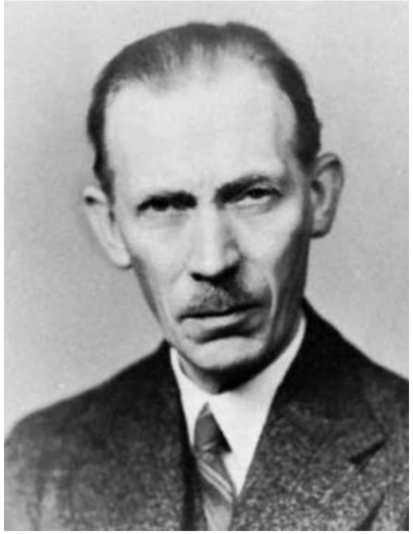
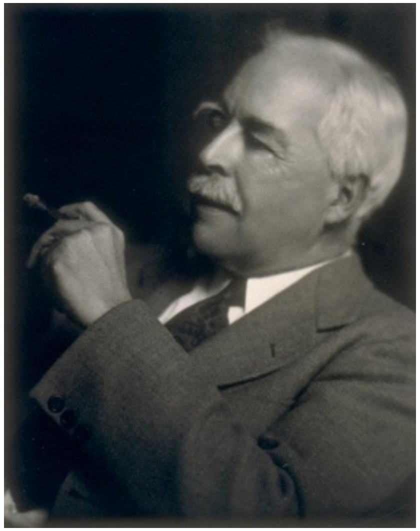
Chemistry of acids and basis

Svante Arrhenius
(1859–1927)



Johannes N. Brønsted
(1879–1947)

Thomas Martin Lowry
(1874-1936)



Gilbert Newton Lewis
(1875-1946)

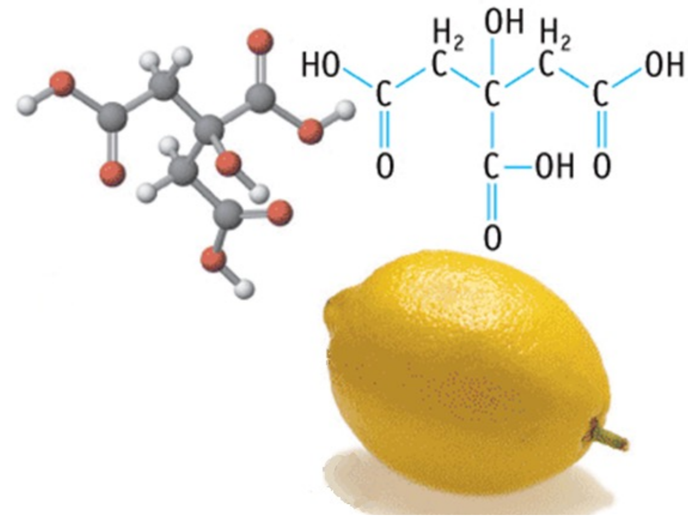
Acids and bases can be roughly divided into: strong electrolytes (HCl, HNO_3 e $NaOH$) and weak electrolytes (CH_3COOH e NH_3)

Alcune immagini sono state prese e modificate da “Chimica” di Kotz, Treichel & Weaver, Edises 2007, III edizione

Acids

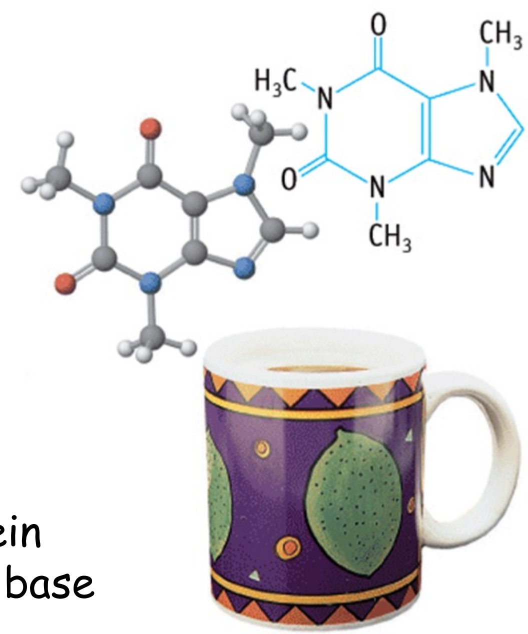
citric acid
A weak acid

- produce hydrogen ions in H2O
- taste sour
- tornasole dye turns red
- are electrolytes in aqueous solution
- neutralize solutions containing hydroxide ions
- react with many metals generating H_2 (g)
- react with carbonates generating CO_2 (g)
- damage tissues
- HCl, HNO_3, CH_3COOH



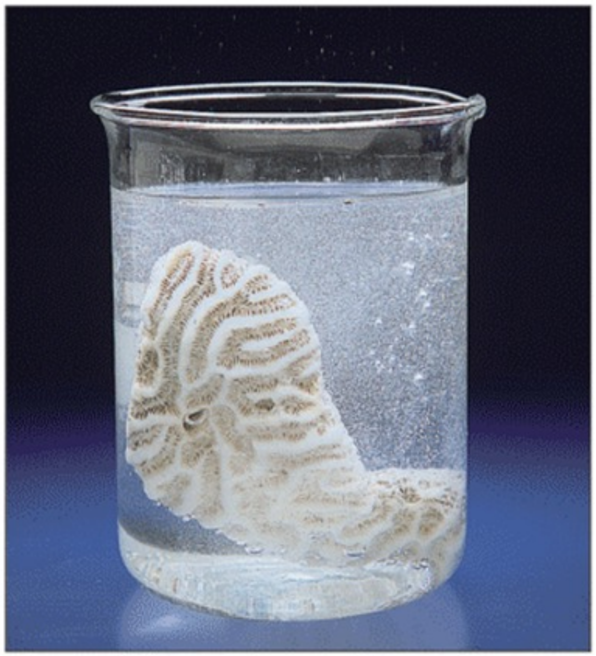
Bases

- produce hydroxil ions H_2O
- bitter taste
- tornasole dye turns blue
- are electrolytes in aqueous solution
- neutralize solutions containing hydrogen ions
- have a soapy texture
- damage tissues (hydrolize lipids)
- NaOH, $Mg(OH)_2$, $Al(OH)_3$, NH_3



caffein
a weak base

Acids react easily with coral (mainly $CaCO_3$) and develop gaseous CO_2 yiealding a salt: ($CaCO_3$) and in general with metal carbonates developing gaseous CO_2 and yielding a salt:



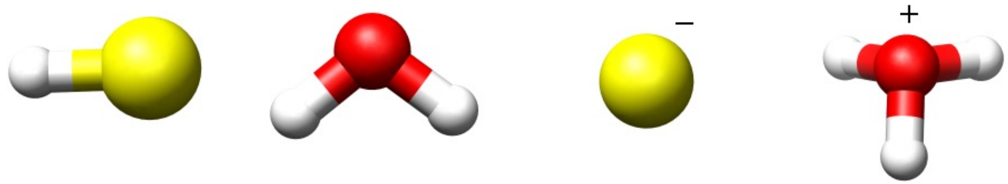
Acids react with many metals developing gaseous H_2 and a salt:

$$Zn\,(s) + 2\,HCl\,(aq) = ZnCl_2\,(aq) + H_2\,(g)$$

$$CaCO_3\,(s) + 2\,HCl\,(aq) = CaCl_2\,(aq) + CO_2\,(g) + H_2O\,(l)$$

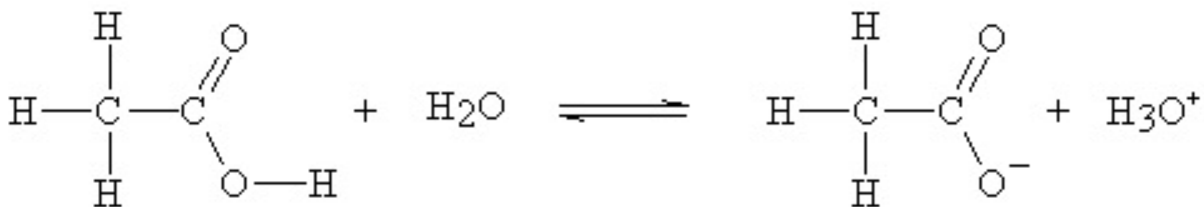
Strong acids (K >>> 1): are fully dissociated (K ≃ ∞)

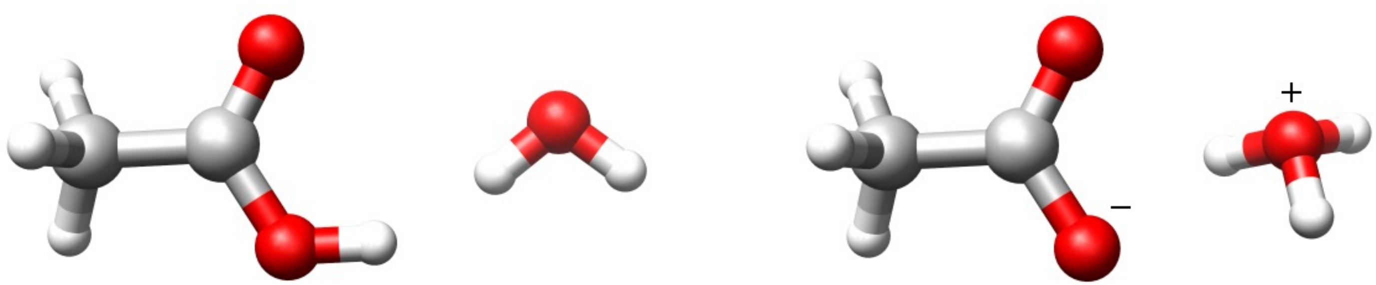
$$HCl\ (aq) + H_2O\ (l) \longrightarrow Cl^-\ (aq) + H_3O^+\ (aq)$$



Weak acids (K<1): do not fully dissociate

$$CH_3COOH\ (aq) + H_2O\ (l) = CH_3COO^-\ (aq) + H_3O^+\ (aq)$$





$$K = \frac{[CH_3COO^-]\cdot[H_3O^+]}{[CH_3COOH]} = 1.8\cdot10^{-5}\ M$$

K allows evaluating the strength of an acid

Acids & bases, definition

Arrhenius Theory (1883)

ACID: Produces H+ in Water
BASE: Produces OH- in Water

Bronsted/Lowry Theory (1923)
ACID: proton, H+ DONOR
BASE: proton, H+ ACCEPTOR

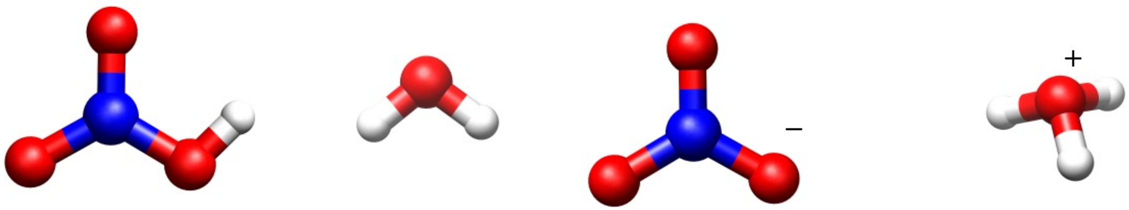
Lewis Theory (1938)
a more general acid base theory.
ACID: accepts pair of electrons for sharing
BASE: donates pair of electrons for sharing

$$X + :Y \rightarrow X:Y$$

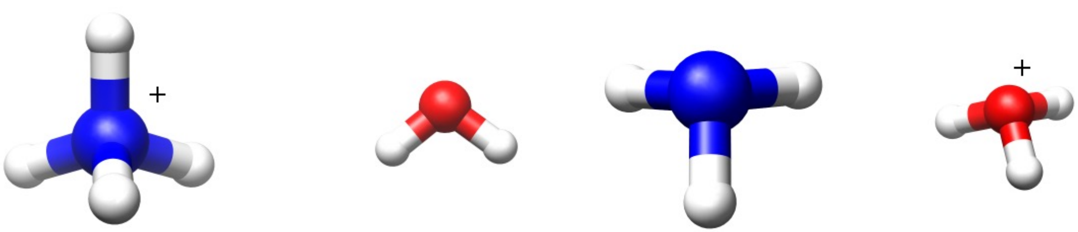
acid base

Brønsted acids

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



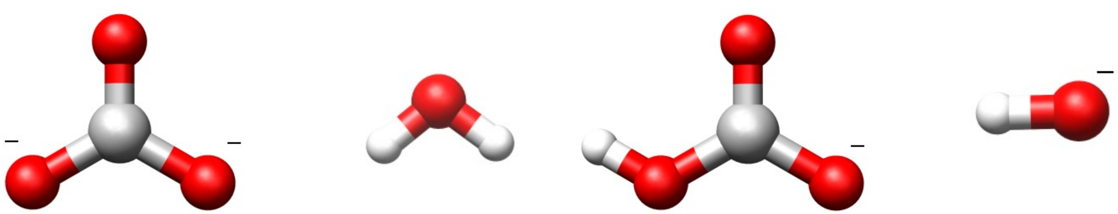
$$NH_4^+\,(aq) + H_2O\,(l) \rightleftarrows NH_3\,(aq) + H_3O^+\,(aq)$$



Brønsted bases

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

$$CO_3^{2-}\,(aq) + H_2O\,(l) \rightleftarrows HCO_3^-\,(aq) + OH^-\,(aq)$$



Polyprotic acids

Acids such as HCl, HNO_3 e CH_3COOH dissociate only one proton and are called "monoprotic". Polyprotic acids can dissocate two or more protons.

