



Module 4

Acids & Bases

Session Slides with Notes

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Brønsted-Lowry Acids & Bases

acid - proton donor
base - proton receiver

An Brønsted-Lowry acid is a proton (H^+) donor.



other systems

An Brønsted-Lowry base is a proton (H^+) receiver.

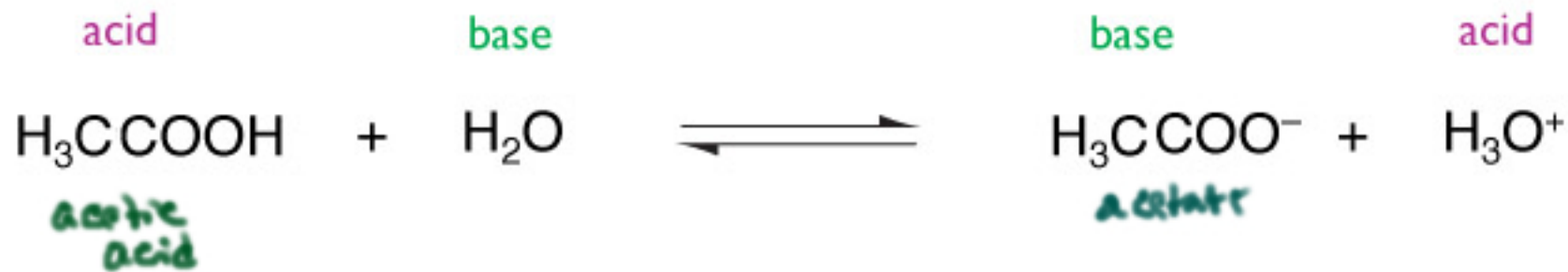


Arrhenius -
acid - H^+ donor
base - OH^- donor

acid + base \rightarrow salt + H_2O

Lewis
acid - electron pair receiver
base - electron pair donor

- context is aqueous solutions



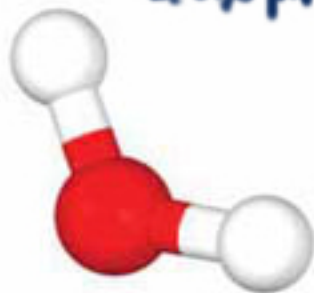
Weak acids and bases - an equilibrium establishes

strong acids and bases - completely dissociate or
the process to completion

HCl, H₂SO₄, HNO₃

NaOH NaNH₂ etc

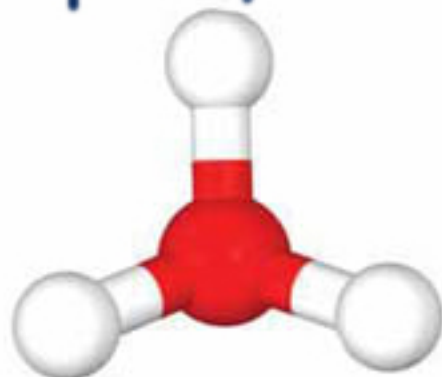
autoprotolysis of H_2O
acid base activity is in coupled equilibrium with
autoprotolysis of H_2O



1 Bonded hydrogen ions dissociate from the water molecules ($2H_2O$)



2 Hydroxide ion (OH^-) forms the conjugate base



3 Oxonium ion forms a conjugate acid by accepting H^+ ion



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

$$= 1.00 \times 10^{-14}$$

At 25°C the autoprotolysis of pure water, shown below, attains equilibrium hydronium and hydroxide ion concentrations of about 1×10^{-7} moles per liter for each. The equilibrium concentrations vary somewhat with temperature, however. At 0°C, the concentrations are about 8×10^{-8} moles per liter, and at 100°C the concentrations are about 7×10^{-7} moles per liter. What does this directly imply about the autoprotolysis of water?

