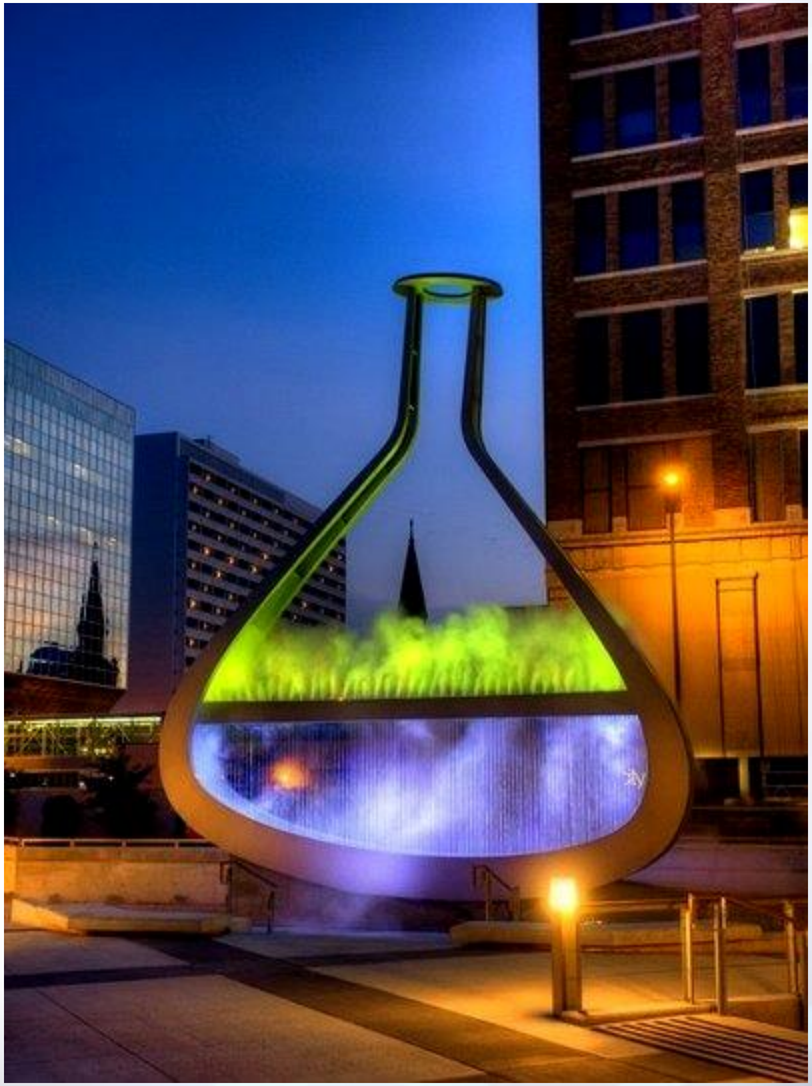
Analytical chemistry

Lecture № 3

Acid - Base equilibria Part I



The Early History of Acid—Base Concepts

The word ***acid*** *derives from Latin acere, meaning sour.* ***Bases*** *were referred to as alkali in early history and that word derives from Arabic al-qili, the ashes of the plant* saltwort, rich in sodium carbonate. In the mid seventeenth century it was recognized that acids and bases (called *alkali in early history) tend to neutralize each other (known* as the Silvio-Tachenio theory) but the concepts were vague. Acids, for example, were thought to be substances that would cause limestone to effervesce and alkalis as those that would effervesce with acids.

In 1675, Boyle objected to the vagueness of the Silvio–Tachenio theory and largely because of his efforts, a set of definitions emerged about acids that sought to incorporate their known properties: acids taste sour, cause limestone to effervesce, turn blue plant dyes to red, and precipitate sulfur from alkaline solutions.

Alkalies are substances that are slippery to the touch and can reverse the effect of acids.

