

## Acid Strength and Structure

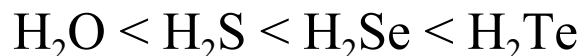
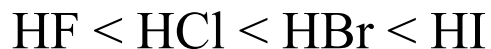
☞ The tendency of an acid to lose a proton to solvent water, as indicated by its  $K_a$  value, depends upon two principal factors:

1. The strength of the H–A bond.
  - ✓ The weaker the bond, the greater is the tendency to lose protons, and the larger  $K_a$  will be.
2. The stability of the conjugate base in solution.
  - ✓ The more stable the conjugate base  $A^-$ , the greater is the tendency to lose protons, and the larger  $K_a$  will be.

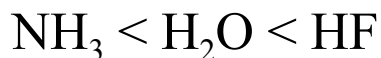
## Binary Acid Strengths

☞ Acid strengths of *binary acids*,  $H_nX$ , increase as the H–X bond weakens. This results in the following trends:

1. The larger the X atom, the weaker the H–X bond is and the stronger the acid is.

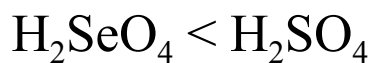


2. Among acids with similar H–X bond strengths, the more electronegative the X atom, the more polar the H–X bond will be.
  - ✓ This makes the H atom more positive, facilitating its removal by solvent water.
  - ✓ Thus, across a period,



## Oxoacids, HOXO<sub>n</sub>

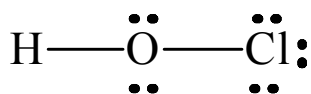
1. Among acids of the same structure type, acid strength increases with the electronegativity of the central X atom.



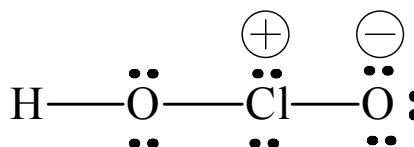
- ✓ The acidic H atom is always part of an –OH group.
- ✓ As electronegativity of X increases, the polarity of the –O–H bond increases, making removal of H<sup>+</sup> by solvent water more favorable.

## Oxoacids, HOXO<sub>n</sub>

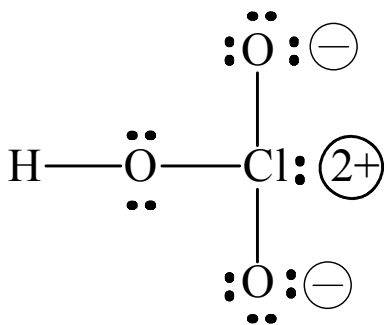
2. Acidity increases as the number of terminal (or non-hydroxy) oxygen atoms attached to X increases.



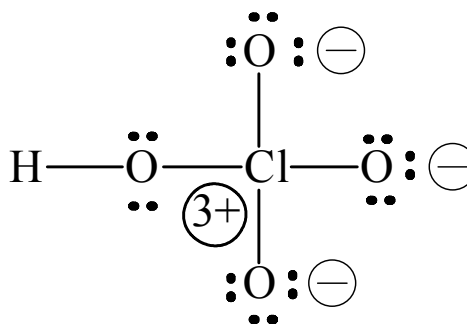
$$K_a = 3.2 \times 10^{-8}$$



$$K_a = 1.1 \times 10^{-2}$$



$$K_a \gg 1$$



$$K_a \gg 1$$

- ✓ The electron withdrawing ability of the terminal –O atoms increases the formal charge on the central X atom, decreasing electron density in the –O–H bond, thereby weakening it. This is an example of an *inductive effect*.

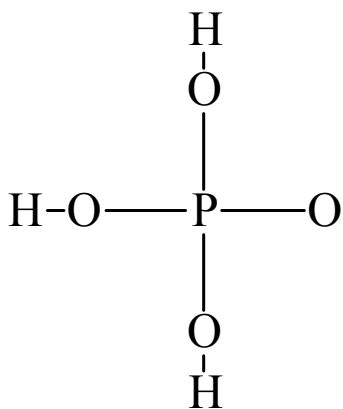
## Oxoacids, HOXO<sub>n</sub>

- ☞ The number of terminal (non-hydroxy) oxygen atoms in the oxoacids bears a strong correlation to  $K_a$ .

