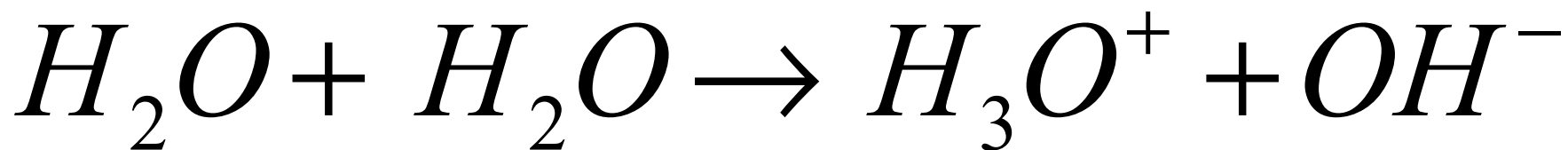


# **ACID-BASE THEORY**

## **EVALUATION OF ACIDS**

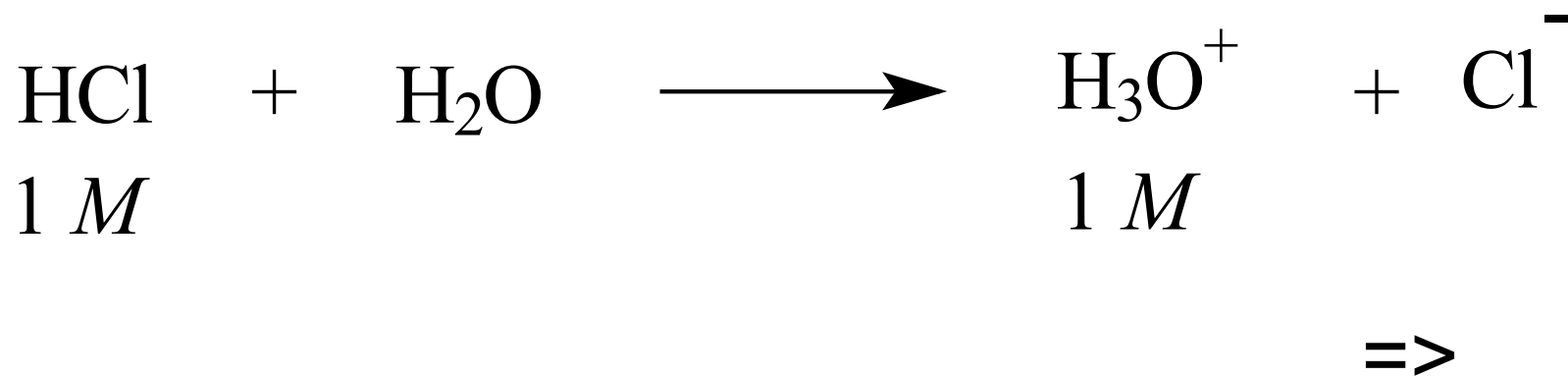
# REVIEW OF MAJOR THEORIES



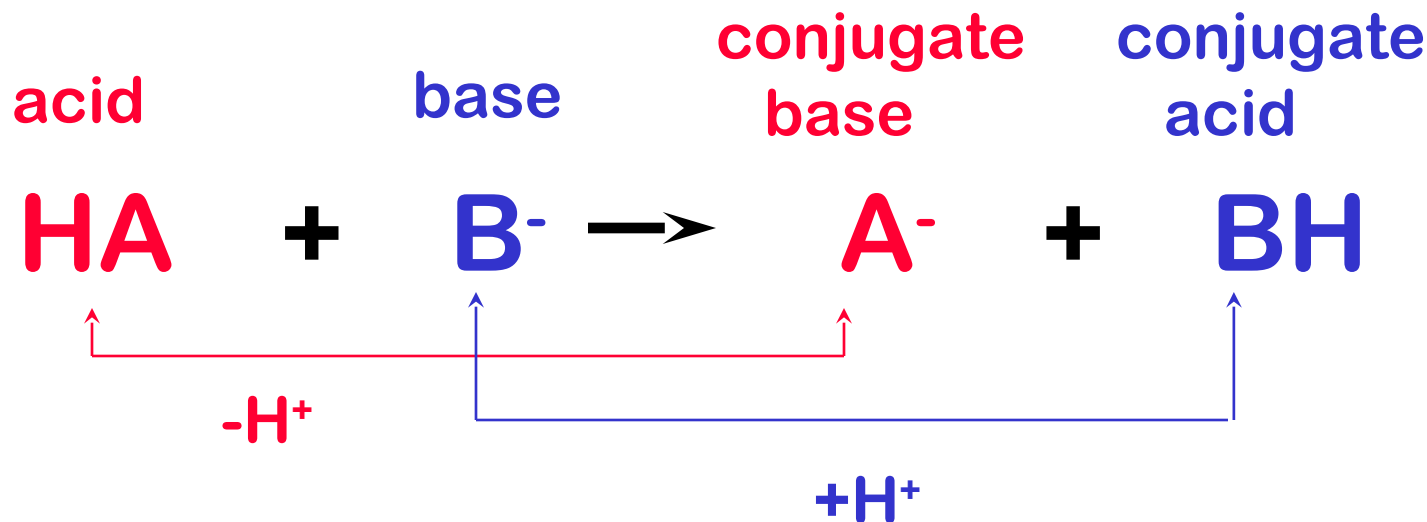
$$K_w = [H_3O^+][OH^-]$$

# Arrhenius Acids and Bases

- Acids dissociate in water to give  $\text{H}_3\text{O}^+$  ions.
- Bases dissociate in water to give  $\text{OH}^-$  ions.
- $K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$  at  $24^\circ\text{C}$
- $\text{pH} = -\log [\text{H}_3\text{O}^+]$
- Strong acids and bases are 100% dissociated.



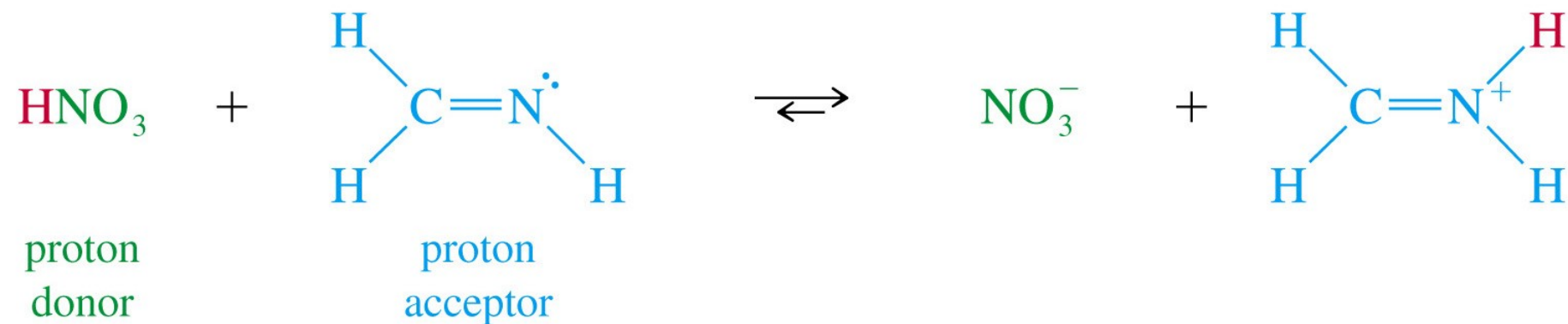
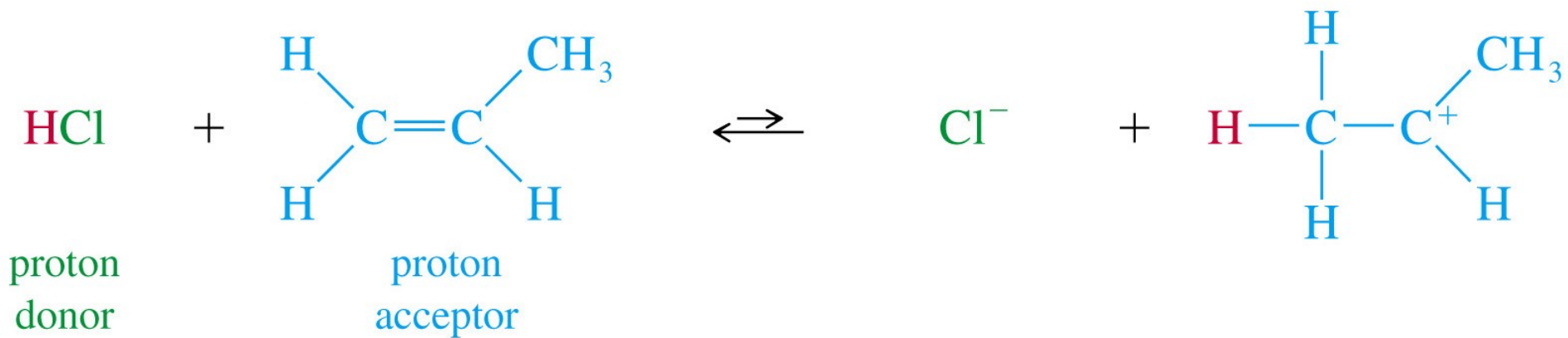
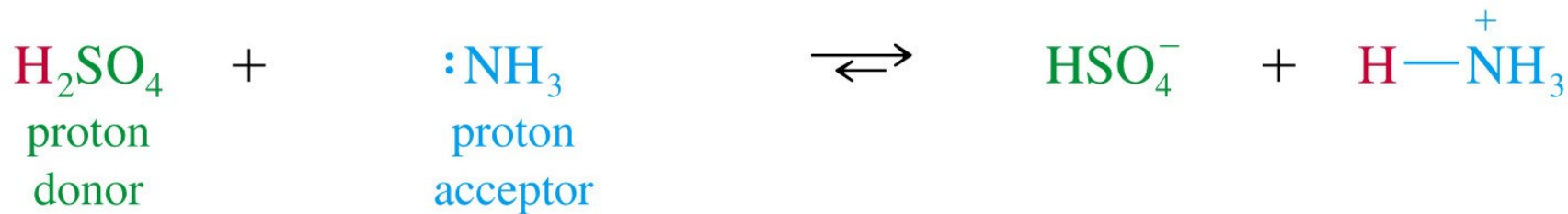
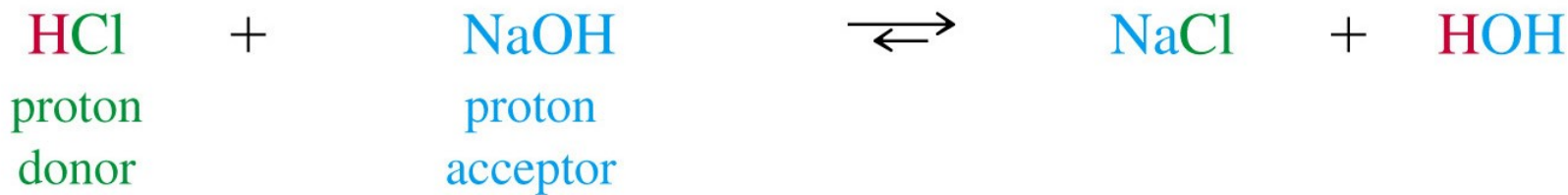
# BRONSTED - LOWRY THEORY



acid = proton donor

base = proton acceptor

Everything is defined in terms of the proton, the only recognized type of acid in B-L theory.



# **pKa's AND ACID STRENGTH**

**$pK_a$  - An alternative to  $K_a$  to describe acid strength.**

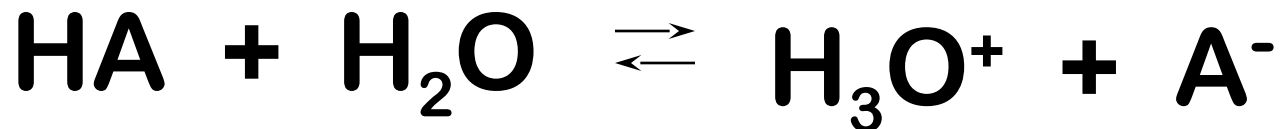
# Acid and Base Strength

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.)



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

Compare the  
definition of pH

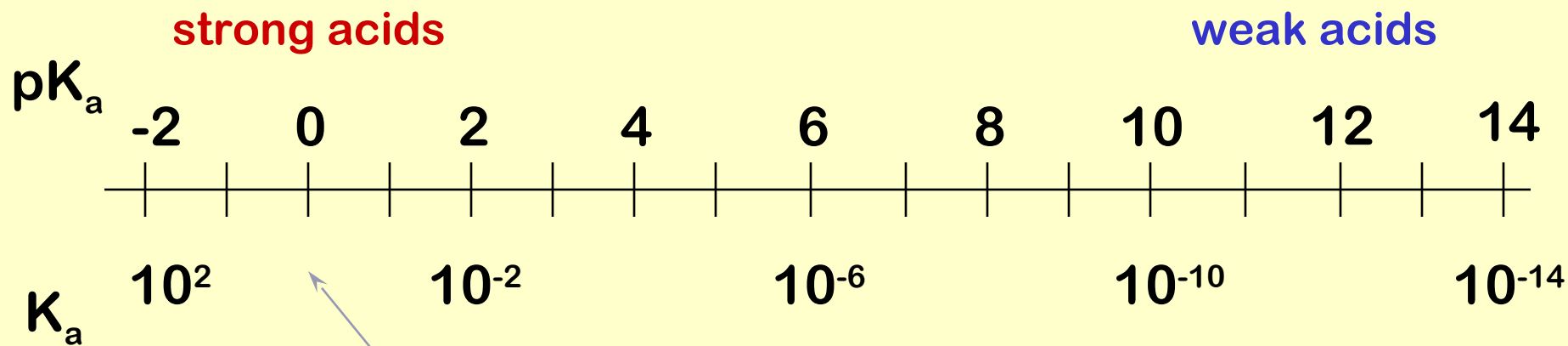
$$pH = -\log[H^+]$$

$$pK_a = -\log K_a$$



# COMPARISON OF $pK_a$ and $K_a$ VALUES

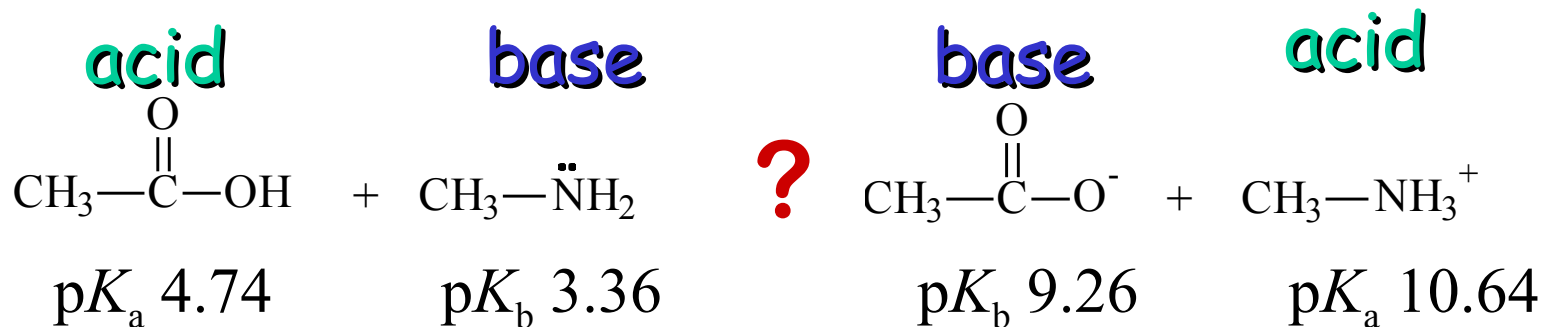
$$pK_a = -\log K_a$$



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.

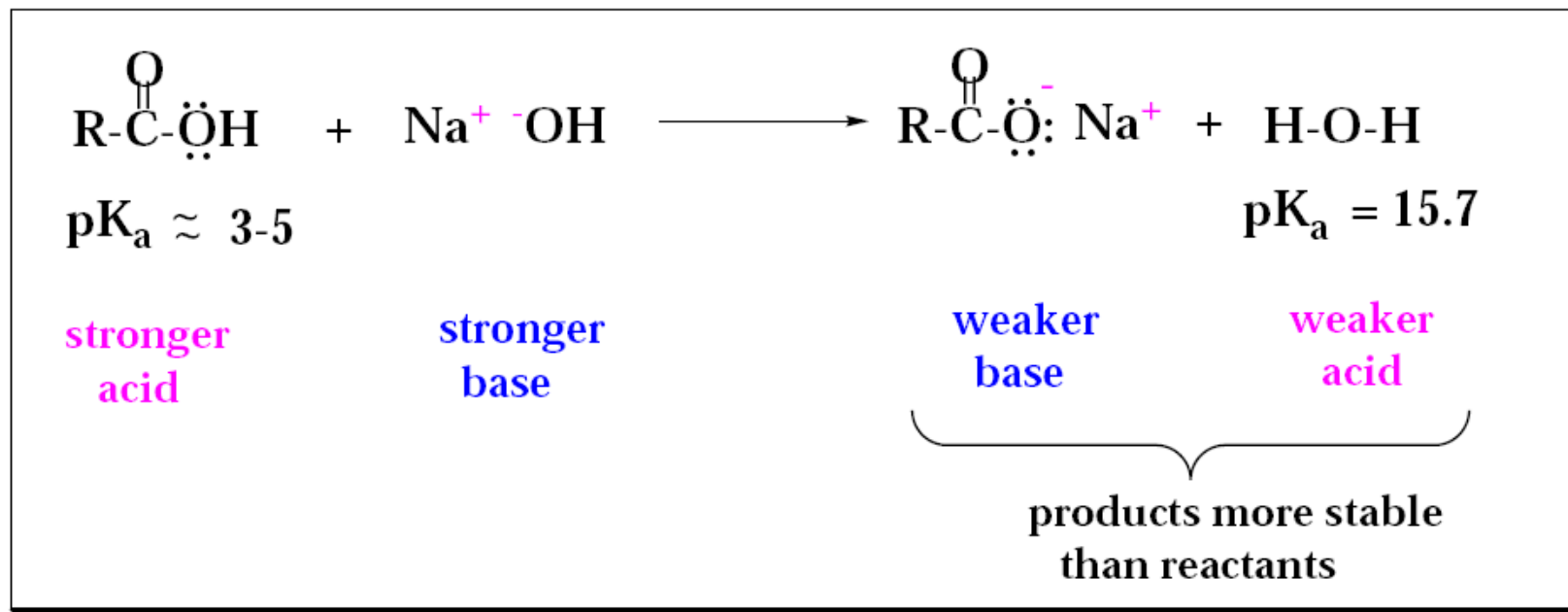
# Spontaneous or not?



