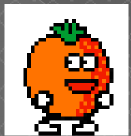
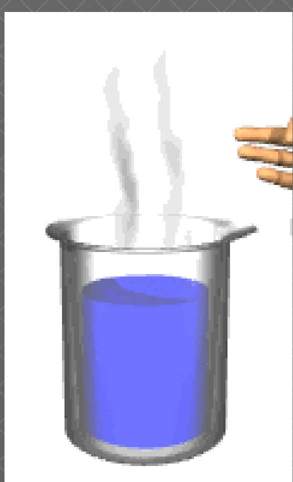
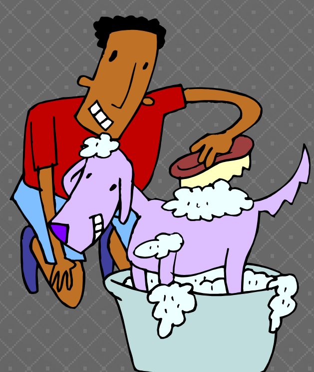


Asam dan Basa





ASAL USUL TEORI ASAM BASA

Lavoisier (1776) mengemukakan teori asam yang hanya terfokus pada asam oksi seperti HNO_3 dan H_2SO_4. sedangkan asam-asam hidro halida tidak dapat didefinisikan

Sir Humphry Davy (1810)memberikan istilah asam untuk senyawa hidrohalida meskiput kurang terstruktur

ASAL USUL TEORI ASAM BASA

Berzelius

Asam → Senyawa-senyawa yang mengandung oksida non logam

Basa → Senyawa-senyawa yang mengandung oksida logam

Hanya berlaku 30 tahun

ASAL USUL TEORI ASAM BASA

Justus von Liebig (1838)

Asam

Zat-zat yang mengandung hidrogen yang dapat digantikan dengan logam

Basa

Zat-zat yang mengandung hidrogen yang tidak dapat digantikan dengan logam

Hanya berlaku 50 tahun

TEORI ASAM BASA

Secara Umum :

Asam	:	Cairan berasa asam dan dapat memerahkan kertas lakmus biru
Basa	:	Cairan berasa pahit dan dapat membirukan kertas lakmus merah
Garam	:	Cairan yang berasa asin

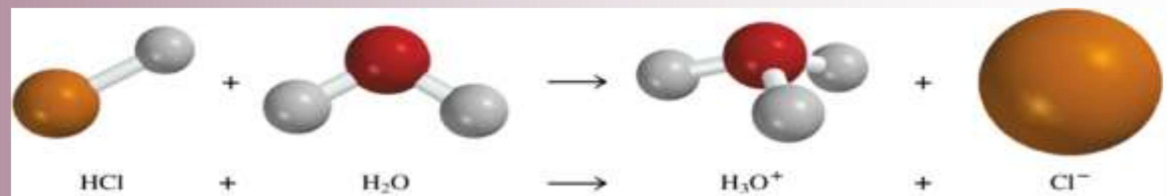
TEORI ASAM BASA

- Terdapat 7 teori Asam Basa yang masih dikenal :
  - Teori Arrhenius
  - Teori Bronstead-Lowry
  - Teori Lewis
  - Teori Pelarut
  - Teori Lux-Flood
  - Teori Usanovich
  - Teori Pearson

Teori Arrhenius (1887)

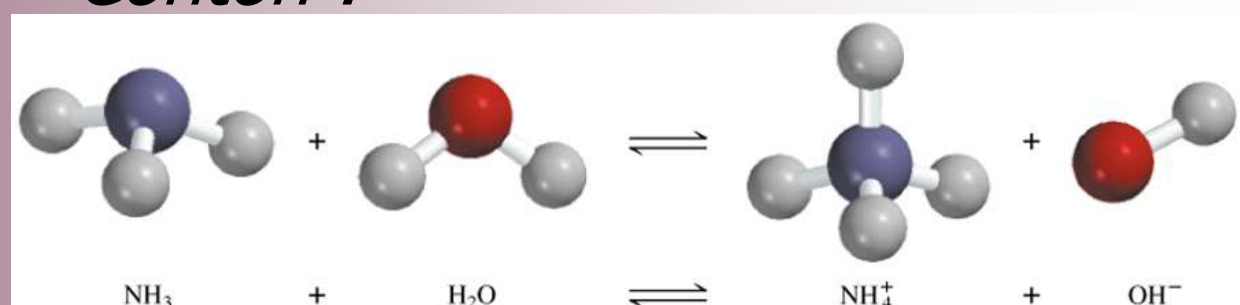
Asam adalah senyawa yang melepaskan H^+ dalam air.

Contoh :



Basa adalah senyawa yang melepaskan OH^- dalam air

Contoh :



Kelemahan : hanya berlaku untuk larutan dalam air saja.

TEORI ASAM BASA

Teori Bronsted - Lowry(1923)


Asam : Senyawa yg dapat memberikan proton (H^+) / donor proton.

Basa: Senyawa yg dapat menerima proton (H^+) / akseptor proton.

CONTOH :

Reaksi tanpa Pelarut Air

$HCl_{(g)} + NH_{3(g)} \rightarrow NH_4^+ + Cl^- \rightarrow NH_4Cl_{(s)}$

Asam Basa

Reaksi dengan Pelarut Air

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

Asam Basa

$NH_4OH_{(g)} + H_2O_{(aq)} \rightarrow NH_4OH_2^+{}_{(aq)} + OH^-_{(aq)}$

Air dapat bersifat asam atau basa → Amfoter

TEORI ASAM BASA

Pasangan Asam Basa Konjugasi

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

Asam 1   Basa 1 ⇌ Asam 2   Basa 2

Konjugasi (Basa 1 – Asam 2)

Konjugasi (Asam 1 – Basa 2)

Pasangan asam basa konjugasi : pasangan asam 1 – basa 2 dan basa 1 – asam 2 → HCl – Cl^- dan H_2O – H_3O^+

<u>Asam konjugasi</u> : Asam yg terbentuk dari basa yang menerima Proton → H_3O^+

<u>Basa konjugasi</u> : Basa yg terbentuk dari asam yang melepaskan Proton → Cl^-

Jelaskan untuk reaksi :

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

a. **Pasangan asam basa konjugasi**

b. **Asam konjugasi**

c. **Basa konjugasi**

Pertanyaan!

- Bagaimana dengan?

$$HF_{(aq)} + SO_3^{2-}{}_{(aq)} \rightarrow F^-{}_{(aq)} + HSO_3^-{}_{(aq)}$$

$$CO_3^{2-}{}_{(aq)} + HC_2H_3O_{2(aq)} \rightarrow C_2H_3O_2^-{}_{(aq)} + HCO_3^-{}_{(aq)}$$

$$H_3PO_{4(aq)} + OCl^-{}_{(aq)} \rightarrow H_2PO_4^-{}_{(aq)} + HOCl_{(aq)}$$

pKa’s AND ACID STRENGTH

pK_a - An alternative to K_a to describe acid strength.

Acid and Base Strength

hint pg 24

- Acid dissociation constant, K_a
- Base dissociation constant, K_b
- For conjugate pairs, $(K_a)(K_b) = K_w$
- Spontaneous acid-base reactions proceed from stronger to weaker.

DEFINITION OF pK_a

(A concise way to state the strength of an acid.)

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

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

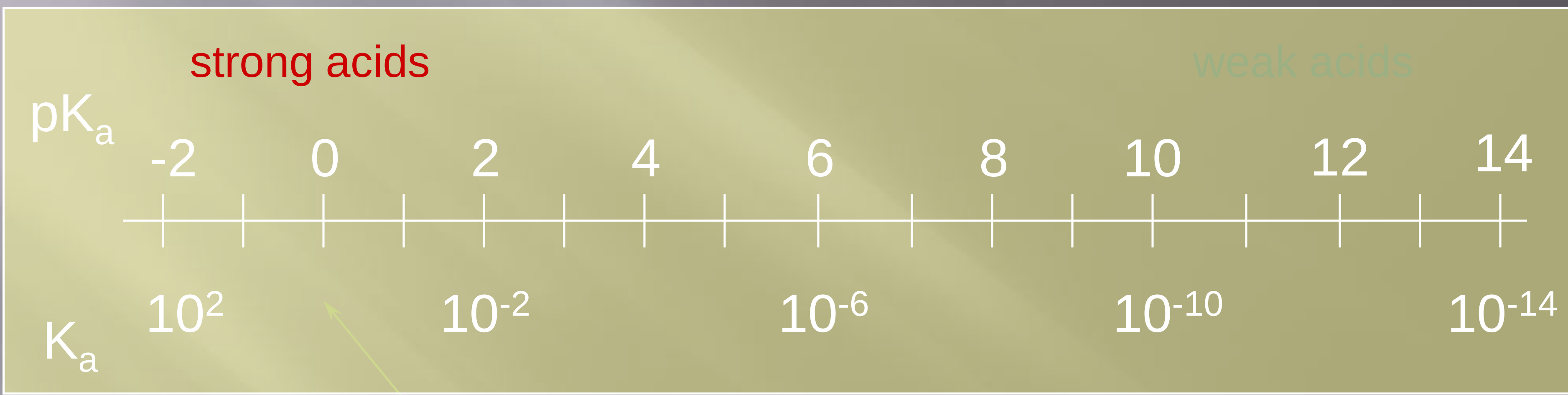
Compare the definition of pH

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

$$pK_a = -\log K_a$$

COMPARISON OF pK_a and K_a VALUES

$$pK_a = - \log K_a$$



The smaller the value of the pK_a the stronger the acid.

We will use pK_a to describe the strengths of acids.
It is a single number, without exponents.

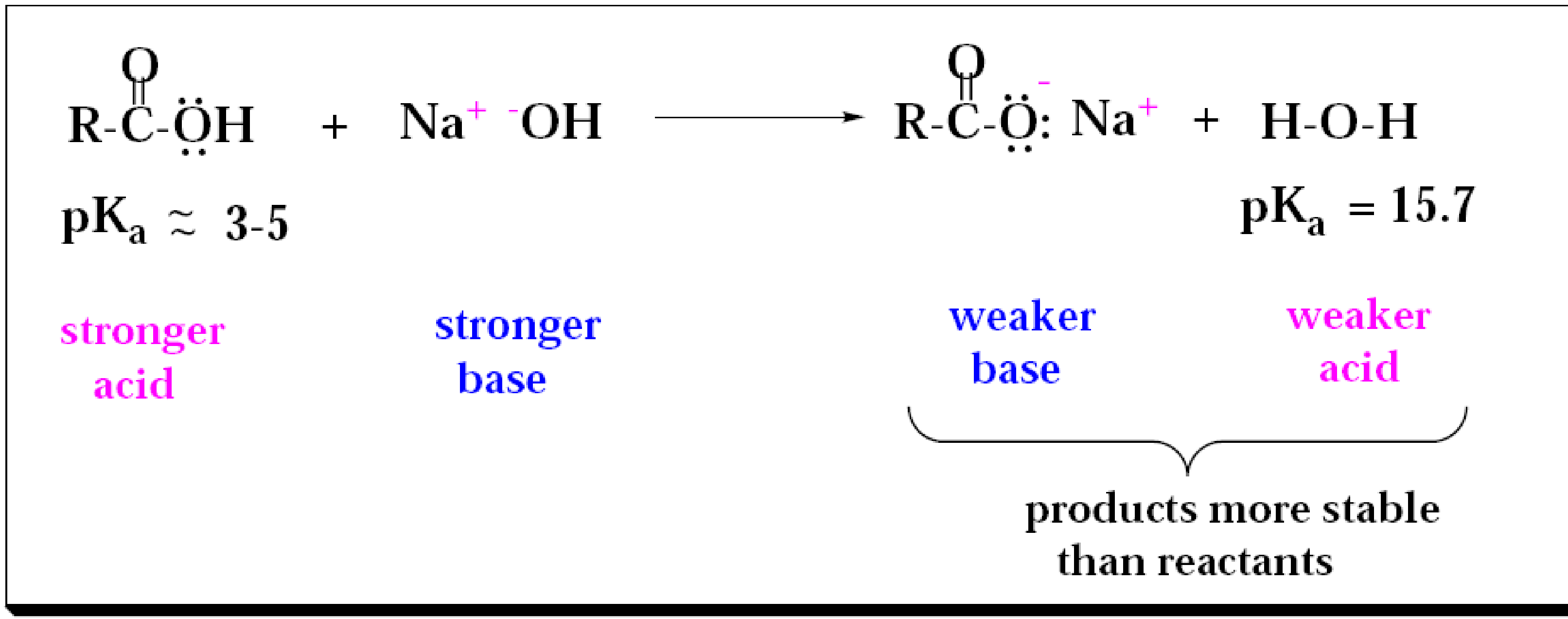
Spontaneous or not?

acid	base		base	acid
$CH_3-C(=O)-OH$	+ $CH_3-\ddot{N}H_2$	[redacted] ?	$CH_3-C(=O)-O^-$	+ $CH_3-NH_3^+$
pK_a 4.74	pK_b 3.36		pK_b 9.26	pK_a 10.64

$pK_a = -\log Ka$ larger pKa = weaker acid

Predicting the Outcome of Acid-Base Reactions

Acid-base reactions proceed to give the weaker acid and weaker base as products. This is the reaction favored by product stability and is the tendency of reactions under equilibrium control.

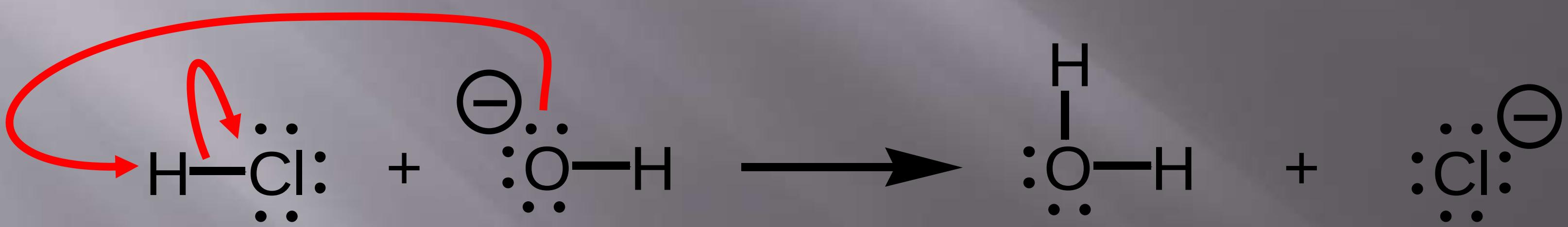


Even though the above reaction is an equilibrium, only a one-way arrow is used because the equilibrium is far to the right (>99%). The practical consequence of the above reaction is that carboxylic acids (RCO_2H) can be dissolved as their carboxylate salts in aqueous NaOH solutions.

Acids and Bases

How are the bonds made and broken?
The "curved arrow" formalism.

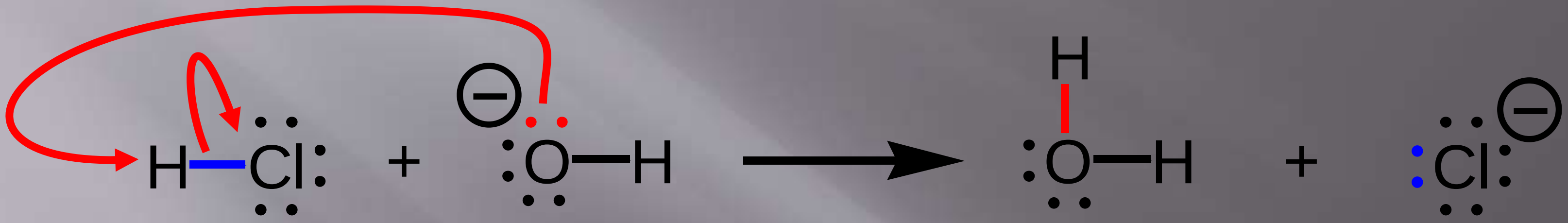
acid base



electron pair acceptor

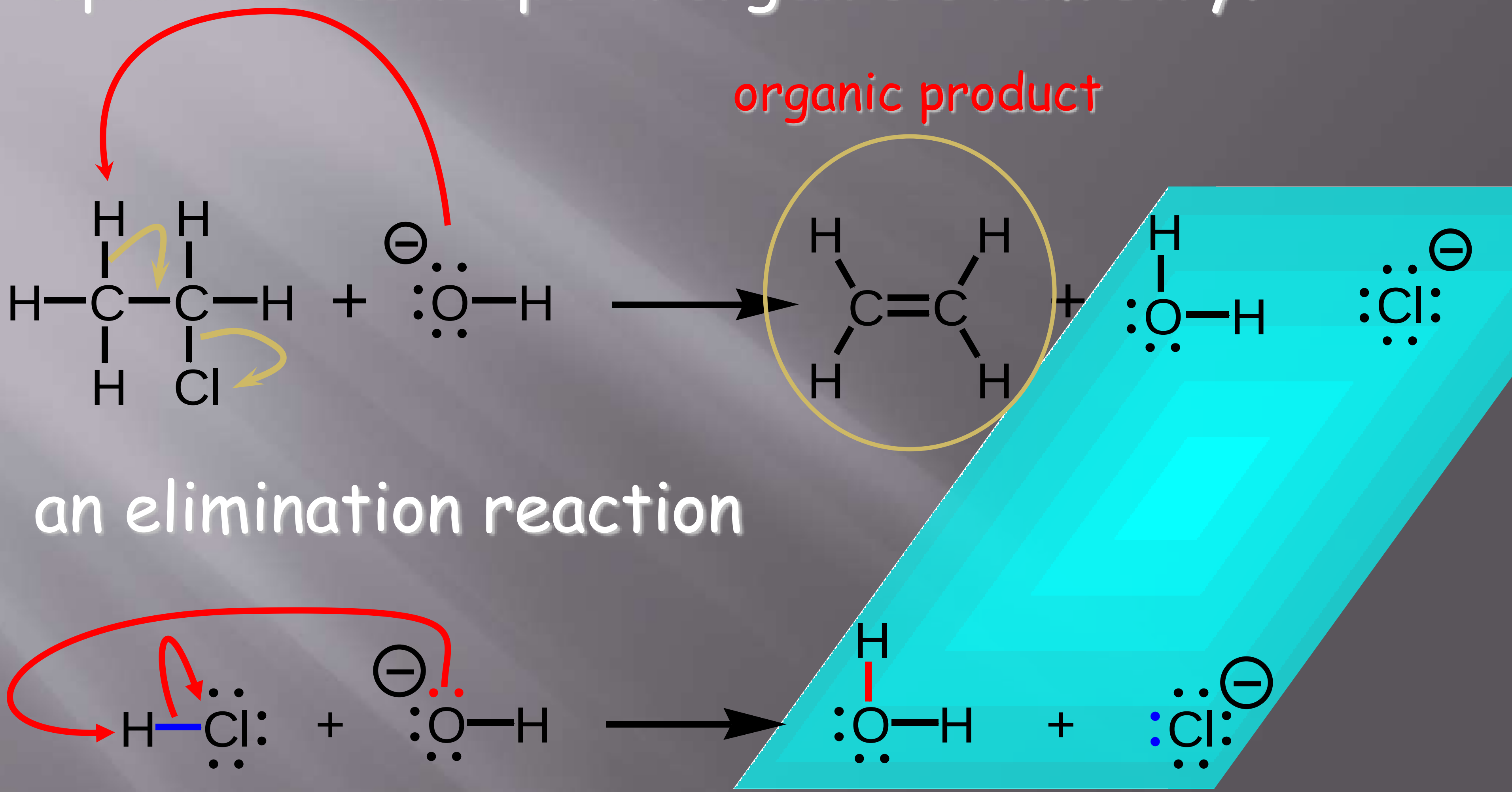
electron pair donor

The "curved arrow formalism" is an extremely important concept in organic chemistry.

