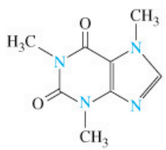
Curso Propedéutico de Química Orgánica

Maestría en Ciencias: Productos Naturales y Alimentos



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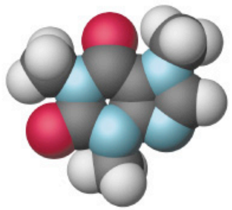

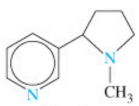

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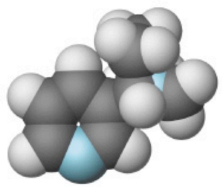

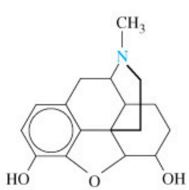

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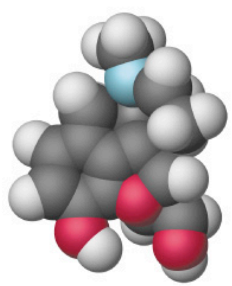


(a) (b)

1ª Parte

Ácidos y Bases

- Ácidos y bases orgánicas; pK_a y pH
- El efecto de la estructura en el pK_a
- El efecto del pH en la estructura de un compuesto orgánico
- Ácidos y bases de Lewis

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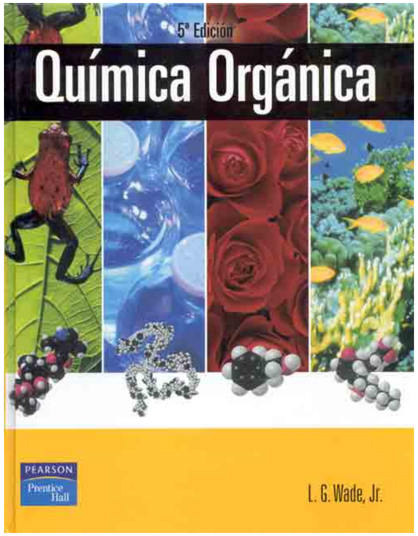

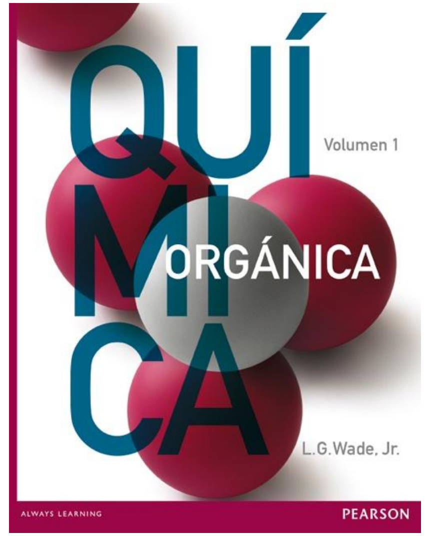

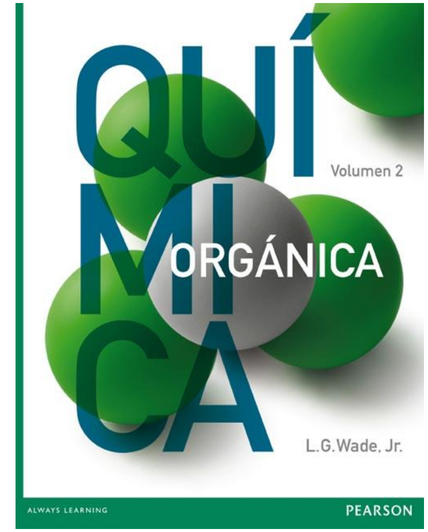

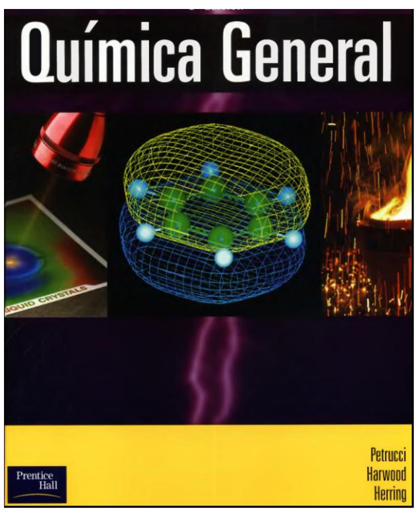

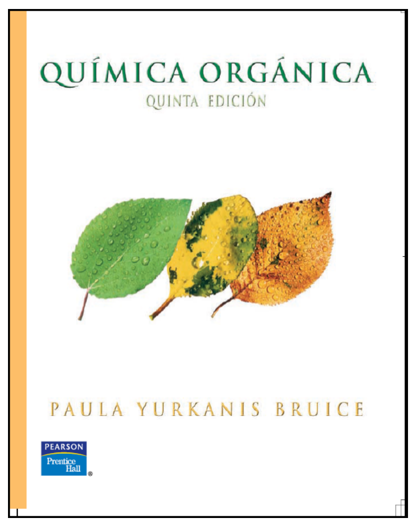

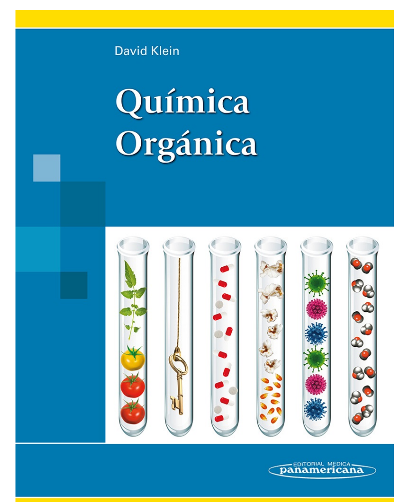

Química Orgánica
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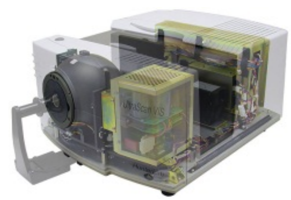
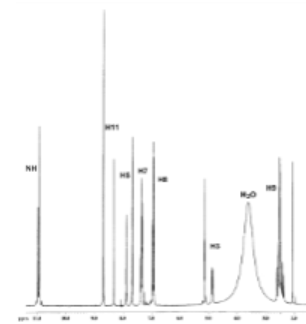
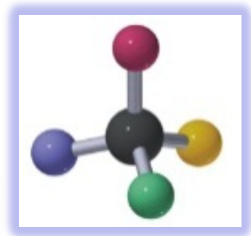
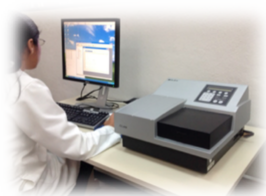
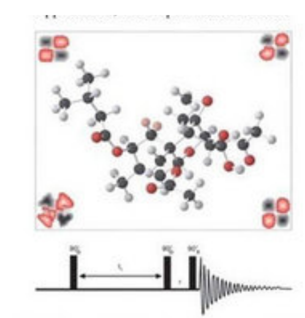