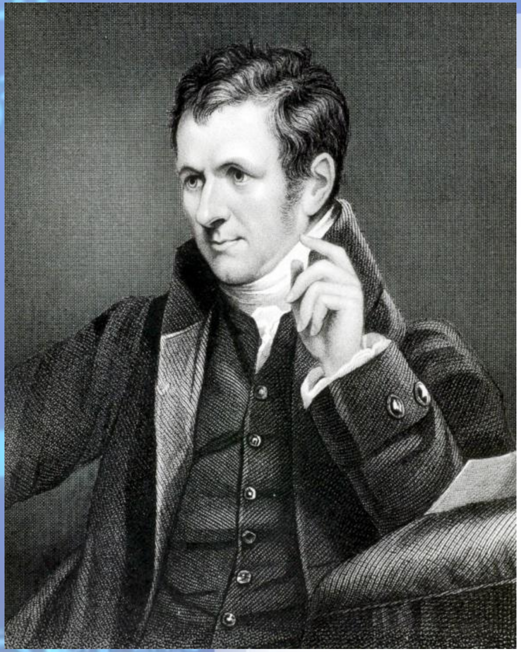
18 century

Antuan Lavuazye

Based primarily on his observations on combustion and respiration, in which carbon is converted to carbon dioxide (the acidic nature of carbon dioxide dissolved in water was already obvious), he named the gas recently (1774) discovered by Joseph Priestley, so essential for combustion or respiration, as oxygen (from Greek, meaning *acid former), since he surmised it was what created the* acidic product.

Acids – substances,
That have oxygen

O

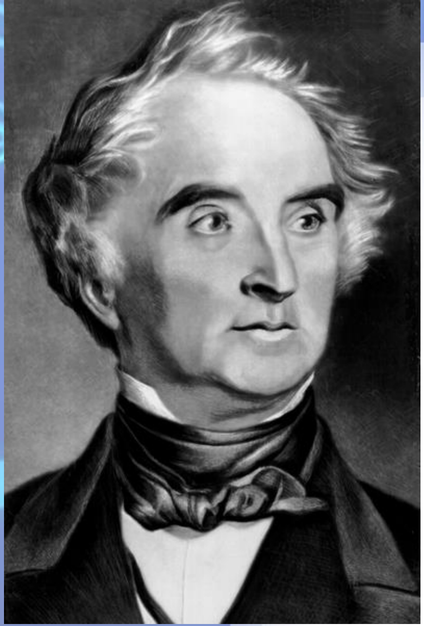


Hemphri Devi

1816 year

Humphry Davy through electrolysis discovered several new elements. In 1807 he electrolyzed fused potash and then soda—substances that many thought to be elements—and isolated potassium and sodium. Davy recognized that these alkali and alkaline earth metals combine with oxygen and form already known oxides that are highly basic, which challenged Lavoisier’s theory that oxygen was the acidifying element. He went on to establish that hydrochloric acid, not “oxymuriatic acid” as Lavoisier called it, was acidifying; by electrolysis he isolated hydrogen and one other element, chlorine (that he so named in 1810), which until then was believed to be a compound containing oxygen. Rather than oxygen, Davy suggested in 1815 that hydrogen may be the acidifying element.

Acids - substances,
That have hydrogen H



Justus Von Liebig (1803–1873) was a German chemist who profoundly enriched agricultural and biological chemistry. Liebig first recognized nitrogen as an essential plant nutrient and is hence often called the father of the fertilizer industry. Liebig first advocated experimentally centered teaching of chemistry. He was also the first to attempt to systematize organic chemistry.

Ustas Libig 1833 year

H/Me

Acids – substances,

That have hydrogen

Able to replaced the atom of metall

80-th years of 19 century

Svante Arrhenius

V. Ostvald

Ionic theory

of acids and basis

1903 year Nobel prize on chemistry

Svante Arrhenius (1859–1927) submitted a 150-page dissertation in 1884 on electrolytic conductivity to Uppsala for the doctorate. It did not impress the professors, and he received a fourth class degree, but upon his defense it was reclassified as third class. Nineteen years later, extensions of this very work would earn him the 1903 Nobel Prize in Chemistry.

Svante Arrhenius

The Arrhenius theory is restricted to aqueous solutions

Acid – any substance that, when dissolved in water, increase the concentration of hydrogen ion H^+

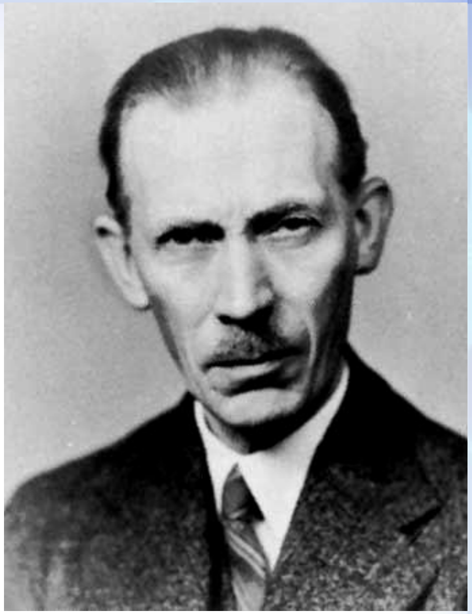
Base – any substance that, when dissolved in water, increase the concentration of hydroxide ion OH^-

