

MSJChem

Tutorials for IB Chemistry

Topic 18

Acids and bases HL

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**Lewis theory of
acids and bases**

Lewis theory of acids and bases

A Lewis acid is an electron pair acceptor.

A Lewis base is an electron pair donor.



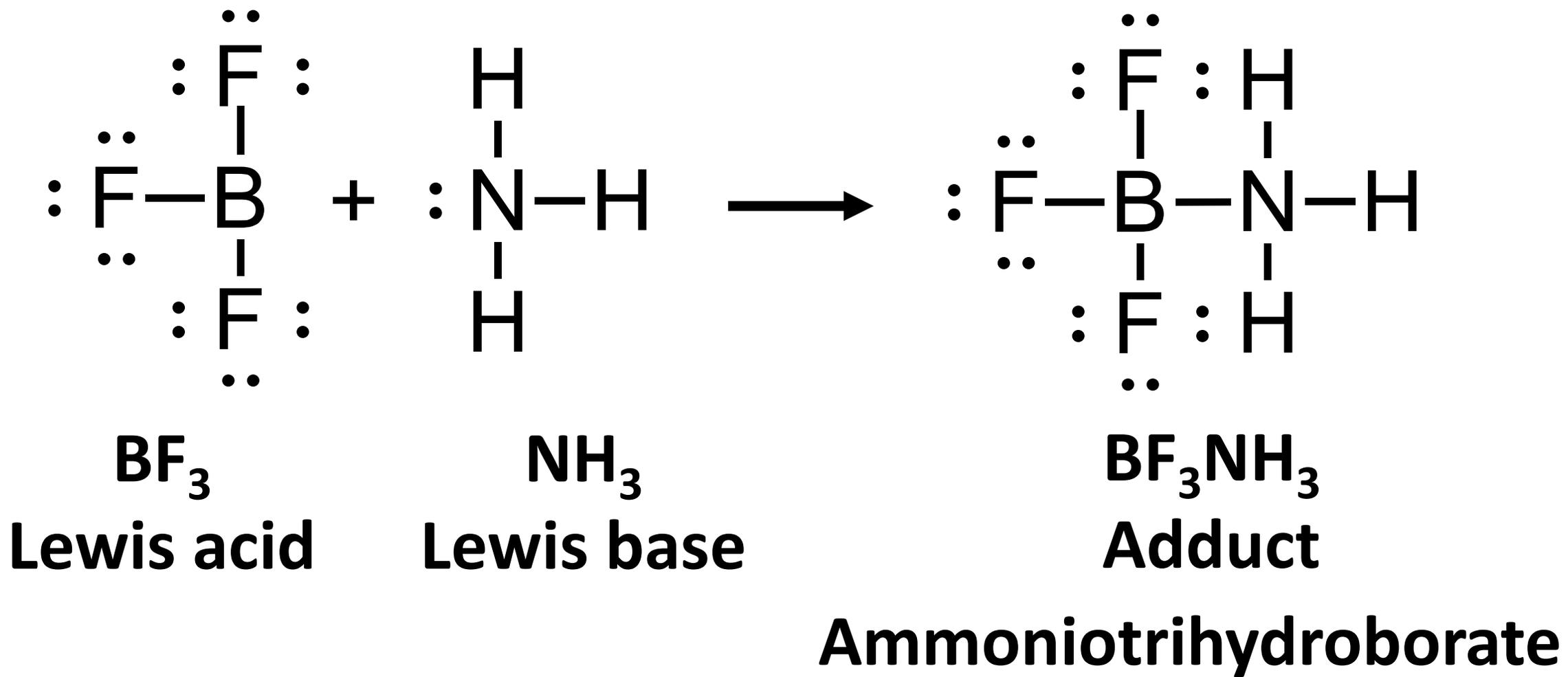
A is a Lewis acid (is electron deficient)

B is a Lewis base (has a lone pair of electrons)

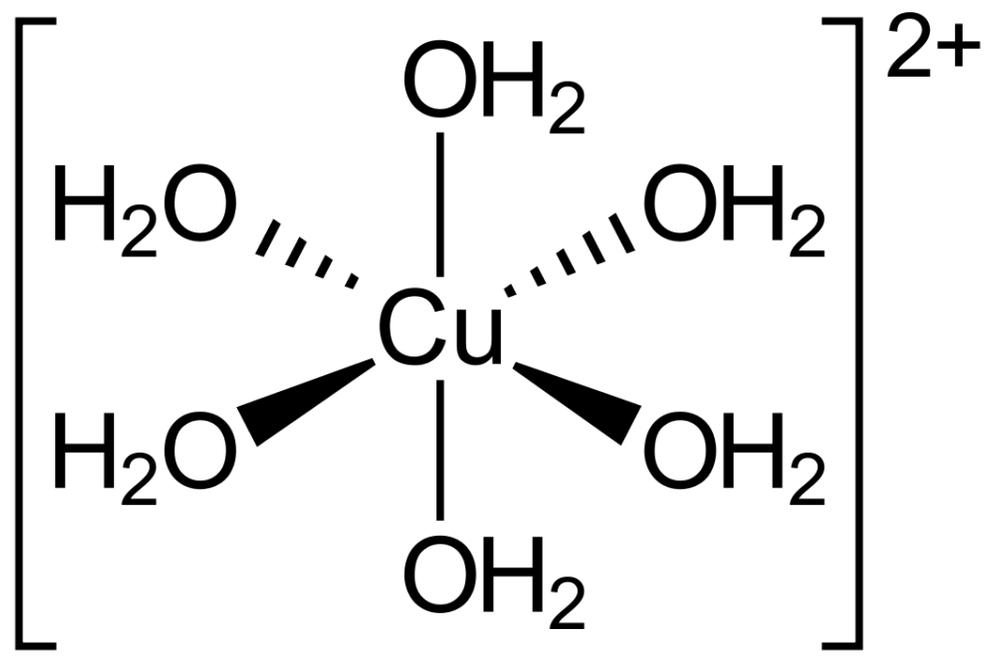
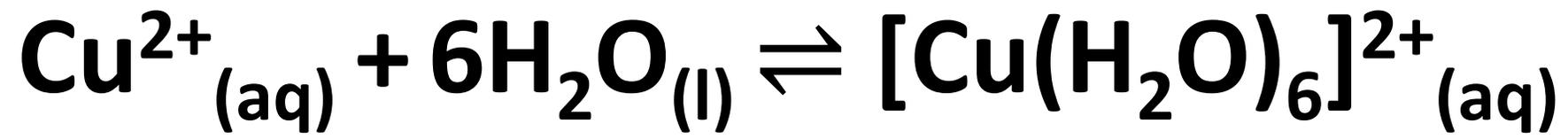
A-B is an adduct

A coordinate covalent bond is formed between the Lewis acid and the Lewis base.