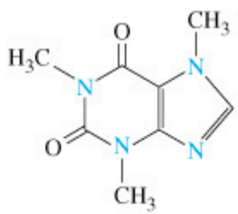




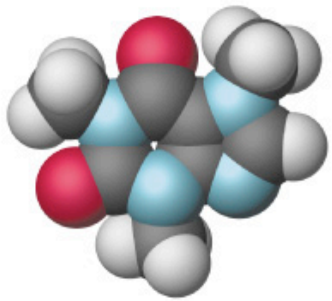


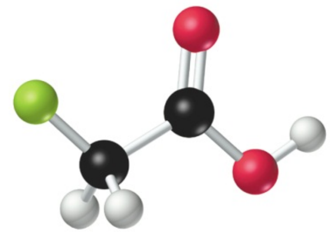


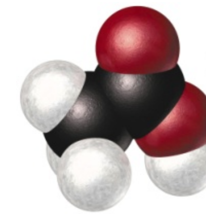
Ácidos y bases orgánicas; pK_a y pH



Caffeine

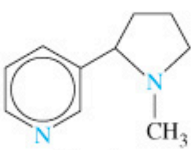




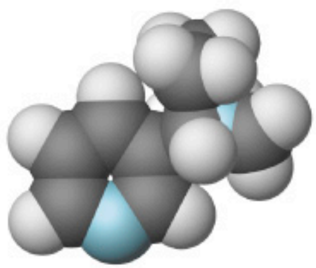


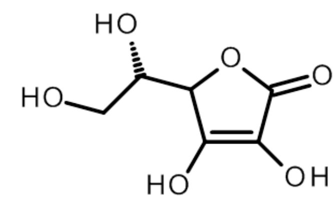
$HC_2H_3O_2$

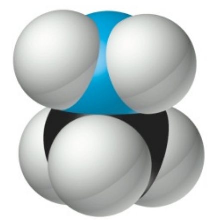
Acetic acid

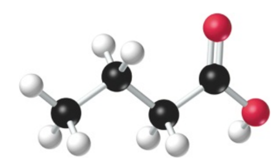


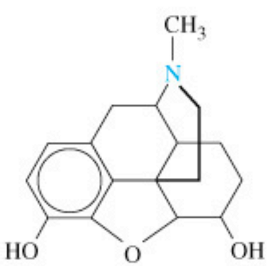
Nicotine



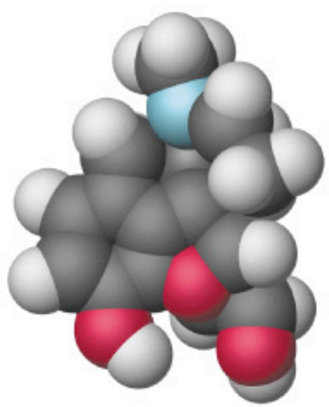


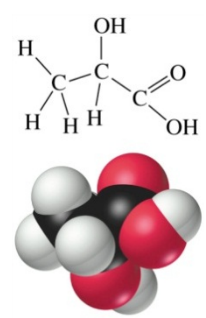




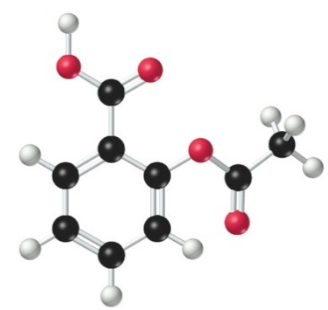


Morphine





Lactic acid



$$\underset{\substack{\text{stronger acid}\\ pK_a = 4.8}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH} + \underset{\text{stronger base}}{NH_3} \rightleftharpoons \underset{\text{weaker base}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O^-} + \underset{\substack{\text{weaker acid}\\ pK_a = 9.4}}{\overset{+}{N}H_4}$$

$$\underset{\substack{\text{weaker acid}\\ pK_a = 15.9}}{CH_3CH_2OH} + \underset{\text{weaker base}}{CH_3NH_2} \rightleftharpoons \underset{\text{stronger base}}{CH_3CH_2O^-} + \underset{\substack{\text{stronger acid}\\ pK_a = 10.7}}{CH_3\overset{+}{N}H_3}$$

Brønsted–Lowry Acids and Bases

- Acid donates a proton
- Base accepts a proton

$CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH$	$+$	NH_3	$\rightleftharpoons$	$CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O^-$	$+$	$\overset{+}{N}H_4$
stronger acid		stronger base		weaker base		weaker acid
$pK_a = 4.8$						$pK_a = 9.4$

CH_3CH_2OH	$+$	CH_3NH_2	$\rightleftharpoons$	$CH_3CH_2O^-$	$+$	$CH_3\overset{+}{N}H_3$
weaker acid		weaker base		stronger base		stronger acid
$pK_a = 15.9$						$pK_a = 10.7$

- Strong reacts to give weak
- The weaker the base, the stronger is its conjugate acid
- Stable bases are weak bases

An Acid/Base Equilibrium

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

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

$$pK_a = -\log K_a$$

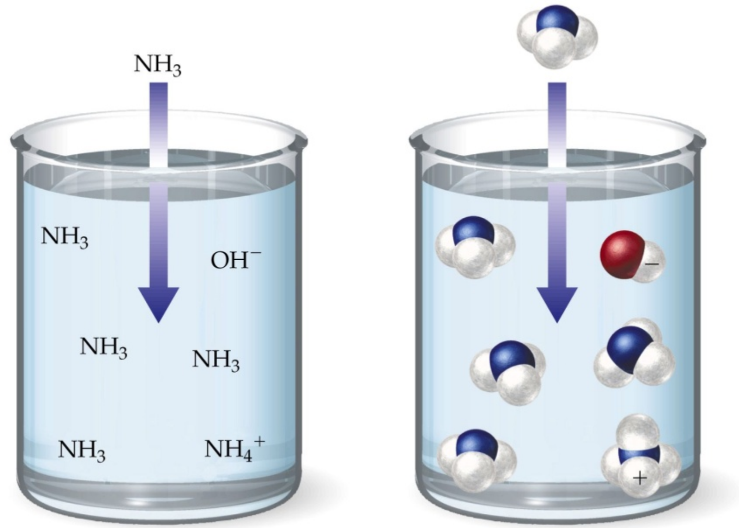
K_a: The acid dissociation constant

1. El pH de una disolución de ácido fórmico ($HCOOH$) 0.10 *M* es 2.39. ¿Cuál es la K_a del ácido? Calcule el porcentaje de ionización del ácido fórmico.

2. El pH de una disolución de un ácido débil monoprótico 0.060 *M* es 3.44. Calcule K_a del ácido.

Respuesta 1: $K_a = 1.73 \times 10^{-4}$, % = 4.1

Bases débiles y su constante de ionización básica



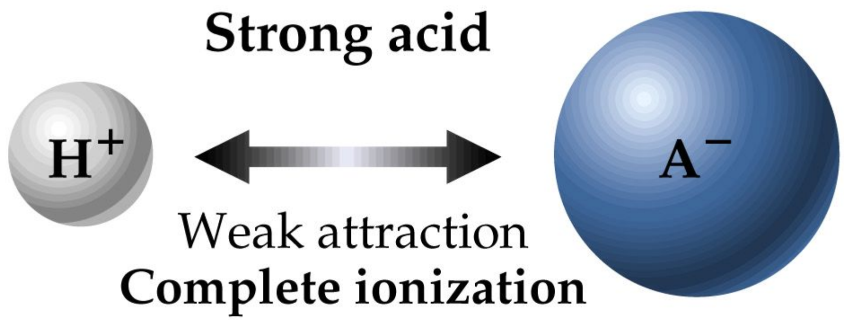
1. ¿Cuál es el pH de una disolución de amoniaco 0.40 *M*? pK_b = 4.74.

   Respuesta: pH = 11.43

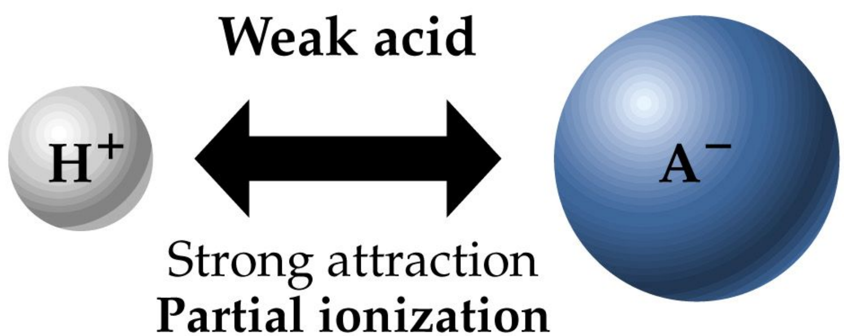
2. Calcule el pH de una disolución de metilamina 0.26 *M*. K_b = 4.4 x 10^{-4}.

   Respuesta: pH = 12.03

very strong acids	$pK_a < 1$
moderately strong acids	$pK_a = 1 – 5$
weak acids	$pK_a = 5 – 15$
extremely weak acids	$pK_a > 15$

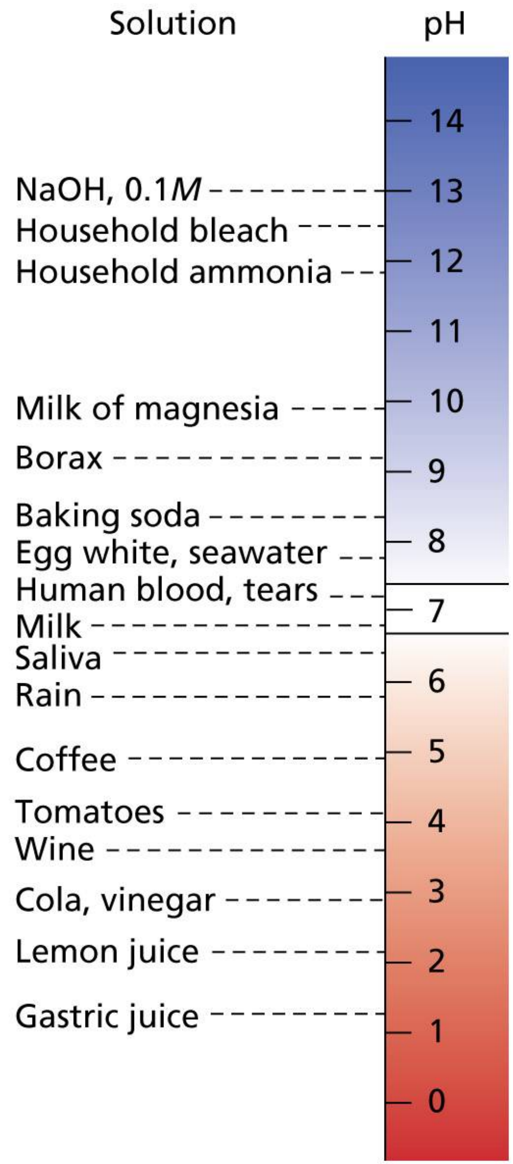


(a) In a strong acid, the attraction between H^+ and A^- is low, resulting in complete ionization.



(b) In a weak acid, the attraction between H^+ and A^- is high, resulting in partial ionization.