$HCl \rightarrow H^+ + Cl^-$ $NaOH \rightarrow OH^- + Na^+$

The reaction of neutralization

$HCl + NaOH \rightarrow NaCl + H_2O$

1923 year



Johanes N. Bronsted

Thomas Lowry

Ptotolytical theory

of acids and basis

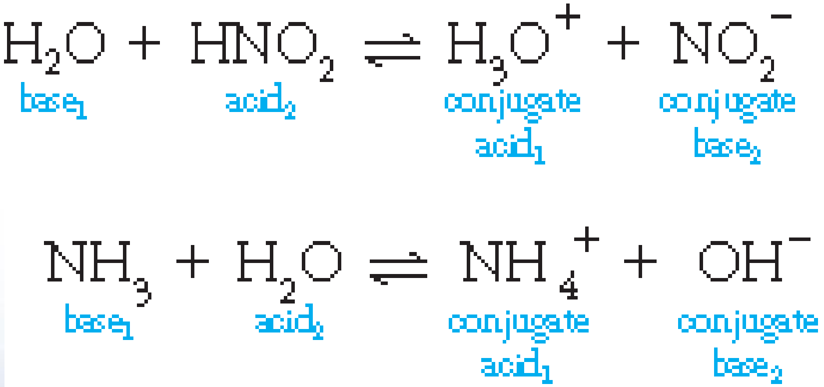
Acid is the species (molecule or ion) that donates a proton to another species in a proton transfer reaction.
Base is the species (molecule or ion) that accepts a proton in a proton-transfer reaction.

$$NH_4^+ + S^{2-} \leftrightarrow NH_3 + HS^-$$

acid *base* *base* *acid*

conjugate acid/base pair, or just a conjugate pair:

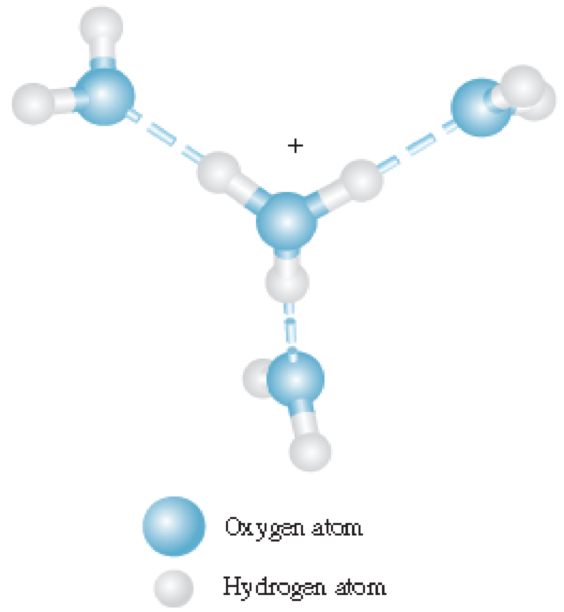
$$NH_4^+/NH_3 \text{ и } HS^-/S^{2-}$$



$$\underset{\text{base}_1}{H_2O} + \underset{\text{acid}_2}{HNO_2} \rightleftharpoons \underset{\substack{\text{conjugate}\\ \text{acid}_1}}{H_3O^+} + \underset{\substack{\text{conjugate}\\ \text{base}_2}}{NO_2^-}$$

$$\underset{\text{base}_1}{NH_3} + \underset{\text{acid}_2}{H_2O} \rightleftharpoons \underset{\substack{\text{conjugate}\\ \text{acid}_1}}{NH_4^+} + \underset{\substack{\text{conjugate}\\ \text{base}_2}}{OH^-}$$

Type of Acids:



- neutral:

H+ H+

$$HCN + H_2O \leftrightarrow CN^- + H_3O^+$$

- anionic:

H+ H+

$$H_2PO_4^- + H_2O \leftrightarrow HPO_4^{2-} + H_3O^+$$

- cationic:

H+ H+

$$NH_4^+ + 2\,H_2O \leftrightarrow NH_3 \cdot H_2O + H_3O^+$$

Type of bases:

- neutral:

$$NH_3{\cdot}H_2O + H_2O \leftrightarrow NH_4^+ + OH^- + H_2O$$

- anionic:

$$CN^- + H_2O \leftrightarrow HCN + OH^-$$

- cationic:

$$N_2H_5^+ + H_2O \leftrightarrow N_2H_6^{2+} + OH^-$$

Species that have both acidic and basic properties are **amphiprotic**

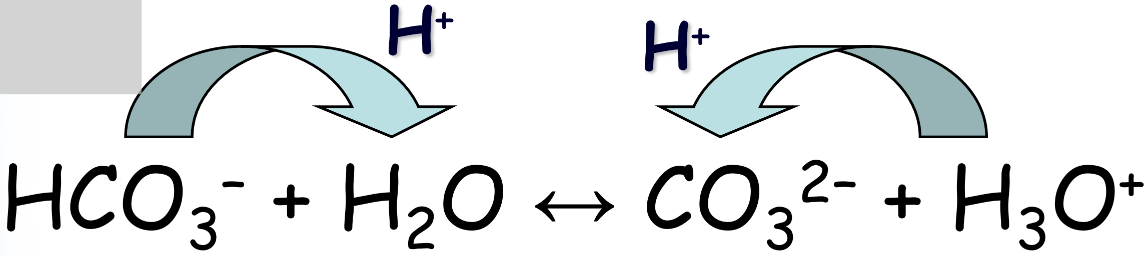
HCO_3^-

H_2NCH_2COOH

NH_4CN

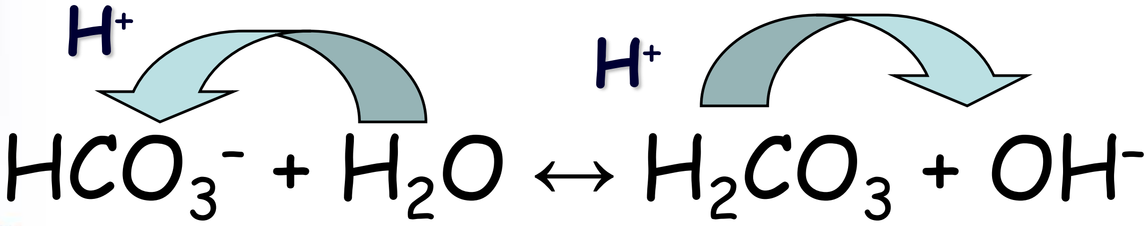
$HA^- + H_2O \leftrightarrow H_3O^+ + A^{2-}$

$HA^- + H_3O^+ \leftrightarrow H_2A + H_2O$



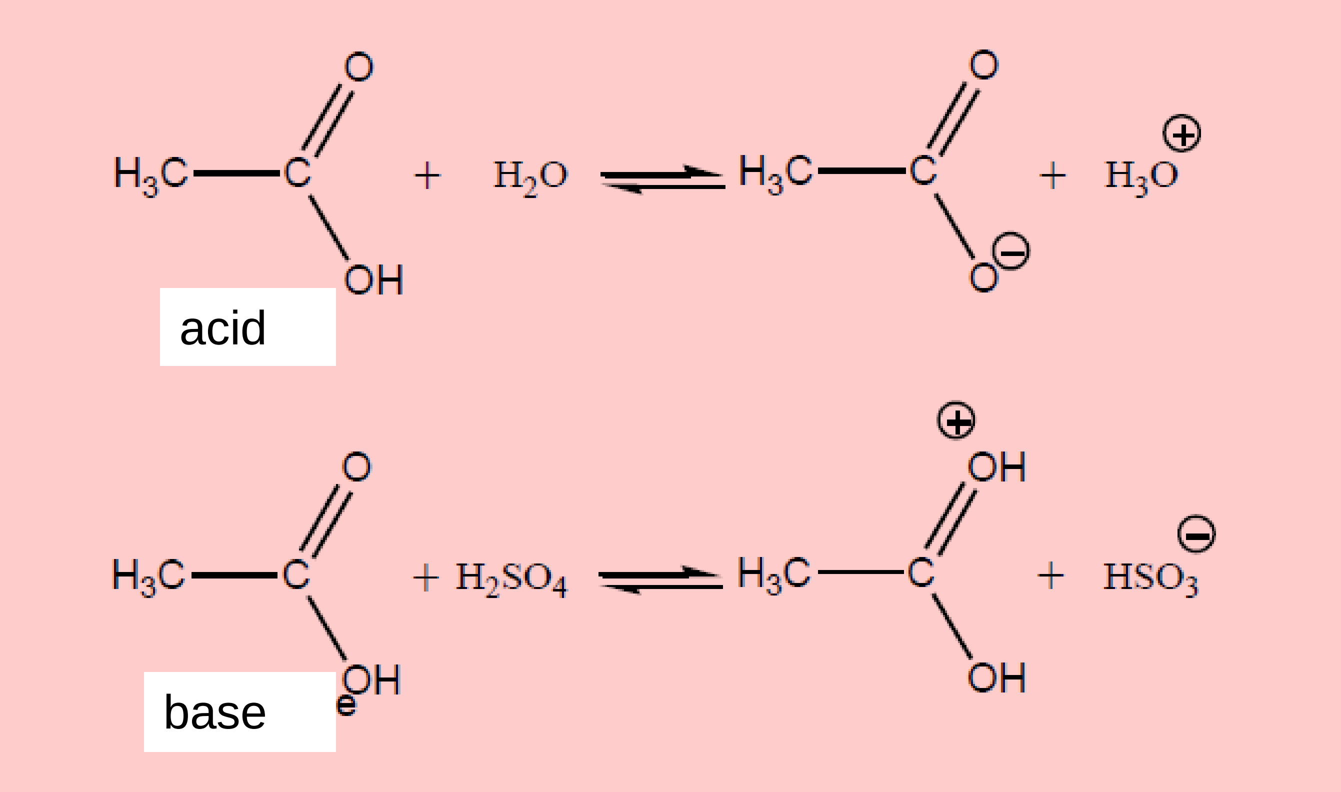
$HCO_3^- + H_2O \leftrightarrow CO_3^{2-} + H_3O^+$

