

Acids & Bases;

pH, K_a , K_b , etc. ...



**Lecturer:
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Acids and Bases

Arrhenius –

An **acid** contains ‘H’ that ionises in water to give H^+ ion;

A **base** contains ‘OH’ that ionises in water to give OH^- ion.



OK for H_2SO_4 , HNO_3 , HClO_3 ...
and for KOH , Mg(OH)_2 ...

but what about ammonia, NH_3 ?

Svante Arrhenius
(1859–1927)

Brønsted–Lowry acids and bases

Brønsted–Lowry –

Acid can **donate** a proton.

Base can **accept** a proton.



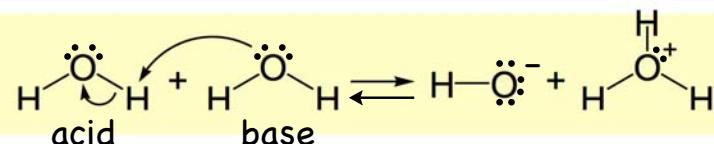
Johannes Brønsted
(1879–1947)



Thomas Lowry
(1874–1936)

Brønsted–Lowry definition of acids and bases

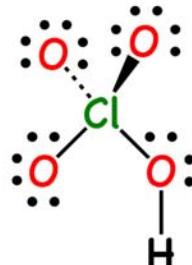
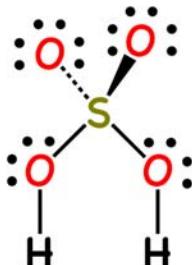
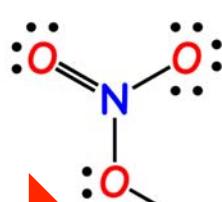
- An **acid** is a **proton donor**
- A **base** is a **proton acceptor**
- An **acid-base reaction** involves the **transfer of a single proton** from one species to another
- A Brønsted–Lowry acid may donate a proton to a Brønsted–Lowry base



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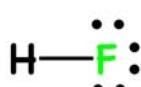
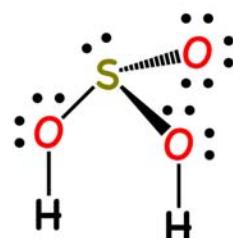
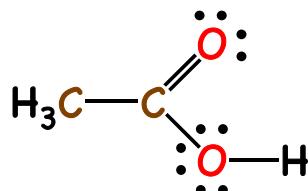
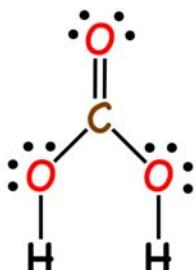
Some Brønsted acids

Strong acids... in water, complete H^+ dissociation



L3

Weak acids... in water, little H^+ dissociation



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HF

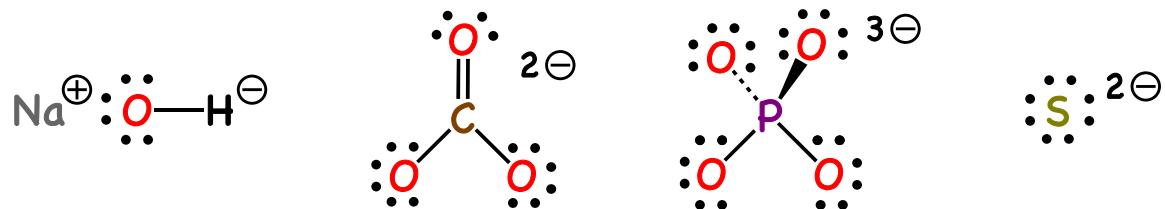


HF burns may not be evident till day after

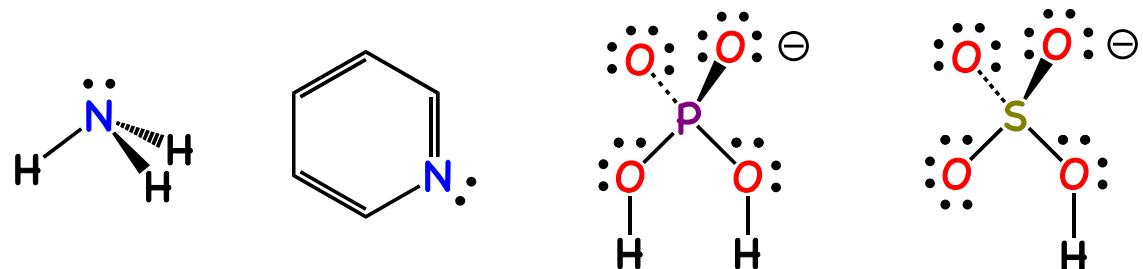
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Some Brønsted bases

Stronger bases... in water, complete dissociation of OH^- or almost complete reaction to give OH^-



Weak bases... in water, little reaction to give OH^-



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Acid-base reactions don't just occur in water – also occur in gas or (other) liquid or solid states

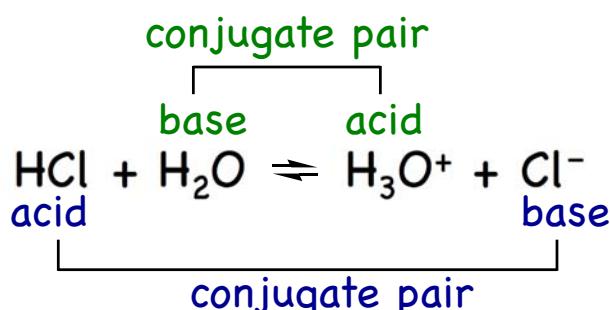
e.g.: ...



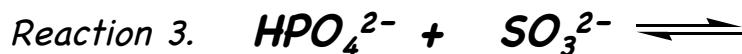
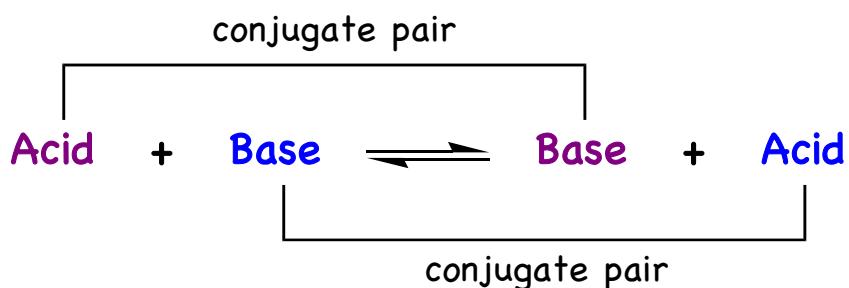
Brønsted-Lowry definition of acids and bases

- Conjugate acid-base pairs

- For Brønsted-Lowry acid-base reactions both the forward and reverse reactions are acid-base reactions
- There are always 2 sets of species on either side of the equation that differ by only one proton
- These are conjugate acid-base pairs



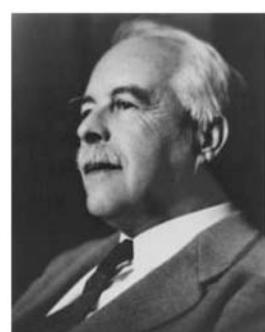
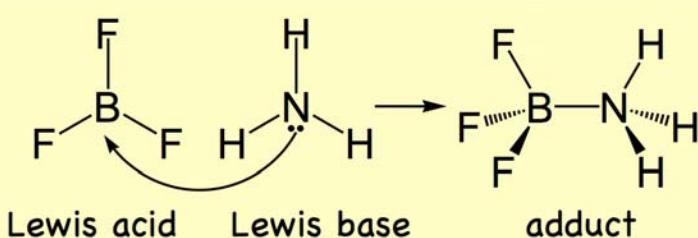
Acid — base conjugate pairs



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Lewis acids and bases

- A **Lewis acid** is an **electron-pair acceptor**
- A **Lewis base** is an **electron-pair donor**



Gilbert N Lewis
(1875–1946)

- Strength of Lewis acids and bases is not as readily quantified as Brønsted-Lowry counterparts

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Nature of H⁺ (aq)

What is H⁺ (aq)?

What is H⁺?

