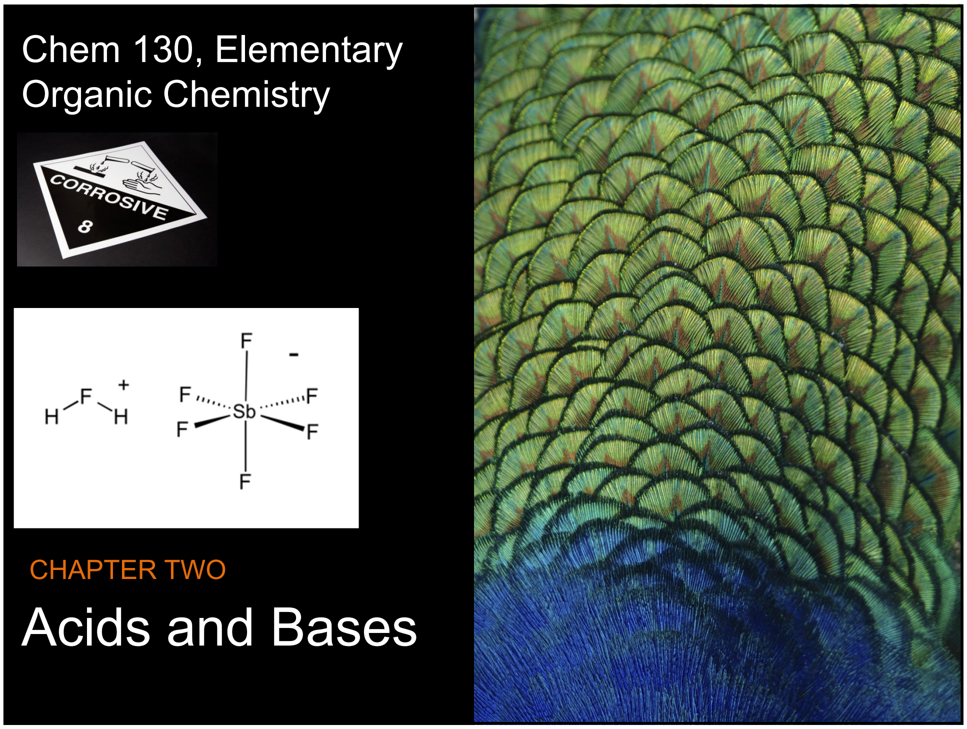


Chem 130, Elementary Organic Chemistry

CHAPTER TWO

Acids and Bases

Table of Contents

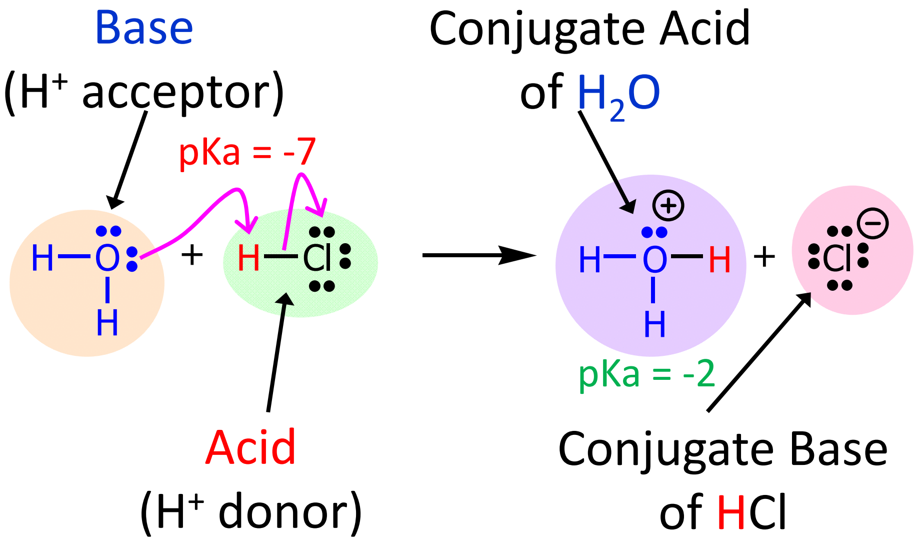
1. Acid–Base Reactions

- Many of the reactions that occur in organic chemistry are either acid–base reactions themselves or they involve an *acid–base reaction* at some stage
- Acid–base reactions are simple fundamental reactions that will enable you to see how chemists use *curved arrows* to represent mechanisms of reactions and how they depict the processes of bond breaking and bond making that occur as molecules react

1A. Brønsted–Lowry Acids and Bases

- **Brønsted–Lowry** acid–base reactions involve the transfer of protons
- A **Brønsted–Lowry acid** is a substance that can donate (or lose) a proton
- A **Brønsted–Lowry base** is a substance that can accept (or remove) a proton