$\text{p}K_{\text{a}} = -\log K_{\text{a}}$  larger  $\text{p}K_{\text{a}}$  = weaker acid

## Predicting the Outcome of Acid-Base Reactions

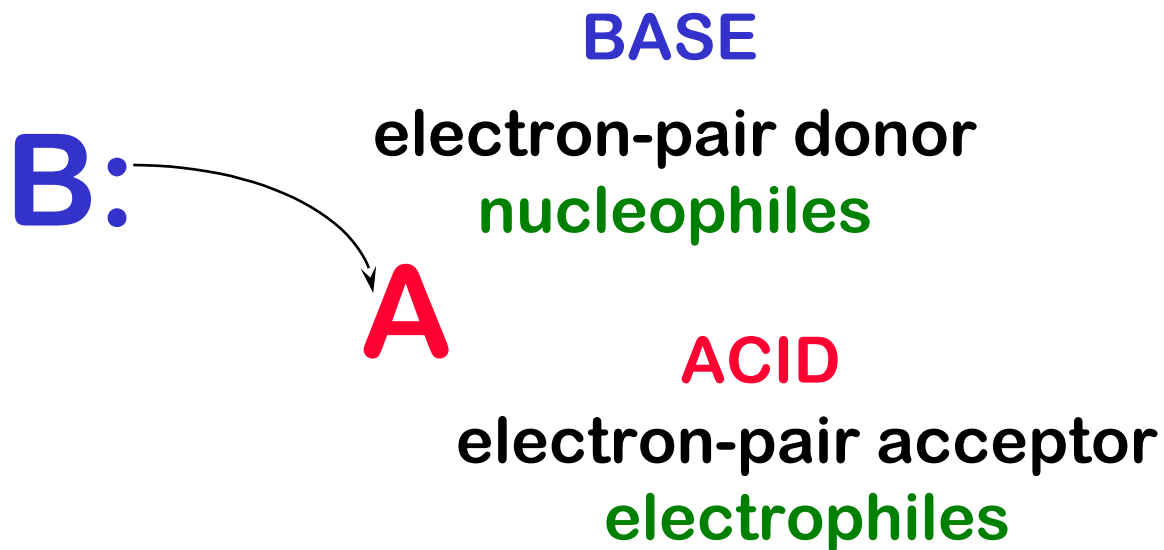
Acid-base reactions proceed to give the **weaker acid and weaker base as products**. This is the reaction favored by product stability and is the tendency of reactions under **equilibrium control**.



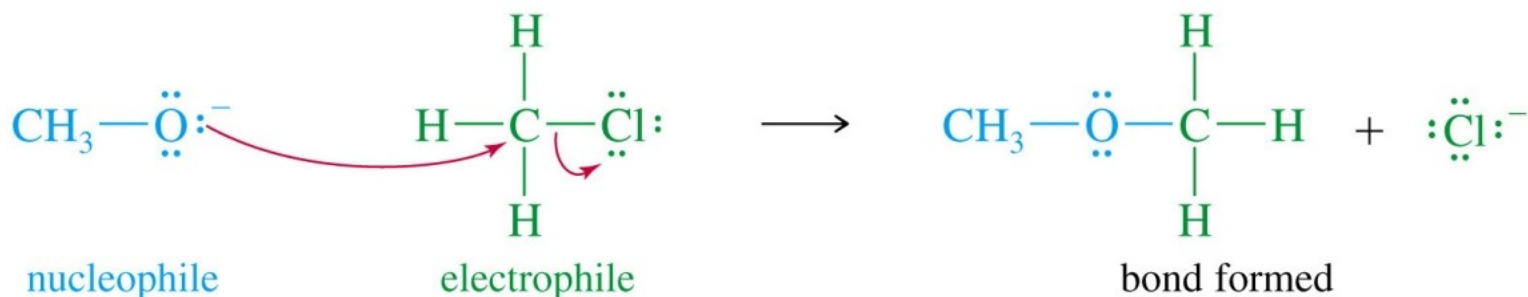
Even though the above reaction is an equilibrium, only a one-way arrow is used because the equilibrium is far to the right (>99%). The practical consequence of the above reaction is that carboxylic acids (RCO<sub>2</sub>H) can be dissolved as their carboxylate salts in aqueous NaOH solutions.

# LEWIS ACID - BASE THEORY

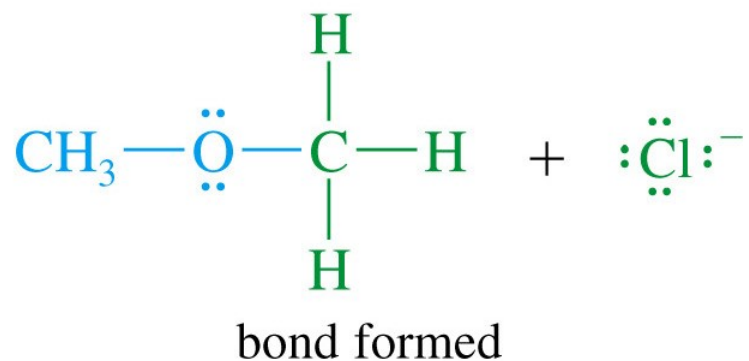
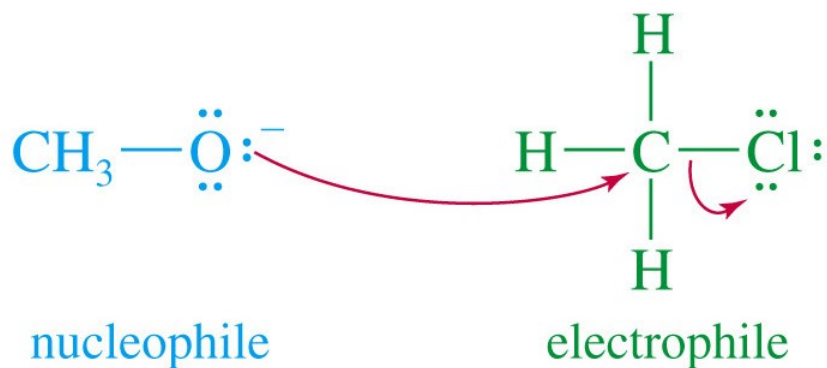
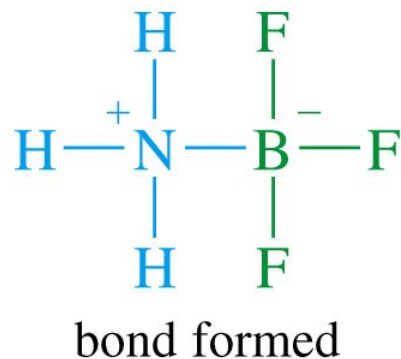
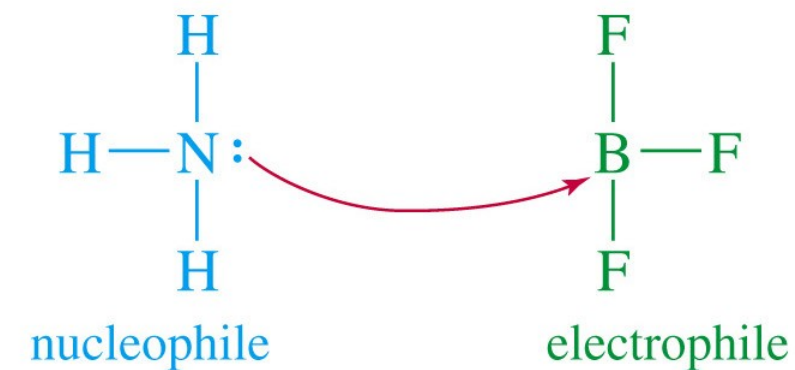
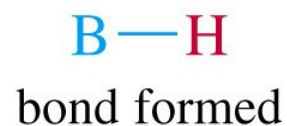
more general than Bronsted theory



Substances other than proton donor and acceptors are recognized as acids and bases.

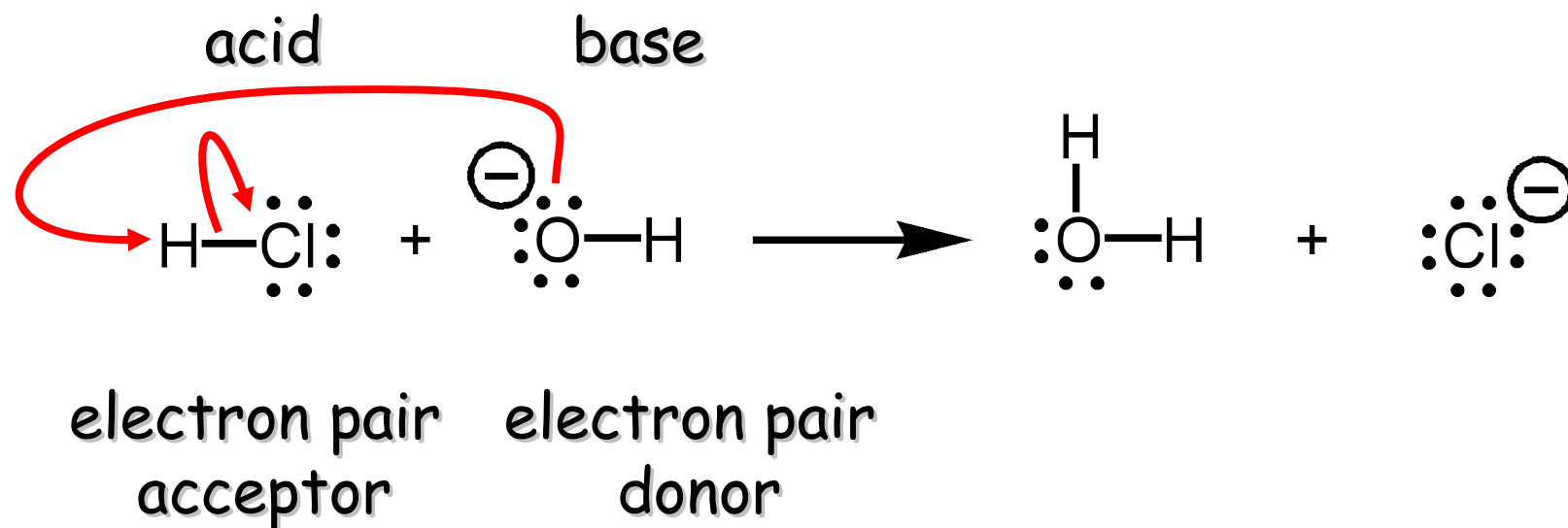


=>

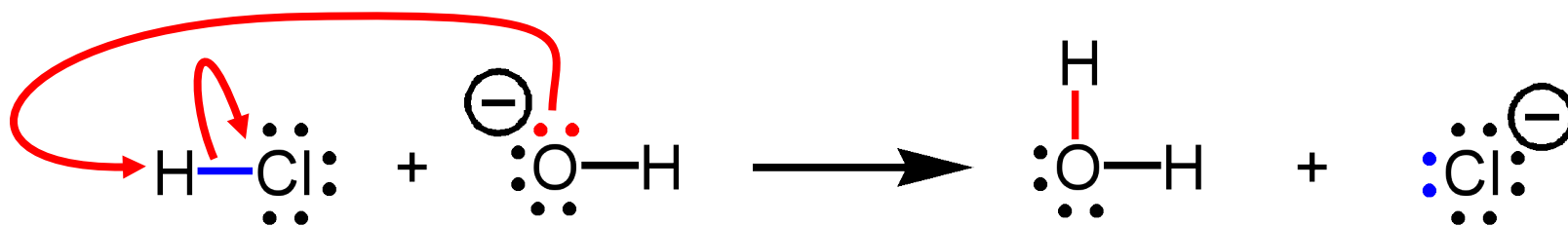


# Acids and Bases

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

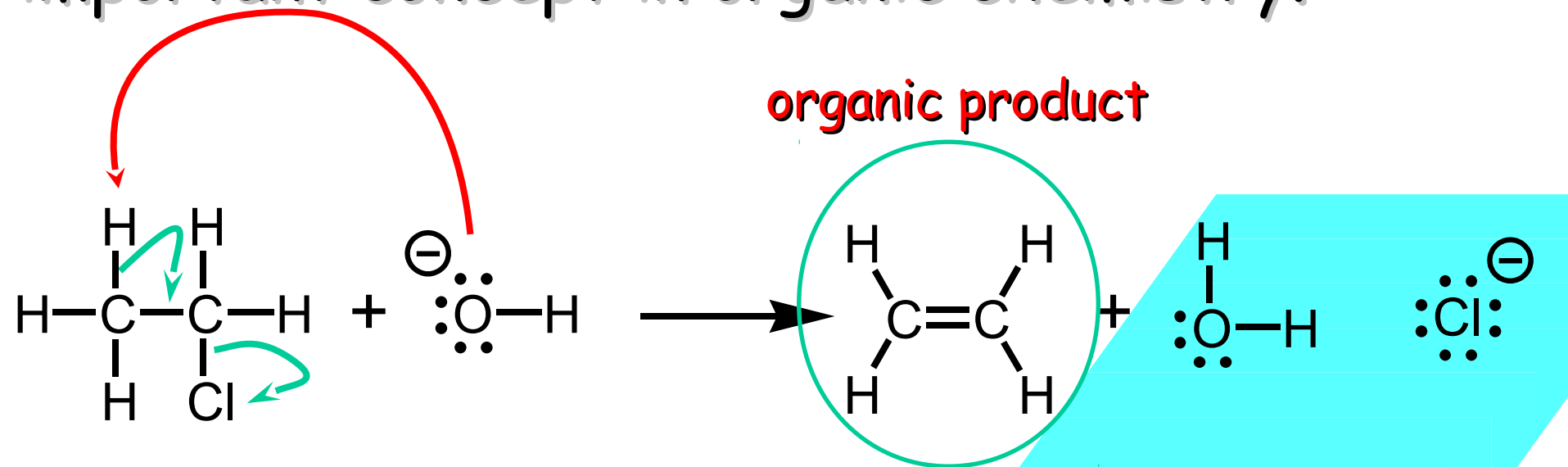


The "curved arrow formalism" is an extremely important concept in organic chemistry.

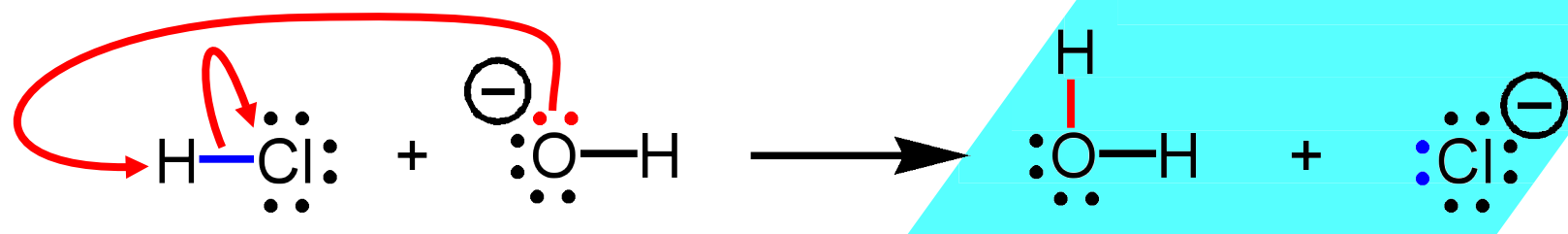


The arrow illustrates the flow of the electrons. This formalism is useful in describing reactivity and bonding.

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

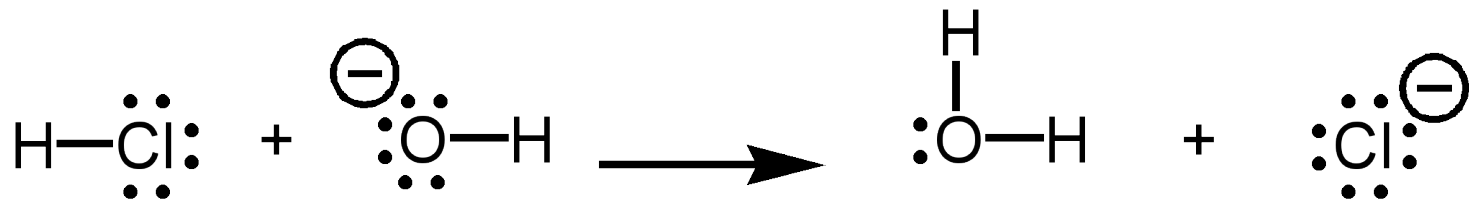
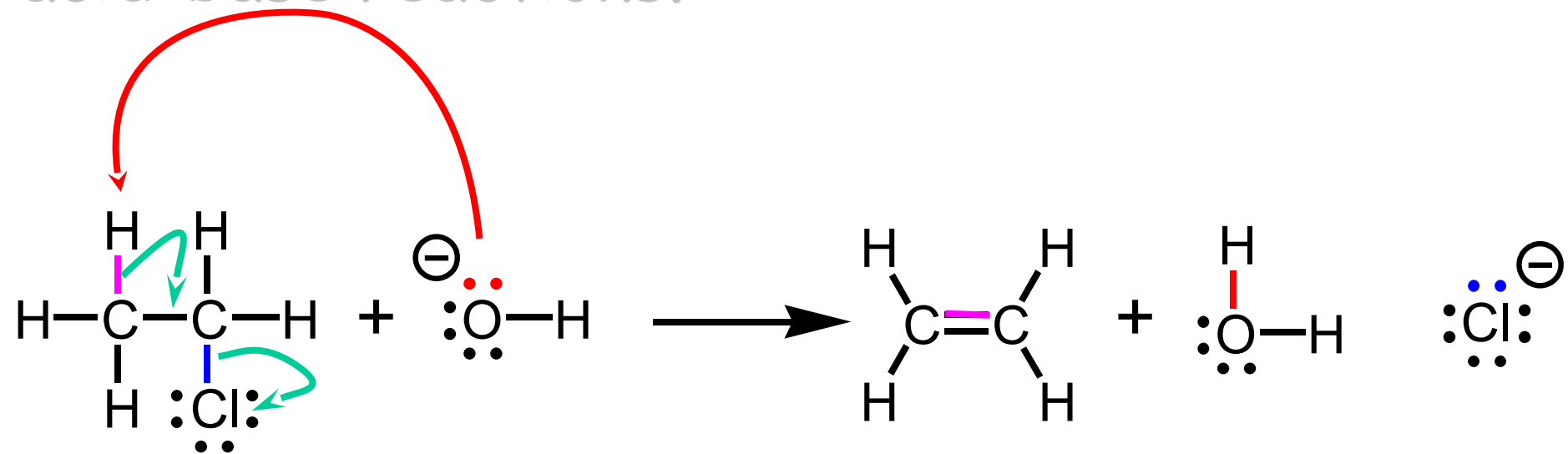