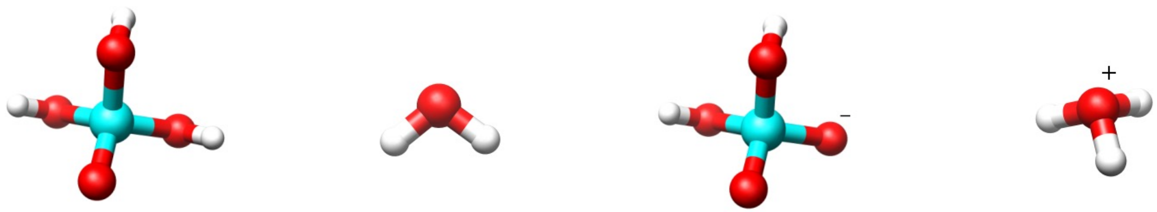
Sulphuric Acid

$$H_2SO_4\ (aq) + H_2O\ (l) \rightarrow HSO_4^-\ (aq) + H_3O^+\ (aq)$$

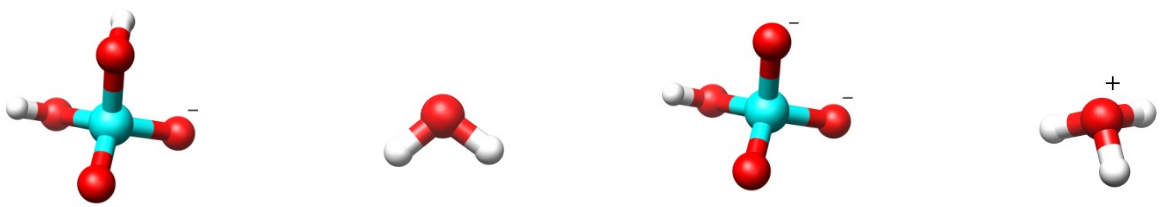
$$HSO_4^-\ (aq) + H_2O\ (l) \rightleftarrows SO_4^{2-}\ (aq) + H_3O^+\ (aq)$$

Phosphoric acid

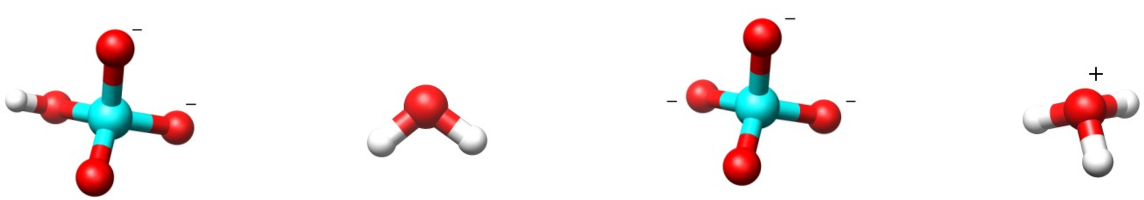
$$H_3PO_4\ (aq) + H_2O\ (l) \rightleftarrows H_2PO_4^-\ (aq) + H_3O^+\ (aq)$$



$$H_2PO_4^-\ (aq) + H_2O\ (l) \rightleftarrows HPO_4^{2-}\ (aq) + H_3O^+\ (aq)$$



$$HPO_4^{2-}\ (aq) + H_2O\ (l) \rightleftarrows PO_4^{3-}\ (aq) + H_3O^+\ (aq)$$



Conjugate acid-base couples

Two compounds that differ for the presence/absence of a proton.
All reactions between Brønsted acid and bases implies the tranfer of a H^+ ion and it involves two conjugate acid-base couples.

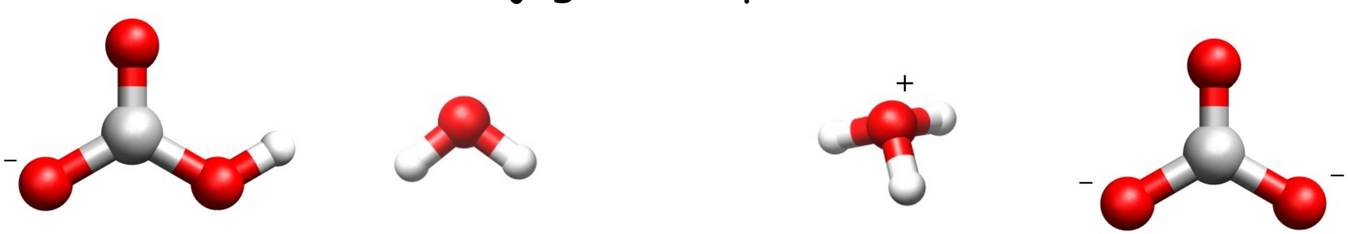
Conjugate couple 1

base 2 acid 2

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

acid 1 base 1

Conjugate couple 2



Conjugate acid-base couples

Conjugate couple 2

$$HNO_2\,(aq) + H_2O(l) \rightleftarrows NO_2^-(aq) + H_3O^+(aq)$$

Conjugate couple 1

The nitrite anion NO_2^- is the conjugate base of nitrous acid and the hydronium ion is tha conjugate acid of water

Conjugate couple 2

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

Conjugate couple 1

The NH_4^+ ion is the conjugate acid of ammonia and the hydroxyl ion is the coniugate base of water

All reactions between Brønsted acid and bases implies the tranfer of a H^+ ion and it involves two conjugate acid-base couples.