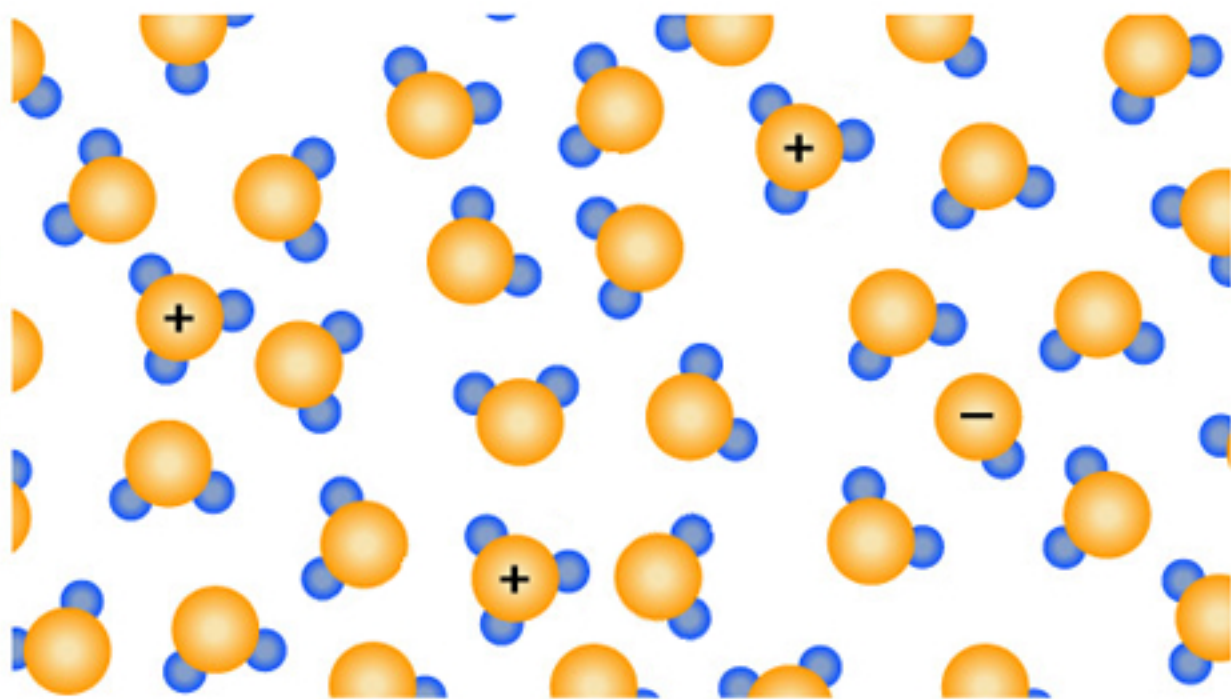


- a. Autoprotolysis of water is a second order reaction.
- b. Autoprotolysis of water is an endothermic process.
- c. Autoprotolysis of water is spontaneous.
- d. Water is a strong electrolyte.





$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = [\text{H}^+][\text{OH}^-] = 1.00 \times 10^{-14}$$



an acidic solution

$$\log(10^a) = a$$

$$\text{pH} = -\log[\text{H}^+]$$

$$\log(1) = 0 \quad \log(10) = 1$$

If 0.1 mol HCl
in a 1L solution

What is the pH?

0.1 M HCl solution

$$[\text{H}^+] = \frac{1}{10} = 10^{-1}$$

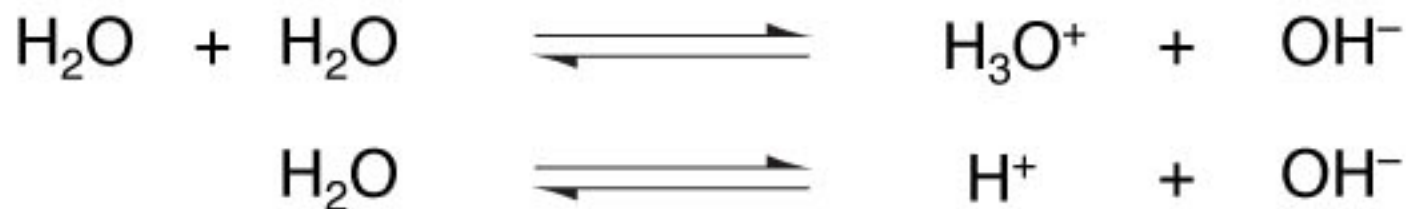
$$-\log(10^{-1}) = \text{pH} = 1$$

acid solutions have
a proton pressure

basic solutions have
a proton pull

$$\log(100) = 2$$

$$\log(1000) = 3$$



$$\begin{aligned} K_w &= [\text{H}^+][\text{OH}^-] \\ &= 1.00 \times 10^{-14} \end{aligned}$$

Calculate the pH of a 0.001M solution of NaOH.

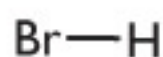
$$\begin{aligned} [\text{OH}^-] &= 10^{-3} \\ [\text{H}^+][\text{OH}^-] &= 10^{-14} \\ [\text{H}^+] &= 10^{-11} \\ \text{pH} &= 11 \end{aligned}$$

Use the following relationship to calculate the pH of a 0.001 M solution of NaOH

$$\text{pH} + \text{pOH} = \text{p}K_w = 14$$

$HA \rightleftharpoons A^- + H^+$ Acids F-H ← weak

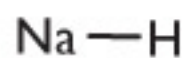
Bases



Nonmetal
Hydrides



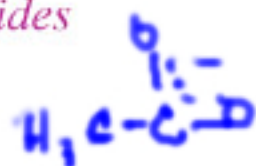
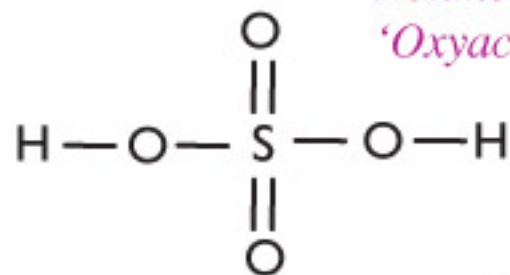
Metal
Hydrides