Lewis theory of acids and bases

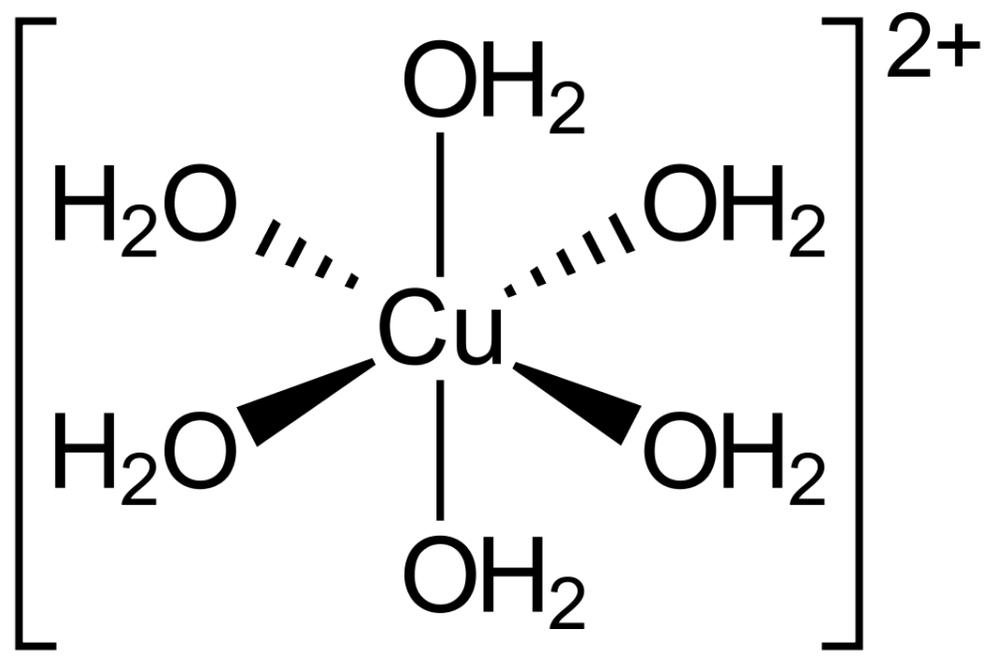
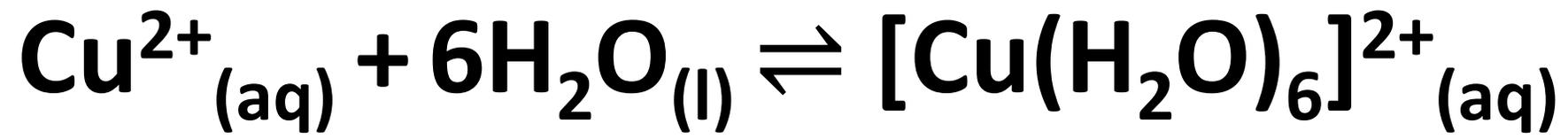


Lewis theory of acids and bases



The central metal ion is a Lewis acid.
The ligands are Lewis bases.

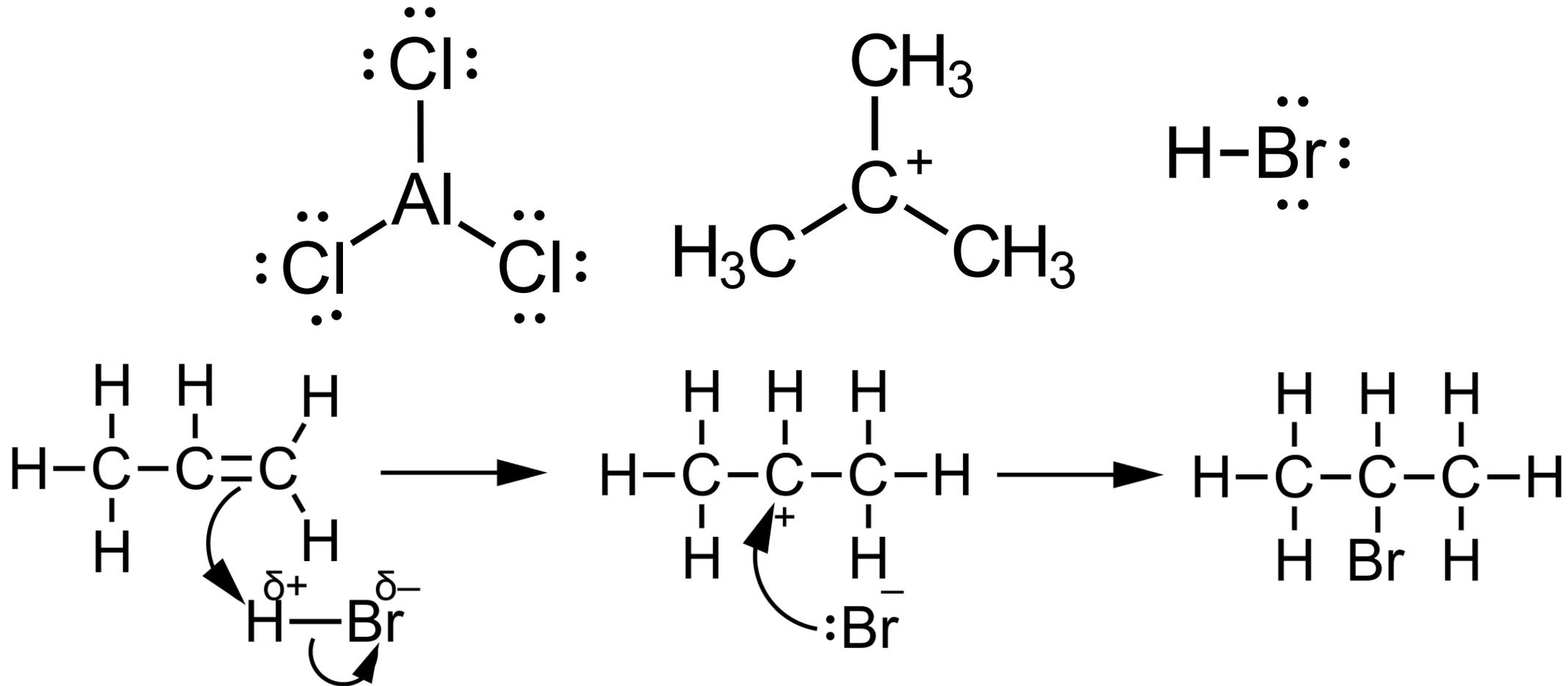
Lewis theory of acids and bases



The central metal ion is a Lewis acid.
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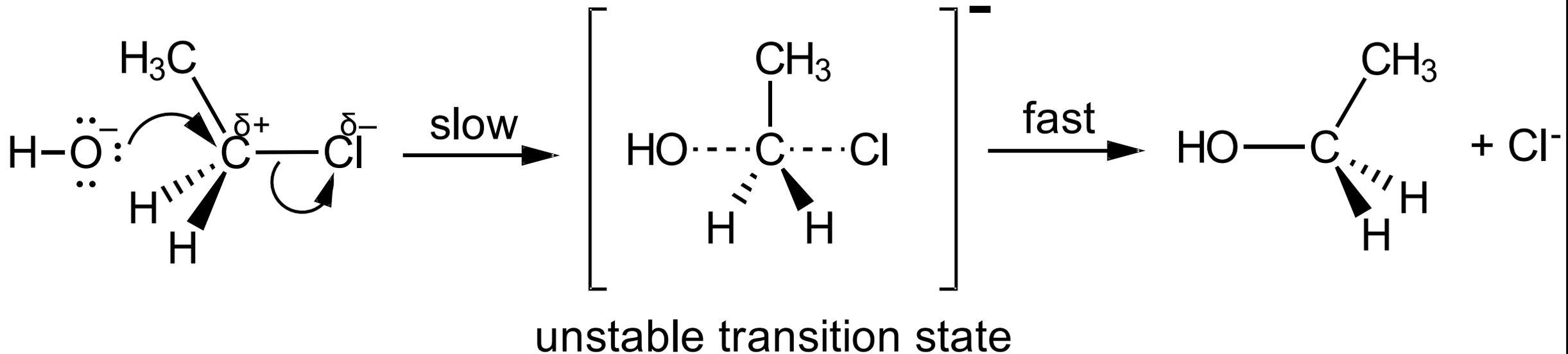
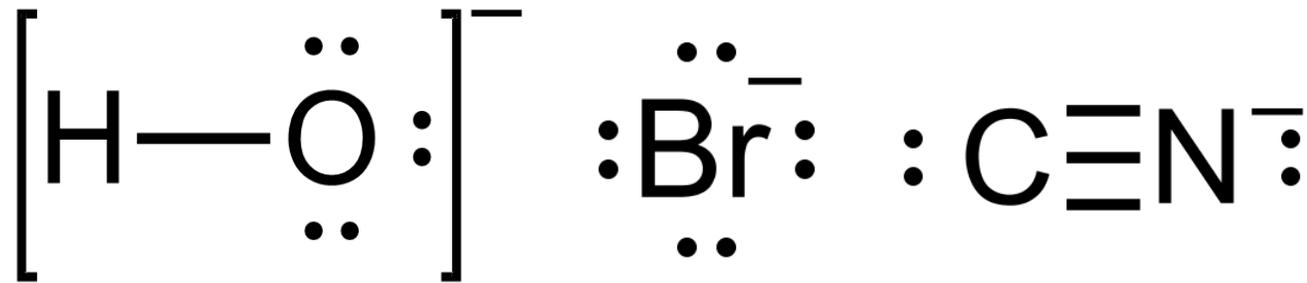
Lewis theory of acids and bases