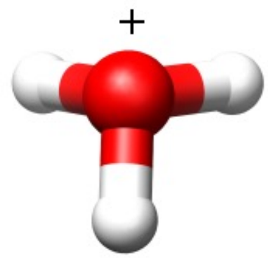
Conjugate acid-base couples

name	acid 1		base 2		base 1		acid 2
Hydrochloric acid	HCl	+	H_2O	→	Cl^-	+	H_3O^+
Nitric acid	HNO_3	+	H_2O	→	NO_3^-	+	H_3O^+
Hydrogen carbonate	HCO_3^-	+	H_2O	⇄	CO_3^{2-}	+	H_3O^+
Acetic acid	CH_3COOH	+	H_2O	⇄	CH_3COO^-	+	H_3O^+
Cianidric acid	HCN	+	H_2O	⇄	CN^-	+	H_3O^+
Sulphidric acid	H_2S	+	H_2O	⇄	HS^-	+	H_3O^+
ammonia	H_2O	+	NH_3	⇄	OH^-	+	NH_4^+
Carbonate ion	H_2O	+	CO_3^{2-}	⇄	OH^-	+	HCO_3^-
water	H_2O	+	H_2O	⇄	OH^-	+	H_3O^+

Water is amphiprotic (or amphoteric) since it cas accept a proton to yield the hydronium ion:

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

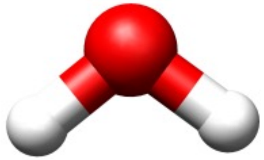
base acid

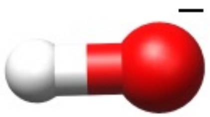


or it can donate a proton to yield the hydroxyl ion:

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

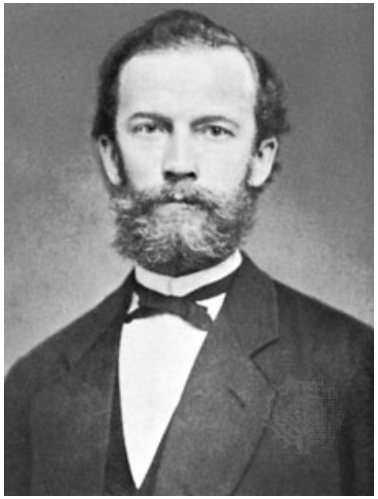
acid base





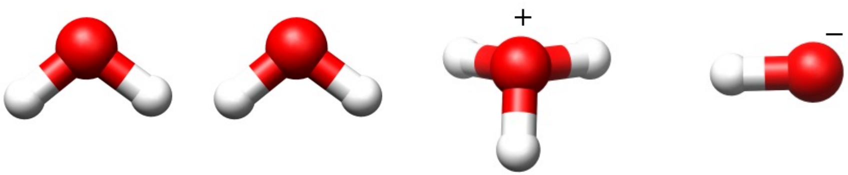
Water autoprotolysis and its constant K_W

There is no need for an acid in water to form the hydronium ion H_3O^+. Two water molecule react to produce one hydronium and one hydroxil.



Friedrich W. G. Kohlrausch (1840-1910)

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



This self-ionization reaction (water ionic product was discovered by Kohlrausch measuring the electrical conductivity of ultra pure water. When water ionizes at 25 ° C only 2 in 10^9 molecules are ionized.

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

Since water concentration variation is neglible (55.5 M)

$$K\cdot[H_2O]^2 = [H_3O^+]\cdot[OH^-] = K_W$$

K_W is known as water ionization constant.

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

$$K_W = [H_3O^+]\cdot[OH^-]$$

In pure water $[H_3O^+] = [OH^-]$.

compound	Electrical conductivity(S/m)
Ag	$6.30\cdot10^7$
Cu	$5.96\cdot10^7$
Au	$4.52\cdot10^7$
Al	$3.78\cdot10^7$
Sea water(35 g/kg Na Cl)	5
tap water	0.0005–0.05
deionized and degassed H_2O	$5.50\cdot10^{-6}$

Electrical conductivity data show that at 25 °C in pure water $[H_3O^+] = [OH^-] = 1.0\cdot10^{-7}$ M.
Therefore K_W at 25 °C is:

$$K_W = [H_3O^+]\cdot[OH^-] = 1.0\cdot10^{-14}\ M^2$$

$$K_W = [H_3O^+]\cdot[OH^-] = 1.0\cdot 10^{-14}\ M^2 \quad a\ 25\ °C$$

When $[H_3O^+] = [OH^-]$ a solution is called a Neutral Solution

If an acid or a base are added the equilibrium is perturbed

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

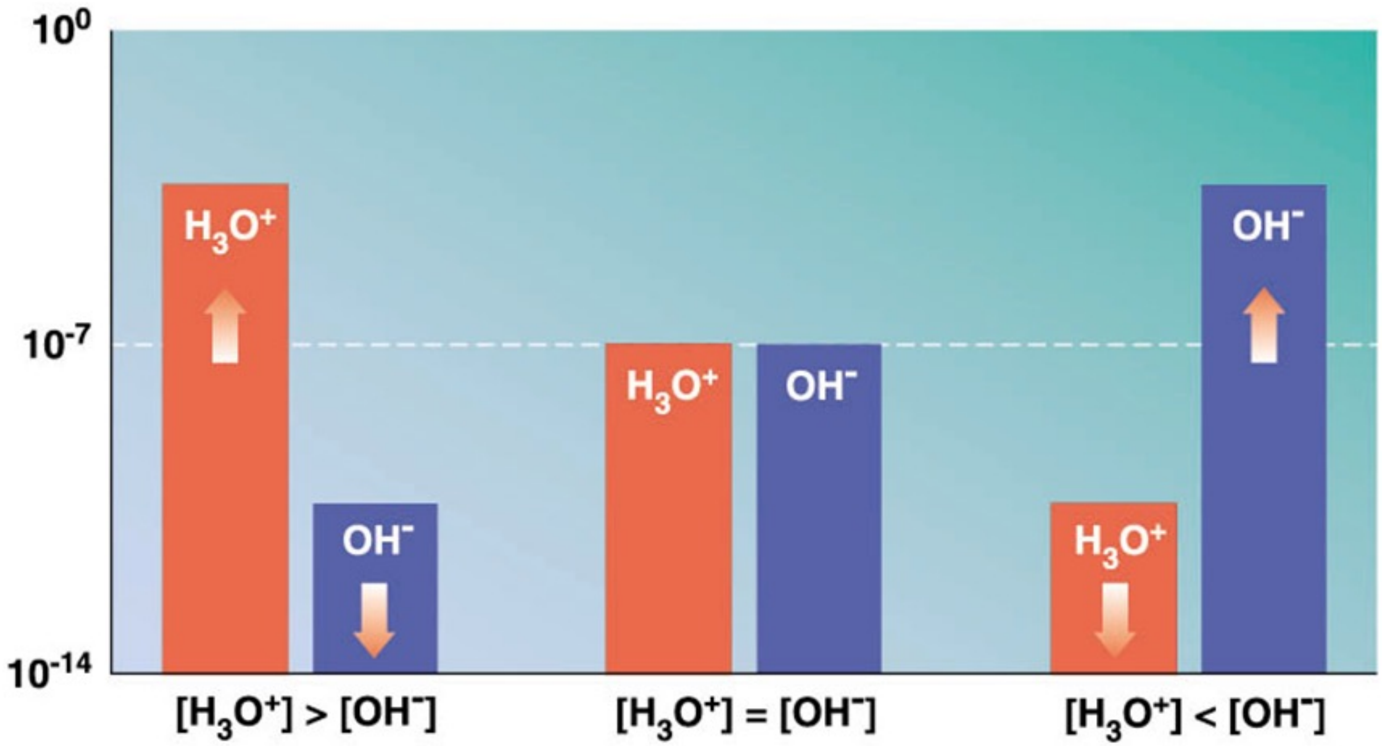
By adding an acid, the $[H_3O^+]$ increases and the solution becomes acidic.
Le Châtelier's principle predicts that a small amount of $[H_3O^+]$ will react with OH^- (from water self-protolysis). This lowers $[OH^-]$ until:
$[H_3O^+] \times [OH^-] = 1.0\times10^{-14}$ at 25 °C