- Example



Base
(H⁺ acceptor)

pKa = -7

Acid
(H⁺ donor)

Conjugate Acid
of H_2O

pKa = -2

Conjugate Base
of HCl

1B. Acids and Bases in Water

- Hydronium ion (H_3O^+) is the strongest acid that can exist in water to any significant extent: *Any stronger acid will simply transfer its proton to a water molecule to form hydronium ions*
- Hydroxide ion (HO^-) is the strongest base that can exist in water to any significant extent: *Any base stronger than hydroxide will remove a proton from water to form hydroxide ions*

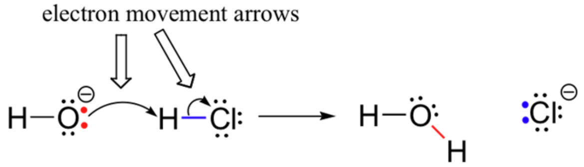
2. How to Use Curved Arrows in Illustrating Reactions

- Curved arrows show the direction of electron flow in a reaction mechanism
  - Draw the curved arrow so that it *points from the source of an electron pair to the atom receiving the pair*. (Curved arrows can also show the movement of single electrons)
  - Always show the flow of electrons from a site of higher electron density to a site of lower electron density (δ- vs. δ+)

- *Never use curved arrows to show the movement of atoms*. Atoms are assumed to follow the *flow of the electrons*

- Make sure that the movement of electrons shown by the curved arrow *does not violate the octet rule* for elements in the second row of the periodic table

❖ Examples



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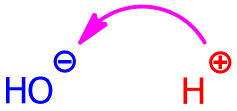
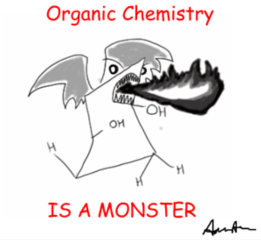
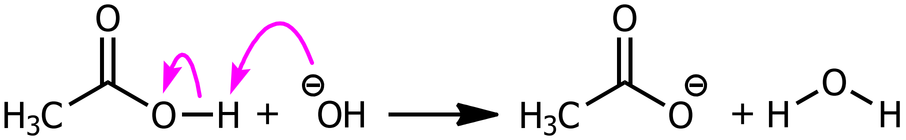




❖ Examples



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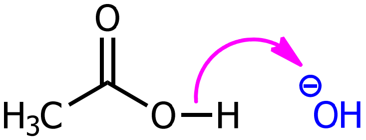
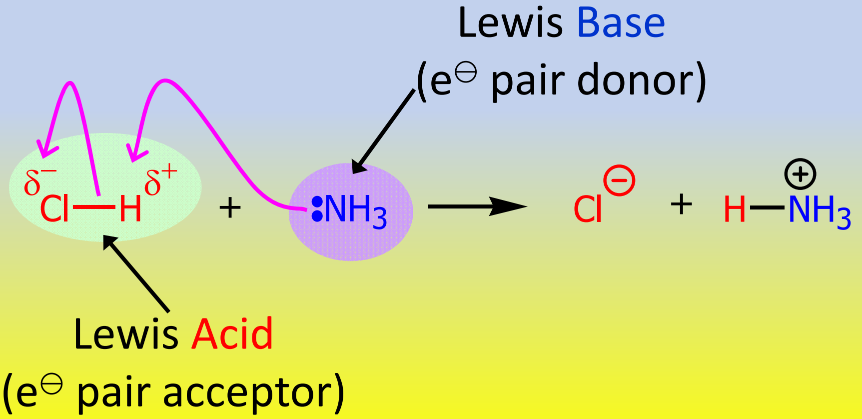


