **amphiprotic**:
Aluminium metal is amphoteric (it reacts with both acids and bases), but it has *no* hydrogen atoms to donate as protons, so it is **not** amphiprotic.

Equilibrium Constant for Water

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$
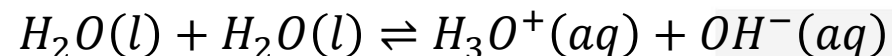
$$K_w = \frac{(a_{H_3O^+})(a_{OH^-})}{(a_{H_2O})^2}$$

K_w is known as the **autoprotolysis** constant of water. In dilute aqueous solutions, the concentration of the solvent (water) is nearly pure, so its activity can be assumed as 1. Additionally, we can treat dilute solutions as ideal, so $a_B = [B]$.

(**Note:** In ideal solutions there are no interactions between solute molecules and the activity is the same as the concentration. We still use the concentration empirically, so without unit.)

$$K_w = \frac{[H_3O^+][OH^-]}{[H_2O]^2} = [H_3O^+][OH^-]$$

In pure water at 25 °C, the molar concentrations of H$_3$O$^+$ and OH$^-$ are equal and are 1.0×10^{-7} mol·L^{-1}. Therefore:

$$K_w = [1.0 \times 10^{-7}][1.0 \times 10^{-7}] = 1.0 \times 10^{-14}$$

Equilibrium Constant for Water

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

The concentrations of H_3O^+ and OH^- are very low, which explains why pure water is such a poor conductor of electricity.

The autoprotolysis reaction is **endothermic** $\left(\Delta H_r^\circ = +56 \ \frac{kJ}{mol}\right)$, so we can expect **$K_w$** to increase with temperature, meaning at higher temperatures there will be higher concentrations of both hydronium and hydroxide ions.

$K_w = [H_3O^+][OH^-] = 1.0\times10^{-14}$

What is the meaning of K_w; an important part of this chapter?

K_w is a constant, meaning the concentrations of H_3O^+ and OH^- can change but K_w cannot.

The autoprotolysis process is like a see-saw, if $[H_3O^+]$ increases, then $[OH^-]$ must decrease.

The **product** of the two values must be K_w or 1.0×10^{-14}.

H_3O^+ concentration
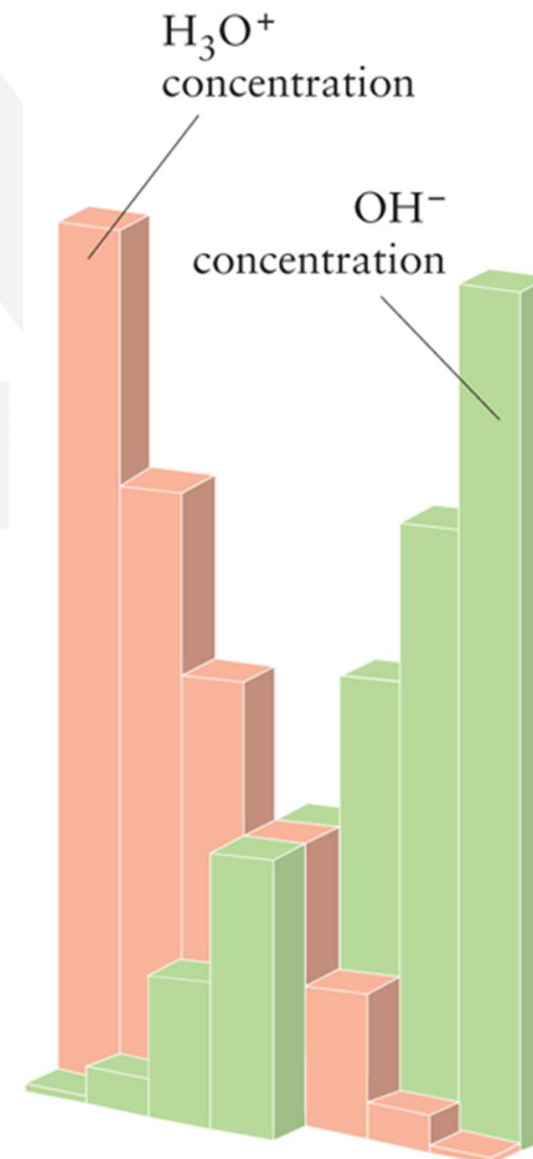
OH^- concentration

Example

What are the concentrations of H_3O^+ and OH^- in 0.0030 M Ba(OH)$_2$(aq) at 25 °C?

Because barium is an alkaline earth metal, it will dissociate to provide OH^-.

$$Ba(OH)_2(s) \rightarrow Ba^{2+}(aq) + 2\,OH^-(aq)$$
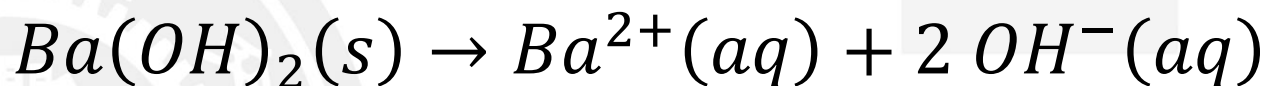
$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

$$[H_3O^+] = \frac{1.0 \times 10^{-14}}{[OH^-]} = \frac{1.0 \times 10^{-14}}{2 \cdot [Ba(OH)_2]} = \frac{1.0 \times 10^{-14}}{2 \times 0.0030} = 1.7 \times 10^{-12}\,\frac{\text{mol}}{\text{L}}$$

The pH Scale

Expressing concentrations of H_3O^+ and OH^- ions, varying over many orders of magnitude from 1 to 10^{-14} mol·L^{-1} is inconvenient.

To avoid the *awkwardness* of this wide range we work in terms of pH:

$$pH = -\log(a_{H_3O^+})$$

For dilute solutions we treat this as ideal, so $a_{H_3O^+} = [H_3O^+]$:

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

Note that: $[H_3O^+] = 10^{-pH} \dfrac{\text{mol}}{\text{L}}$

For example, the pH of pure water where $[H_3O^+] = 1.0 \times 10^{-7} \dfrac{\text{mol}}{\text{L}}$:

$$pH = -\log(1.0 \times 10^{-7}) = 7$$

The pH Scale

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

The **negative sign** means that as the pH rises, the concentration of H_3O^+ ions decreases.

The pH of pure water at 25 °C is 7.

The pH of an acidic solution is <7 (low pH).

The pH of a basic solution is >7 (high pH).

"Dihydrogen monoxide is an acid with a pH of 7, which is higher than the pH of any other acid!"

- "How to scare people that know nothing about Chemistry"