Electrophiles are electron deficient species that accept a lone pair of electrons (Lewis acids).



Lewis theory of acids and bases

Nucleophiles are electron rich species that donate a lone pair of electrons (Lewis bases).



Lewis theory of acids and bases

	Lewis acid	Lewis base
Definition	Electron pair acceptor	Electron pair donor
Example	BF_3	NH_3
Complex ions	Central metal ions $\text{Cu}^{2+} / \text{Fe}^{3+} / \text{Cr}^{3+}$	Ligands $\text{H}_2\text{O} / \text{NH}_3 / \text{CN}^-$
Organic chemistry	Electrophiles $\text{AlCl}_3 / \text{HBr}$	Nucleophiles $\text{H}_2\text{O} / \text{OH}^-$

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Lewis theory vs

Bronsted-Lowry theory

Bronsted-Lowry theory

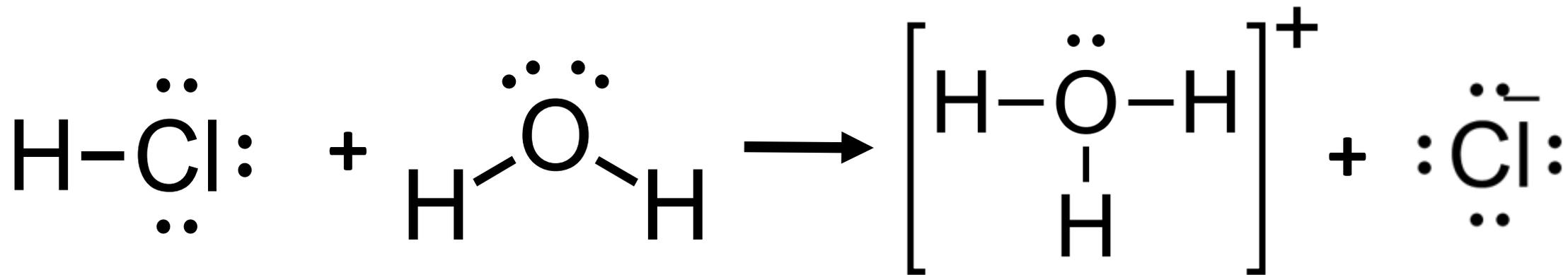
An acid is a proton donor

A base is a proton acceptor

Lewis theory

An acid is an electron pair acceptor

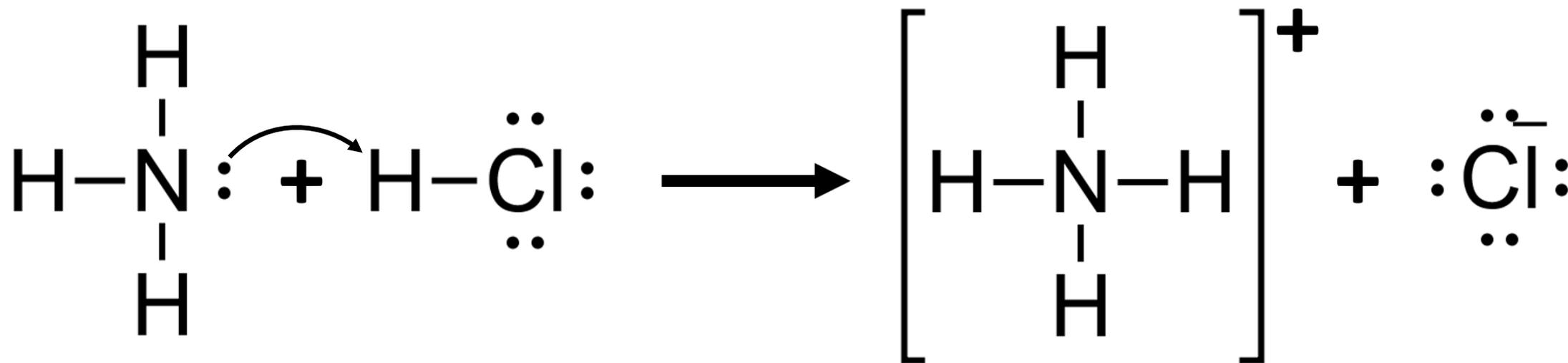
A base is an electron pair donor



HCl donates a proton to H₂O.

HCl accepts a lone pair of electrons from H₂O.

All Bronsted-Lewis acids are also Lewis acids.

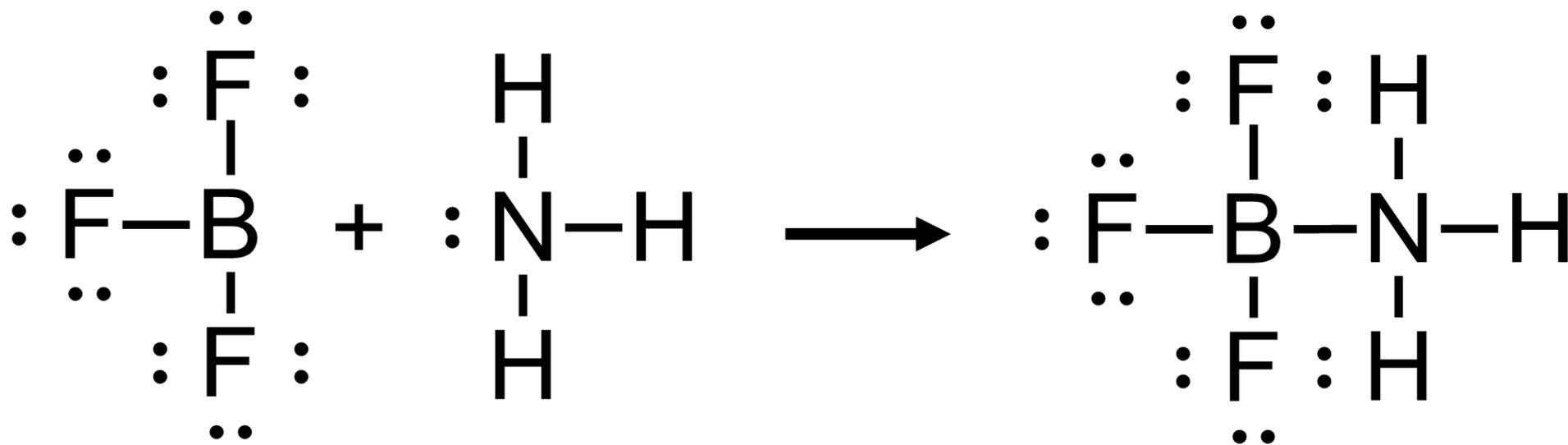


NH₃ accepts a proton from HCl.