3. Lewis Acids and Bases

- Lewis Acids are electron pair acceptors
- Lewis Bases are electron pair donors

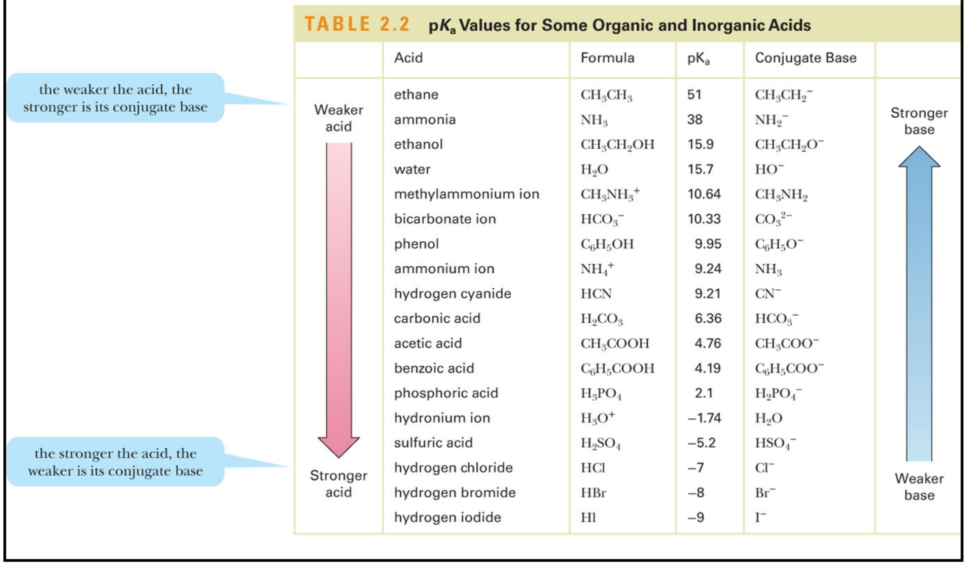


Lewis Base
(e⊖ pair donor)

$$\overset{\delta-}{Cl}-\overset{\delta+}{H} + :NH_3 \longrightarrow Cl^{\ominus} + H-\overset{\oplus}{N}H_3$$

Lewis Acid
(e⊖ pair acceptor)

pK_a Values for Some Organic and Inorganic Acids



the weaker the acid, the stronger is its conjugate base

the stronger the acid, the weaker is its conjugate base

TABLE 2.2 **pK_a Values for Some Organic and Inorganic Acids**

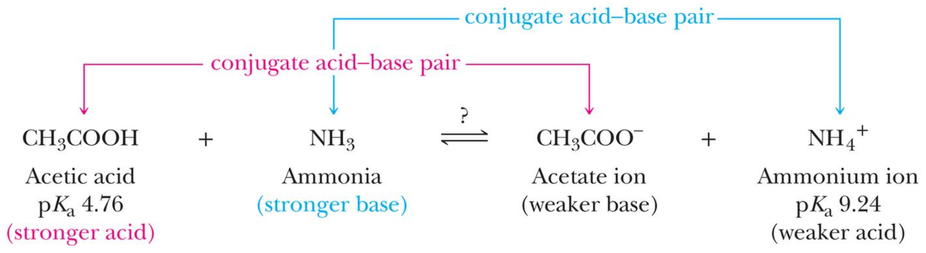
	Acid	Formula	pK_a	Conjugate Base	
Weaker acid	ethane	CH_3CH_3	51	$CH_3CH_2^-$	
	ammonia	NH_3	38	NH_2^-	Stronger base
	ethanol	CH_3CH_2OH	15.9	$CH_3CH_2O^-$	
	water	H_2O	15.7	HO^-	
	methylammonium ion	$CH_3NH_3^+$	10.64	CH_3NH_2	
	bicarbonate ion	HCO_3^-	10.33	CO_3^{2-}	
	phenol	C_6H_5OH	9.95	$C_6H_5O^-$	
	ammonium ion	NH_4^+	9.24	NH_3	
	hydrogen cyanide	HCN	9.21	CN^-	
	carbonic acid	H_2CO_3	6.36	HCO_3^-	
	acetic acid	CH_3COOH	4.76	CH_3COO^-	
	benzoic acid	C_6H_5COOH	4.19	$C_6H_5COO^-$	
	phosphoric acid	H_3PO_4	2.1	$H_2PO_4^-$	
	hydronium ion	H_3O^+	−1.74	H_2O	
	sulfuric acid	H_2SO_4	−5.2	HSO_4^-	
Stronger acid	hydrogen chloride	HCl	−7	Cl^-	Weaker base
	hydrogen bromide	HBr	−8	Br^-	
	hydrogen iodide	HI	−9	I^-	

4. Acid-Base Equilibrium

- To determine the position of equilibrium in an acid-base reaction:
  - Identify the two acids in the equilibrium; one on the left and one on the right.
  - Use the information in Table 2.2 to determine which is the stronger acid and which is the weaker acid.
  - Remember that the stronger acid gives the weaker conjugate base, and the weaker acid gives the stronger conjugate base.
  - The stronger acid reacts with the stronger base to give the weaker acid and weaker base.
  - **Equilibrium lies on the side of the weaker acid and the weaker base.**

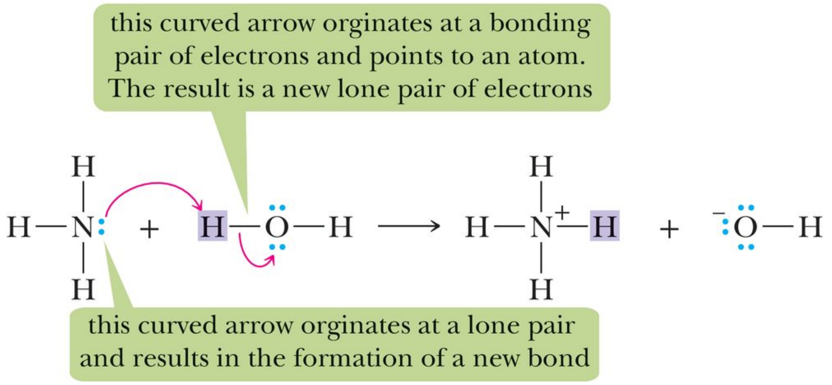
Acid-Base Equilibrium

- Equilibrium in the following acid-base reaction lies to the right, on the side of the weaker acid and the weaker base.