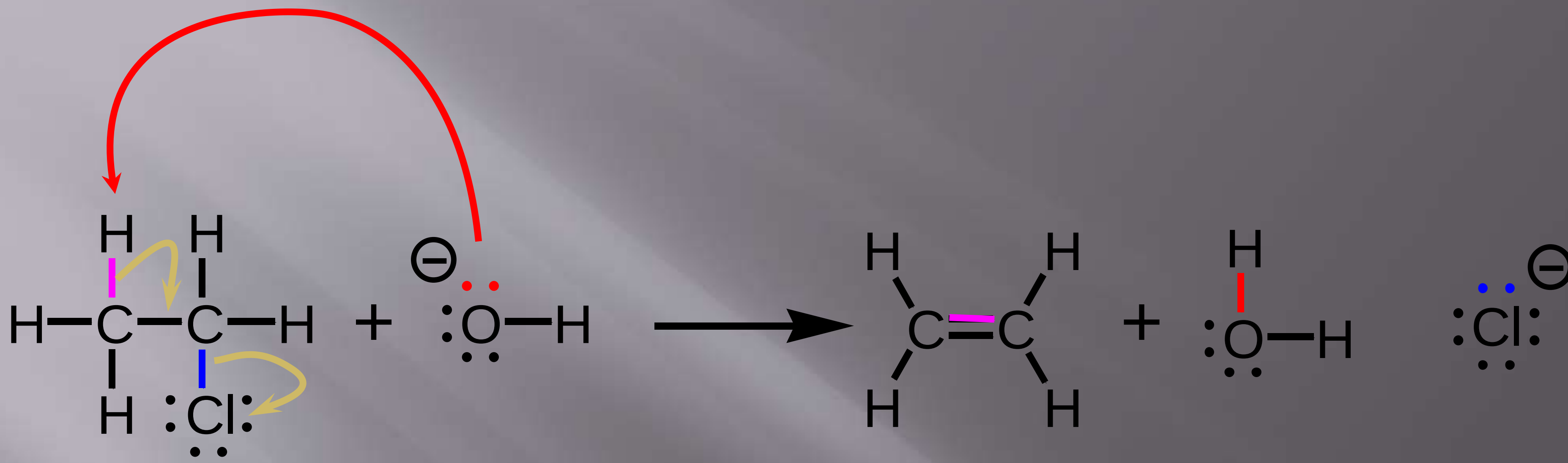


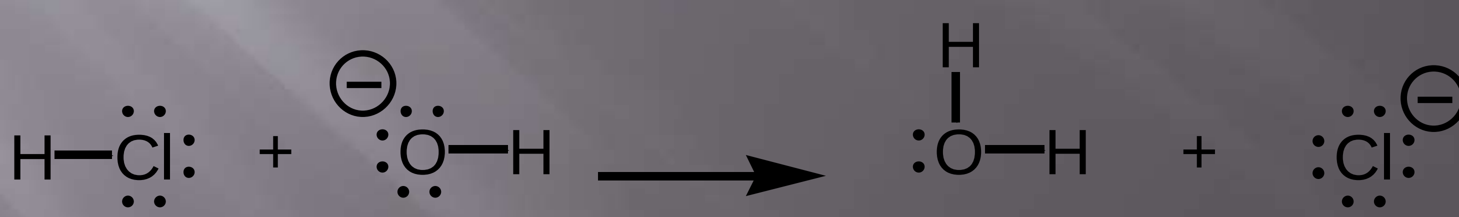
The arrow illustrates the flow of the electrons. This formalism is useful in describing reactivity and bonding.

The "curved arrow formalism" is an extremely important concept in organic chemistry.

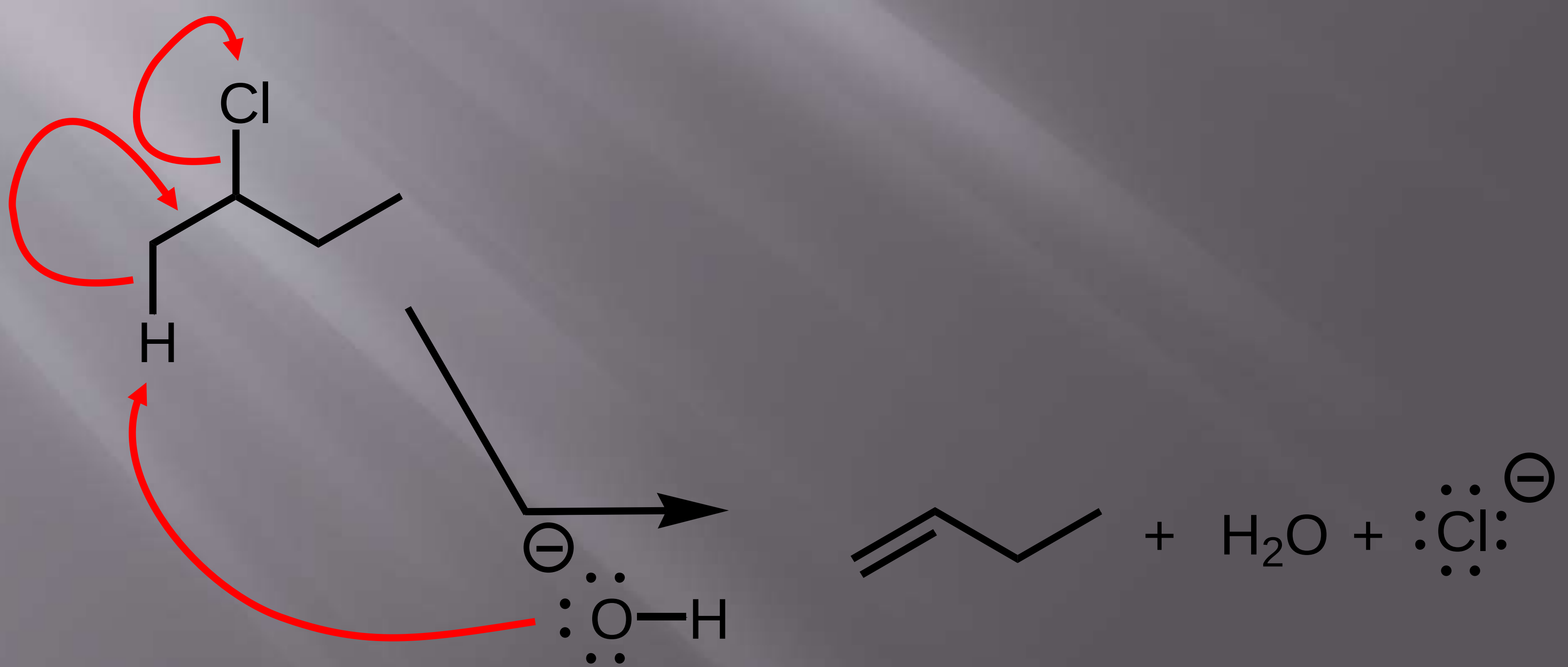


Organic compounds can behave as acids in acid-base reactions.

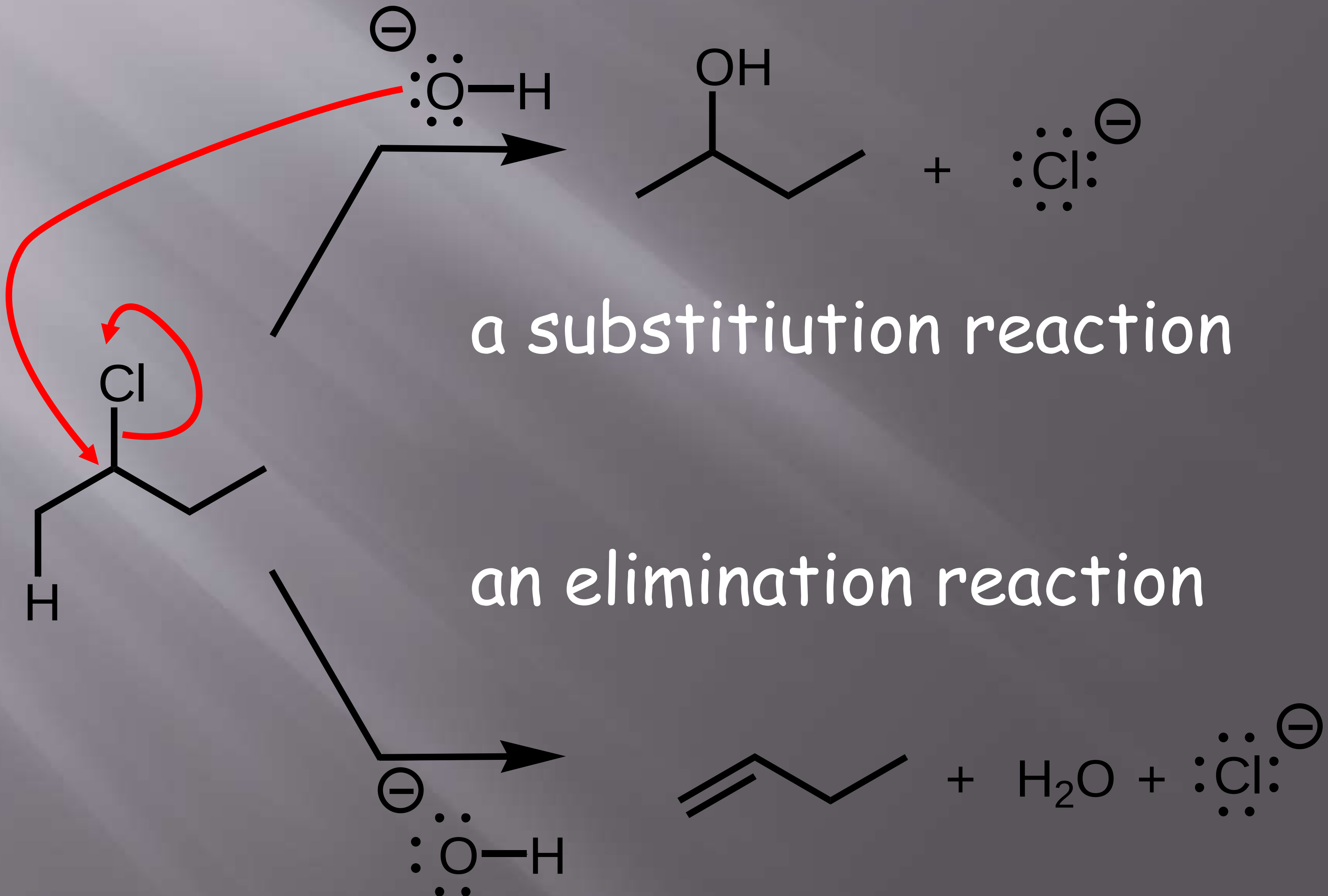




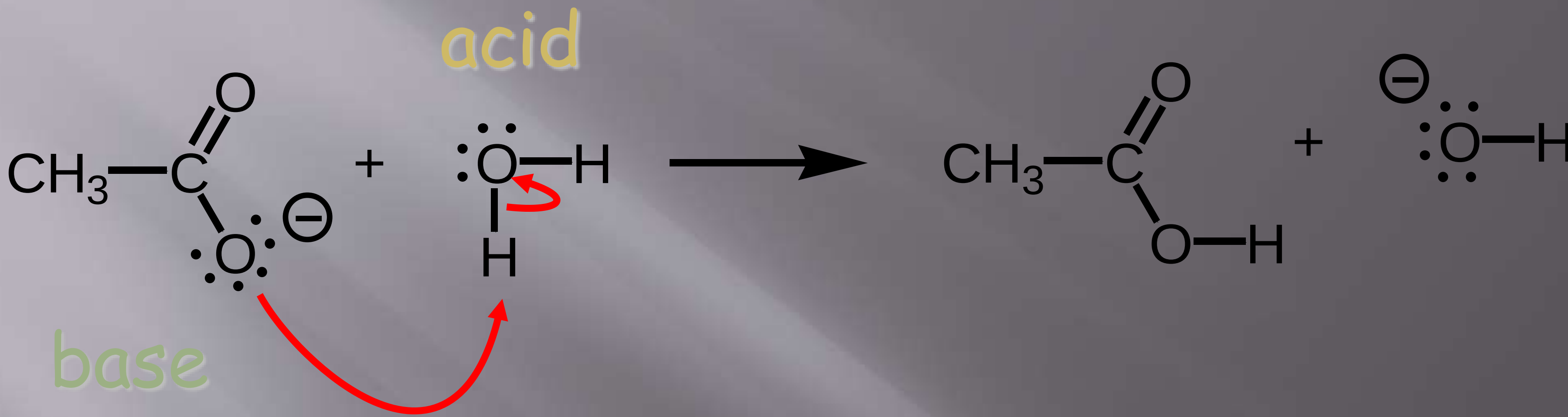
In organic chemistry two or more acid base reactions can compete.

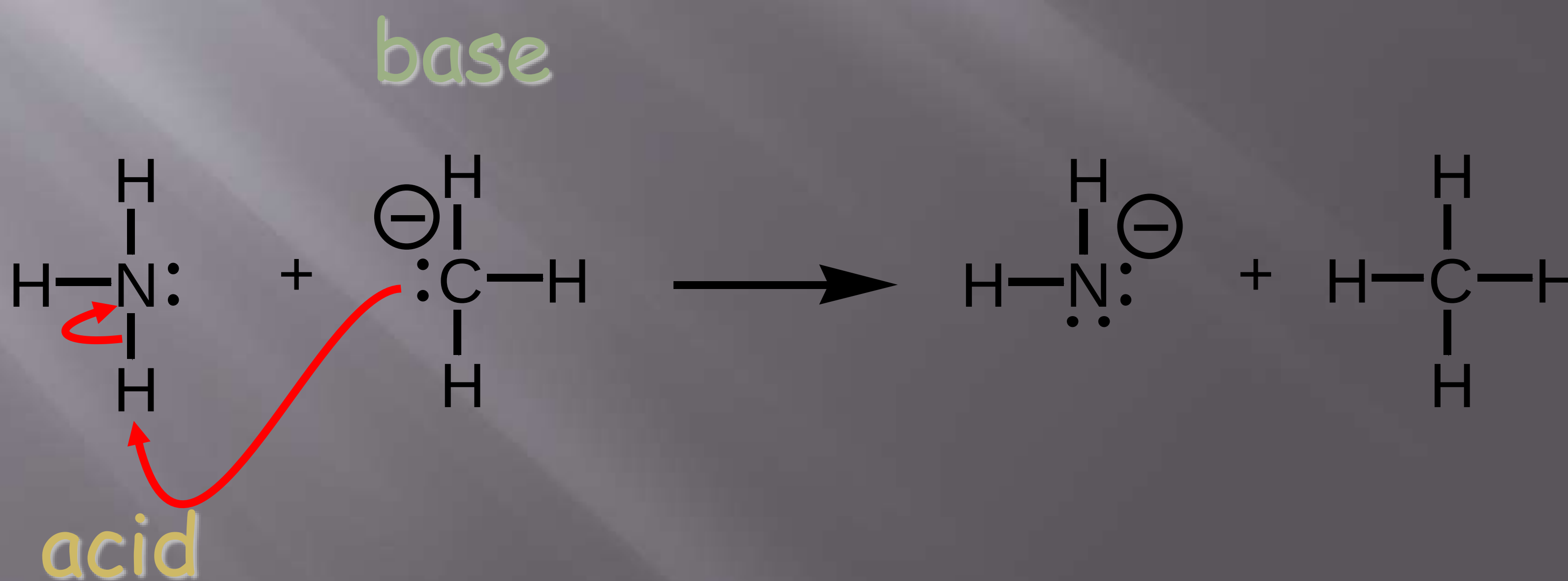


In organic chemistry two or more acid base reactions can compete.

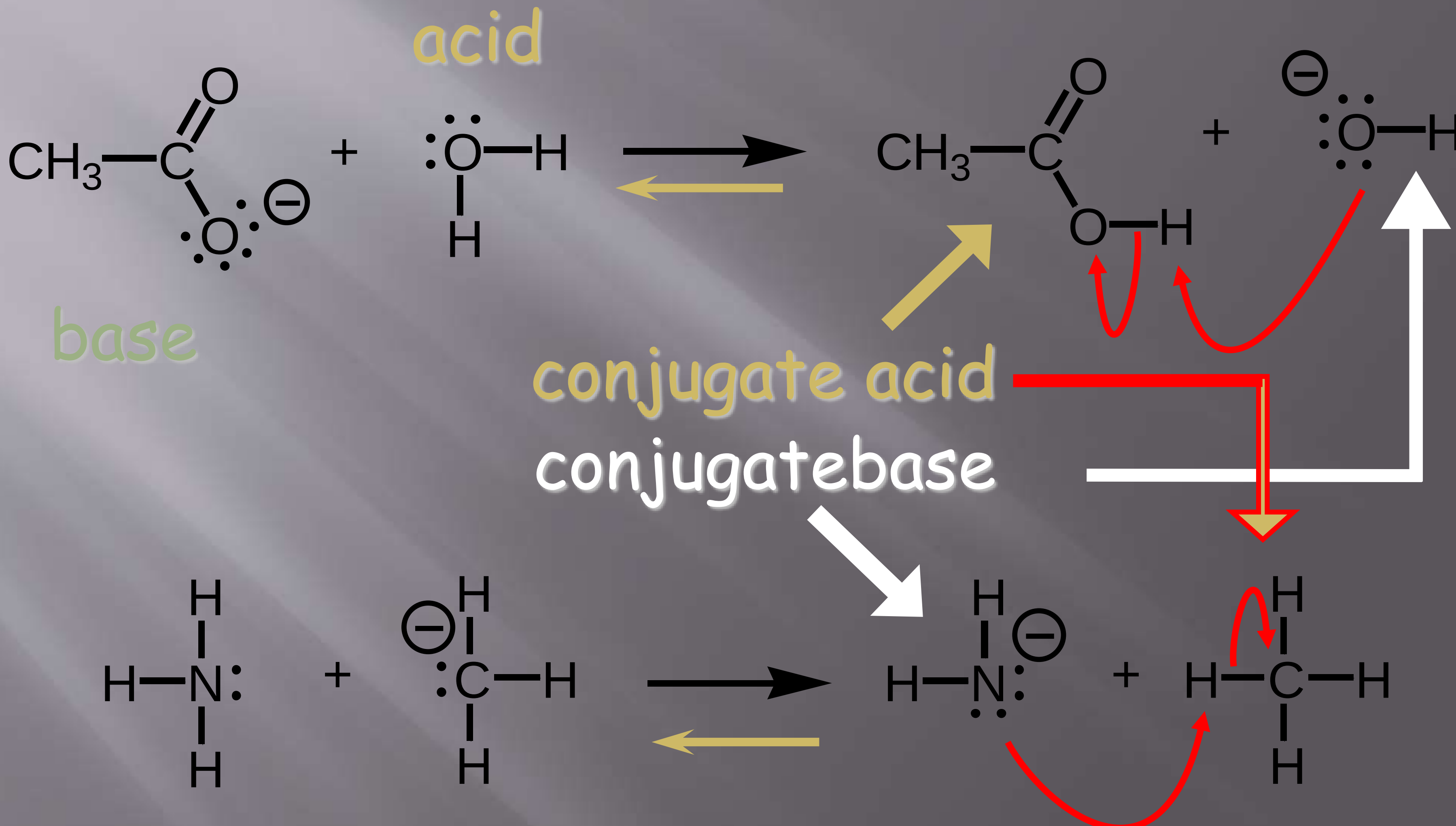


Identify the acid and base in the following reactions.