The pH Scale
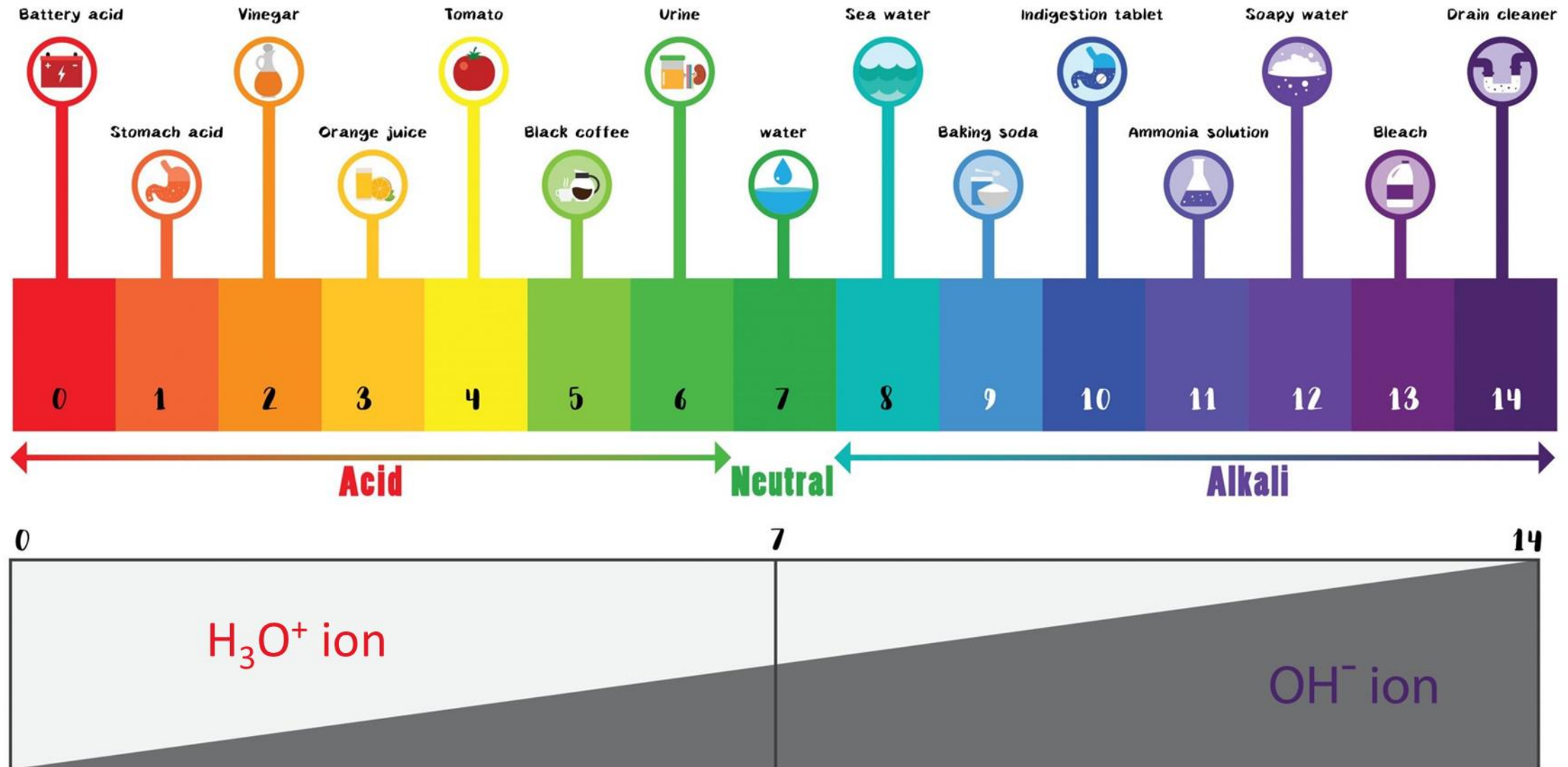
pH Values of Some Liquids

Natural (unpolluted) rain, with an acidity due largely to dissolved carbon dioxide, typically has a pH of about 5.7.
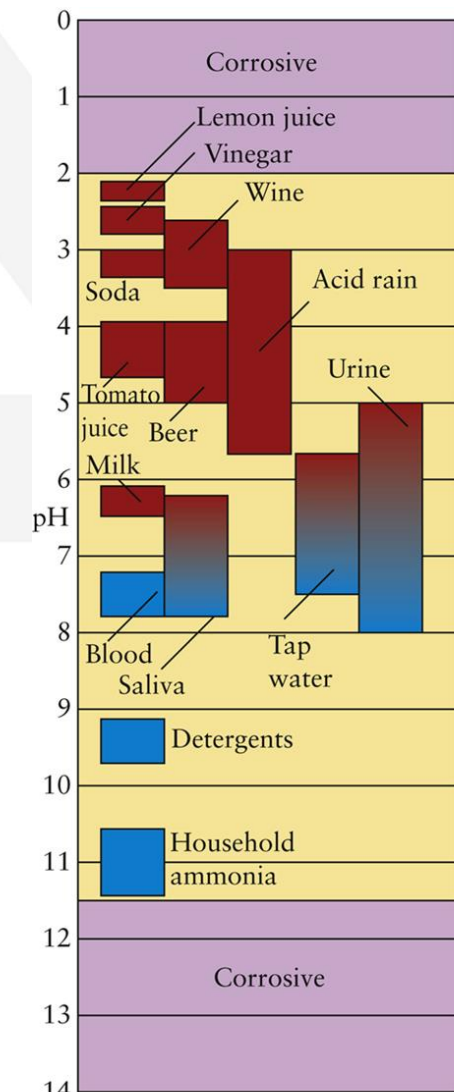
Figure 6B.2
Atkins, *Chemical Principles: The Quest for Insight*, 7e
W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, al

The pH Scale

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

Because pH is a common logarithm (base 10), a change of **one pH** unit means that the concentration of H_3O^+ ions has changed by a **factor of 10**.

For example, **increasing** the concentration of H_3O^+ by a factor of 10, from 10^{-5} mol·L^{-1} to 10^{-4} mol·L^{-1}, is a pH **decrease** from 5 to 4.

Most solutions used in chemistry have a pH ranging from 0 to 14, but values outside this range **are possible**.

Example

What is the pH of (a) human blood, in which the concentration of H_3O^+ ions is 4.0×10^{-8} mol·L^{-1}; (b) 0.020 M HCl(aq)?

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

a) $[H_3O^+] = 4.0 \times 10^{-8} \frac{mol}{L}$

$$pH = -\log(4.0 \times 10^{-8}) = 7.4$$

b) $[HCl] = 0.020 \frac{mol}{L}, HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$

HCl is a strong acid, therefore: $[H_3O^+] = 0.020 \frac{mol}{L}$

$$pH = -\log(0.020) = 1.7$$

pH Values of Basic Solutions

How to calculate the pH of a strong basic solution, e.g., 0.01 M NaOH?
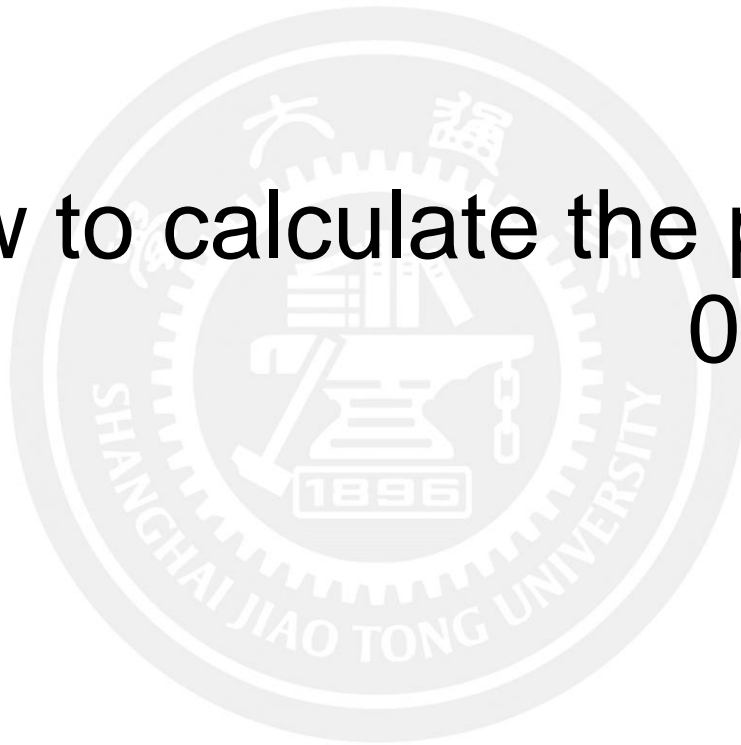
pOH of Solutions

A function of p is generalized as $pX = -\log(X)$

Therefore:

$$pOH = -\log(a_{OH^-})$$

For dilute solutions we can simplify to:

$$pOH = -\log([OH^-])$$

Note that: $[OH^-] = 10^{-pOH}\ \dfrac{\mathrm{mol}}{\mathrm{L}}$

$pH = -\log([H_3O^+])$ and $pOH = -\log([OH^-])$ are often applied to K_w to simplify it as well.

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

$pK_w = -\log(K_w) = -\log([H_3O^+][OH^-])$ leads to:

$$pH + pOH = pK_w = 14$$

If pH = 6
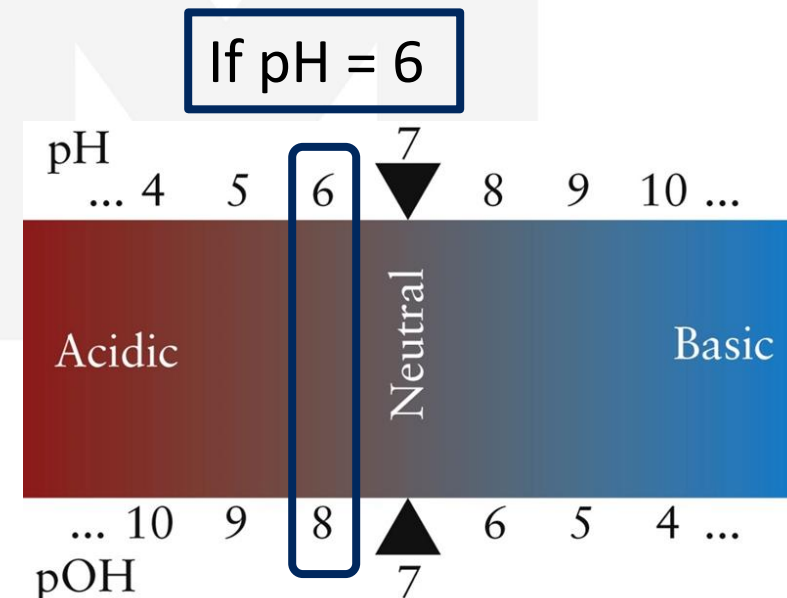
Figure 6B.3
Atkins, *Chemical Principles: The Quest for Insight*, 7e
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then pOH = 8

Weak Acids and Bases

We begin to develop a **quantitative measure** of the <u>strengths of weak acids</u> and <u>bases</u>.

0.1 M CH_3COOH has a pH close to 3

versus

0.1 M HCl has a pH close to 1

This says that **only a little** of CH_3COOH is deprotonated whereas **all** of HCl is deprotonated.

Weak Acids and Bases

Because conjugate acids and bases are in equilibrium in a solution, we use the equilibrium constant.

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$
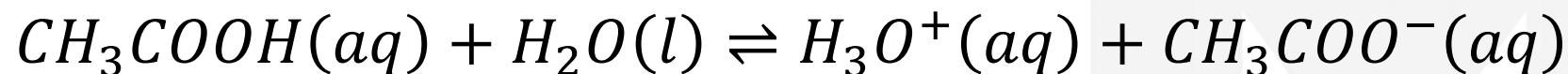
$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = 1.8 \times 10^{-5}$$

K_a refers to the equilibrium constant for an acid.

This is very small and says that <1% molecules of CH_3COOH deprotonate.

The generic form for any K_a is:

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

Weak Acids and Bases

The equilibrium constant for the proton transfer of a weak base (aqueous ammonia) in water is:

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

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

K_b refers to the equilibrium constant for a base.

