Acids and Bases
An Introduction

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Properties of Acids

1. Sour taste

   (examples: vinegar, citric acid, lemon juice)
2. Turns litmus from blue to red (also affects other indicators)
3. Reacts with metals to liberate H_2
4. Reacts with base losing its acid properties
5. Reacts with salts to give a new acid and a new salt
6. Conducts electricity (electrolyte)

Properties of Bases

1. Bitter taste (examples: baking soda, soap)
2. Turns litmus from red to blue (also affects other indicators – best known is phenolphthalein)
3. Soapy feel
4. Reacts with acid losing its basic properties
5. Conducts electricity (electrolyte)

The Arrhenius Theory

- **Svante August Arrhenius (1859 –1927)**
  - **Acid: Substance that produces hydrogen ions in water solution.**

$$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

  - **Base: Substance that produces hydroxide ions in water solution.**

$$NaOH_{(aq)} \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$$

  - **An acid neutralizes a base**

$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$$

The Arrhenius Theory

- **Acid strength depends on the amount of hydrogen ions produced.**
  - **Definition includes acids such as HCl, HBr, HI, HNO_3, H_2SO_4, HSO_4^-, $HC_2H_3O_2$, etc.**
- **Base strength depends on amount of hydroxide ions produced.**
  - **Definition includes bases such as NaOH, KOH, $Ca(OH)_2$, $Mg(OH)_2$, $Al(OH)_3$, etc.**

The Arrhenius Theory

- **Problems with the Arrhenius Theory**
  - The solvent is limited to water, but water is not involved in the acid-base reaction
  - A solution of CO_2 in water is acidic, but H_2CO_3 exists at a concentration less than 1% of the CO_2
  - A solution of NH_3 in water is basic, but NH_4OH does not exist (Note: the formula NH_4OH was invented by Arrhenius to explain the basic nature of NH_3 solutions)
  - The reaction of HCl and NH_3 results in an acidic solution

A Generalized Arrhenius Theory

The solvent (water) can ionize to produce H^+ and OH^- ions

$$H_2O_{(l)} \leftrightarrows H^+_{(aq)} + OH^-_{(aq)}$$

Acid: Substance that increases the concentration of hydrogen ions in solution.

$$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

A strong acid is 100% dissociated

A weak acid is only slightly dissociated

A Generalized Arrhenius Theory

Base: Substance that increases the concentration of hydroxide ions in water solution.

$$NaOH_{(aq)} \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$$

A strong base is 100% dissociated

A weak base is only slightly dissociated

Hydrolysis reactions can change H^+ and OH^- concentration in water solution

$$CO_2 + H_2O \leftrightarrows H^+ + HCO_3^-$$ **CO_2 is an acid**

$$NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-$$ **NH_3 is a base**

A Generalized Arrhenius Theory

Solvents other than water can be used:

The solvent can ionize to produce positive and negative ions

Example: liquid ammonia, NH_3

$$2\ NH_3 \leftrightarrows NH_4^+ + NH_2^-$$

Acid: Substance that increases the concentration of the positive ion in solution.

$$HCl + NH_3 \rightarrow NH_4^+ + Cl^-$$

Base: Substance that increases the concentration of the negative ion in water solution.

$$NaOH + NH_3 \rightarrow Na^+ + NH_2^- + H_2O_{(l)}$$

A Generalized Arrhenius Theory

Solvents other than water (continued)

Neutralization produces the solvent:

Example: In liquid ammonia, NH_3

$$NH_4^+ + NH_2^- \rightarrow 2\ NH_3$$

The Brønsted–Lowry Theory

Johannes Nicolaus Brønsted (*1879-1947)* *and* Thomas Martin Lowry (1874-1936)

independently proposed the proton definition of acids and bases in 1923

Quoting Brønsted:

". . . acids and bases are substances that are capable of splitting off or taking up hydrogen ions, respectively."

or

An acid-base reaction consists of the transfer of a proton (or hydrogen ion) from an acid to a base

The Brønsted–Lowry Theory

An acid is a proton donor

That is, an acid is a substance from which a proton (H^+) can be removed.

A Base is a proton acceptor

That is, a base is a substance that has a non-bonded electron pair that can bond with a proton (H^+) from an acid.

No solvent is specified

The Brønsted–Lowry Theory

If a substance can either lose a proton or gain a proton, then it is **amphiprotic**

Some examples are

HCO_3^- , HSO_4^- , and H_2O

Using HCO_3^-:

as an acid: $HCO_3^- + H_2O \leftrightarrows H_3O^+ + CO_3^{2-}$

as a base: $HCO_3^- + H_3O^+ \leftrightarrows H_2CO_3 + H_2O$

Note that the proton (H^+) is combined with water forming H_3O^+

The Brønsted–Lowry Theory

$$HCl + H_2O \leftrightarrows H_3O^+ + Cl^-$$

Looking at the forward reaction:

HCl is an acid, because it has a proton available to be transferred.

H_2O is a base, since it bonds with the proton that the acid lost.

Looking at the reverse reaction:

H_3O^+ is an acid, because it can give a proton to the Cl^-

Cl^- is a base, since it can bond with the proton from H_3O^+

Note that each pair HCl and Cl^-, and, H_2O and H_3O^+ differ by one proton. These pairs are called conjugate acid-base pairs