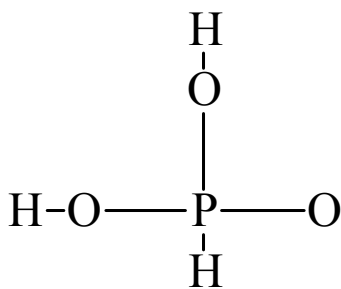
-O atoms	$K_a$ range	Strength
0	$10^{-7} - 10^{-10}$	very weak
1	$10^{-1} - 10^{-4}$	weak
2	$>10^{-1}$	strong
3	$\gg 1$	very strong

## Oxoacids, HOXO<sub>n</sub>

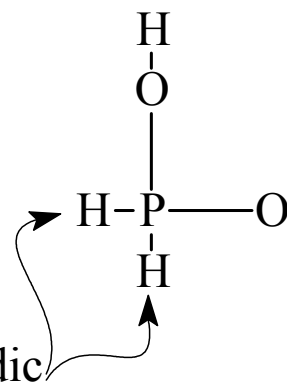
- ☞ Some care must be used in predicting acid strengths from formulas, because the actual structure may not be apparent.
- ✓ For example, H<sub>3</sub>PO<sub>4</sub>, H<sub>3</sub>PO<sub>3</sub>, and H<sub>3</sub>PO<sub>2</sub> all have only one terminal –O in their structures and therefore have similar strengths.



$$K_a = 7.6 \times 10^{-3}$$



$$K_a = 1.6 \times 10^{-2}$$



$$K_a = 1 \times 10^{-2}$$

## Carboxylic Acids, $\text{RCO}_2\text{H}$

☞ *Carboxylic acids*, an important class of organic acids, contain the *carboxyl group*,  $-\text{CO}_2\text{H}$ .

$\text{HCO}_2\text{H}$   
formic acid

$\text{CH}_3\text{CO}_2\text{H}$   
acetic acid

$\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$   
propionic acid

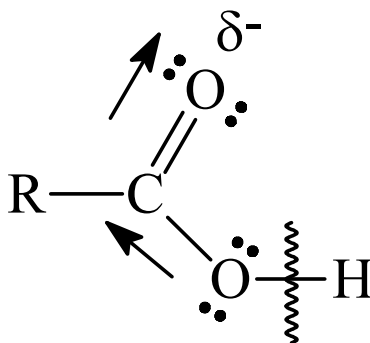
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$   
butyric acid

$\text{C}_6\text{H}_5\text{CO}_2\text{H}$   
benzoic acid

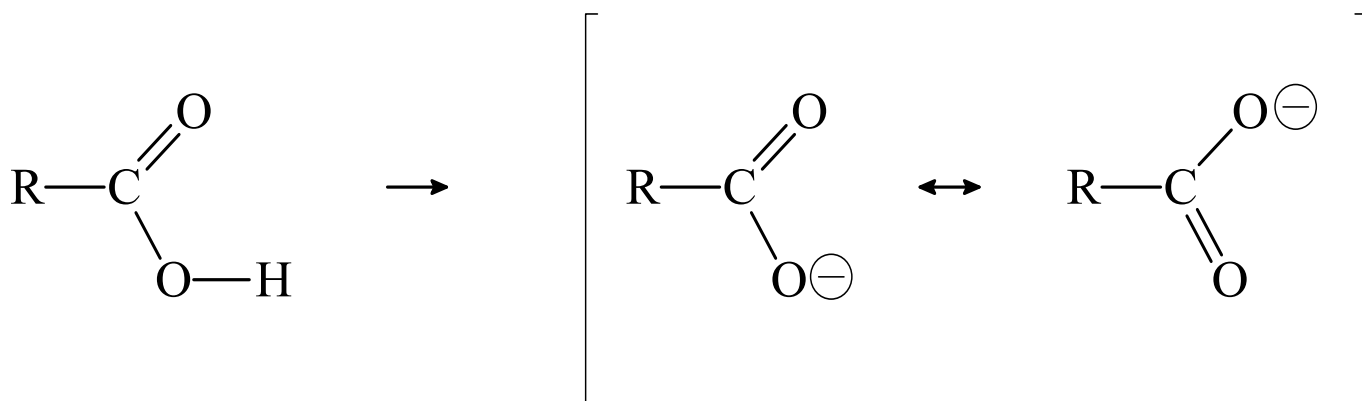
$\text{HO}_2\text{CCO}_2\text{H}$   
oxalic acid  
(diprotic)

## Acidity of the Carboxyl Group

- The acidity of the carboxyl group is partly due to the electronegativity of the double-bonded oxygen, which withdraws electron density from the  $\text{-O-H}$  bond, thereby facilitating the loss of  $\text{H}^+$  to solvent water.