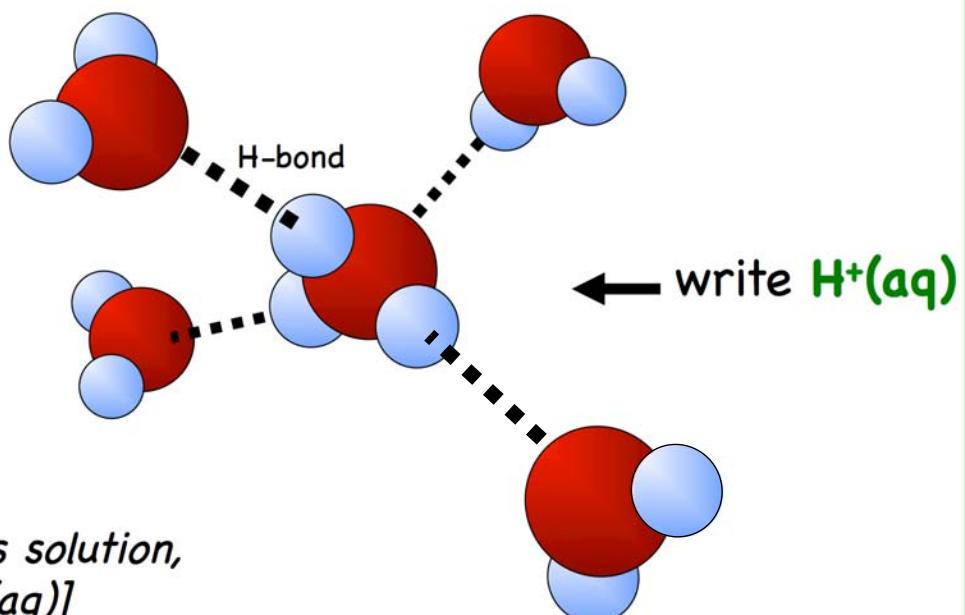
So could H⁺ exist in aqueous solution?

So what does H⁺(aq) mean?

What is H⁺(aq)?

Nature of H⁺ (aq)

H⁺ (aq): a bare proton has *NO existence*; it is always solvated... simplest species is H(H₂O)₅⁺



The concept of pH

p(Anything) =
-log(Anything)

- ◆ To avoid working with inconveniently small numbers we commonly express $[H^+]$ in terms of the pH of the solution



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

- ◆ log means \log_{10} , as opposed to natural logarithms (\ln or \log_e)

$$[H^+] = 10^{-\text{pH}}$$
$$[OH^-] = 10^{-\text{pOH}}$$

pH

Can you have a
negative pH ?



- The pH scale is typically between 0 (i.e. $[H^+] = 1 \text{ mol L}^{-1}$) and 14 ($[H^+] = 10^{-14} \text{ mol L}^{-1}$)
- Example
What is the pH of a solution of $[H^+] = 3.7 \times 10^{-4} \text{ M}$?

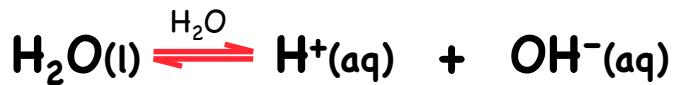
Answer

$$\text{pH} = -\log_{10}(3.7 \times 10^{-4} \text{ M}/1 \text{ M}) = 3.43$$

(i.e. 2 sig figs **after** the decimal point)

Water equilibrium & the pH scale

Pure water – is almost a **non-electrolyte**; only trace **self-ionisation**



Define...

dissociation constant
for water (K_w)

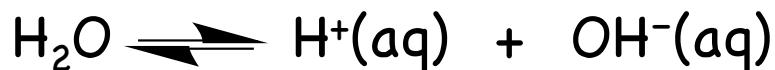
$$K_w = [\text{H}^+][\text{OH}^-]$$

$$= 1.008 \times 10^{-14}$$

pure water
at 25 °C

Neutral water

For self-ionization of water



$$K_w = 1.0 \times 10^{-14} = [\text{H}^+][\text{OH}^-]$$

In neutral water: $[\text{H}^+] = [\text{OH}^-]$

So substituting $[\text{H}^+]$ for $[\text{OH}^-]$ into K_w ,

$$\text{get } [\text{H}^+]^2 = 1.0 \times 10^{-14}$$

$$\text{so } [\text{H}^+] = (1.0 \times 10^{-14})^{1/2} = 1.0 \times 10^{-7} \text{ mol L}^{-1}$$

$$\text{and pH} = -\log [\text{H}^+] = 7.0$$

Typical pH's

- Pure water at 25 °C

- $\text{pH} = -\log[\text{H}^+] = -\log(1.0 \times 10^{-7}) = 7.00$
- $\text{pOH} = -\log[\text{OH}^-] = -\log(1.0 \times 10^{-7}) = 7.00$

L4

- Acidic solutions

- $[\text{H}^+] > [\text{OH}^-]$
- At 25 °C $\text{pH} < 7$

- Basic solutions

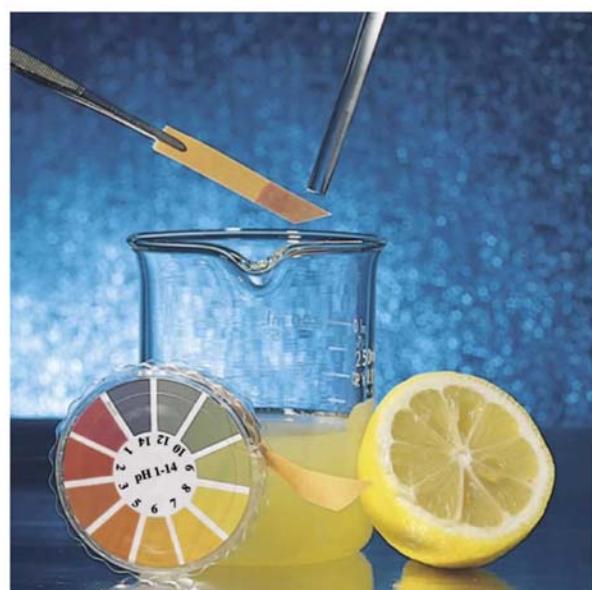
- $[\text{H}^+] < [\text{OH}^-]$
- At 25 °C $\text{pH} > 7$

Measuring pH

Use...