- neutral solution: $[H_3O^+] = [OH^-] = 1.0\cdot10^{-7}$ M
- acidic solution: $[H_3O^+] > [OH^-]$ e $[H_3O^+] > 1.0\times10^{-7}$ M and $[OH^-] < 1.0\times10^{-7}$ M
- basic solution: $[H_3O^+] < [OH^-]$ e $[H_3O^+] < 1.0\times10^{-7}$ M and $[OH^-] > 1.0\times10^{-7}$ M

In conclusion:

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

$$K_w = [H_3O^+]\cdot[OH^-] = 1.0\cdot10^{-14}\ M^2\ \text{a}\ 25\,°C$$



acidic neutral basic

Exercise 1. What are the concentrations of $[H_3O^+]$ and $[OH^-]$ of 0.01 M di HCl at 25 °C.

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

0.01 mol/L of H_3O^+ and 0.01 mol/L of Cl^- are formed

$$[H_3O^+]_{total} = [H_3O^+]_{HCl} + [H_3O^+]_{H2O} = 0.01 + 10^{-7} \approx 0.01\ M$$

$$Q = [H_3O^+]_{total} \times [OH^-] = 0.01 \times 10^{-7} = 10^{-9} \gg K_W = 10^{-14}\ M^2$$

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

$$[OH^-] = K_W / [H_3O^+]_{total} = 10^{-14} / 0.01 = 10^{-12}\ M$$

Logarithm

The logarithm function in base = b is the inverse function with respect to the eponential funcion in base b. The logarithm in base b of a number x is th number to whic b must be raised to obtain x.

therefore: $$x = b^y$$

$$y = \log_b x$$

Example, $\log_3 81 = 4$, since $3^4 = 81$. Logarithm transforms products into sums, divisions into subtractions and exponentiations into products.

$$\log_b (x \cdot y) = \log_b x + \log_b y$$

$$\log_b \frac{x}{y} = \log_b x - \log_b y$$

$$\log_b x^y = y \cdot \log_b x$$

pH scale

pH is defined as the decimal logarithm of the reciprocal of the hydronium concentration:

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

pOH isdefined as the decimal logarithm of the reciprocal of the oxydril concentration:

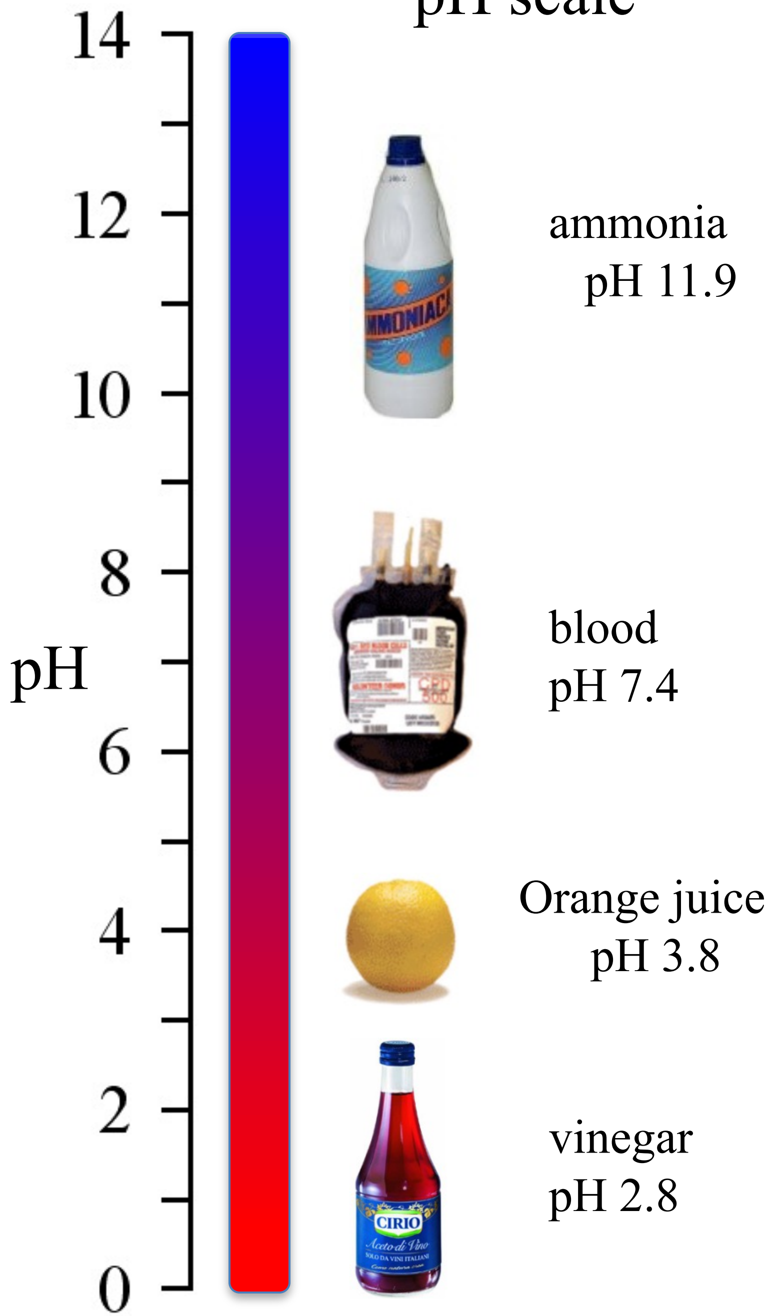
$$pOH = -\log_{10}[OH^-]$$

In water$[H_3O^+] = [OH^-] = 10^{-7}$ M and pH = pOH = 7
$pH = -\log_{10}[H_3O^+] = -\log_{10}10^{-7} = 7$

For constants: $NH_4^+ (aq) + H_2O (l) \rightleftarrows NH_3 (aq) + H_3O^+ (aq)$

$$K = \frac{[NH_3]\cdot[H_3O^+]}{[NH_4^+]} = 5.6\cdot 10^{-10}\ M \qquad pK = -\log_{10}(5.6\times 10^{-10}) = 9.25$$

pH scale



solution	pH
1 M HCl	0.0
gastric juice	1.0
Lemon juice	2.3
vinegar	2.8
wine	3.5
Tomato juice	4.1
coffee	5.0
Acidic rain	5.6
urine	6.0
rain	6.5
milk	6.6
pure water	7.0
blood	7.4
Bicarbonate solution	8.4
Tooth paste	9.9
NH_3	11.9

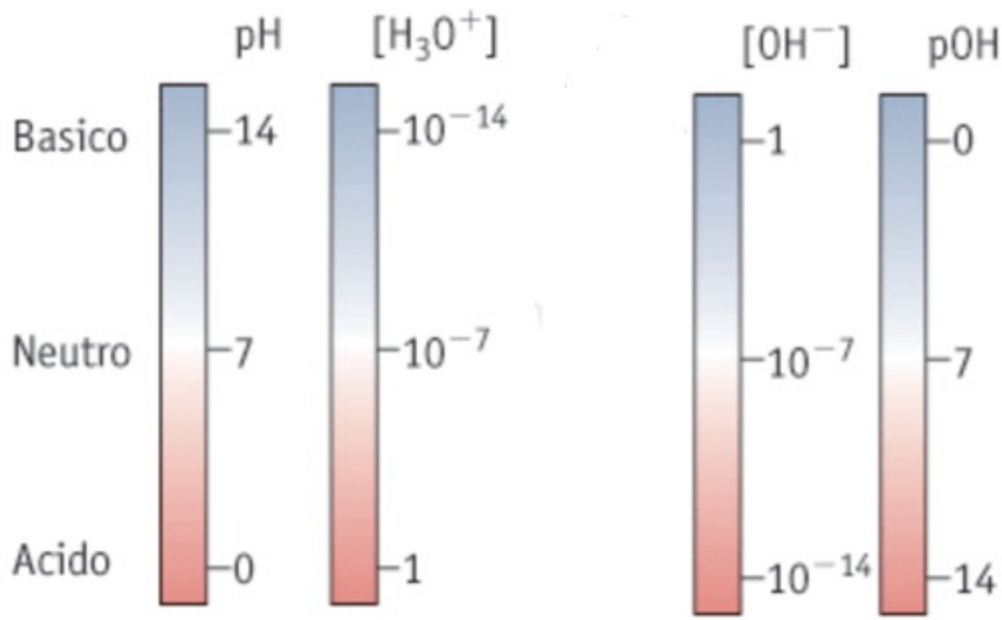
The sum of pH and pOH at 25 ° C is 14:

$$K_W = [H_3O^+]\cdot[OH^-] = 1.0\cdot 10^{-14}\ M^2 \quad a\ 25\,°C$$

$$-\log_{10}K_W = -\log_{10}\left([H_3O^+]\cdot[OH^-]\right) = -\log_{10}1.0\cdot 10^{-14}$$