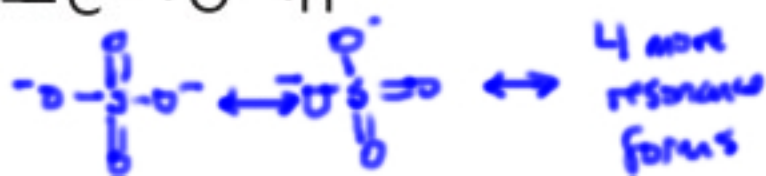
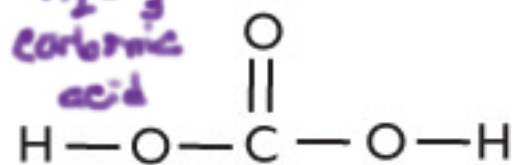
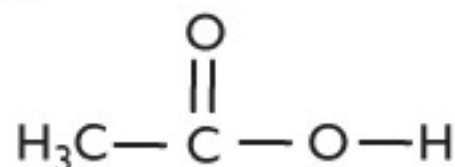
Metal
Oxides



Nonmetal Hydroxides
'Oxyacids'



H_2CO_3
carbonic
acid



Metal
Hydroxides



Ammonia &
Amines



most important organic bases



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

or

$$\frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

EXAMPLE

$$\frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{H}_2\text{CO}_3]}$$

$$\text{p}K_a = -\log[K_a]$$

For weak acids,
 K_a is a number
 with a negative exponent

The weaker the acid, the higher
 $\text{p}K_a$.

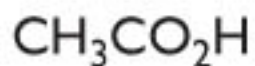
Determine the $\text{p}K_a$:

$$K_a \text{ of } \text{HNO}_2 : 7 \times 10^{-4}$$

$$K_a \text{ of } \text{CH}_3\text{CO}_2\text{H} : 1.8 \times 10^{-5} = 4.8$$

$-\log(7 \times 10^{-4})$
 shortcut · say $4 - 0.7 = 3.3$

Which is the stronger acid?



↙ *unlust*
 $pK_a \approx 15.9$

$$K_a : 5.9 \times 10^{-1}$$

$$K_a : 1.8 \times 10^{-5}$$

$$K_a : 1.3 \times 10^{-16}$$



$$K = e^{-\Delta G^\circ/RT}$$

True or false?: The larger the pK_a the weaker the acid.



$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

$$pK_b = -\log[K_b]$$

EXAMPLE

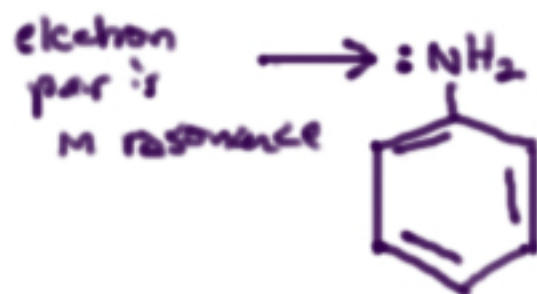
$$\frac{[NH_4^+][OH^-]}{[NH_3]}$$

Determine the pK_b :

$$K_b \text{ of } CH_3NH_2 : 4.4 \times 10^{-4} \quad 3.6$$

$$K_b \text{ of } CN^- : 1.6 \times 10^{-5} \quad 4.8$$

Which is the stronger base?



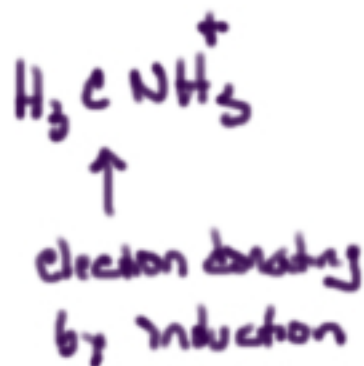
$K_b : 1.8 \times 10^{-5}$



$K_b : 4.4 \times 10^{-4}$



$K_b : 4.3 \times 10^{-10}$





K_a acetic acid $\sim 10^{-5}$

K_b acetate $\sim 10^{-9}$

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad K_b = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]}$$

$$K_a \times K_b = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \times \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} = [\text{H}^+][\text{OH}^-] = K_w$$