The generic form for any K_b is:

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

Equilibrium Constants for Acids

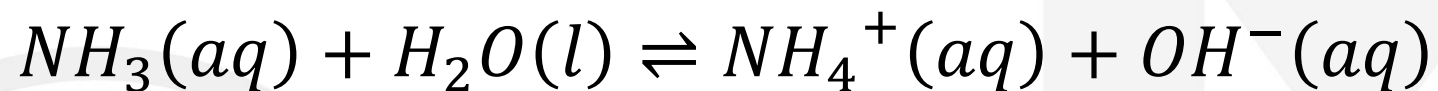| Acid	K_a (@25 °C)	pK_a (@25 °C)
Trichloroacetic acid, CCl_3COOH	3.0×10^{-1}	0.52
Benzene sulfonic acid, $C_6H_5SO_3H$	2.0×10^{-1}	0.70
Iodic acid, HIO_3	1.7×10^{-1}	0.77
Sulfurous acid, H_2SO_3	1.5×10^{-2}	1.81
Chlorous acid, $HClO_2$	1.0×10^{-2}	2.00
Phosphoric acid, H_3PO_4	7.6×10^{-3}	2.12
Chloroacetic acid, $CH_2ClCOOH$	1.4×10^{-3}	2.85
Lactic acid, $CH_3CH(OH)COOH$	8.4×10^{-4}	3.08
Nitrous acid, HNO_2	4.3×10^{-4}	3.37
Hydrofluoric acid, HF	3.5×10^{-4}	3.45
Formic acid, HCOOH	1.8×10^{-4}	3.75
Benzoic acid, C_6H_5COOH	6.5×10^{-5}	4.19
Acetic acid, CH_3COOH	1.8×10^{-5}	4.75
Carbonic acid, H_2CO_3	4.3×10^{-7}	6.37
Hypochlorous acid, HClO	3.0×10^{-8}	7.53
Hypobromous acid, HBrO	2.0×10^{-9}	8.69
Boric acid, $B(OH)_3$	7.2×10^{-10}	9.14
Hydrocyanic acid, HCN	4.9×10^{-10}	9.31
Phenol, C_6H_5OH	1.3×10^{-10}	9.89
Hypoiodous acid, HIO	2.3×10^{-11}	10.64

Strong acids

$$pK_a = -log(K_a)$$

Note:

As K_a increases, pK_a decreases. Therefore, stronger acids have lower pK_a values, which can also become negative.

Equilibrium Constants for Bases

$$pK_b = -log(K_b)$$

Note:

As K_b increases, pK_b decreases. Therefore, stronger bases have lower pK_b values, which can also become negative.

Strong bases

Base	K_b (@25 °C)	pK_b (@25 °C)
Urea, $CO(NH_2)_2$	1.3×10^{-14}	13.90
Aniline, $C_6H_5NH_2$	4.3×10^{-10}	9.37
Pyridine, C_5H_5N	1.8×10^{-9}	8.75
Hydroxylamine, NH_2OH	1.1×10^{-8}	7.97
Nicotine, $C_{10}H_{14}N_2$	1.0×10^{-6}	5.98
Morphine, $C_{17}H_{19}O_3N$	1.6×10^{-6}	5.79
Hydrazine, NH_2NH_2	1.7×10^{-6}	5.77
Ammonia, NH_3	1.8×10^{-5}	4.75
Trimethylamine, $(CH_3)_3N$	6.5×10^{-5}	4.19
Methylamine, CH_3NH_2	3.6×10^{-4}	3.44
Dimethylamine, $(CH_3)_2NH$	5.4×10^{-4}	3.27
Ethylamine, $C_2H_5NH_2$	6.5×10^{-4}	3.19
Triethylamine, $(C_2H_5)_3N$	1.0×10^{-3}	2.99

The Conjugate Seesaw

Strong acids like HCl completely react with water:

$$HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$$
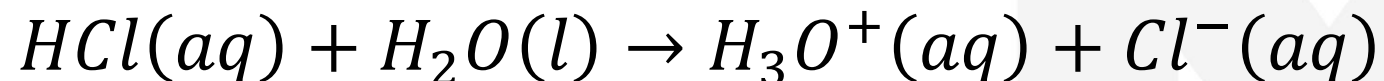
The K_a for HCl is large, 1×10^8.

Every time Cl^- takes a H^+ from H_3O^+ to make HCl, the HCl immediately disassociates back to Cl^-. *In other words, the Cl^- is not strong enough to hold onto the H^+.* We call Cl^- a weak conjugate base.

Therefore the K_b for Cl^- is very small or 1×10^{-22}.

The Conjugate Seesaw

For a weak acid we see **both** the acid and the conjugate base.

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$
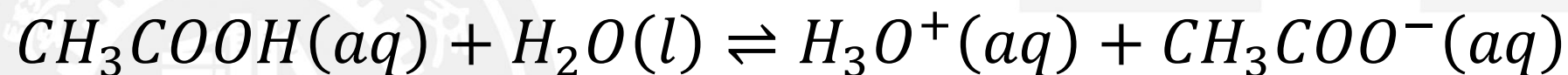
Here, since K_a is small, we expect K_b to be equally small (but not very small).

The Conjugate Seesaw

$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$, NH$_4^+$ as an acid

$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$, NH$_4^+$ a conjugate acid

Equilibrium expressions:

$$K_a = \frac{[H_3O^+][NH_3]}{[NH_4^+]} \qquad K_b = \frac{[OH^-][NH_4^+]}{[NH_3]}$$

Combining the equilibrium expressions:

$$K_a \cdot K_b = \frac{[H_3O^+][NH_3]}{[NH_4^+]} \cdot \frac{[OH^-][NH_4^+]}{[NH_3]} = [H_3O^+][OH^-]$$

$$K_a \cdot K_b = [H_3O^+][OH^-] = K_w = 1.0 \times 10^{-14}$$

$$\boldsymbol{pK_a + pK_b = pK_w = 14}$$

Conjugate Acid-Base Pairs

pK_a pK_b

Chlorous acid 2.00 / 12.00
Acetic acid 4.75 / 9.25
Hypochlorous acid 7.53 / 6.47
Ammonia 9.25 / 4.75
Methylamine 10.56 / 3.44
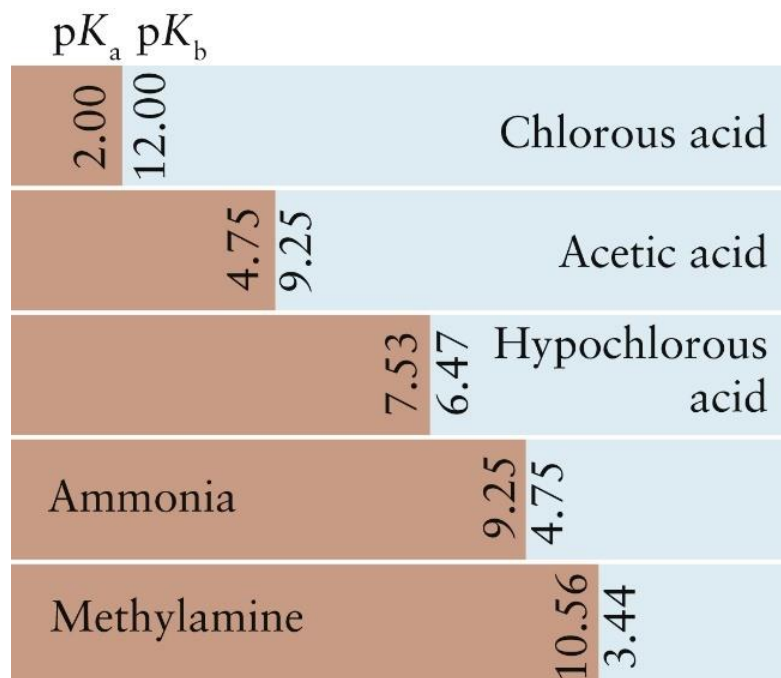
Figure 6C.4
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CH_3COOH and CH_3COO^-

$$pK_a + pK_b = 14$$
$$4.75 + 9.25 = 14$$
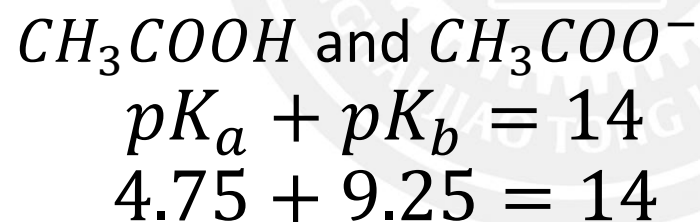
pK_a	Acid name	Acid formula	Base formula	Base name	pK_b
	Strong acid			*Very weak base*	
	Hydroiodic acid	HI	I$^-$	Iodide ion	
	Perchloric acid	$HClO_4$	ClO_4^-	Perchlorate ion	
	Hydrobromic acid	HBr	Br$^-$	Bromide ion	
	Hydrochloric acid	HCl	Cl$^-$	Chloride ion	
	Sulfuric acid	H_2SO_4	HSO_4^-	Hydrogen sulfate ion	
	Chloric acid	$HClO_3$	ClO_3^-	Chlorate ion	
	Nitric acid	HNO_3	NO_3^-	Nitrate ion	
	Hydronium ion	H_3O^+	H_2O	*Water*	
	Weak acid			*Weak base*	
1.92	Hydrogen sulfate ion	HSO_4^-	SO_4^{2-}	Sulfate ion	12.08
3.37	Nitrous acid	HNO_2	NO_2^-	Nitrite ion	10.63
3.45	Hydrofluoric acid	HF	F$^-$	Fluoride ion	10.55
4.75	Acetic acid	CH_3COOH	CH_3COO^-	Acetate ion	9.25
6.37	Carbonic acid	H_2CO_3	HCO_3^-	Hydrogen carbonate ion	7.63

Example

Decide which is the stronger acid in water: HF or HIO_3.

The greater the K_a of a weak acid, the stronger is the acid and the weaker is its conjugate base.

Similarly, the greater the K_b of a weak base, the stronger the base and the weaker its conjugate acid.

HF: $K_a = 3.5 \times 10^{-4}$ $pK_a = 3.45$

HIO_3: $K_a = 1.7 \times 10^{-1}$ $pK_a = 0.77$

$$pK_{a,HIO_3} < pK_{a,HF}$$

HIO_3 is the stronger acid.

