#### Robert Boyle 1680



"acids...substances able to turn to red the indicator paper and to react with bases being neutralised..."



Chrozophora tinctoria

#### Roccella tinctoria also called tornasole





2-hydroxyphenazine

What do you notice in this structure ?!



Acids & bases, definition

**Arrhenius Theory** (1883)

ACID: Produces H<sup>+</sup> in Water BASE: Produces OH<sup>-</sup> in Water

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

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

 $\mathbf{X} + : \mathbf{Y} \rightarrow \mathbf{X} : \mathbf{Y}$ acid base

### OPERATIVE DEFINITIONS

*generally*, •an acid donates one (or more) H<sup>+</sup> to an acceptor base

•An acid accepts one (or more) *lone pair(s)* form a donor base

•H<sup>+</sup> is a very efficient *lone pair* acceptor
•OH<sup>-</sup> is avery efficient *lone pair(s)*3 of them) *donor*...!.

HCl is an acid, since it releases H<sup>+</sup> (accepting a *lone pair*) NaOH is a base, since it releases OH<sup>-</sup> (donating a *lone pair*)

### Acid base reaction (most common )

# HC1 + NaOH



 $\Delta G \ll 0 \approx$  - 57 KJ/mol

The calorie, again



1 cal  $\sim$  4.18 joules

#### Acids and bases of biomedical interest

<b>ACIDS</b>			
HCll	hydrochloric ac.	Strong	gastric jouce
HNO <sub>3</sub>	nitric ac.	strong	caustic
$H_2SO_4$	sulphoric ac.	strong	caustic
H <sub>2</sub> SO <sub>3</sub>	sulphoric ac.	strong	caustic
H <sub>3</sub> PO <sub>4</sub>	phosphoric ac.	weak	biological buffer
H <sub>3</sub> BO <sub>3</sub>	boric ac.	weak	external disinfectant
H <sub>2</sub> CO <sub>3</sub>	carbonic ac.	weak	biological buffer
НСООН	formic ac.	weak	
CH <sub>3</sub> COOH	acetic ac.	weak	vinegar
BASES (HYDROX)	(DES)		
NaOH	sodium hydroxide	strong	caustic
КОН	potassium hydroxide	caustic	
Ca(OH) <sub>2</sub>	calcium hydroxide	caustic	
$Mg(OH)_2$	magnesium hydroxide	estrong	caustic
Al(OH) <sub>3</sub>	aluminum hydroxide	strong	caustic
NH <sub>3</sub> .H <sub>2</sub> O	ammonia	weak	
NH <sub>4</sub> OH	ammonium hydroxide	e	

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### Acid-base conjugated couple (Brönsted & Lowry)



### Acid-base reaction

Conjugated couple 1



After H+ donation, the acid turns into the conjugated base while the base turns into the conjugated acid **The cojugated species have opposite strength** !







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Water auto-protolysis

 $H_2O \leftarrow H^+ + OH^ 2H_2O \leftarrow H_3O^+ + OH^-$ 



 $2 H_2 O \longrightarrow H_3 O^+ + OH^-$ 

Keq = 
$$\frac{[H_3O^+] [OH^-]}{[H_2O]^2}$$
 =  $\frac{(10^{-7}) (10^{-7})}{(55.5)^2}$  = 3.2 x 10<sup>-18</sup>

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$$H_2O \leftarrow H^+ + OH^-$$



$$[H_2O] = 55.\overline{5} M$$
, costant !!