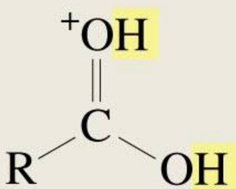
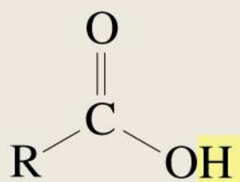
pH Values of Some Common Substances



CH_3OH
methanol
pK_a = 15.5

CH_3NH_2
methylamine
pK_a = 40

Table 1.8 Approximate pK_a Values

pK_a < 0	pK_a ~ 5	pK_a ~ 10	pK_a ~ 15
$R\overset{+}{O}H_2$ a protonated alcohol  H_3O^+ protonated water	 a carboxylic acid	$R\overset{+}{N}H_3$ a protonated amine	ROH an alcohol H_2O water

El efecto de la estructura en el pK_a

- When atoms are very different in size, the stronger acid will have its proton attached to the largest atom

relative electronegativities: $F > Cl > Br > I$

most electronegative (F)

largest (I)

relative stabilities: $F^- < Cl^- < Br^- < I^-$

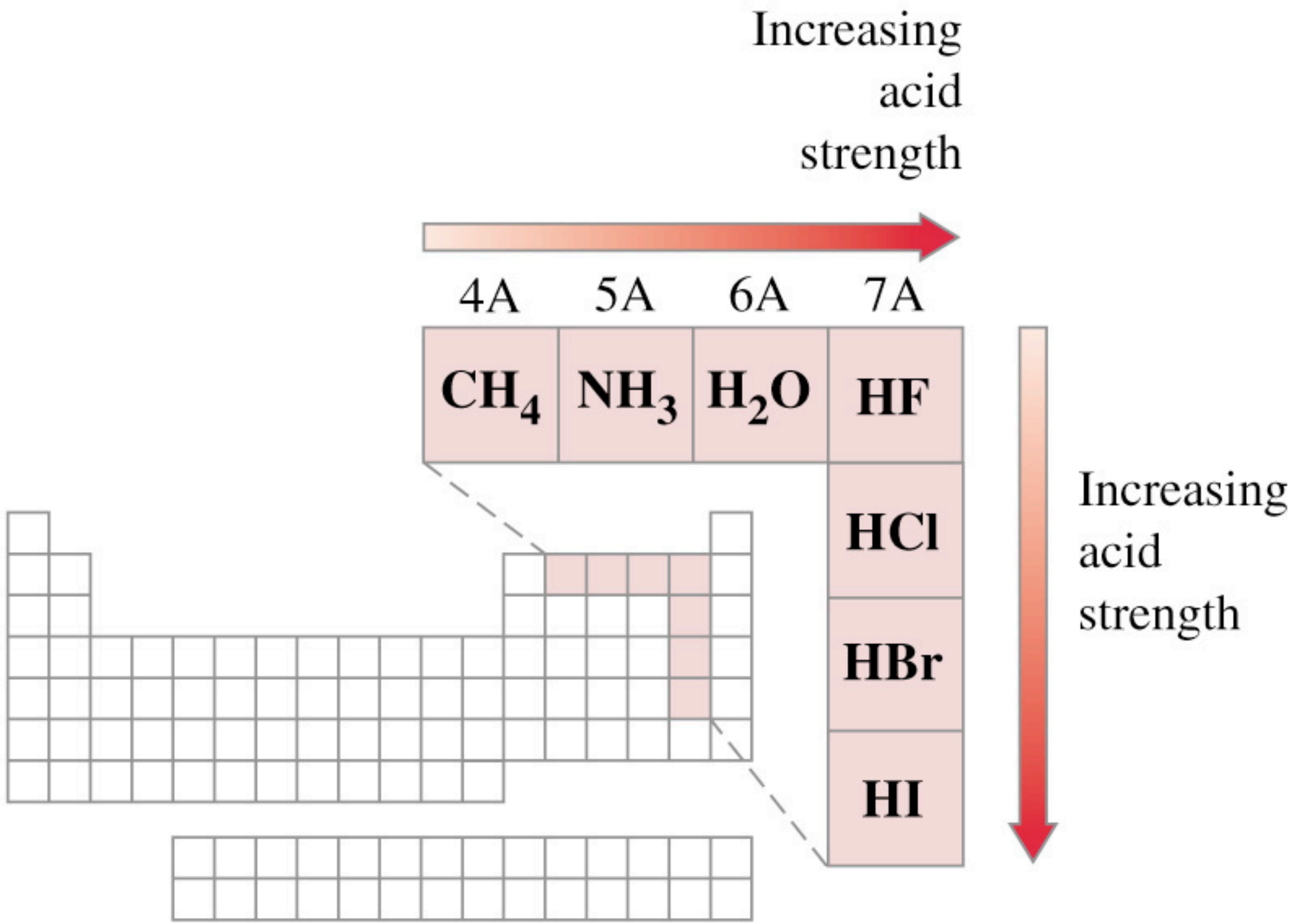
most stable (I^-)

relative acidities: $HF < HCl < HBr < HI$

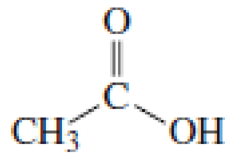
strongest acid (HI)

Table 1.9 The pK_a Values of Some Simple Acids

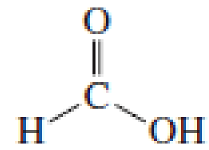
CH_4	NH_3	H_2O	HF
pK_a = 50	pK_a = 36	pK_a = 15.7	pK_a = 3.2
		H_2S	HCl
		pK_a = 7.0	pK_a = −7
			HBr
			pK_a = −9
			HI
			pK_a = −10


Increasing acid strength
4A
5A
6A
7A
CH_4
NH_3
H_2O
HF
HCl
HBr
HI
Increasing acid strength