$$K_a \times K_b = K_w$$

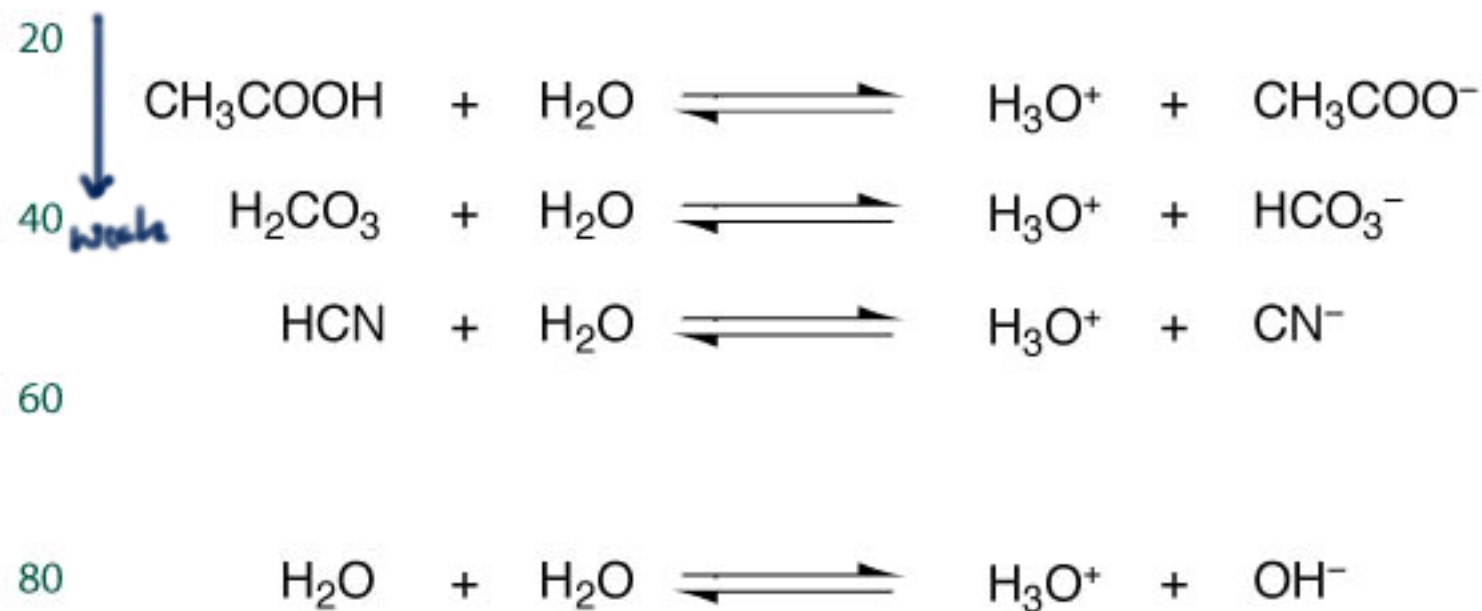
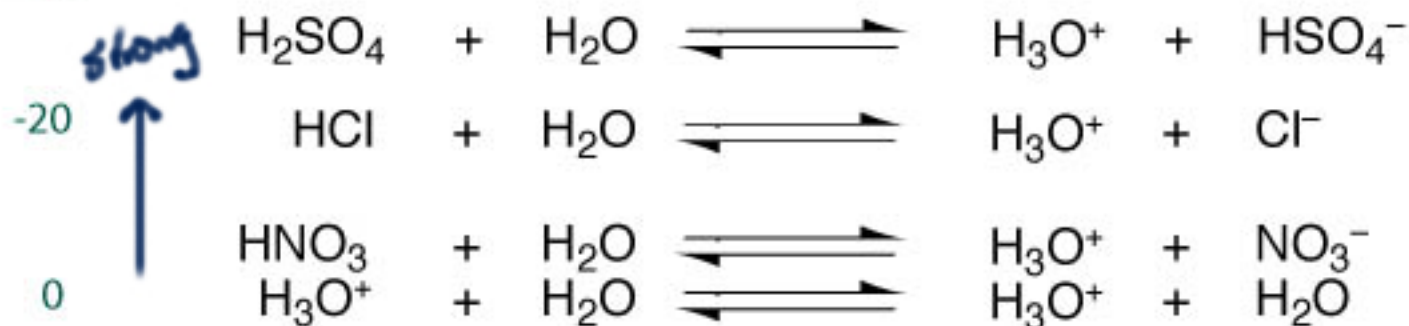
K_a of an acid

K_b of its conjugate base

The stronger a weak acid the weaker its conjugate base.

ΔG°

$$K = e^{-\Delta G^\circ / RT}$$



Acid		pK _a	Base	pK _b	
H ₂ SO ₄	↑ strong	sulfuric acid	-3	HSO ₄ ⁻	17
HCl		hydrochloric acid	-3	Cl ⁻	17
HNO ₃		nitric acid	-1	NO ₃ ⁻	15
H ₃ O ⁺		hydronium ion	0	H ₂ O	14
HSO ₄ ⁻		bisulfate	1.8	SO ₄ ²⁻	12.1
H ₃ PO ₄	↓ weak	phosphoric acid ★	2.1	H ₂ PO ₄ ⁻	11.9
HF		hydrofluoric acid	3.2	F ⁻	10.8
CH ₃ COOH		acetic acid ★	4.7	CH ₃ COO ⁻	9.3
H ₂ CO ₃		carbonic acid : CO ₂ (aq) ★	6.3 ←	HCO ₃ ⁻	7.7
H ₂ PO ₄ ⁻		dihydrogen phosphate ★	7.2	HPO ₄ ²⁻	11.9
HCN		hydrogen cyanide	9.2	CN ⁻	4.8
NH ₄ ⁺		ammonium ion	9.25	NH ₃	4.75
HCO ₃ ⁻		bicarbonate ★	10.3	CO ₃ ²⁻	3.7
HPO ₄ ²⁻		hydrogen phosphate ★	12.3	PO ₄ ³⁻	1.7
H ₂ O		water	14	OH ⁻	0
NH ₃		ammonia	23	NH ₂ ⁻	-9

What is the pH of a 0.1M $\text{CH}_3\text{CO}_2\text{H}$ solution? $K_a : 1.8 \times 10^{-5}$



$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]} = 1.8 \times 10^{-5}$$

$[\text{H}^+] \approx [\text{CH}_3\text{CO}_2^-]$ so approximate $[\text{H}^+] = [\text{CH}_3\text{CO}_2^-]$ ← ignoring $[\text{H}^+]$ already there

$[\text{CH}_3\text{CO}_2\text{H}] \approx 0.1\text{M}$ so approximate $[\text{CH}_3\text{CO}_2\text{H}] = 0.1\text{M}$ ← assuming not too much dissociated

$$K_a = \frac{[\text{H}^+]^2}{0.1} = 1.8 \times 10^{-5}$$

$$[\text{H}^+]^2 = 1.8 \times 10^{-6}$$

$$[\text{H}^+] = 1.4 \times 10^{-3}$$

$$\sqrt{10^{2x}} = 10^x$$

$$(10^x)(10^x) = 10^{x+x}$$

⇒ 2 ways to look at it

1) What's the pH of a buffer solution?