pH meter



indicator paper

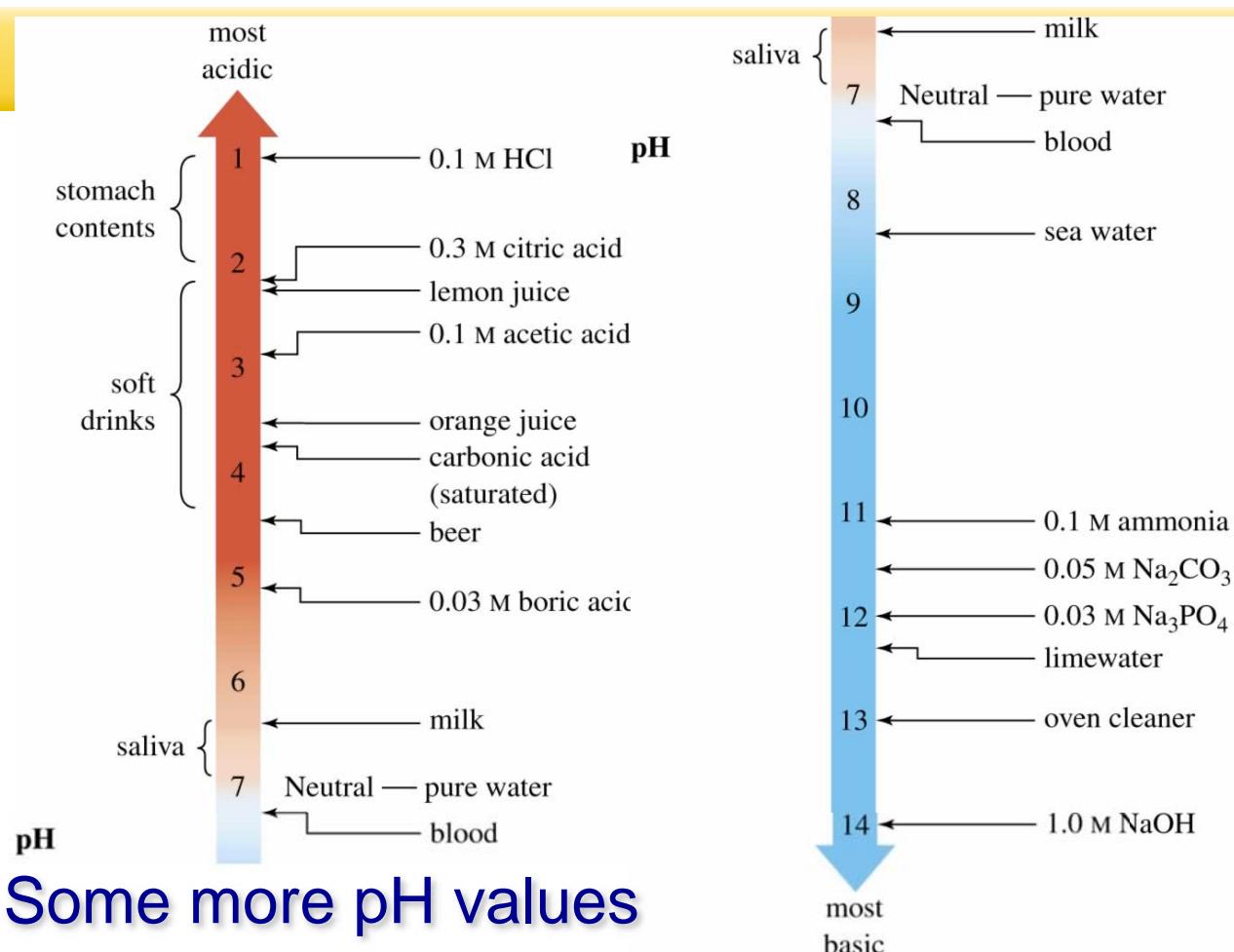
pH of aqueous solutions

- Pure water exposed to air eventually has a pH of about 5.5 because of dissolved carbon dioxide ($\rightarrow \text{H}_2\text{CO}_3$ = carbonic acid)
- Blood is around pH 7.4
- Spit is \sim pH 6.5
- Gastric juice in the stomach is pH 1 to 2

A note about significant figures — because pH is a logarithm, the number of significant figures in the concentration is the number of figures **after** the decimal point of the pH

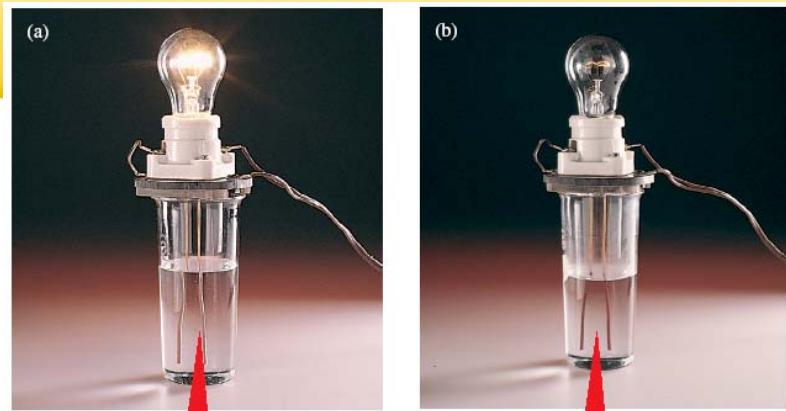


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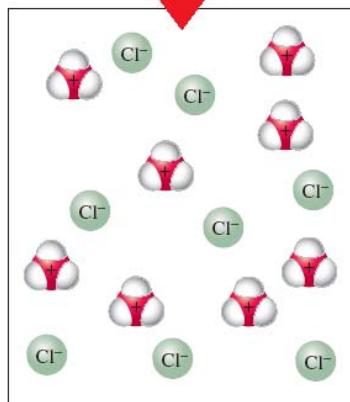


acid/base strengths

Dissociation produces ions and **increases** the electrical conductivity of a solution

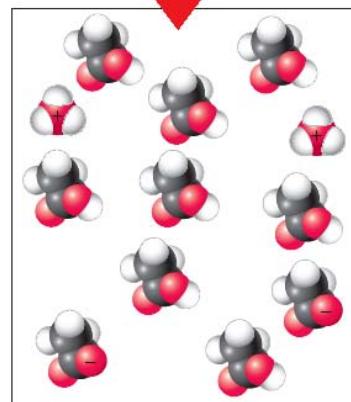


Strong acids and bases dissociate completely



All the HCl reacts with water, so there are many ions present.

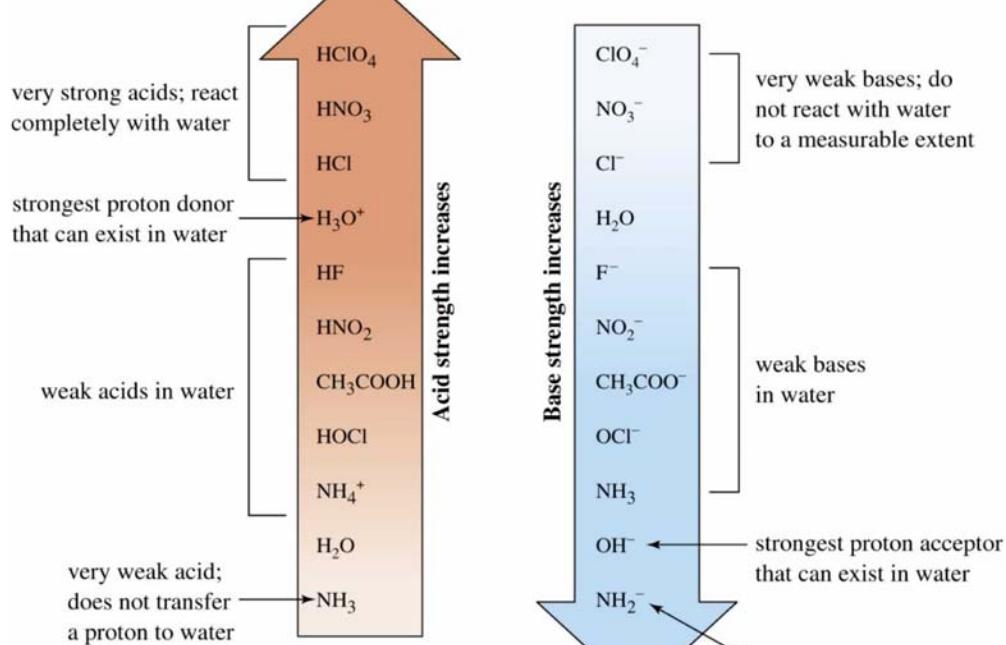
For weak acids and bases only a small fraction of the molecules dissociate



Only a small fraction of the acetic acid reacts with water, so there are few ions to conduct electricity. Most of the acetic acid is present as neutral molecules of CH_3COOH .

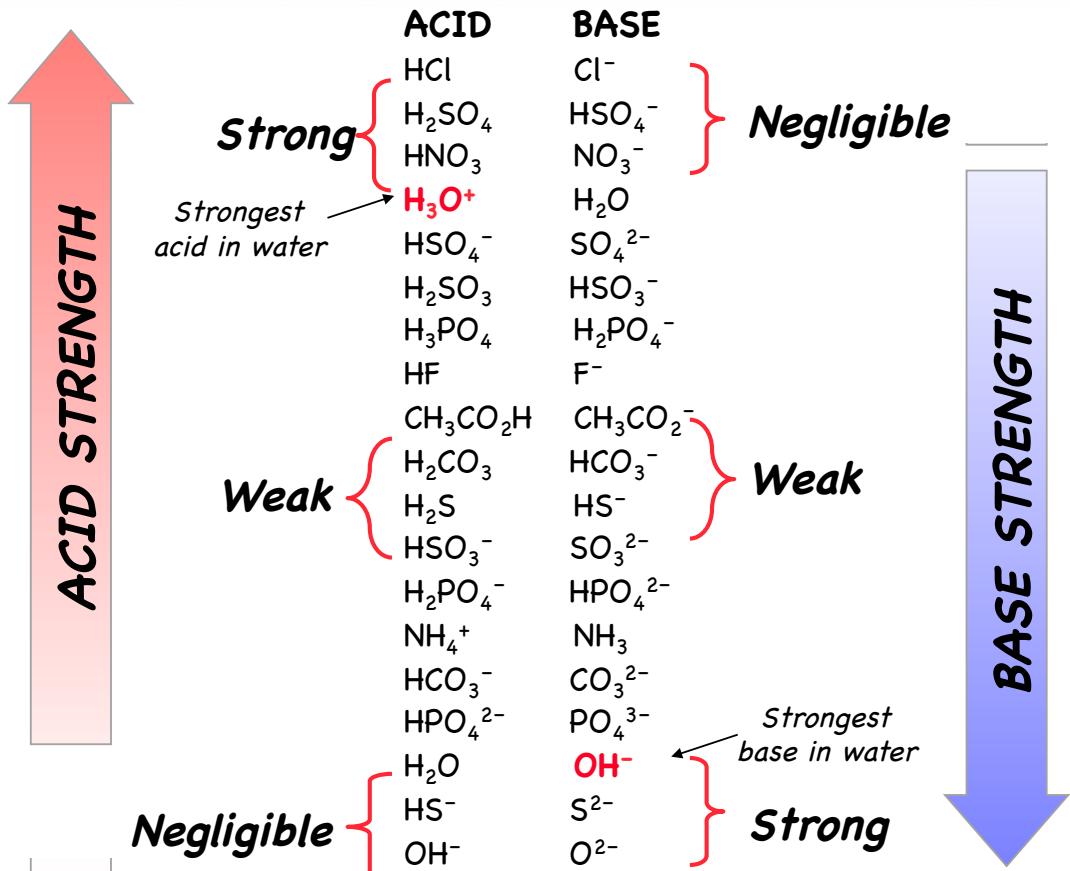
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There is an inverse relationship between the strengths of the acid and base members of a conjugate pair