El efecto del pH en la estructura de un compuesto orgánico



acetic acid
$pK_a = 4.76$



formic acid
$pK_a = 3.75$

CH_3OH
methanol
$pK_a = 15.5$

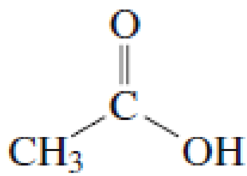
CH_3CH_2OH
ethanol
$pK_a = 15.9$

$$CH_3OH + HO^- \rightleftharpoons CH_3O^- + H_2O$$

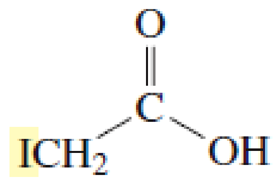
an acid

$$CH_3OH + H_3O^+ \rightleftharpoons CH_3\overset{+}{\underset{H}{O}}H + H_2O$$

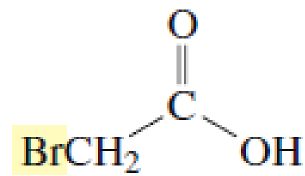
a base



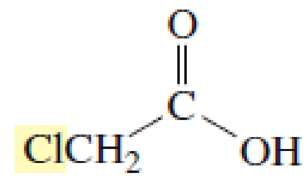
pK_a = 4.76



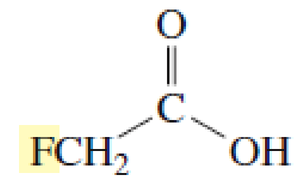
pK_a = 3.15



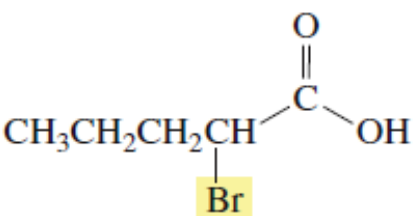
pK_a = 2.86



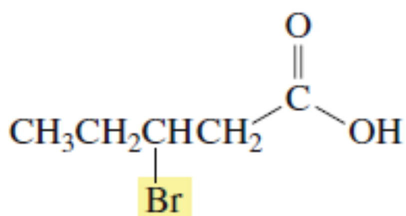
pK_a = 2.81



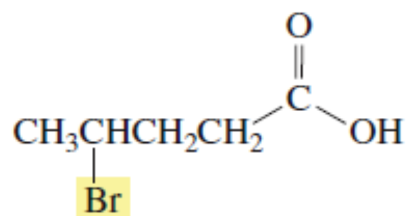
pK_a = 2.66



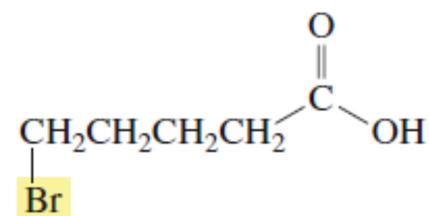
pK_a = 2.97



pK_a = 4.01

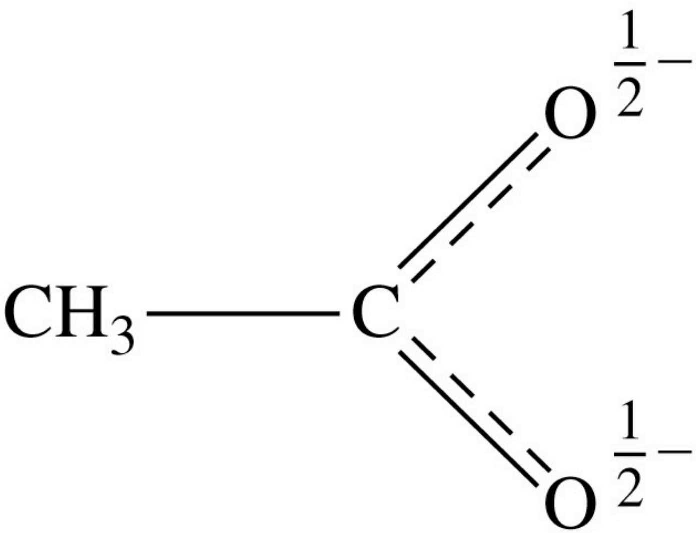


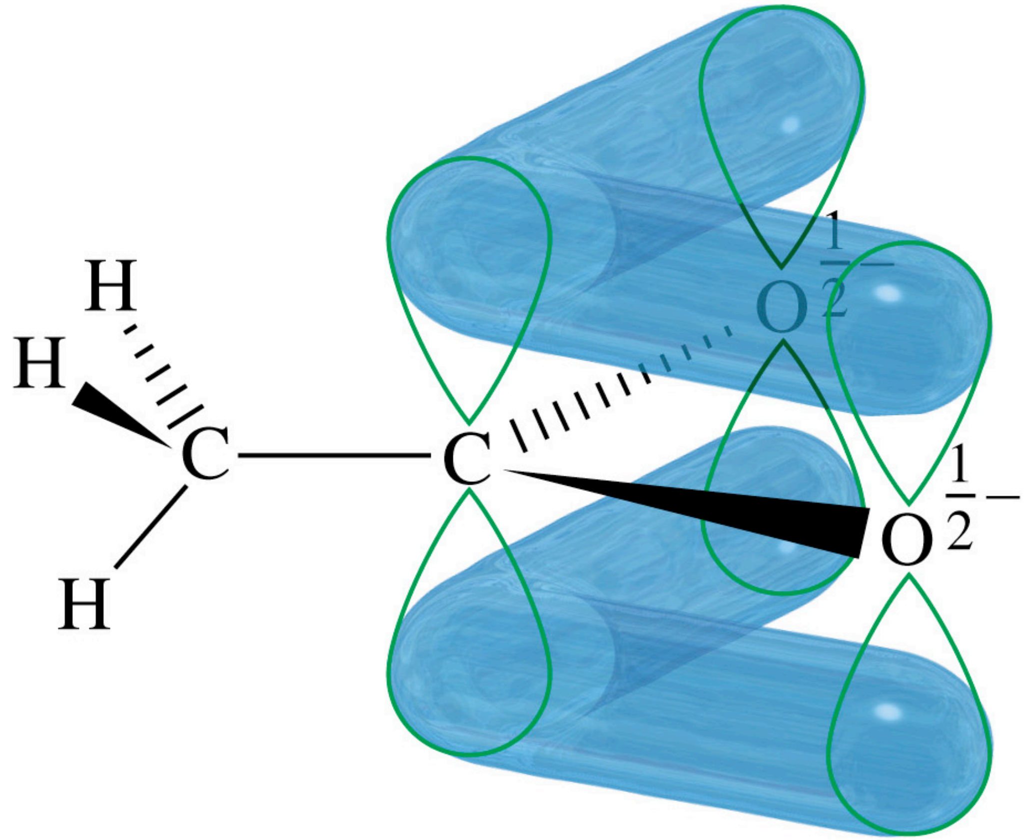
pK_a = 4.59



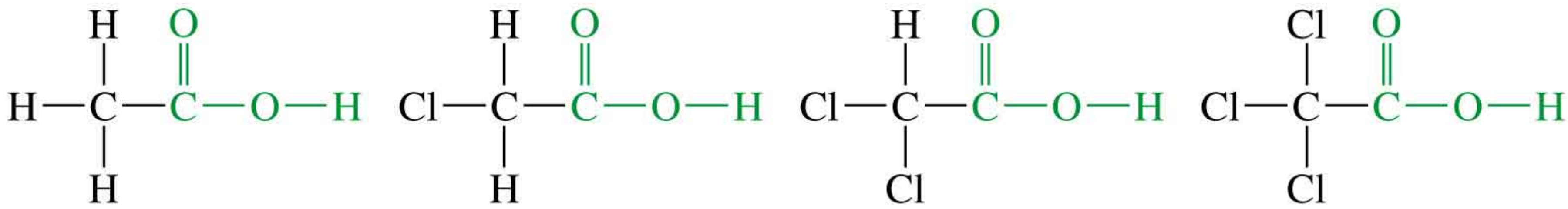
pK_a = 4.71

Ion Carboxilato

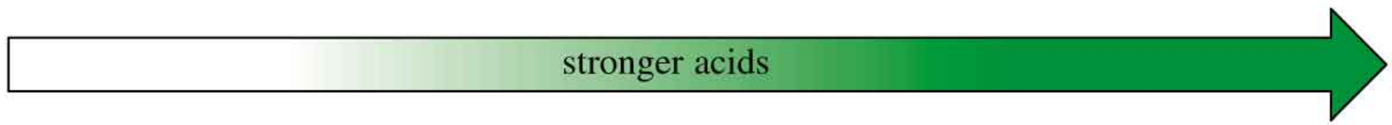


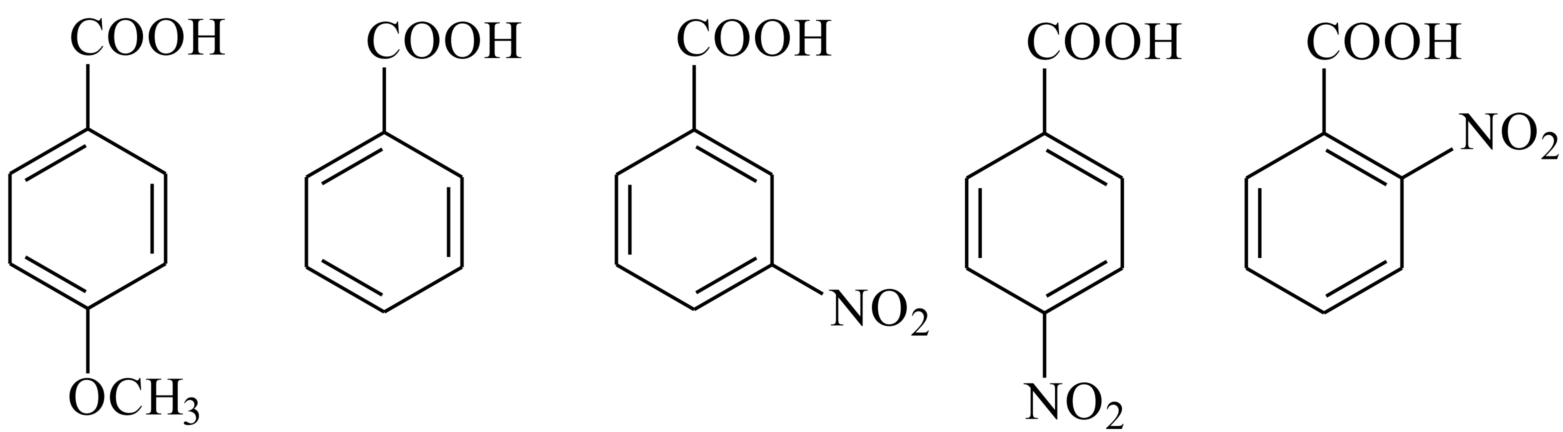


Substituent Effects on Acidity



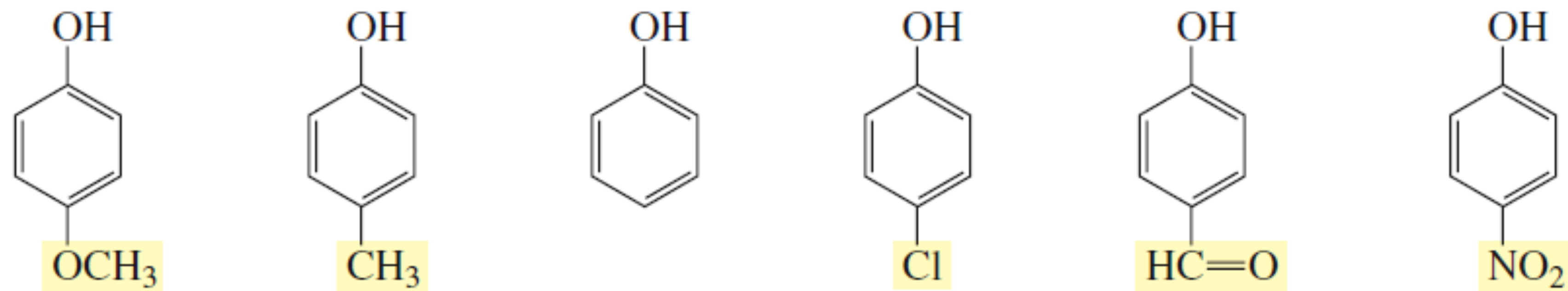
acetic acid $pK_a = 4.74$ | chloroacetic acid $pK_a = 2.86$ | dichloroacetic acid $pK_a = 1.26$ | trichloroacetic acid $pK_a = 0.64$





p-methoxy | benzoic acid | *m*-nitro | *p*-nitro | *o*-nitro

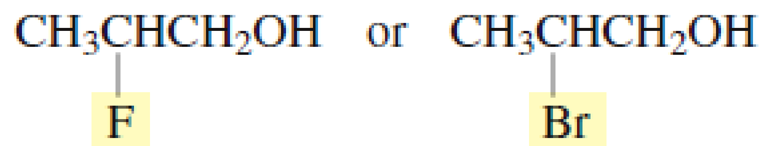
pK_a = 4.46 | **pK_a = 4.19** | **pK_a = 3.47** | **pK_a = 3.41** | **pK_a = 2.16**