an elimination reaction

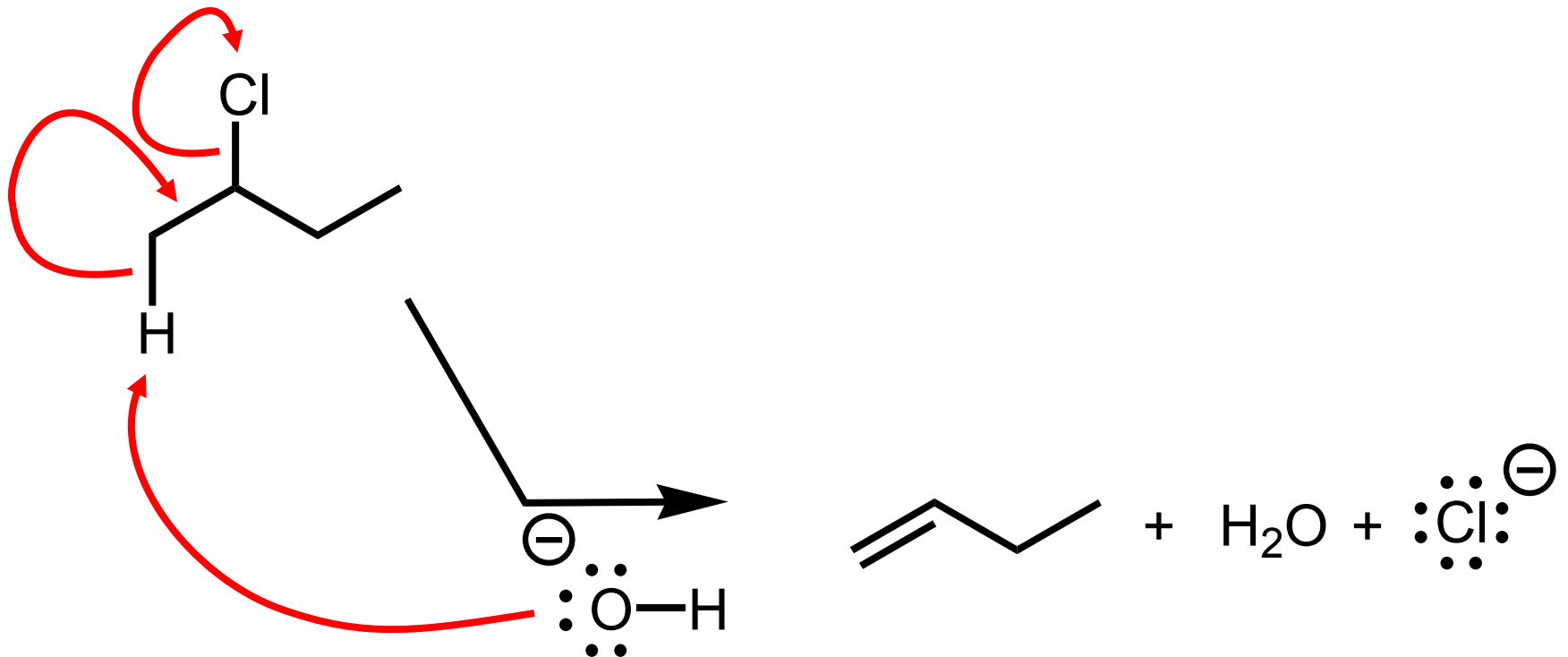




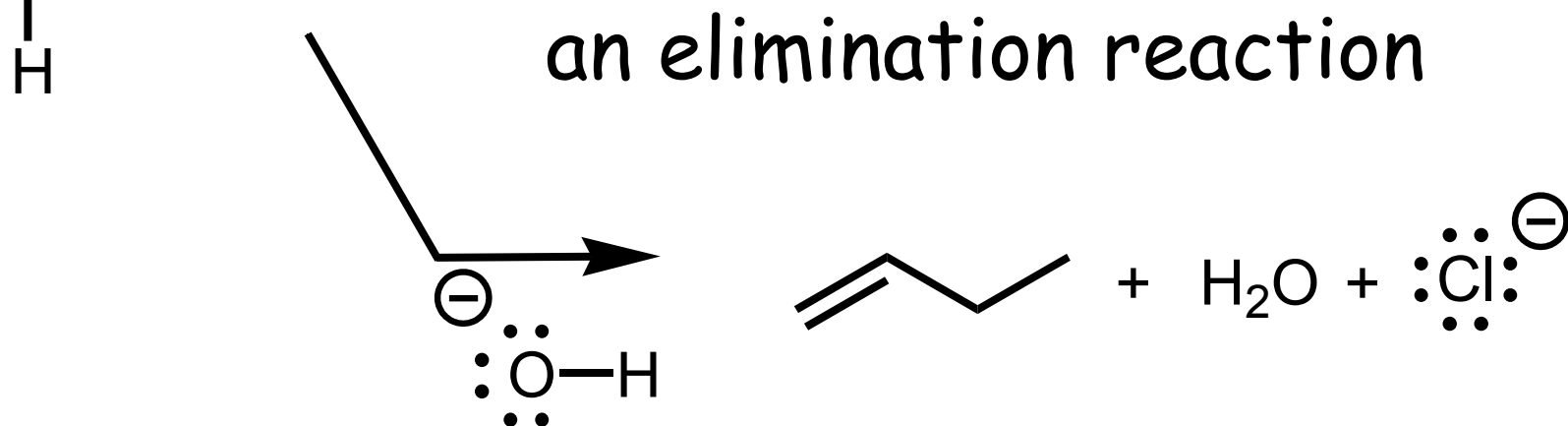
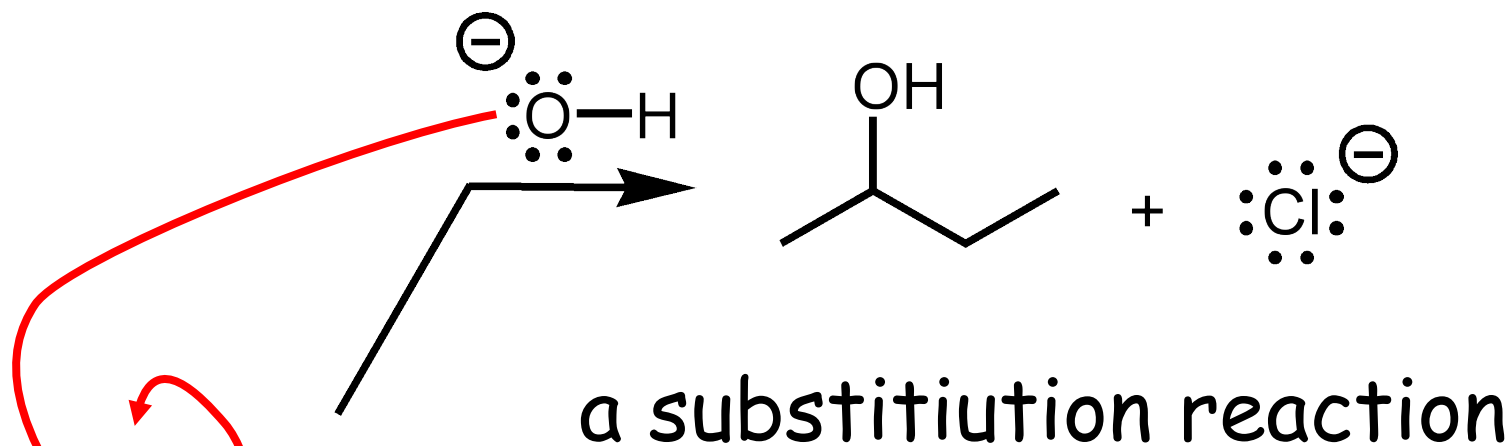
Organic compounds can behave as acids in acid-base reactions.



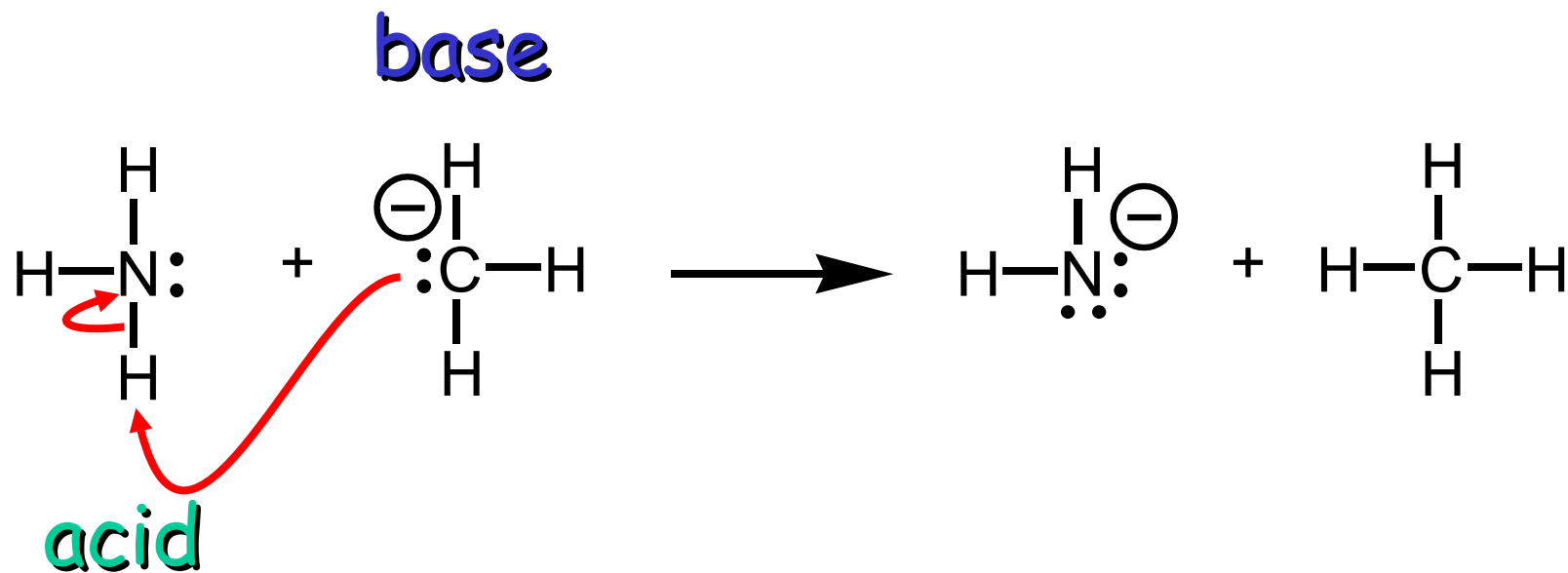
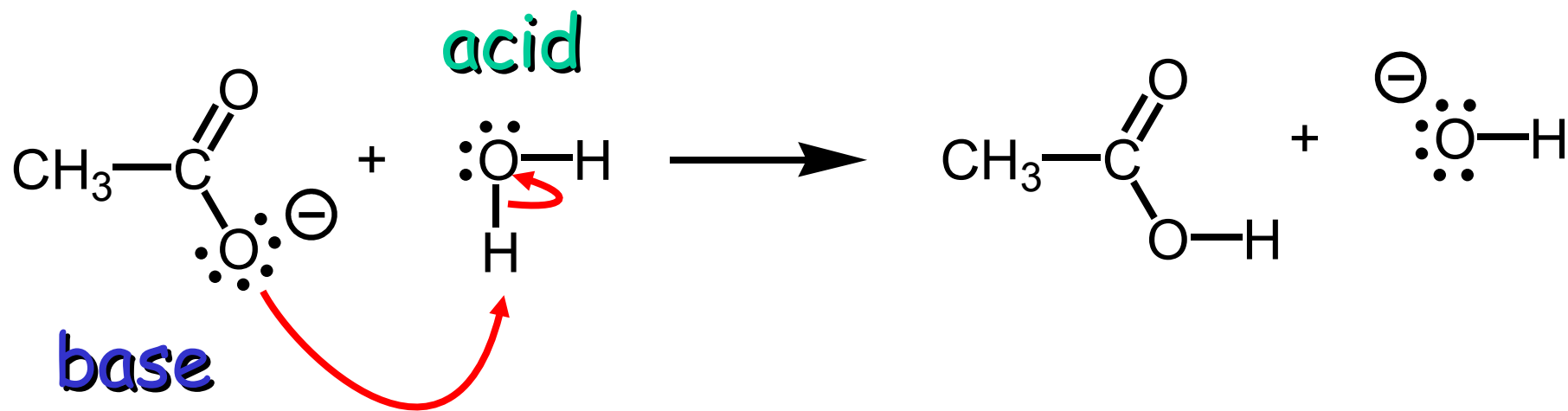
In organic chemistry two or more acid base reactions can compete.



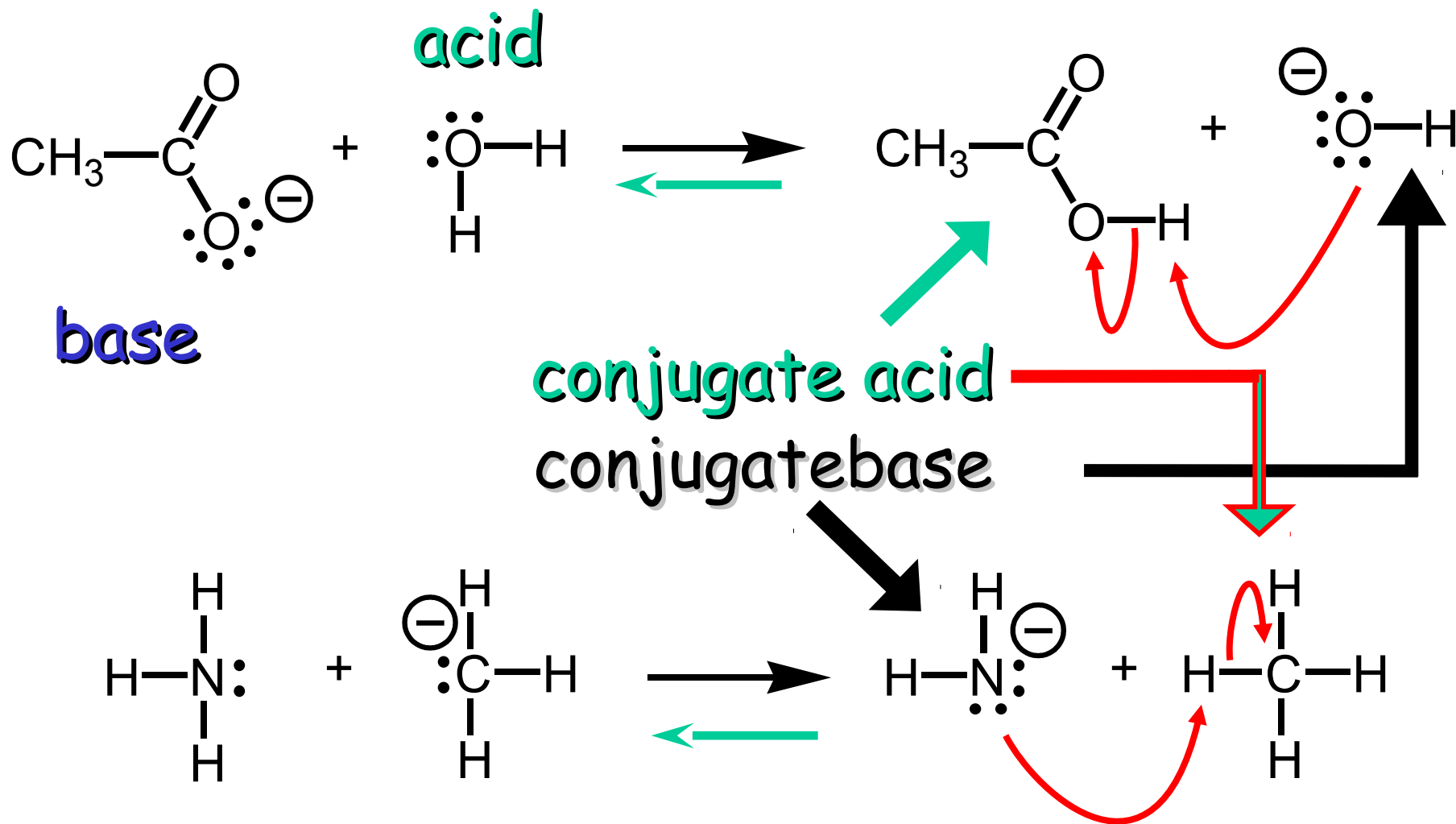
In organic chemistry two or more acid base reactions can compete.



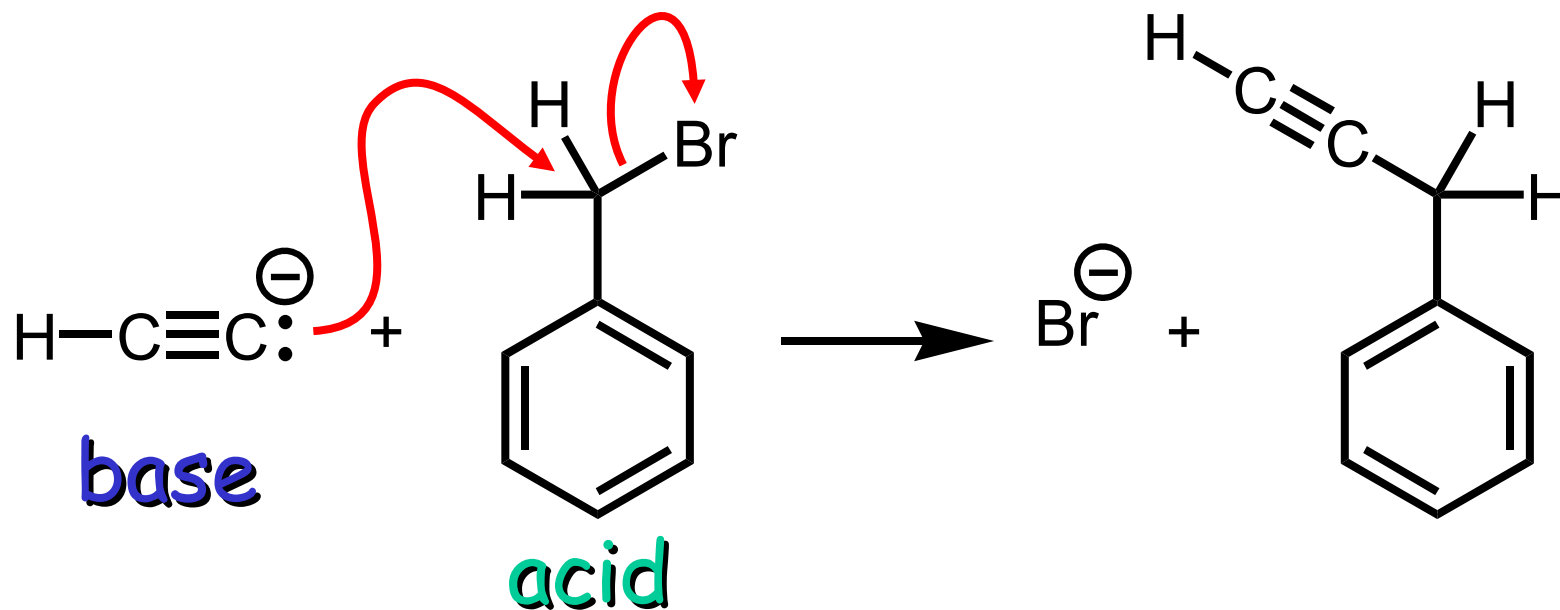
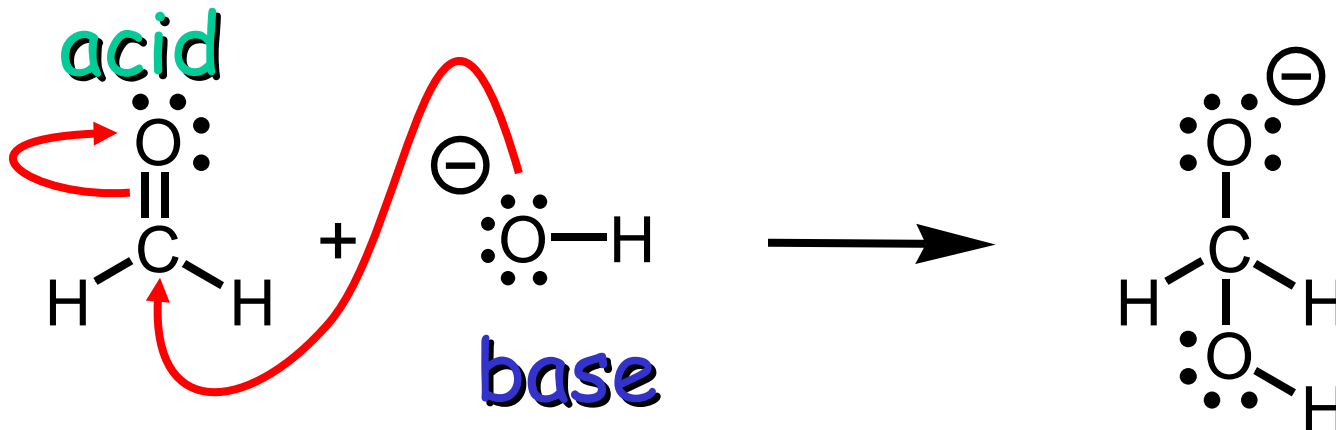
Identify the acid and base in the following reactions.