Molecular Structure and Acid Strength

There is **no general theory** that describes acid strength. We only have **general trends** to work with and **compare**.

Two competing factors complicate our description.

1) Since equilibrium constants, K_a and K_b, are related to **Gibbs free energy**, acid-base strengths are subject to correlations between both entropy and energy.

2) The **solvent** plays an equally important role.

We'll look at trends in binary acids as well as oxoacids.

Molecular Structure and Acid Strength

Two different trends can be observed, one for **periods and** the other for **groups**.

1) In a **period**, acid strength is based on <u>bond polarity</u>

2) In a **group**, acid strength is based on <u>bond strength</u>

H-C, H-N, H-F

Electronegativity increases across a period from carbon to fluorine which <u>increases</u> <u>the partial positive charge</u> on the hydrogen:
$H^{\delta+}$-$C^{2.5}$, $H^{\delta+}$-$N^{3.0}$, $H^{\delta+}$-$F^{4.0}$, making the proton more acidic.
In HF, F being the most electronegative, it can remove electron density away from its H and thereby making it easier for water to remove the proton:
$H_2O \cdots H - F \rightleftharpoons H_3O^+ + F^-$, making HF the most acidic.

Molecular Structure and Acid Strength

Two different trends can be observed, one for **periods and** the other for **groups**.

1) In a **period**, acid strength is based on <u>bond polarity</u>

2) In a **group**, acid strength is based on <u>bond strength</u>

For groups, there is the opposite effect

In group acidity, *electronegativity decreases* down the group. Therefore, bond strength weakens going down the group, making it easier for the proton to leave. For Group 17 hydrides, bond strength decreases, and acidity increases accordingly, $HF < HCl < HBr < HI$ which makes hydroiodic acid the strongest acid in that group.

Molecular Structure and Acid Strength: Oxoacids

There are two ways to compare oxoacids:

1) A group with the **same number of oxygen atoms**

(HClO, HBrO, HIO)

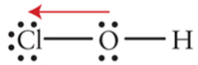1) A family of the same element with **different numbers of oxygen atoms**
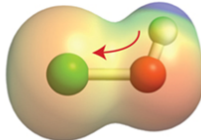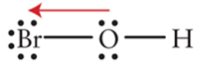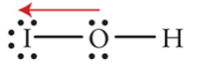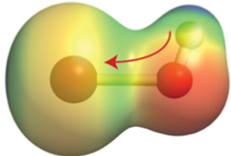
(HClO, $HClO_2$, $HClO_3$, $HClO_4$)

In groups with the **same number of oxygen atoms**, we see that the greater the electronegativity the greater the acidity:

$$HClO > HBrO > HIO$$

A partial explanation is that electrons are withdrawn slightly from the O-H bond as the electronegativity of the halogen increases (group effect).

TABLE 6C.5 Correlation of Acid Strength and Electronegativity

Acid, HAO	Structure*	Electronegativity of atom A	pKa
hypochlorous acid, HClO	Cl—O—H	3.2	7.53
hypobromous acid, HBrO	Br—O—H	3.0	8.69
hypoiodous acid, HIO	I—O—H	2.7	10.64

*The red arrows indicate the direction of the shift of electron density away from the O—H bond.

Table 6C.5
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TABLE 6C.6   Correlation of Acid Strength and Oxidation Number

Acid	Structure*	Oxidation number of Cl atom	pK_a	
hypochlorous acid, HClO		+1	7.53	
chlorous acid, HClO₂		+3	2.00	
chloric acid, HClO₃		+5	strong	
perchloric acid, HClO₄		+7	strong	

*The red arrows indicate the direction of the shift of electron density away from the O—H bond. The Lewis structures shown are the ones with the most favorable formal charges, but it is unlikely that the bond orders are as high as these structures suggest.

Table 6C.6
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In a family of the same element with **different numbers of oxygen atoms**:
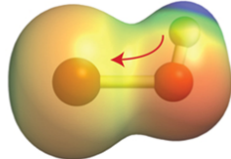$$HClO < HClO_2 < HClO_3 < HClO_4$$

Here, the **greater the number of oxygen atoms**, the stronger the acid due to an **increase** in the **oxidation** number on the central atom, which causes **polarization**.

Carboxylic acid, is a weak acid, though it is a **much stronger acid than alcohols** with the same number of carbon atoms.

In fact, alcohols are usually not regarded as oxoacids.

The second O atom in the carboxyl group, -COOH,

- increases the oxidation number of the carbon, polarizing the C-O-H bond, and

- helps stabilize the conjugate base by delocalizing electrons.

2 Ethanol, CH_3CH_2OH

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3 Acetic acid, CH_3COOH

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4 Acetate ion, $CH_3CO_2^-$

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Summary
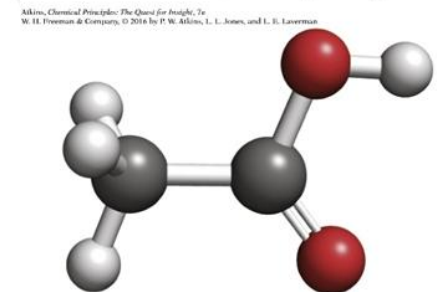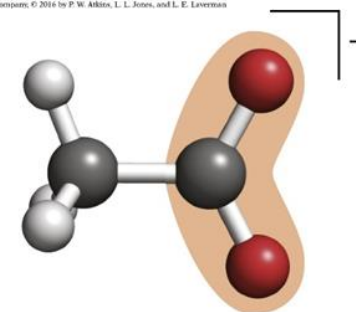
TABLE 6C.7   Correlations of Molecular Structure and Acid Strength*

Acid type	Trend	
binary	The more polar the H—A bond, the stronger the acid.	
	This effect is dominant for acids of the same period.	
	The weaker the H—A bond, the stronger the acid.	
	This effect is dominant for acids of the same group.	
oxoacid	The greater the number of O atoms attached to the central atom (the greater the oxidation number of the central atom), the stronger the acid.	
	For the same number of O atoms attached to the central atom, then the greater the electronegativity of the central atom, the stronger the acid.	
carboxylic	The greater the electronegativities of the groups attached to the carboxyl group, the stronger the acid.	
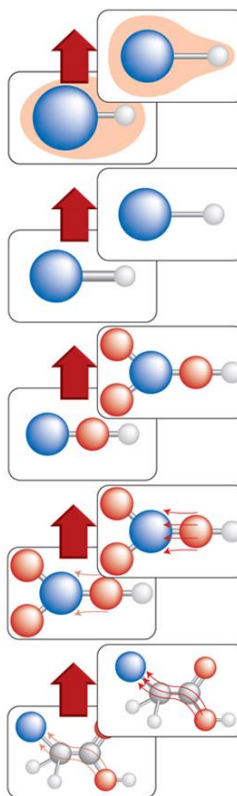
*In each diagram, the arrows indicate the corresponding increase in acid strength.

The greater the number of oxygen atoms and the more electronegative the atoms present in the molecules of an acid, the stronger is the acid. These trends are summarized in Table 6C.7.

Table 6C.7
Atkins, *Chemical Principles: The Quest for Insight*, 7e
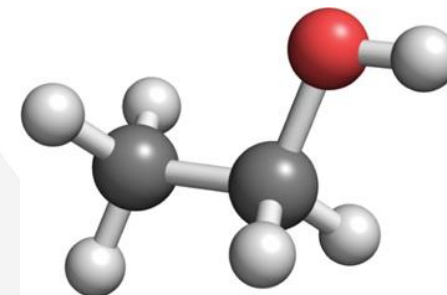W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

1. Groups: bond strength ⬇

2. Periods: polarity ⬆

3. Oxidation number ⬆

4. Number of oxygen atoms: polarity ⬆

5. Resonances stabilized ⬆

Example

Predict from their molecular structures which acid in each of the following pairs is the stronger one: (a) H_2S and H_2Se; (b) H_2SO_4 and H_2SO_3; (c) H_2SO_4 and H_3PO_4.

a) H_2S and H_2Se: When comparing in the same group we look for the larger, more polarized atom. Here Se is larger, more polarizable than S, so H_2Se > H_2S.

b) H_2SO_4 and H_2SO_3: When comparing the same atom with a different number of oxygen atoms, the molecule with the greater number of oxygen atoms also has the greater oxidation number on the central atom. The sulfur in H_2SO_4 has a +6 oxidation number and the sulfur in H_2SO_3 has a +4, so H_2SO_4 > H_2SO_3.

c) H_2SO_4 and H_3PO_4: We can only compare the oxidation numbers. The sulfur in H_2SO_4 has a +6 oxidation number and the phosphorous in H_3PO_4 has a +5, so H_2SO_4 > H_3PO_4.

The pH of Solutions of Weak Acids and Bases

We will use ICE **tables** to calculate K_a/K_b and initial/finial concentrations.

One notable difference is that **pH** will be used as a way to find the final concentrations of the solutions.

Equilibrium reactions have an (1) initial concentration, (2) a change in concentration, and (3) an equilibrium concentration. These are easy to calculate in a table. These tables are often referred to as ICE tables.

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$$

	H_2	I_2	HI
initial			
change			
equilibrium (final)			

$$relative\ chage = \frac{change\ in\ activity}{initial\ activity} = \frac{x}{a_{initial}}$$

This was helpful when we wanted to simplify our calculations by **ignoring "x"** when the equilibrium constant was very small, or when there was less than **5%** change.

In this chapter, the change is commonly a **degree of protonation** or **deprotonation**, depending on the reaction being a **base** reaction or an **acid** reaction.