- When a carboxyl group loses  $\text{H}^+$ , it forms a resonance stabilized anion, called a *carboxylate ion*:





## Enhancing Carboxylic Acid Strength

- ☞ The acidity of a carboxylic acid can be enhanced by adding electronegative atoms to the rest of the molecule.
- ✓ The electron-withdrawing ability of electronegative atoms weakens the  $\text{O-H}$  bond (inductive effect), thereby enhancing the ability of solvent water to remove  $\text{H}^+$ .

Acid	$K_a$
$\text{CH}_3\text{CO}_2\text{H}$	$1.77 \times 10^{-5}$
$\text{BrCH}_2\text{CO}_2\text{H}$	$2.05 \times 10^{-3}$
$\text{ClCH}_2\text{CO}_2\text{H}$	$1.40 \times 10^{-3}$
$\text{Cl}_2\text{CHCO}_2\text{H}$	$3.32 \times 10^{-2}$
$\text{Cl}_3\text{CCO}_2\text{H}$	$2 \times 10^{-1}$
$\text{F}_3\text{CCO}_2\text{H}$	$5 \times 10^{-1}$

## Hydrated Cations

- ☞ The *total hydration sphere* is the total number of water molecules associated with an ion in solution.
- ✓ The number of water molecules in the total hydration sphere is determined by the *charge density* of the ion.

### Crystallographic and Hydrated Radii of Alkali Metal Ions

Ion	Crystal radii, Å	Approx. hydrated radii, Å	Approx. Hydration Number
Li <sup>+</sup>	0.60	3.40	25
Na <sup>+</sup>	0.95	2.76	17
K <sup>+</sup>	1.33	2.32	11
Rb <sup>+</sup>	1.48	2.28	10
Cs <sup>+</sup>	1.69	2.28	10

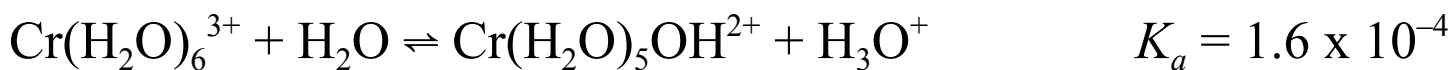
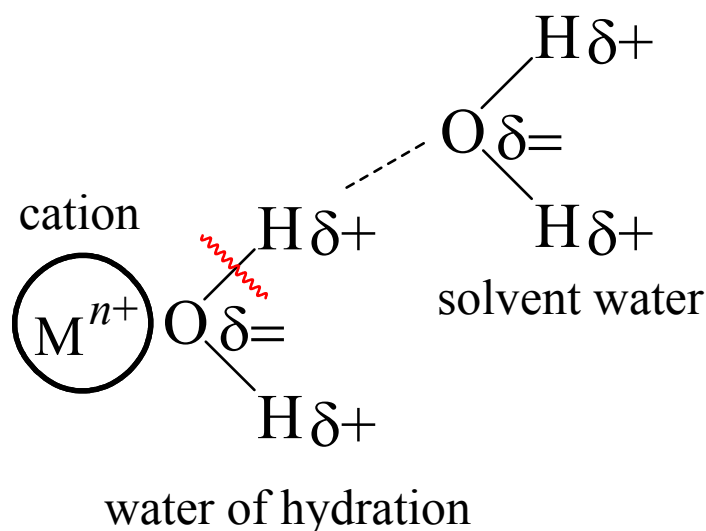
## First Hydration Sphere

- ☞ The *first hydration sphere* is defined as the number of water molecules in *direct contact* with the ion.
- ✓ The number of water molecules in the first hydration sphere depends only on the size of the ion.
  - ✓ Typical cations have first hydration spheres with four to six water molecules; e.g.,



## Acidic Hydrated Cations

- ☞ Ion-dipole attractions have an inductive effect on the O–H bonds of the water molecules in the first hydration sphere, which weakens the bond and may allow  $\text{H}^+$  to be lost to solvent water.



- ✓ This means that when we dissolve an ionic compound in water, the cation may affect the acid-base character of the solution.