Arrhenius Acids and Bases

- – We use curved arrows to show the transfer of a proton from water to ammonia.



this curved arrow orginates at a bonding pair of electrons and points to an atom. The result is a new lone pair of electrons

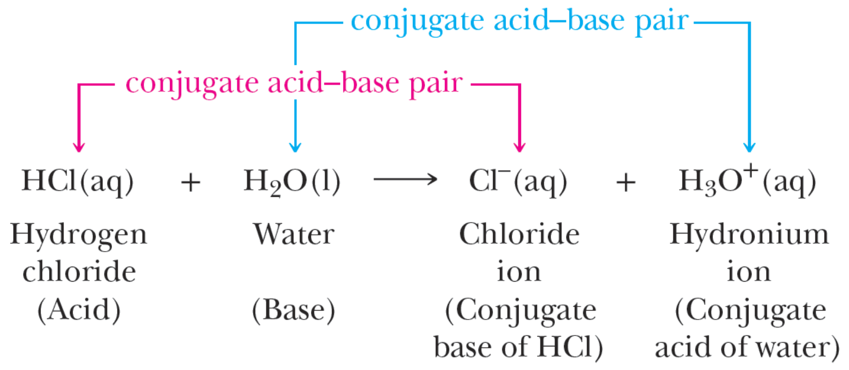
this curved arrow orginates at a lone pair and results in the formation of a new bond

Brønsted-Lowry Acids & Bases

- **Acid**: A proton donor.
- **Base**: A proton acceptor.
- **Conjugate base**: The species formed from an acid when an acid donates a proton to a base.
- **Conjugate acid**: The species formed from a base when the base accepts a proton from an acid.
  - – Acid-base reaction: A proton-transfer reaction.
  - – Conjugate acid-base pair: Any pair of molecules or ions that can be interconverted by transfer of a proton.

Conjugate Acids & Bases

- We illustrate these relationships by the reaction of hydrogen chloride with water:

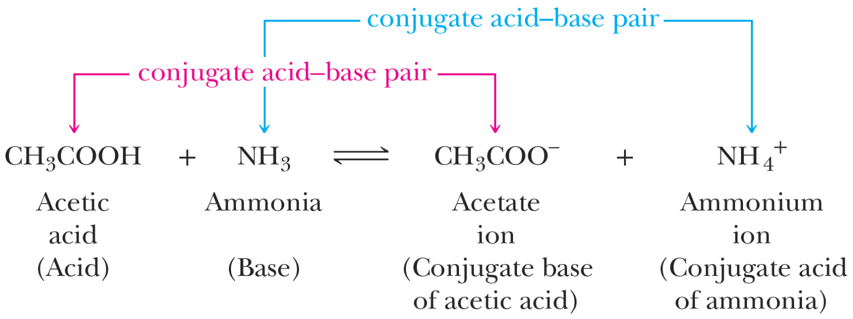


$$HCl(aq) + H_2O(l) \longrightarrow Cl^-(aq) + H_3O^+(aq)$$

Hydrogen chloride (Acid)	Water (Base)	Chloride ion (Conjugate base of HCl)	Hydronium ion (Conjugate acid of water)

Brønsted-Lowry Acids & Bases

- Brønsted-Lowry definitions do not require water as a reactant.

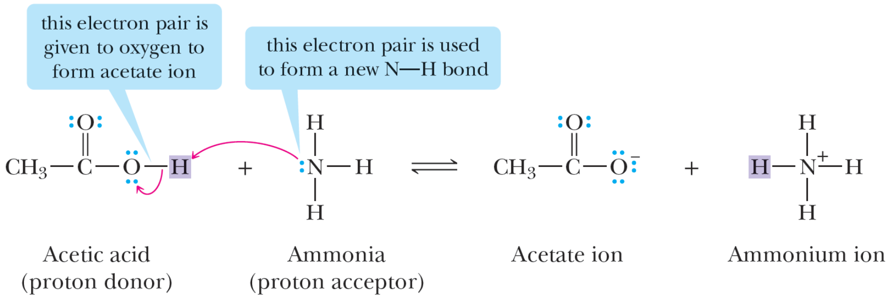


$$CH_3COOH + NH_3 \rightleftharpoons CH_3COO^- + NH_4^+$$

Acetic acid (Acid)	Ammonia (Base)	Acetate ion (Conjugate base of acetic acid)	Ammonium ion (Conjugate acid of ammonia)