For a generic weak acid reaction $\left(HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)\right)$:

$$degree\ of\ deprotonation = \frac{[H_3O^+]}{[HA]_{initial}}$$

The **autoprotolysis** of water:

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$
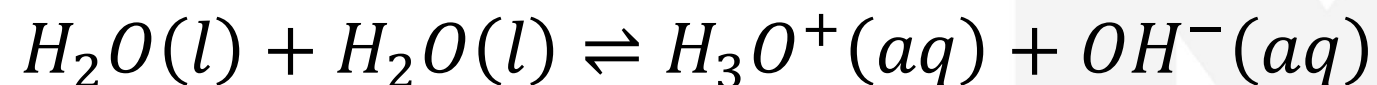
$$K_w = \frac{[H_3O^+][OH^-]}{[H_2O]^2} = [H_3O^+][OH^-]$$

$$K_w = [1.0 \times 10^{-7}][1.0 \times 10^{-7}] = 1.0 \times 10^{-14}$$

We note that 1.0×10^{-14} is so small that neither the $[H_3O^+]$ nor $[OH^-]$ concentrations are high enough to be considered a factor in our calculations. Therefore, these concentrations are very often ignored.

We can always use the quadratic formula for solving our ICE tables. However, this can be time consuming. It's sometimes faster to make a guess before solving with the quadratic formula.

For instance, if $K = 7.6 \times 10^{-3}$ and a solution has an initial concentration of 0.10 M we could:

1) Solve using the 5% rule; like we learned Chapter 10, or

2) before doing any calculations, we make a quick check by multiplying K with 100. So, if $K \times 100 < 0.10$ M (**initial concentration**), we can assume we won't need the quadratic formula. However, always check that the change in the initial concentration is <5%.

Calculate the pH and percentage deprotonation of 0.10 M $CH_3COOH(aq)$, given that K_a for acetic acid is 1.8×10^{-5}.
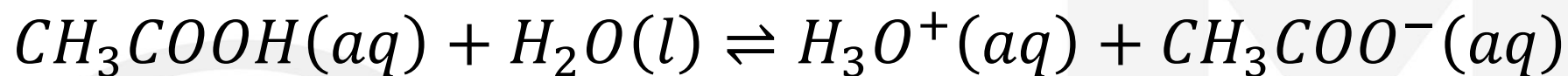
$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

First, we create our ICE table with the known values.

Note: -x means the concentration is decreasing, +x means the concentration is increasing.

	CH_3COOH	H_3O^+	CH_3COO^-
initial	0.10	0	0
change	-x	+x	+x
equilibrium (final)	0.10-x	x	x

$K_a = 1.8 \times 10^{-5} \ll 0.1$, so we can ignore the change in initial acid concentration.

$$K_a = \frac{x^2}{[CH_3COOH]}$$

$$x = \sqrt{K_a \cdot [CH_3COOH]} = \sqrt{1.8 \times 10^{-5} \times 0.10} = 1.3 \times 10^{-3}$$

$$[CH_3COOH] = 0.10 \ \frac{mol}{L} \qquad [H_3O^+] = [CH_3COO^-] = 1.3 \times 10^{-3} \ \frac{mol}{L}$$

$$pH = -\log([H_3O^+]) = -\log(1.3 \times 10^{-3}) = 2.89$$

(since pH < 6, ignoring the autoprotolysis of water is valid)

$$degree\ of\ deprotonation = \frac{x}{[CH_3COOH]_{initial}} = \frac{1.3 \times 10^{-3}}{0.10} = 0.013$$

Calculate the pH and percentage deprotonation of 0.22 M aqueous chloroacetic acid. Be sure to check any approximation to see whether it is valid. The K_a for chloroacetic acid is 1.4×10^{-3}. *K_a is 100 times larger than in the previous example.*
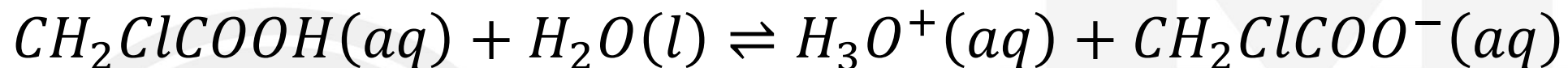
$$CH_2ClCOOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_2ClCOO^-(aq)$$

First, we create our ICE table with the known values.

Note: *-x* means the concentration is decreasing, *+x* means the concentration is increasing.

	$CH_2ClCOOH$	H_3O^+	CH_2ClCOO^-
initial	0.22	0	0
change	-x	+x	+x
equilibrium (final)	0.22-x	x	x

$$K_a = \frac{x^2}{[CH_2ClCOOH]}$$

$$x = \sqrt{K_a \cdot [CH_2ClCOOH]} = \sqrt{1.4 \times 10^{-3} \times 0.22} = 1.8 \times 10^{-2}$$

$$degree\ of\ deprotonation = \frac{x}{[CH_2ClCOOH_{initial}]} = \frac{1.8 \times 10^{-2}}{0.22} = 0.082 \quad ✗$$

Which means we'll have to use the quadratic formula.

$$K_a = \frac{x^2}{[CH_2ClCOOH] - x} = \frac{x^2}{0.22 - x} = 1.4 \times 10^{-3}$$

$$0 = x^2 + 1.4 \times 10^{-3}x - 3.1 \times 10^{-4}$$

Solving for x, using $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$:

$$x = \frac{-1.4 \times 10^{-3} \pm \sqrt{(1.4 \times 10^{-3})^2 - 4 \times 1 \times (-3.1 \times 10^{-4})}}{2 \times 1} = 0.017$$

$$[CH_2ClCOOH] = 0.22 - 0.017 = 0.20 \frac{mol}{L} \qquad [CH_2ClCOO^-] = [H_3O^+] = 0.017 \frac{mol}{L}$$

$$pH = -\log([H_3O^+]) = -log(0.017) = 1.77$$

$$degree\ of\ deprotonation = \frac{x}{[CH_2ClCOOH]_{initial}} = \frac{0.017}{0.22} = 0.077$$

Example

The pH of a 0.010 M aqueous solution of mandelic acid, C₆H₅CH(OH)COOH, an antiseptic, is 2.95. What is the K_a of mandelic acid?

$$C_6H_5CH(OH)COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_6H_5CH(OH)COO^-(aq)$$
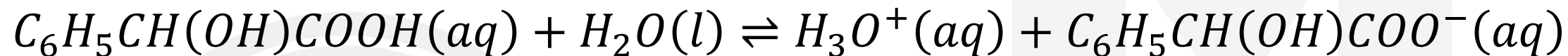
$$[H_3O^+] = 10^{-pH} = 10^{-2.95} = 0.0011 \frac{mol}{L}$$

	C₆H₅CH(OH)COOH	H₃O⁺	C₆H₅CH(OH)COO⁻
initial	0.010	0	0
change	-0.0011	+0.0011	+0.0011
equilibrium (final)	0.0089	0.0011	0.0011

Example

$$C_6H_5CH(OH)COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_6H_5CH(OH)COO^-(aq)$$
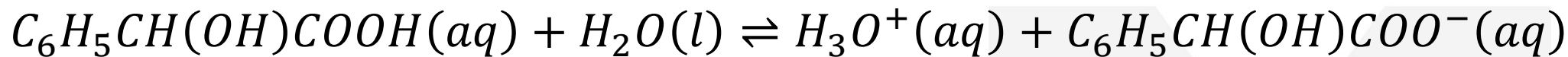
Calculating K_a:

$$K_a = \frac{[H_3O^+][C_6H_5CH(OH)COO^-]}{[C_6H_5CH(OH)COOH]} = \frac{(0.0011)^2}{0.0089} = 1.4 \times 10^{-4}$$

	$C_6H_5CH(OH)COOH$	H_3O^+	$C_6H_5CH(OH)COO^-$
initial	0.010	0	0
change	-0.0011	+0.0011	+0.0011
equilibrium (final)	0.0089	0.0011	0.0011

Solutions of Weak Bases

In the next section we examine weak base equilibrium. We treat these the same way we did with weak acids.

Example

Calculate the pH and degree of protonation of a 0.20 M aqueous solution of methylamine, CH_3NH_2. The K_b for CH_3NH_2 is 3.6×10^{-4}.

This is a base reaction in water:
$$CH_3NH_2(aq) + H_2O(aq) \rightleftharpoons CH_3NH_3{}^+(aq) + OH^-(aq)$$
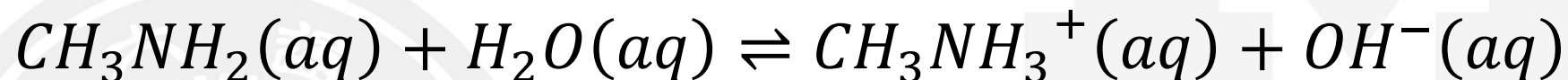
First, we create our ICE table with the known values.

Note: -*x* means the concentration is decreasing, +*x* means the concentration is increasing.

	CH_3NH_2	$CH_3NH_3{}^+$	OH^-
initial	0.20	0	0
change	-*x*	+*x*	+*x*
equilibrium (final)	0.20-*x*	*x*	*x*

$K_b = 3.6 \times 10^{-4} \ll 0.2$, so we can ignore the change in initial base concentration.

$$K_b = \frac{x^2}{[CH_3NH_2]}$$

$$x = \sqrt{K_b \cdot [CH_3NH_2]} = \sqrt{3.6 \times 10^{-4} \times 0.20} = 8.5 \times 10^{-3}$$

$$[CH_3NH_2] = 0.20 \,\frac{mol}{L} \qquad [OH^-] = [CH_3NH_3^+] = 8.5 \times 10^{-3} \,\frac{mol}{L}$$

$$pOH = -\log([OH^-]) = -\log(8.5 \times 10^{-3}) = 2.07$$

$$pH = 14 - pOH = 14 - 2.07 = 11.9$$

(since pH > 8, ignoring the autoprotolysis of water is valid)

$$degree\ of\ protonation = \frac{x}{[CH_3NH_2]_{initial}} = \frac{8.5 \times 10^{-3}}{0.20} = 0.043$$

The pH of Salt Solutions

Earlier we saw that a neutralization reaction between acids and bases produces salt and water. In general, a strong acid and a metal hydroxide react accordingly.

$$Acid + Metal\ hydroxide \rightarrow Salt + Water$$
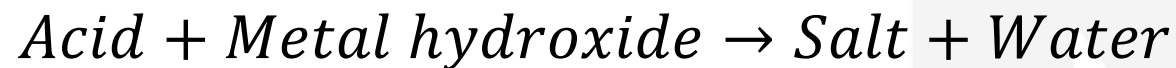
An example is hydrochloric acid and sodium hydroxide reacting to produce table salt, sodium chloride, and water.