$$pK_W = -\log_{10}[H_3O^+] - \log_{10}[OH^-] = 14$$

$$pK_W = pH + pOH = 14$$

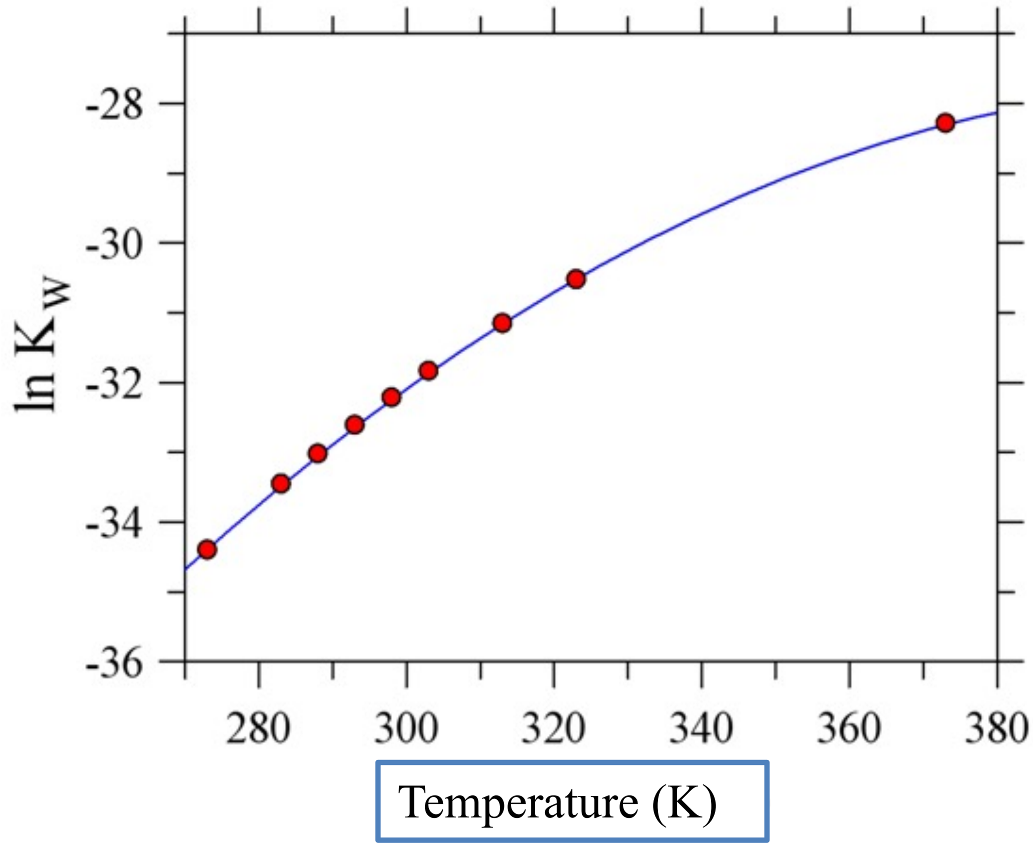


Water self-ionization is endothermic

$$2\,H_2O\,(l) + \text{heat} \rightleftarrows H_3O^+(aq) + OH^-(aq)$$

T °C	K_W (M^2)	pH=pOH
0	$0.114\cdot10^{-14}$	7.47
10	$0.293\cdot10^{-14}$	7.27
15	$0.450\cdot10^{-14}$	7.17
20	$0.681\cdot10^{-14}$	7.08
25	$1.008\cdot10^{-14}$	7.00
30	$1.471\cdot10^{-14}$	6.92
40	$2.916\cdot10^{-14}$	6.77
50	$5.476\cdot10^{-14}$	6.63
100	$51.3\cdot10^{-14}$	6.14

$\Delta H = 52$ kJ/mol



At all temperatures $[H_3O^+] = [OH^-]$

Calculate the pH at 25 ° C of:

a) 0.01 M di HCl; b) 0.1 M NaOH e c) 0.2 M $HClO_4$.

Calculate the pH at 25 ° C of:
a) 0.01 M di HCl; b) 0.1 M NaOH e c) 0.2 M $HClO_4$.

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

$[H_3O^+] = [HCl] = 0.01\ M \rightarrow pH = -\log_{10}(0.01) = -\log_{10}(10^{-2}) = 2$

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

$[OH^-] = [NaOH] = 0.1\ M \rightarrow pOH = -\log_{10}(0.1) = -\log_{10}(10^{-1}) = 1$
$pH = 14 - pOH = 13$

c) $HClO_4\ (aq) + H_2O\ (l) \rightarrow ClO_4^- \ (aq) + H_3O^+ \ (aq)$

$[H_3O^+] = [HClO_4\ ] = 0.2\ M \rightarrow pH = -\log_{10}(0.2) = -\log_{10}(2x10^{-1}) = 0.698$

If pH = 8.5 what is $[H_3O^+]$?

If pOH = 8.5, what is $[H_3O^+]$?

If pH = 8.5 what is $[H_3O^+]$?

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

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

$$[H_3O^+] = 10^{-8.5} = 3.16 \cdot 10^{-9}\ M$$

If pOH = 8.5, what is $[H_3O^+]$?

$$pH = 14 - pOH = 5.5$$

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

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

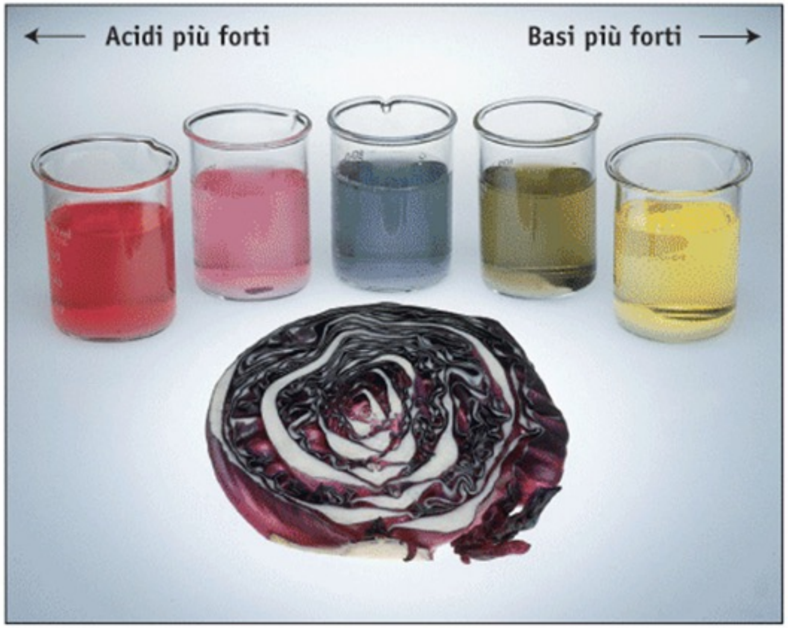
$$[H_3O^+] = 10^{-5.5} = 3.16 \cdot 10^{-6}\ M$$

Measuring pH: indirect and direct methods

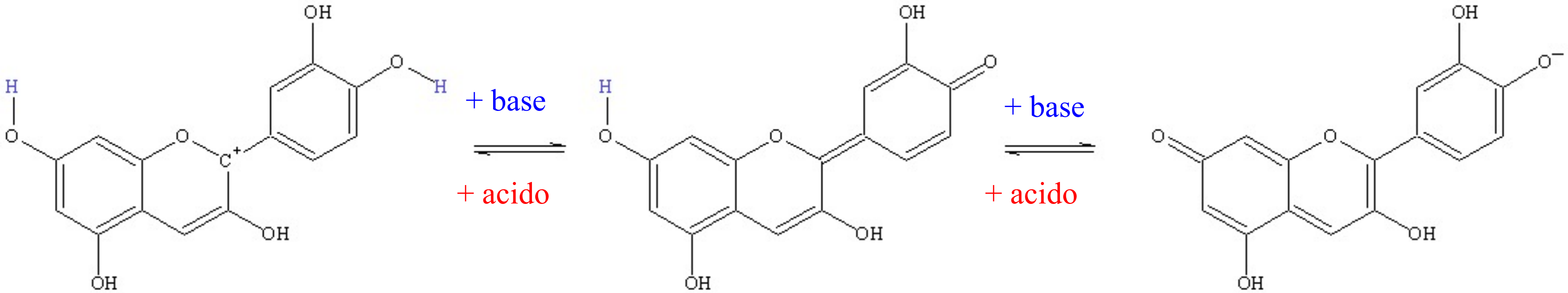
Tornasole is a dye extracted from lichens of the *Rocella* genus.