acid



$HCO_3^- + H_2O \leftrightarrow H_2CO_3 + OH^-$

base



$$\underset{\text{base}_1}{H_2PO_4^-} + \underset{\text{acid}_2}{H_3O^+} \rightleftharpoons \underset{\text{acid}_1}{H_3PO_4} + \underset{\text{base}_2}{H_2O}$$

$$\underset{\text{acid}_1}{H_2PO_4^-} + \underset{\text{base}_2}{OH^-} \rightleftharpoons \underset{\text{base}_1}{HPO_4^{2-}} + \underset{\text{acid}_2}{H_2O}$$

The acid and base of a half-reaction are called **conjugate pairs. Free protons do not** exist in solution, and there must be a proton acceptor (base) before a proton donor (acid) will release its proton.

The Brønsted-Lowry concept of acids and bases has greater scope than the Arrhenius concept:

1. **A base is a species that accept protons; the OH^- ions is only one example of a base.**
2. **Acids and bases can be ions as well as molecular substances.**
3. **Acid-base reactions are not restricted to aqueous solutions.**
4. **Some species can act as either acids or bases, depending on what the other reactant is.**

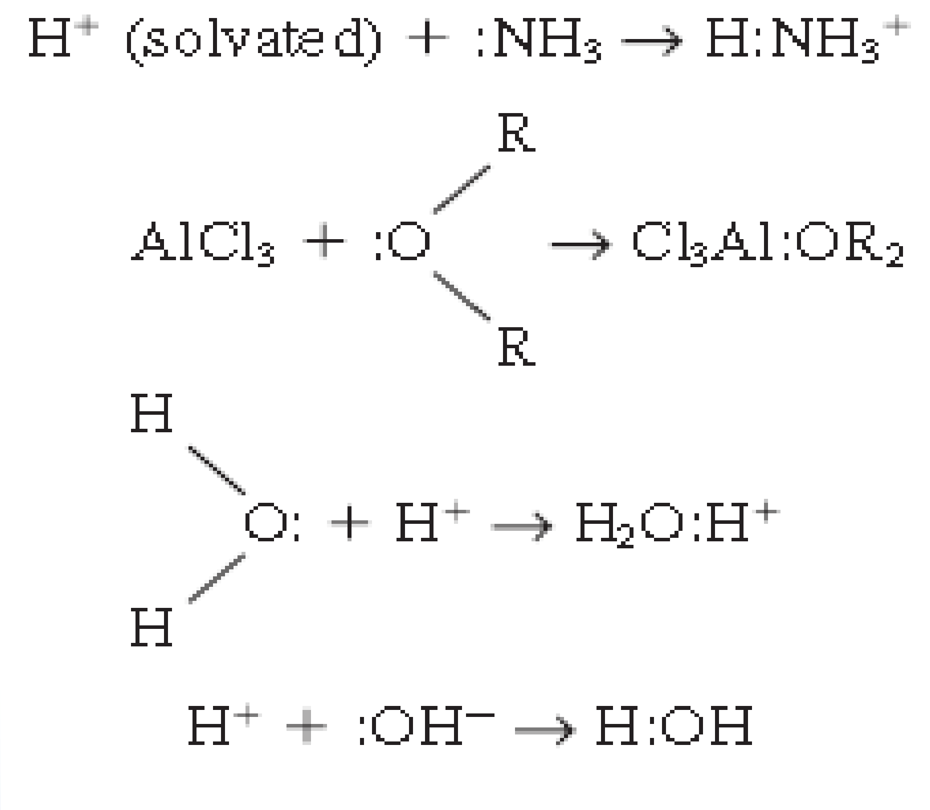
1923 year

Gilbert Lewis

Electronic theory

of acids and bases

Lewis acid is a species that can form a covalent bond by accepting an electron pair from another species. **Lewis base** is a species that can form a covalent bond by donating an electron pair to another species.



$$H^+ \text{ (solvated)} + :NH_3 \rightarrow H:NH_3^+$$

$$AlCl_3 + :OR_2 \rightarrow Cl_3Al:OR_2$$

$$H_2O: + H^+ \rightarrow H_2O:H^+$$

$$H^+ + :OH^- \rightarrow H:OH$$

Acid–Base Equilibria in Water