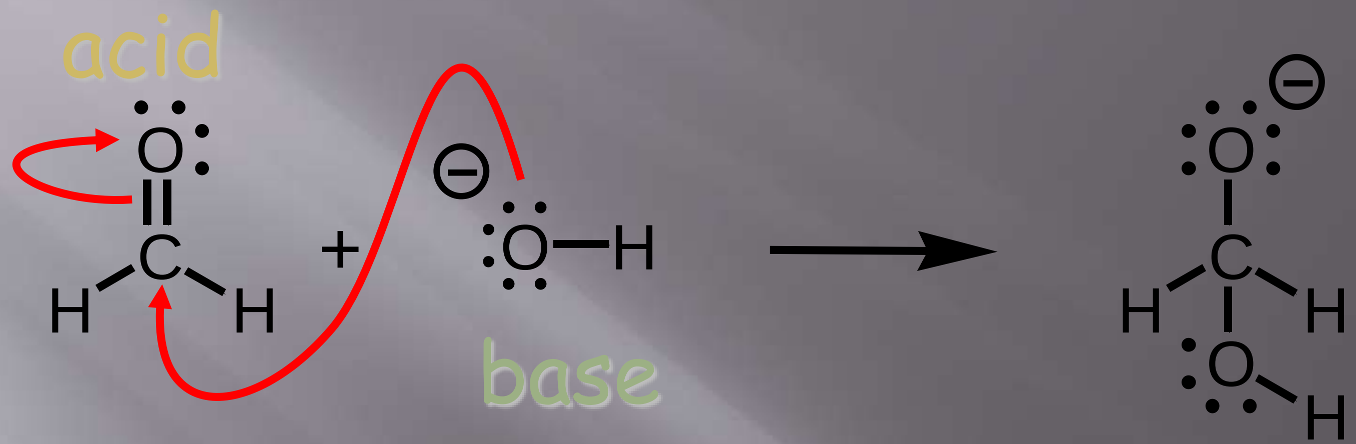


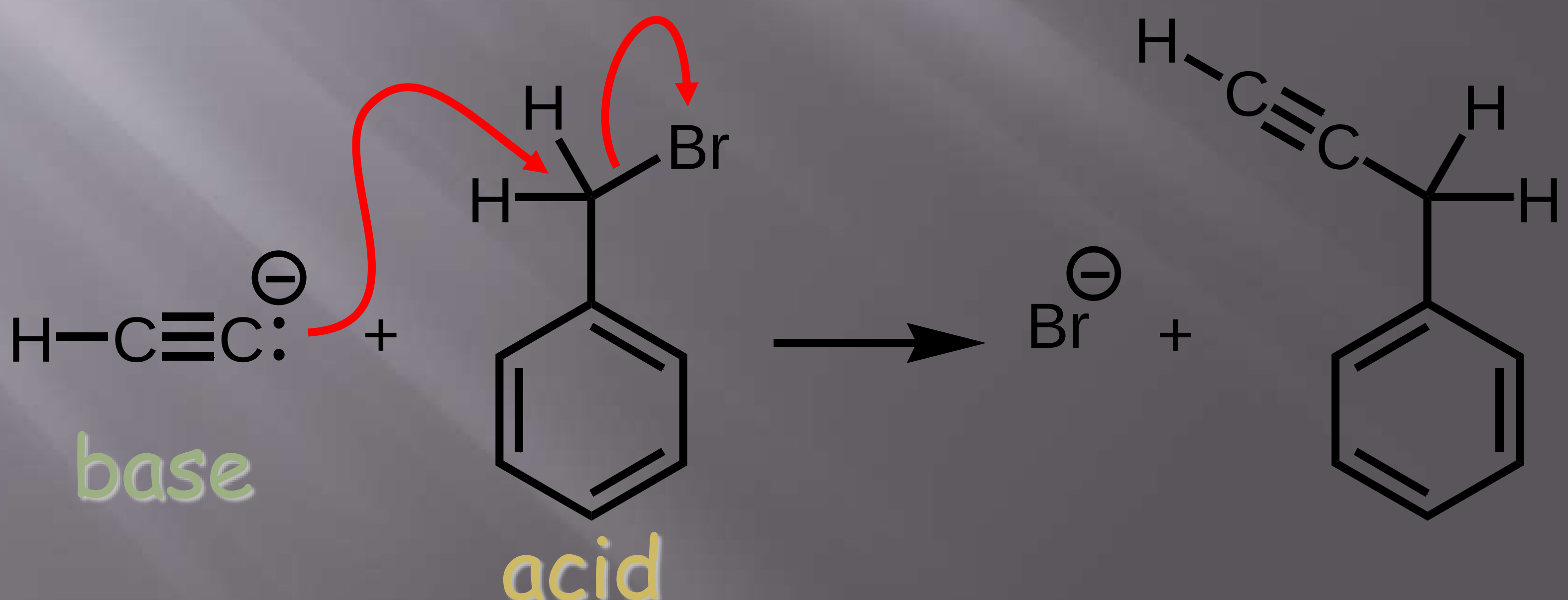


Identify the conjugate acid and conjugate base in the following reactions.



Identify the acid and base in the following reactions.

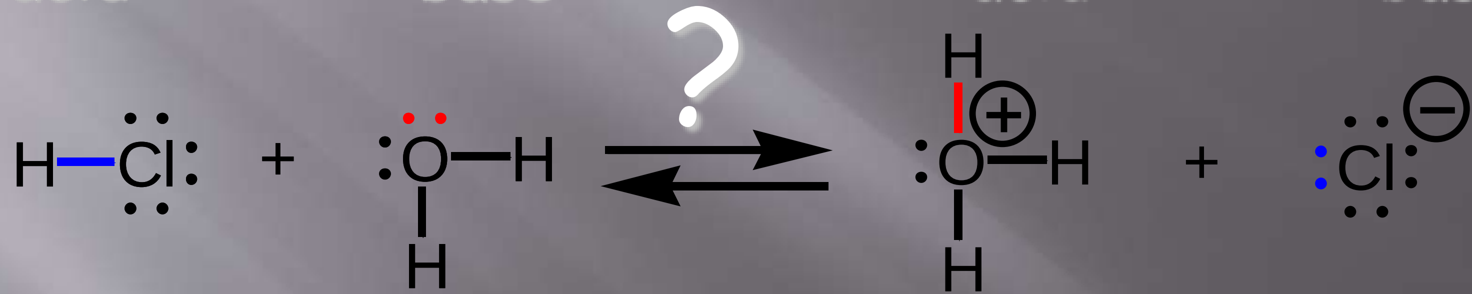




which is the stronger acid?

which is the stronger base?

acid | base | conjugate acid | conjugate base

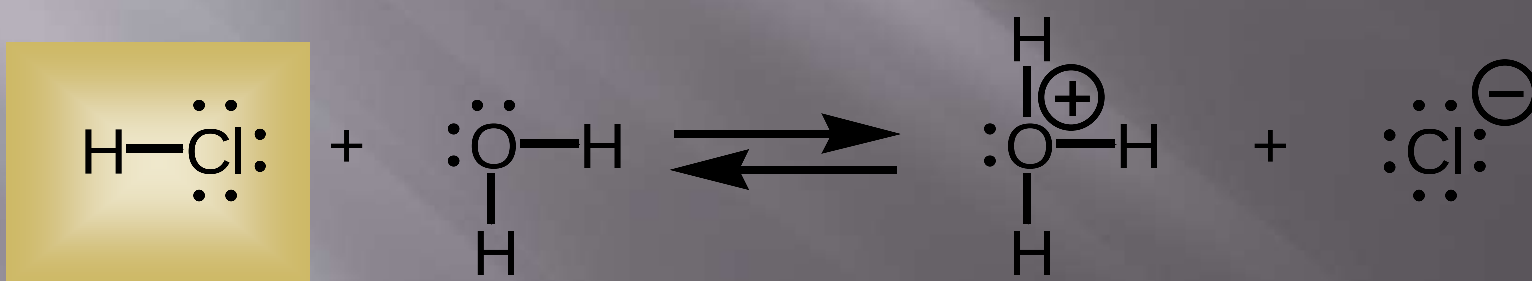


electron pair acceptor | electron pair donor | electron pair acceptor | electron pair donor

which are the major species present at equilibrium?

which is the stronger acid?

acid base acid base

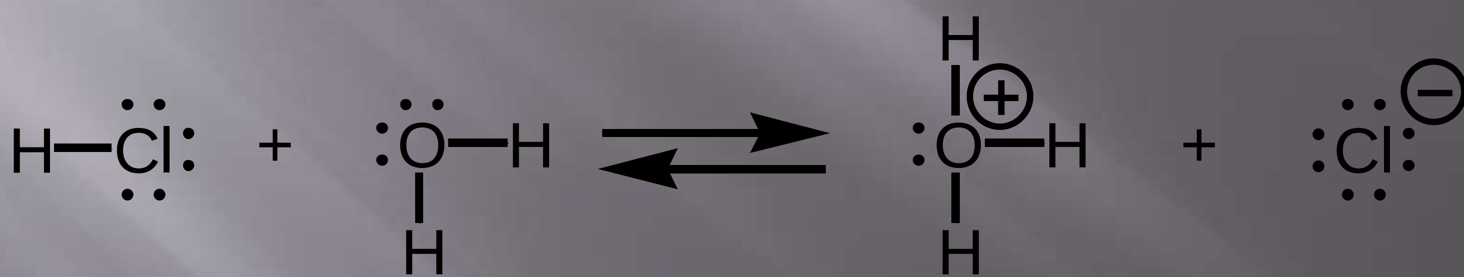


$pK_a = -7$ -1.74

$K_a = 10^7$ $K_a = 10^{1.74}$

which is the stronger base?

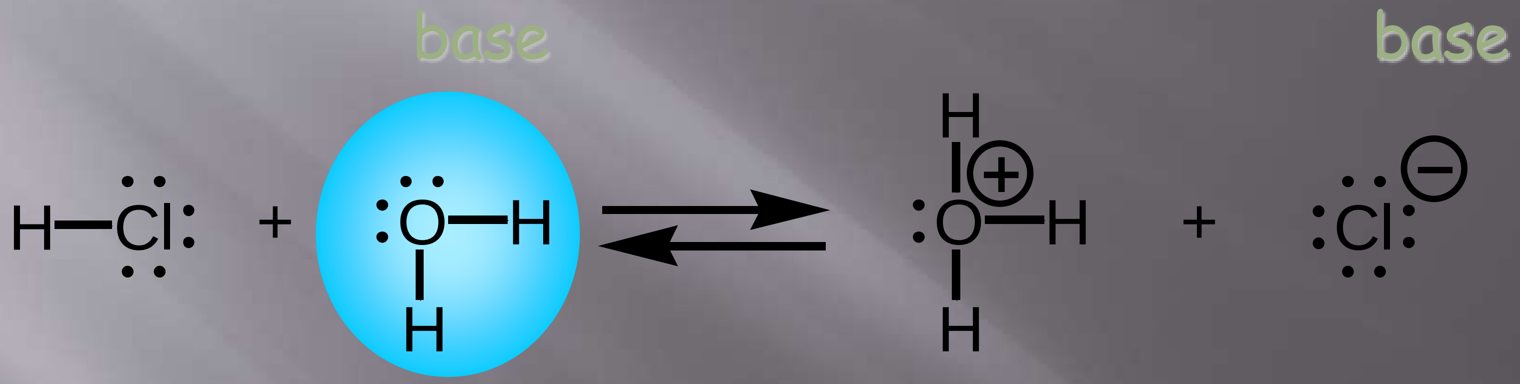
base | base

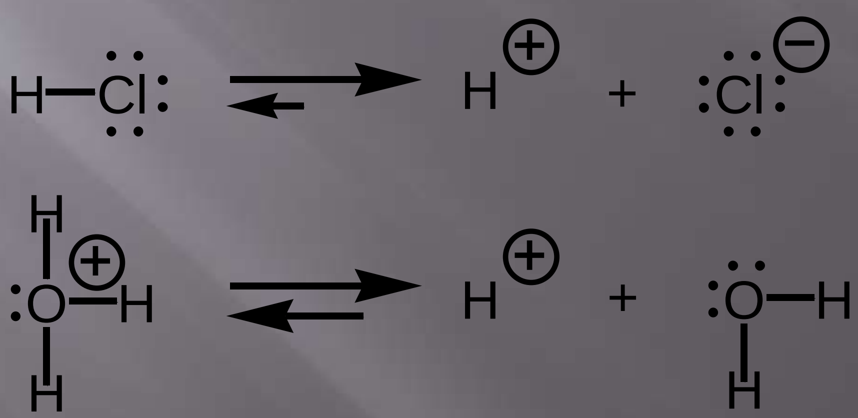


pK_a= -7 | -1.74

the stronger acid gives the weaker base

the weaker acid gives the stronger base

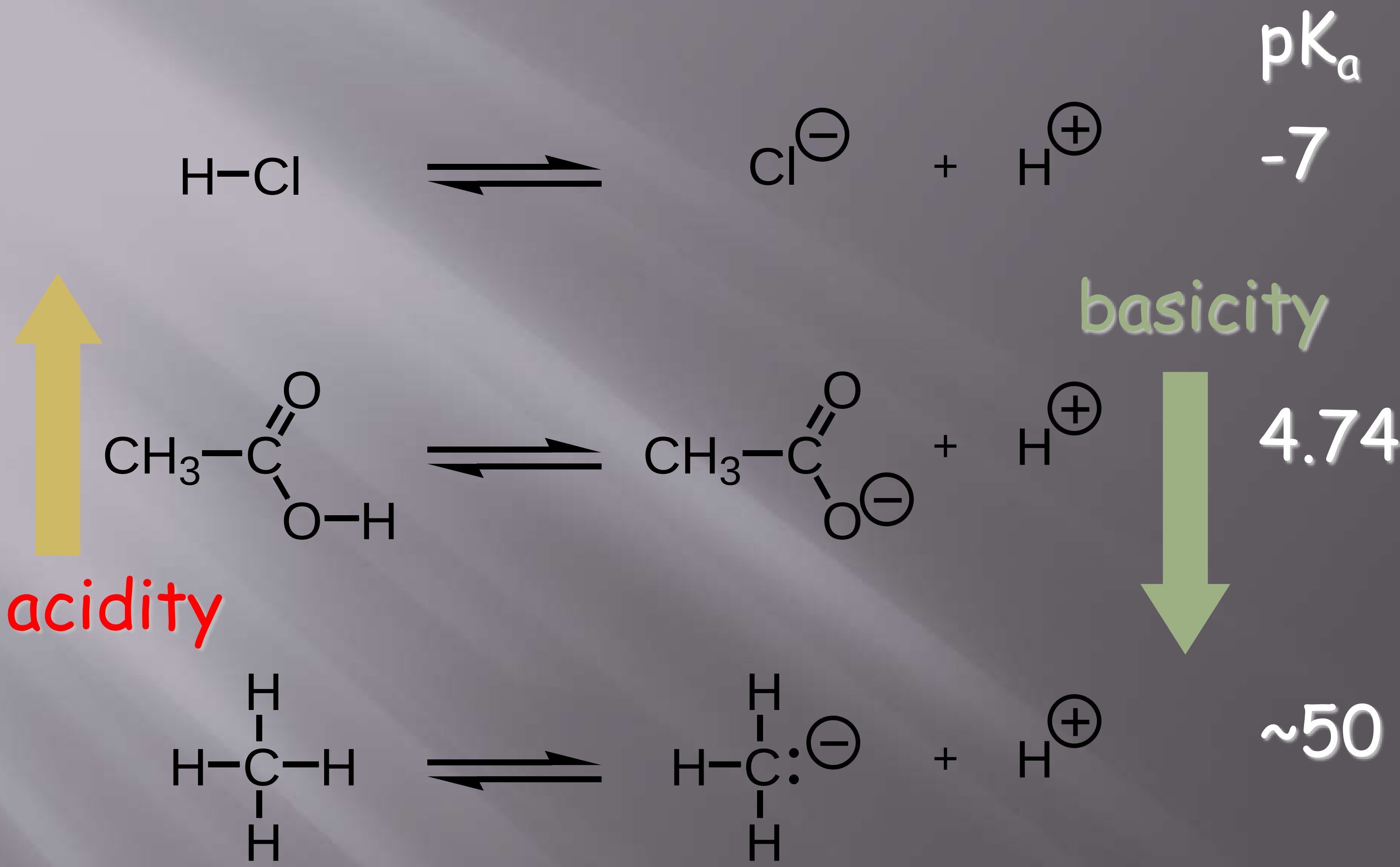




pK_a

-7

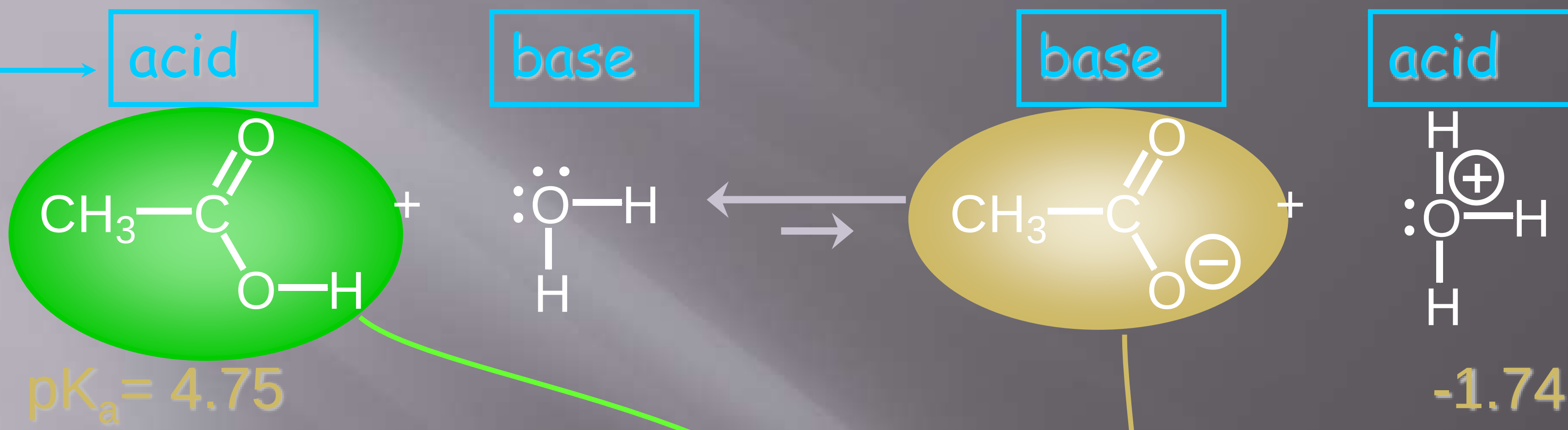
-1.74



Strong acids give weak bases.