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$
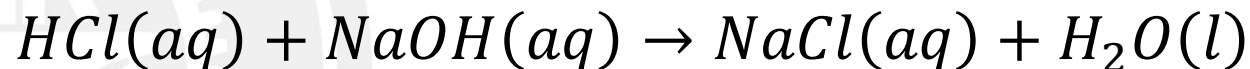
The pH of this solution will be 7, or neutral.

We are familiar with the meaning of a forward arrow, →, <u>implying</u> the reaction <u>never proceeds in the reverse direction</u>.

The pH of Salt Solutions

In <u>another neutralization</u>, a somewhat unexpected result appears:

$$CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COO^-Na^+(aq) + H_2O(l)$$
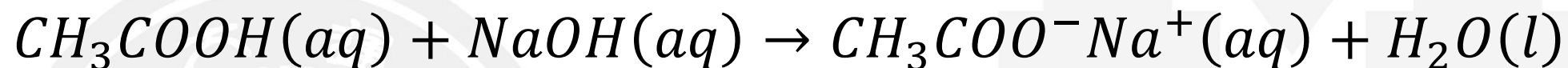
Even though this is a neutralization reaction, **the measured pH is 9**.

In Brønsted–Lowry theory the **conjugate acid** or **base** can be either **acidic** or **basic**.

The pH of Salt Solutions

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

In the example above, a <u>weak acid reacts</u> **completely** with a <u>strong base</u>.

The salt product $CH_3COO^-Na^+$ is soluble in water and there are two possible reactions that this salt can still go through with water:

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

$$Na^+(aq) + H_2O(l) \;\cancel{\rightleftharpoons}\; H_3O^+(aq) + NaOH(aq)$$
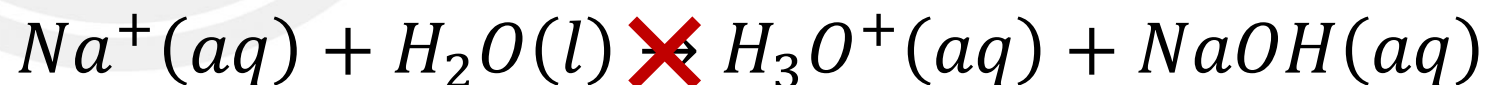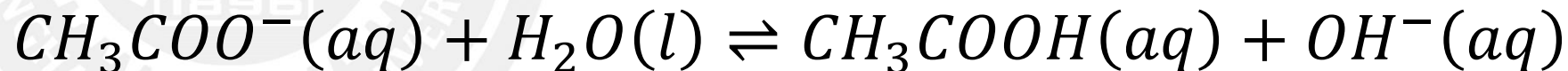
The pH of Salt Solutions

While comparing pK_a and pK_b values, we can make some observations:

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

$$pK_b = 9.25 \qquad\qquad pK_a = 4.75$$

$$Na^+(aq) + H_2O(l) \;❌\; H_3O^+(aq) + NaOH(aq)$$
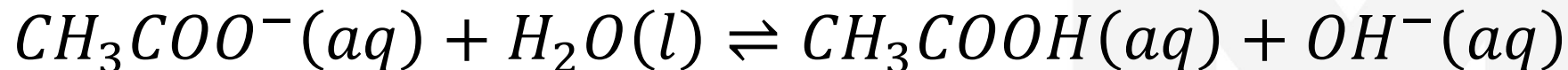
$$pK_a = 13.8 \qquad\qquad pK_b = 0.2$$

NaOH is a strong base and CH$_3$COOH is a weak acid, so NaCH$_3$COO is basic.

The pH of Salt Solutions

$$Cl^-(aq) + H_2O(l) \xcancel{\rightleftharpoons} OH^-(aq) + HCl(aq)$$

$$pK_b = 22 \qquad\qquad\qquad pK_a = -8$$

$$Na^+(aq) + H_2O(l) \xcancel{\rightleftharpoons} H_3O^+(aq) + NaOH(aq)$$

$$pK_a = 13.8 \qquad\qquad\qquad pK_b = 0.2$$
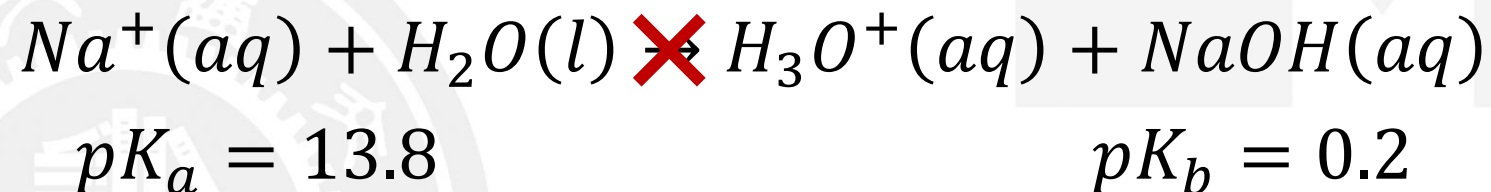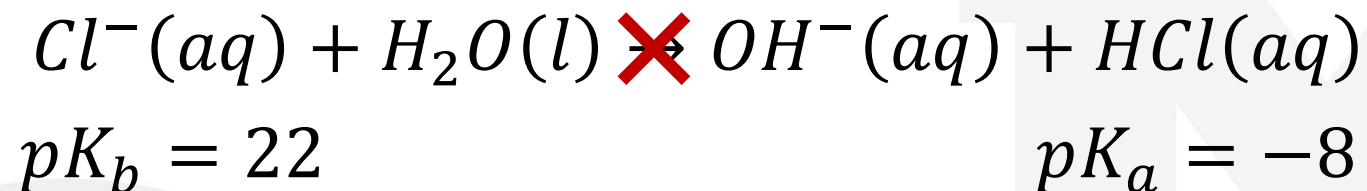
Both Cl$^-$ and Na$^+$ are <u>very weak</u>, while HCl and NaOH are <u>very strong.</u> Notice the *pK* values.

The pH of Salt Solutions – Cations

Character	Examples	K_a	pK_a
Acidic			
Conjugate acids of weak bases	Anilinium ion, $C_6H_5NH_3^+$	2.3×10^{-5}	4.64
	Pyridinium ion, $C_5H_5NH^+$	5.6×10^{-6}	5.24
	Ammonium ion, NH_4^+	5.6×10^{-10}	9.25
	Methylammonium ion, $CH_3NH_3^+$	2.8×10^{-11}	10.56
Small, highly charged metal cations	Fe^{3+} as $Fe(H_2O)_6^{3+}$	3.5×10^{-3}	2.46
	Cr^{3+} as $Cr(H_2O)_6^{3+}$	1.3×10^{-4}	3.89
	Al^{3+} as $Al(H_2O)_6^{3+}$	1.4×10^{-5}	4.85
	Cu^{2+} as $Cu(H_2O)_6^{2+}$	3.2×10^{-8}	7.49
	Ni^{2+} as $Ni(H_2O)_6^{2+}$	9.3×10^{-10}	9.03
	Fe^{2+} as $Fe(H_2O)_6^{2+}$	8×10^{-11}	10.1
Neutral			
Group 1 and 2 cations metal cations with charge +1	Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Ag^+		
Basic	none		

Small, highly charged metal cations that can act as Lewis acids in water, such as Al^{3+} and Fe^{3+}, produce acidic solutions.

$$Fe^{3+}(aq) + 2\, H_2O(l) \rightleftharpoons H_3O^+(aq) + Fe(OH)^{2+}(aq)$$
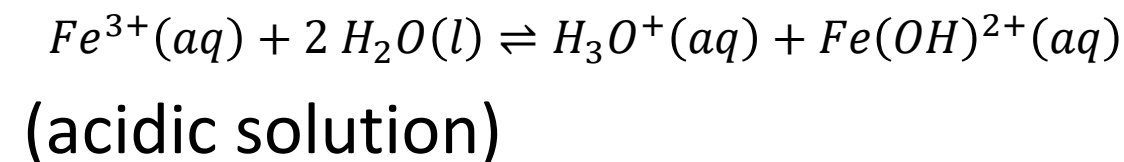
(acidic solution)

The pH of Salt Solutions – Anions

Hydrogen sulfate continues to react with water, so it is considered a strong acid.

$$HSO_4^-(aq) + H_2O(l) \rightarrow H_3O^+(aq) + SO_4^{2-}(aq)$$
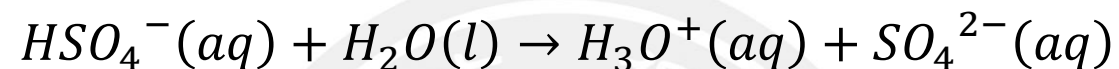
Basic solutions, here fluoride, react with water to make hydroxide, a base, and a weak acid HF and so make basic solutions.

$$F^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + HF(aq)$$
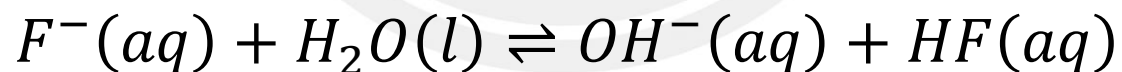
Character	Examples
Acidic	
Very few	HSO_4^-, $H_2PO_4^-$
Neutral	
Conjugate bases of strong acids	Cl^-, Br^-, I^-, NO_3^-, ClO_4^-
Basic	
Conjugate bases of weak acids	F^-, O^{2-}, S^{2-}, HS^-, CN^-, CO_3^{2-}, PO_4^{3-}, NO_2^-, CH_3COO^-, other carboxylate ions

Estimate the pH of 0.15 M NH$_4$Cl(aq), K_b of NH$_3$ is 1.8 × 10^{-5}.