When an acid or base is dissolved in water, it will dissociate, or **ionize, the amount of ionization being dependent on the strength of the acid or the base.** A “strong” electrolyte is completely dissociated, while a “weak” electrolyte is partially dissociated.

Hydrochloric acid is a strong acid, and in water, its ionization is complete:

$$\mathrm{HCl} + \mathrm{H_2O} \rightarrow \mathrm{H_3O^+} + \mathrm{Cl^-}$$

The proton H^+ exists in water as a hydrated ion, the **hydronium ion, H_3O^+.** Higher hydrates probably exist, particularly $H_9O_4^+$. The hydronium ion is written as **H_3O^+** for convenience and to emphasize Bronsted behavior.

Acetic acid is a weak acid, which ionizes only partially in water (a few percent):

$$\mathrm{HOAc} + \mathrm{H_2O} \rightleftharpoons \mathrm{H_3O^+} + \mathrm{OAc^-}$$

$$K_a^\circ = \frac{a_{\mathrm{H_3O^+}} \cdot a_{\mathrm{OAc^-}}}{a_{\mathrm{HOAc}}}$$

thermodynamic acidity constant

Strengths of Acids and Bases

Strong Weak

H^+

$$HA + H_2O \leftrightarrow A^- + H_3O^+$$

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

SOLVENT - растворитель

$$HA + SH \;\square\; A^- + SH_2^+$$

acid

base

$$K^0_a = \frac{a(A^-)\cdot a(SH_2^+)}{a(HA)}$$

$$pK_a = -\lg K_a$$

acid dissociation constant

$$K_a = \frac{[A^-]\cdot[SH_2^+]}{[HA]}$$

Weak acids are acids that are only partly ionised as the result of equilibrium reaction with water.

Conjugate acid-base pair	K_a
CH_3COOH / CH_3COO^-	$1{,}7 \cdot 10^{-5}$
$Al^{3+} \cdot H_2O$ / $AlOH^{2+}$	$9{,}6 \cdot 10^{-6}$
H_2S / HS^-	$1{,}1 \cdot 10^{-7}$
$B(OH)_3 \cdot H_2O / [B(OH)_4]^-$	$5{,}8 \cdot 10^{-10}$

Strengths of acid

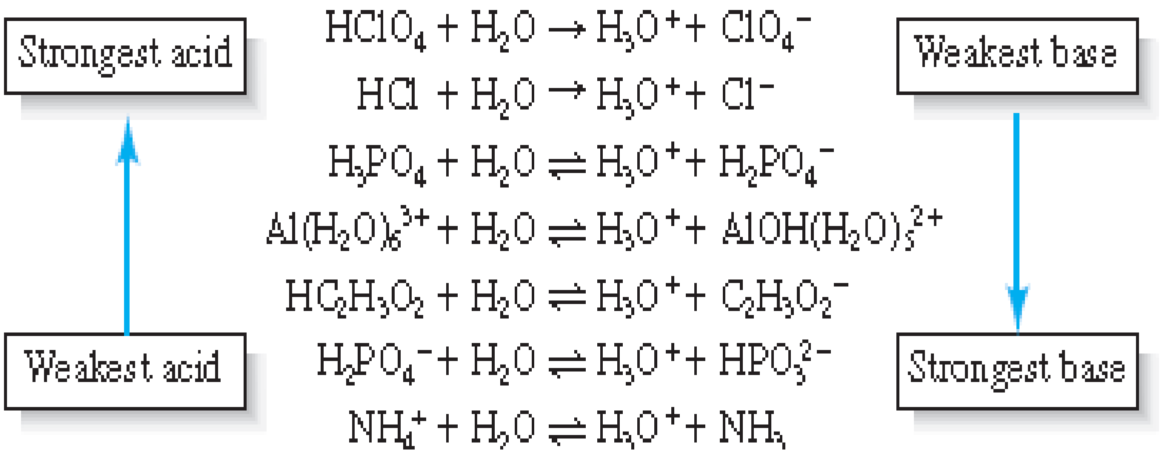
$$CH_3COOH + H_2O \leftrightarrow CH_3COO^- + H_3O^+$$