 $K_{eq} \times [H_2O] = [H^+] [OH^-] = 10^{-14} = K_W (costant, at cost T)$ *ion product* of water

### Cojugated (acid-base) couples (Brönsted & Lowry)



strength of an acid/base in H<sub>2</sub>O

Defined by the tendency to donate/accept  $H^+$ 



 $[H_2O] \approx costant!$ 





#### Examples



Sapienza

*Let's figure out: The same equilibrium read from left to right and vice-versa...!* 

AH 
$$\xrightarrow{\text{on}}$$
 A<sup>-</sup> + H<sup>+</sup>





BUT pay attention to approximations !

$$B + H_2O \longrightarrow HB^+ + OH^-$$

$$K_{eq} \rightarrow K_b = \frac{[HB^+][OH^-]}{[B]} \qquad [OH^-] = \frac{K_w}{[H^+]} \qquad in H_2O \quad Kw = [H^+][OH^-]$$

$$K_b = \frac{[HB^+]K_w}{[B][H^+]} = \frac{K_w}{K_a}$$

Thus Kb and Ka are inversely related...!

$$K_b \propto 1/K_a \rightarrow K_b = K_w/K_a$$
 and

 $K_a \propto 1/K_b \rightarrow K_a = K_w/K_b$ 

The strength of the hydroxides (inorganic strong bases) is commonly expressed as dissociation of OH<sup>-</sup>

# $BOH = B^+ + OH^-$



#### **CONCLUDING:**

- •The stronger the acid, the larger  $K_a$
- •The stronger the base, the larger K<sub>b</sub>



			K <sub>a</sub> an	id K <sub>b</sub> Values		
	Name of Acid	Acid	Ka	Name of Base	Base	Kb
•	Sulfuric acid	H <sub>2</sub> SO <sub>4</sub>	large	hydrogen sulfate ion	HSO4-	very small
	Hydrochloric acid	HC1	large	chloride ion	C1-	very small
	Nitric acid	HNO <sub>3</sub>	large	nitrate ion	NO3"	very small
	Hydronium ion	H <sub>2</sub> O <sup>+</sup>	55.5	water	H <sub>2</sub> O	1.8 × 10-16
•	Hydrogen sulfate ion	HSO4-	1.2 × 10 <sup>-2</sup>	sulfate ion	SO42-	8.3 × 10-1
•	Phosphoric acid	H <sub>2</sub> PO <sub>4</sub>	7.5 x 10 <sup>-3</sup>	dihudrogen phosphate ion	H-PO4-	1.3 × 10-12
	Hexaaguairon(III) ion	Fe(H2O)63+	6.3 × 10 <sup>-3</sup>	pentaaguahydroxoiron(III) ion	Fe(H <sub>2</sub> O) <sub>5</sub> OH <sup>2+</sup>	1.6 × 10-12
	Hydrofluoric acid	HF	7.4 × 10 <sup>-4</sup>	fluoride ion	F-	1.4 × 10-11
•	Formic acid	HCO <sub>2</sub> H	$1.8 \times 10^{-4}$	formate ion	HCO2"	5.6 x 10-1
	Benzoic acid	CeHsCO2H	6.3 × 10 <sup>-5</sup>	benzoate ion	CeHsCO2-	1.6 × 10 <sup>-10</sup>
•	Acetic acid	CH3CO2H	1.8 × 10 <sup>-5</sup>	acetate ion	CH2CO2	5.6 x 10 <sup>-1</sup>
	Hexaaguaaluminum ion	A1(H2O)63+	7.9 × 10 <sup>-6</sup>	pentaaguahydroxoaluminum ion	A1(H2O)50H2+	1.3 × 10-9
•	Carbonic acid	H <sub>2</sub> CO <sub>3</sub>	4.2 × 10-7	hydrogen carbonate ion	HCO3-	2.4 × 10-8
	Hydrogen sulfide	Hos	1 × 10 <sup>-7</sup>	hudrogen sulfide ion	HS-	1 × 10 <sup>-7</sup>
•	Dihudrogen phosphate ion	H-PO4-	6.2 x 10 <sup>-8</sup>	hydrogen phosphate ion	HPO42-	1.6 × 10-7
	Hypochlorous acid	HÊIO	3.5 × 10 <sup>-8</sup>	hypochlorite ion	C10-	2.9 × 10-7
	Ammonium ion	NH4+	5.6 x 10 <sup>-10</sup>	ammonia	NHa	1.8 × 10-5
	Hydrocyanic acid	HCN	4.0 × 10 <sup>-10</sup>	cuanide ion	CN-	2.5 × 10-5
	Hexaaguairon(II) ion	Fe(H2O)62+	3.2 × 10 <sup>-10</sup>	pentaaguahydroxoiron(II) ion	Fe(H2O)sOH+	$3.1 \times 10^{-5}$
•	Hydrogen carbonate ion	HCO3-	4.8 × 10-11	carbonate ion	CO22-	$2.1 \times 10^{-4}$
•	Hydrogen phosphate ion	HPO42-	3.6 x 10 <sup>-13</sup>	phosphate ion	PO43-	2.8 × 10-2
	Water	HO	1.8 × 10 <sup>-16</sup>	hudroxide ion	OH-	55.5
	Hudrogen sulfide ion	HS-	1 × 10-19	sulfide ion	S2-	$1 \times 10^{5}$