Weak acids give strong bases.

Consider the following equilibrium.



(a) Identify the acids and bases.

(b) Identify the weakest acid.

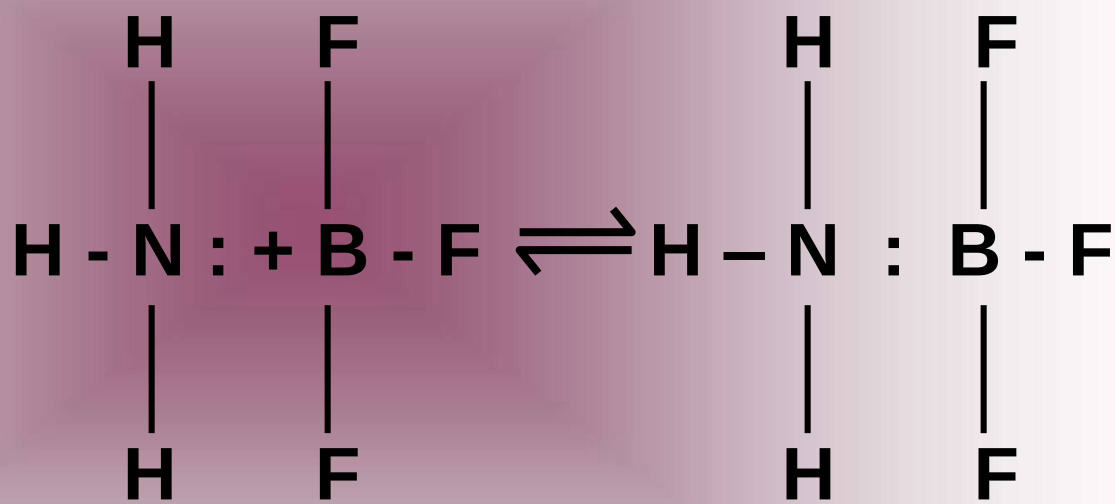
(c) Identify the strongest base.

(d) Does this equilibrium lie to the right or left?

Teori Lewis (1916)

Ada beberapa reaksi yang tidak dapat dijelaskan dengan kedua teori sebelumnya, misalnya reaksi :

$NH_3 + BF_3 \dashrightarrow H_3N - BF_3$



Asam : **Senyawa yang dapat menerima pasangan elektron** → BF_3

Basa : **Senyawa yang dapat memberikan pasangan elektron** → NH_3

Kesetimbangan Air

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

Pada keadaan setimbang

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

$Kw = [H^+]\,[OH^-]$

Pada suhu kamar T= 25°C $Kw = 10^{-14}$

sehingga

$[H^+] = [OH^-] = 10^{-7}$

- Air sebagai amfotir
- Amfotir : senyawa yang bisa berfungsi sebagai asam dan basa
- Autoionisasi pada air

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

$K = [H_3O^+][OH^-] = [H^+][OH^-]$

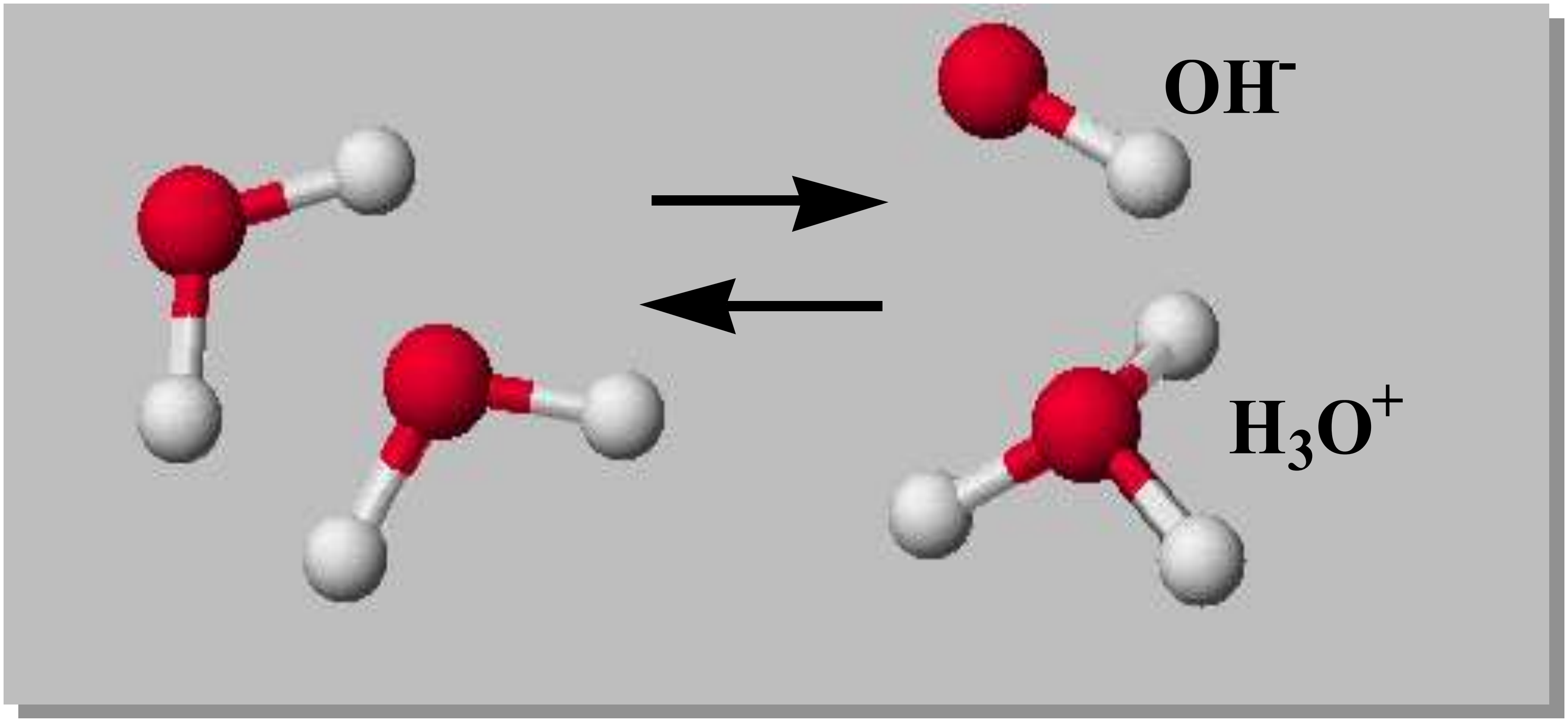
- K = tetapan ionisasi air , Kw

  nilai kw tetap pada suhu 25^0C. bila suhu berubah Kw akan berubah

$H^+] = [OH^-] = 1.0\ x10^{-7}\ M$

$Kw = [H^+][OH^-]=(1.0 \times 10^{-7}\ M)^2 = 1.0 \times 10^{-14}\ M$ (SUHU 25^0C)

AUTOIONISASI AIR



Acid – Base Strength

Strong Acid - Transfers all protons to water;
completely ionizes;
strong electrolyte;
conjugate base is weaker and has negligible tendency to be protonated.

Weak Acid - Fraction of protons transferred to water;
partly ionized;
weak electrolyte;
conjugate base is stronger readily accepting protons from water

- **As acid strength decreases, base strength increases.**
- **The stronger the acid, the weaker its conjugate base**
- **The weaker the acid, the stronger its conjugate base**

Acid strength	ACID	BASE	Base strength
Strong (100 percent ionized in H_2O)	HCl	Cl^-	Negligible
Strong (100 percent ionized in H_2O)	H_2SO_4	HSO_4^-	Negligible
Strong (100 percent ionized in H_2O)	HNO_3	NO_3^-	Negligible
	$H_3O^+(aq)$	H_2O	
Weak	HSO_4^-	SO_4^{2-}	Weak
Weak	H_3PO_4	$H_2PO_4^-$	Weak
Weak	HF	F^-	Weak
Weak	$HC_2H_3O_2$	$C_2H_3O_2^-$	Weak
Weak	H_2CO_3	HCO_3^-	Weak
Weak	H_2S	HS^-	Weak
Weak	$H_2PO_4^-$	HPO_4^{2-}	Weak
Weak	NH_4^+	NH_3	Weak
Weak	HCO_3^-	CO_3^{2-}	Weak
Weak	HPO_4^{2-}	PO_4^{3-}	Weak
	H_2O	OH^-	
Negligible	OH^-	O^{2-}	Strong (100 percent protonated in H_2O)
Negligible	H_2	H^-	Strong (100 percent protonated in H_2O)
Negligible	CH_4	CH_3^-	Strong (100 percent protonated in H_2O)

Acid strength increases ↑

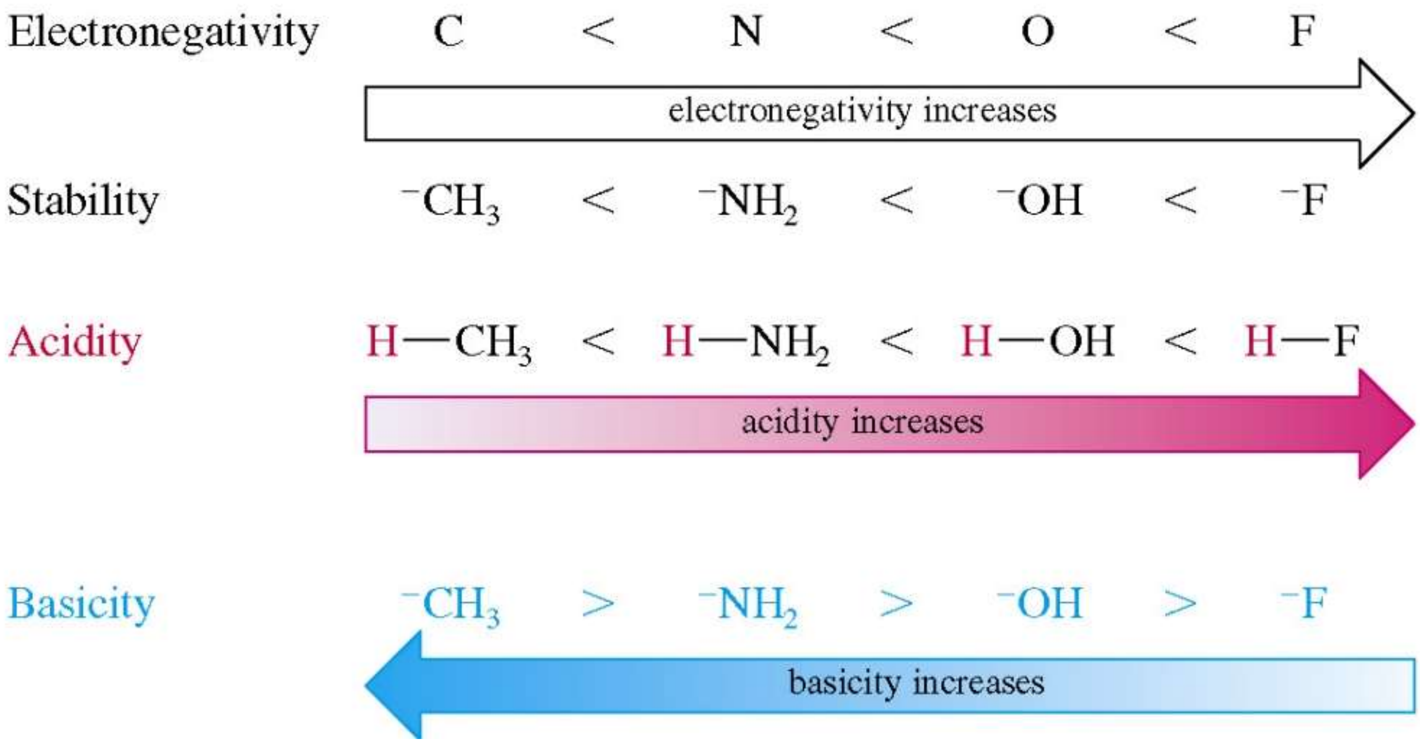
Base strength increases ↓

FACTORS THAT INCREASE ACIDITY

STABILIZATION OF A CONJUGATE BASE

Electronegativity

As the bond to H becomes more polarized, H becomes more positive and the bond is easier to break.



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ELECTRONEGATIVITY

When comparing two acids in the same period ...

placing the negative charge on a more electronegative element in the conjugate base leads to a stronger acid

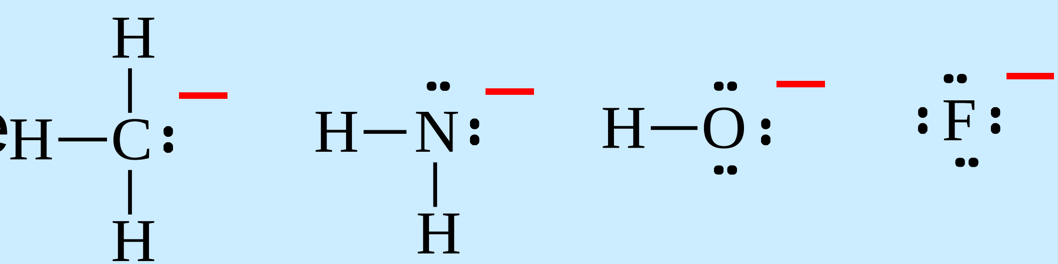
EFFECT OF ELECTRONEGATIVITY

increasing electronegativity ↓

pKa Values

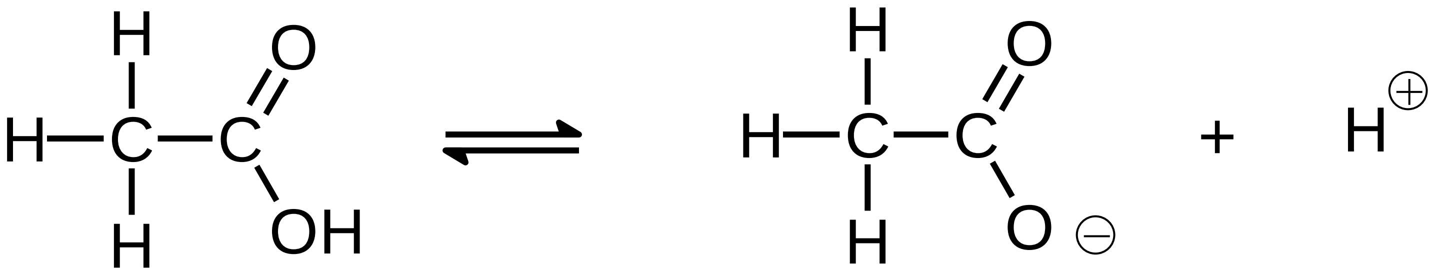
CH_4	>45	RCH_3	45	$R-C(=O)-CH_3$	20
NH_3	34	RNH_2	35	$R-C(=O)-NH_2$	15
H_2O	16	ROH	18	$R-C(=O)-OH$	5
HF	3.5				

conjugate bases :



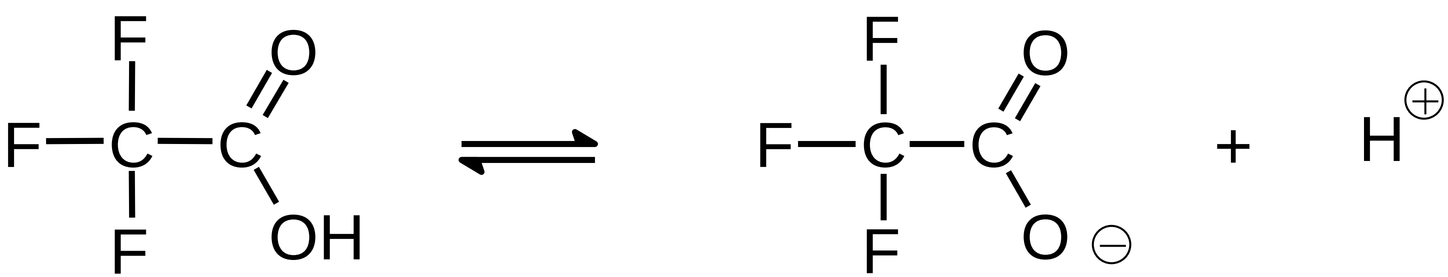
Predict whether trifluoroacetic acid will be a stronger or weaker acid than acetic acid.

K_a



$10^{-4.74}$

acetic acid



$10^{-0.23}$

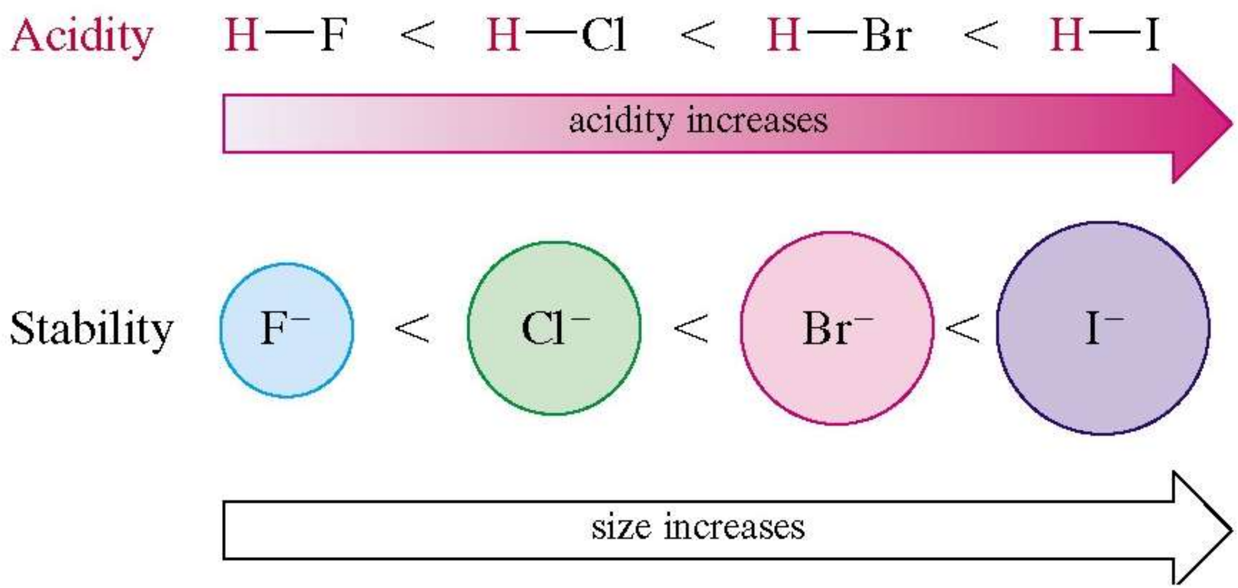
trifluoroacetic acid

more acidic acid

Fluorine is more electro-negative than hydrogen. Anion is more stable.