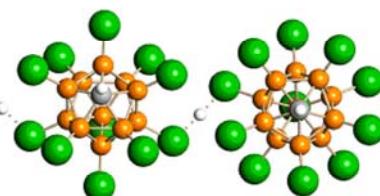
stronger acid → weaker conjugate base
weaker acid → stronger conjugate base

Relative (conjugate) acid/base strengths



The world's strongest acids

> million times stronger
than H₂SO₄



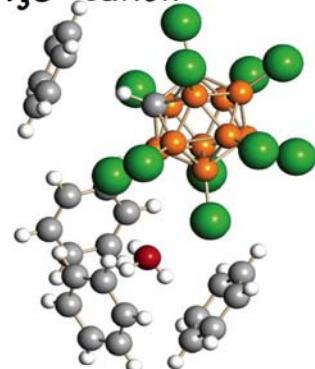
Chris Reed,
New Zealander,
works USA
@uc.riverside

Carborane 'superacids'

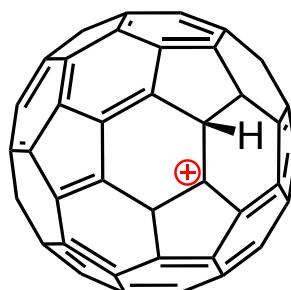
Angew. Chem. Int. Ed. 2004, 43, 5352

Chem. Commun. 2005, 1669

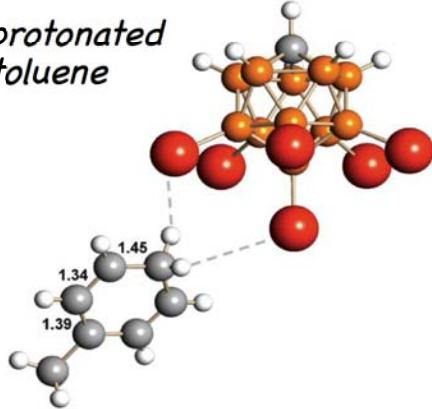
benzene-solvated
 H_3O^+ cation



C_{60}H^+ cation



protonated
toluene



J. Am. Chem. Soc. 2005, 127, 7664

Science, 2000, 289, 101

J. Am. Chem. Soc. 2003, 125, 1796

Direction of acid/base reactions

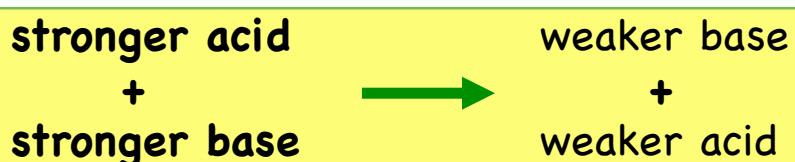


e.g. Do chlorate and ammonium ions react together
or does ammonia react with chloric acid?

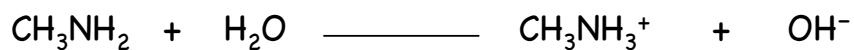
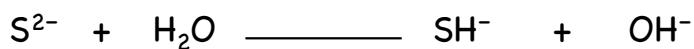
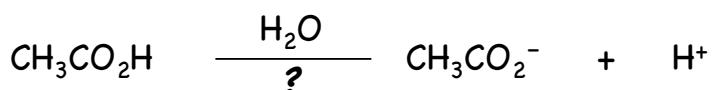
?

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Direction of acid/base reactions



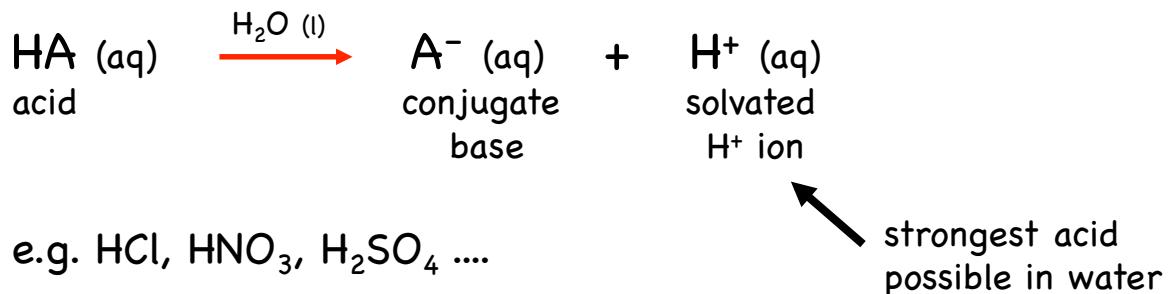
Examples: predict the reaction direction? (draw arrows)



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Strong acids in water

Strong acids – dissociate completely in water



$$\begin{aligned}\text{so pH} &= -\log [\text{H}^+] \\ &= -\log [\text{acid}]\end{aligned}$$

Acid strength in water

Weak acids – incomplete dissociation, equilibrium established



define
acid dissociation constant (K_a)

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

← for a dilute (ideal) solution

Acid strength:

larger K_a ⇒ stronger acid

Relationship between K_a and pK_a

$$pK_a = -\log_{10} K_a$$

Acid

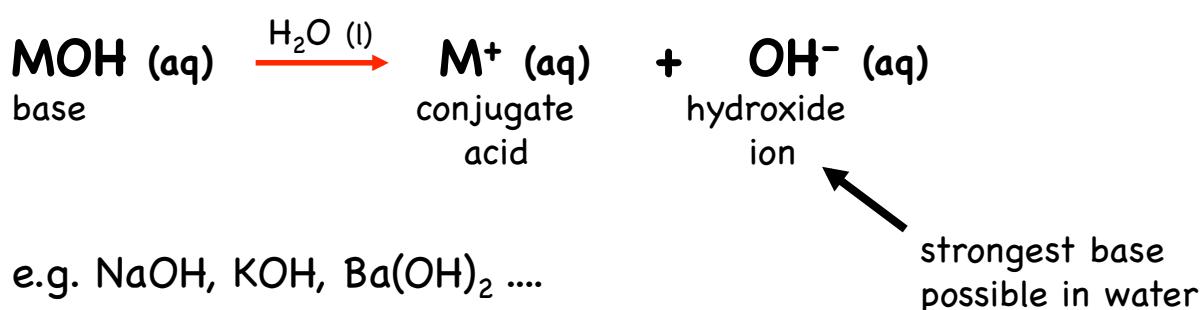
Hydrogen sulfate ion (HSO_4^-)
Nitrous acid (HNO_2)
Acetic acid (CH_3COOH)
Hypobromous acid (HBrO)
Phenol ($\text{C}_6\text{H}_5\text{OH}$)

$K_a @ 25^\circ\text{C}$	pK_a
1.0×10^{-2}	2.00
7.1×10^{-4}	3.15
1.8×10^{-5}	4.74
2.3×10^{-9}	8.64
1.0×10^{-10}	10.00

stronger acid
(higher K_a ; lower pK_a)

Strong bases in water

Strong bases – dissociate completely in water



$$\begin{aligned} \text{so } p\text{OH} &= -\log [\text{OH}^-] \\ &= -\log [\text{base}] \end{aligned}$$

Base strength in water

Weak bases – incomplete dissociation,
equilibrium established



define
BASE dissociation
constant (K_b)