The Brønsted–Lowry Theory

So, in the reaction:

$$HCl + H_2O \leftrightarrows H_3O^+ + Cl^-$$

Acid	Base	Conjugate Acid	Conjugate Base

One acid-base conjugate pair is HCl and Cl^-

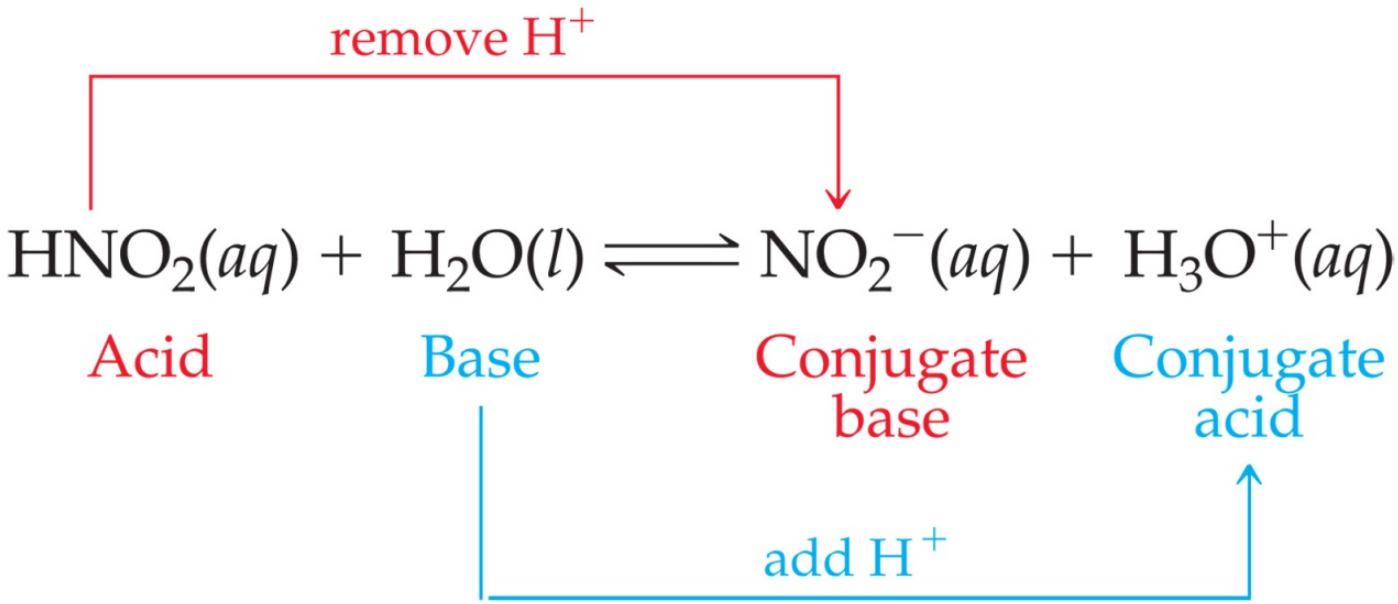
HCl is an acid, and Cl^- is the conjugate base of HCl

The second acid-base conjugate pair is H_2O and H_3O^-

H_2O is a base, and H_3O^+ is the conjugate acid of H_2O

Conjugate Acids and Bases:

- From the Latin word ***conjugare***, meaning "to join together."
- Reactions between acids and bases always yield their conjugate bases and acids.
- Another example is:



Strong Acids

HNO_3, HCl, H_2SO_4 and $HClO_4$ are the most commonly known strong acids.