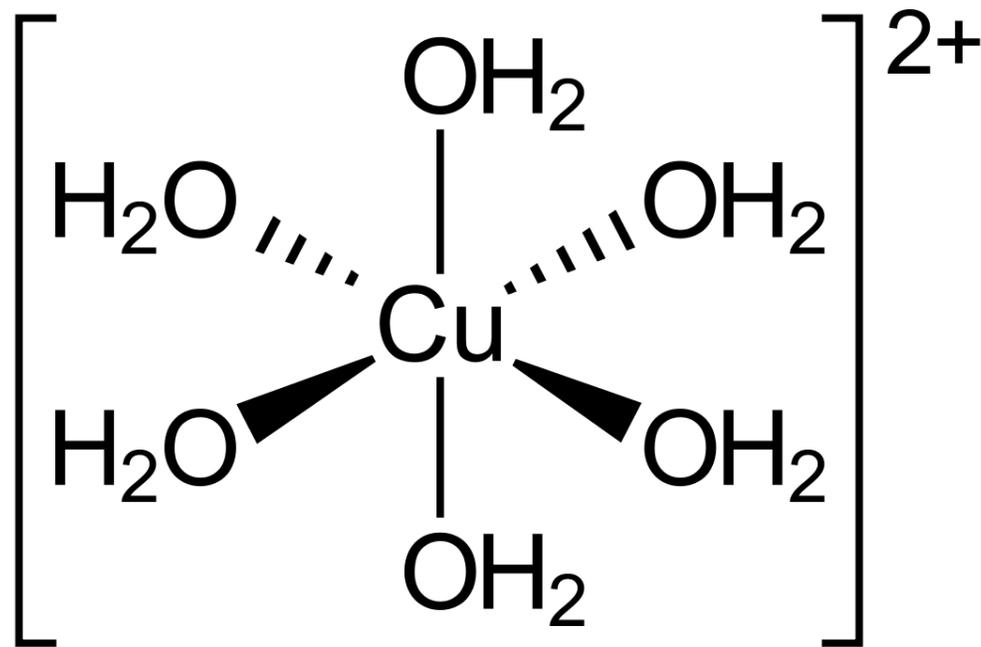
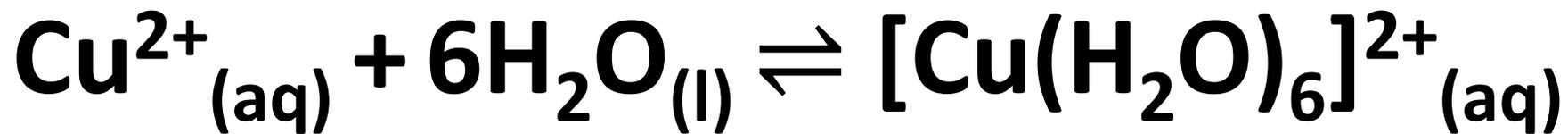
NH₃ donates a lone pair of electrons to HCl.

All Bronsted-Lowry bases are also Lewis bases.

Lewis theory vs Bronsted-Lowry theory

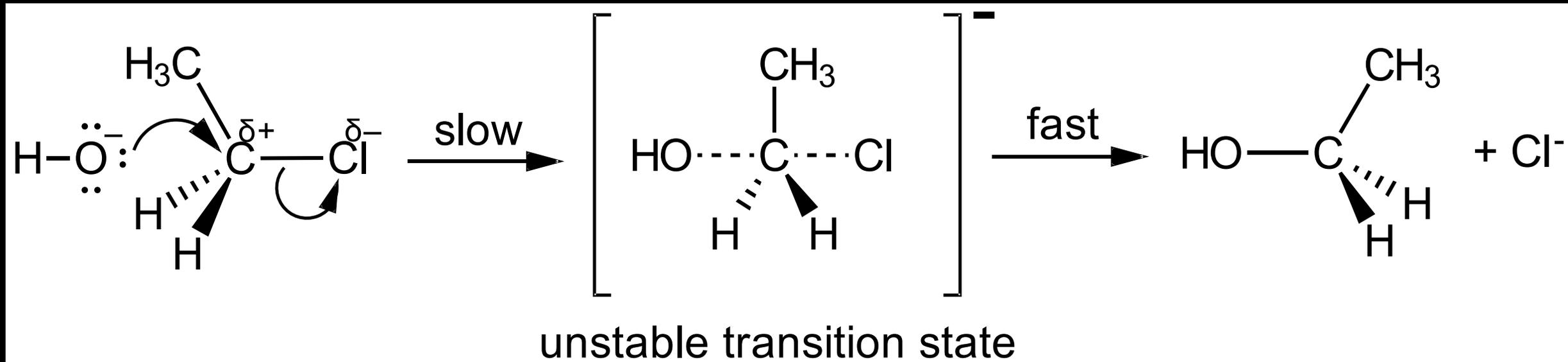
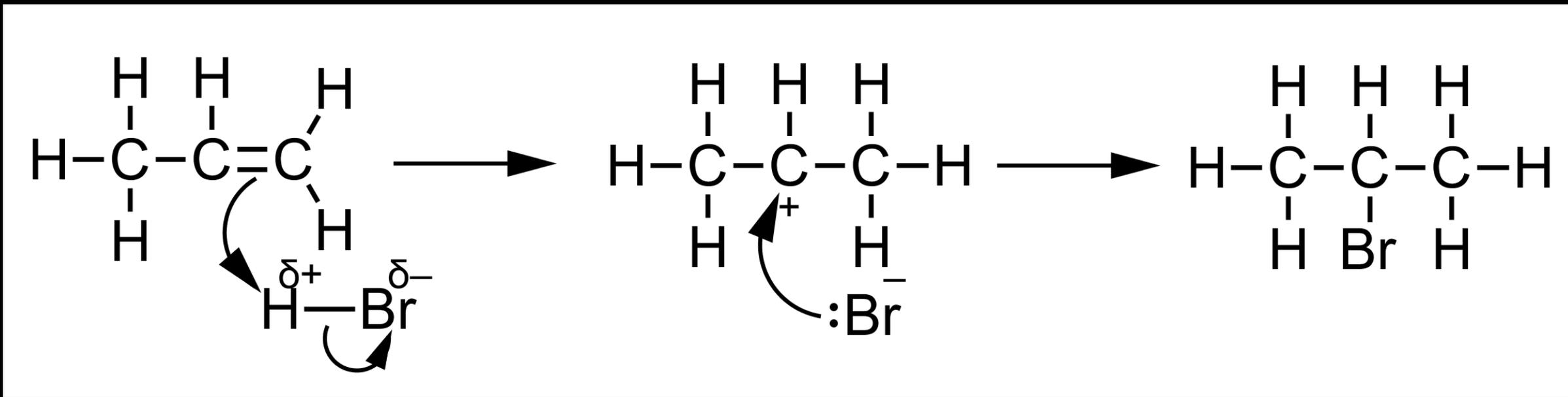


BF₃ accepts a lone pair of electrons from NH₃.
NH₃ donates a lone pair of electrons to BF₃.
BF₃ acts as a Lewis acid and NH₃ as a Lewis base.



The central metal ion is a Lewis acid.
The ligands are Lewis bases.