Brønsted-Lowry Acids & Bases

- We use curved arrows to show the flow of electrons that occurs in the transfer of a proton from acetic acid to ammonia.



this electron pair is given to oxygen to form acetate ion

this electron pair is used to form a new N—H bond

Brønsted-Lowry Acids & Bases

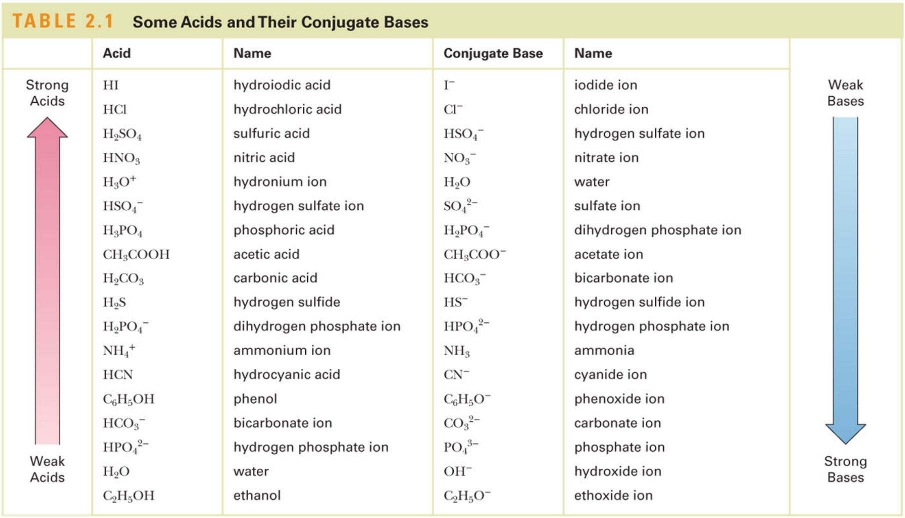


TABLE 2.1 **Some Acids and Their Conjugate Bases**

	Acid	Name	Conjugate Base	Name	
Strong Acids	HI	hydroiodic acid	I^-	iodide ion	Weak Bases
	HCl	hydrochloric acid	Cl^-	chloride ion	
	H_2SO_4	sulfuric acid	HSO_4^-	hydrogen sulfate ion	
	HNO_3	nitric acid	NO_3^-	nitrate ion	
	H_3O^+	hydronium ion	H_2O	water	
	HSO_4^-	hydrogen sulfate ion	SO_4^{2-}	sulfate ion	
	H_3PO_4	phosphoric acid	$H_2PO_4^-$	dihydrogen phosphate ion	
	CH_3COOH	acetic acid	CH_3COO^-	acetate ion	
	H_2CO_3	carbonic acid	HCO_3^-	bicarbonate ion	
	H_2S	hydrogen sulfide	HS^-	hydrogen sulfide ion	
	$H_2PO_4^-$	dihydrogen phosphate ion	HPO_4^{2-}	hydrogen phosphate ion	
	NH_4^+	ammonium ion	NH_3	ammonia	
	HCN	hydrocyanic acid	CN^-	cyanide ion	
	C_6H_5OH	phenol	$C_6H_5O^-$	phenoxide ion	
	HCO_3^-	bicarbonate ion	CO_3^{2-}	carbonate ion	
	HPO_4^{2-}	hydrogen phosphate ion	PO_4^{3-}	phosphate ion	
Weak Acids	H_2O	water	OH^-	hydroxide ion	Strong Bases
	C_2H_5OH	ethanol	$C_2H_5O^-$	ethoxide ion	

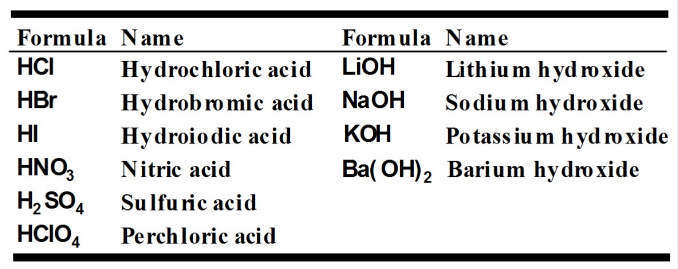
Brønsted-Lowry Acids & Bases

There is an inverse relationship between the strength of an acid and the strength of its conjugate base.

- The stronger the acid, the weaker its conjugate base.
- HI, for example, is the strongest acid in Table 2.1 and its conjugate base, I^-, is the weakest base in the table.
- CH_3COOH (acetic acid) is a stronger acid that H_2CO_3 (carbonic acid); conversely, CH_3COO^- (acetate ion) is a weaker base that HCO_3^- (bicarbonate ion).