Size

- As size increases, the H is more loosely held and the bond is easier to break.
- A larger size also stabilizes the anion.



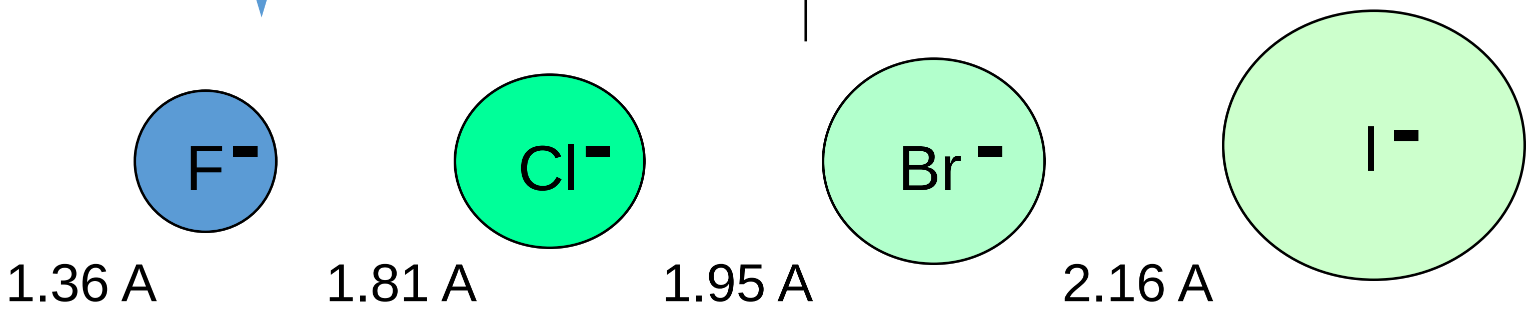
When comparing two acids in the <u>same group</u> ...
placing the negative charge on a larger atom
in the conjugate base leads to a stronger acid.

EFFECT OF ATOMIC SIZE

increasing atom size

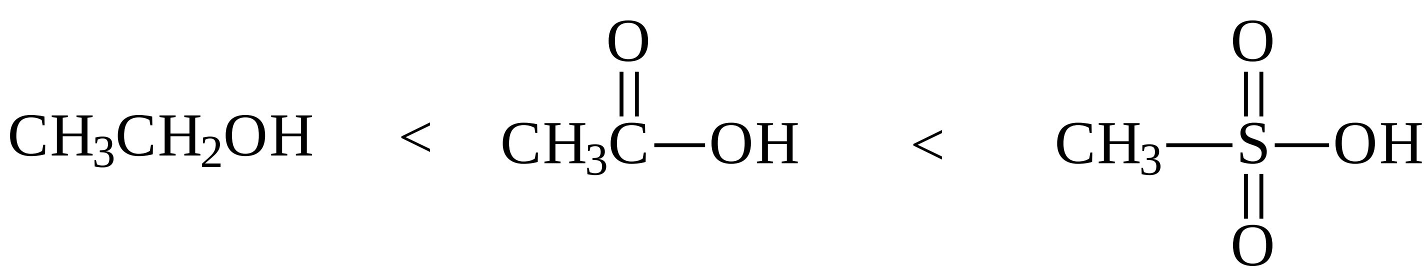
pKa Values

HF	3.5	**HOH**	16
HCl	-7	**HSH**	7
HBr	-9	**HSeH**	4
HI	-10	**HTeH**	3



Resonance

- Delocalization of the negative charge on the conjugate base will stabilize the anion, so the substance is a stronger acid.
- More resonance structures usually mean greater stabilization.



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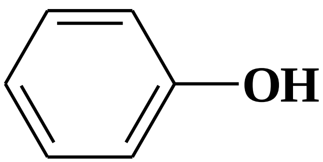
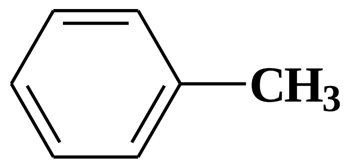
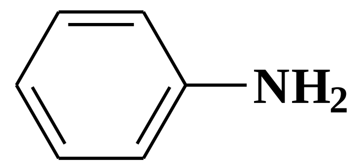
RESONANCE EFFECTS

increasing quality of resonance

pKa Values

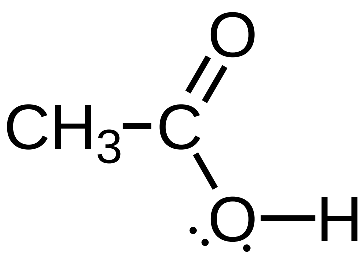
$R-OH$	18	$R-CH_3$	45	$R-NH_2$	28
	10		30		25
$R-C(=O)-OH$	5	$CH_3O-C(=O)-CH_3$	25	$R-C(=O)-NH_2$	15
		$R-C(=O)-CH_3$	20		
		$R-C(=O)-CH_2-C(=O)-R$	9		

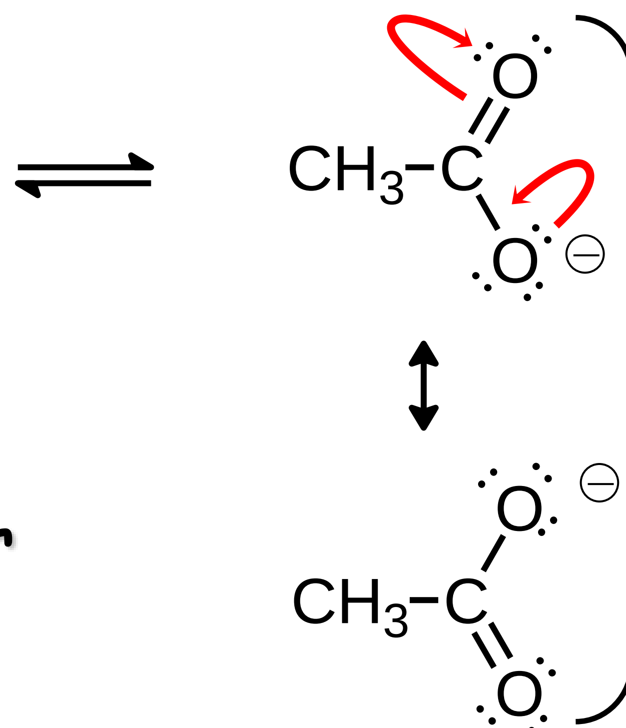
Which molecule is the stronger acid, ethanol or acetic acid?

K_a

$$CH_3CH_2OH \rightleftharpoons CH_3CH_2\ddot{\underset{\cdot\cdot}{O}}{:}^{\ominus} + H^{\oplus} \qquad 10^{-16}$$

ethanol





$+ \quad H^{\oplus} \qquad 10^{-4.74}$

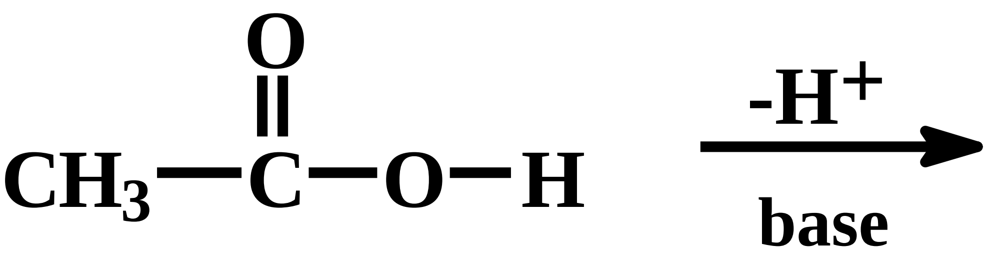
acetic acid

more stable anion because of resonance and inductive effects

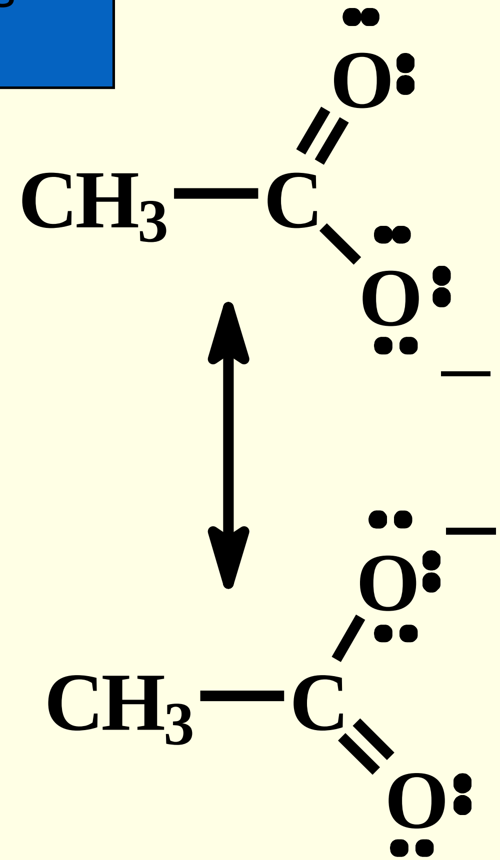
the stronger acid

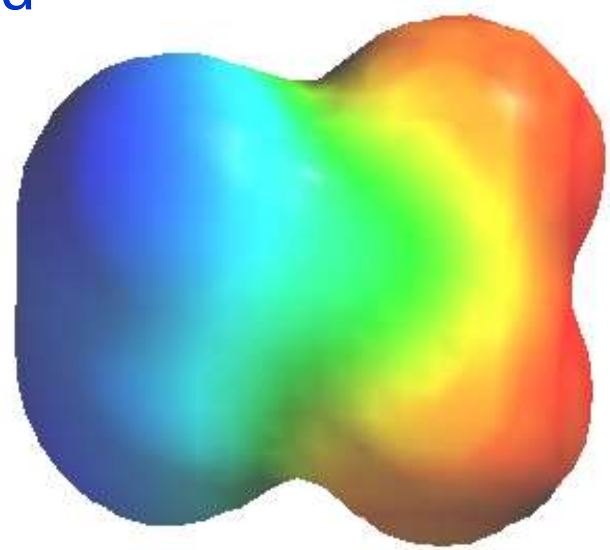
RESONANCE IN THE ACETATE ION

equivalent structures
charge on oxygens



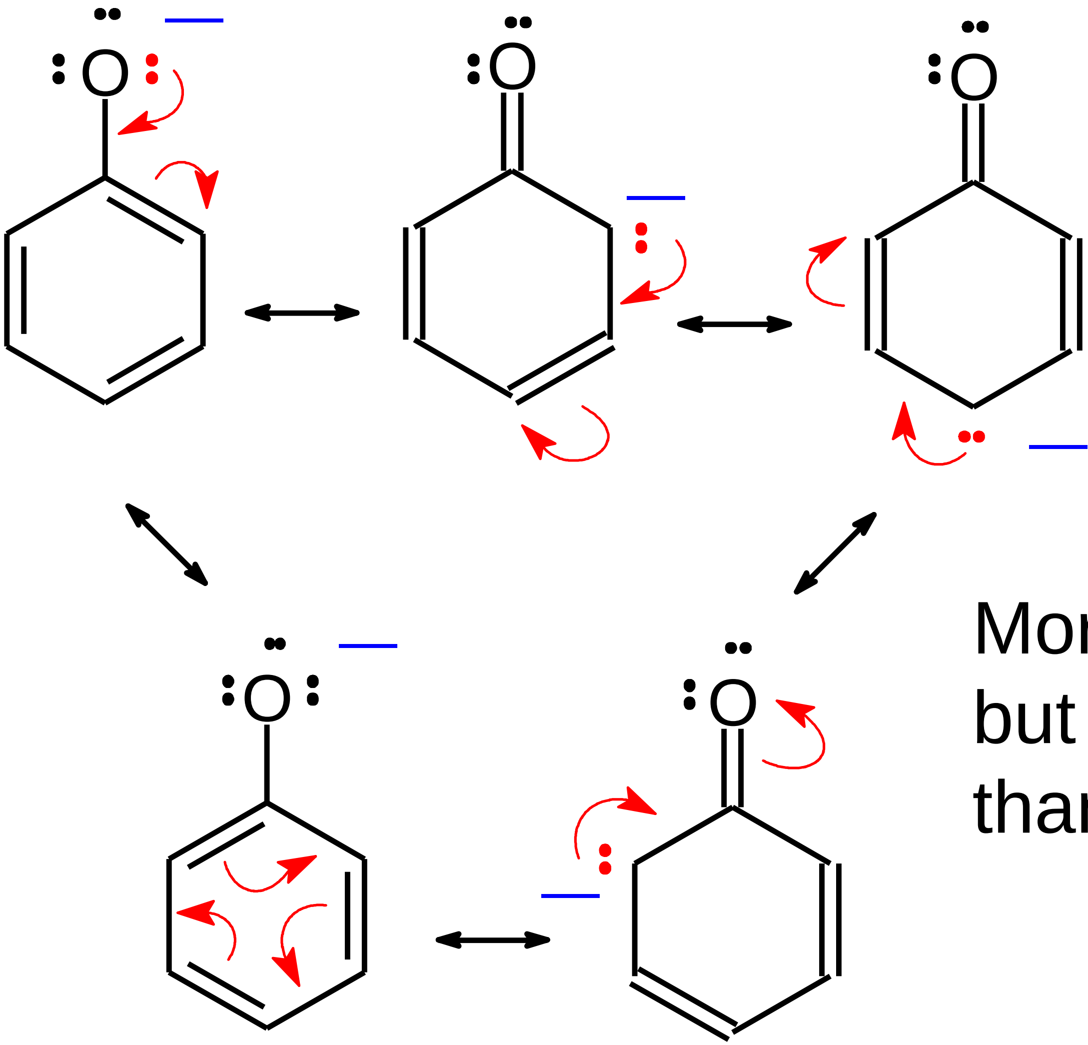
acetic acid

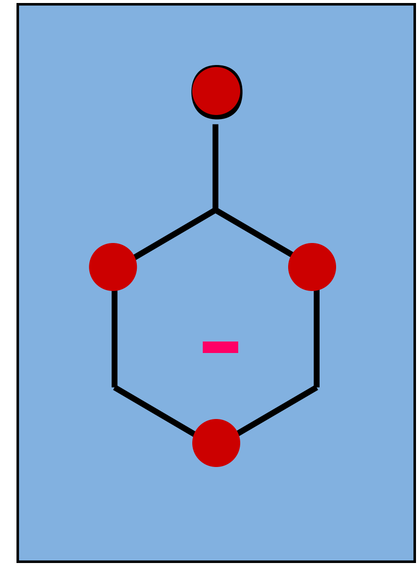




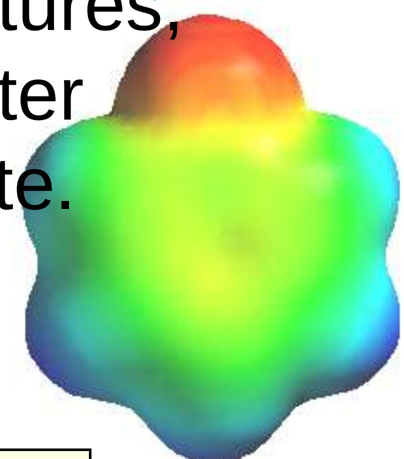
acetate ion

PHENOLATE ION RESONANCE





More structures, but not better than acetate.



Non-equivalent structures
charge on carbon and oxygen

DEPENDENCE OF ACIDITY ON SIZE AND ELECTRONEGATIVITY

PERIOD: Acidity → ; Electronegativity →

GROUP: Size ↓ ; Acidity ↓

CH_4 50	NH_3 36	H_2O 16	HF 3.2
SiH_4 35	PH_3 27	H_2S 7	HCl -7
GeH_4 25	AsH_3 23	H_2Se 3.7	HBr -8
		H_2Te 3.0	HI -9

Molecular Structure and Acid Strength

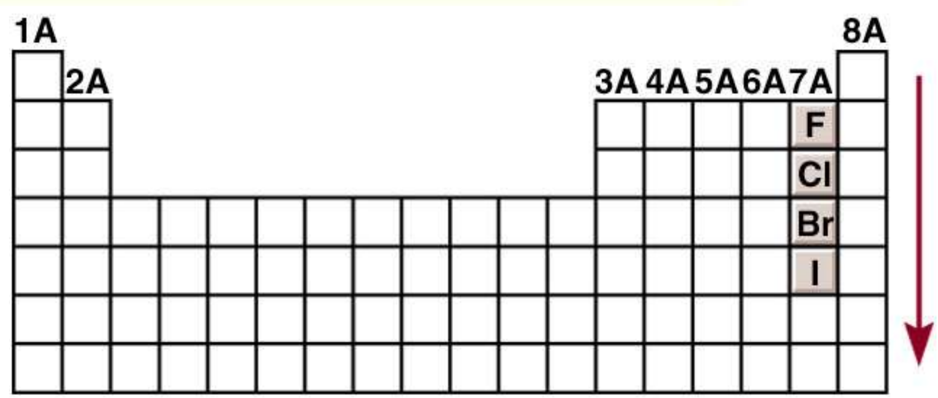
$$H{-}X \longrightarrow H^+ + X^-$$

The stronger the bond → The weaker the acid

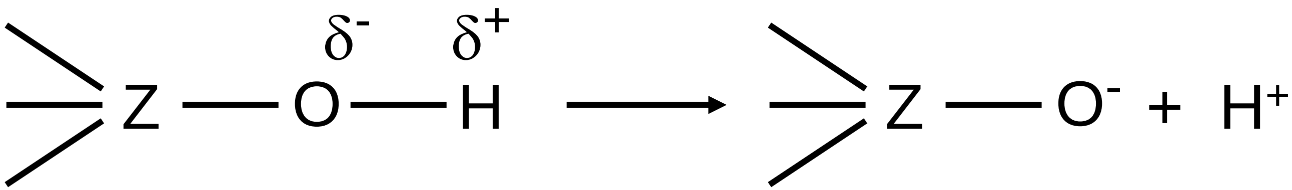
TABLE 15.6 Bond Enthalpies for Hydrogen Halides and Acid Strengths for Hydrohalic Acids

Bond	Bond Enthalpy (kJ/mol)	Acid Strength
H—F	568.2	weak
H—Cl	431.9	strong
H—Br	366.1	strong
H—I	298.3	strong