Suppose a solution:
0.1 M acetic acid
1.0 M acetate

$$\text{pH} = \text{pK}_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$$
$$= 5 + \log\left(\frac{1}{0.1}\right)$$
$$= 6$$

after adding 0.1 mol HCl to 1L

$$\text{pH} = 5 + \log\left(\frac{0.9}{0.1}\right)$$
$$= 5.5$$

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

$$[\text{H}^+] = \frac{[\text{HA}]}{[\text{A}^-]} \times K_a$$

$$\log [\text{H}^+] = \log K_a + \log\left(\frac{[\text{HA}]}{[\text{A}^-]}\right)$$

$$\text{pH} = \text{pK}_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$$

! Henderson-Hasselbach Equation !

2) What is the state of ionization of a solution component?

$$\text{pH} = \text{pK}_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$$

Aspirin $\text{asp} - \text{COOH} \leftarrow \text{pK}_a \sim 4$

$$7 = 4 + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$$

$$\log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right) = 3$$

$$\frac{[\text{A}^-]}{[\text{HA}]} = \frac{1000}{1}$$

lys - $\text{NH}_3^+ \leftarrow \text{pK}_a \sim 10.5$

$$7 = 10.5 + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$$

$$\frac{[\text{A}^-]}{[\text{HA}]} = \frac{1}{3000}$$



$$\text{pH} = \text{p}K_{\text{ind}} + \log \left(\frac{[\text{A}^-]}{[\text{HA}]} \right)$$

4 7





$$N_a V_a = N_b V_b$$

$$N_a (0.1 \text{ L}) = (0.2 \text{ N})(.025)$$

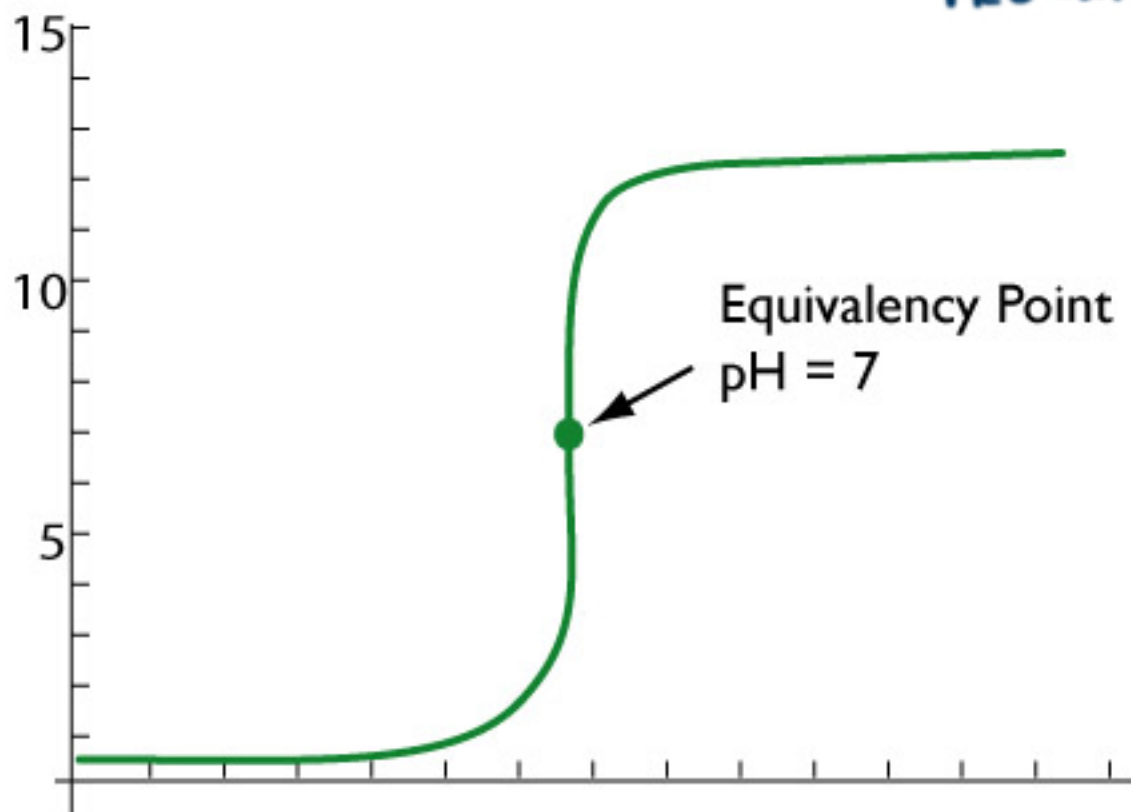
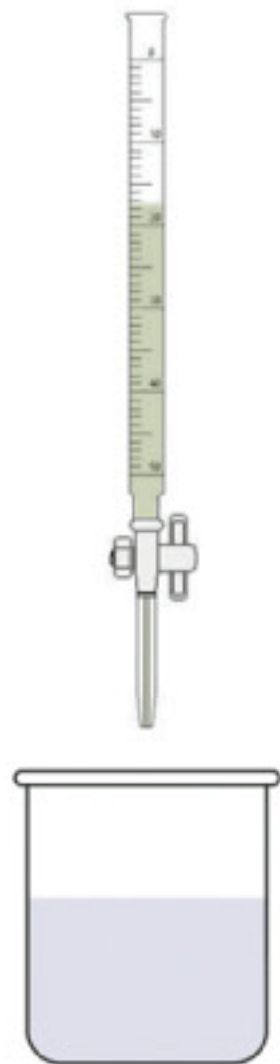
$$N_a = .05 \text{ N}$$