Lewis theory vs Bronsted-Lowry theory



Lewis theory vs Bronsted-Lowry theory

Species	Bronsted-Lowry base	Lewis base	Bronsted-Lowry acid	Lewis acid
NH_3 H_2O	Yes	Yes	No	No
HCl HNO_3	No	No	Yes	Yes
BF_3 AlCl_3	No	No	No	Yes
Cu^{2+} Cr^{3+}	No	No	No	Yes

Bronsted-Lowry theory involves the transfer of protons; if there is no transfer of protons taking place, then the reaction cannot be described using Bronsted-Lowry theory.

All Bronsted-Lowry acids are also Lewis acids and all Bronsted-Lowry bases are also Lewis bases.

Not all Lewis acids are Bronsted-Lowry acids (BF_3 , Cu^{2+}). The formation of a complex ion can be described using Lewis theory, but not Bronsted-Lowry theory.

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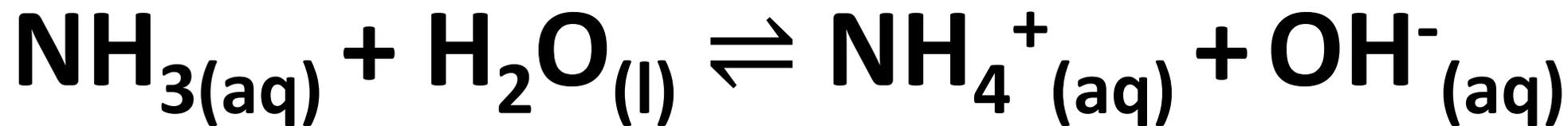
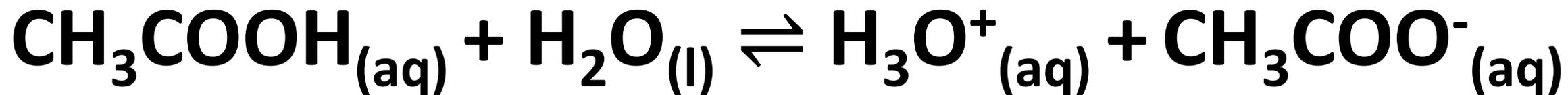
Acid and base

dissociation constants

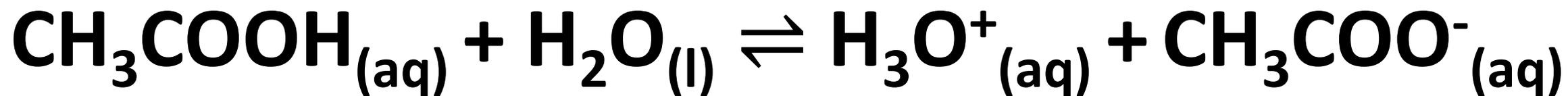
K_a and K_b

Weak acids and bases

Weak acids and bases partially dissociate (ionise) in solution.

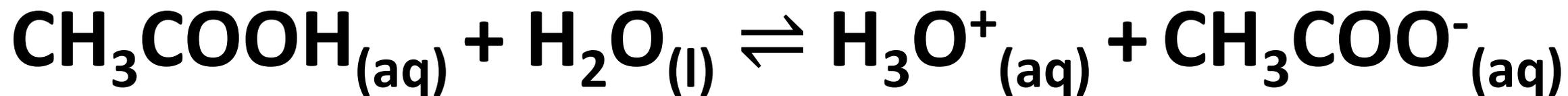


The position of equilibrium in these reactions lies to the left (reactants side).



$$K_c = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}][\text{H}_2\text{O}]}$$

$$K_c[\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

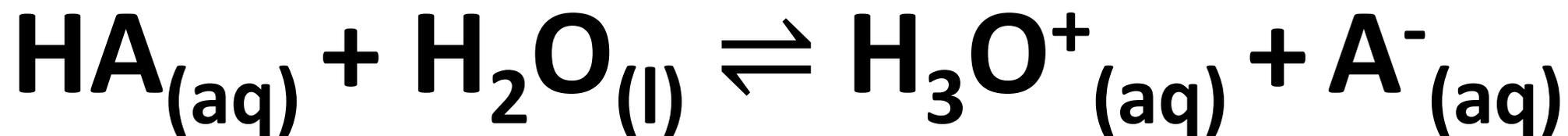


$$K_c = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}][\text{H}_2\text{O}]}$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

Acid dissociation constant K_a

K_a (the acid dissociation constant) is an equilibrium constant that refers to the dissociation or ionisation of an acid.



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

Acid dissociation constant K_a

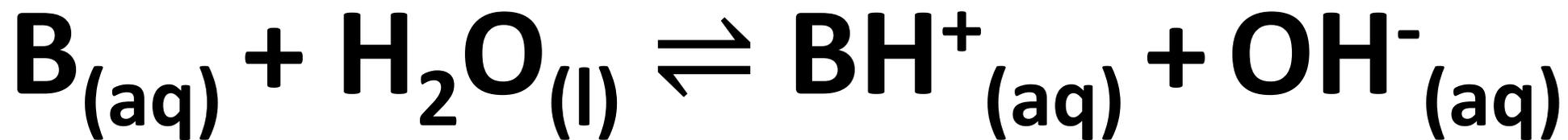
The magnitude of the K_a tells us the extent of dissociation and the strength of the acid.

Acid	K_a
HCOOH	1.78×10^{-4}
CH ₃ COOH	1.74×10^{-5}

The larger the value of the K_a , the greater the degree of dissociation and the stronger the acid.

Base dissociation constant K_b

K_b (the base dissociation constant) is an equilibrium constant that refers to the dissociation or ionisation of a base.



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

Base dissociation constant K_b

The magnitude of the K_b tells us the extent of dissociation and the strength of the base.

Base	K_b
CH_3NH_2	4.57×10^{-4}
NH_3	1.78×10^{-5}

The larger the value of the K_b , the greater the degree of dissociation and the stronger the base.

Weak acids and bases

The K_a and K_b tell us the extent of the dissociation and the strength of the acid or base.

The higher the value of the K_a , the higher the $[H_3O^+]$ at equilibrium and the stronger the acid.

The higher the value of the K_b , the higher the $[OH^-]$ at equilibrium and the stronger the base.

Stronger acids and bases have higher K_a and K_b values than weaker acids and bases.

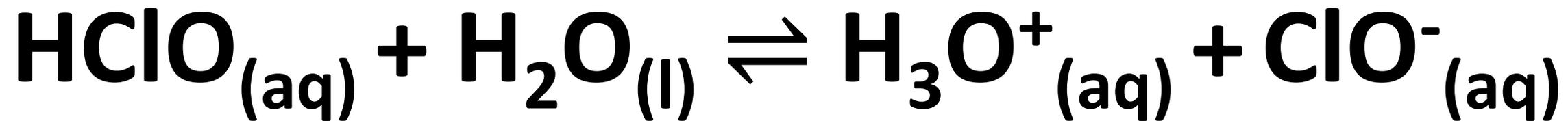
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Calculating the K_a or K_b
of a weak acid or base

Calculating the K_a of a weak acid

A $0.100 \text{ mol dm}^{-3}$ solution of HClO has a pH of 4.23. Calculate the K_a of HClO.



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

Calculating the K_a of a weak acid

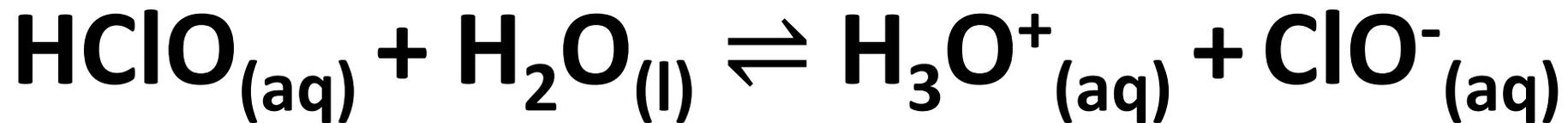
A $0.100 \text{ mol dm}^{-3}$ solution of HClO has a pH of 4.23. Calculate the K_a of HClO.