Acido acetico	1,75-10-5
Acido amminoacetico	Ka1 4,47 · 10 <sup>-3</sup>
(glicina)	Ka2 1,67-10-10
Acido amminobenzensolfonico (solfanilico)	K <sub>a</sub> 5,86-10 <sup>-4</sup>
Acido arsenico	$K_{a1} 5,8 \cdot 10^{-3}$ $K_{a2} 1,10 \cdot 10^{-7}$ $K_{a3} 3,2 \cdot 10^{-12}$
Acido arsenioso	5,1.10-10
Acido aspartico	K <sub>a1</sub> 1,02 · 10 <sup>-2</sup> K <sub>a2</sub> 1,26 · 10 <sup>-4</sup> K <sub>a3</sub> 9,95 · 10 <sup>-11</sup>
Acido benzoico	6,28 - 10-5
Acido borico	$K_{a1} 5,81 \cdot 10^{-10}$ $K_{a2} 1,82 \cdot 10^{-13}$ $K_{a3} 1,58 \cdot 10^{-14}$
Acido butanoico	1,52 - 10 - 5
Acido cis-butendioico (maleico)	K <sub>a1</sub> 1,23 · 10 <sup>-2</sup> K <sub>a2</sub> 4,66 · 10 <sup>-7</sup>
Acido trans-butendioico (fumarico)	K <sub>a1</sub> 8,85 · 10 <sup>-4</sup> K <sub>a2</sub> 3,21 · 10 <sup>-5</sup>
Acido carbonico	$K_{a1} 4,45 \cdot 10^{-7}$ $K_{a2} 4,69 \cdot 10^{-11}$
Acido cianidrico	6,2.10-10
Acido cítrico	$K_{a1} 7,44 \cdot 10^{-4}$ $K_{a2} 1,73 \cdot 10^{-5}$ $K_{a3} 4,02 \cdot 10^{-7}$
Acido cloroacetico	1,36.10-3
Acido cloroso	1,12 · 10 - 2
Acido cromico	$K_{a1}$ 1,6 $K_{a2}$ 3,1 · 10 <sup>-7</sup>
Acido	
D-2,3-diidrossibutandioico (D-tartarico)	$K_{a1} 9,20 \cdot 10^{-4}$ $K_{a2} 4,31 \cdot 10^{-5}$