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

hydrochloric acid
strong electrolyte
= 100% ionized

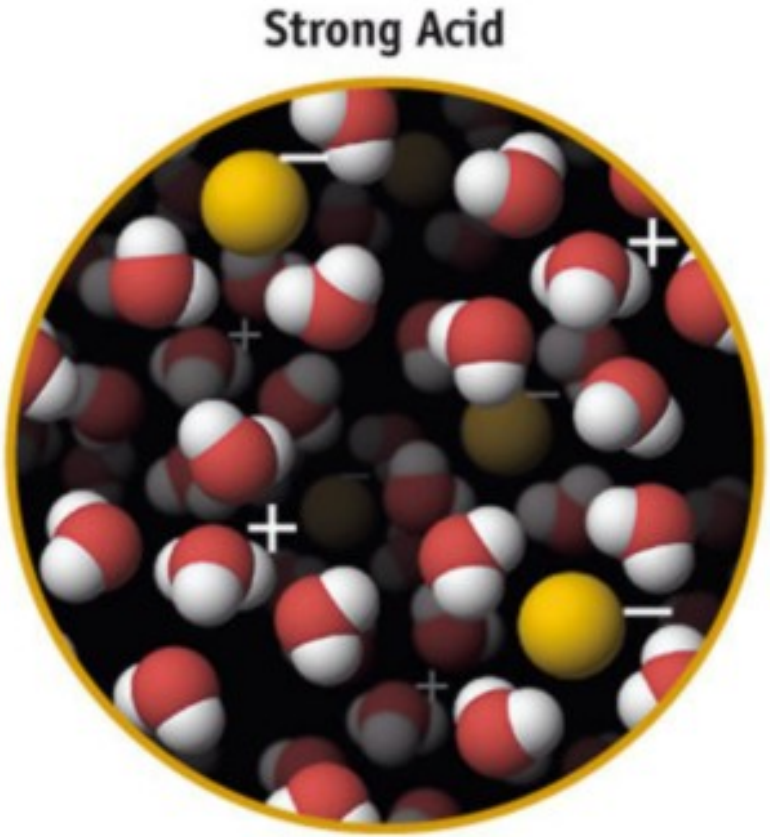
water

hydronium ion

chloride ion

Strong Acids

This is a “submicroscopic” artist’s view

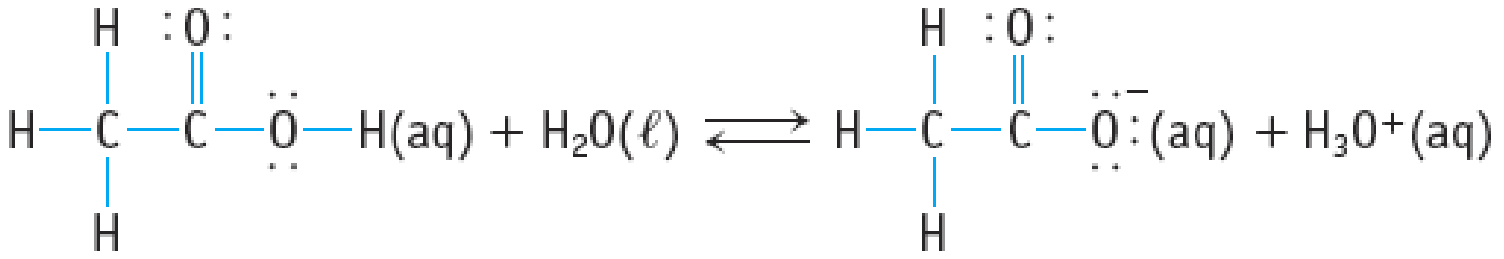


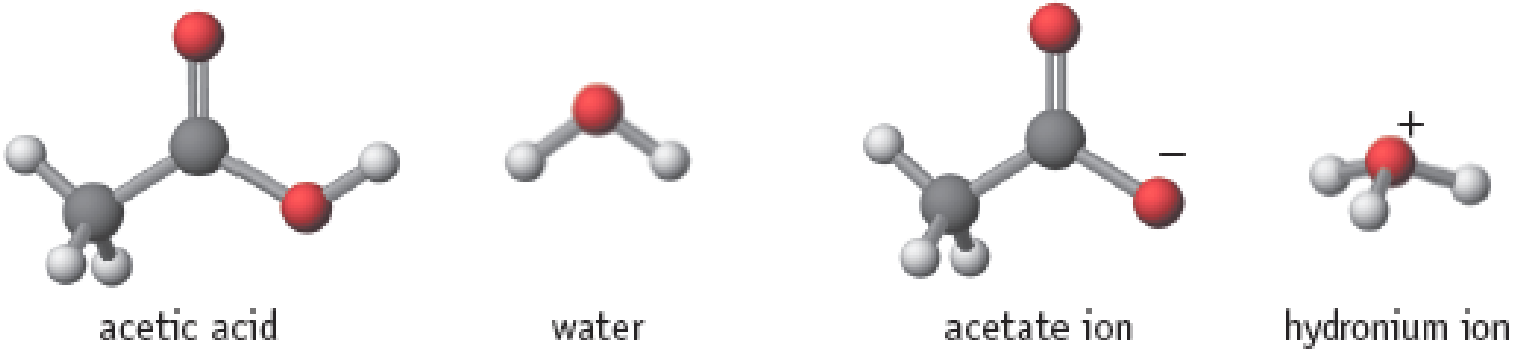
HCl completely ionizes in aqueous solution.

Weak Acids

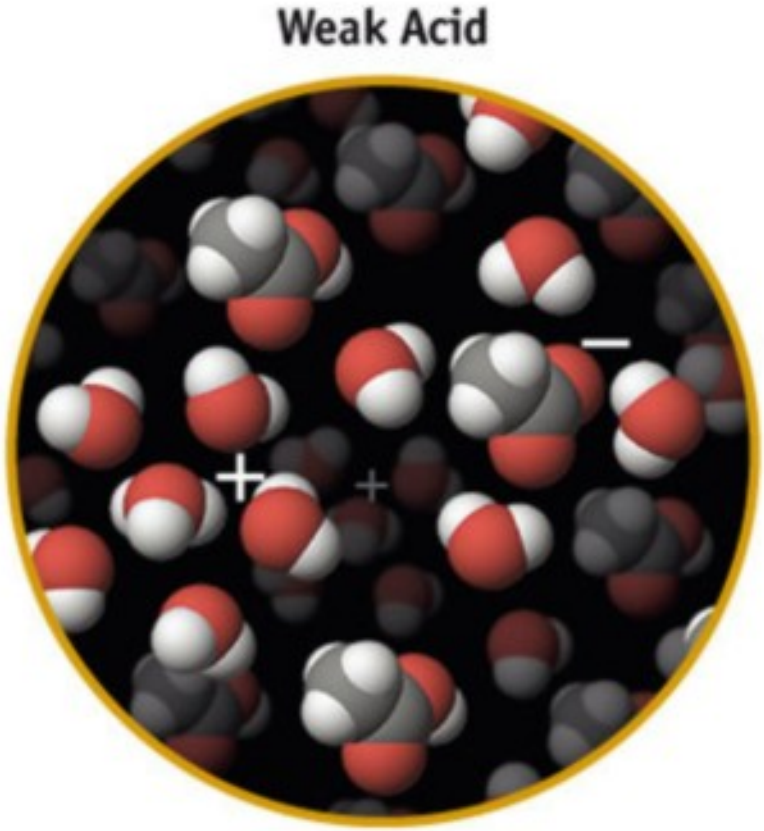
Weak acids are much less than 100% ionized in water (usually 5% ionic or less)

One of the best known weak acids is acetic acid, CH_3CO_2H





Weak Acids



Acetic acid, CH_3CO_2H, ionizes only slightly in water.

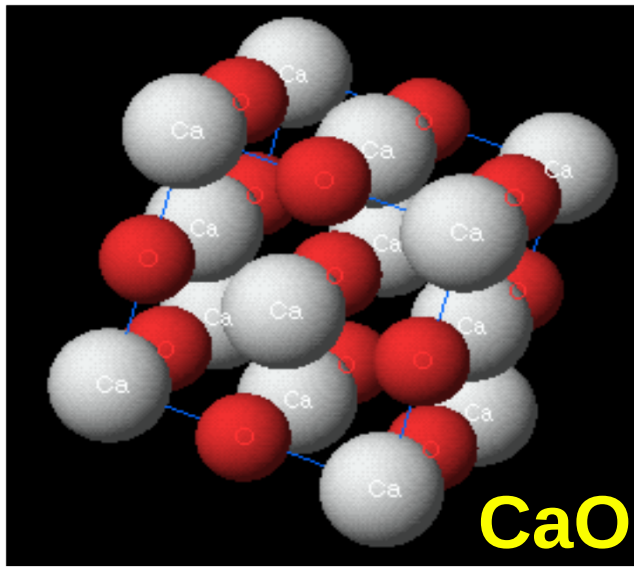
Strong Bases

A Strong Base is 100% dissociated in water.