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$
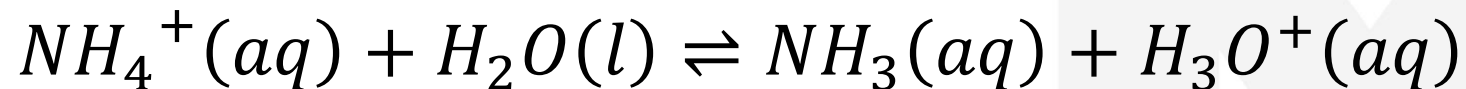
(Yes, weak acid to weak base will occur)

$$Cl^-(aq) + H_2O(l) \ \cancel{\rightleftharpoons}\ OH^-(aq) + HCl(aq)$$

(No, weak base to strong acid will not occur)

	NH$_4^+$	H$_3$O$^+$	NH$_3$
initial	0.15	0	0
change	-x	+x	+x
equilibrium (final)	0.15-x	x	x

$K_b = 1.8 \times 10^{-5} \ll 0.15$, so we can ignore the change in initial base concentration.

However, our reaction is written as an acid reaction, so we need K_a. $\left(NH_4{}^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)\right)$

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

$$K_a = \frac{x^2}{\left[NH_4{}^+\right]}$$

$$x = \sqrt{K_a \cdot \left[NH_4{}^+\right]} = \sqrt{5.6 \times 10^{-10} \times 0.15} = 9.2 \times 10^{-6}$$

$$\left[NH_4{}^+\right] = 0.15 \ \frac{\text{mol}}{\text{L}} \qquad\qquad \left[H_3O^+\right] = [NH_3] = 9.2 \times 10^{-6} \ \frac{\text{mol}}{\text{L}}$$

$$pH = -\log\left(\left[H_3O^+\right]\right) = -\log\left(9.2 \times 10^{-6}\right) = 5.04$$

$$degree \ of \ deprotonation = \frac{x}{\left[NH_4{}^+\right]_{initial}} = \frac{9.2 \times 10^{-6}}{0.15} = 6.13 \times 10^{-5}$$

Polyprotic Acids and Bases

A polyprotic acid is a compound that can **donate more than one** proton.

Common polyprotic acids include sulfuric acid, **H_2SO_4**, and carbonic acid, **H_2CO_3**, each of which can donate **two protons**, and phosphoric acid, H_3PO_4, which can donate **three protons**.

Polyprotic acids play a critical role in biological systems, because many enzymes can be regarded as polyprotic acids that carry out their vital functions.

Polyprotic Acids and Bases

A polyprotic base is a species that can accept more than one proton.

Examples include the **CO_3^{2-}** and **SO_3^{2-}** anions, both of which can **accept two protons**, and the PO_4^{3-} anion, which can accept three protons.

The existence of each of these species is dependent on pH.

The pH of Polyprotic Acids

Carbonic acid takes part in two successive proton transfer equilibria:

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq) \qquad K_{a1} = 4.3 \times 10^{-7}$$

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq) \qquad K_{a2} = 5.6 \times 10^{-11}$$
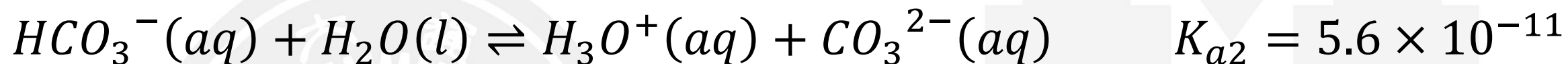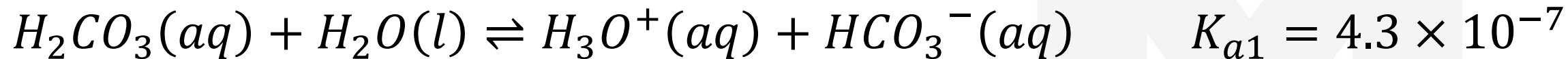
The conjugate base of H_2CO_3 in the first equilibrium, HCO_3^-, acts as an acid in the second equilibrium. That ion produces in turn its own conjugate base, CO_3^{2-}.

We *notice* that the acidity decreases significantly with each successive proton loss $\boldsymbol{K_{a1} \gg K_{a2}}$.

The pH of Polyprotic Acids

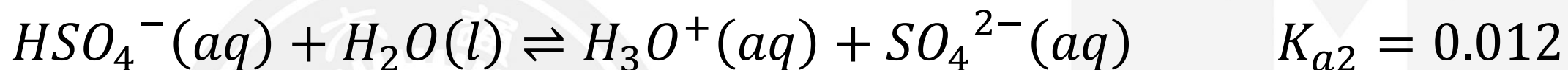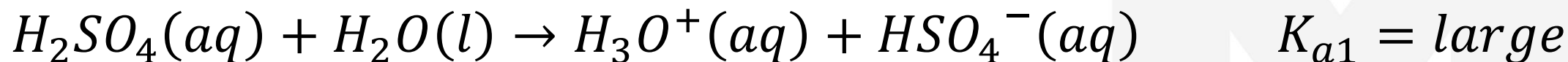| Acid	K_{a1}	pK_{a1}	K_{a2}	pK_{a2}	K_{a3}	pK_{a3}
Sulfuric acid, H_2SO_4	strong		1.2×10^{-2}	1.92		
Oxalic acid, $H_2C_2O_4$	5.9×10^{-2}	1.23	6.5×10^{-5}	4.19		
Sulfurous acid, H_2SO_3	1.5×10^{-2}	1.91	1.2×10^{-7}	6.91		
Phosphorous acid, H_3PO_3	1.0×10^{-2}	2.00	2.6×10^{-7}	6.59		
Phosphoric acid, H_3PO_4	7.6×10^{-3}	2.12	6.2×10^{-8}	7.21	2.1×10^{-13}	12.68
Tartaric acid, $C_2H_4O_2(COOH)_2$	6.0×10^{-4}	3.22	1.5×10^{-5}	4.82		
Carbonic, H_2CO_3	4.3×10^{-7}	6.37	5.6×10^{-11}	10.25		
Hydrosulfuric acid, H_2S	1.3×10^{-7}	6.89	7.1×10^{-15}	14.15		

For all polyprotic acids or bases, K_{a1} is always the **greatest contributor** to **the overall pH** of the solution—except for H_2SO_4.

Only H_2SO_4 has a large K_{a1} and K_{a2}.

Example

Estimate the pH of 0.10 M H_2SO_4. K_{a1} = large, K_{a2} = 0.012

$$H_2SO_4(aq) + H_2O(l) \rightarrow H_3O^+(aq) + HSO_4^-(aq) \qquad K_{a1} = large$$

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq) \qquad K_{a2} = 0.012$$

As the first reaction is complete, H_2SO_4 already produces 0.10 M H_3O^+ and we use K_{a2} in our ICE table to find the deprotonation of HSO_4^-.

	HSO_4^-	H_3O^+	SO_4^{2-}
initial	0.10	0.10	0
change	-x	+x	+x
equilibrium (final)	0.10-x	0.10+x	x

Example

As K_{a2} is of a similar order as the initial concentration, we have to use the quadratic formula to solve for x.

$$K_{a2} = \frac{(0.10 + x)x}{0.10 - x} = 0.012$$

$$0 = x^2 + 0.11x - 0.0012$$

Solving for x, using $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$:

$$x = \frac{-0.11 \pm \sqrt{(0.11)^2 - 4 \times 1 \times (-0.0012)}}{2} = 0.010$$

$$[HSO_4{}^-] = 0.10 - 0.010 = 0.09 \; \frac{mol}{L} \quad [SO_4{}^{2-}] = 0.010 \; \frac{mol}{L} \quad [H_3O^+] = 0.10 \; \frac{mol}{L} + 0.010 \; \frac{mol}{L} = 0.11 \; \frac{mol}{L}$$

$$pH = -\log([H_3O^+]) = -log(0.11) = 0.95$$

Reminder: This is rare, and only happens with strong acids.

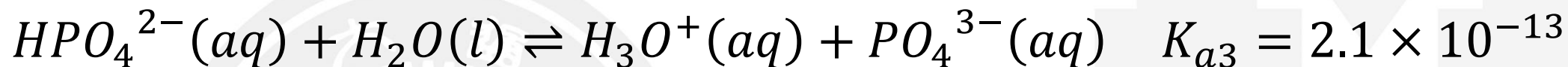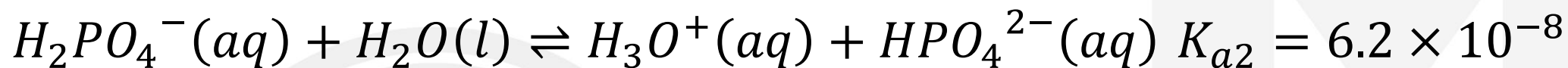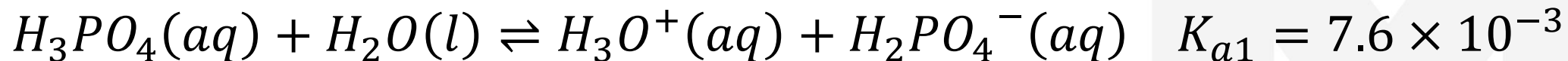# The Concentrations of Solute Species

Next, **we learn to calculate the concentrations** of all the solute species in solution, from pH.