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

$$[\text{H}^+] = 10^{-4.23}$$

$$[\text{H}^+] = 5.89 \times 10^{-5} \text{ mol dm}^{-3}$$

Calculating the K_a of a weak acid



	HClO	H_3O^+	ClO^-
Initial	0.100	0	0
Change	-5.89×10^{-5}	$+5.89 \times 10^{-5}$	$+5.89 \times 10^{-5}$
Equilibrium	$0.100 - 5.89 \times 10^{-5}$	5.89×10^{-5}	5.89×10^{-5}

$$[\text{HClO}]_{\text{eq}} = [\text{HClO}]_{\text{initial}}$$

Calculating the K_a of a weak acid

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

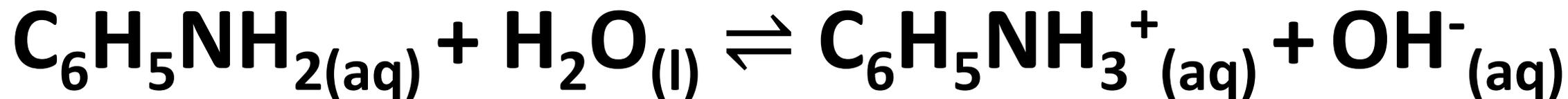
$$K_a = \frac{(5.89 \times 10^{-5})^2}{0.100}$$

$$K_a = 3.47 \times 10^{-8}$$

$$K_a = \frac{(5.89 \times 10^{-5})^2}{(0.100 - 5.89 \times 10^{-5})}$$

Calculating the K_b of a weak base

A $0.100 \text{ mol dm}^{-3}$ solution of $\text{C}_6\text{H}_5\text{NH}_2$ has a pH of 8.79. Calculate the K_b of $\text{C}_6\text{H}_5\text{NH}_2$.



$$K_b = \frac{[\text{C}_6\text{H}_5\text{NH}_3^+][\text{OH}^-]}{[\text{C}_6\text{H}_5\text{NH}_2]}$$

Calculating the K_b of a weak base

A $0.100 \text{ mol dm}^{-3}$ solution of $\text{C}_6\text{H}_5\text{NH}_2$ has a pH of 8.79. Calculate the K_b of $\text{C}_6\text{H}_5\text{NH}_2$.

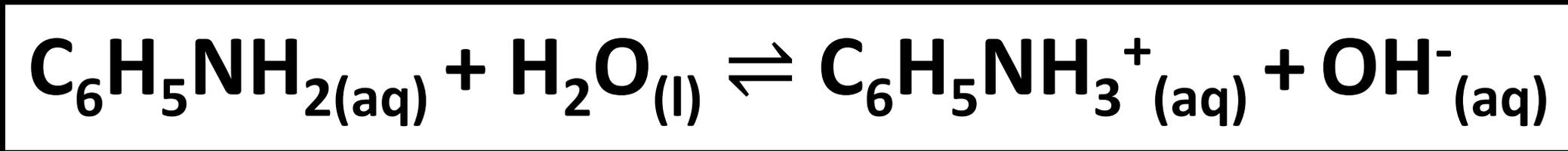
$$\text{pH} + \text{pOH} = 14.00 \text{ (at 298 K)}$$

$$\text{pOH} = 14.00 - 8.79 = 5.21$$

$$[\text{OH}^-] = 10^{-5.21}$$

$$[\text{OH}^-] = 6.17 \times 10^{-6} \text{ mol dm}^{-3}$$

Calculating the K_b of a weak base



	$\text{C}_6\text{H}_5\text{NH}_2$	$\text{C}_6\text{H}_5\text{NH}_3^+$	OH^-
Initial	0.100	0	0
Change	-6.17×10^{-6}	$+6.17 \times 10^{-6}$	$+6.17 \times 10^{-6}$
Equilibrium	$0.100 - 6.17 \times 10^{-6}$	6.17×10^{-6}	6.17×10^{-6}

$$[\text{C}_6\text{H}_5\text{NH}_2]_{\text{eq}} = [\text{C}_6\text{H}_5\text{NH}_2]_{\text{initial}}$$

Calculating the K_b of a weak base

$$K_b = \frac{[\text{C}_6\text{H}_5\text{NH}_3^+][\text{OH}^-]}{[\text{C}_6\text{H}_5\text{NH}_2]}$$

$$K_b = \frac{(6.17 \times 10^{-6})^2}{0.100}$$

$$K_b = 3.81 \times 10^{-10}$$

$$K_b = \frac{(6.17 \times 10^{-6})^2}{(0.100 - 6.17 \times 10^{-6})}$$

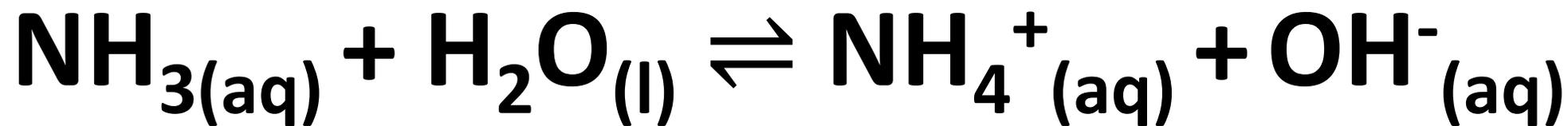
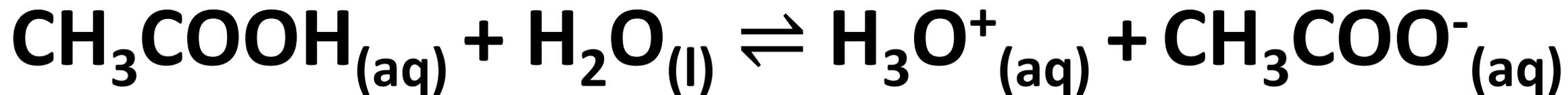
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**Calculating the pH of
weak acids and bases**

Weak acids and bases

Weak acids and bases partially dissociate (ionise) in solution.



The position of equilibrium in these reactions lies to the left (reactants side).

Calculating pH of weak acids

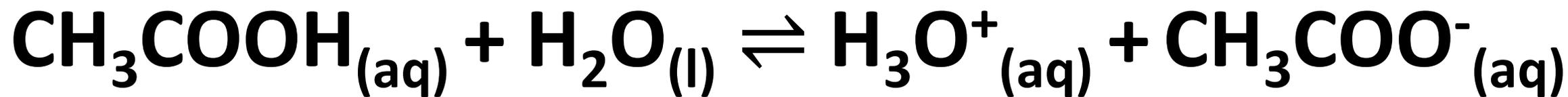
A $0.500 \text{ mol dm}^{-3}$ solution of CH_3COOH has a K_a of 1.8×10^{-5} . Calculate the pH of the solution.

	CH_3COOH	H_3O^+	CH_3COO^-
Initial	0.500	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.500-x$	x	x

$$[\text{CH}_3\text{COOH}]_{\text{eq}} = [\text{CH}_3\text{COOH}]_{\text{initial}}$$

Calculating pH of weak acids

A $0.500 \text{ mol dm}^{-3}$ solution of CH_3COOH has a K_a of 1.8×10^{-5} . Calculate the pH of the solution.