$$NaOH_{(aq)} \rightarrow Na^{+}_{(aq)} + OH^{-}_{(aq)}$$

Other common strong bases include KOH and $Ca(OH)_2$

$$CaO \text{ (lime)} + H_2O \rightarrow Ca(OH)_2 \text{ (slaked lime)}$$

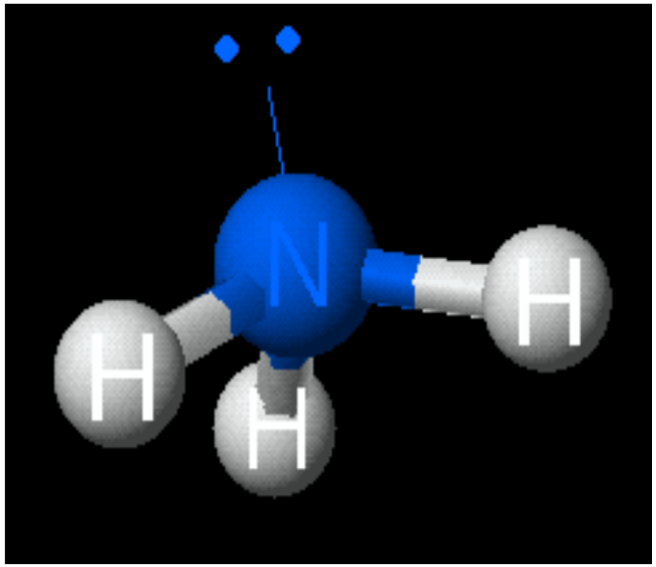


Weak Bases

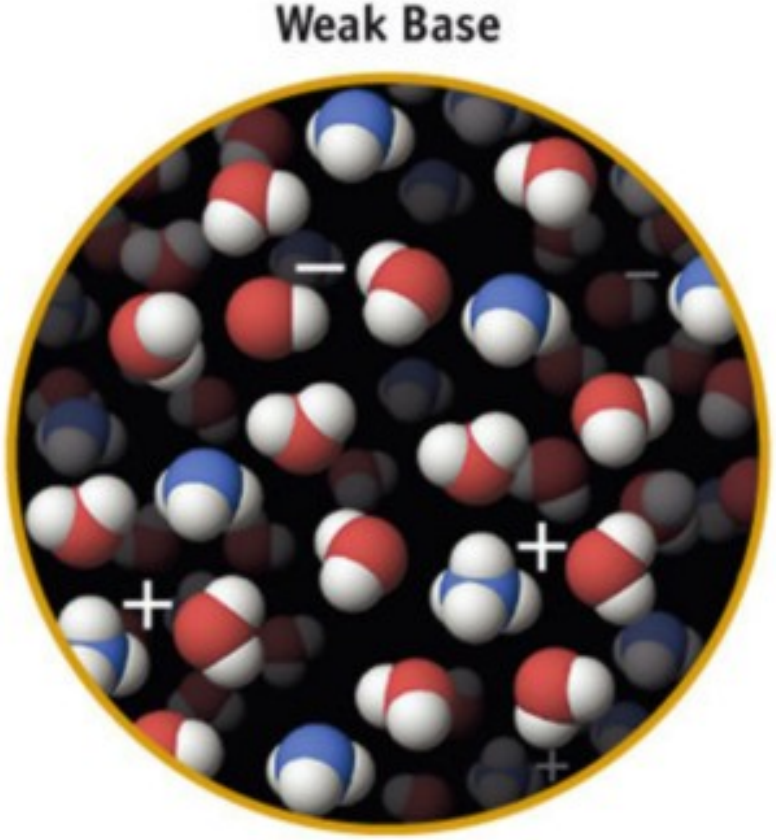
A Weak base is less than 100% ionized in water

One of the best known weak bases is ammonia

$$NH_{3(aq)} + H_2O_{(l)} \leftrightarrows NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$$



Weak Bases



The weak base ammonia reacts to a small extent with water to give a weakly basic solution.

Strong Acids

- The seven strong acids are HCl, HBr, HI, HNO_3, H_2SO_4, $HClO_3$, and $HClO_4$.

- These are, by definition, strong electrolytes and exist totally as ions in aqueous solution (i.e.,they are 100% ionic in solution)

- For the monoprotic strong acids, the concentration of H_3O^+ is equal to the concentration of the acid:

$$[H_3O^+] = [\text{acid}]$$

Strong Bases

- Strong bases are the soluble hydroxides, which are the alkali metal and heavier alkaline earth metal hydroxides (Ca^{2+}, Sr^{2+}, and Ba^{2+}).

- Strong bases dissociate completely in aqueous solution (i.e., they are 100% ionic in solution).

- For a monohydroxy strong base, the concentration of OH^- is equal to the concentration of the base:

$$[OH^-] = [base]$$

Weak Acids

Acetic acid, $HC_2H_3O_2$, is a weak acid

$$HC_2H_3O_{2(aq)} + H_2O_{(l)} \rightleftarrows H_3O^+_{(aq)} + C_2H_3O_2^-{}_{(aq)}$$

Acetate is a stronger base than H_2O, so the molecular form (the left side of the equation) is favored.

Only about 1% of the acetic acid is ionic.