5. Acid and Base Strength

- **Strong acid**: One that reacts completely or almost completely with water to form H_3O^+ ions.
- **Strong base**: One that reacts completely or almost completely with water to form OH^- ions.
  - Here are the six most common strong acids and the four most common strong bases.



Formula	Name	Formula	Name
HCl	Hydrochloric acid	$LiOH$	Lithium hydroxide
HBr	Hydrobromic acid	$NaOH$	Sodium hydroxide
HI	Hydroiodic acid	KOH	Potassium hydroxide
HNO_3	Nitric acid	$Ba(OH)_2$	Barium hydroxide
H_2SO_4	Sulfuric acid		
$HClO_4$	Perchloric acid		

Acid and Base Strength

- **Weak acid**: A substance that only partially dissociates in water to produce H_3O^+ ions.
  - Acetic acid, for example, is a weak acid; in water, only 4 out every 1000 molecules are converted to acetate ions.

$$\underset{\text{Acetic acid}}{CH_3COOH} + H_2O \rightleftharpoons \underset{\text{Acetate ion}}{CH_3COO^-} + H_3O^+$$

- **Weak base**: A substance that only partially dissociates in water to produce OH^- ions.
  - ammonia, for example, is a weak base.

$$\mathbf{NH_3\,(aq) + H_2O\,(l) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq)}$$

Acid-Base Reactions

- Acetic acid is incompletely ionized in aqueous solution.

$$CH_3\overset{\overset{\displaystyle O}{\|}}{C}OH + H_2O \rightleftharpoons CH_3\overset{\overset{\displaystyle O}{\|}}{C}O^- + H_3O^+$$

Acid (weaker acid)

Base (weaker base)

Conjugate base of CH_3COOH (stronger base)

Conjugate acid of H_2O (stronger acid)

- The equation for the ionization of a weak acid, HA, is:

$$HA + H_2O \rightleftharpoons A^- + H_3O^+ \qquad K_a = K_{eq}[H_2O] = \frac{[H_3O^+][A^-]}{[HA]}$$

6. Structure and Acidity

- The most important factor in determining the relative acidity of an organic acid is the relative stability of the anion, A^-, formed when the acid, HA, transfers a proton to a base.
- We consider these four factors:
  1. The electronegativity of the atom bonded to H in HA.
  2. Resonance stabilization of A^-.
  3. The inductive effect.
  4. The size and delocalization of charge in A^-.

Relationships between Structure and Acidity

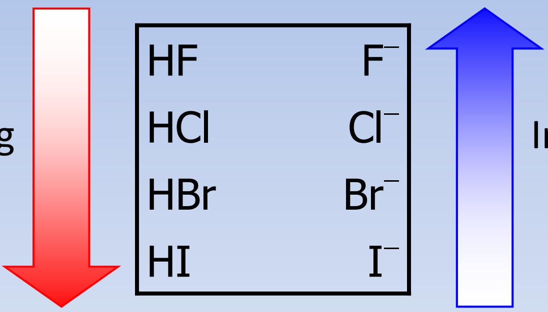
	H–F	H–Cl	H–Br	H–I
Bond Length (Å)	0.92	1.28	1.41	1.60
pK_a	3.2	-7	-9	-10

Increasing acidity

- The strength of H–X bond
  - H–F > H–Cl > H–Br > H–I

The stronger the H–X bond, the weaker the acid.

- Thus acidity increases as we descend a vertical column in a group in the Periodic Table



Increasing acidity

HF	F^-
HCl	Cl^-
HBr	Br^-
HI	I^-

Increasing basicity

The stronger the acid, the weaker the conjugate base.

	δ^- H_3C	δ^+ —H	δ^- H_3N	δ^+ —H	δ^- HO	δ^+ —H	δ^- F	δ^+ —H
Electro-negativity	2.5	2.1	3.0	2.1	3.5	2.1	4.0	2.1
pK_a	50		~35		15.7		3.2	

The higher the electronegativity of an atom, the easier it will acquire a negative charge.