$$\alpha = \frac{[H_3O^+]}{c_0(HA)} = \frac{[A^-]}{c_0(HA)}$$

The degree of ionisation

Strong acids are acids that ionise completely in water (that is, they react completely to give ions).

The common strong acids include HCl, HBr, HI, $HClO_4$, HNO_3, the first proton in H_2SO_4, and the organic sulfonic acid RSO_3H.



$$HClO_4 + H_2O \rightarrow H_3O^+ + ClO_4^-$$

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

$$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-$$

$$Al(H_2O)_6^{3+} + H_2O \rightleftharpoons H_3O^+ + AlOH(H_2O)_5^{2+}$$

$$HC_2H_3O_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_2^-$$

$$H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{2-}$$

$$NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3$$

$$B + SH \;\square\; BH^{+} + S^{-}$$

Base acid

$$K^{0}_{b} = \frac{a(BH^{+})\cdot a(S^{-})}{a(B\ )}$$

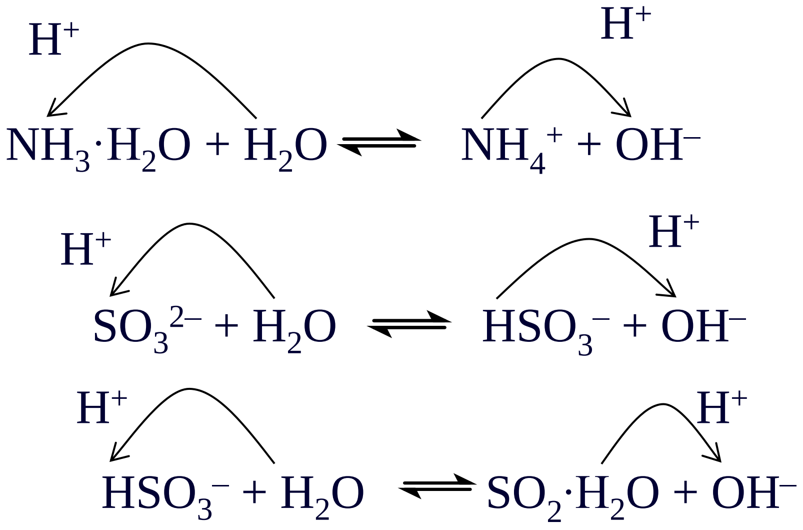
$$K_{b} = \frac{[BH^{+}]\cdot[S^{-}]}{[B]}$$

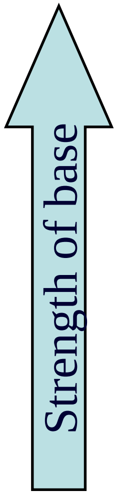
$$A^{-} + H_2O \leftrightarrow HA + OH^{-}$$

$$K_{O}(K_{b}) = \frac{[OH^{-}][HA]}{[A^{-}]}$$

base dissociation constant

Weak bases are bases that are only partly ionised as the result of equilibrium reactions with water.





The reaction equation	Conjugate pair	K_b
$NH_3{\cdot}H_2O + H_2O \rightleftharpoons NH_4^+ + OH^-$	$NH_4^+/ NH_3{\cdot}H_2O$	$1{,}8 \cdot 10^{-5}$
$SO_3^{2-} + H_2O \rightleftharpoons HSO_3^- + OH^-$	HSO_3^- / SO_3^{2-}	$1{,}6{\cdot}10^{-7}$
$HSO_3^- + H_2O \rightleftharpoons SO_2{\cdot}H_2O + OH^-$	$SO_2{\cdot}H_2O / HSO_3^-$	$6{,}0{\cdot}10^{-13}$

The common strong bases include NaOH, KOH, $Ba(OH)_2$, and the quaternary ammonium hydroxide R_4NOH, where R is an alkyl group such as CH_3 or C_2H_5