Acido etilendiamminotetraacetico	Ka1 1.0
	Kaz 0,032
	K <sub>a3</sub> 0,010
	Ka4 0,0021
	Ka5 7,8.10-7
	K <sub>a6</sub> 6,8 10 <sup>-11</sup>
Acido formico	1,80.10-4
Fenolo	1,05.10-10
Fluoruro di idrogeno	6,8·10 <sup>-4</sup>
Acido fosforico	Kai 7.11.10 <sup>-3</sup>
*	Ka2 6,32.10 <sup>-8</sup>
	$K_{a3}$ 7,1.10 <sup>-13</sup>
Acido fosforoso	Ka1 3.10-2
	Ka2 1,62 10-7
Acido o-ftalico	Ka1 1,12.10 <sup>-3</sup>
	Ka2 3,90-10 <sup>-6</sup>
Acido glutammico	Ka1 5,9.10 <sup>-3</sup>
*	Ka2 3,8.10-5
	K <sub>a3</sub> 1,12 · 10 <sup>-10</sup>
Acido idrossiacetico (glicolico)	1,48.10-4
Acido 2-idrossibenzoico	$K_{a1}$ 1,07 $\cdot$ 10 <sup>-3</sup>
salicilico)	$K_{a2}$ 1,82 $\cdot$ 10 <sup>-14</sup>
Acido L- idrossibutandioico	Ka1 3,48.10 <sup>-4</sup>
(malico)	Kaz 8.00-10 <sup>-6</sup>
Acido iodico	0,17
Acido ipobromoso	2,3.10-9
Acido ipocloroso	3,0.10-8
Acido ipofosforoso	5,9.10-2
Acido ipoiodoso	2,3.10-11
Acido lattico 🔸	1,37.10-4
Acido malonico	$K_{a1}$ 1,42 $\cdot$ 10 <sup>-3</sup>
*	$K_{a2} 2,01 \cdot 10^{-6}$

Acido mandelico	3,88-10-4
Acido nitroso	7,1.10-4
Acido ossalico	$K_{a1} 5,60 \cdot 10^{-2}$ $K_{a2} 5,42 \cdot 10^{-5}$
Acido ossobutandioico (ossalacetico)	$K_{a1} 2.8 \cdot 10^{-3}$ $K_{a2} 4.3 \cdot 10^{-5}$
Acido ossopropanoico (piruvico)	2,8.10-3
Acido piridin-2-carbossilico (picolinico)	$K_{a1} 9.8 \cdot 10^{-2}$ $K_{a2} 4.1 \cdot 10^{-6}$
Acido piridin-3-carbossilico (nicotinico)	$K_{41} 8,9 \cdot 10^{-3}$ $K_{42} 1,55 \cdot 10^{-5}$
Acido pirofosforico	$K_{a1} 0.16$ $K_{a2} 6 \cdot 10^{-3}$ $K_{a3} 2.0 \cdot 10^{-7}$ $K_{a4} 4.0 \cdot 10^{-10}$
Acido propanoico	1,34.10-5
Acido propenoico (acrilico)	5,52 · 10-5
Acido solfidrico	$K_{a1} 9,5 \cdot 10^{-5}$ $K_{a2} 1,3 \cdot 10^{-14}$
Acido solforico (seconda dissoc.)	1,02.10-2
Acido solforoso	$K_{a1} 1.23 \cdot 10^{-2}$ $K_{a2} 6.6 \cdot 10^{-8}$
Acido succinico (butandioico) 😽	$K_{a1} 6,21 \cdot 10^{-5}$ $K_{a2} 2,31 \cdot 10^{-6}$
Acido tiasolforico	K <sub>a1</sub> 0,3 K <sub>a2</sub> 3·10 <sup>-2</sup>
and the second second second second second	0.22

### Thus

The stronger the acid:

• the higher its Ka (H<sup>+</sup> dissociation)

#### The stronger the base:

- the higher its Kb value (H+ association)
- the lower the Ka value (of the conjugated acid)
- the higher the efficiency to dissociate OH- (hydroxides only)

Ka or Kb values can be numbers *difficult to handle*, e.g. rather small (10<sup>-x</sup>) whose, again, small variations induce big effects !