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

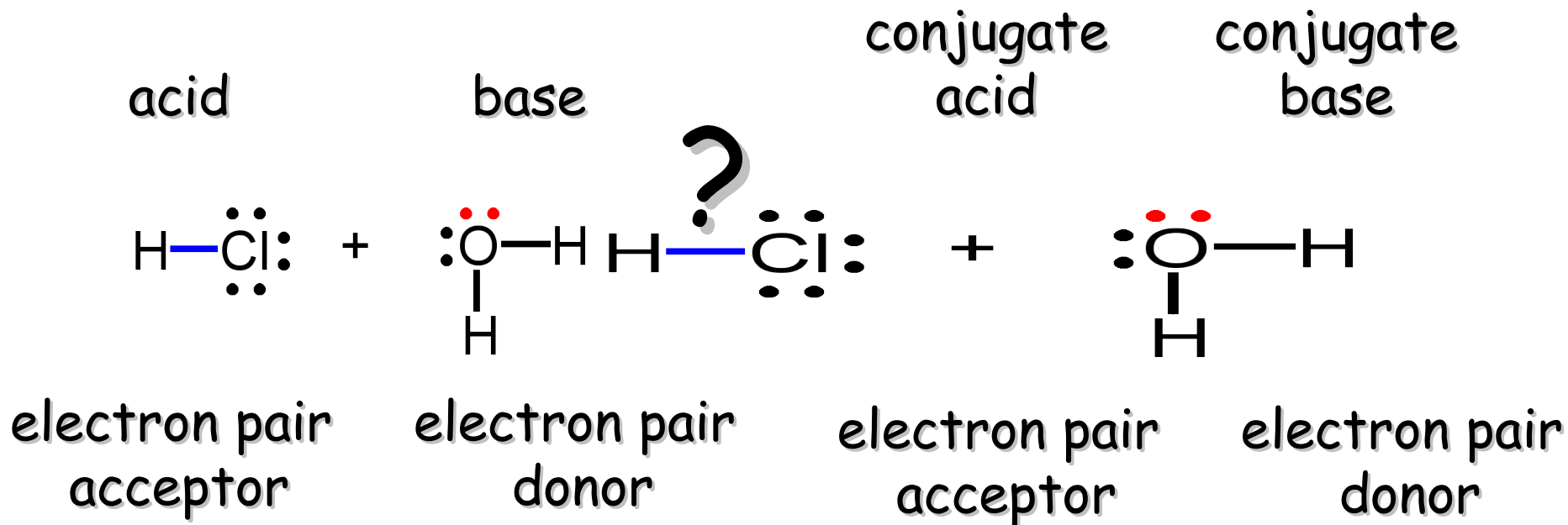


Identify the acid and base in the following reactions.



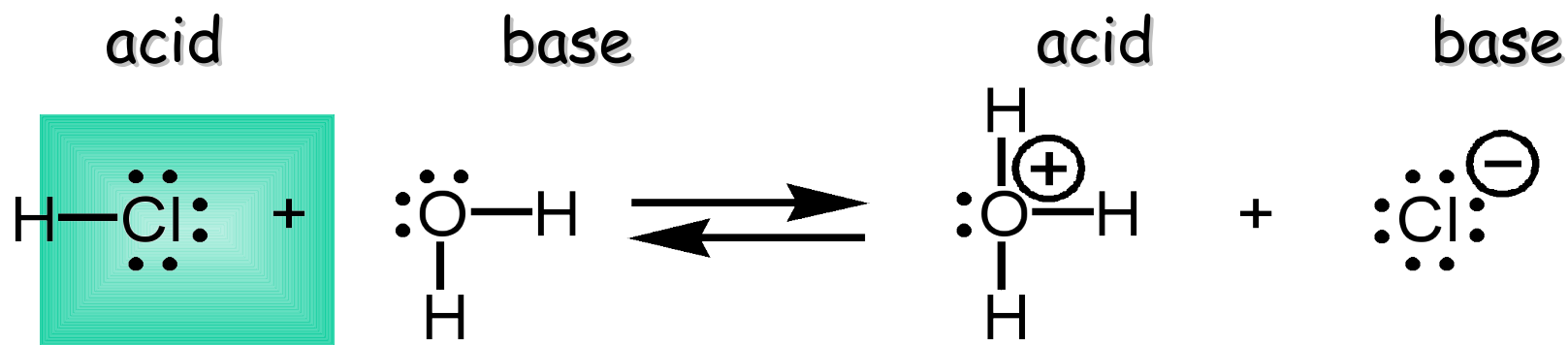
which is the stronger acid?

which is the stronger base?



which are the major species present at equilibrium?

which is the stronger acid?



$$\text{p}K_a = -7$$

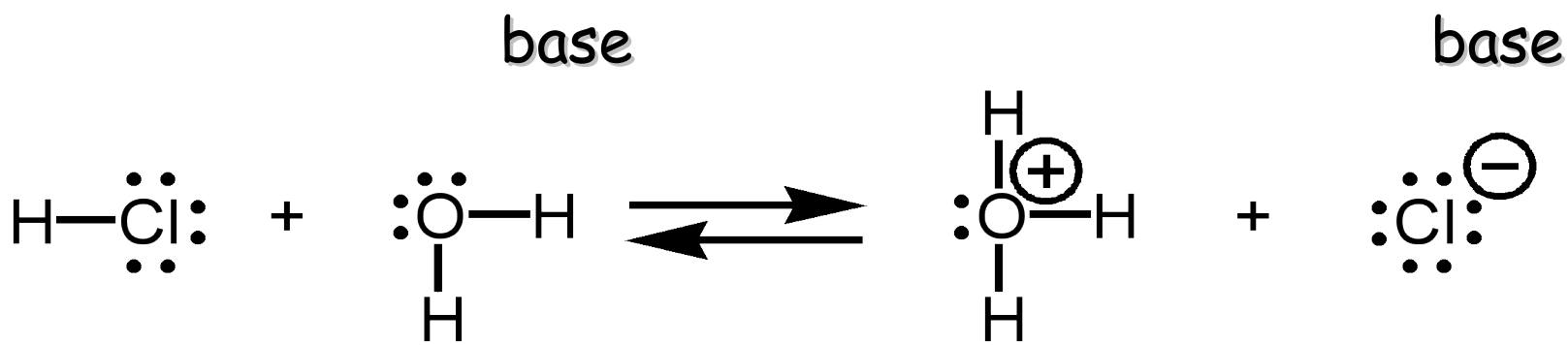
$$-1.74$$

$$K_a = 10^7$$

$$K_a = 10^{1.74}$$



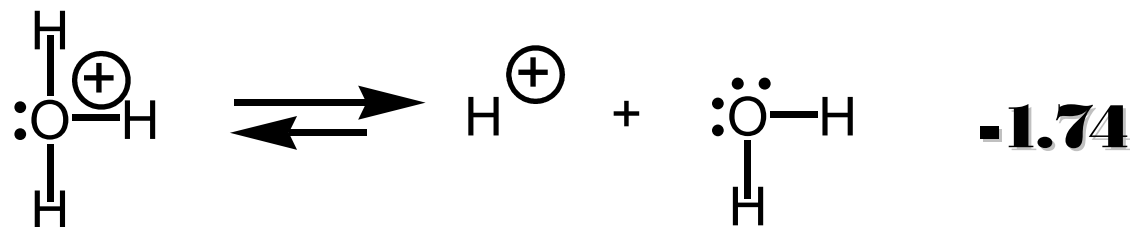
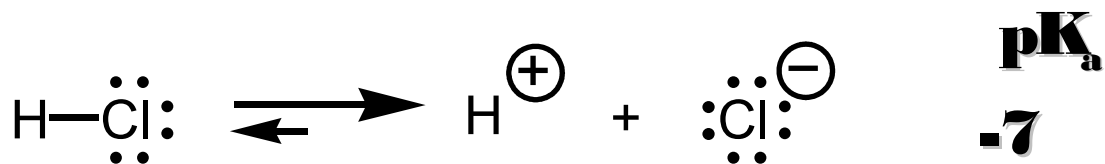
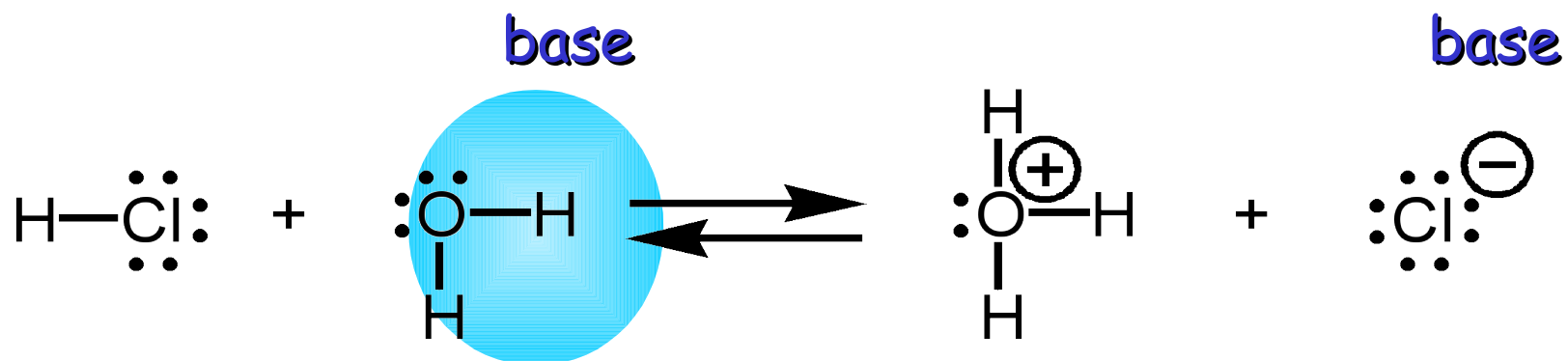
which is the stronger base?

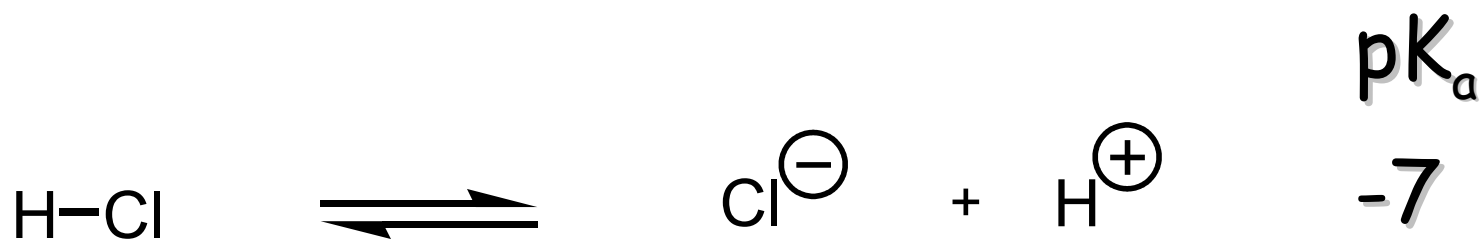



$\text{p}K_{\text{a}} = -7$

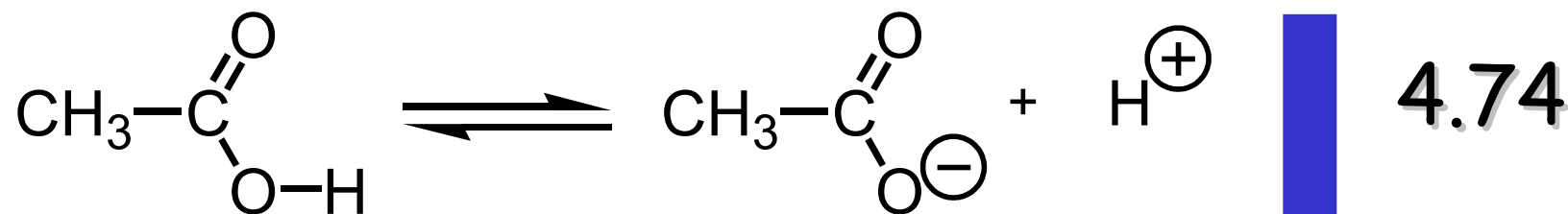
$-1.74$

the stronger **acid** gives the weaker **base**  
 the weaker **acid** gives the stronger **base**

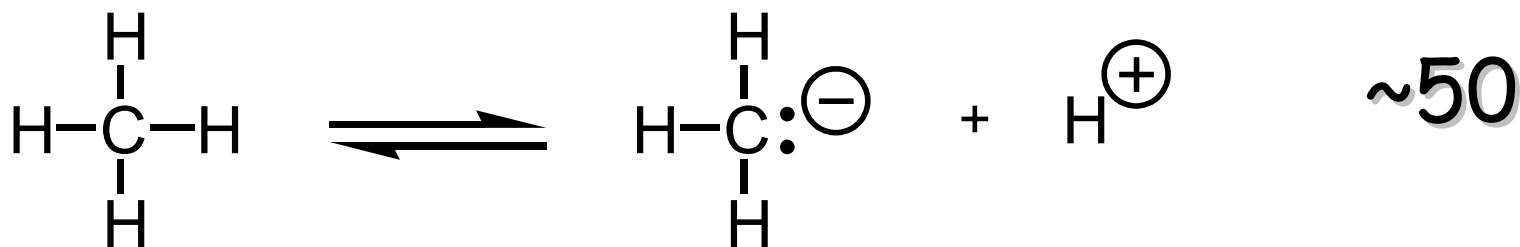




  
**acidity**



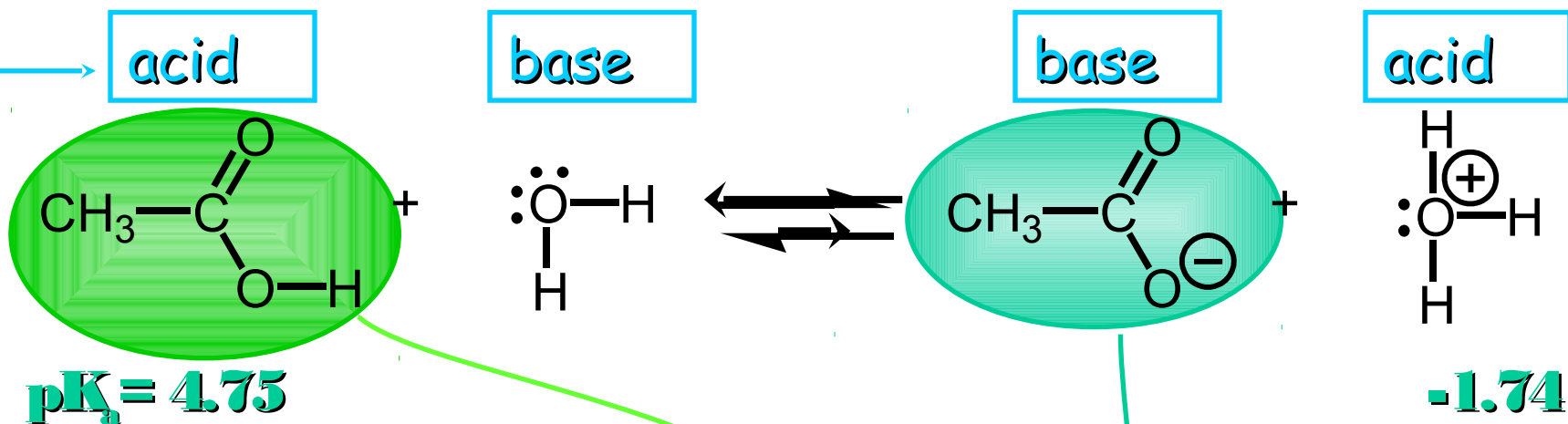
**basicity**



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?

# Acids and Bases. Summary

Acids are electron pair **acceptors**.

Bases are electron pair **donors**.

$$K_a = \frac{[H^+][A^-]}{[H-A]} \quad pK_a = -\log K_a \quad K_a = 10^{-pK_a}$$

An acid base equilibrium will always favor the weak acid and weak base.

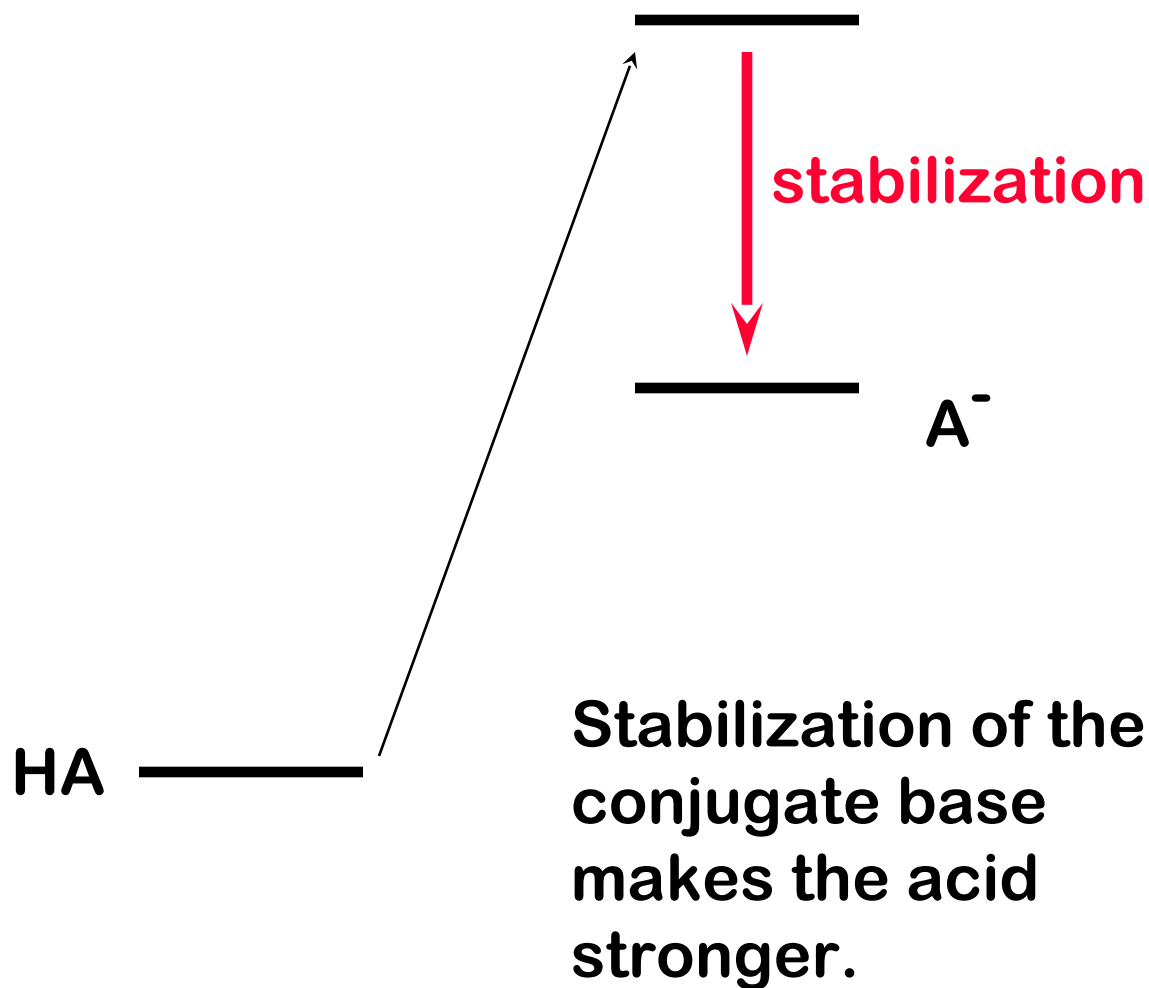
Strong acids give weak bases.