100 ml of HCl solution was completely neutralized by 25ml of 0.2N NaOH solution. What was the normality of the HCL solution?

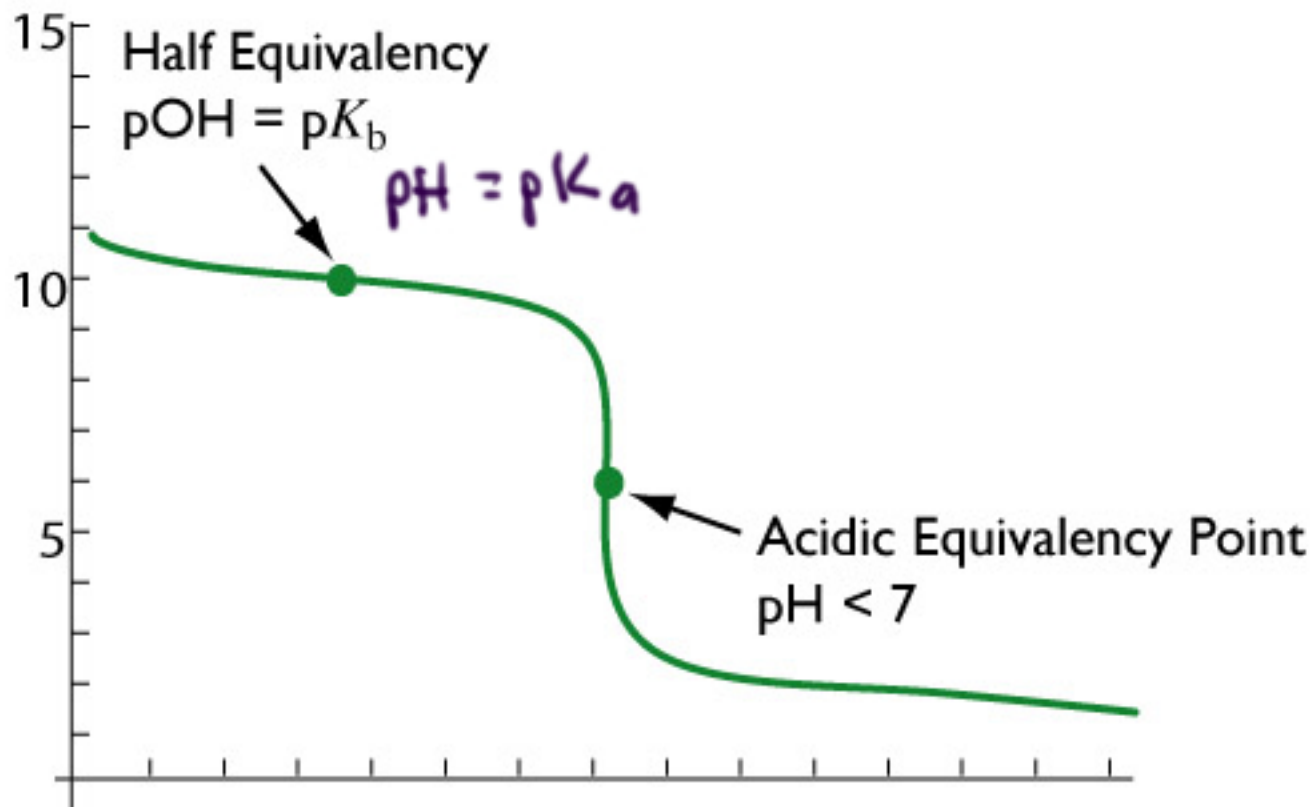
$$\text{H}_2\text{SO}_4 \quad \frac{2 \text{ equiv}}{\text{mol}} \cdot 1 \text{ M} \left(\frac{\text{mol}}{\text{L}} \right) = 2 \text{ N}$$

$$\text{HCl} \quad \frac{1 \text{ equiv}}{\text{mol}} \cdot 1 \text{ M} = 1 \text{ N}$$