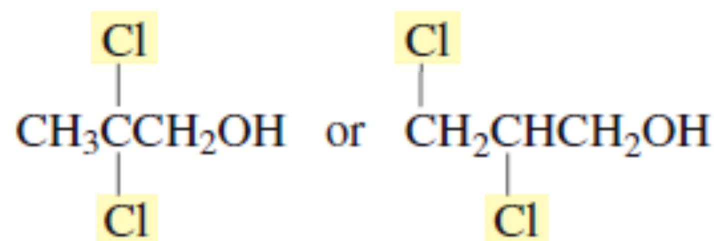
$pK_a = 10.20$ | $pK_a = 10.19$ | $pK_a = 9.95$ | $pK_a = 9.38$ | $pK_a = 7.66$ | $pK_a = 7.14$

phenol

a. Which is a stronger acid?



b. Which is a stronger acid?



PROBLEM 31◆

a. Which is a stronger base, CH_3COO^- or $HCOO^-$? (The pK_a of CH_3COOH is 4.8; the pK_a of HCOOH is 3.8.)

b. Which is a stronger base, HO^- or $^-NH_2$? (The pK_a of H_2O is 15.7; the pK_a of NH_3 is 36.)

c. Which is a stronger base, H_2O or CH_3OH? (The pK_a of H_3O^+ is −1.7; the pK_a of $CH_3OH_2^+$ is −2.5.)

PROBLEM 32◆

Using the pK_a values in Section 1.17, rank the following species in order of decreasing base strength:

$$CH_3NH_2 \quad CH_3NH^- \quad CH_3OH \quad CH_3O^- \quad CH_3\overset{\overset{\displaystyle O}{\|}}{C}O^-$$

PROBLEM 34◆

For each of the following compounds, indicate which is the stronger acid:

a. $CH_3OCH_2CH_2OH$ or $CH_3CH_2CH_2CH_2OH$

b. $CH_3CH_2CH_2\overset{+}{N}H_3$ or $CH_3CH_2CH_2\overset{+}{O}H_2$

c. $CH_3OCH_2CH_2CH_2OH$ or $CH_3CH_2OCH_2CH_2OH$

d. $CH_3\overset{\overset{O}{\|}}{C}CH_2OH$ or $CH_3CH_2\overset{\overset{O}{\|}}{C}OH$

PROBLEM 35◆

List the following compounds in order of decreasing acidity:

$CH_3\underset{\underset{F}{|}}{C}HCH_2OH$ $\quad$ $CH_3CH_2CH_2OH$ $\quad$ $\underset{\underset{Cl}{|}}{C}H_2CH_2CH_2OH$ $\quad$ $CH_3\underset{\underset{Cl}{|}}{C}HCH_2OH$

PROBLEM 36◆

For each of the following compounds, indicate which is the stronger base:

a. $CH_3\underset{\underset{Br}{|}}{C}H\overset{\overset{O}{\|}}{C}O^-$ or $CH_3\underset{\underset{F}{|}}{C}H\overset{\overset{O}{\|}}{C}O^-$

b. $CH_3\underset{\underset{Cl}{|}}{C}HCH_2\overset{\overset{O}{\|}}{C}O^-$ or $CH_3CH_2\underset{\underset{Cl}{|}}{C}H\overset{\overset{O}{\|}}{C}O^-$

c. $BrCH_2\overset{\overset{O}{\|}}{C}O^-$ or $CH_3CH_2\overset{\overset{O}{\|}}{C}O^-$

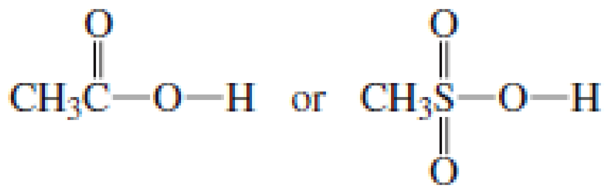
d. $CH_3\overset{\overset{O}{\|}}{C}CH_2CH_2O^-$ or $CH_3CH_2\overset{\overset{O}{\|}}{C}CH_2O^-$

PROBLEM 37 SOLVED

HCl is a weaker acid than HBr. Why, then, is $ClCH_2COOH$ a stronger acid than $BrCH_2COOH$?

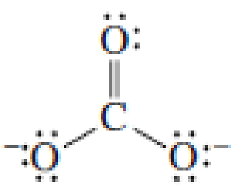
PROBLEM 41

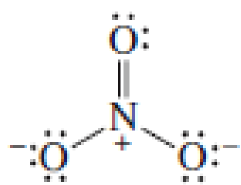
Which compound would you expect to be a stronger acid? Why?

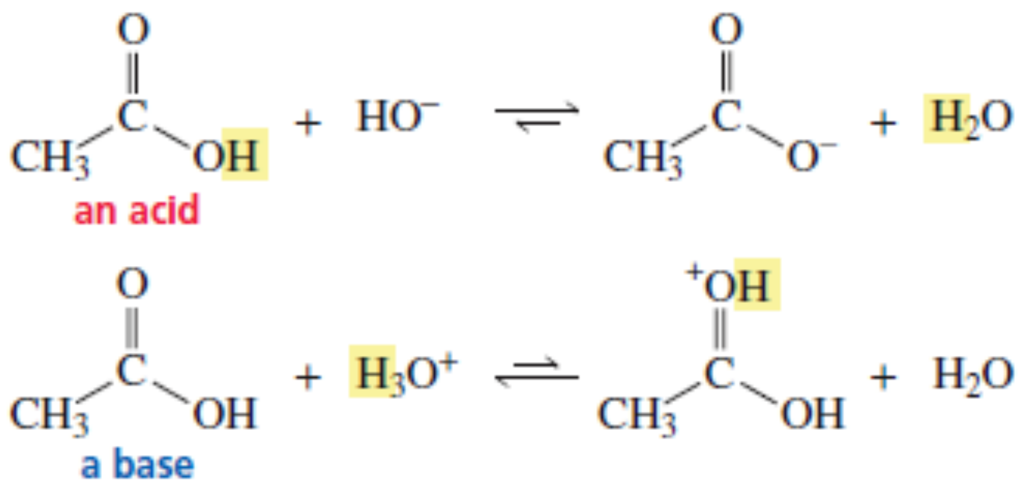


PROBLEM 42◆

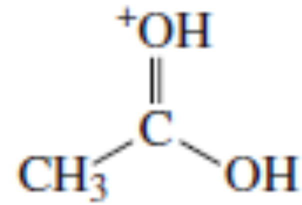
Draw resonance contributors for the following compounds:

a. 

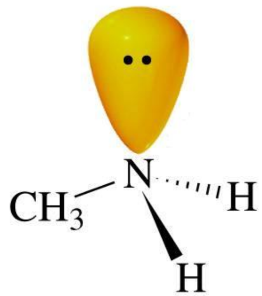
b. 



an acid
a base

$\mathrm{CH_3\underset{H}{\overset{+}{O}}H}$	$\mathrm{CH_3CH_2\underset{H}{\overset{+}{O}}H}$	
protonated methanol	protonated ethanol	protonated acetic acid
$pK_a = -2.5$	$pK_a = -2.4$	$pK_a = -6.1$

... Proponga lo propio para la metilamina



methylamine
a primary amine

$$CH_3NH_2 + HO^- \rightleftharpoons CH_3\bar{N}H + H_2O$$

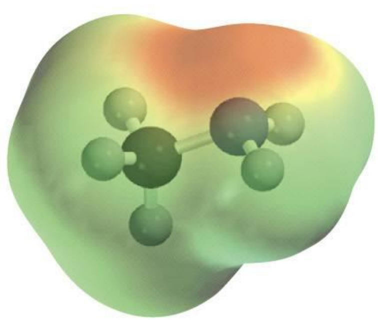
an acid

$$CH_3NH_2 + H_3O^+ \rightleftharpoons CH_3\overset{+}{N}H_3 + H_2O$$

a base

CH_3NH_2
methylamine
$pK_a = 40$

NH_3
ammonia
$pK_a = 36$



$CH_3\overset{+}{N}H_3$
protonated methylamine
$pK_a = 10.7$

$CH_3CH_2\overset{+}{N}H_3$
protonated ethylamine
$pK_a = 11.0$

electrostatic potential maps

methylamine

$$\underset{\substack{\text{stronger acid}\\ pK_a = 4.8}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH} + \underset{\text{stronger base}}{NH_3} \rightleftharpoons \underset{\text{weaker base}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O^-} + \underset{\substack{\text{weaker acid}\\ pK_a = 9.4}}{\overset{+}{N}H_4}$$

$$\underset{\substack{\text{weaker acid}\\ pK_a = 15.9}}{CH_3CH_2OH} + \underset{\text{weaker base}}{CH_3NH_2} \rightleftharpoons \underset{\text{stronger base}}{CH_3CH_2O^-} + \underset{\substack{\text{stronger acid}\\ pK_a = 10.7}}{CH_3\overset{+}{N}H_3}$$

$CH_3\underset{H}{\overset{+}{O}}H$

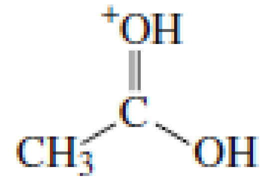
protonated methanol

$pK_a = -2.5$

$CH_3CH_2\underset{H}{\overset{+}{O}}H$

protonated ethanol

$pK_a = -2.4$



protonated acetic acid

$pK_a = -6.1$

CH_3NH_2

methylamine

$pK_a = 40$

NH_3

ammonia

$pK_a = 36$

$CH_3\overset{+}{N}H_3$

protonated methylamine

$pK_a = 10.7$

$CH_3CH_2\overset{+}{N}H_3$

protonated ethylamine

$pK_a = 11.0$

Efecto del ion común en los equilibrios ácido-base

Una mezcla de un ácido débil-ácido fuerte

Demostración del efecto del ion común: Una disolución de un ácido débil y ácido fuerte.