Weak acids give strong bases.

# **FACTORS THAT INCREASE ACIDITY**

**STABILIZATION OF A CONJUGATE BASE**

We will study the factors that lead to lower energy (stabilization) in the conjugate base.



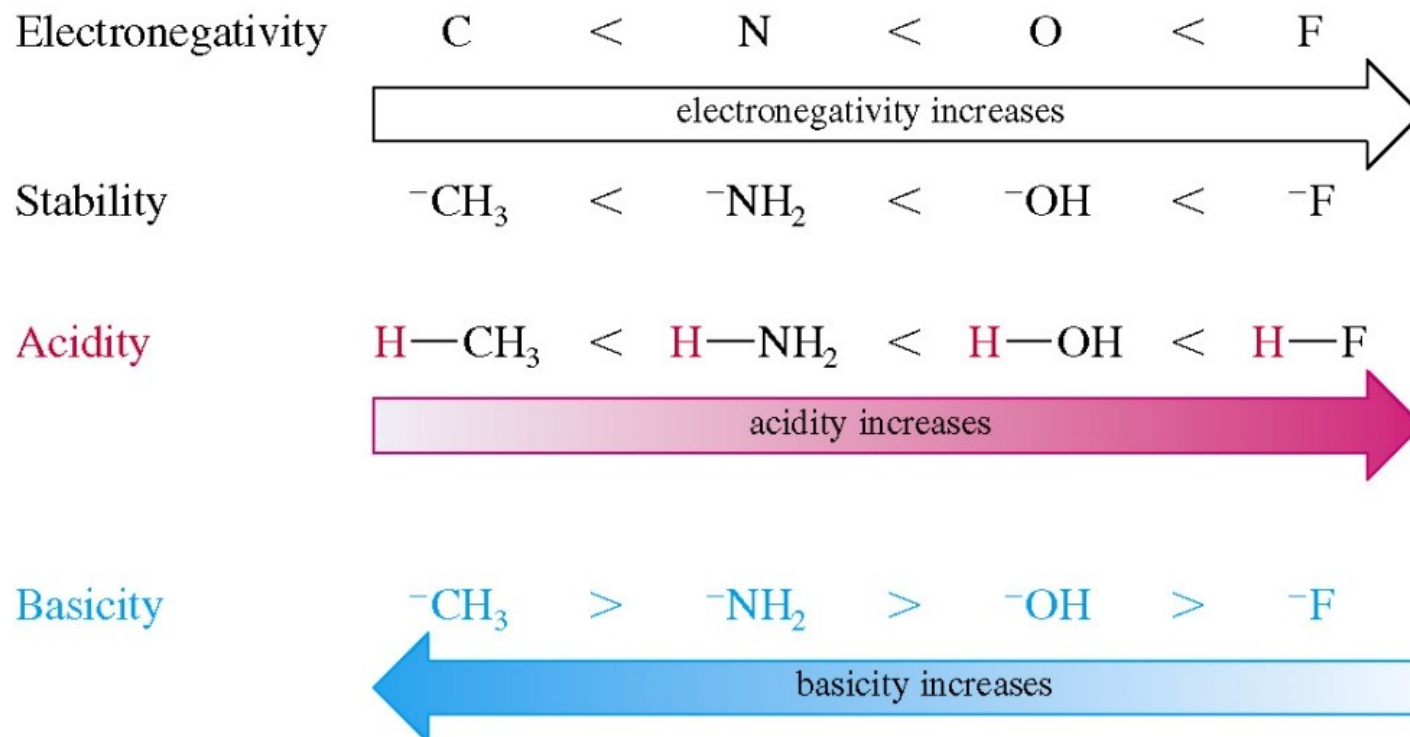
## STABILIZATION FACTORS

- 1 Resonance
- 2 Electronegativity
- 3 Size of Atoms
- 4 Hybridization
- 5 Inductive Effects
- 6 Charge
- 7 Solvation
- 8 Steric Effects\*

\* usually destabilize

# Electronegativity

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



=>



# 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

$\text{CH}_4$  >45

$\text{NH}_3$  34

$\text{H}_2\text{O}$  16

$\text{HF}$  3.5

$\text{RCH}_3$  45

$\text{RNH}_2$  35

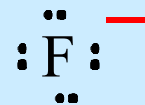
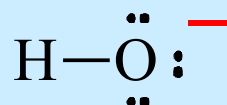
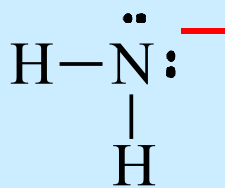
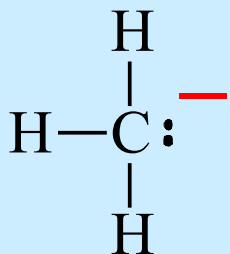
$\text{ROH}$  18

$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$  20

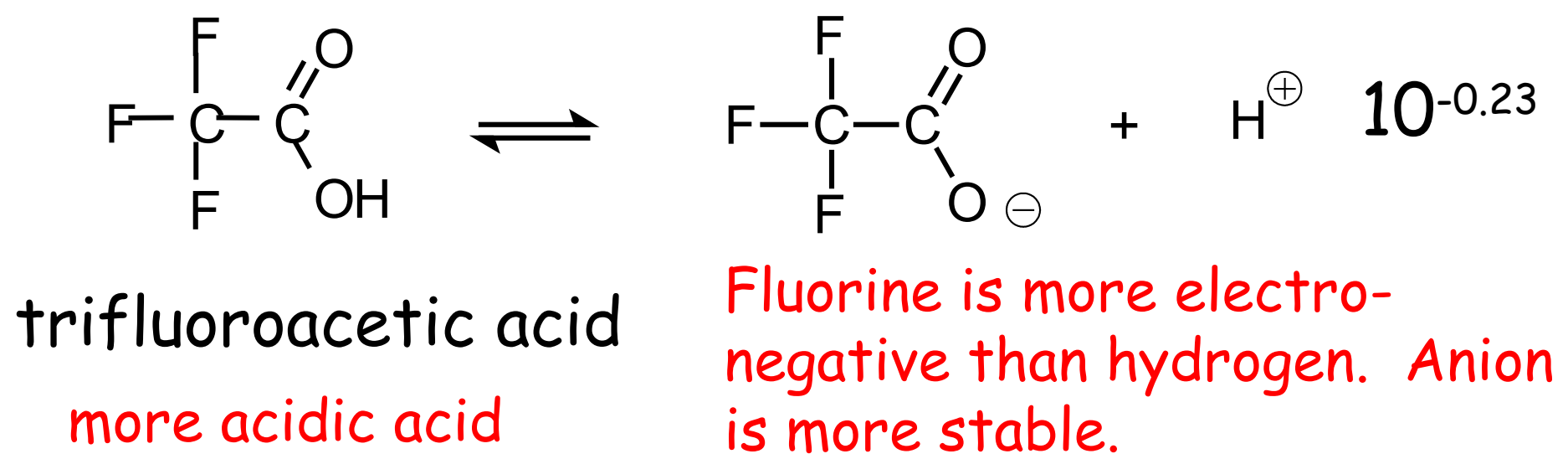
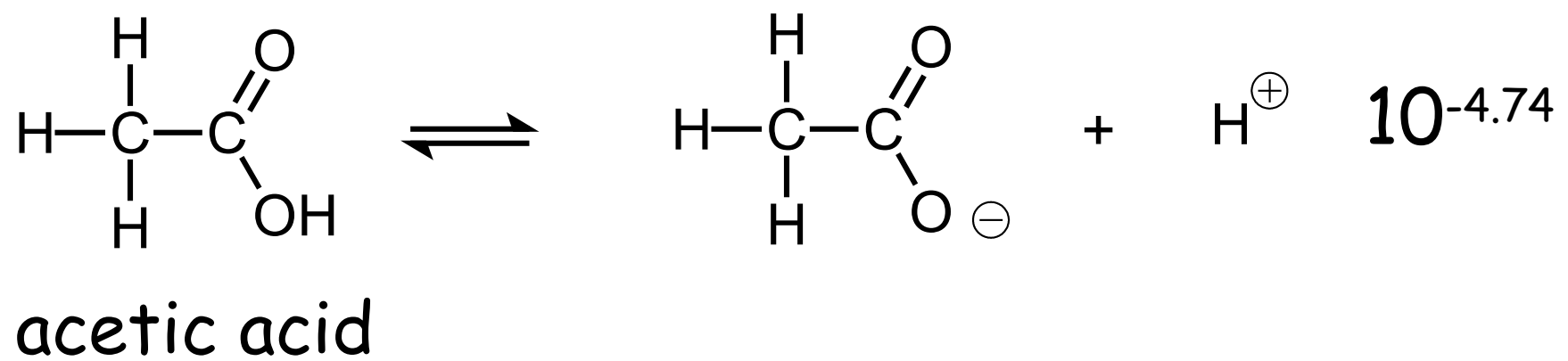
$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2$  15

$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$  5

conjugate  
bases :

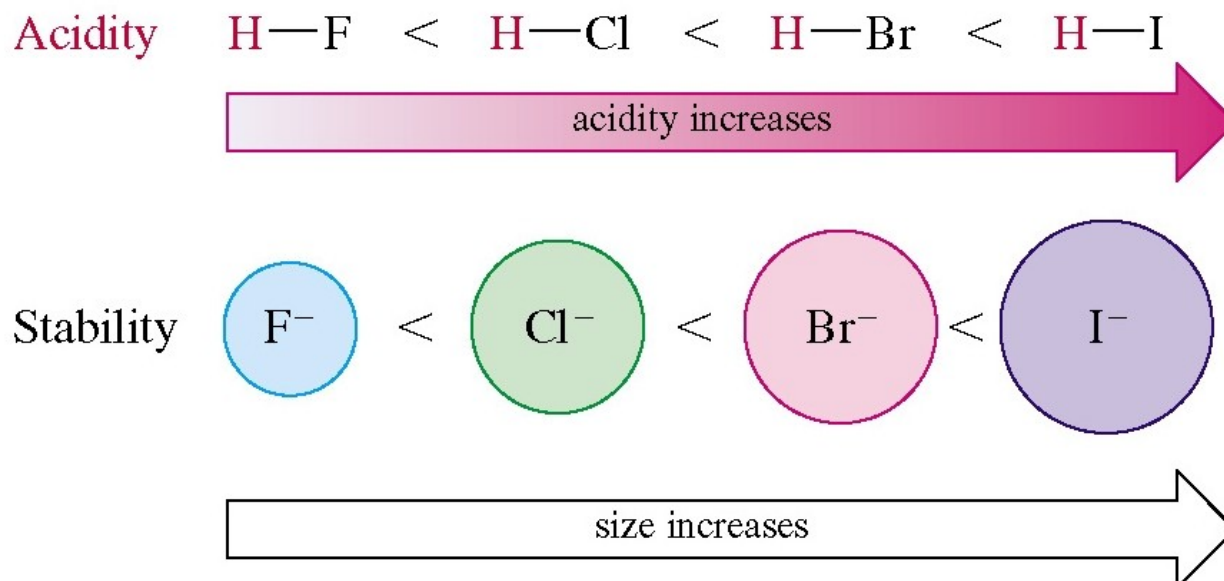


Predict whether trifluoroacetic acid will be a stronger or weaker acid than acetic acid.



# 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 same group ... 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

HCl -7

HBr -9

HI -10

HOH 16

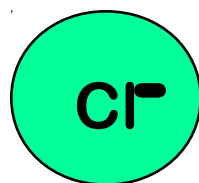
HSH 7

HSeH 4

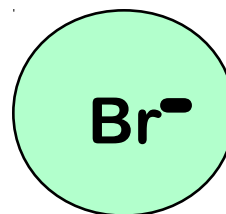
HTeH 3



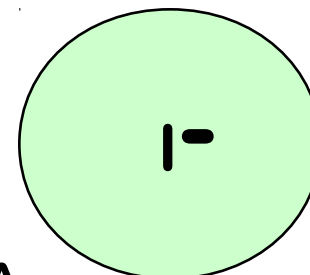
1.36 A



1.81 A



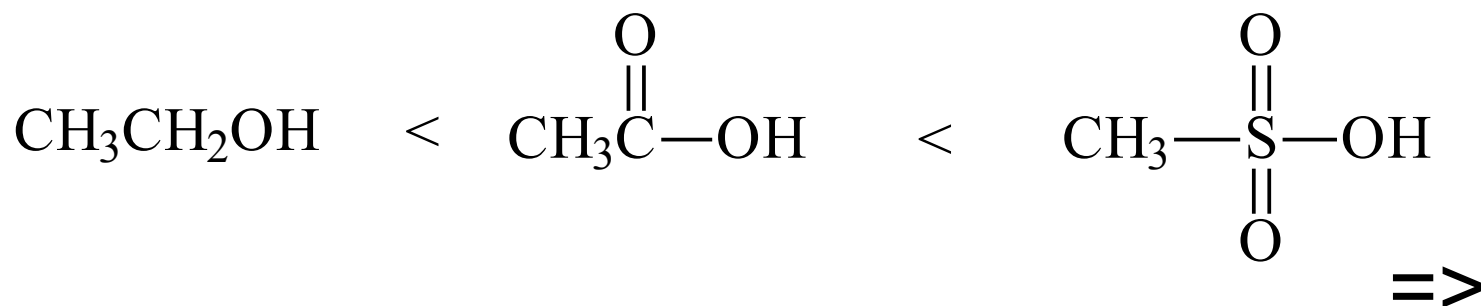
1.95 A



2.16 A

# Resonance

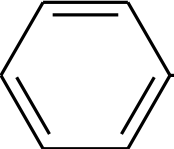
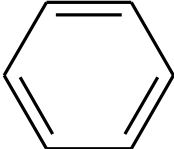
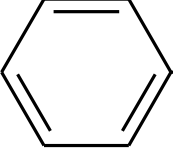
- Delocalization of the negative charge on the conjugate base will stabilize the anion, so the substance is a stronger acid.
- More resonance structures usually mean greater stabilization.



# RESONANCE EFFECTS

increasing quality  
of resonance

pKa Values

$R-OH$	18	$R-CH_3$	45	$R-NH_2$	28
	10		30		25
$R-\overset{O}{\parallel}C-OH$	5	$CH_3O-\overset{O}{\parallel}C-CH_3$	25	$R-\overset{O}{\parallel}C-NH_2$	15
		$R-\overset{O}{\parallel}C-CH_3$	20		
		$R-\overset{O}{\parallel}C-CH_2-\overset{O}{\parallel}C-R$	9		

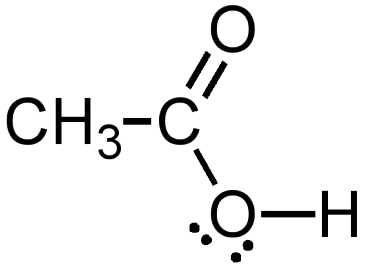
Which molecule is the stronger acid, ethanol or acetic acid?

$K_a$



$10^{-16}$

ethanol



acetic acid

the stronger acid



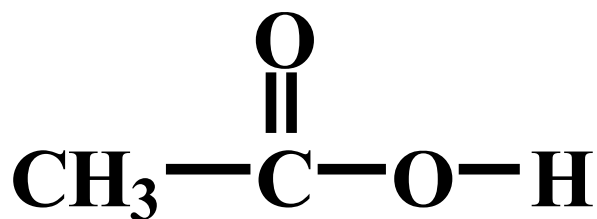
$10^{-4.74}$

more stable anion because of resonance and inductive effects

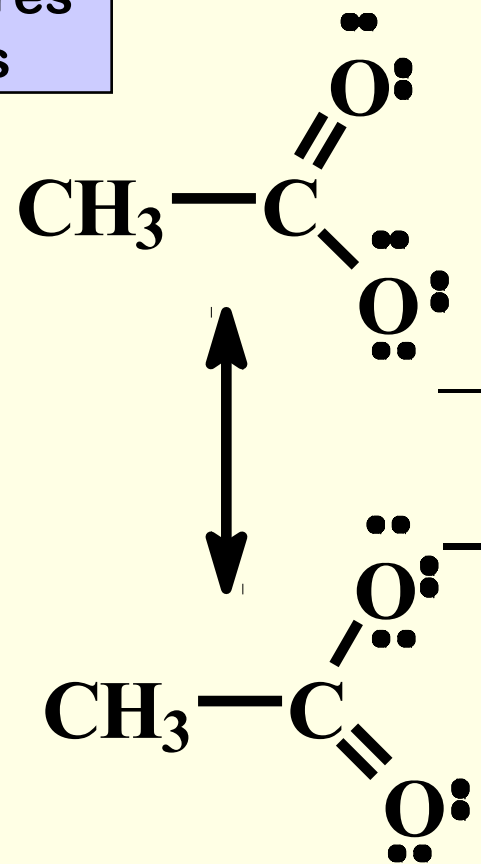
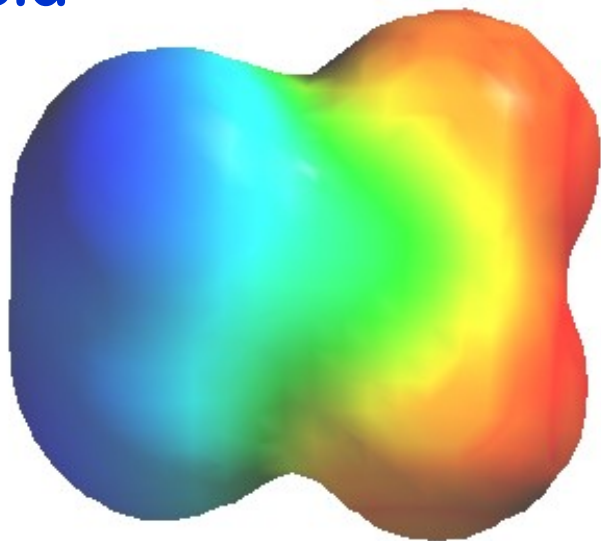
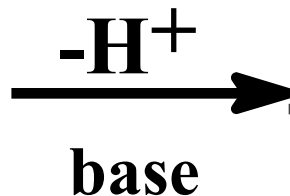