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

Calculating pH of weak acids

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

$$1.8 \times 10^{-5} = \frac{x^2}{0.500}$$

$$x = \sqrt{9.0 \times 10^{-6}} \quad x = 3.0 \times 10^{-3}$$

$$x = 3.0 \times 10^{-3}$$

$$[\text{H}^+] = 3.0 \times 10^{-3} \text{ mol dm}^{-3}$$

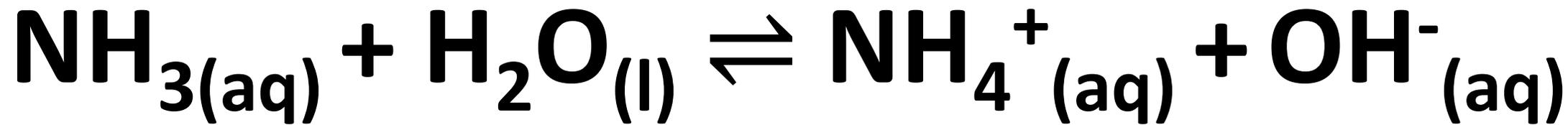
$$\text{pH} = -\log[\text{H}^+]$$

$$\text{pH} = -\log(3.0 \times 10^{-3})$$

$$\text{pH} = 2.5$$

Calculating pH of weak bases

A 0.200 mol dm⁻³ solution of NH₃ has a K_b of 1.8×10^{-5} .
Calculate the pH of the solution.



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

Calculating pH of weak bases

A $0.200 \text{ mol dm}^{-3}$ solution of NH_3 has a K_b of 1.8×10^{-5} . Calculate the pH of the solution.

	NH_3	NH_4^+	OH^-
Initial	0.200	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.200-x$	x	x

$$[\text{NH}_3]_{\text{eq}} = [\text{NH}_3]_{\text{initial}}$$

Calculating pH of weak bases

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

$$1.8 \times 10^{-5} = \frac{x^2}{0.200}$$

$$x = \sqrt{3.6 \times 10^{-6}} \quad x = 1.9 \times 10^{-3}$$

Calculating pH of weak bases

$$x = 1.9 \times 10^{-3}$$

$$[\text{OH}^-] = 1.9 \times 10^{-3} \text{ mol dm}^{-3}$$

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

$$\text{pOH} = -\log(1.9 \times 10^{-3})$$

$$\text{pOH} = 2.7$$

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

$$\text{pH} = 14.00 - 2.7 = 11.3$$

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K_a / pK_a

K_b / pK_b

K_w / pK_w

pK_a and pK_b

$$pK_a = -\log_{10} K_a \quad pK_b = -\log_{10} K_b$$

$$K_a = 10^{-pK_a} \quad K_b = 10^{-pK_b}$$

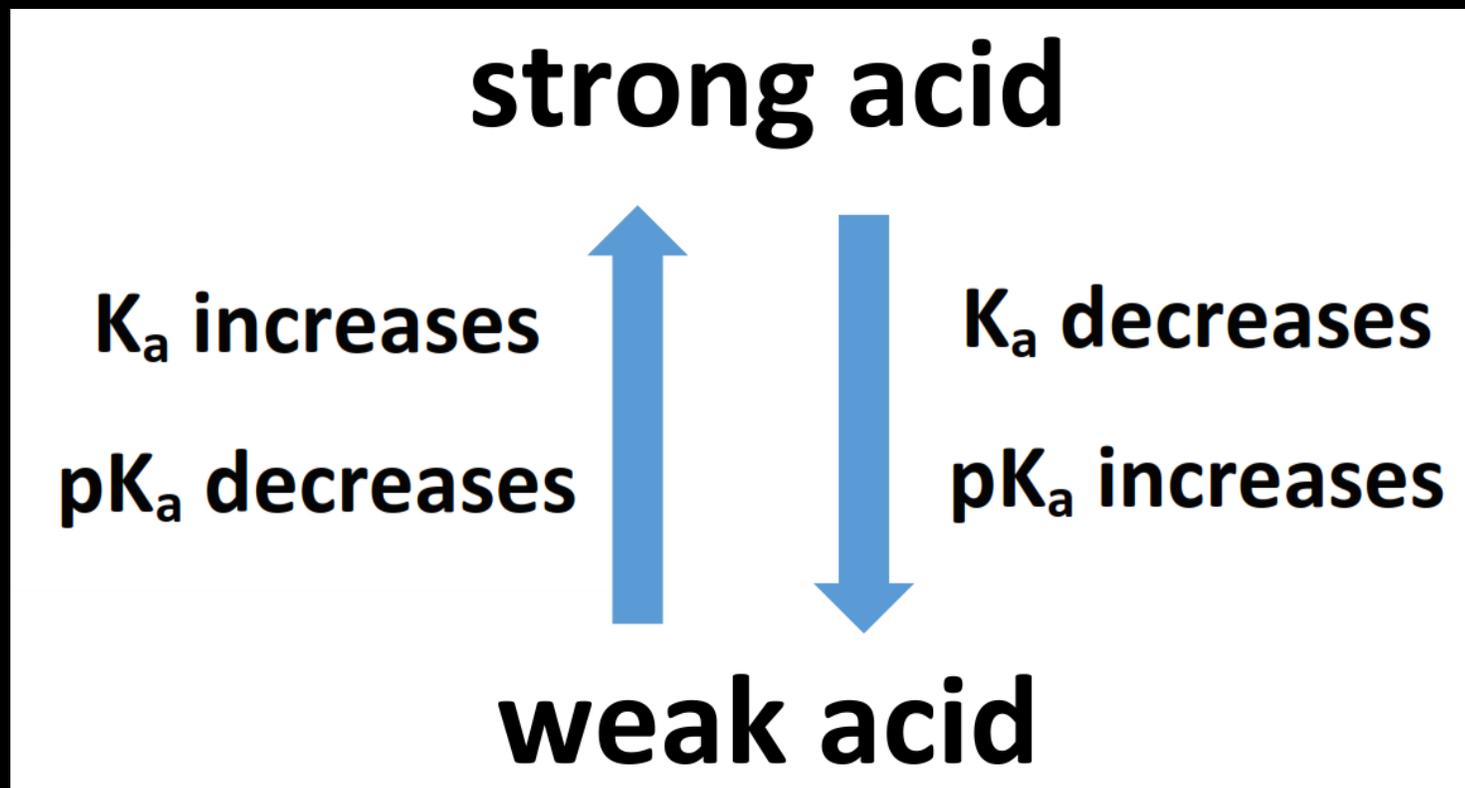
pK_a and pK_b are usually positive and have no units.

A change of one unit of pK_a or pK_b represents a ten-fold change in the value K_a or K_b.

pK_a and pK_b must be quoted at a specific temperature.