HF << HCl < HBr < HI

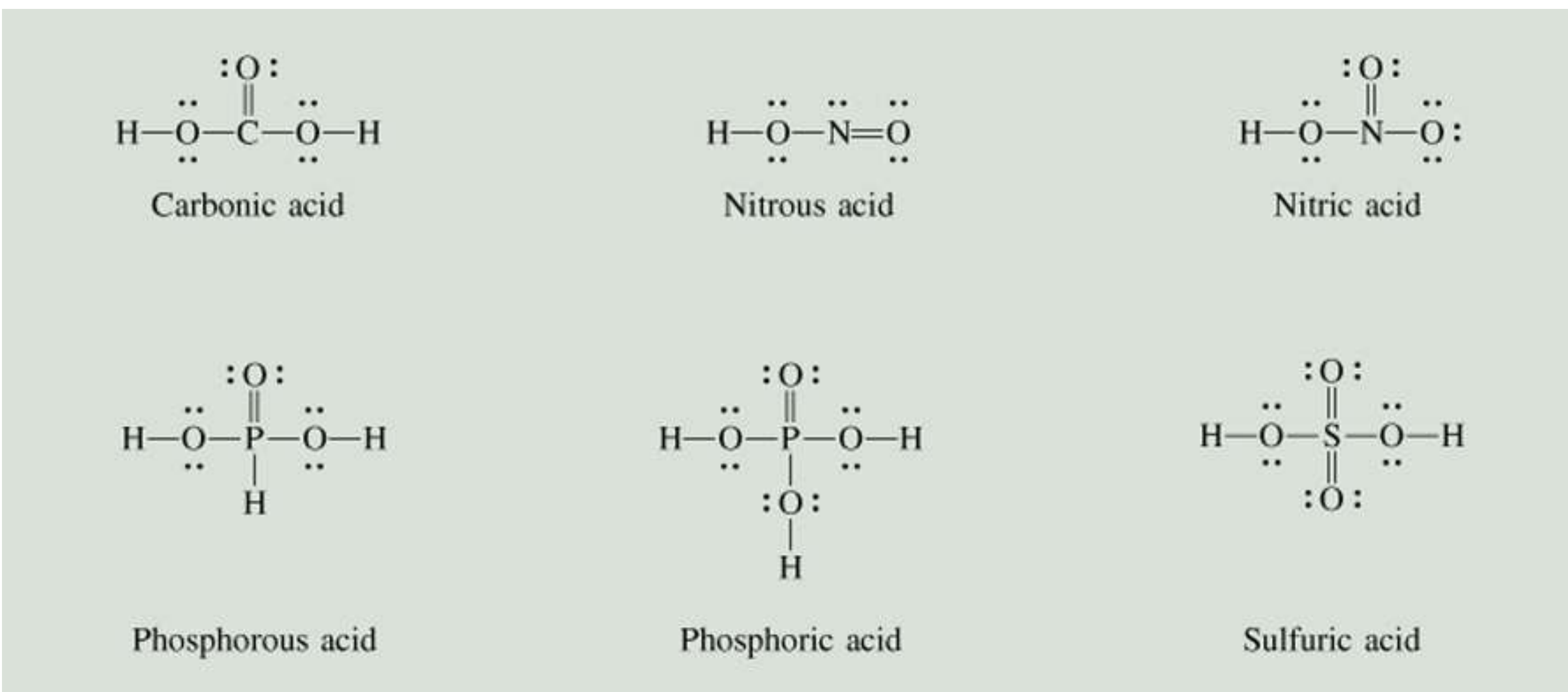


Molecular Structure and Acid Strength



The O-H bond will be more polar and easier to break if:

- Z is very electronegative or
- Z is in a high oxidation state



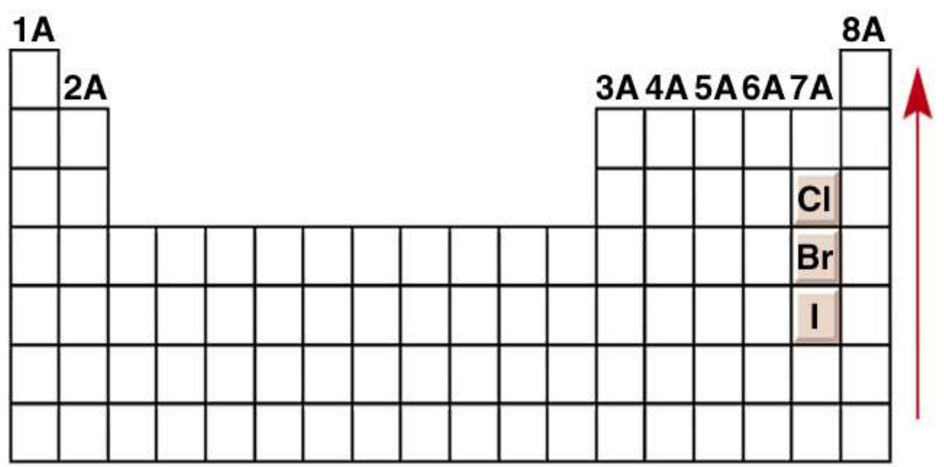
Molecular Structure and Acid Strength

1. Oxoacids having different central atoms (Z) that **are from the same group** and that have the **same oxidation number**.

Acid strength increases with increasing electronegativity of Z

Cl is more electronegative than Br

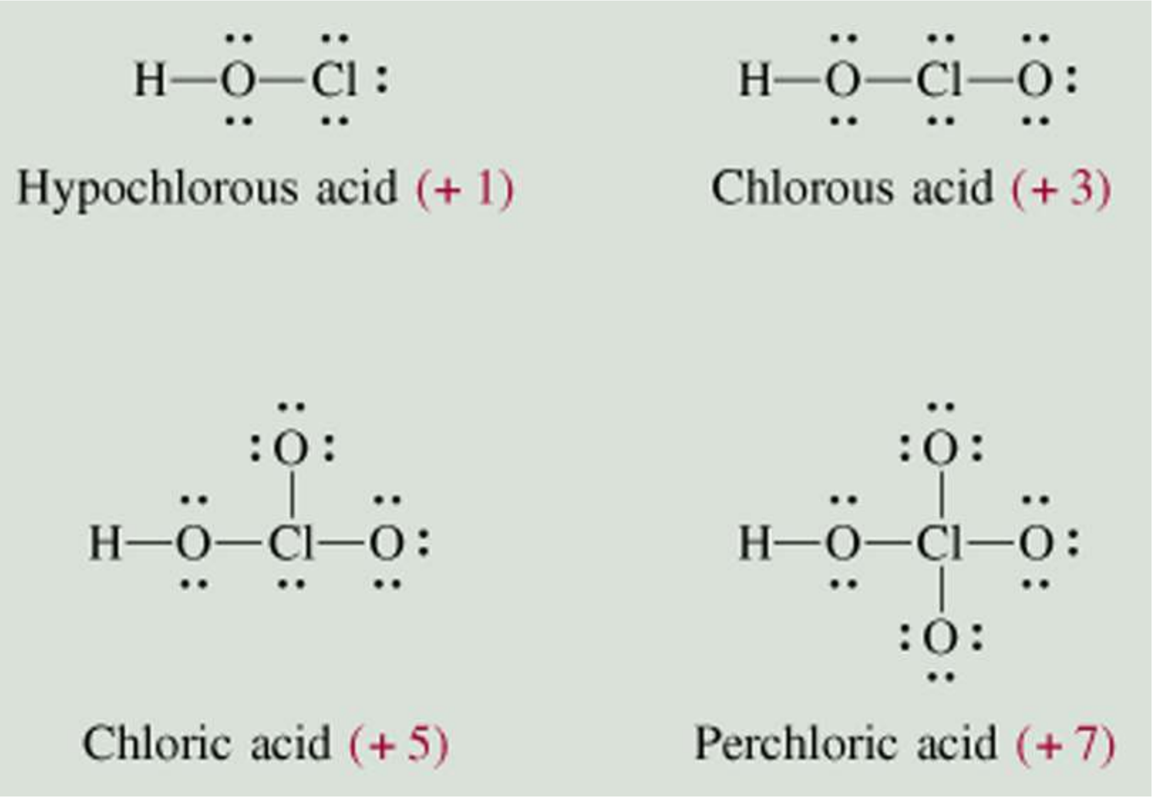
$HClO_3 > HBrO_3$



Molecular Structure and Acid Strength

2. Oxoacids having the same central atom (Z) but different numbers of attached groups.

Acid strength increases as the oxidation number of Z increases.



$HClO_4 > HClO_3 > HClO_2 > HClO$

Acid-Base Properties of Salts

Neutral Solutions:

Salts containing an alkali metal or alkaline earth metal ion (except Be^{2+}) **and** the conjugate base of a **strong** acid (*e.g.* Cl^-, Br^-, and NO_3^-).

$$NaCl\ (s) \xrightarrow{H_2O} Na^+\ (aq) + Cl^-\ (aq)$$

Basic Solutions:

Salts derived from a strong base **and** a **weak** acid.

$$NaCH_3COO\ (s) \xrightarrow{H_2O} Na^+\ (aq) + CH_3COO^-\ (aq)$$

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

Acid-Base Properties of Salts

Acid Solutions:

Salts derived from a strong acid and a weak base.

$$NH_4Cl\ (s) \xrightarrow{H_2O} NH_4^+\ (aq) + Cl^-\ (aq)$$

$$NH_4^+\ (aq) \rightleftharpoons NH_3\ (aq) + H^+\ (aq)$$

Salts with small, highly charged metal cations (*e.g.* Al^{3+}, Cr^{3+}, and Be^{2+}) and the conjugate base of a strong acid.

$$Al(H_2O)_6^{3+}(aq) \rightleftharpoons Al(OH)(H_2O)_5^{2+}(aq) + H^+\ (aq)$$

Acid-Base Properties of Salts

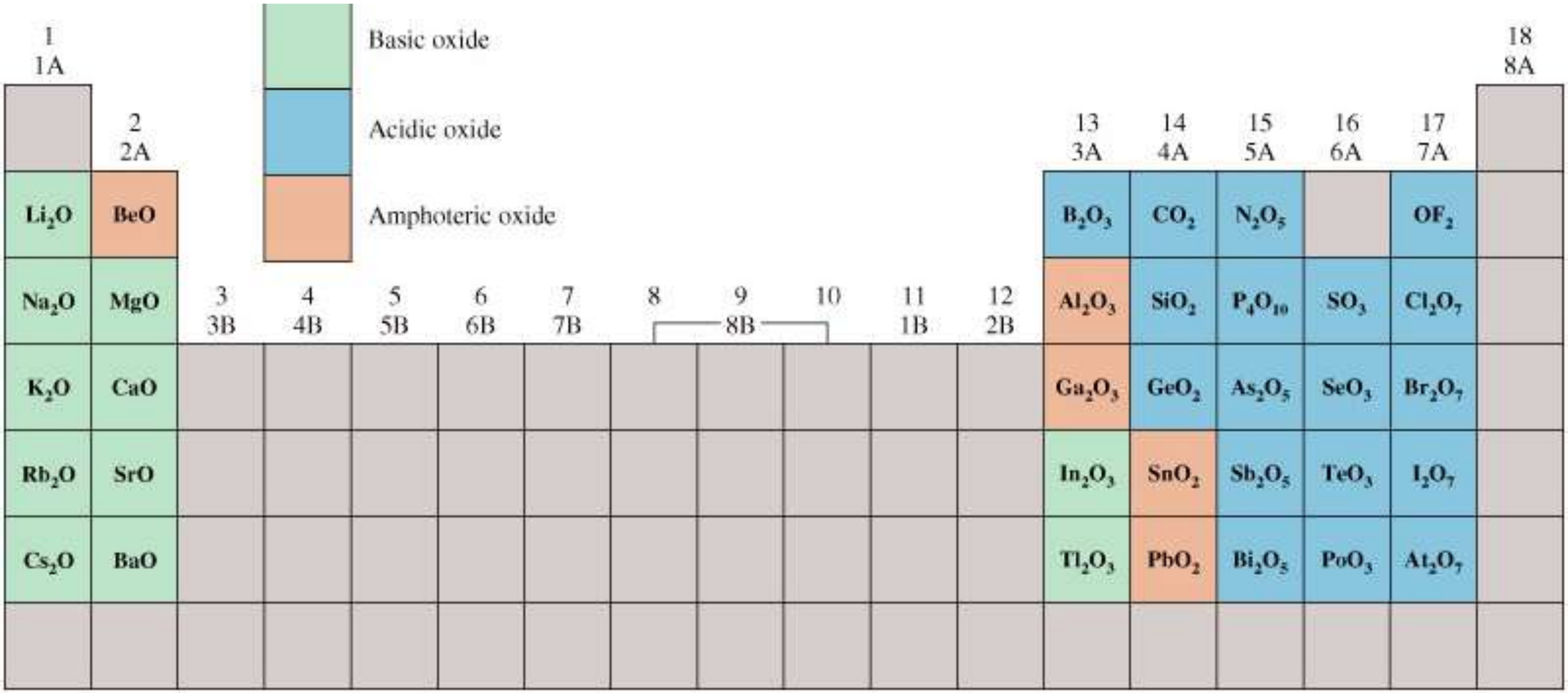
Solutions in which both the cation and the anion hydrolyze:

- K_b for the anion > K_a for the cation, solution will be basic
- K_b for the anion < K_a for the cation, solution will be acidic
- K_b for the anion ≈ K_a for the cation, solution will be neutral

TABLE 15.7 Acid-Base Properties of Salts

Type of Salt	Examples	Ions That Undergo Hydrolysis	pH of Solution
Cation from strong base; anion from strong acid	NaCl, KI, KNO_3, RbBr, $BaCl_2$	None	≈ 7
Cation from strong base; anion from weak acid	CH_3COONa, KNO_2	Anion	> 7
Cation from weak base; anion from strong acid	NH_4Cl, NH_4NO_3	Cation	< 7
Cation from weak base; anion from weak acid	NH_4NO_2, CH_3COONH_4, NH_4CN	Anion and cation	< 7 if $K_b < K_a$ ≈ 7 if $K_b \approx K_a$ > 7 if $K_b > K_a$
Small, highly charged cation; anion from strong acid	$AlCl_3$, $Fe(NO_3)_3$	Hydrated cation	< 7

Oxides of the Representative Elements In Their Highest Oxidation States



$$CO_2\,(g) + H_2O\,(l) \rightleftharpoons H_2CO_3\,(aq)$$

$$N_2O_5\,(g) + H_2O\,(l) \rightleftharpoons 2HNO_3\,(aq)$$

LEVELING EFFECT

The term **leveling effect** refers to a solvent's ability to level the effect of a strong acid or base dissolved in it.

When a strong acid is dissolved in water, it reacts with it to form H_3O^+ in the following reaction (where "HA" is a generic strong acid such as "HCl"):

$$\mathbf{HA + H_2O \longrightarrow A^- + H_3O^+}$$

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. This is true with any solvent, although usually to a lesser extent than with water. Bases may be also leveled in solvents

The acidity and basicity in the aqueous solutions are limited by H^+ and OH^-. The acidity of any substance is stronger than H^+ or the basicity is stronger than OH^- will be leveled off. This is called “*leveling effect*”.

Which one is stronger?

A) HCl **B) $HClO_4$**

Because of this leveling effect, $HClO_4$ and HCl behave as if they had the same acid strength; both are leveled to H_3O^+:

$$HClO_4 + H_2O \longrightarrow H_3O^+ + ClO^-$$

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

In acetic acid solvent, which is less basic than H_2O, $HClO_4$ and HCl are not leveled to the same strength:

$$HClO_4 + CH_3COOH \rightleftharpoons CH_3COOH_2^+ + ClO_4^- \qquad K= 1.3 \times 10^{-5}$$

$$HCl + CH_3COOH \rightleftharpoons CH_3COOH_2^+ + Cl^- \qquad K= 2.8 \times 10^{-9}$$

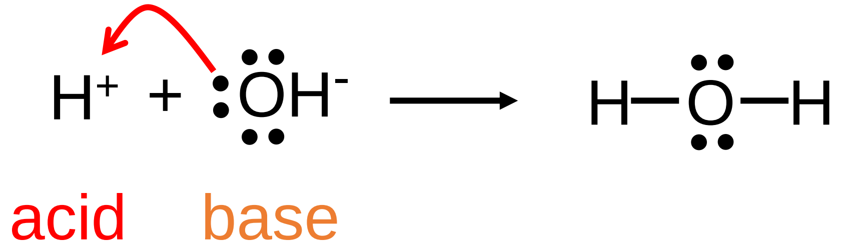
Definition of An Acid

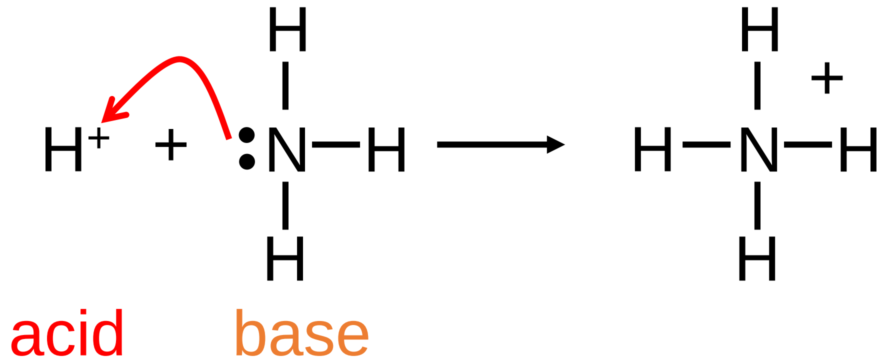
Arrhenius acid is a substance that produces H^+ (H_3O^+) in water

A ***Brønsted acid*** is a proton donor

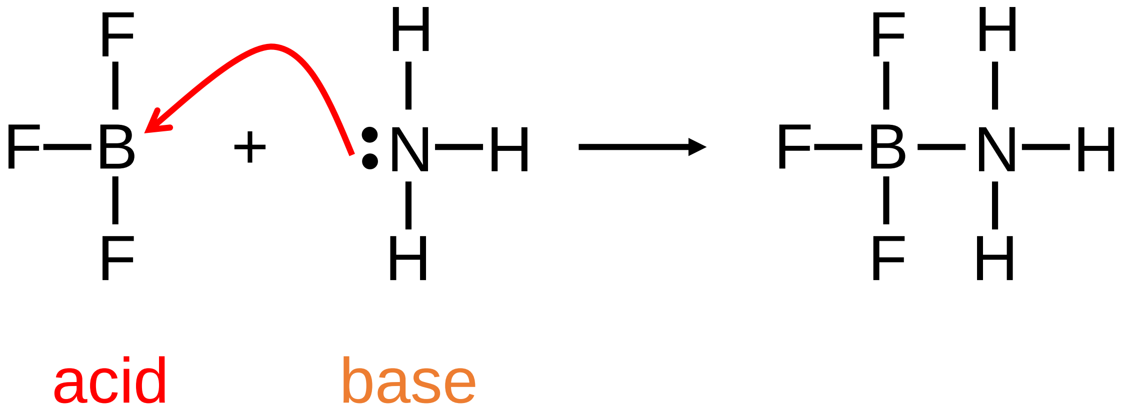
A ***Lewis acid*** is a substance that can *accept* a pair of electrons

A ***Lewis base*** is a substance that can *donate* a pair of electrons





Lewis Acids and Bases



No protons donated or accepted!