# RESONANCE IN THE ACETATE ION

equivalent structures  
charge on oxygens

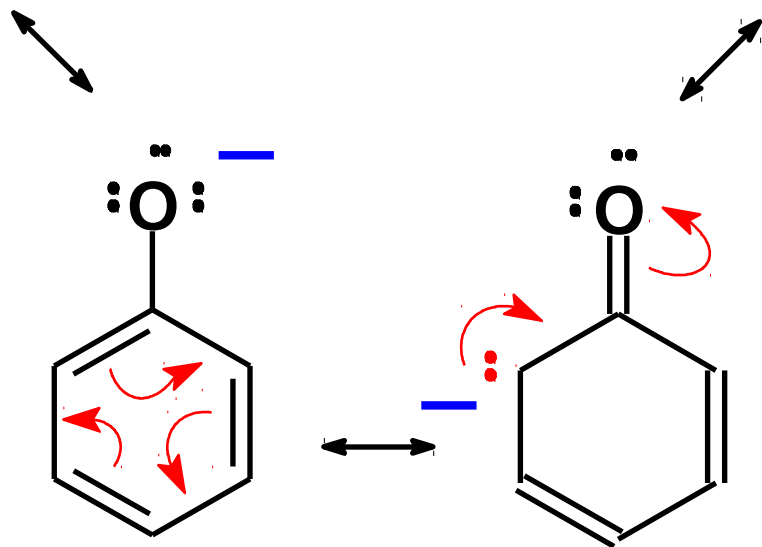
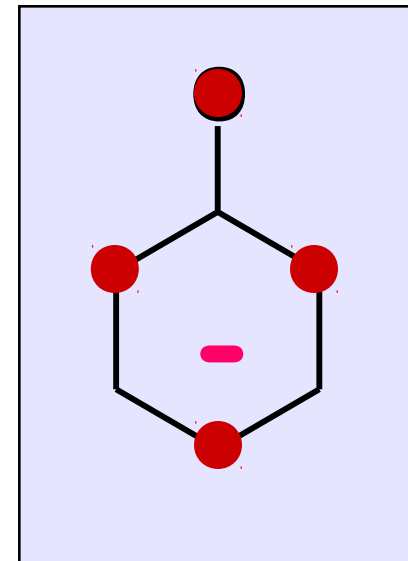
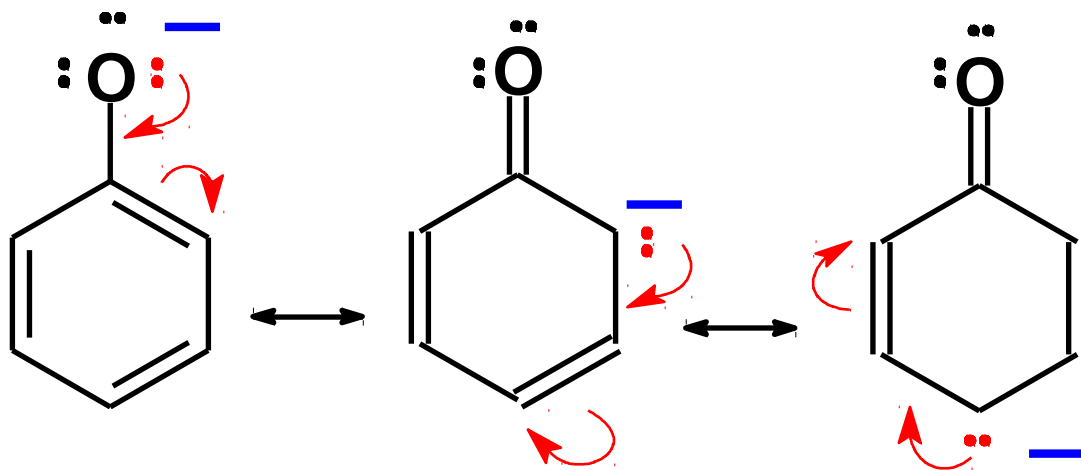


acetic acid

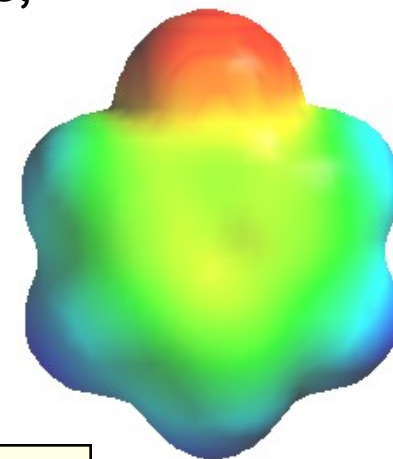


acetate ion

# 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  $\longrightarrow$   
Electronegativity  $\longrightarrow$

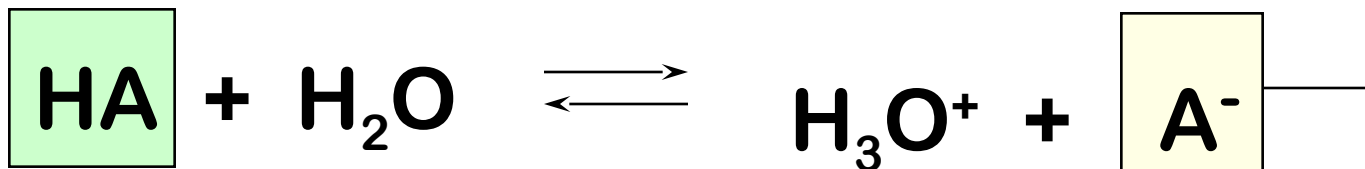
<b>CH<sub>4</sub></b> 50	<b>NH<sub>3</sub></b> 36	<b>H<sub>2</sub>O</b> 16	<b>HF</b> 3.2
<b>SiH<sub>4</sub></b> 35	<b>PH<sub>3</sub></b> 27	<b>H<sub>2</sub>S</b> 7	<b>HCl</b> -7
<b>GeH<sub>4</sub></b> 25	<b>AsH<sub>3</sub></b> 23	<b>H<sub>2</sub>Se</b> 3.7	<b>HBr</b> -8
		<b>H<sub>2</sub>Te</b> 3.0	<b>HI</b> -9

**GROUP**  
Size      Acidity



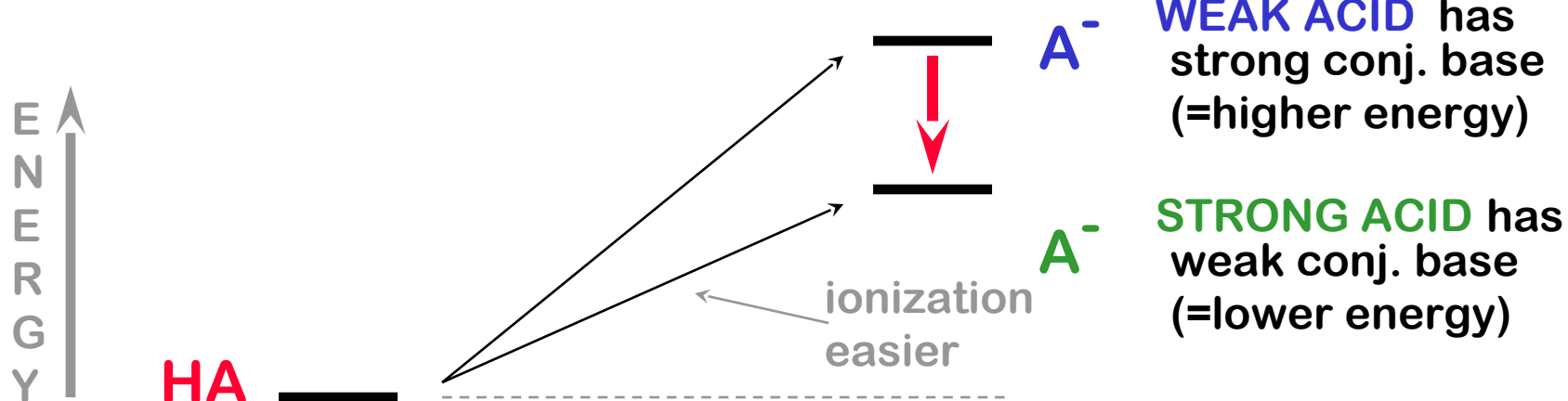
# **EVALUATION OF ACID STRENGTH**

# EVALUATION OF ACID STRENGTH

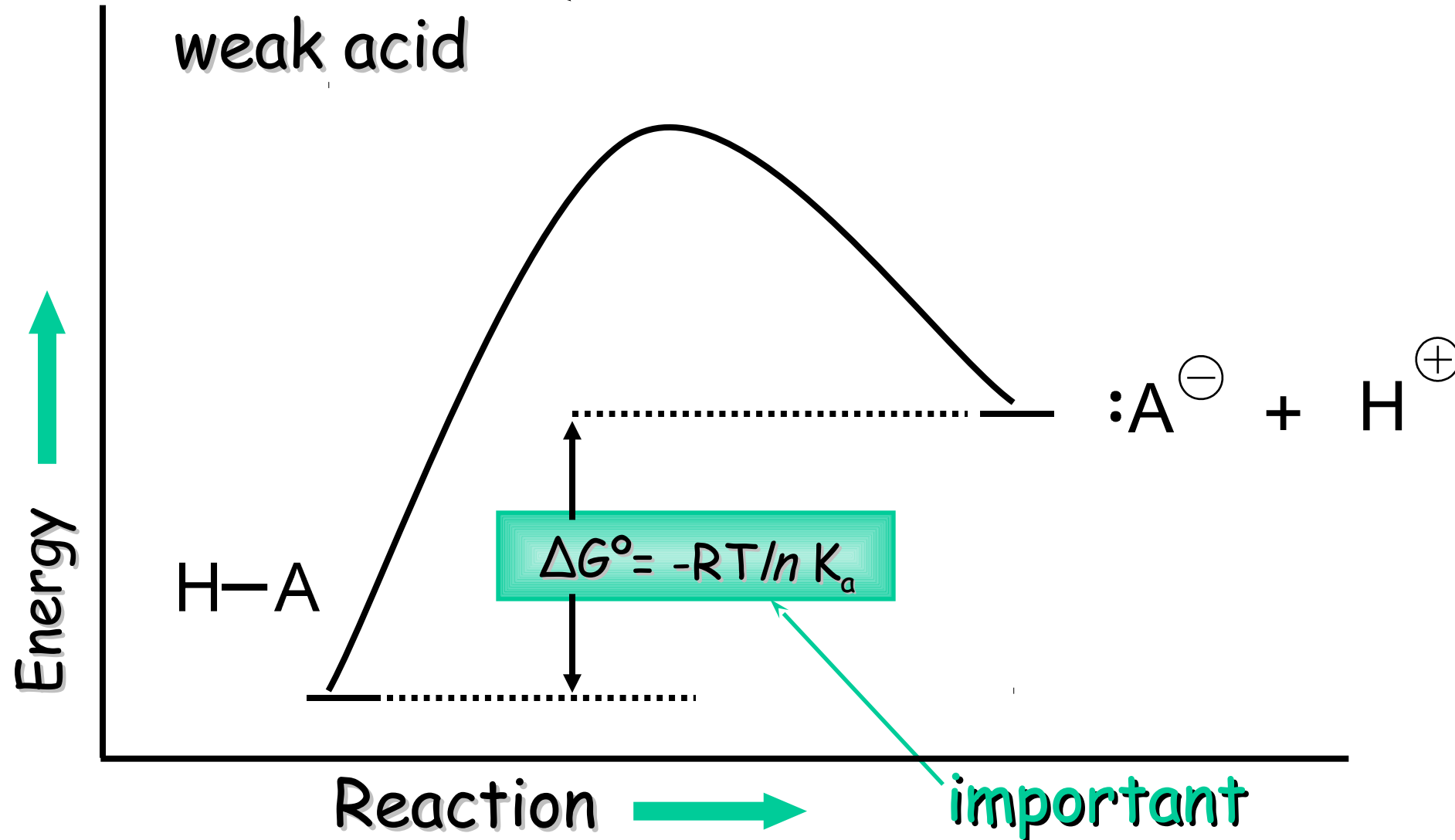
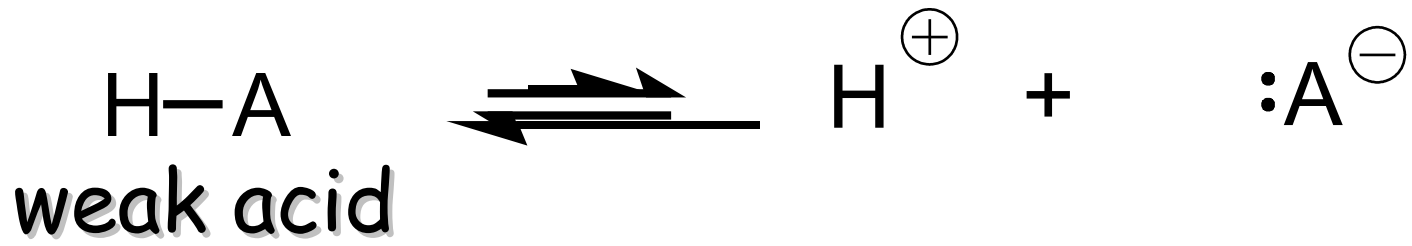


In water, all acids form hydronium ion, the important factor of difference is the conjugate base.

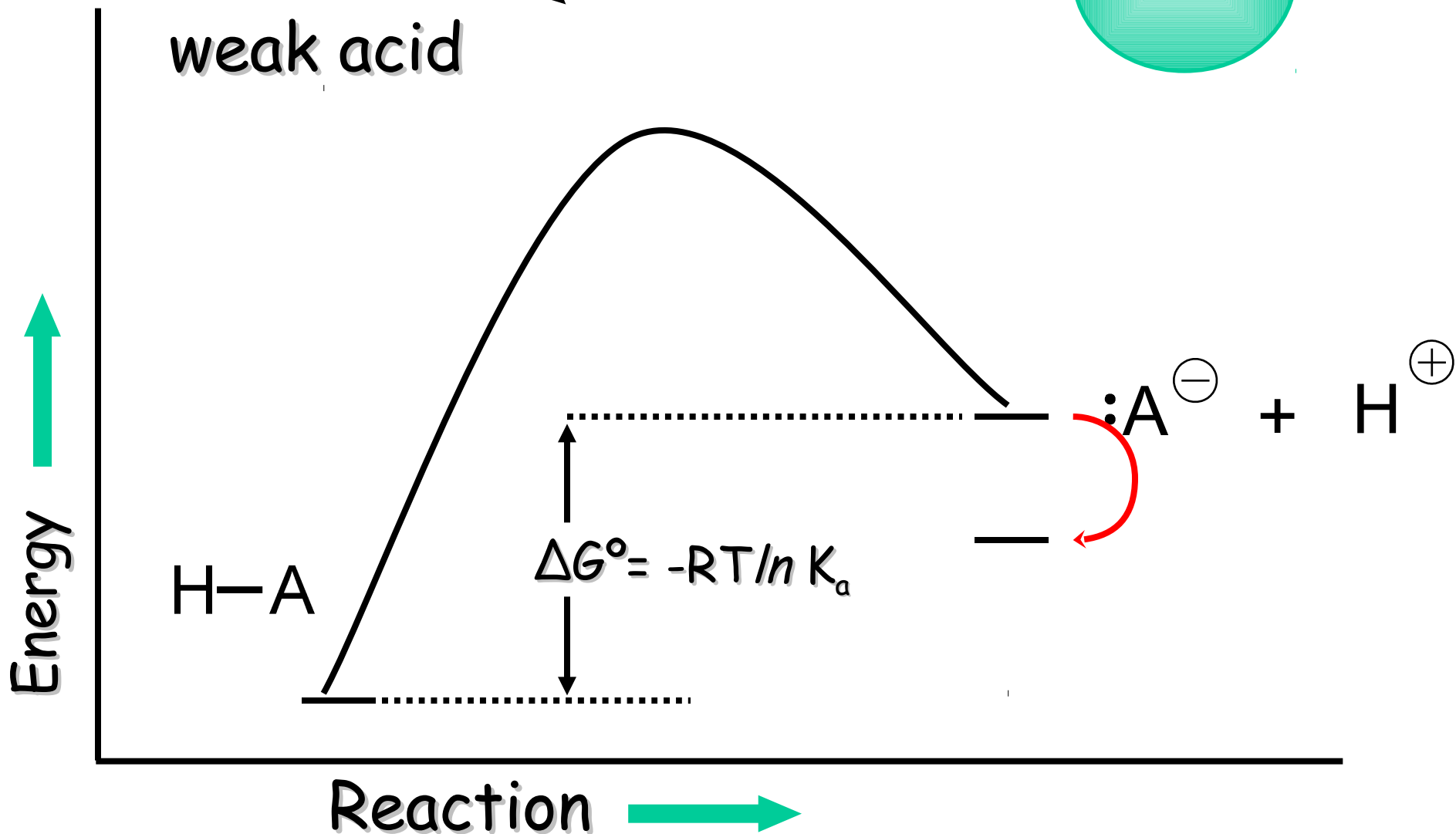
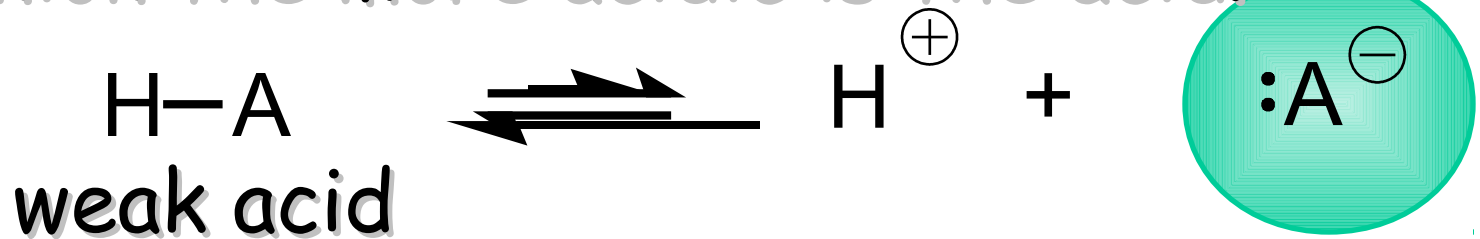
The difference between a strong acid and a weak acid is in the stability of the conjugate base.