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

for a dilute
(ideal) solution

Base strength:

larger K_b \Rightarrow stronger base

Relationship between K_b and pK_b

$$pK_b = -\log_{10} K_b$$

N-Base

Methylamine (CH_3NH_2)
Ethanolamine ($HOCH_2CH_2NH_2$)
Ammonia (NH_3)
Pyridine (C_6H_5N)
Aniline ($C_6H_5NH_2$)

$K_b @ 25^\circ C$	pK_b
4.4×10^{-4}	3.36
3.2×10^{-5}	4.49
1.76×10^{-5}	4.754
2.3×10^{-9}	8.64
4.0×10^{-10}	9.40



**stronger
base**
(higher K_b ; lower pK_b)

Inter-relationships ~ pH, pOH, K_w , K_a , K_b

for any solution (at 25 °C (298 K)):

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

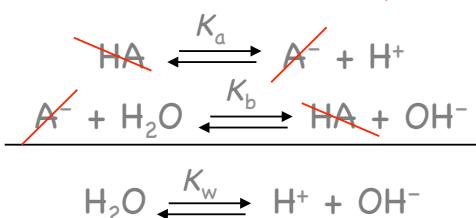
$$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+]$$

$$\text{pOH} = -\log_{10}[\text{OH}^-]$$

$$\text{pH} + \text{pOH} = 14.0$$

Learn these

for any {
base - conjugate acid
acid - conjugate base } pair:



So: $K_w = K_a \times K_b$ which gives: $\text{p}K_a + \text{p}K_b = \text{p}K_w = 14.0$ at 298 K

Calculations pH, pOH, $[\text{H}^+]$, $[\text{OH}^-]$

1. Strong acids

Q. Calculate the pH and $[\text{OH}^-]$ of 0.01 M HCl

A. Solution. HCl (aq) \longrightarrow H^+ (aq) + Cl^- (aq)

- strong acid \Rightarrow dissociation is 100% complete
- assume $[\text{H}^+]$ from dissociation of water ($\ll 10^{-7}$ M) is *negligible*

So $[\text{H}^+] = 0.01 \text{ M}$

$$\text{pH} = -\log_{10}(1.0 \times 10^{-2}) =$$

$$\text{pOH} = 14 - \text{pH} =$$

$$[\text{OH}^-] =$$

Calculations pH, pOH, [H⁺], [OH⁻]

2. Strong bases

Q. Calculate the pH of 0.01 M NaOH

A. Solution. NaOH (aq) \longrightarrow Na⁺ (aq) + OH⁻ (aq)

- strong base \Rightarrow dissociation is 100% complete

$$[\text{OH}^-] = 0.01 \text{ M} = 10^{-2} \text{ M},$$

$$\text{so } \text{pOH} = \quad \text{and } \text{pH} = 14 - \text{pOH} =$$

3. Weak acids

Q. Calculate the pH and % ionization in 0.10 M acetic acid (K_a (HOAc) = 1.80×10^{-5})

A. <u>Solution</u>	HOAc	$\xrightleftharpoons{\text{H}_2\text{O}}$	H ⁺	+	OAc ⁻
Initial	0.10		0		0
Change	- x		+ x		+ x
Final (equilbm)	$0.10 - x \approx 0.1$		+ x		+ x

KEY ASSUMPTION: Acid is WEAK, so **x** is VERY SMALL compared to 0.10, and **so negligible**. Therefore: $0.1 - x \approx 0.1$

$$K_a = \frac{[\text{H}^+][\text{OAc}^-]}{[\text{HOAc}]} = \frac{x^2}{0.10} = 1.80 \times 10^{-5}$$

Solve x = [H⁺] =

Assumption OK
(to within $\pm 5\%$)

so pH = $-\log_{10} () =$

$$\begin{aligned}\% \text{ ionization} &= \frac{[\text{acid dissociated}]_{\text{equilbm}}}{[\text{acid}]_{\text{initial}}} \times 100 = \frac{[\text{OAc}^-]_{\text{equilbm}} \times 100}{[\text{HOAc}]_{\text{initial}}} \\ &= () / \times 100/1 =\end{aligned}$$

Weak acid (HA) calcs cont'd

- When K_a is small, can always make the assumption ...

$$[\text{HA}] - x \approx [\text{HA}] \quad \text{where } [\text{HA}] = [\text{HA}]_{\text{initial}}$$

Then $K_a = \frac{x^2}{[\text{HA}]}$ where $x = [\text{H}^+]$

so $x = \sqrt{K_a [\text{HA}]} = [\text{H}^+]$

or $\text{pH} = \frac{1}{2} \text{p}K_a - \frac{1}{2} \log_{10}[\text{HA}]$

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Q. Calculate the pH in 0.10 M acetic acid
($K_a (\text{HOAc}) = 1.80 \times 10^{-5}$)

$$K_a = \frac{x^2}{[\text{HA}]}$$

So the working for the previous problem becomes ...

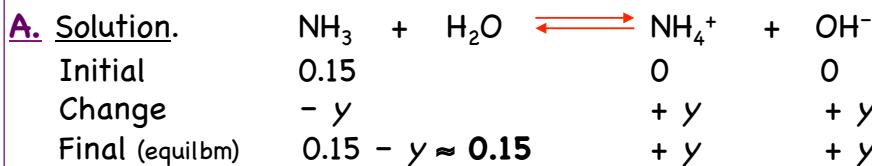
$$\begin{aligned} [\text{H}^+] &= x = (K_a \times [\text{HA}])^{1/2} \\ &= ()^{1/2} \\ &= \end{aligned}$$

$$\begin{aligned} \text{pH} &= -\log [\text{H}^+] \\ &= \end{aligned}$$

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4. Weak bases

Q. Calculate the pH and % ionization in 0.15 M ammonia (K_b (NH_3) = 1.60×10^{-5})



Key assumption: NH_3 is a weak base, so y will be negligible compared to the initial $[\text{NH}_3]$

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{y^2}{0.15} =$$

Solve $y = [\text{OH}^-] = ()^{1/2} =$

so $\text{pOH} = -\log_{10} () =$

and $\text{pH} = 14 - \text{pOH} = 14.00 - =$

Assumption OK
(to within $\pm 5\%$)

$$\% \text{ ionization} = \frac{[\text{conjugate ion}]_{\text{equilbm}}}{[\text{base}]_{\text{initial}}} \times \frac{100}{1} = \frac{[\text{NH}_4^+]_{\text{equilbm}}}{[\text{NH}_3]} \times \frac{100}{1}$$
$$= () / \times 100/1 =$$

Weak base (B) calcs cont'd

- If K_b is small, then can always make the assumption... $[B] - y \approx [B]_{\text{initial}}$

Then $K_b = \frac{y^2}{[B]}$ where $y = [\text{OH}^-]$

so $y = \sqrt{K_b[B]} = [\text{OH}^-]$

or $\text{pOH} = \frac{1}{2} \text{p}K_b - \frac{1}{2} \log_{10}[B]$

Q. Calculate the pH in 0.15 M ammonia
(K_b (NH_3) = 1.60×10^{-5})

$$K_b = \frac{y^2}{[B]}$$

So the working for the previous problem becomes ...

$$\begin{aligned} [\text{OH}^-] &= y = (K_b \times [B])^{1/2} \\ &= (\quad \quad \quad \times \quad \quad \quad)^{1/2} \\ &= \end{aligned}$$

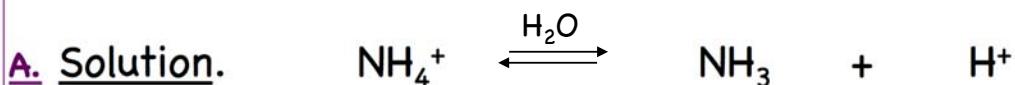
$$\text{pOH} = -\log [\text{OH}^-] =$$

$$\text{pH} = 14.00 - \text{pOH} =$$

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5. K_a , K_b ...

Q. Calculate the pK_a of ammonium ion given that 0.2 M NH_4Cl solution has a pH of 5.0.



Weak Acid, so use... $K_a = x^2/[\text{HA}]$ (where $x = [\text{H}^+]$)

Therefore...