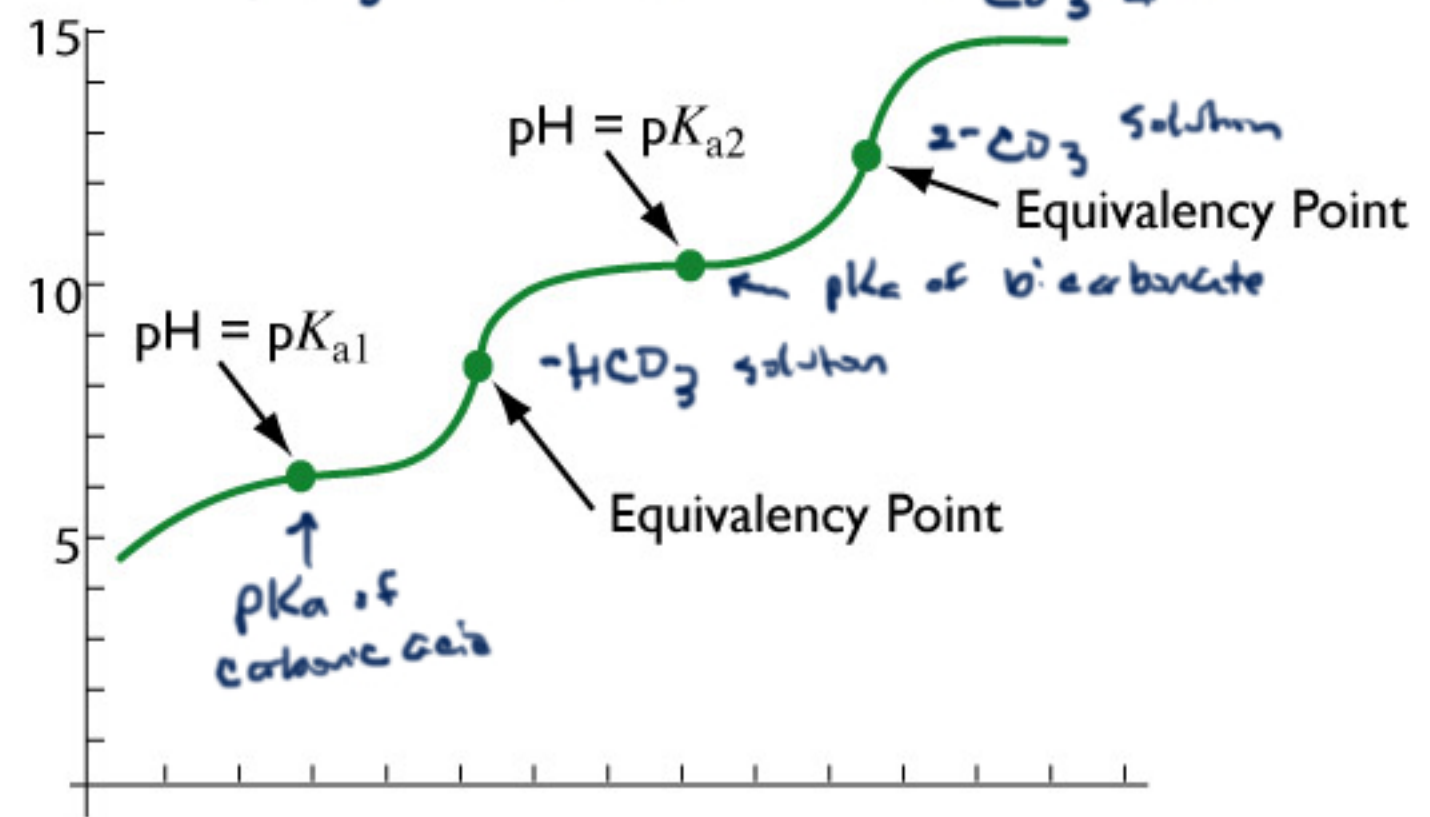
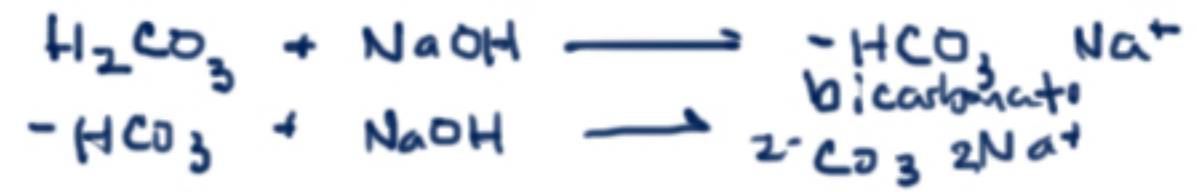
equivalency point -
when you add exactly
as many equivalents of
base as acid.