The Lewis definition of acid base reactions, devised by Gilbert N. Lewis in 1923 is an encompassing theory to the Brønsted-Lowry and solvent-system definitions with regards to the premise of a donation mechanism, which conversely attributes **the donation of electron pairs from bases and the acceptance by acids**, rather than protons or other bonded substances and spans both aqueous and non-aqueous reactions

$$Ag^{+} + 2\ :NH_3 \rightarrow [H_3N:Ag:NH_3]^{+}$$

A silver cation reacts as an acid with ammonia which acts as an electron-pair donor, forming an ammonia-silver adduct

Acid - An electron pair acceptor

Base - An electron pair donor

Solvent-system definition

This definition is based on a generalization of the earlier Arrhenius definition to all autodissociating solvents. In all such solvents there is a certain concentration of a positive species, **solvonium cations** and negative species, **solvate anions**, in equilibrium with the neutral solvent molecules. For example:

$2H_2O \rightleftharpoons H_3O^+$ (hydronium) + OH^- (hydroxide)

$2NH_3 \rightleftharpoons NH_4^+$ (ammonium) + NH_2^- (amide)

or even some aprotic systems:

$N_2O_4 \rightleftharpoons NO^+$ (nitrosonium) + NO_3^- (nitrate)

$2SbCl_3 \rightleftharpoons SbCl_2^+$ (*dichloroantimonium*) + $SbCl_4^-$ (*tetrachloroantimonate*)

A solute causing an increase in the concentration of the solvonium ions and a decrease in the solvate ions is an **acid** and one causing the reverse is a **base**.

Thus, in liquid ammonia, KNH_2 (supplying NH_2^-) is a strong base, and NH_4NO_3 (supplying NH_4^+) is a strong acid.

Thus, in Solvent system concept

acid - a species that increases the concentration of the **solvent cation**

base - a species that increases the concentration of the **solvent anion**

ex. i) NH_3 solvent

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

$$NH_3 + CH_3COOH \rightarrow NH_4^+ + CH_3COO^-$$

strong acid

$$NH_3 + H_2NC(O)NH_2 \rightarrow NH_4^+ + H_2NC(O)NH^-$$

acid

ii) BrF_3 solvent

$$2BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-$$

$$BrF_3 + SbF_5 \rightarrow BrF_2^+ + SbF_6^-$$

acid

$$BrF_3 + KF \rightarrow K^+ + BrF_4^-$$

base

solvent		*acid*		*base*
$2H_2O(\ell)$	$\rightleftharpoons$	$H_3O^+(aq)$	+	$OH^-(aq)$
$2NH_3(\ell)$	$\rightleftharpoons$	$NH_4^+(NH_3)$	+	$NH_2^-(NH_3)$
$2H_2SO_4(\ell)$	$\rightleftharpoons$	$H_3SO_4^+(H_2SO_4)$	+	$HSO_4^-(H_2SO_4)$
$2OPCl_3(\ell)$	$\rightleftharpoons$	$OPCl_2^+(OPCl_3)$	+	$OPCl_4^-(OPCl_3)$

Acids increase the concentration of the cationic solvent while bases increase those of the anionic solvent

$$\mathbf{OPCl_3}(\ell) + \mathbf{PCl_5}(OPCl_3) \rightleftharpoons \mathbf{OPCl_2^+}(OPCl_3) + \mathbf{PCl_6^-}(OPCl_3)$$

Particular example:

$$(CH_3)_4N^+ Cl^-(OPCl_3) + FeCl_3(OPCl_3) \longrightarrow (CH_3)_4N^+ FeCl_4^-(OPCl_3)$$

Gutmann rendered the following reaction steps:

$$(CH_3)_4N^+ Cl^-(\ell) + OPCl_3(\ell) \longrightarrow (CH_3)_4N^+(OPCl_3) + \mathbf{Cl^-}(OPCl_3)$$

$$FeCl_3(s) + OPCl_3(\ell) \rightleftharpoons \mathbf{OPCl_2^+}(OPCl_3) + FeCl_4^-(OPCl_3)$$

$$\mathbf{OPCl_2^+}(OPCl_3) + \mathbf{Cl^-}(OPCl_3) \longrightarrow OPCl_3(\ell)$$

$$HClO_4(\ell) + \mathbf{H_2O}(aq) \longrightarrow \mathbf{H_3O^+}(aq) + ClO_4^-(aq)$$

$$HCl(g) + \mathbf{H_2O}(aq) \longrightarrow \mathbf{H_3O^+}(aq) + Cl^-(aq)$$

$$CH_3COOH(\ell) + \mathbf{H_2O}(aq) \rightleftharpoons \mathbf{H_3O^+}(aq) + CH_3COO^-(aq)$$

$$HClO_4(\ell) + \mathbf{NH_3}(\ell) \longrightarrow \mathbf{NH_4^+}(NH_3) + ClO_4^-(NH_3)$$

$$CH_3COOH(\ell) + \mathbf{NH_3}(\ell) \longrightarrow \mathbf{NH_4^+}(NH_3) + CH_3COO^-(NH_3)$$

$$NH_2CONH_2(s) + \mathbf{NH_3}(\ell) \rightleftharpoons \mathbf{NH_4^+}(NH_3) + NH_2CONH^-(NH_3)$$

Acid-Base Models

- Lux-Flood
  – Acid accepts oxide ion
  – Base is an oxide ion donor
  – Neutralization is transfer of oxide ion from base to acid
  – Can be generalized to transfer of any negative ion
  – Useful in ceramics and metallurgy

Lux-Flood concept

acid - oxide ion (O^{2-}) acceptor
base - oxide ion (O^{2-}) donor

ex. · $CaO + SiO_2 \rightarrow CaSiO_3$ (= $Ca^{2+}[SiO_3]^{2-}$)
base   acid

This definition, proposed by German chemist Hermann Lux in 1939, further improved by Håkon Flood circa 1947 and now commonly used in modern geochemistry and electrochemistry of molten salts, describes an **acid** as an oxide ion acceptor and a **base** as an oxide ion donor. For example:

- MgO (base) + CO_2 (acid) → $MgCO_3$
- CaO (base) + SiO_2 (acid) → $CaSiO_3$
- NO_3^- (base) + $S_2O_7^{2-}$ (acid) → $NO_2^+ + 2SO_4^{2-}$

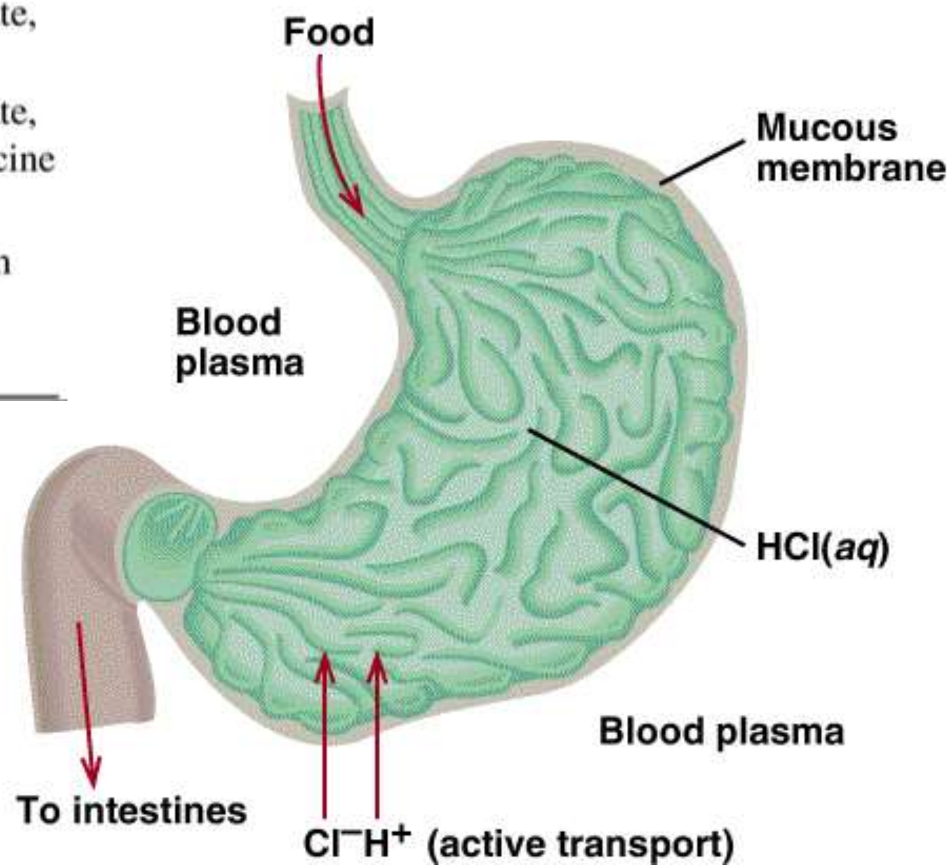
- **Usanovich definition**
- The most general definition is that of the Russian chemist Mikhail Usanovich, and can basically be summarized as defining an acid as "anything that accepts negative species or donates positive ones," and a base as the reverse. This tends to overlap the concept of redox (oxidation-reduction), and so is not highly favored by chemists. This is because redox reactions focus more on physical electron transfer processes, rather than bond making/bond breaking processes, although the distinction between these two processes is somewhat ambiguous.

Chemistry In Action: Antacids and the Stomach pH Balance

Some Common Commercial Antacid Preparations

Commercial Name	Active Ingredients
Alka-2	Calcium carbonate
Alka-Seltzer	Aspirin, sodium bicarbonate, citric acid
Bufferin	Aspirin, magnesium carbonate, aluminum glycinate
Buffered aspirin	Aspirin, magnesium carbonate, aluminum hydroxide-glycine
Milk of magnesia	Magnesium hydroxide
Rolaids	Dihydroxy aluminum sodium carbonate
Tums	Calcium carbonate

$$NaHCO_3\ (aq) + HCl\ (aq) \longrightarrow NaCl\ (aq) + H_2O\ (l) + CO_2\ (g)$$



$$Mg(OH)_2\ (s) + 2HCl\ (aq) \longrightarrow MgCl_2\ (aq) + 2H_2O\ (l)$$

Properties of Solvents

Protic solvents

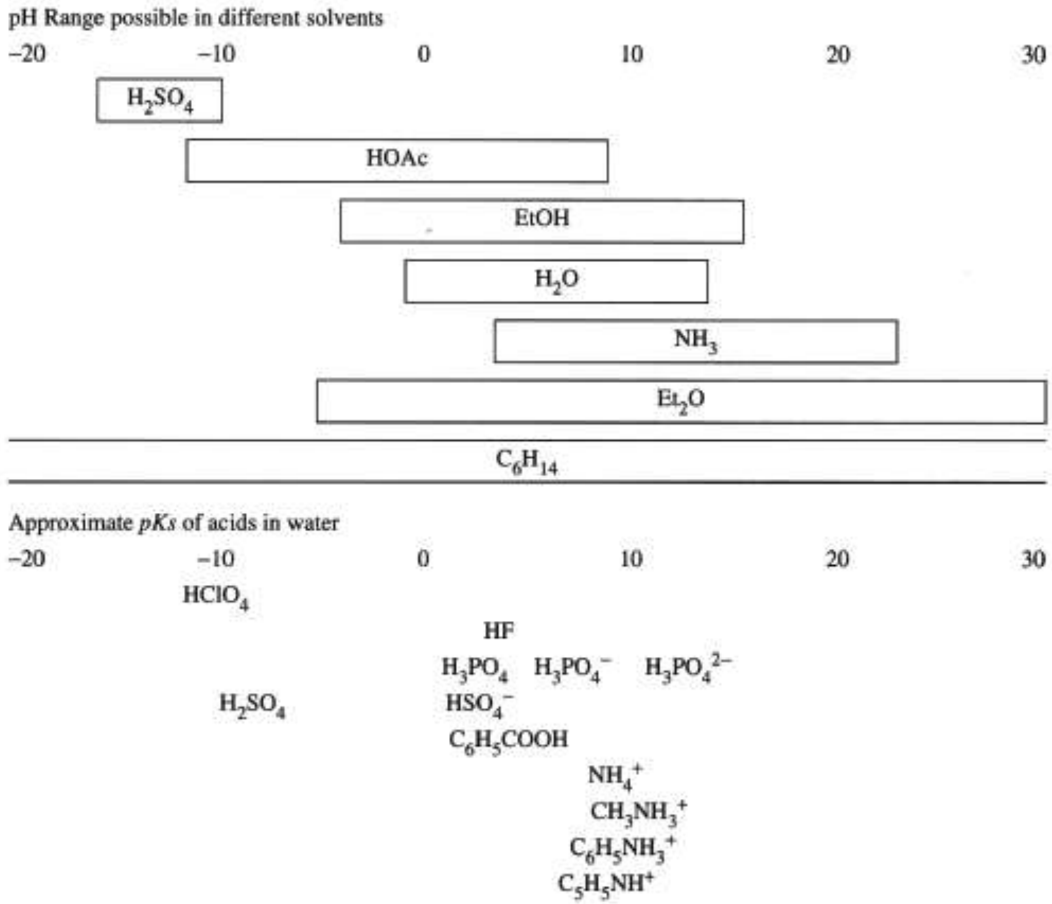
Solvent	*Acid cation*	*Base anion*	pK_{ion} *(25°C)*	*Boiling point (°C)*
Ammonia, NH_3	NH_4^+	NH_2^-	27	−33.38
Sulfuric acid, H_2SO_4	$H_3SO_4^+$	HSO_4^-	3.4 (10°)	330
Acetic acid, CH_3COOH	$CH_3COOH_2^+$	CH_3COO^-	14.45	118.2
Acetonitrile, CH_3CN	CH_3CNH^+	CH_2CN^-	28.6	81
Hydrogen fluoride, HF	H_2F^+	HF_2^-	~12 (0°)	19.51
Methanol, CH_3OH	$CH_3OH_2^+$	CH_3O^-	18.9	64.7
Water, H_2O	H_3O^+	OH^-	14	100

Aprotic solvents

Solvent	*Boiling point (%C)*
Dinitrogen tetroxide, N_2O_4	21.15
Sulfur dioxide, SO_2	−10.2
Pyridine, C_5H_5N	115.5
Diglyme, $CH_3(OCH_2CH_2)_2OCH_3$	162
Bromine trifluoride, BrF_3	127.6

SOURCE: Data from W. L. Jolly, *The Synthesis and Characterization of Inorganic Compounds*, Prentice-Hall, Englewood Cliffs, N.J., 1970, pp. 99–101. Data for many other solvents are also given by Jolly.

pH Range in Various Solvents



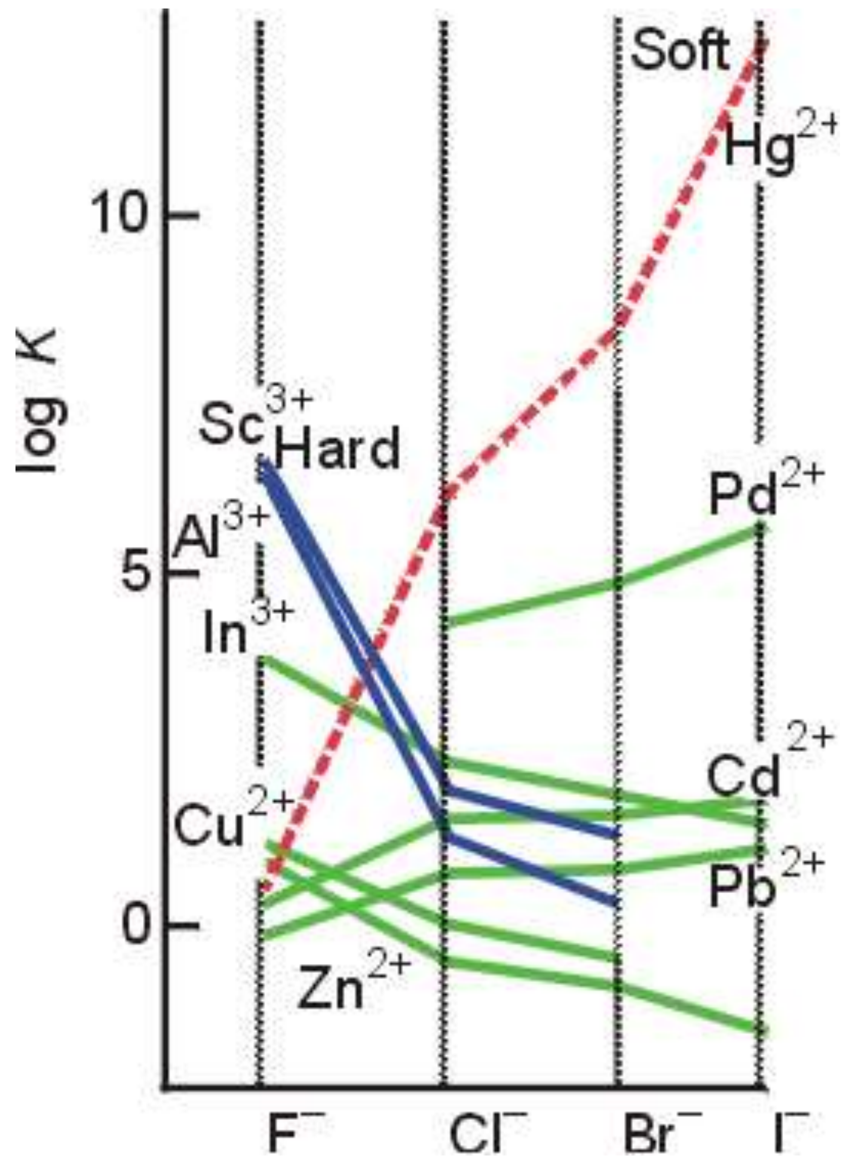
Pearson Classification of Lewis Acids and Bases

- Two Groupings
  - *Hard*: high charge or large charge to size ratio
  - *Soft*: low charge or low charge to size ratio
  - *Borderline*: intermediate hardness/softness
- Pearson Classification is *Qualitative* and *Relative*

- HSAB concept
- by Pearson

" <u>Hard likes Hard & Soft likes Soft</u> "

Trends in K_f



	Acid	Base
<Hard>	ex. Ti^{4+}, Si^{4+}, Cr^{3+}, Mo^{3+} · high oxidation state · small size · not very polarizable	ex. H_3N, RO^-, O^{2-} · localized(= tight) lone pair
<Soft>	ex. Hg^{2+}, Pt^{2+}, Au^+ · low oxidation state · large size · very polarizable	ex. R_2S, RS^-, R_3P · diffuse(= soft) lone pair

Hard/Soft Lewis Acids

Hard	Soft
H^+, Li^+, Na^+, K^+, Be^{2+}, Mg^{2+} Ca^{2+}, Al^{3+}, Sc^{3+}, Ga^{3+}, In^{3+} Fe^{3+}, Cr^{3+}, La^{3+}, Zr^{4+}, BF_3, AlH_3, $AlCl_3$, CO_2	Cu^+, Ag^+, Au^+, Hg^+, Hg^{2+}, Tl^+, Pd^{2+}, Pt^{2+}, Cd^{2+}, BH_3, Br_2, I_2, metals with formal charges ≤ 0

Borderline: Fe^{2+}, Ru^{2+}, Os^{2+}, Rh^{3+}, Ir^{3+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Pb^{2+}, Sn^{2+}, SO_2, NO^+, BMe_3

Notes:

- Higher charges and smaller ions are hard
- Larger ions are softer (except highly charged)