This is why it was introduced the notation **p**;  $\mathbf{p} = \operatorname{colog} (-\log x = \log 1/x) \ base = 10$ of Ka or Kb

if [Ka] = 
$$10^{-5}$$
  
**p**Ka = 5  
-log 10<sup>-5</sup>, log 1/10<sup>-5</sup> = log 10<sup>5</sup> = 5

The weaker the acid:

•The lower its Ka value &

•The higher its pKa value

### Ka & pKa

Acids	Ka	pKa	
Trichloroethanoic acid	5.10 × 10 <sup>-2</sup>	1.29	Stronger
Chloroethanoic acid	$1.38 \times 10^{-3}$	2.86	Acid
Methanoic acid	1.77 x 10 <sup>-4</sup>	3.75	
Ethanoic acid	$1.78 \times 10^{-5}$	4.75	
Propanoic acid	1.26 × 10 <sup>-5</sup>	4.90	
Carbonic acid	3.98 × 10-7	6.40	
Water	1.00 x 10 <sup>-7</sup>	7.00	Weak
	Ka increas	es pKa Decrea	ses Acid
Si	trong Acid - High Veak Acid - Low K	Ka - Low pKa a - High pKa	



Remember relationship between Ka and  $\alpha$  ?



What happens to  $\alpha$  upon diluting a solution of a weak electrolyte ?!



What is the molecular reason for different acid/base strength?

Different H+ bond energy (covalent etheropolar) (electronegativity + inductive effects + charge distribution)

#### Strenght of hydro-chloro acids



# Bond energy !



# Poly-functional acids (*poly*-protic)

Electronegativity  $\rightarrow f(E_i, A_e)$ 

**Distribution of electronegativity** 



### polyfunctional acids

$$H_2SO_4 \longrightarrow HSO_4^- + H^+ \qquad K_{a1} = \infty$$

 $HSO_4^- \longrightarrow SO_4^{2-} + H^+ \qquad K_{a2} = 10^{-2}$ 



 $[H^+] = 10^{-7} M$  ? The log  $1/10^{-7} = \log 10^7 = 7$ pH = 7 (neutral pH!)

Ex.s: 
$$[H^+] = 2,5119 \times 10^{-8} \rightarrow pH 7.6$$
  
 $[H^+] = 3,9810 \times 10^{-8} \rightarrow pH 7.4$   
 $[H^+] = 5,0118 \times 10^{-8} \rightarrow pH 7.3$   
 $[H^+] = 6,3095 \times 10^{-8} \rightarrow pH 7.2$   
 $[H^+] = 3,1623 \times 10^{-7} \rightarrow pH 6.5$ 

### [H<sup>+</sup>] to pH conversion



#### Biological fluids



 $[H^+] \times [OH^-] = cost = 10^{-14}$ pH + pOH = 14



pH = log 1/0.1 = 1.0

pH of a weak acid solution

 $AH \longrightarrow A^- + H^+$ 

 $Ka = \frac{[A^{-}] [H_{3}O^{+}]}{[AH]} = \frac{[H^{+}]^{2}}{[AH]}$ 

 $[H^+]^2 = Ka [AH]$ 

$$[H^+] = \sqrt{Ka \times Ca}$$

#### How many atoms are in the human body?

A 70 kg body would have approximately 7\*10<sup>27</sup> atoms. That is, 7 followed by 27 zeros: 7,000,000,000,000,000,000,000,000,000

Of that, 4.7\*10<sup>27</sup> would be hydrogen atoms, which have one proton and one electron each.

Another 1.8\*1027 would be oxygen, which has 8 protons, 8 neutrons and 8 electrons.

There are 7.0\*1026 carbon atoms, which have 6 protons, 6 neutrons and 6 electrons. Now, let's add that all up:

	Protons	Neutrons	Electrons
Hydrogen	4.7*10 <sup>27</sup>	0	4.7*10 <sup>27</sup>
Oxygen	1.4*10 <sup>28</sup>	1.4*10 <sup>28</sup>	1.4*10 <sup>28</sup>
Carbon	4.2*10 <sup>27</sup>	4.2*10 <sup>27</sup>	4.2*10 <sup>27</sup>
Total	2.3*10 <sup>28</sup>	1.8*10 <sup>28</sup>	2.3*10 <sup>28</sup>

Well, you'll have to agree that really is a whole bunch.

#### Acid-base conjugated couples