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

$$= -\log[\text{H}^+]^2 + \log[\text{HA}]$$

$$= 2(\text{pH} + \frac{1}{2}\log[\text{HA}])$$

$$= 2(\quad + \frac{1}{2}\log \quad) =$$

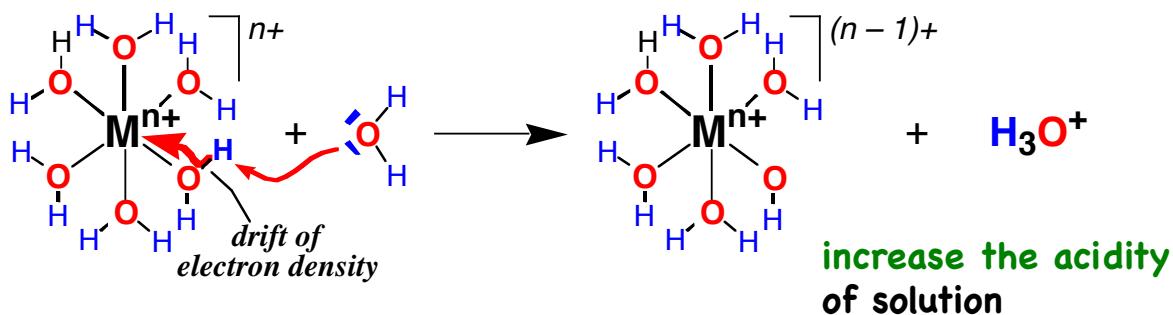
L5

$$\log x^y = y \log x$$

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pH of salt solutions: Cation hydrolysis

(a) polarising metal ions (all M^{z+} except Na^+ , K^+ , Rb^+ , Cs^+ ; Ca^{2+} , Sr^{2+} , Ba^{2+})



(b) cations from weak bases

weak base \Rightarrow cation is a weak – moderate conjugate acid

\therefore cations **increase the acidity of solution** (lower the pH)

e.g. ammonium ion



(NH_3 weak base $\Rightarrow NH_4^+$ "gives up" H^+)

Anion hydrolysis

(a) anions from strong acids

strong acid \Rightarrow anion is a very weak conjugate base

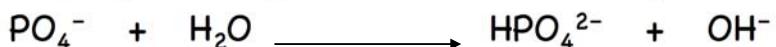
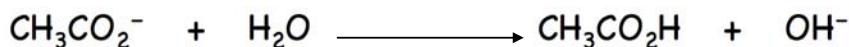
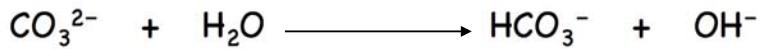
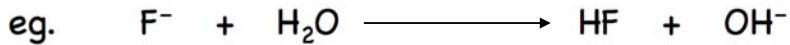
\therefore no reaction with water (**do not alter the pH**)

e.g. Cl^- , Br^- , I^- , NO_3^- , ClO_3^- , ClO_4^- , etc.

(b) anions from weak acids

weak acid \Rightarrow anion is weak – moderate conjugate base

\therefore **increase basicity** of solution (raise the pH)



↑
anions (= conjugate base) weak acids

pH of salts: qualitative prediction

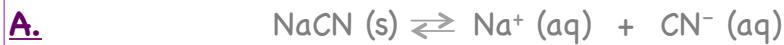
1. Anion from strong acid, cation from strong base $\text{pH} = 7$
(e.g. NaCl, KNO₃)
2. Anion from weak acid, cation from strong base $\text{pH} > 7$
(e.g. CH₃COONa, NaF)
3. Anion from strong acid, cation from weak base $\text{pH} < 7$
(e.g. NH₄Cl, NH₄NO₃)
4. Anion from weak acid, cation from weak base
If K_a (acid) > K_b (base) $\text{pH} < 7$
 K_a (acid) < K_b (base) $\text{pH} > 7$
 K_a (acid) = K_b (base) $\text{pH} = 7$

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pH of salts: calculations

Example question

Q. Calculate the pH of 0.1 M NaCN given $\text{p}K_a$ (HCN) = 9.22.



So need K_b ...

From $\text{p}K_a$ (HCN): $\text{p}K_a = 9.22$

$$\text{so: } \text{p}K_b (\text{CN}^-) = 14.00 - 9.22 = 4.78$$

$$\text{Therefore: } K_b (\text{CN}^-) = 10^{-4.78} = y^2 / [\text{CN}^-] \text{ where } y = [\text{OH}^-] = [\text{HCN}]$$

$$\text{Solve for } y: y = [\text{OH}^-] = (0.1 \times 10^{-4.78})^{1/2} (= 1.28 \times 10^{-3} \text{ M})$$

$$\text{so: } \text{pOH} = -\log_{10} [\text{OH}^-] = 2.89$$

$$\text{and: } \text{pH} = 14 - \text{pOH} = 14.00 - 2.89 = 11.11 \leftarrow \text{basic as expected}$$

Buffers

Mixture of acid + salt



Some of
this ...

fixes this

... and some of
this

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

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

So...

$$\text{pH} = \text{p}K_a + \log_{10} \frac{[\text{A}^-]}{[\text{HA}]} \text{ ...is } \underline{\text{constant}}$$

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How buffers work

Buffers resist pH change

(when small amounts of acid or base are added)



↑
Add OH^- –
reacts with HA and
 $\text{pH} \approx \text{constant}$

↑
Add H^+ –
reacts with A^- and
 $\text{pH} \approx \text{constant}$



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Some buffers

Buffers resist pH change

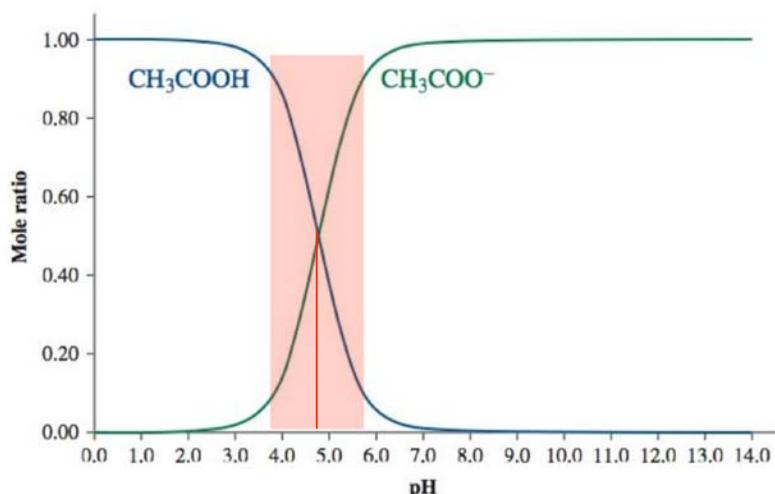
(when small amounts of acid or base are added)

Examples:

	pK_a
HClO_2 & ClO_2^-	2.0
HNO_2 & NO_2^-	3.4
$\text{CH}_3\text{CO}_2\text{H}$ & CH_3CO_2^-	4.7
H_2PO_4^- & HPO_4^{2-}	7.2
CO_2 & HCO_3^- (<i>blood</i>)	7.4
NH_3 & NH_4^+	9.3

Buffers

Since a buffer must have roughly equal concentrations of acid/conjugate base, it can only function at pH's close to the pK_a of the acid.

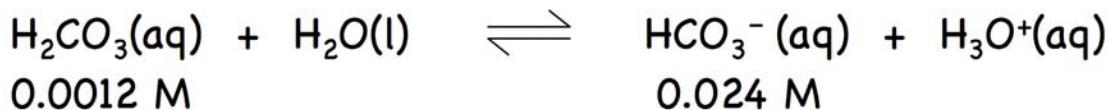


Real life example of a buffer



Human blood has a pH of 7.25 – 7.45. If your blood pH falls **below 6.8**, or rises **above 7.8** you may well be dead!

The major buffer system that controls your blood pH is the $\text{H}_2\text{CO}_3 : \text{HCO}_3^-$ buffer.



$$[\text{HCO}_3^-] / [\text{H}_2\text{CO}_3] = 20$$

Analysis of Buffers

We can use the expression for K_a directly in the Henderson – Hasselbalch equation

$$\text{pH} = \text{pK}_a + \log_{10} \frac{[\text{A}^-]}{[\text{HA}]}$$

in general, this
is the base ...