Polyprotic Acids

- Have more than one ionizable H
- A common polyprotic acid is sulfuric acid, H_2SO_4
- The dissociation of a polyprotic acid is written to take place in steps:

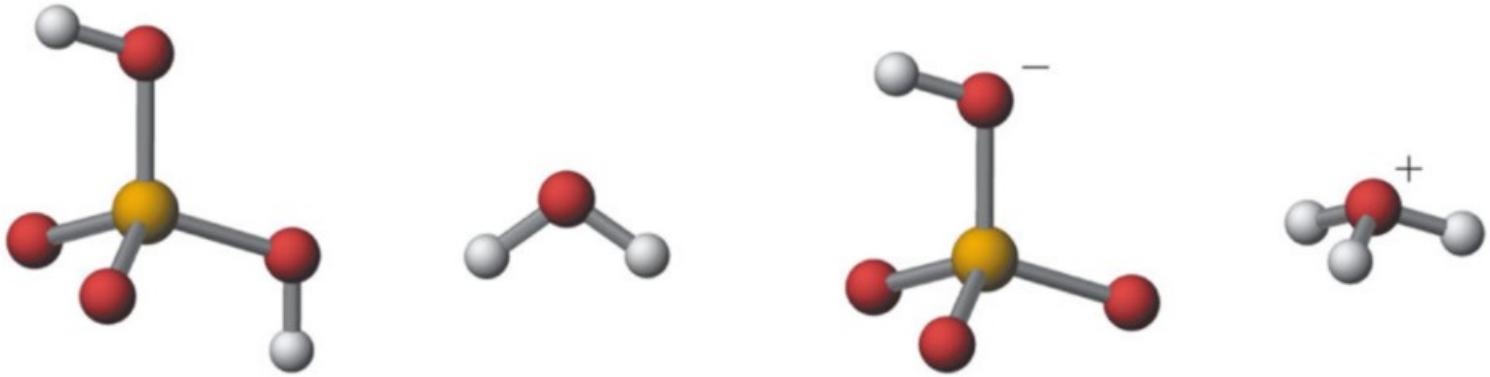
$$H_2SO_{4\,(aq)} + H_2O_{\,(l)} \leftrightarrows HSO_4^-{}_{(aq)} + H_3O^+_{(aq)}$$

$$HSO_4^-{}_{(aq)} + H_2O_{\,(l)} \leftrightarrows SO_4^{2-}{}_{(aq)} + H_3O^+_{(aq)}$$

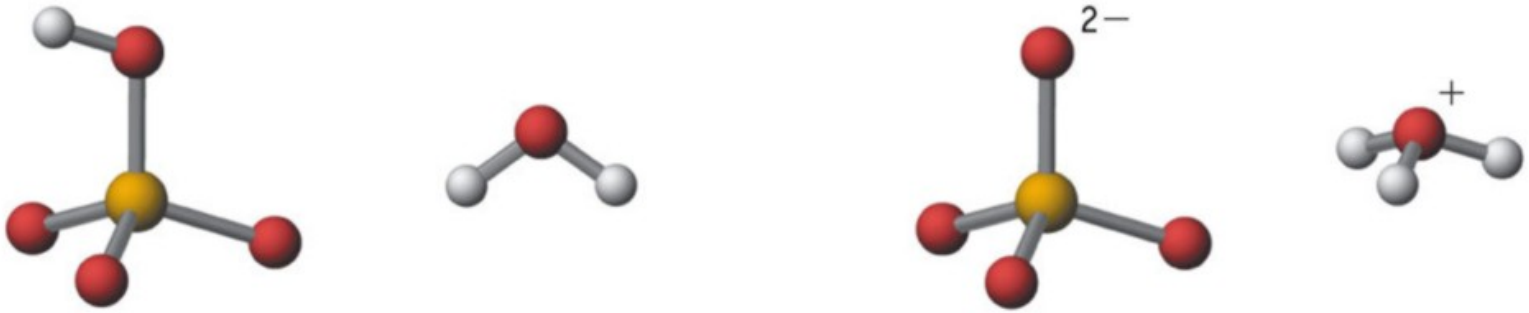
- For a weak acid or weak base, all the ions shown in the equation are present in solution.

Polyprotic Acids

$$H_2SO_4(aq) + H_2O(\ell) \rightleftharpoons HSO_4^-(aq) + H_3O^+(aq)$$



$$HSO_4^-(aq) + H_2O(\ell) \rightleftharpoons SO_4^{2-}(aq) + H_3O^+(aq)$$



Polyprotic Acids

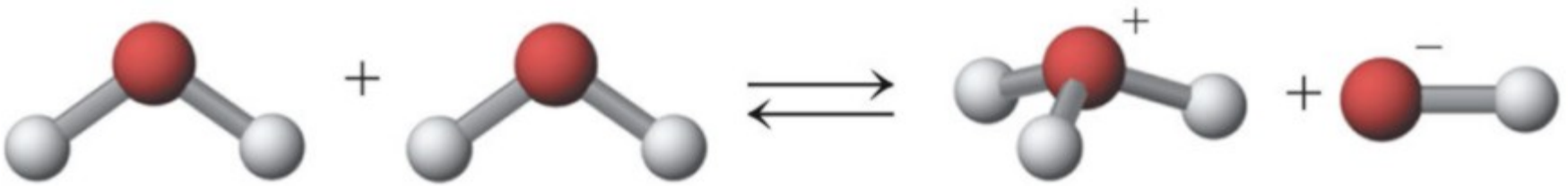
Names of Some Common Polyprotic Acids and Bases

Acid Form	Amphiprotic Form	Base Form
H_2S (hydrosulfuric acid or hydrogen sulfide)	HS^- (hydrogen sulfide ion)	S^{2-} (sulfide ion)
H_3PO_4 (phosphoric acid)	$H_2PO_4^-$ (dihydrogen phosphate ion)	PO_4^{3-} (phosphate ion)
	HPO_4^{2-} (hydrogen phosphate ion)	
H_2CO_3 (carbonic acid)	HCO_3^- (hydrogen carbonate ion or bicarbonate ion)	CO_3^{2-} (carbonate ion)
$H_2C_2O_4$ (oxalic acid)	$HC_2O_4^-$ (hydrogen oxalate ion)	$C_2O_4^{2-}$ (oxalate ion)

Autoionization of Water

- Water is amphoteric.
- In pure water, a few molecules act as bases and a few act as acids.

$$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$



- This process is referred to as **autoionization**.