- Thus acidity increases from left to right when we compare compounds in the same row of the Periodic Table

Increasing acidity

$H_3C{-}H$ $H_2N{-}H$ $HO{-}H$ $F{-}H$

$^{\ominus}CH_3$ $^{\ominus}NH_2$ $^{\ominus}OH$ $^{\ominus}F$

Increasing basicity

Acidity increases within a given row (electronegativity effect)

	C	N	O	F
Hydride	$(H_3C{-}H)$	$(H_2N{-}H)$	(HO–H)	(F–H)
pK_a	50	~33	15.7	3.2
			S	Cl
			(HS–H)	(Cl–H)
			7.0	-7
			Se	Br
			(HSe–H)	(Br–H)
			3.9	-9
				I
				(I–H)
				-10

Acidity increases within a given column (bond strength effect)

Structure and Acidity

- Resonance delocalization of the charge on A⁻
  - Compare the acidity of a carboxylic acid and an alcohol, both of which contain an –OH group.
  - Carboxylic acids are weak acids. Values of pK_a for most unsubstituted carboxylic acids fall within the range of 4 to 5.

$$\underset{\text{A carboxylic acid}}{CH_3COOH} + H_2O \rightleftharpoons \underset{\text{A carboxylate anion}}{CH_3COO^-} + H_3O^+ \quad pK_a = 4.76$$

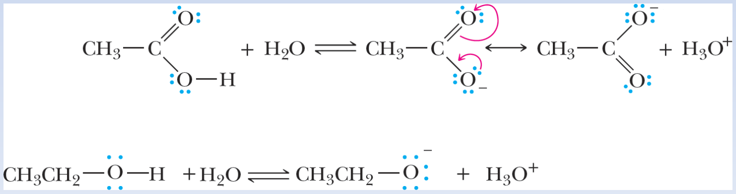
  - Alcohols are very weak acids. Values of pK_a for most alcohols fall within the range of 15 to 18.

$$\underset{\text{An alcohol}}{CH_3CH_2O{-}H} + H_2O \rightleftharpoons \underset{\text{An alkoxide ion}}{CH_3CH_2O^-} + H_3O^+ \quad pK_a = 15.9$$

  - How do we account for the fact that carboxylic acids are stronger acids than alcohols?

Structure and Acidity

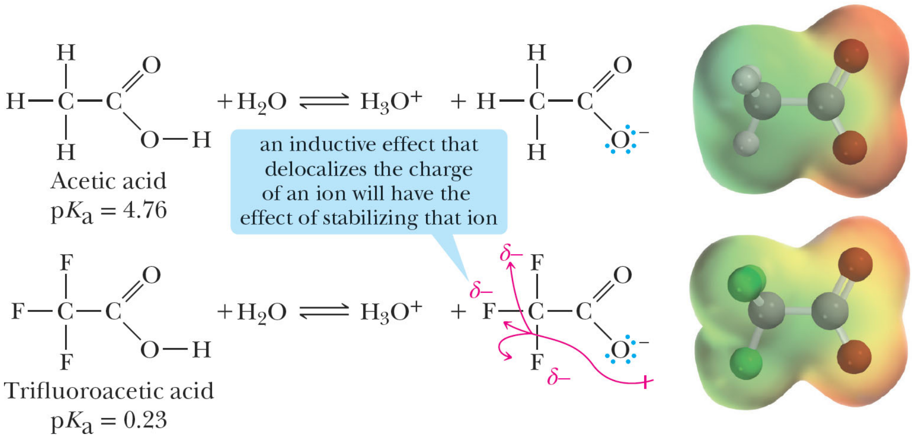
- The greater the resonance stabilization of the anion, the more acidic the compound.
- There is no resonance stabilization in an alkoxide anion.
- We can write two equivalent contributing structures for the carboxylate anion; the negative charge is delocalized evenly over the two oxygen atoms.



7. Inductive Effects

- Inductive effects are electronic effects transmitted through bonds (*σ-bonds*)
- The inductive effect of a group can be *electron donating* or *electron withdrawing*
- Inductive effects weaken as the *distance* from the group increases

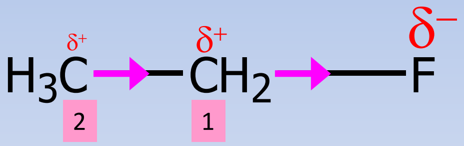
- **Inductive** polarization of electron density transmitted through covalent bonds caused by a nearby atom of higher electronegativity



an inductive effect that delocalizes the charge of an ion will have the effect of stabilizing that ion

$H_3C{-}CH_3$

The C–C bond is nonpolar.



- The positive charge that the fluorine imparts to C1 is greater than that imparted to C2 because the fluorine is closer to C1

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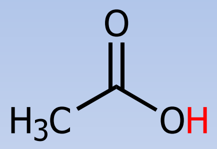
8. Acidity: Resonance Effects