To **simplify the calculations**, species with a **greater amount** are <u>not significantly affected</u> by concentrations of species present in the **smaller amount**.

Example

Calculate the concentrations of all solute species in 0.10 M H_3PO_4(aq).

$$H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_2PO_4^-(aq) \quad K_{a1} = 7.6 \times 10^{-3}$$

$$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HPO_4^{2-}(aq) \quad K_{a2} = 6.2 \times 10^{-8}$$

$$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + PO_4^{3-}(aq) \quad K_{a3} = 2.1 \times 10^{-13}$$

We need to set up an ICE table for each **K**, so there will be **three** ICE tables. This will help us find the concentrations of H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, H_3O^+, OH^-, and the pH value.

	H_3PO_4	H_3O^+	$H_2PO_4^-$
initial	0.10	0	0
change	-x	+x	+x
equilibrium (final)	0.10-x	x	x

As K_{a1} is of a similar order as the initial concentration, we have to use the quadratic formula to solve for x.

$$K_{a1} = \frac{x^2}{0.10 - x} = 7.6 \times 10^{-3}$$

$$0 = x^2 + 7.6 \times 10^{-3}x - 7.6 \times 10^{-4}$$

Solving for x, using $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$:

$$x = \frac{-7.6 \times 10^{-3} \pm \sqrt{(7.6 \times 10^{-3})^2 - 4 \times 1 \times (-7.6 \times 10^{-4})}}{2} = 0.024$$

$$[H_3PO_4] = 0.10 - 0.024 = 0.08 \frac{\text{mol}}{\text{L}} \qquad \boxed{[H_2PO_4^-] = [H_3O^+] = 0.024 \frac{\text{mol}}{\text{L}}}$$

Note: $H_2PO_4^-$ is not a strong acid, so the majority of H_3O^+ comes from the dissociation of H_3PO_4.

These values are the starting values for our **next ICE table**.

For our next K, K_{a2}, we find HPO_4^{2-}, noting $[H_3O^+]$ and $[H_2PO_4^-]$ come from our previous table, due to the strength of acid coming from the first step.

	$H_2PO_4^-$	H_3O^+	HPO_4^{2-}
initial	0.024	0.024	0
change	$-x$	$+x$	$+x$
equilibrium (final)	$0.024-x$	$0.024+x$	x

Solving for K_{a2}, two things happen: (1) in both $0.024 - x$, and $0.024 + x$, "x" the amount dissociated, 6.2×10^{-8} is so small that we ignore the change, and (2) our $x = 6.2 \times 10^{-8} = [HPO_4^{2-}]$.

$$K_{a2} = \frac{(0.024 + x)x}{0.024 - x} = \frac{(0.024)x}{0.024} = 6.2 \times 10^{-8}$$

$$[H_2PO_4^-] = \boxed{[H_3O^+] = 0.024 \, \frac{\text{mol}}{\text{L}}} \qquad \boxed{[HPO_4^{2-}] = 6.2 \times 10^{-8} \, \frac{\text{mol}}{\text{L}}}$$

Example

Using similar assumptions, we approach our third ICE table:

	HPO_4^{2-}	H_3O^+	PO_4^{3-}
initial	6.2×10^{-8}	0.024	0
change	$-x$	$+x$	$+x$
equilibrium (final)	$6.2 \times 10^{-8} - x$	$0.024 + x$	x

$$K_{a3} = \frac{(0.024 + x)x}{6.2 \times 10^{-8} - x} = \frac{(0.024)x}{6.2 \times 10^{-8}} = 2.1 \times 10^{-13}$$

$$x = 5.4 \times 10^{-19}$$

$$[H_3O^+] = 0.024 \ \frac{mol}{L} \quad [HPO_4^{2-}] = 6.2 \times 10^{-8} \ \frac{mol}{L} \quad [PO_4^{3-}] = 5.4 \times 10^{-19} \ \frac{mol}{L}$$

All concentrations:

$[H_3PO_4] = 0.080 \, \frac{\text{mol}}{\text{L}}$, from K_{a1}

$[H_2PO_4{}^-] = 0.024 \, \frac{\text{mol}}{\text{L}}$, from K_{a1}

$[HPO_4{}^{2-}] = 6.2 \times 10^{-8} \, \frac{\text{mol}}{\text{L}}$, from K_{a2}

$[PO_4{}^{3-}] = 5.4 \times 10^{-19} \, \frac{\text{mol}}{\text{L}}$, from K_{a3}

$[H_3O^+] = 0.024 \, \frac{\text{mol}}{\text{L}}$, from K_{a1} (no contribution from other equilibria)

$[OH^-] = \frac{1.0 \times 10^{-14}}{[H_3O^+]} = 4.2 \times 10^{-13} \, \frac{\text{mol}}{\text{L}}$, from $K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$

$pH = -\log([H_3O^+]) = -\log(0.024) = 1.62$

Autoprotolysis and pH

Asked to estimate the pH of 1.0×10^{-8} M HCl(aq) we might say pH = 8.00.

That is **absurd**, because pH of 8.00 is basic, whereas HCl is an acid!

Two sources of error occur with hydronium ions:

1) At very low acid concentrations, the supply of hydronium ions from the **autoprotolysis of water** is close to the **original source of acid**

2) Both sources must be taken into account!

We discuss this in the next two sections, first taking into account autoprotolysis for <u>strong</u> acids and bases and then for <u>weak</u> ones.

Very Dilute Solutions of Strong Acids and Bases

We have to include the contribution of autoprotolysis to pH only when the concentration of strong acid or base is **less than about 10^{-6} mol·L^{-1}**.

We need to consider **all** species in solution.

HCl, a strong acid would have, besides water, H_3O^+, OH^-, and Cl^- ions in a solution. We need **three equations** to find all their concentrations.

The first equation takes the **charge balance** into account for an <u>electrically neutral solution</u>. As there is only one type of cation, H_3O^+:

$$[H_3O^+] = [OH^-] + [Cl^-] \text{ or } [OH^-] = [H_3O^+] - [Cl^-]$$

(charge-balance relation)

Very Dilute Solutions of Strong Acids and Bases

The second equation takes **material balance** into account; all <u>added solute</u> must be accounted for. Because HCl is a strong acid, the concentration of Cl⁻ ions in the solution is equal to the initial concentration of HCl:

$$[Cl^-] = [HCl]_{initial}$$

(material balance)

$$[OH^-] = [H_3O^+] - [Cl^-] = [H_3O^+] - [HCl]_{initial}$$

The third equation is K_w:

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

$$[OH^-] = [H_3O^+] - [Cl^-]$$ charge-balance

$$[Cl^-] = [HCl]_{initial}$$ material balance

$$K_w = [H_3O^+][OH^-]$$ autoprotolysis of water

Combining:

$$K_w = [H_3O^+]([H_3O^+] - [HCl]_{initial})$$

$$[H_3O^+]^2 - ([H_3O^+][HCl]_{initial}) - K_w = 0 \text{ for any acid around pH 6.}$$

For a base, we consider NaOH and arrive at a similar solution:

$$[H_3O^+]^2 - ([H_3O^+][NaOH]_{initial}) - K_w = 0 \text{ for any acid around pH 8.}$$

Example

What is the pH of 8.0×10^{-8} M HCl(aq) solution?

$$[H_3O^+]^2 - ([H_3O^+][HCl]_{initial}) - K_w = 0$$

$$[H_3O^+]^2 - ([H_3O^+]8.0 \times 10^{-8}) - 1.0 \times 10^{-14} = 0$$

Solving with the quadratic formula:

$$[H_3O^+] = \frac{-8.0 \times 10^{-8} \pm \sqrt{(8.0 \times 10^{-8})^2 - 4 \times 1 \times (-1.0 \times 10^{-14})}}{2} = 1.5 \times 10^{-7} \frac{mol}{L}$$

$$pH = -\log([H_3O^+]) = -\log(1.5 \times 10^{-7}) = 6.82$$

Very Dilute Solutions of Weak Acids

For weak acids autoprotolysis of water often is the greatest contributing factor to pH.

Four species exist for a weak acid in a solution: HA, A⁻, H_3O^+, and OH⁻.

Both $K_w = [H_3O^+][OH^-]$ and $K_a = \dfrac{[H_3O^+][A^-]}{[HA]}$ are used to arrive at the following cubic equation (derivation is shown in the textbook).

$$[H_3O^+]^3 - K_a[H_3O^+]^2 - (K_w + K_a[HA]_{initial})[H_3O^+] - K_aK_w = 0$$

Example

Estimate the pH of a 1.0×10^{-4} M aqueous phenol solution.

The $K_a = 1.3 \times 10^{-10}$.

$$[H_3O^+]^3 - K_a[H_3O^+]^2 - (K_w + K_a[HA]_{initial})[H_3O^+] - K_aK_w = 0$$

$$[H_3O^+]^3 - 1.3 \times 10^{-10}[H_3O^+]^2 - (1.0 \times 10^{-14} + 1.3 \times 10^{-10}[HA]_{initial})[H_3O^+] - 1.3 \times 10^{-10} \times 1.0 \times 10^{-14} = 0$$

Solving for $[H_3O^+]$ yields:

$$[H_3O^+] = 1.5 \times 10^{-7} \frac{\text{mol}}{\text{L}}$$

$$pH = -\log([H_3O^+]) = -\log(1.5 \times 10^{-7}) = 6.82$$