The tendency of a solvent to accept or donate protons determines the strength of a solute acid or base dissolved in it. For example, perchloric and hydrochloric acids are strong acids in water. If anhydrous acetic acid, a weaker proton acceptor than water, is substituted *as the solvent, neither of these acids undergoes complete dissociation.*

$$\underset{\text{base}_1}{CH_3COOH} + \underset{\text{acid}_2}{HClO_4} \rightleftharpoons \underset{\text{acid}_1}{CH_3COOH_2^{\,+}} + \underset{\text{base}_2}{ClO_4^{\,-}}$$

Perchloric acid is, however, about 5000 times stronger than hydrochloric acid in this solvent. Acetic acid thus acts as a differentiating solvent toward the two acids byrevealing the inherent differences in their acidities. Water, on the other hand, is a leveling solvent for perchloric, hydrochloric, and nitric acids because all three are completely ionized in this solvent and show no differences in strength. There are differentiating and leveling solvents for bases as well.

In a differentiating solvent, various acids dissociate to different degrees and have different strengths. In a leveling solvent, several acids are completely dissociated and show the same strength.

The acid strength depends

- **first on its own ability to donate protons,**
- **on the solvent’s ability (here water) to accept protons, that is, on its basic character.**

This second factor is often underestimated. For example, hydrogen chloride is strong in water.

$$HCl + H_2O \rightarrow Cl^-_{(w)} + H_3O^+_{(w)}.$$

Hence, in acetic acid playing the part of the solvent, hydrogen chloride is a weak acid.

$$HCl + CH_3COOH \rightleftharpoons Cl^-_{(solv)} + CH_3COOH_2{}^+_{(solv)}.$$

In this example, ethanoic acid is the solvent, but it also plays the part of a base since it accepts a proton from the hydrogen chloride to give the solvated proton $CH_3COOH_2^+$, which has sometimes been called the acetylium ion. Quite obviously, ethanoic acid is less basic than water since the proton transfer to it is equilibrated, whereas it is total to water. Hydrogen chloride is a weak acid in ethanoic acid and is a strong one in water.

Autoprotolysis (also called autoionization) is the spontaneous reaction of molecules of a substance to give a pair of ions.

$$SH + SH \rightleftarrows S^- + SH_2^+$$

Liat Lionium

$$H_2O + H_2O \rightleftarrows H_3O^+ + OH^-$$

$$CH_3COOH + CH_3COOH \rightleftarrows CH_3COO^- + CH_3COOH_2^+$$

$$C_2H_5OH + C_2H_5OH \rightleftarrows C_2H_5O^- + C_2H_5OH_2^+$$

$$NH_3 + NH_3 \rightleftarrows NH_2^- + NH_4^+$$

$$\underline{K^0_{SH} = a_{SH_2^+} \cdot a_{S^-}}$$

$$K_{SH} = [SH_2^+][S^-]$$

Ion-product constant for water

Aqueous solutions contain small concentrations of hydronium and hydroxide ions as a result of the dissociation reaction

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

autoprotolysis

An equilibrium constant for this reaction can be written

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

$$K[H_2O]^2 = K_w = [H_3O^+][OH^-]$$

ion-product constant for water

$$K_w^\circ = a_{H_3O^+} \cdot a_{OH^-}$$

thermodynamic autoprotolysis, or self-ionization, constant

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

molar equilibrium constants

Ion-product constant for water

$$K_a \cdot K_b = \frac{[H_3O^+]\,[A^-]}{[HA]} \cdot \frac{[HA]\,[OH^-]}{[A^-]} = [H_3O^+]\,[OH^-] = K_w$$

$$K_b = K_w / K_a$$

$$2H_2O \leftrightarrow H_3O^+ + OH^-$$

$K_w = [H_3O^+]\,[OH^-] = 1 \cdot 10^{-14}$

t=25 °C:

$[H_3O^+] = [OH^-] = K_B = 10^{-7}$ mol/l

Ostwald’s dilution rule

$$HA + H_2O \rightleftharpoons A^- + H_3O^+.$$

$$\alpha = [A^-]/C, \qquad \alpha = [A^-]/([HA] + [A^-])$$

$$[A^-] = \alpha C \text{ and } [HA] = C(1 - \alpha).$$

$$K_a = \alpha^2 C/(1 - \alpha). \qquad \alpha = K_a/(K_a + [H_3O^+]).$$

If $\alpha \ll 1$ ($\alpha < 0,05$):

$$\alpha = \sqrt{K_a / c_0}$$