Autoionization of Water

- The product of the concentrations of H_3O^+ and OH^- is given by the equation:

$$K_w = [H_3O^+]\,[OH^-] = 1.00 \times 10^{-14} \text{ at } 25\ ^oC$$

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

so $[H_3O^+] = [OH^-] = 1.00 \times 10^{-7}$ M

pH

A common way to express acidity and basicity is with pH

pH is defined as the negative logarithm (to the base 10) of the hydrogen ion (hydronium) concentration

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

In a neutral solution,

$$[H_3O^+] = [OH^-] = 1.00 \times 10^{-7} \text{ at } 25\ ^oC$$

$$pH = -\log (1.00 \times 10^{-7})$$

$$= - (-7) = 7$$

pH

- **Therefore, in pure water,**

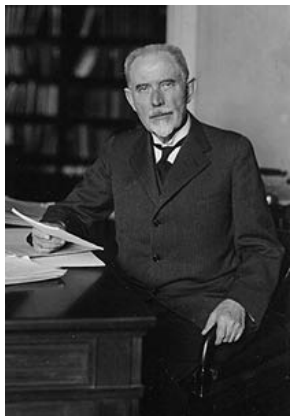
$$pH = -\log (1.0 \times 10^{-7}) = 7.00$$

- **An acid has a higher $[H_3O^+]$ than pure water, so its pH is <7**
- **A base has a lower $[H_3O^+]$ than pure water, so its pH is >7.**

Solution Type	$[H^+]$ (M)	$[OH^-]$ (M)	pH Value
Acidic	$>1.0 \times 10^{-7}$	$<1.0 \times 10^{-7}$	<7.00
Neutral	$=1.0 \times 10^{-7}$	$=1.0 \times 10^{-7}$	=7.00
Basic	$<1.0 \times 10^{-7}$	$>1.0 \times 10^{-7}$	>7.00

pH

- **The concept of pH was first introduced by Danish chemist Søren Peder Lauritz Sørensen (1868-1939), the head of the Carlsberg Laboratory's Chemical Department, in 1909**
- **Dr. Sørensen developed the pH scale during his pioneering research into proteins, amino acids and enzymes - the basis of today's protein chemistry in a paper titled "Enzyme Studies II. The Measurement and Meaning of Hydrogen Ion Concentration in Enzymatic Processes":**



> **The value of the hydrogen ion concentration will accordingly be expressed by the hydrogen ion based on the normality factor of the solution used, and this factor will have the form of a *negative power of 10.* Since in the following section I usually refer to this, I will explain here that *I use the name "hydrogen ion exponent" and the designation P_H for the numerical value of the exponents of this power.***

Sørensen and the Carlsberg Chemistry Department

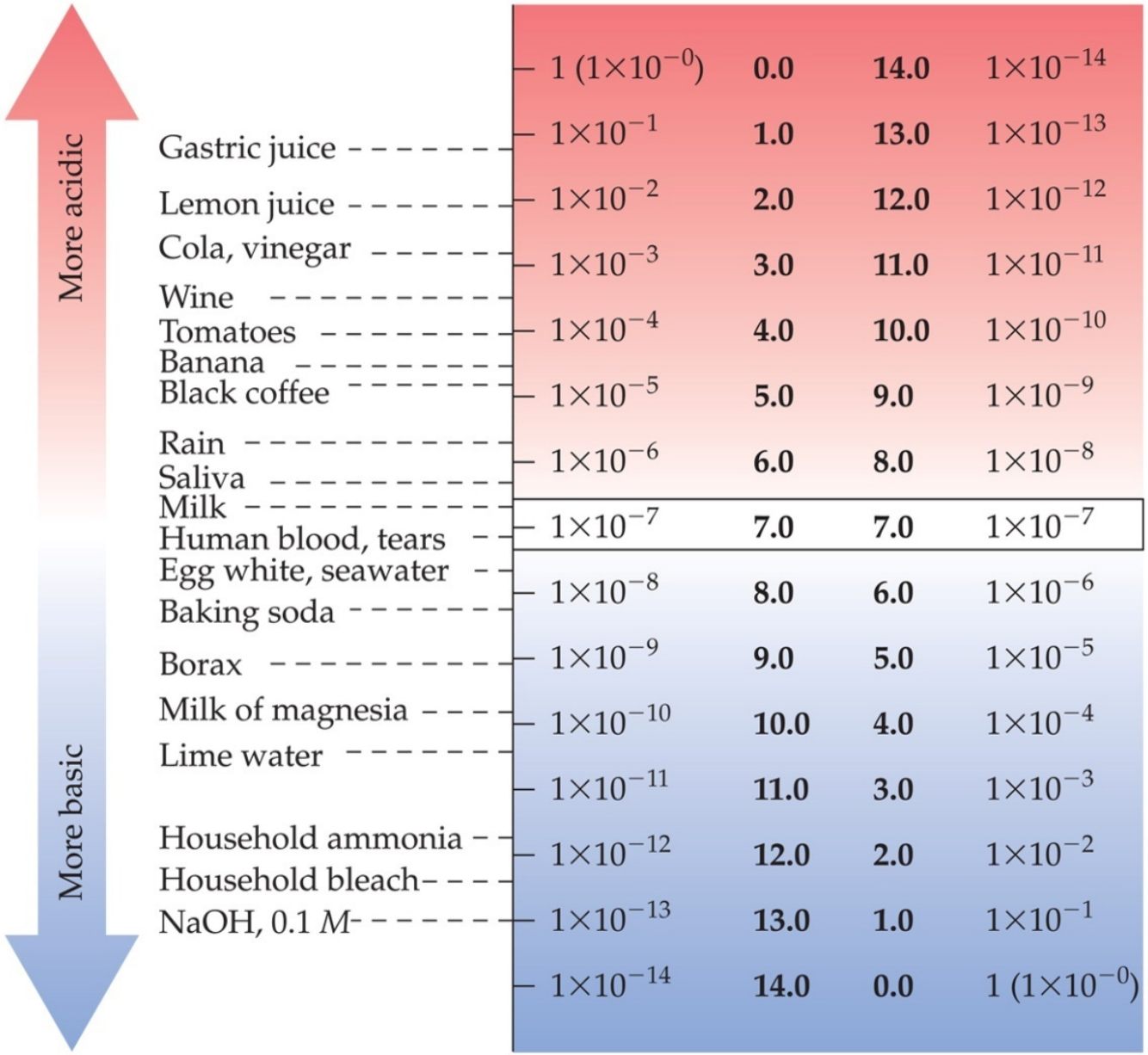
pH

- Today, we refer to pH as meaning ‘the power of hydrogen’.
- The pH scale provides a simple and universal measurement of the amount of hydrogen ions in a solution, which affects its acidity and how it reacts chemically.
- Each value of pH means the H^+ concentration changes by a factor of 10
- As the H^+ concentration decreases, the OH^- concentration increases

pH 1 **strong acid** | **weak acid** | **pH 7** **neutral** | **weak base** | **pH 14** **strong base**