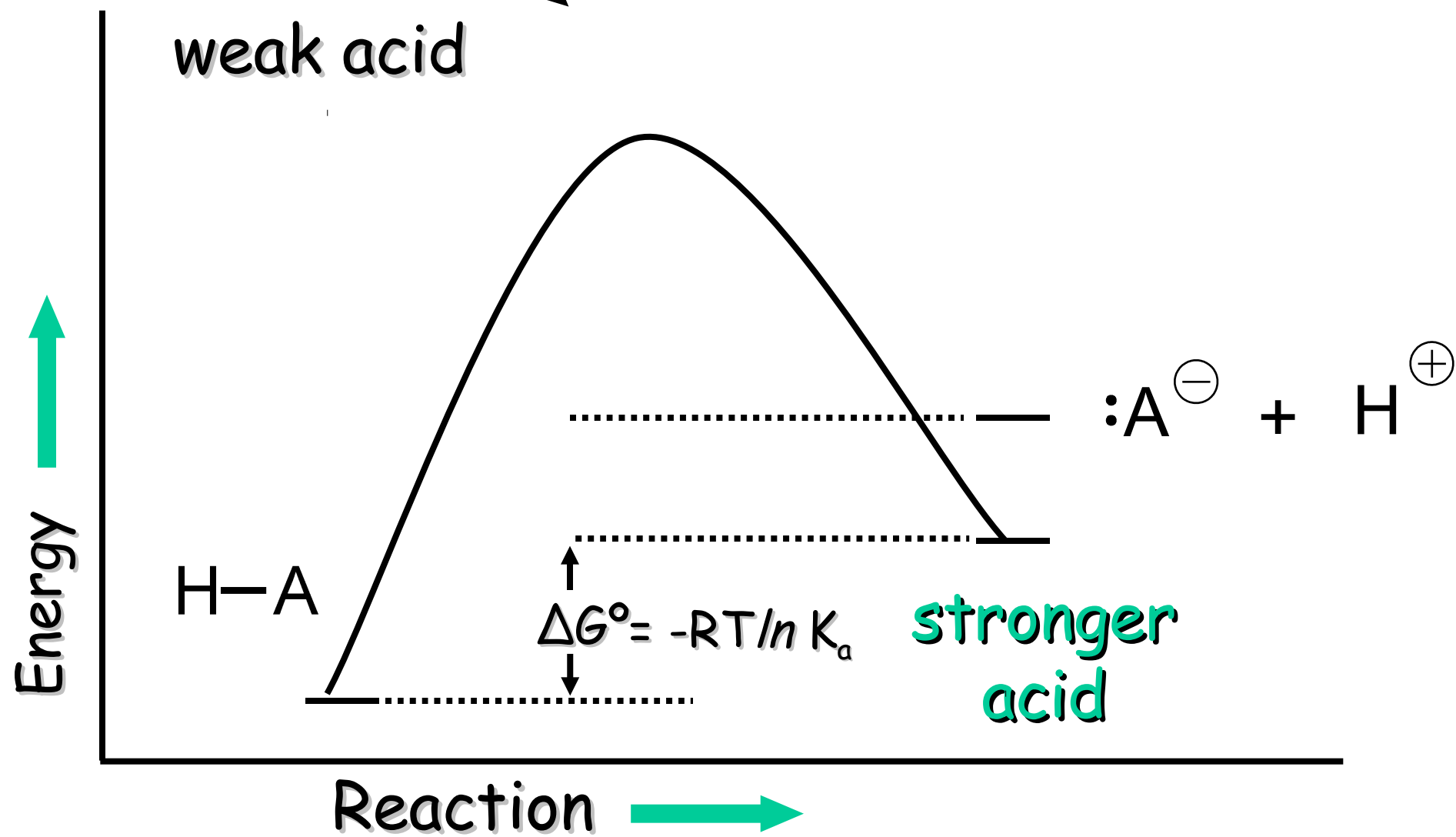
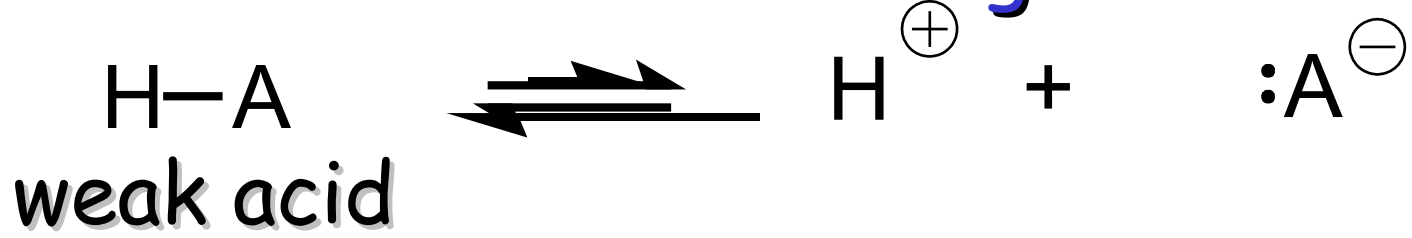
# A model for the ionization of an acid.



It is a general principle that the more stable the anion the more acidic is the acid.

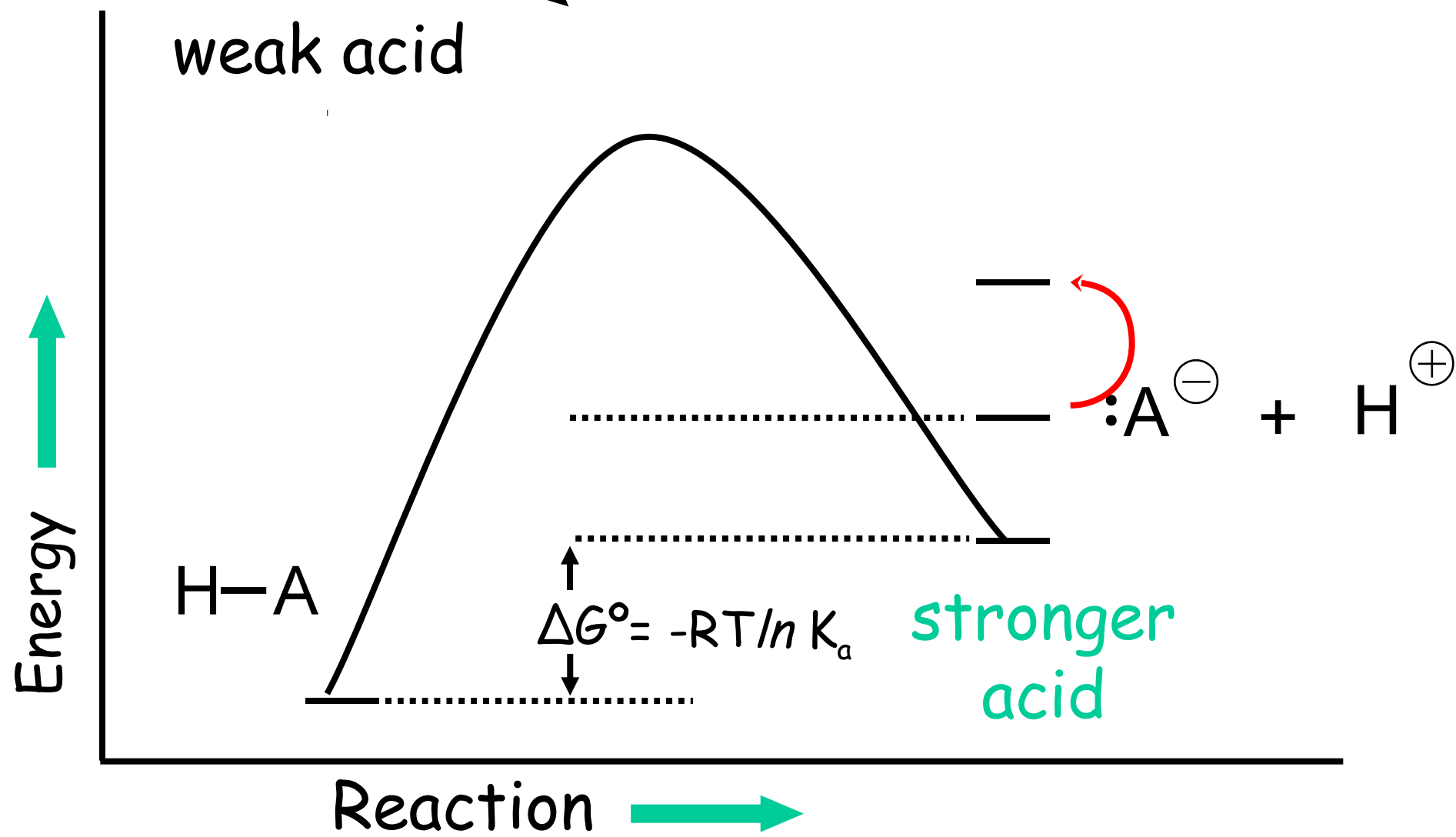
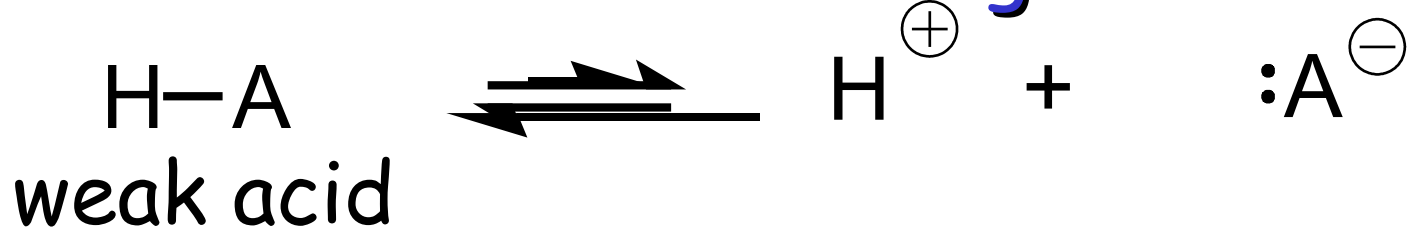


Consider another acid where the anion is more stable. Will this acid be stronger or weaker?

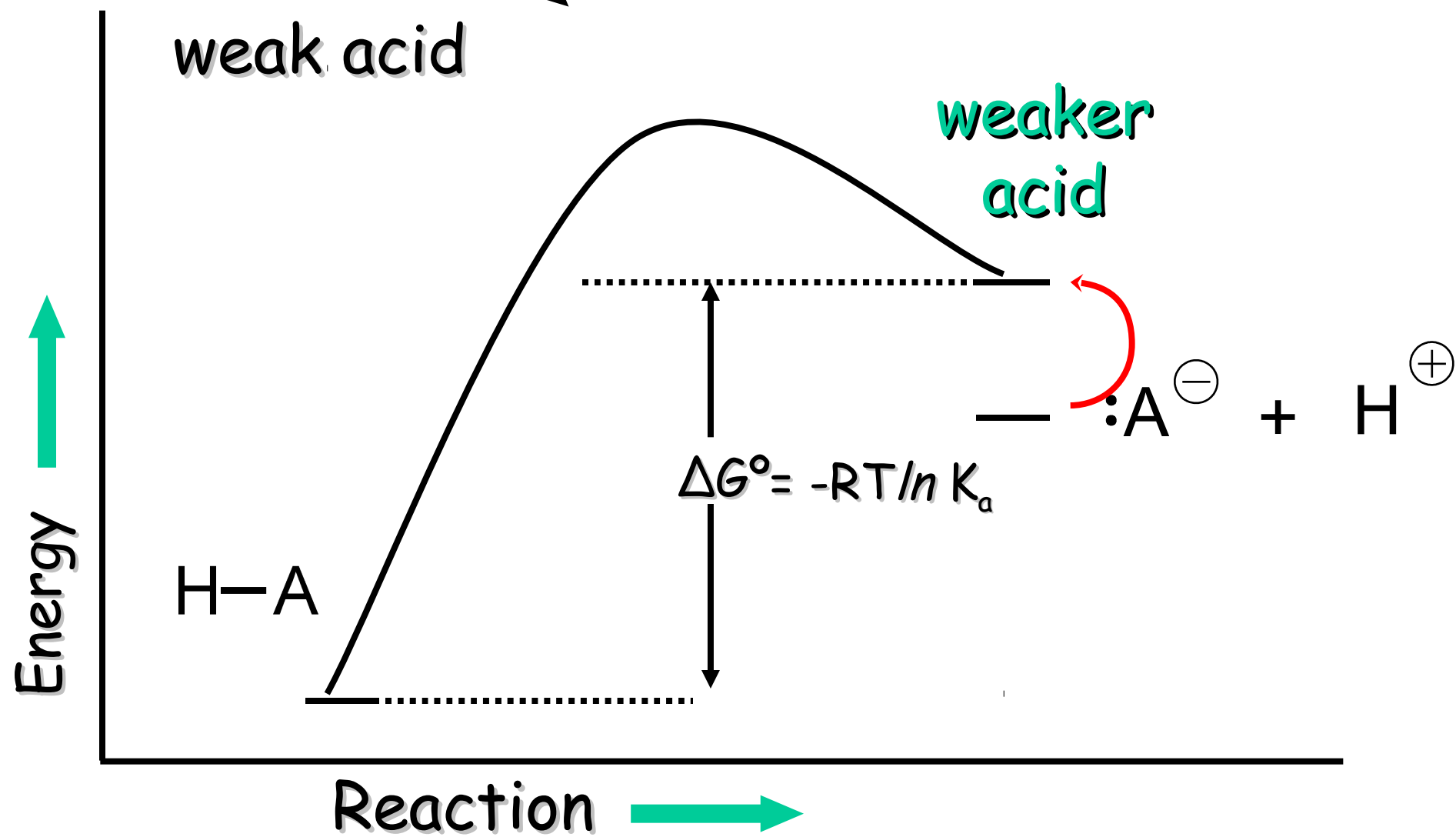
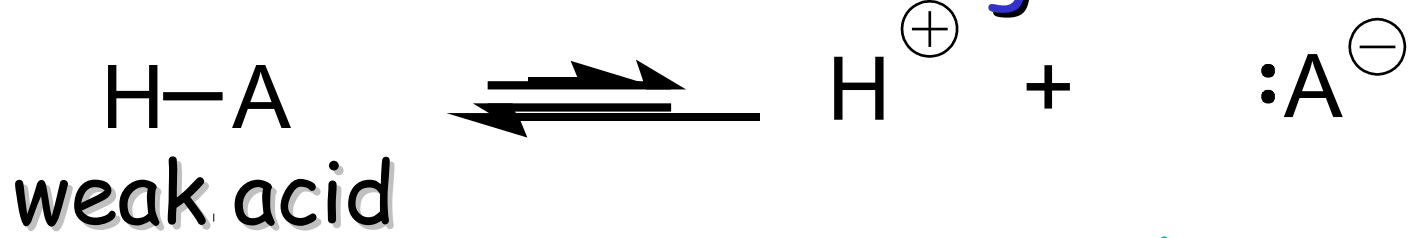




Consider another acid where the anion is less stable. Will this acid be stronger or weaker?



Consider another acid where the anion is less stable. Will this acid be stronger or weaker?



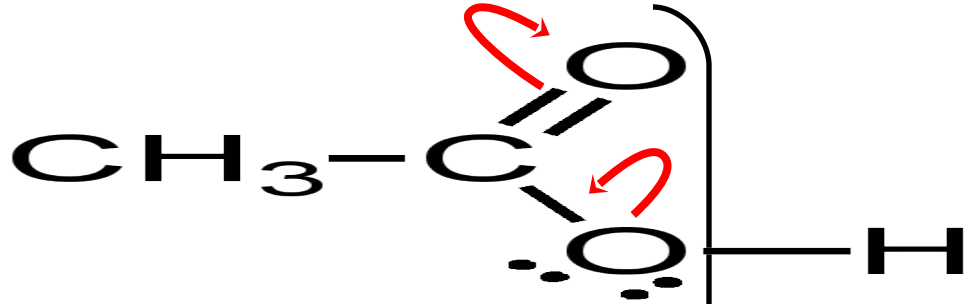
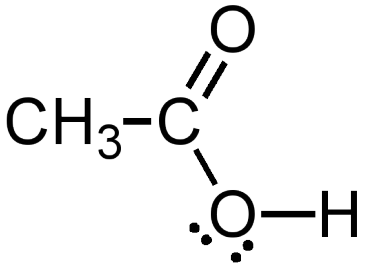
Which molecule is the stronger acid, ethanol or acetic acid?

$K_a$



$10^{-16}$

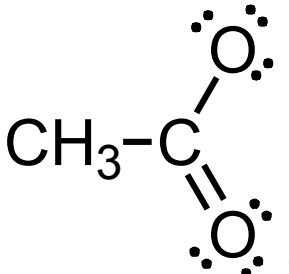
ethanol



$10^{-4.74}$

acetic acid

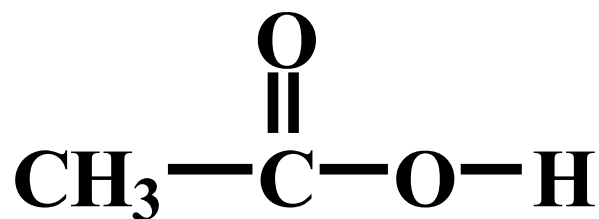
the stronger acid



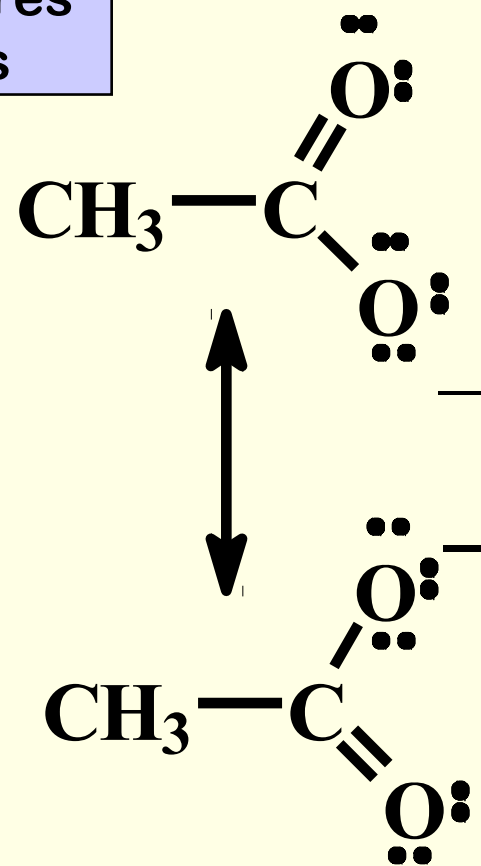
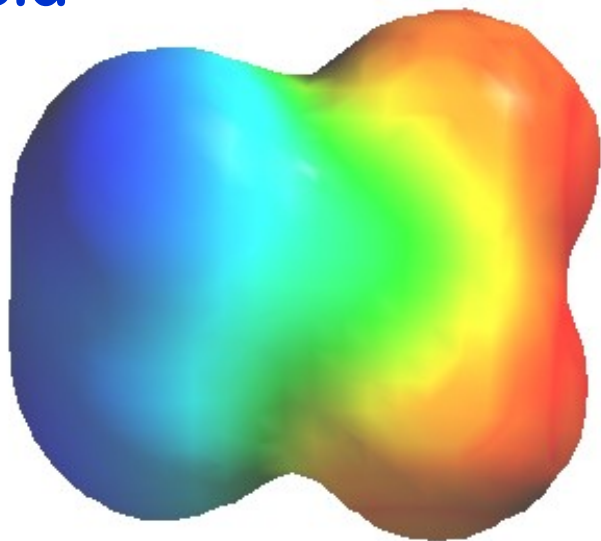
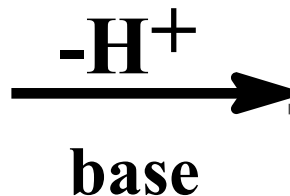
more stable anion because of resonance and inductive effects