(**a**) Determine $[H_3O^+]$ y $[C_2H_3O_2^-]$ en $HC_2H_3O_2$ 0.100 M (K_a = 1.8×10^{-5}). (**b**) Después, determine las mismas cantidades en una disolución que es 0.100 M en los dos ácidos $HC_2H_3O_2$ y HCl.

R = (**a**) $[H_3O^+] = [CH_3CO_2^-] = 1.3 \times 10^{-3}$ M

(**b**) $[H_3O^+] = 0.100$ M, $[CH_3CO_2^-] = 1.8 \times 10^{-5}$ M

Disoluciones de ácidos débiles y sus sales:

Una mezcla de un ácido débil y su sal

(a) (b)

(**a**) Disolución de $HC_2H_3O_2$ 0.100 M, pH calculado de 2.89 (K_a = 1.8 x 10^{-5}), pero (**b**) si la disolución es también 0.100 M en $NaC_2H_3O_2$ el pH calculado es 4.74.

When a strong acid supplies the common ion H_3O^+, the equilibrium shifts to form more $HC_2H_3O_2$.

Added H_3O^+

$$HC_2H_3O_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_2^- \quad K_a = 1.8 \times 10^{-5}$$

Equilibrium shifts to form more $HC_2H_3O_2$

When a salt supplies the common anion $C_2H_3O_2^-$, the equilibrium shifts to form more $HC_2H_3O_2$.

$$NaC_2H_3O_2(aq) \longrightarrow Na^+ + C_2H_3O_2^-$$

Added $C_2H_3O_2^-$

$$HC_2H_3O_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_2^- \qquad K_a = 1.8 \times 10^{-5}$$

Equilibrium shifts to form more $HC_2H_3O_2$

Demostración del efecto del ion común: Una disolución de un ácido débil y una sal del ácido débil.

Calcule $[H_3O^+]$ y $[C_2H_3O_2^-]$ en una disolución de $HC_2H_3O_2$ y NaO_2CCH_3 0.100 M para ambos compuestos (K_a = 1.8 x 10^{-5}).

R = $[H_3O^+]$ = 1.8 X 10^{-5} M
$[CH_3CO_2^-]$ = 0.100 M

Calcule $[H_3O^+]$ y $[CHO_2^-]$ en una disolución que es 0.100 M en $HCHO_2$ y 0.150 M en $NaCHO_2$ (K_a = 1.8 x 10^{-4}).

¿Qué masa de NaO_2CCH_3 se debería de añadir a 1.00 L de $HC_2H_3O_2$ 0.100 M para obtener una disolución con pH = 5.00? Suponga que el volumen se mantiene en 1.00 L.

Disoluciones de bases débiles y sus sales:

Una mezcla de una base débil y su sal

(a) (b)

(**a**) pH del NH_3 0.100 M es superior a 10 (valor calculado 11.11). (**b**) Si la disolución es también 0.100 M en NH_4Cl, el pH desciende por debajo de 10 (valor calculado: 9.26).

When a salt supplies the common cation NH_4^+, the equilibrium shifts to form more NH_3.

$$NH_4Cl(aq) \longrightarrow NH_4^+ + Cl^-$$

Added NH_4^+

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \quad K_b = 1.8 \times 10^{-5}$$

Equilibrium shifts to form more NH_3

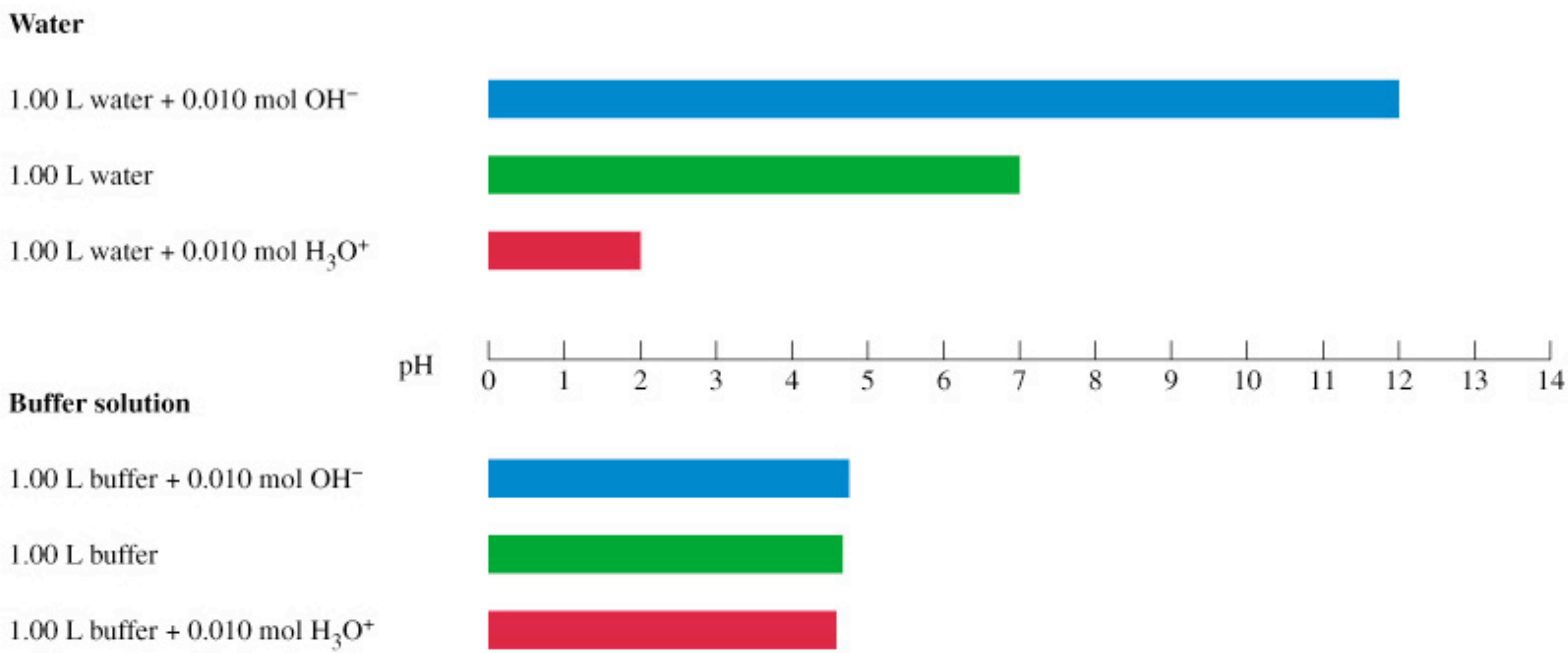
When a strong base supplies the common ion OH^-, the equilibrium shifts to form more NH_3.

Added OH^-

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \qquad K_b = 1.8 \times 10^{-5}$$

Equilibrium shifts to form more NH_3

Disoluciones reguladoras



The pH of pure water undergoes very large changes in pH when a small amount of either an acid or a base is added. Water has no buffering ability. In contrast, the corresponding pH changes in a buffer solution that is 1.00 M in CH_3COOH and 1.00 M in CH_3COONa are almost imperceptible.