The pH scale according to the late Dr. Hubert Alyea, Princeton University

pH values for some common substances



$[H^+]$ (*M*)	pH	pOH	$[OH^-]$ (*M*)
1 (1×10^{-0})	**0.0**	**14.0**	1×10^{-14}
1×10^{-1}	**1.0**	**13.0**	1×10^{-13}
1×10^{-2}	**2.0**	**12.0**	1×10^{-12}
1×10^{-3}	**3.0**	**11.0**	1×10^{-11}
1×10^{-4}	**4.0**	**10.0**	1×10^{-10}
1×10^{-5}	**5.0**	**9.0**	1×10^{-9}
1×10^{-6}	**6.0**	**8.0**	1×10^{-8}
1×10^{-7}	**7.0**	**7.0**	1×10^{-7}
1×10^{-8}	**8.0**	**6.0**	1×10^{-6}
1×10^{-9}	**9.0**	**5.0**	1×10^{-5}
1×10^{-10}	**10.0**	**4.0**	1×10^{-4}
1×10^{-11}	**11.0**	**3.0**	1×10^{-3}
1×10^{-12}	**12.0**	**2.0**	1×10^{-2}
1×10^{-13}	**13.0**	**1.0**	1×10^{-1}
1×10^{-14}	**14.0**	**0.0**	1 (1×10^{-0})

The Leveling Effect

- The pH scale ranges from 0 to 14
- Can an acid or base have a pH lower than 0 or higher than 14?
- When a strong acid, such as HCl, is dissolved in water, it reacts to form H_3O^+ in the following reaction:

$$HCl_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$$

- Any acid that is stronger than H_3O^+ reacts with H_2O to form H_3O^+; therefore, no acid can be stronger than H_3O^+ in H_2O.

The Leveling Effect

- In the same way, a base which is stronger than the conjugate base of water, such as sodium oxide, will react with water to give the weaker base which is the hydroxide ion, OH^-:

$$Na_2O_{(s)} + H_2O \rightarrow 2OH^-_{(aq)} + 2Na^+_{(aq)}$$

Note: The actual base here is the oxide ion since the sodium ion is an extremely weak acid or base.

- All bases which are stronger than the hydroxide ion will react with water to produce hydroxide ion.
- Although oxide ion, amide ion, ethoxide ion, and methoxide ion are all stronger bases than hydroxide ion, their strength in aqueous solution is leveled to that of hydroxide ion.
- Any base that is stronger than OH^- reacts with H_2O to form OH^-; therefore, no base can be stronger than OH^- in H_2O.

The Leveling Effect

- Can the strengths of strong acids or bases can be differentiated?
- The leveling effect operates in any protonic solvent. If a solvent other than water is used, differences between strengths of strong acids or bases can be measured.
- In liquid ammonia, for example, all acids are levelled to the strength of the ammonium ion, NH_4^+, and all bases are leveled to the strength of the amide ion, NH_2^-.

$$2\ NH_3 \leftrightarrows NH_4^+ + NH_2^-$$

- Many of the acids which are weak in water act as strong acids in liquid ammonia because they are stronger than ammonium ion.
- Not all of the bases which are strong in water are also strong in liquid ammonia.

The Leveling Effect

- Glacial acetic acid is another protonic solvent in which the leveling effect takes place.

$$HC_2H_3O_2 \leftrightarrows H^+ + C_2H_3O_2^-$$

- Glacial acetic acid can be used to show that hydrogen chloride is a weaker acid than is perchloric acid, since hydrogen chloride behaves as a weak acid in glacial acetic acid.
- Methanol is also a protonic solvent in which some of the acids which are strong (completely dissociated) in water are found partially in molecular form

pH and pOH

Previous we saw:

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

If we take the negative log of $[H_3O^+]$ and $[OH^-]$

$$-\log [H_3O^+] + -\log [OH^-] = -\log K_w = 14.00$$

or, in other words,

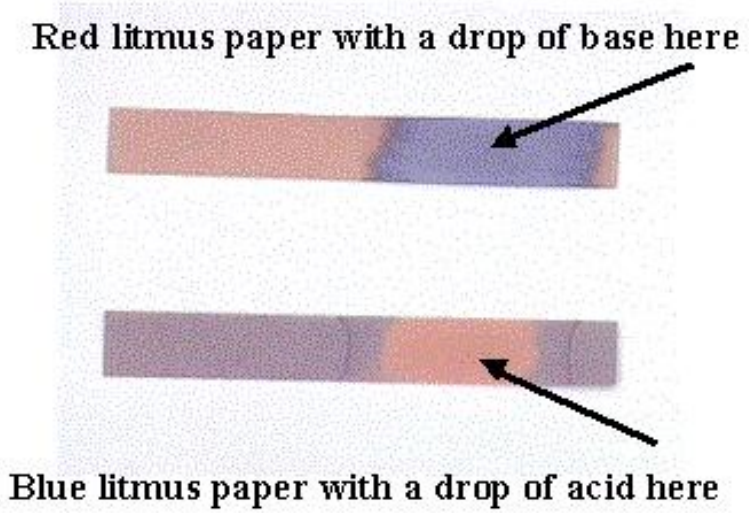
$$pH + pOH = pK_w = 14.00$$

Measuring pH

- **For a simple acid or base determination we use an indicator known as Litmus paper**
  - **Litmus is a water soluble mixture of different dyes extracted from lichens, especially *Roccella tinctoria*.**
  - **The name litmus comes from Middle English litemose (of Scandinavian origin; akin to Old Norse *litmosi*, dyer's herbs : litr, color, dye + mosi, bog, moss) and Middle English lykemose (from Middle Dutch lijkmoes, variant of lēcmoes : lēken, to drip + moes, moss).**