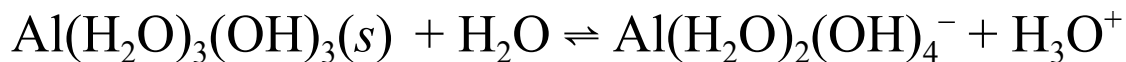
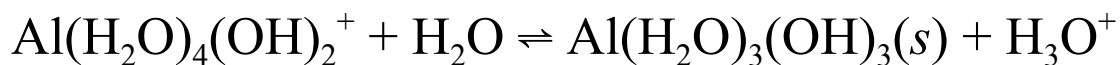
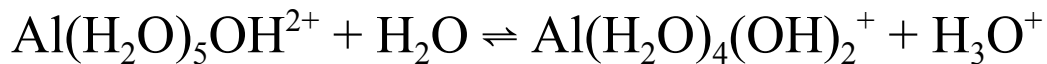
## Acidic and Non-Acidic Hydrated Cations

- ☞ As the charge density experienced by water molecules in the first hydration sphere increases the acidity increases.
- ✓ Smaller and more highly charged cations tend to be acidic.
  - ✓ The alkali and alkaline earth cations (with the exceptions of  $\text{Be}^{2+}$  and  $\text{Mg}^{2+}$ ) are too large and too lowly charged to have any appreciable acidity.
  - ✓ Transition metal cations tend to be more acidic than non-transition metal ions of comparable charge and size, because the poorer shielding  $d$ -subshell allows more of the nuclear charge to be experienced by the attached water molecules; i.e., they have higher effective nuclear charges,  $Z^*$ .

## Hydrated Cations as Polyprotic Acids

☞ Hydrated cations with appreciable acidity often act as polyprotic acids.

✓ Hydrated  $\text{Al}^{3+}$  can act as a tetraprotic acid:



✓ The addition of a strong base, such as  $\text{OH}^-$ , is necessary to drive the equilibria to the right by removal of the  $\text{H}_3\text{O}^+$  by neutralization.

# Lewis Acid-Base Theory

G. N. Lewis

**Lewis acid** - an electron-pair acceptor

**Lewis base** - an electron-pair donor

- ✓ Lewis acids are "seeking" an electron-pair, and so are called *electrophiles*.
- ✓ Lewis bases are "seeking" a nucleus to give an electron-pair, and so are called *nucleophiles*.

(Gk. *philos*, beloved, dear)

- ✓ The product of a Lewis acid-base reaction is often called an *adduct*.

## Comparison of Theories

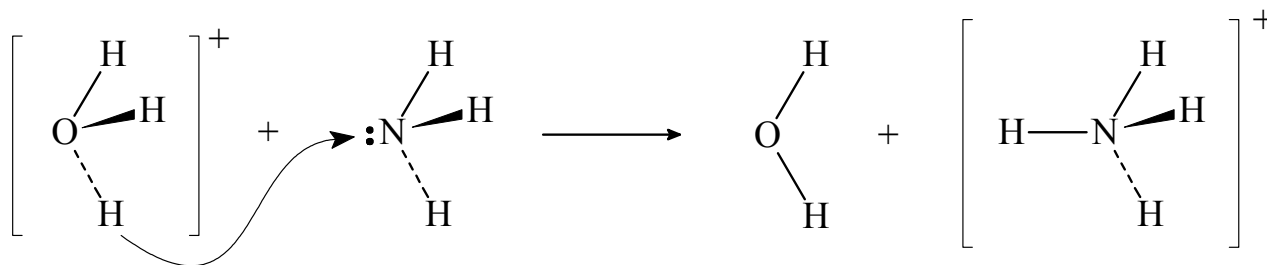
- ✓ Acids and bases in Arrhenius and Brønsted-Lowry theories are also acids and bases in Lewis theory:

hydronium ion

ammonia

water

ammonium ion

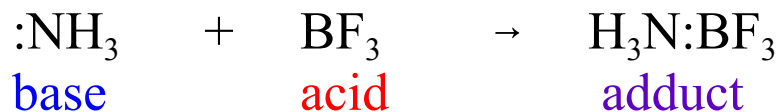


*e*-pair acceptor  
= acid = electrophile

*e*-pair donor  
= base = nucleophile

adduct

- ✓ Some acid-base reactions in Lewis theory are not seen as such by the other theories:





## Examples of Lewis Acid-Base Reactions