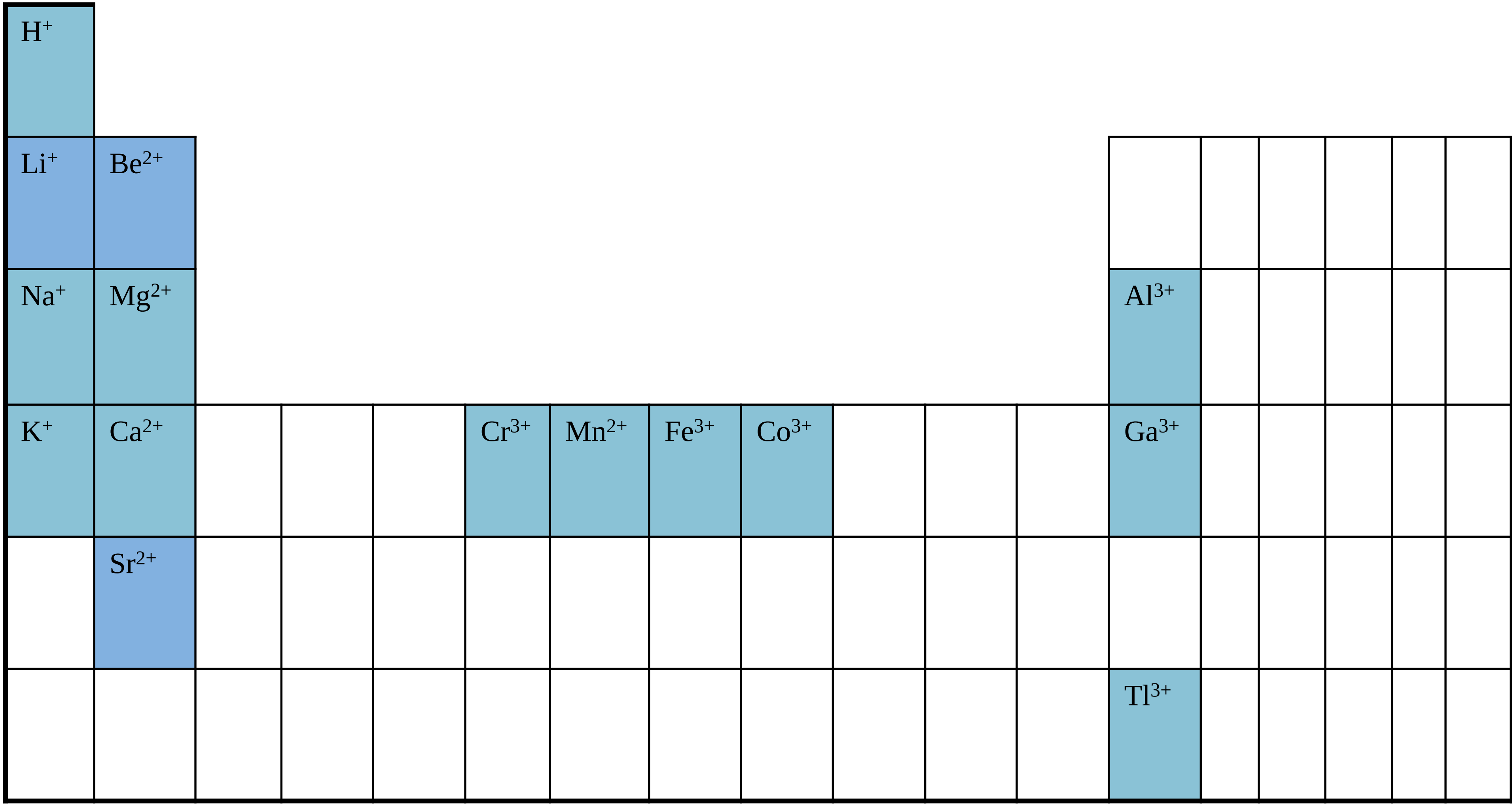
Hard/Soft Lewis Bases

Hard	Soft
CO_3^{2-}, RCO_2^-, NH_3, NH_2, O^{2-}, H_2O, OH^-, ROH, RO^-, R_2O, F^-, Cl^-, NO_3^-, ClO_4^-, PO_4^{3-}, SO_4^{2-}, N_2H_4, $RCONR^-$	CO, CN^-, RNC, C_2H_4, C_6H_6, R_3P, R_2S, RSH, RS^-, H^-, R^-, SCN^-, I^-
Borderline: $C_6H_5NH_2$, C_5H_5N, N_3^-, N_2, NO_2^-, SO_3^{2-}, Br^-	

Notes:

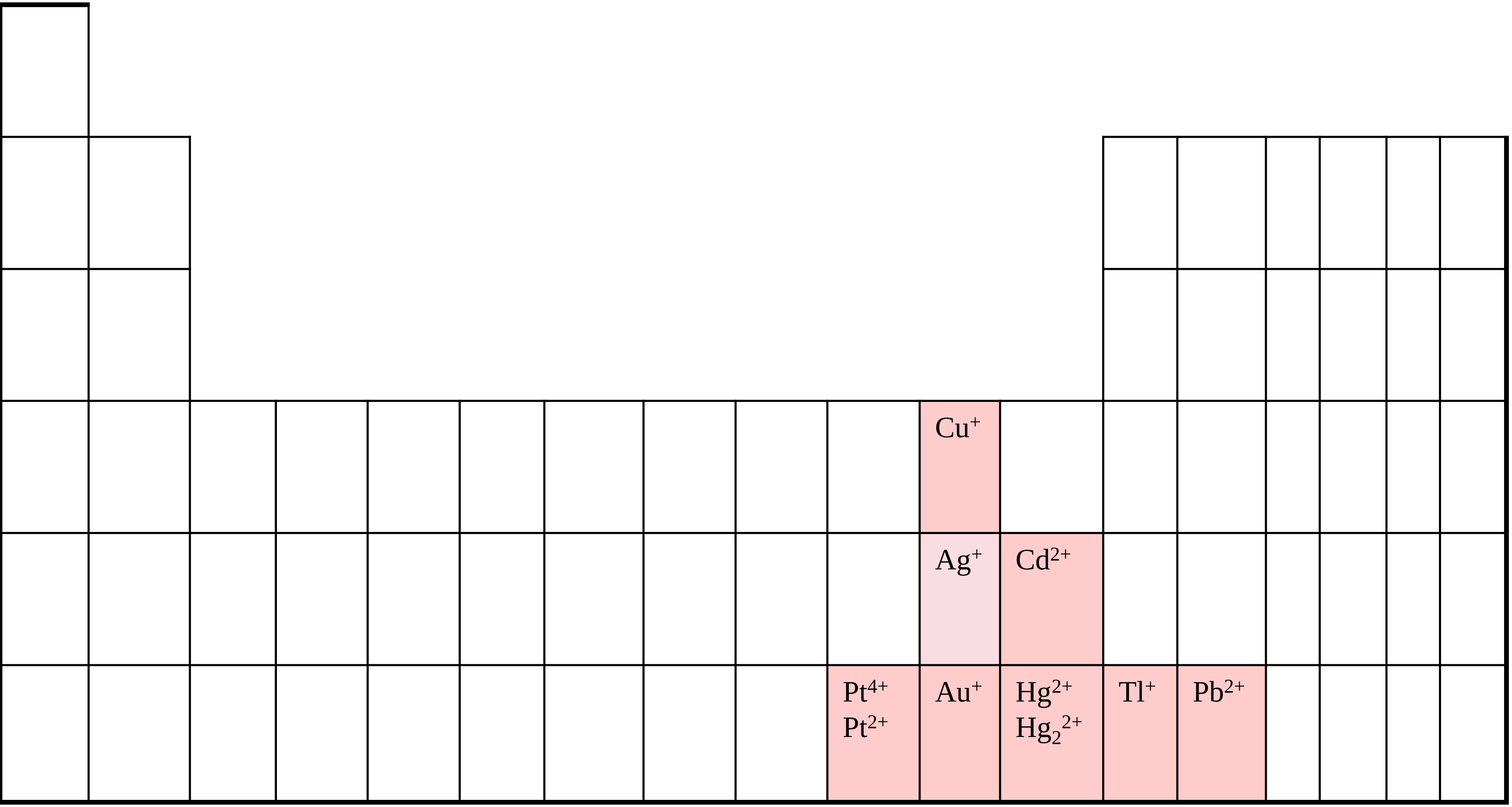
- N, O donors tend to be hard
- C, S, P donors tend to be soft
- Hard/soft not related to acid/base strength

Hard acids



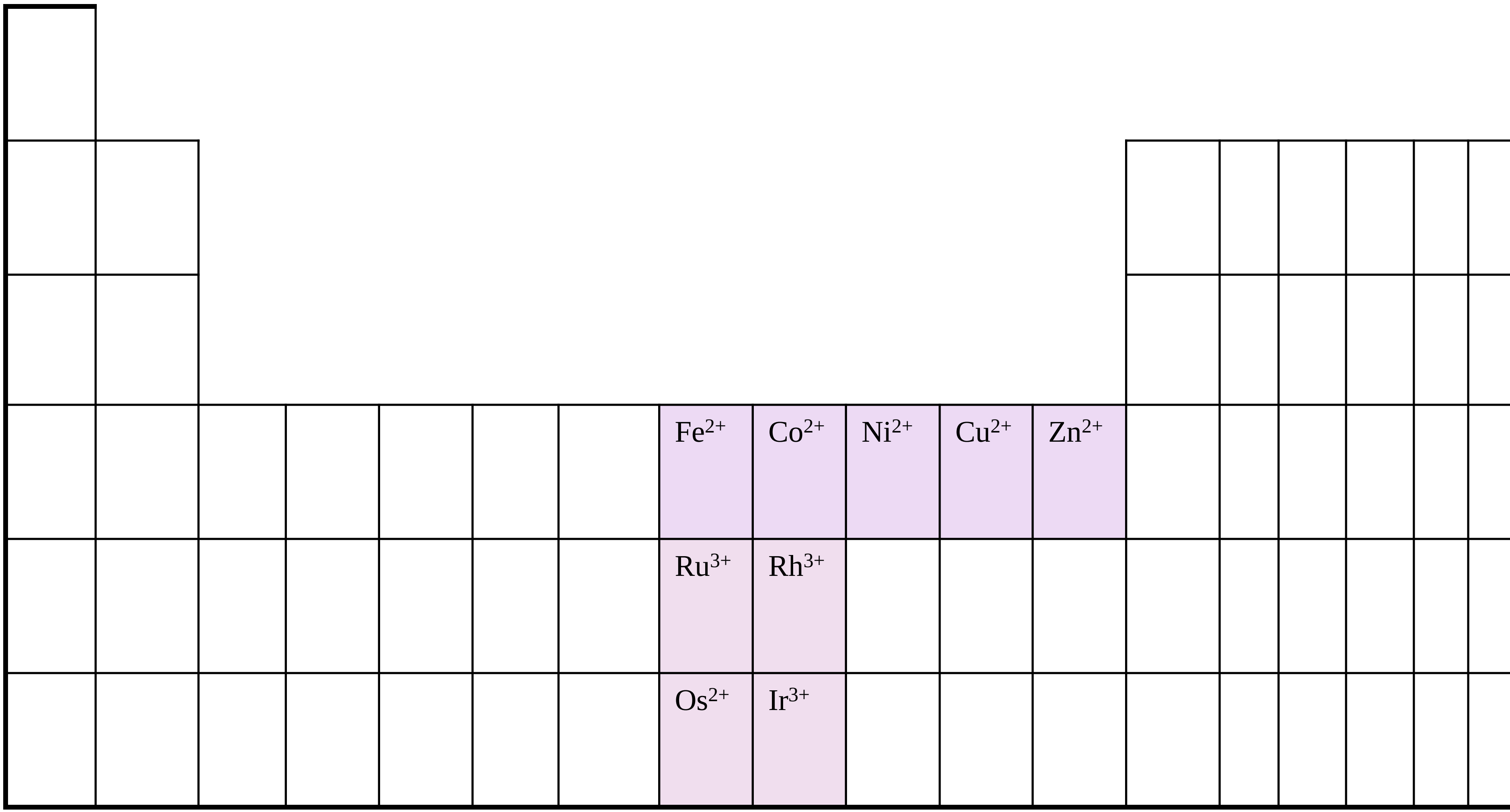
All ions with ox # =4 or higher

Soft acids



Metals with ox # = 0

Borderline acids



Hard and soft bases

Hard bases	Borderline bases	Soft bases
		H^-
F^-	Br^-, Cl^-	I^-
H_2O, OH^-, O^{2-}		H_2S, HS^-, S^{2-}
ROH, RO^-, R_2O, CH_3COO^-		RSH, RS^-, R_2S
NO_3^-, ClO_4^-	NO_2^-, N_3^-, NSC^-	SCN^-, CN^-, RNC, CO
CO_3^{2-}, SO_4^{2-}, PO_4^{3-}	SO_3^{2-}	$S_2O_3^-$
NH_3, RNH_2, N_2H_4	$C_6H_5NH_2$, C_5H_5N, N_2	R_3P, $(RO)_3P$, R_3As, C_2H_4, C_6H_6

Hard & Soft Bases

- Hard ligands
  - Oxygen ligands in H_2O, CO_3^{2-}, NO_3^-, PO_4^{3-}, $ROPO_3^{2-}$, $(RO)_2PO^{3-}$, CH_3COO^-, OH^-, RO^-, R_2O, and crown ethers
  - Nitrogen ligands in NH_3, N_2H_4, RNH_2
- Intermediate ligands
  - Br_-, SO_3^{2-}
  - nitrogen ligands in NO_2^-, N_3^-, N_2, aniline, imidazole
- Soft ligands
  - Sulfur ligands in RSH, RS^-, R_2S
  - R_3P, RNC, CN^-, CO, R^-, H^-, I^-, $S_2O_3^{2-}$, $(RS)_2PO_2^-$, $(RO)_2P(O)S^-$

Adapted from: Roat-Malone, R.M. Bioinorganic Chemistry: A Short Course, Wiley: New Jersey, 2002, p.6.

$HgF_2(g)$ + $BeI_2(g)$ ⟶ $HgI_2(g)$ + $BeF_2(g)$

soft - hard   *hard - soft*   *soft - soft*   *hard - hard*

$CH_3HgF(aq)$ + $HSO_3^-(aq)$ ⟶ $CH_3HgSO_3^-(aq)$ + $HF(aq)$

soft - hard   *hard - soft*   *soft - soft*   *hard - hard*

$CH_3HgOH(aq)$ + $HSO_3^-(aq)$ ⟶ $CH_3HgSO_3^-(aq)$ + $HOH(\ell)$

soft - hard   *hard - soft*   *soft - soft*   *hard - hard*

soft base **B**

$$BH^+ + CH_3Hg^+ \rightleftharpoons CH_3HgB^+ + H^+$$

hard base **B**

← **SCN⁻** →   **- ambidentate ligand**

soft   hard

$[Ag(SCN)_2]^-$

$[Cr(NCS)_6]^{3-}$

Symbiosis

- termed by Jørgensen

- BF_3 + F^- → BF_4^-
  hard hard

- BH_3 + H^- → BH_4^-
  soft soft

- BH_3F^- + BF_3H^- → BH_4^- + BF_4^-

- CH_3F + CF_3H → CH_4 + CF_4

<Acid & Base Strength>

1. acidity of oxyacids:

   a) electronegativity of central atom

   H_2CO_3, H_3PO_4, H_2SO_4, HNO_3, $HClO_4$

   → stronger acid

   b) inductive effect of substituent

   CH_3COOH, CH_2FCOOH, CHF_2COOH, CF_3COOH

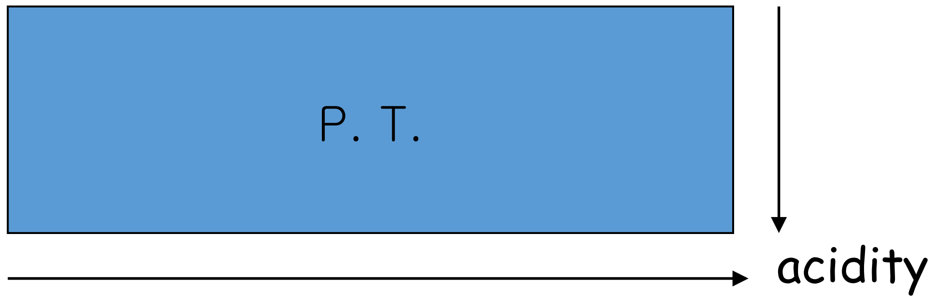
   → stronger acid

   c) number of oxygen atoms

   $HClO$, $HClO_2$, $HClO_3$, $HClO_4$

   → stronger acid

2. acidity of binary hydrogen compounds:



3. basicity of metal oxides:

BeO, MgO, CaO, SrO, BaO
$\longrightarrow$
more basic

(∵) Be^{2+} size 〈 Mg^{2+} size 〈 …
→ Be-O bond energy 〉 Mg-O bond energy 〉 …

What is a strong Acid?

An Acid that is 100% ionized in water.

Strong Acids:

100% ionized (completely dissociated) in water.

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

often written as:

$$HCl \rightarrow H^+ + Cl^-$$

Strong Acids:

100% ionized (completely dissociated) in water.

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

Strong Acids:	
Perchloric	HClO4
Chloric,	$HClO_3$
Hydrobromic,	HBr
Hydrochloric,	HCl
Hydroiodic,	HI
Nitric,	HNO_3
Sulfuric,	H_2SO_4

What is a strong Base?

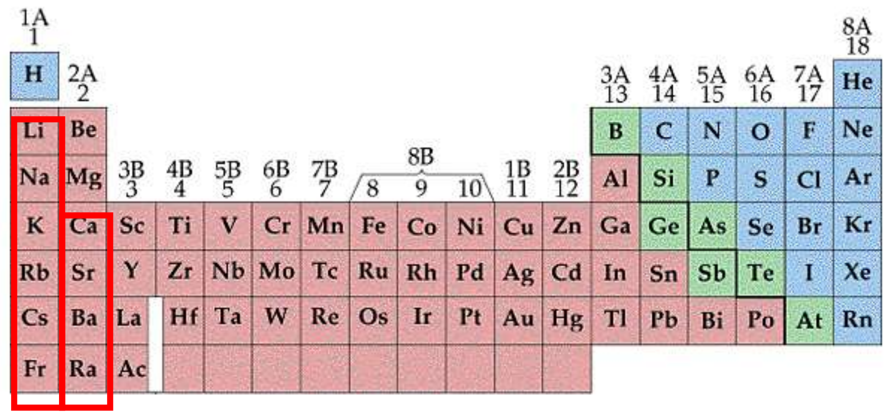
A base that is completely dissociated in water (highly soluble).

$$NaOH(s) \rightarrow Na^{+} + OH^{-}$$

Strong Bases:

Group 1A metal hydroxides
($LiOH$, $NaOH$, KOH, $RbOH$, $CsOH$)

Heavy Group 2A metal hydroxides
[$Ca(OH)_2$, $Sr(OH)_2$, and $Ba(OH)_2$]



Strong Acids:

100% ionized (completely dissociated) in water.

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

Note the "one way arrow".

Weak Acids:

Only a small % (dissociated) in water.

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

Note the "2-way" arrow.

Why are they different?

Super acid

$$HClO_4(H_2SO_4) + H_2SO_4(\ell) \rightleftharpoons H_3SO_4^+(H_2SO_4) + ClO_4^-(H_2SO_4)$$

$$C_3H_6(HSO_3F) + H_2SO_3F^+(HSO_3F) \longrightarrow C_3H_7^+(HSO_3F) + HSO_3F(\ell)$$