The Henderson–Hasselbalch Equation

The pH indicates the concentration of hydrogen ions (H^+)

$$pK_a = pH + \log \frac{[HA]}{[A^-]}$$

- A compound will exist primarily in its acidic form at a pH < its pK_a

- A compound will exist primarily in its basic form at a pH > its pK_a

- A buffer solution maintains a nearly constant pH upon addition of small amount of acid or base

Disoluciones reguladoras

$$K_a = \frac{[H_3O^+][C_2H_3O_2^-]}{[C_2H_3O_2H]} = 1.8 \times 10^{-5}$$

$$[H_3O^+] = K_a \times \frac{\cancel{[C_2H_3O_2H]}}{\cancel{[C_2H_3O_2^-]}} = 1.8 \times 10^{-5}\ M$$

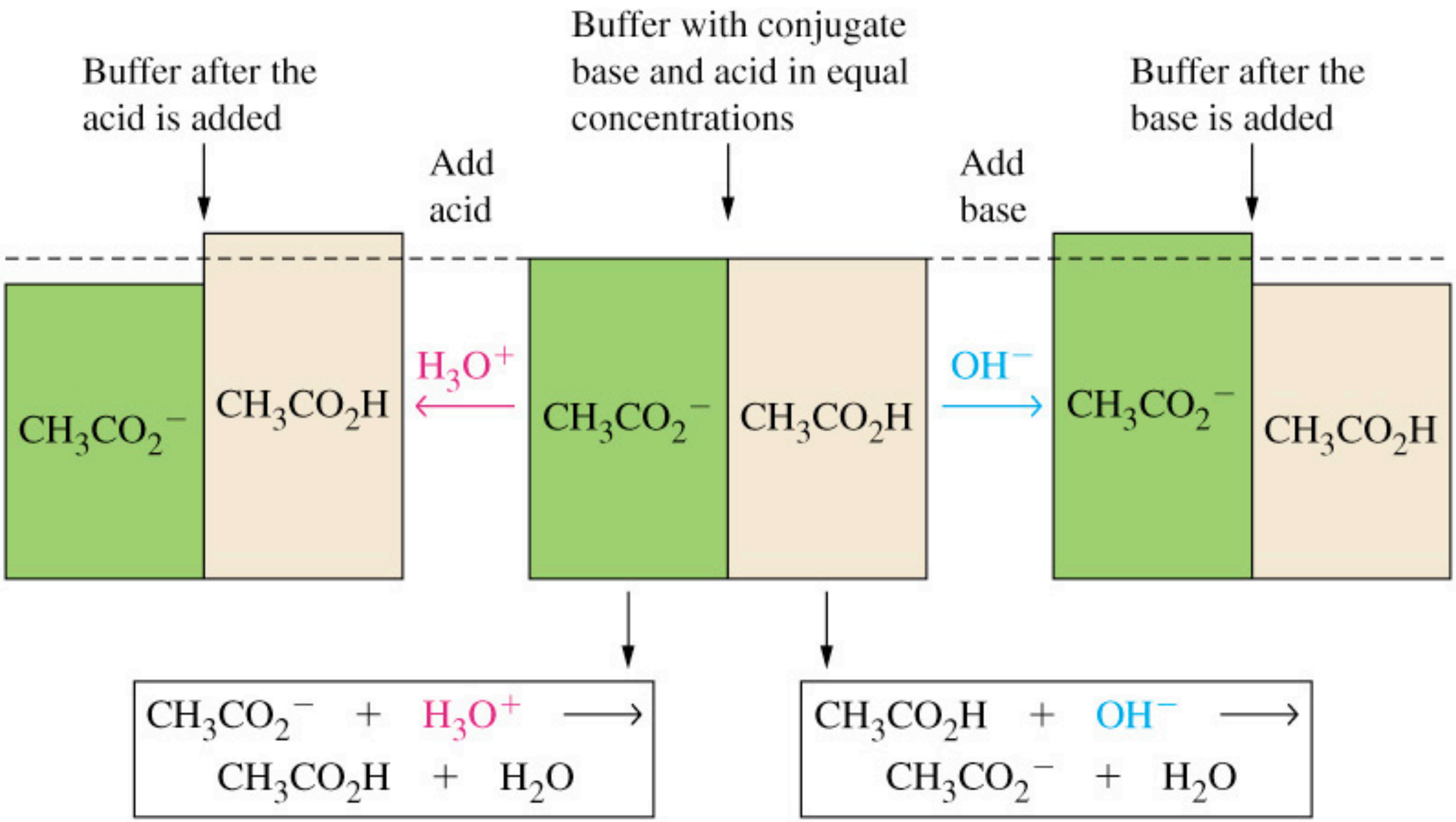
pH = ?

$$[H_3O^+] = K_a \times \frac{\cancel{[C_2H_3O_2H]}}{\cancel{[C_2H_3O_2^-]}} = 1.8 \times 10^{-5}\ M$$

Ahora añadimos una pequeña cantidad de un ácido fuerte...

Ahora añadimos una pequeña cantidad de una base fuerte...

Cómo funciona una disolución reguladora



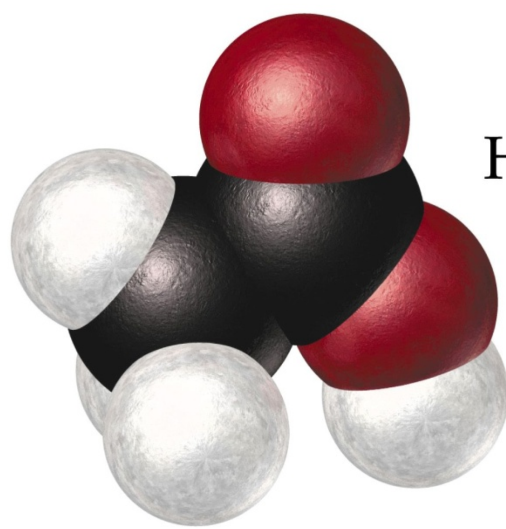
Comprobación de las propiedades reguladoras de una disolución.

1. Demuestre que una disolución de NH_3-NH_4Cl es una disolución reguladora. ¿En qué intervalo de pH espera que sea eficaz? ($K_b = 1.8 \times 10^{-5}$).

2. Justifique que una mezcla de un ácido fuerte (como el HCl) y una sal de un ácido débil (como el NaO_2CCH_3) puede ser una disolución reguladora.
(*Sugerencia*: ¿Cuál es la reacción que produce HO_2CCH_3? ¿qué proporción se necesita para obtener una disolución reguladora?

Cálculo del pH de una disolución reguladora. ¿Cuál es el pH de una disolución reguladora que se prepara disolviendo 25.5 g de NaO_2CCH_3 en un volumen suficiente de HO_2CCH_3 0.550 M para obtener 500.0 mL de la disolución?

pH = 4.80



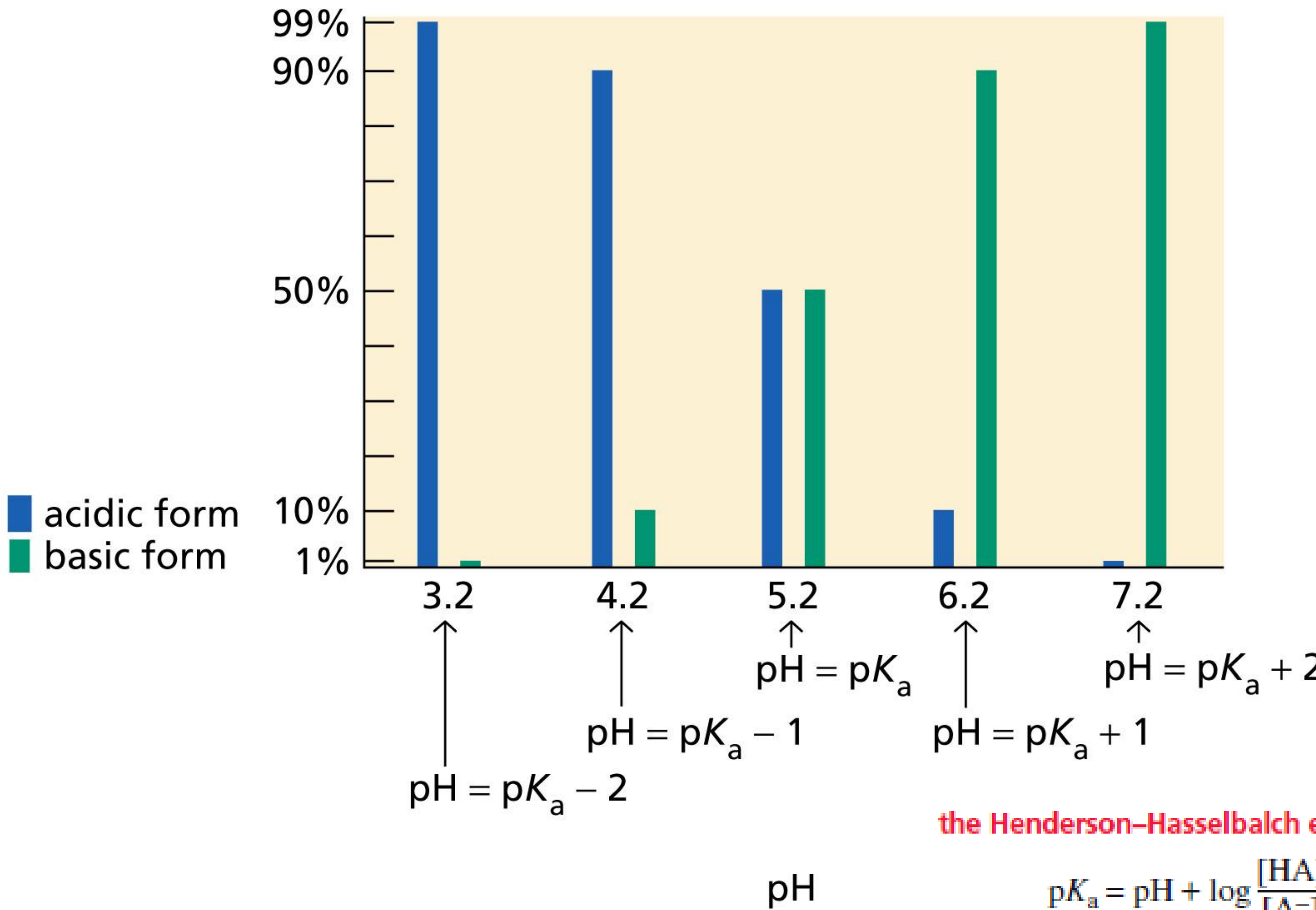
$HC_2H_3O_2$

Acetic acid

¿Cuál es el pH de una disolución reguladora que se prepara disolviendo 23.1 g de $NaCHO_2$ en un volumen suficiente de $HCHO_2$ 0.432 M para obtener 500.0 mL de la disolución? (K_a = 1.8 x 10^{-4}).