"Red" litmus paper turns blue above ~pH = 8

"Blue" litmus paper turns red below ~pH = 5



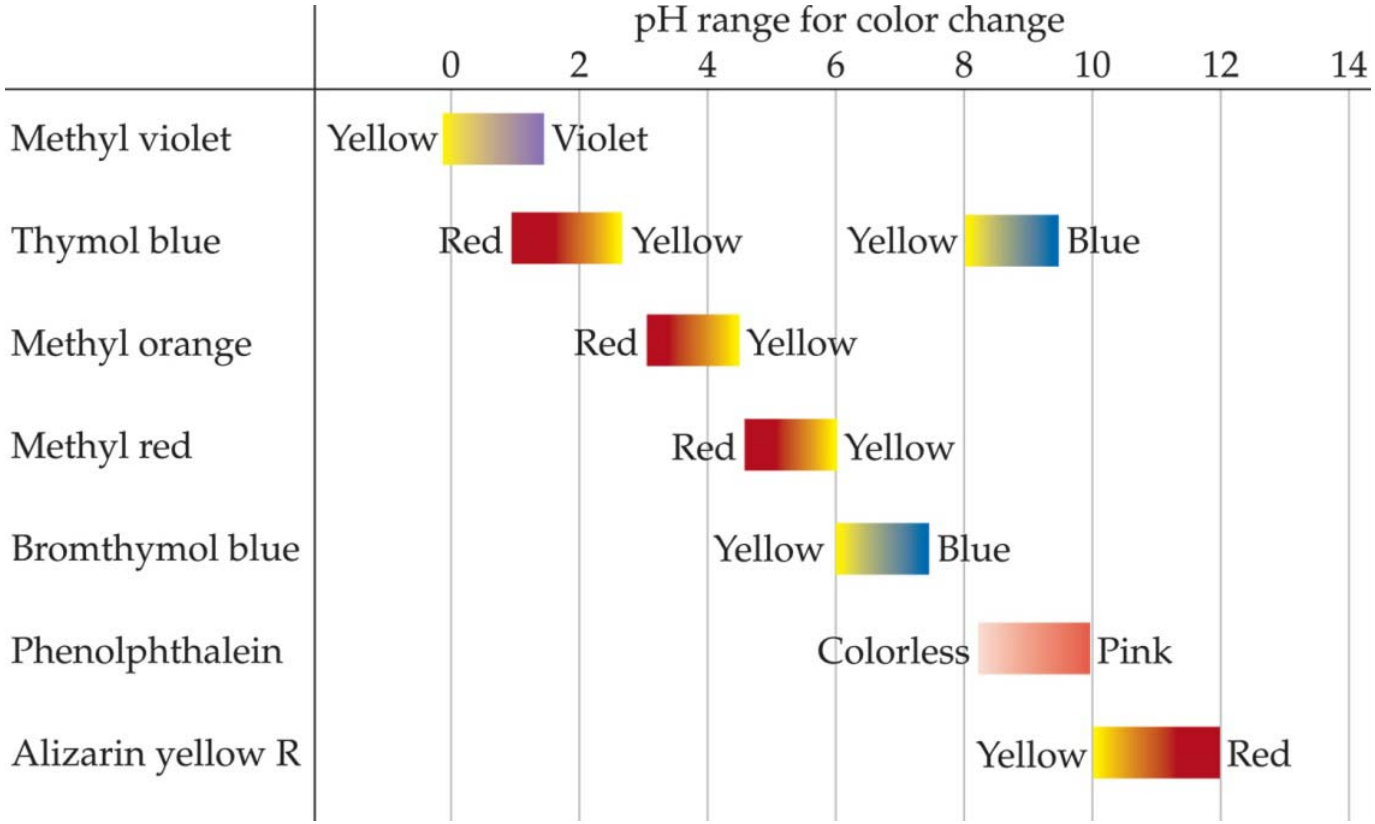
Measuring pH

- pH test papers are made using a mixture of dyes to indicate pH values over a wide range or, for more accurate measurements, there are short range papers.

Measuring pH

Indicators are dyes or mixtures of dyes that can be added to solutions of acids or bases to determine pH.

Some common indicators and their color changes are shown in the chart below:



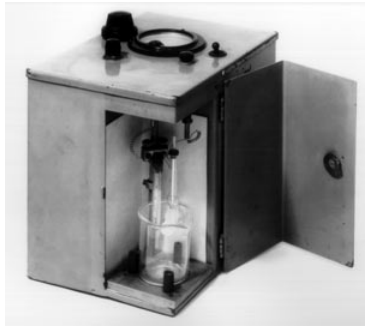
Measuring pH

For more accurate measurements, a pH meter is used.

Using special glass electrodes, the meter measures the voltage of the solution as a function of the activity of the hydrogen ions near the tip of the electrode.

The pH Meter

- **First pH meter was constructed in 1934 by Arnold Beckman (1900-2004).**
- **A glass pH electrode that had a potential dependent on activity of H^+ ions had been constructed in 1906 by Fritz Haber and Zygmunt Klemensiewicz, but there were technical difficulties due to a large internal resistance of glass electrodes. To obtain reliable results one was forced to use very sensitive galvanoscope - expensive and difficult to maintain.**
- **To overcome the problem Arnold Beckman proposed to use simple high-gain amplifier made using two vacuum tubes. Amplified current was much easier to measure with cheap miliamperometers.**



Beckman's first pH meter, 1934 (middle photo)

The Model G pH meter, the first successful marketed pH meter, 1936 (bottom photo)