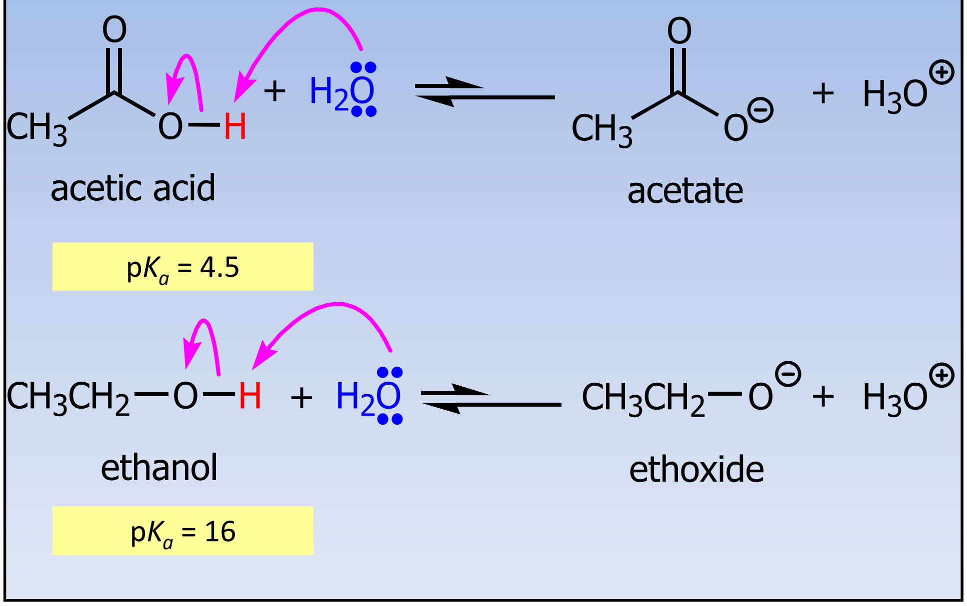
Acetic acid

$pK_a = 4.75$

$CH_3CH_2{-}OH$

Ethanol

$pK_a = 16$



acetic acid

acetate

pK_a = 4.5

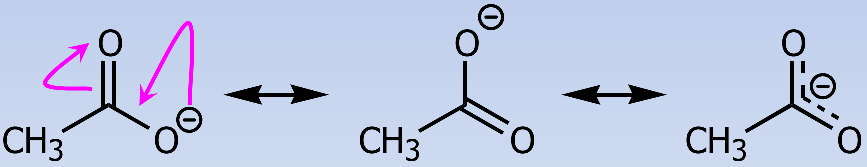
ethanol

ethoxide

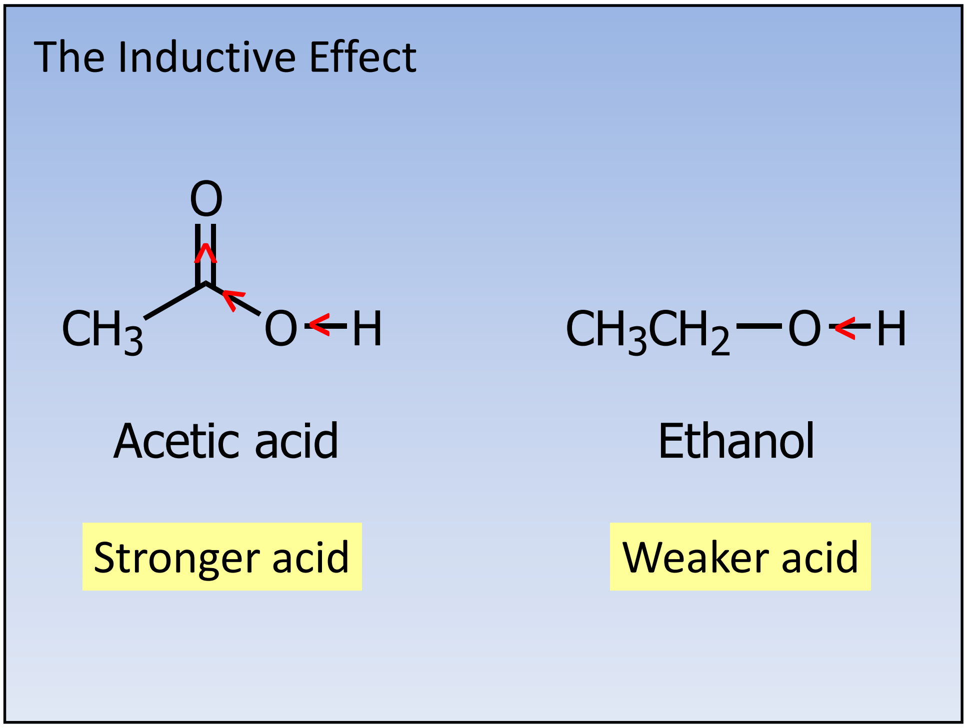
pK_a = 16

The Effect of Delocalization

- The conjugate base acetate is more stable (the anion is more delocalized) than ethoxide due to resonance stabilization



Thus, acetic acid is a stronger acid than ethanol



The Inductive Effect

CH_3CH_2-O-H

Acetic acid

Ethanol

Stronger acid

Weaker acid