A pHmeter measures pH directly using a potentiometric method

Red cabbage contains natural dyes. These can be easily extracted by boiling red cabbage in water: the concentrated extract is red-purple. There are many different types of colored substances in plants, such as chlorophylls, carotenoids and anthocyanins.



The colour dpends on the protonation state



Equilibrium constants for acids and bases

They allow to evaluate the tendency of a compound to react with water.
The relative strength of acids can be inferred from the pH of their solution at the same concentration: the lower the pH the stronger the acid.

The relative strength of an acid or base can be expressed quantitatively using the equilibrium constant.

For a generic weak acid

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

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

For a generic weak base

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

$$K_B = \frac{[OH^-]\cdot[BH^+]}{[B]}$$

The stregth increases as K_A or K_B increase.

Which of these acids is the strongest?

$HNO_2\ (aq) + H_2O\ (l) \rightleftarrows NO_2^-\ (aq) + H_3O^+\ (aq)$

$$K_A = \frac{[H_3O^+]\cdot[NO_2^-]}{[HNO_2]} = 4.5\cdot10^{-4}\,M \quad a\ 25\ °C$$

$HF\ (aq) + H_2O\ (l) \rightleftarrows F^-\ (aq) + H_3O^+\ (aq)$

$$K_A = \frac{[H_3O^+]\cdot[F^-]}{[HF]} = 7.2\cdot10^{-4}\,M \quad a\ 25\ °C$$

$H_2CO_3\ (aq) + H_2O\ (l) \rightleftarrows HCO_3^-\ (aq) + H_3O^+\ (aq)$

$$K_A = \frac{[H_3O^+]\cdot[HCO_3^-]}{[H_2CO_3]} = 4.2\cdot10^{-7}\,M \quad a\ 25\ °C$$

Whic of these bases is the strongest?

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

$$K_B = \frac{[OH^-]\cdot[NH_4^+]}{[NH_3]} = 1.8\cdot10^{-5}\,M \quad a\ 25\,°C$$

$CH_3NH_2\ (aq) + H_2O\ (l) \rightleftarrows CH_3NH_3^+\ (aq) + OH^-\ (aq)$ metilammina

$$K_B = \frac{[OH^-]\cdot[CH_3NH_3^+]}{[CH_3NH_2]} = 5.0\cdot10^{-4}\,M \quad a\ 25\,°C$$

$CO_3^{2-}\ (aq) + H_2O\ (l) \rightleftarrows HCO_3^-\ (aq) + OH^-\ (aq)$

$$K_B = \frac{[OH^-]\cdot[HCO_3^-]}{[CO_3^{2-}]} = 2.1\cdot10^{-4}\,M \quad a\ 25\,°C$$

Polyprotic acids

Phosphoric acid

$H_3PO_4\ (aq) + H_2O\ (l) \rightleftarrows H_2PO_4^-\ (aq) + H_3O^+\ (aq)$ $K_1 = 7.1 \cdot 10^{-3}$

$H_2PO_4^-\ (aq) + H_2O\ (l) \rightleftarrows HPO_4^{2-}\ (aq) + H_3O^+\ (aq)$ $K_2 = 6.2 \cdot 10^{-8}$

$HPO_4^{2-}\ (aq) + H_2O\ (l) \rightleftarrows PO_4^{3-}\ (aq) + H_3O^+\ (aq)$ $K_3 = 4.4 \cdot 10^{-13}$

Carbonic acid

$H_2CO_3\ (aq) + H_2O\ (l) \rightleftarrows HCO_3^-\ (aq) + H_3O^+\ (aq)$ $K_1 = 4.7 \cdot 10^{-7}$

$HCO_3^-\ (aq) + H_2O\ (l) \rightleftarrows CO_3^{2-}\ (aq) + H_3O^+\ (aq)$ $K_2 = 4.7 \cdot 10^{-11}$

Sulphuric acid

$H_2SO_4\ (aq) + H_2O\ (l) \rightleftarrows HSO_4^-\ (aq) + H_3O^+\ (aq)$ $K_1 = \sim 10^2$

$HSO_4^-\ (aq) + H_2O\ (l) \rightleftarrows SO_4^{2-}\ (aq) + H_3O^+\ (aq)$ $K_2 = 1.2 \cdot 10^{-2}$

Ionization constants of some acids and their conjugate bases at 25 ° C

acid	acido	K_A	base	K_B	base
hydrochloric	HCl	>>1	Cl^-	<<1	chloride
nitric	HNO_3	>>1	NO_3^-	<<1	nitrate
hydronium	H_3O^+	1	H_2O	$1.0 \cdot 10^{-14}$	water
phosphoric	H_3PO_4	$7.5 \cdot 10^{-3}$	$H_2PO_4^-$	$1.3 \cdot 10^{-12}$	Di-hydrogen phosphate
fluoridric	HF	$7.2 \cdot 10^{-4}$	F^-	$1.4 \cdot 10^{-11}$	flluorure
acetic	CH_3COOH	$1.8 \cdot 10^{-5}$	CH_3COO^-	$5.6 \cdot 10^{-10}$	acetate
carbonic	H_2CO_3	$4.2 \cdot 10^{-7}$	HCO_3^-	$2.4 \cdot 10^{-8}$	Hydrogen carbonate
sulphidric	H_2S	$1.0 \cdot 10^{-7}$	HS^-	$1.0 \cdot 10^{-7}$	Hydrogen sulphite
Di-hydrogen phosphate	$H_2PO_4^-$	$6.2 \cdot 10^{-8}$	$H_2PO_4^{2-}$	$1.6 \cdot 10^{-7}$	Hydrogen phosphate
ammonium	NH_4^+	$5.6 \cdot 10^{-10}$	NH_3	$1.8 \cdot 10^{-5}$	ammonia
cianidric	HCN	$4.0 \cdot 10^{-10}$	CN^-	$2.5 \cdot 10^{-5}$	cianate
Hydrogen carbonate	HCO_3^-	$4.8 \cdot 10^{-11}$	CO_3^{2-}	$2.1 \cdot 10^{-4}$	carbonate
Hydrogen phosphate	HPO_4^{2-}	$3.6 \cdot 10^{-13}$	PO_4^{3-}	$2.8 \cdot 10^{-2}$	phosphate
wa	H_2O	$1.0 \cdot 10^{-14}$	OH^-	1	hydroxil

Increasing sthregth of the acid

Increasing strength of the base