Titration of a Strong Acid with a Strong Base



Titration of a Weak Base with a Strong Acid



Titration of a Diprotic Acid with a Strong Base



Maintainance of acid-base balance in physiology

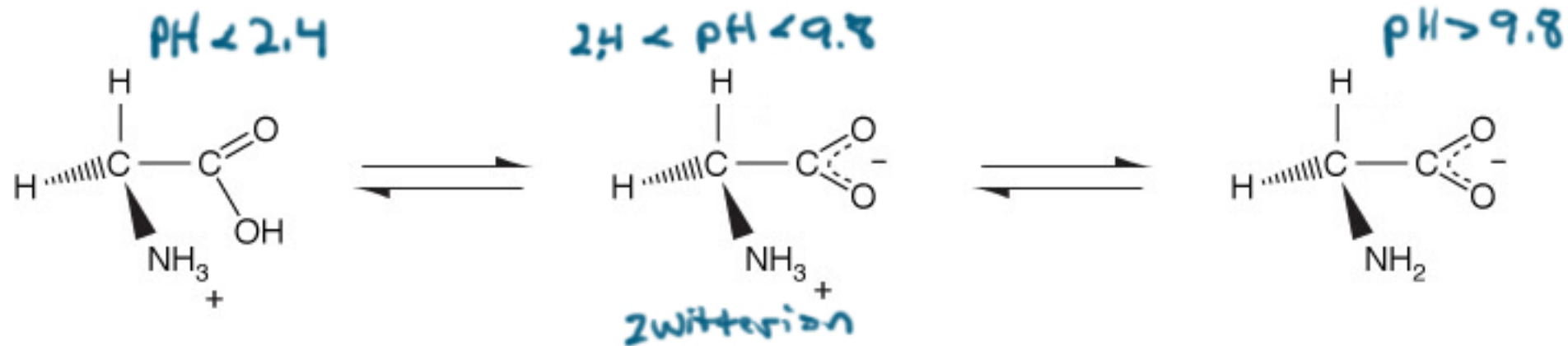
- Exhalation of CO_2
- Excretion of $H_2PO_4^-$ and NH_4^+ by the kidneys
- $NaHCO_3$ buffer system
- Secondary buffer systems including phosphates and proteins

Which results from combining a concentrated solution of HCl with concentrated K_2CO_3 ?

forms carbonic acid

- A. formation of a colored complex
- B. precipitation
- C. liberation of gas
- D. a solution of weak base



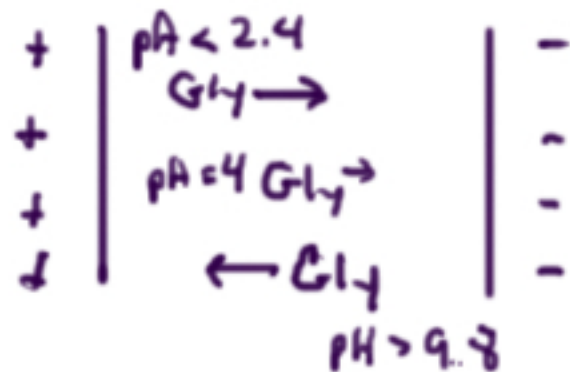


$$K_1 = \frac{[\text{H}^+][\text{HGly}]}{[\text{H}_2\text{Gly}^+]}$$

$$\text{p}K_1 = 2.4$$

$$K_2 = \frac{[\text{H}^+][\text{Gly}^-]}{[\text{HGly}]}$$

$$\text{p}K_2 = 9.8$$

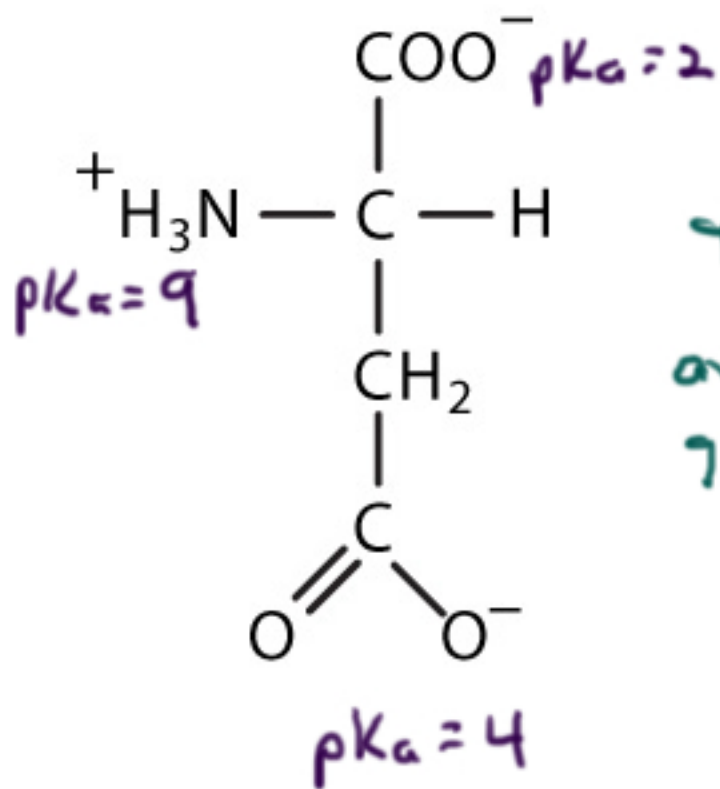


at pI it doesn't migrate

$$\frac{2.4 + 9.8}{2} = 6.1$$

$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$$

Aspartate



To find pI
average the like
groups.

$$\text{pI} = \frac{4 + 2}{2} = 3$$

(rough pKa's)

histidine side-chain

$pK_a \sim 6$