# RESONANCE IN THE ACETATE ION

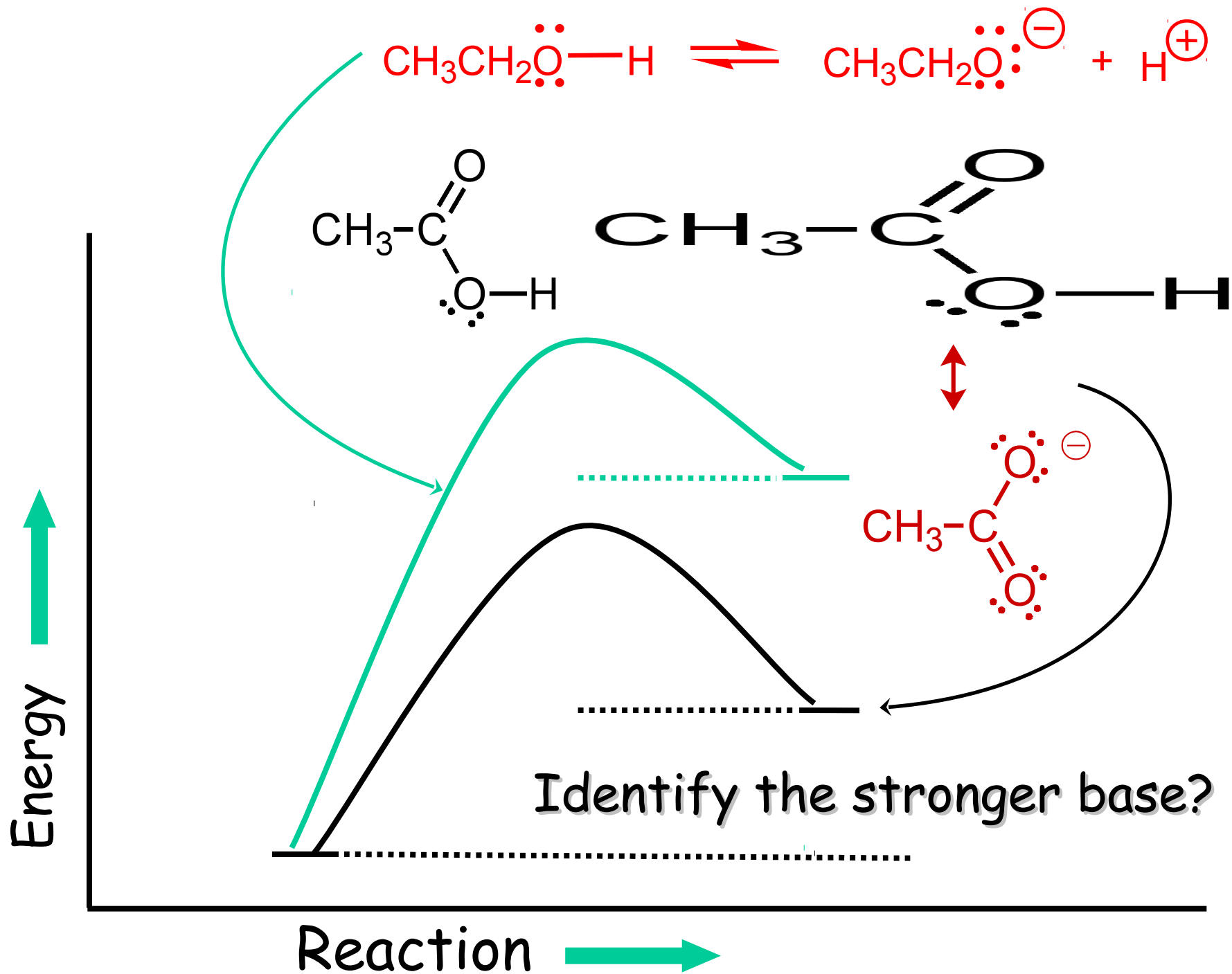
equivalent structures  
charge on oxygens



acetic acid

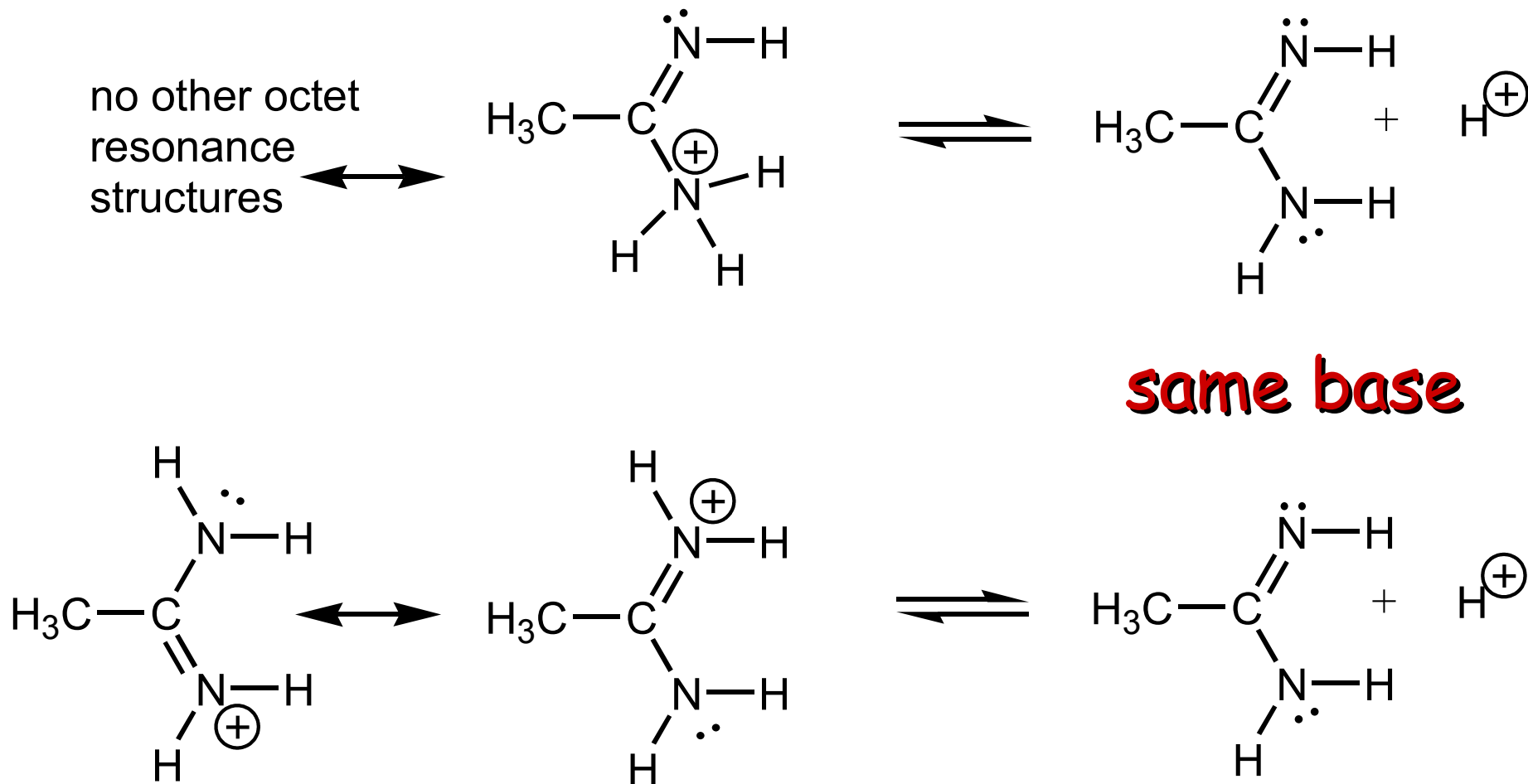


acetate ion

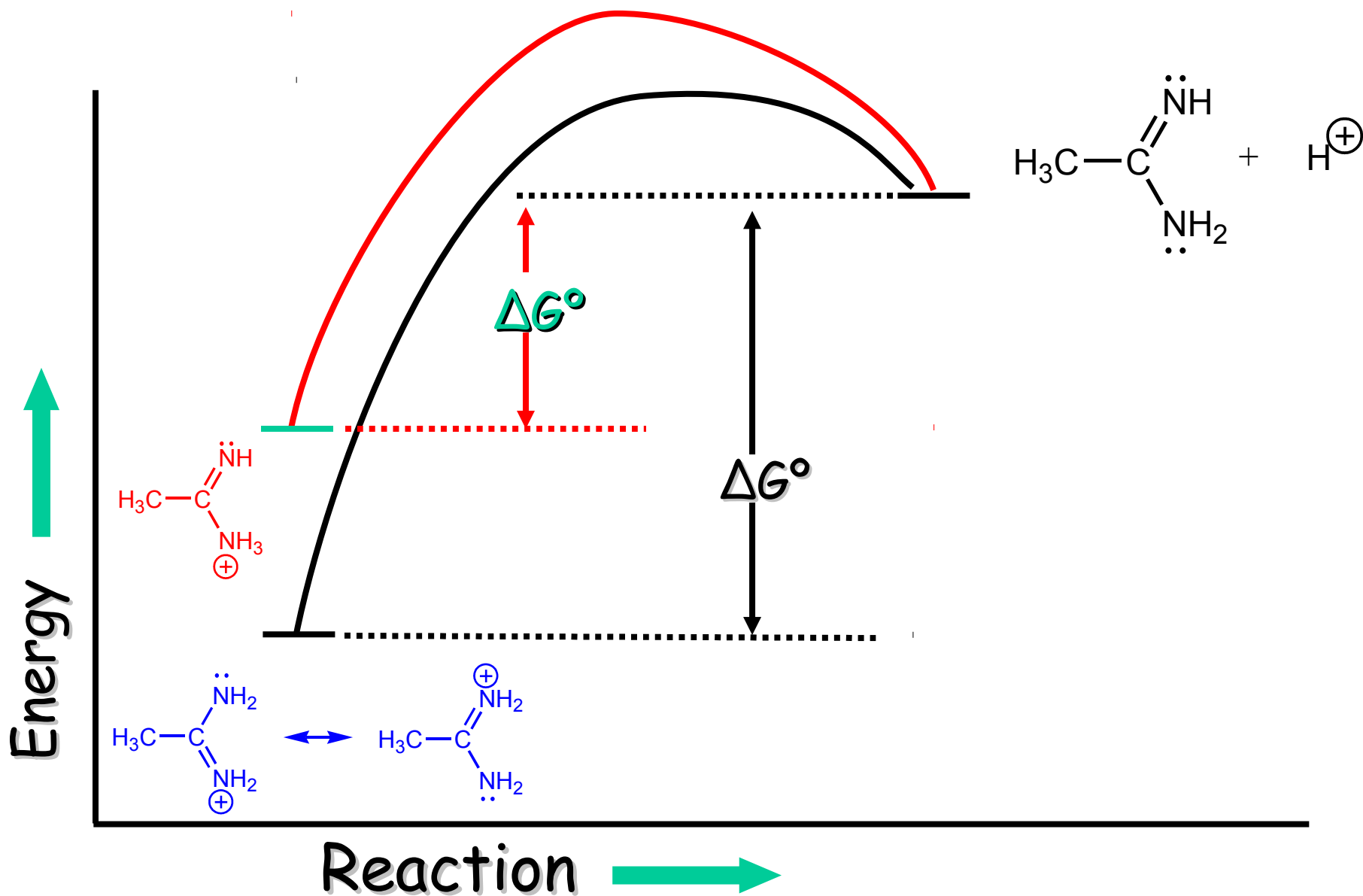


Circle the stronger acid with an explanation for your choice.

no other octet resonance structures



Circle the stronger acid with an explanation for your choice.

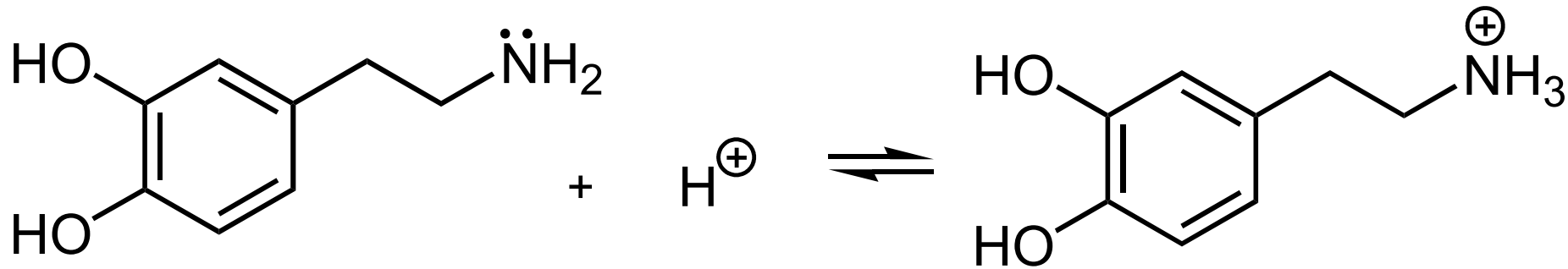


# Buffers and pH changes



In chemistry, particularly biology, a large number of compounds are acids and bases.

dopamine



Biological fluids are often buffered (constant  $pH$ ) and it is useful to know the predominant species present at a given  $pH$ .



$$K_a = \frac{[\text{H}^{\oplus}] [\text{:A}^{\ominus}]}{[\text{H-A}]} \quad \text{p}K_a = \text{pH} + \log \frac{[\text{H-A}]}{[\text{A}^{\ominus}]}$$

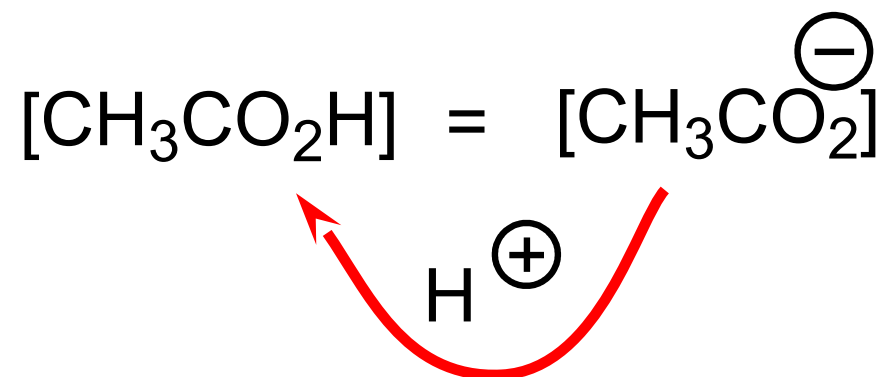
a useful concept:

$$\text{when } [\text{H-A}] = [\text{A}^{\ominus}]$$

Biological fluids are often buffered (constant *pH*) and it is useful to know the predominant species present at a given *pH*.

Consider acetic acid with a  $K_a = 10^{-4.74}$

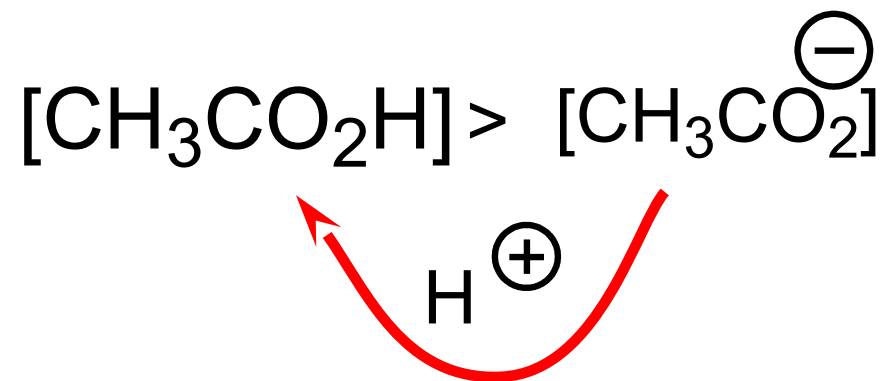
at  $pH = 4.74$



at lower  $pH$ , more acidic  
than 4.74, acetic acid is the  
major species present

Consider acetic acid with a  $K_a = 10^{-4.74}$

at  $pH = 4.74$

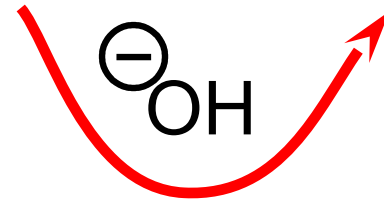
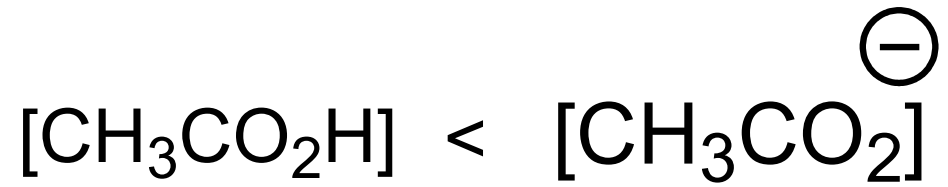


at lower  $pH$ , more acidic than 4.74, acetic acid is the major species present



Consider acetic acid with a  $K_a = 10^{-4.74}$

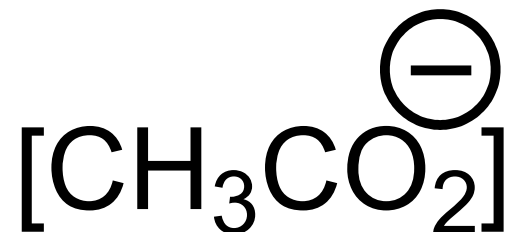
at  $pH = 4.74$



at lower  $pH$ , more acidic than 4.74, acetic acid is the major species present



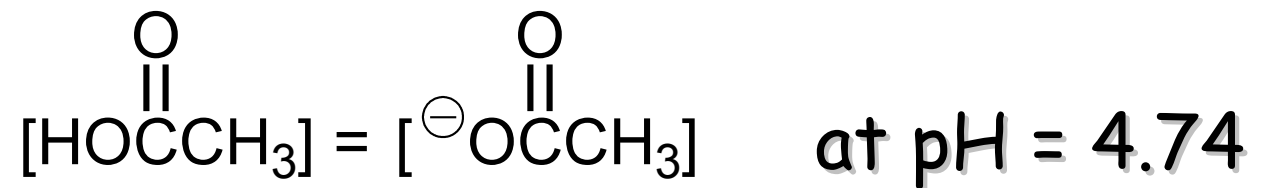
at higher  $pH$ , less acidic than 4.74, acetate ion is the major species present



If acetic acid is introduced into the blood what will be the predominant species present? Will it be acetate ion or acetic acid?

The pH of blood is maintained at  $pH \sim 7.4$

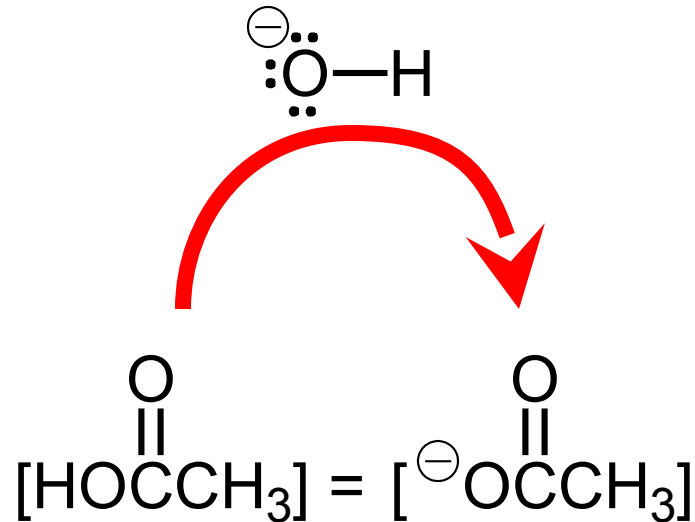
If the pH of blood was 4.74 then the acetate ion would be equal to the acetic acid ion concentration.



If the pH is raised to 7.4 will the concentration of acetate ion increase or decrease?

If acetic acid is introduced into the blood what will be the predominant species present? Will it be acetate ion or acetic acid?

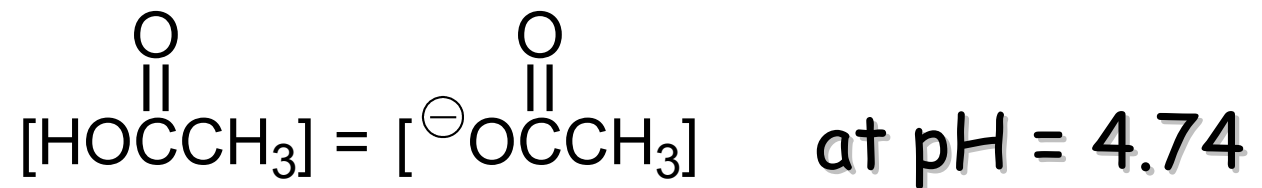
pH 4.74  $\Rightarrow$  7.4



If the pH is raised to 7.4 (more basic) will the concentration of acetate ion increase or decrease?

If acetic acid is introduced into the blood what will be the predominant species present? Will it be acetate ion or acetic acid?

Acetate ion is the major species present if acetic acid is introduced into blood.



If the pH is raised to 7.4 will the concentration of acetate ion increase or decrease?



a useful concept:

when

then