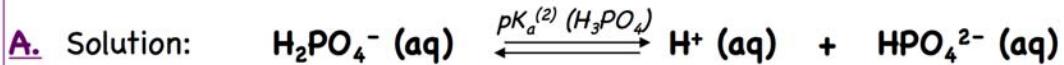
and this the acid

You can remember the sign and which way up
they go, as the more base, the higher the pH



Calculation — pH of buffers

Q. Calculate the pH of a solution of 0.04 M Na_2HPO_4 (aq) and 0.08 M KH_2PO_4 (aq) given $\text{p}K_a^{(2)}(\text{H}_3\text{PO}_4) = 7.21$



Initial	0.08	0	0.04
Change	- x	+ x	+ x
Final _(equilb)	$0.08 - x \approx 0.08$	+ x	$0.04 + x \approx 0.04$

$$\text{pH} = \text{p}K_a + \log_{10} \frac{[\text{base}]_{\text{initial}}}{[\text{acid}]_{\text{initial}}}$$

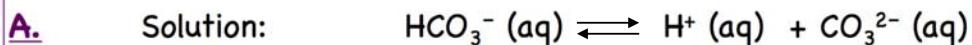
← start here

$$\begin{aligned}\text{pH} &= \text{p}K_a^{(2)} + \log_{10} [\text{HPO}_4^{2-}]/[\text{H}_2\text{PO}_4^-] \\ &= \quad + \log_{10} (\quad / \quad) \\ &= \end{aligned}$$

Henderson-Hasselbalch equation, base on top;
simplifying assumption:
use initial concentrations

Calculations — preparing a buffer

Q. What mass of Na_2CO_3 must be added to 500 mL of 0.40 M NaHCO_3 (aq) to give a pH 9.50 buffer solution? ($\text{p}K_a^{(2)}(\text{CO}_2) = 10.25$)



$$\begin{aligned}K_a^{(2)} &= [\text{CO}_3^{2-}][\text{H}^+]/[\text{HCO}_3^-] \\ \text{rearrange ...} \quad [\text{CO}_3^{2-}] &= (K_a^{(2)} \times [\text{HCO}_3^-])/\text{[H}^+\text{]} \quad [\text{H}^+] = 10^{-\text{pH}} \\ &= (10^{-10.25} \times 0.40)/10^{-9.50}\end{aligned}$$

$$\begin{aligned}\Rightarrow n(\text{Na}_2\text{CO}_3) &= c \times V \\ &= (10^{-10.25} \times 0.40)/10^{-9.50} \times 500/1000 \\ &= 0.036 \text{ mol}\end{aligned}$$

$$\Rightarrow m(\text{Na}_2\text{CO}_3) = n \times M = \frac{\text{x}}{\text{Molar mass}} = \text{g}$$



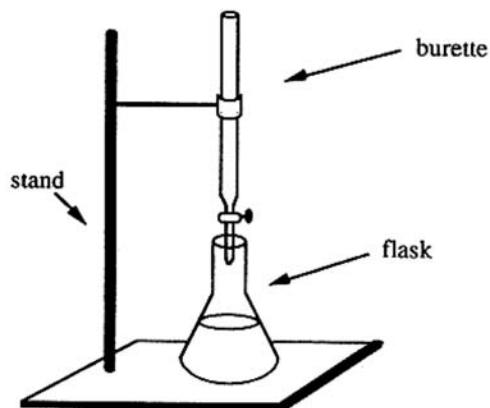
Despite the heavy flak, McAlister's aim was true, and his carefully measured aliquot of hydrochloric acid found its mark deep in the enemy's reservoir of sodium hydroxide.



McAlister grinned wryly: finally, one of the enemy's strongest bases had been completely neutralized.

Titrations

- Titrations are used to determine the concentration of an unknown solution by reacting a known volume with a standard solution (ie. known concentration) of a reactant
- Usually the standard is in the burette and titrates a known volume of the test solution pipetted into a conical flask



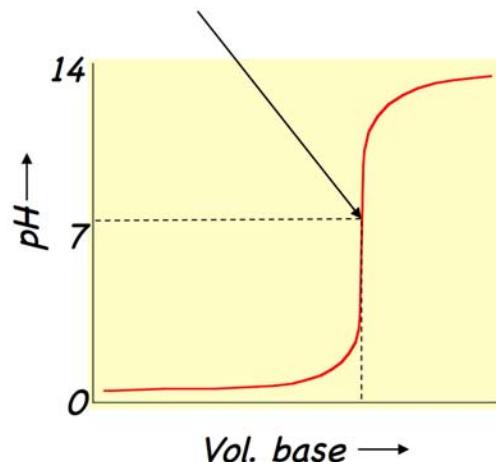
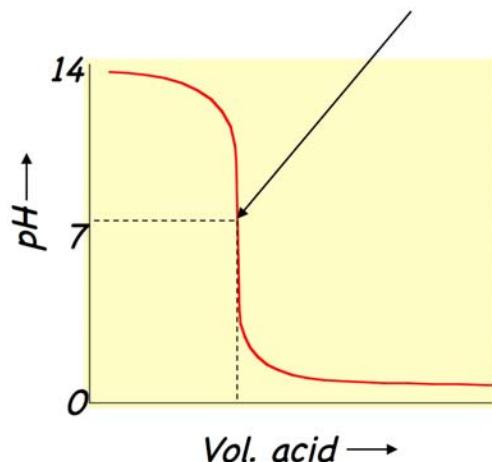
Titrations

1. strong base + strong acid or strong acid + strong base

at equivalence point

$$[\text{H}^+] = [\text{OH}^-] \text{ so... } \text{pH} = 7.0$$

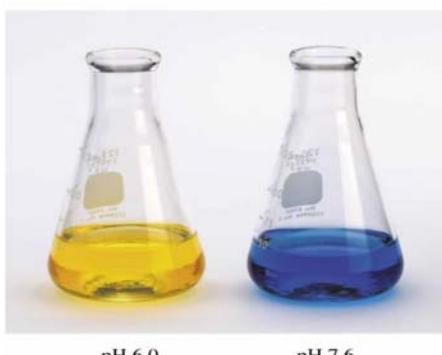
(equal amounts of acid & base in solution)



Calculations – must account for:

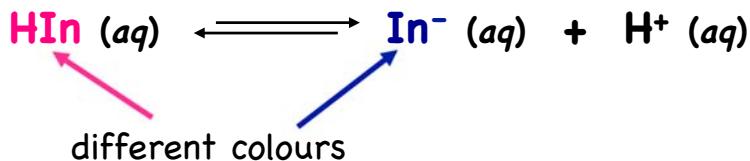
1. neutralisation ($\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$)
2. dilution

Indicators



Acid-base indicators

= weak acids or weak bases with chromophores that change colour with pH

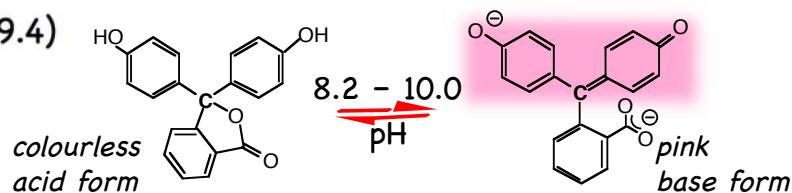


- *change colour at: $\text{pH} = \text{p}K_a(\text{indicator}) \pm 1$*
- *examples*