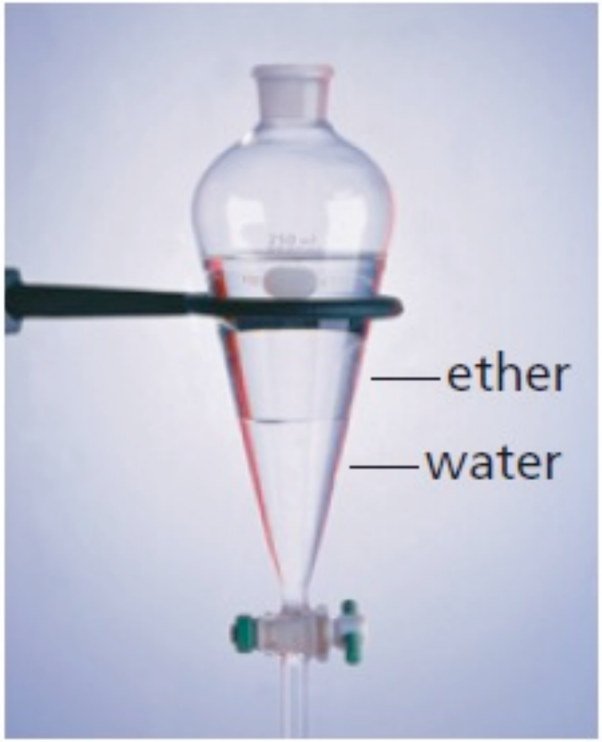
En un manual de datos se encuentra que para obtener una determinada disolución reguladora se mezclan 63.0 mL de HO_2CCH_3 0.200 M con 37.0 mL de NaO_2CCH_3 0.200 M. ¿Cuál es el pH de esta disolución reguladora?

Conjugate Acid/Base Composition and pH



the Henderson–Hasselbalch equation

$$pK_a = pH + \log \frac{[HA]}{[A^-]}$$



Un ácido carbóxílico y una amina a un pH de 2

a. At what pH will 99% of a compound with a pK_a of 8.4 be in its basic form?
b. At what pH will 91% of a compound with a pK_a of 3.7 be in its acidic form?
c. At what pH will 9% of a compound with a pK_a of 5.9 be in its basic form?
d. At what pH will 50% of a compound with a pK_a of 7.3 be in its basic form?
e. At what pH will 1% of a compound with a pK_a of 7.3 be in its acidic form?

PROBLEM 45◆

a. Indicate whether a carboxylic acid (RCOOH) with a pK_a of 5 will be mostly charged or mostly neutral in solutions with the following pH values:

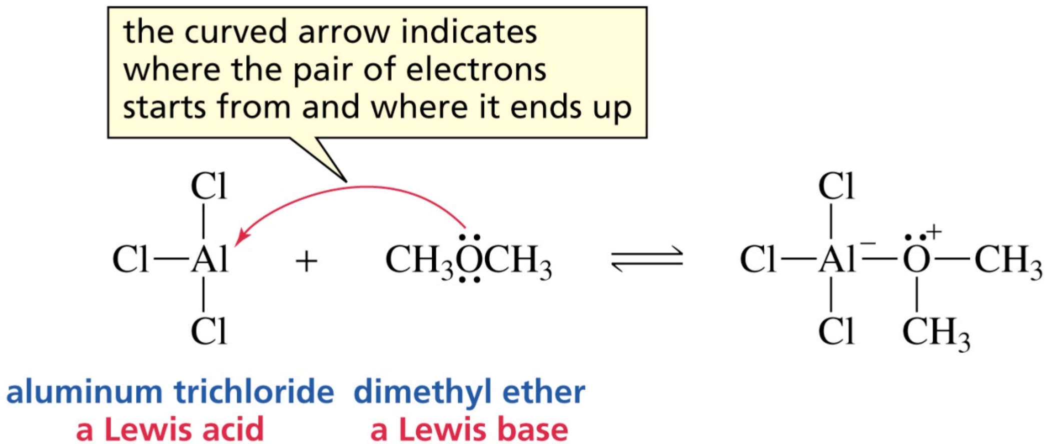
1. pH = 1
2. pH = 3
3. pH = 5
4. pH = 7
5. pH = 9
6. pH = 11
7. pH = 13

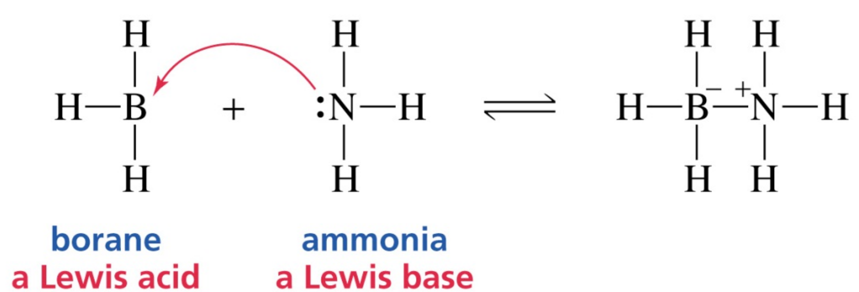
b. Answer the same question for a protonated amine ($R\overset{+}{N}H_3$) with a pK_a of 9.

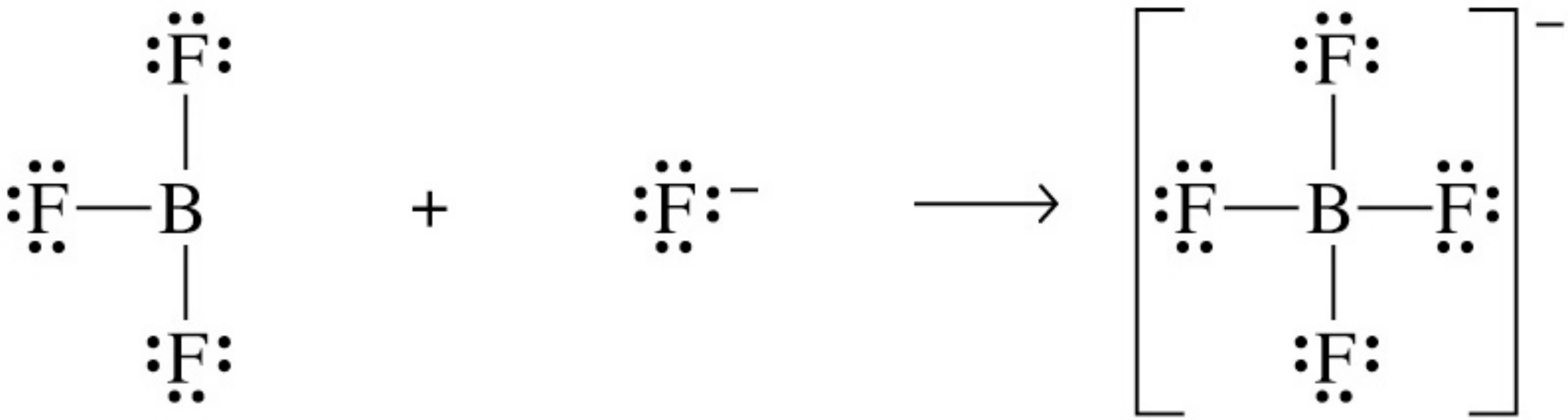
c. Answer the same question for an alcohol (ROH) with a pK_a of 15.

Lewis acid: non-proton-donating acid; will accept two electrons

Lewis base: electron pair donors







Lewis acid Lewis base

Ácidos y bases de Lewis

PROBLEM 48

What is the product of each of the following reactions?

a. $ZnCl_2 + CH_3OH \rightleftharpoons$

b. $FeBr_3 + Br^- \rightleftharpoons$

c. $AlCl_3 + Cl^- \rightleftharpoons$

d. $BF_3 + \mathrm{H\overset{\overset{\displaystyle O}{\|}}{C}H} \rightleftharpoons$

PROBLEM 49

Show how each of the following compounds reacts with HO^-:

a. CH_3OH

b. $^+NH_4$

c. $CH_3\overset{+}{N}H_3$

d. BF_3

e. $^+CH_3$

f. $FeBr_3$

g. $AlCl_3$

h. CH_3COOH