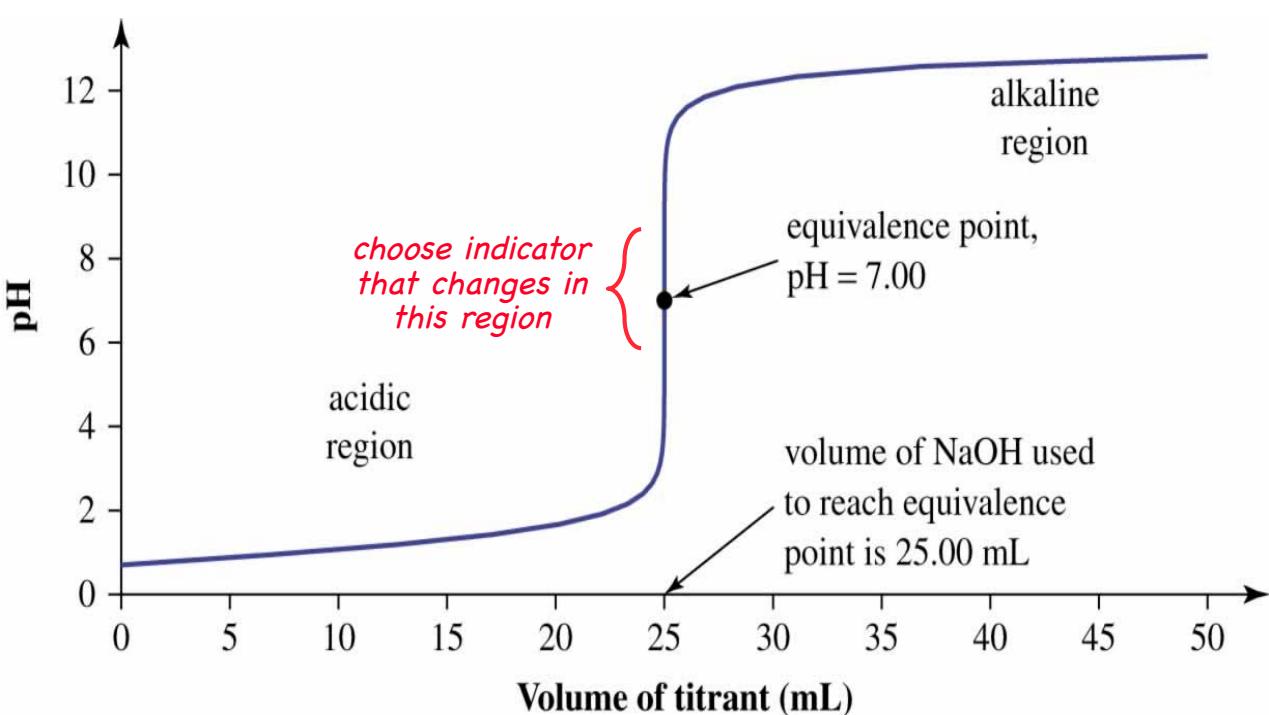
bromophenol blue ($\text{p}K_a$ 3.9): yellow $\xrightarrow[\text{pH}]{3.0 - 4.6}$ blue

litmus ($\text{p}K_a$ 6.5): red $\xrightarrow[\text{pH}]{5.0 - 8.0}$ blue

phenolphthalein ($\text{p}K_a$ 9.4)



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Acid-base indicators

The pK_{In} of an indicator should be equal or close to the pH at the equivalence point, i.e. we want the **endpoint** (where the colour changes) to be close to the equivalence point.

When performing a titration we want to use as little indicator as possible.



pH 4.8 pH 5.4

methyl purple

Titrations

- The concentration of the unknown acid or base may be calculated from the **endpoint** of an acid-base titration
- For $H^+ \text{ (acid)} + OH^- \text{ (base)} \rightarrow H_2O$

at the **equivalence point**:

$$n \text{ (acid)} = n \text{ (base)} \text{ in mol}$$

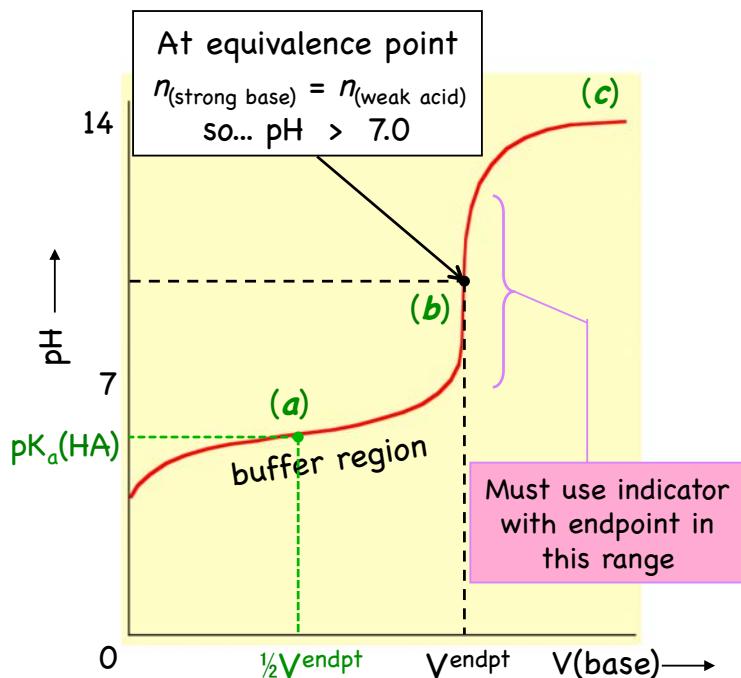
so $C_A V_A = C_B V_B$

note: not $n(H^+) = n(OH^-)$
since endpoint isn't at pH=7
for titrations with weak acids
or weak bases

where c_A is the concentration of acid and c_B is the concentration of base and V_A (V_B) are the volume(s) of A (B) at the **equivalence point**

Titrations

Strong base added to weak acid



Calculations

account for dilution,
neutralisation and –

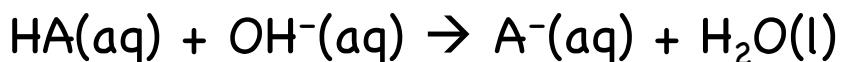
(a) before equivalence point: the solution contains HA and A⁻
⇒ buffer region
– *treat as a buffer* –

(b) at the equivalence point:
the solution only contains
A⁻ (the conjugate base)
⇒ basic ($\text{pH} > 7.0$)
– *treat as a salt of A⁻* –

(c) after the equivalence point:
the solution contains excess
OH⁻ (from the base)
⇒ basic ($\text{pH} \gg 7.0$)
– *treat as a strong base* –

Obtaining pK_a (pK_b)

For titration of a weak acid (HA) with a strong base:



At endpoint ($V_{\text{OH}^-}^{\text{endpoint}}$): $n(\text{OH}^-) = n(\text{HA})$

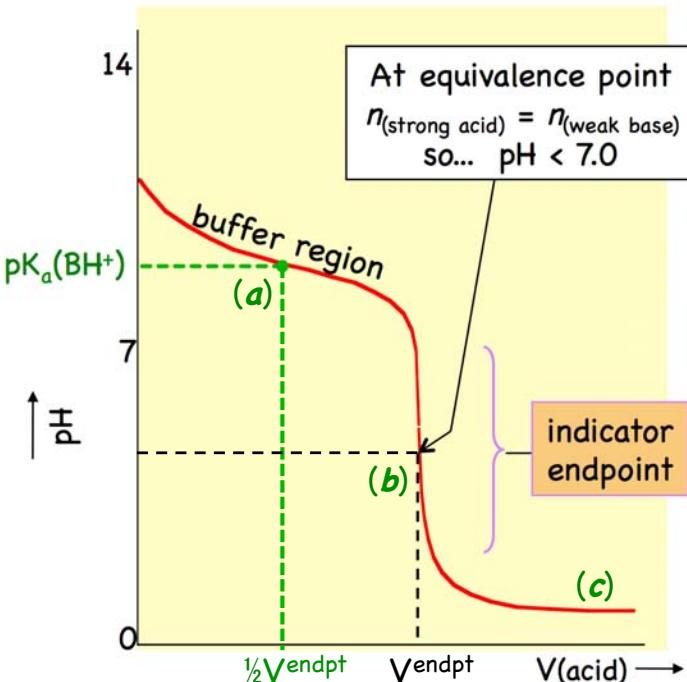
i.e., all HA is converted to A⁻

So at $\frac{1}{2} V_{\text{OH}^-}^{\text{endpoint}}$: half the weak acid is neutralised
i.e., $n(\text{HA}) = n(\text{A}^-)$
and the solution acts as a buffer

so $\text{pH} = \text{pK}_a + \log ([\text{A}^-]/[\text{HA}])$
becomes $\text{pH} = \text{pK}_a$ (since $\log 1 = 0$)

Titrations

Strong acid added to weak base



Calculations

account for dilution , neutralisation and –

(a) before equivalence point:
the solution contains
 BH^+ and B (or HA & A^-)
⇒ buffer region
– treat as a buffer –

(b) at the equivalence point:
the solution only contains
 BH^+ (conjugate acid) (or HA)
⇒ acidic ($\text{pH} < 7.0$)
– treat as weak acid –

(c) after the equivalence point:
the solution contains
excess H^+ (from the acid)
⇒ acidic ($\text{pH} \ll 7.0$)
– treat as a strong acid –

How should I study for this topic?

THINK CRITICALLY!!

Ask yourself: Do I understand everything presented? Can I do all the problems... from lectures, worksheets & tutes?

Try to understand the material...
(use the syllabus & lectures as a guide)

Attend lectures, do worksheets...

Read lecture notes & textbook ...

Do some more problems ...
(from tutorials, textbook & sample exams)

Do some more problems ...



repeat till you
understand it all!!