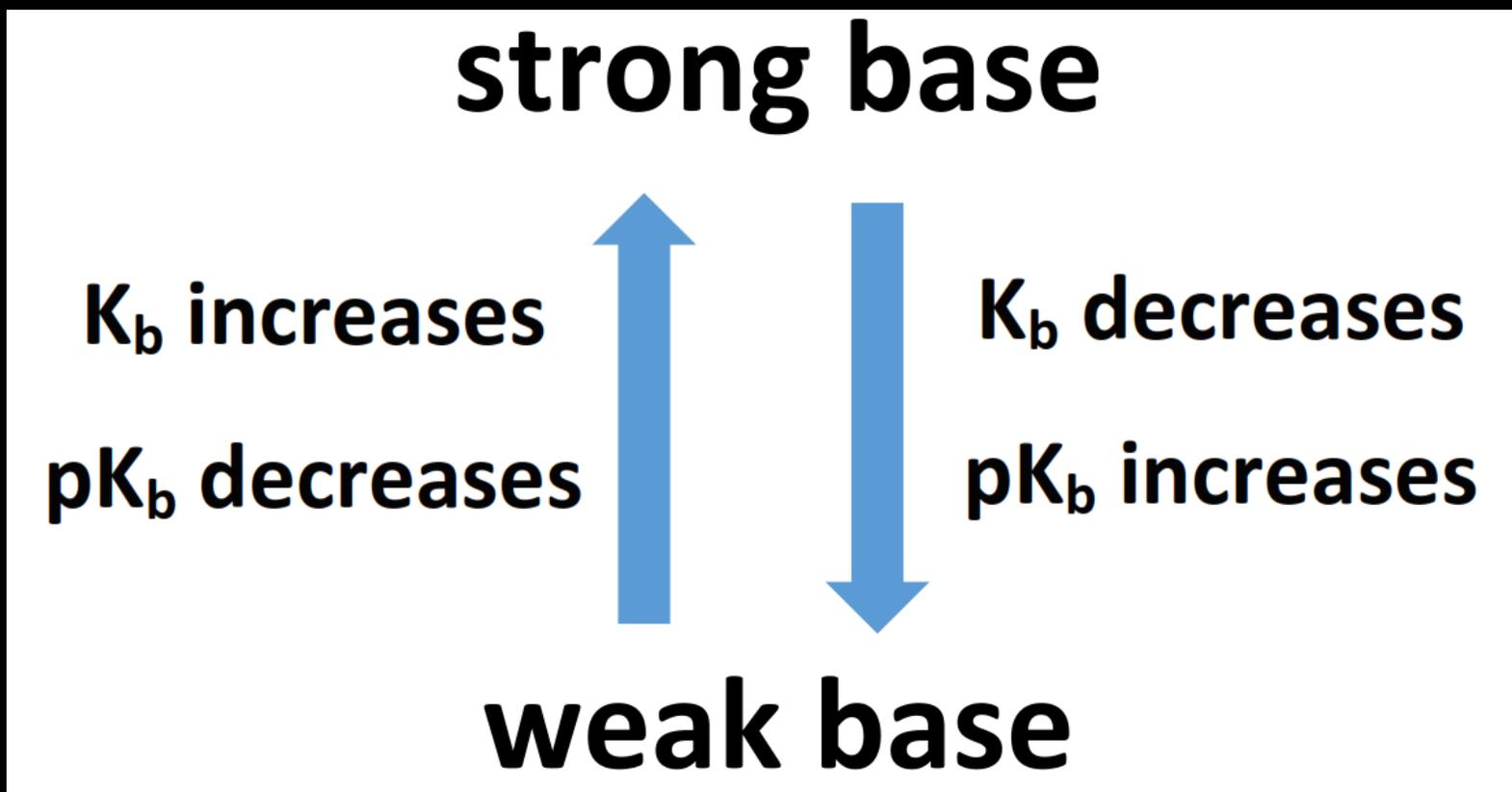
K_a and pK_a

K_a and pK_a have an inverse relationship; the stronger the acid, the higher the value of K_a and the lower the value of pK_a



K_b and pK_b

K_b and pK_b have an inverse relationship; the stronger the base, the higher the value of K_b and the lower the value of pK_b



pK_a and pK_b

At 298 K

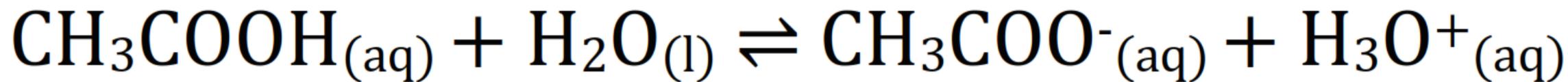
acid	pK_a	base	pK_b
methanoic acid	3.75	ammonia	4.75
ethanoic acid	4.76	methylamine	3.34

Methanoic acid is a stronger acid than ethanoic acid (lower pK_a , higher K_a).

Methylamine is a stronger base than ammonia (lower pK_b , higher K_b).

K_a and K_b

For a conjugate acid-base pair $K_a \times K_b = K_w$



$$K_a \text{ CH}_3\text{COOH} = 1.75 \times 10^{-5}$$

$$\text{At } 298 \text{ K, } K_w = 1.00 \times 10^{-14}$$

$$K_b \text{ CH}_3\text{COO}^- = \frac{1.00 \times 10^{-14}}{1.75 \times 10^{-5}} = 5.71 \times 10^{-10}$$

pK_a , pK_b and pK_w

$$K_a \times K_b = K_w$$

$$pK_a + pK_b = pK_w$$

$$pK_w = -\log (1.00 \times 10^{-14}) = 14$$

$$\text{At } 298 \text{ K, } pK_a + pK_b = 14$$

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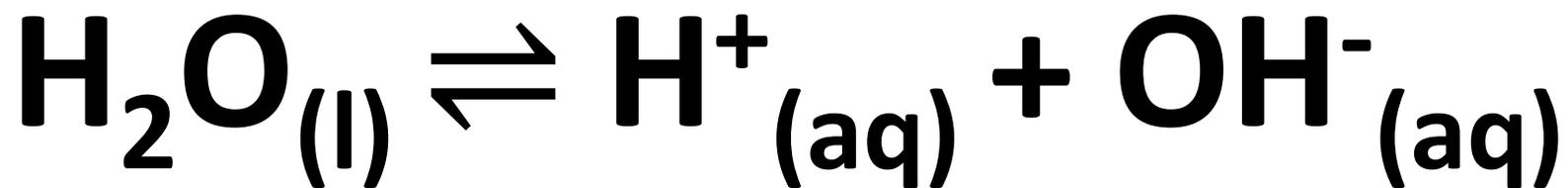
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**Temperature
dependence of K_w**

Ionic product constant K_w

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

$$K_w = 1.00 \times 10^{-14} \text{ at } 298 \text{ K}$$

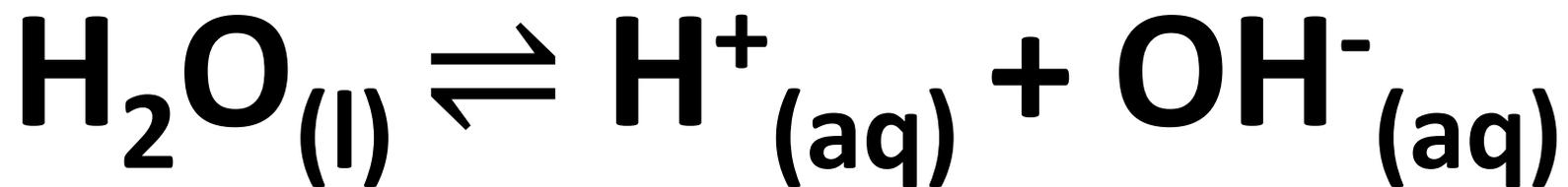


The dissociation of water requires energy - the forward reaction is endothermic.

Temperature dependence of K_w

An increase in temperature shifts the equilibrium to the right and $[H^+]$ and $[OH^-]$ increase.

$[H^+]$ and $[OH^-]$ increase



$[H^+]$ and $[OH^-]$ decrease

A decrease in temperature shifts the equilibrium to the left and $[H^+]$ and $[OH^-]$ decrease.

Temperature dependence of K_w

Temperature (K)	K_w	[H ⁺] in pure water $\sqrt{K_w}$	pH of pure water pH = -log[H ⁺]
273	1.14×10^{-15}	3.38×10^{-8}	7.47
298	1.00×10^{-14}	1.00×10^{-7}	7.00
313	2.92×10^{-14}	1.71×10^{-7}	6.77

K_w is temperature dependent, therefore, the pH of pure water is only 7.00 at 298 K.

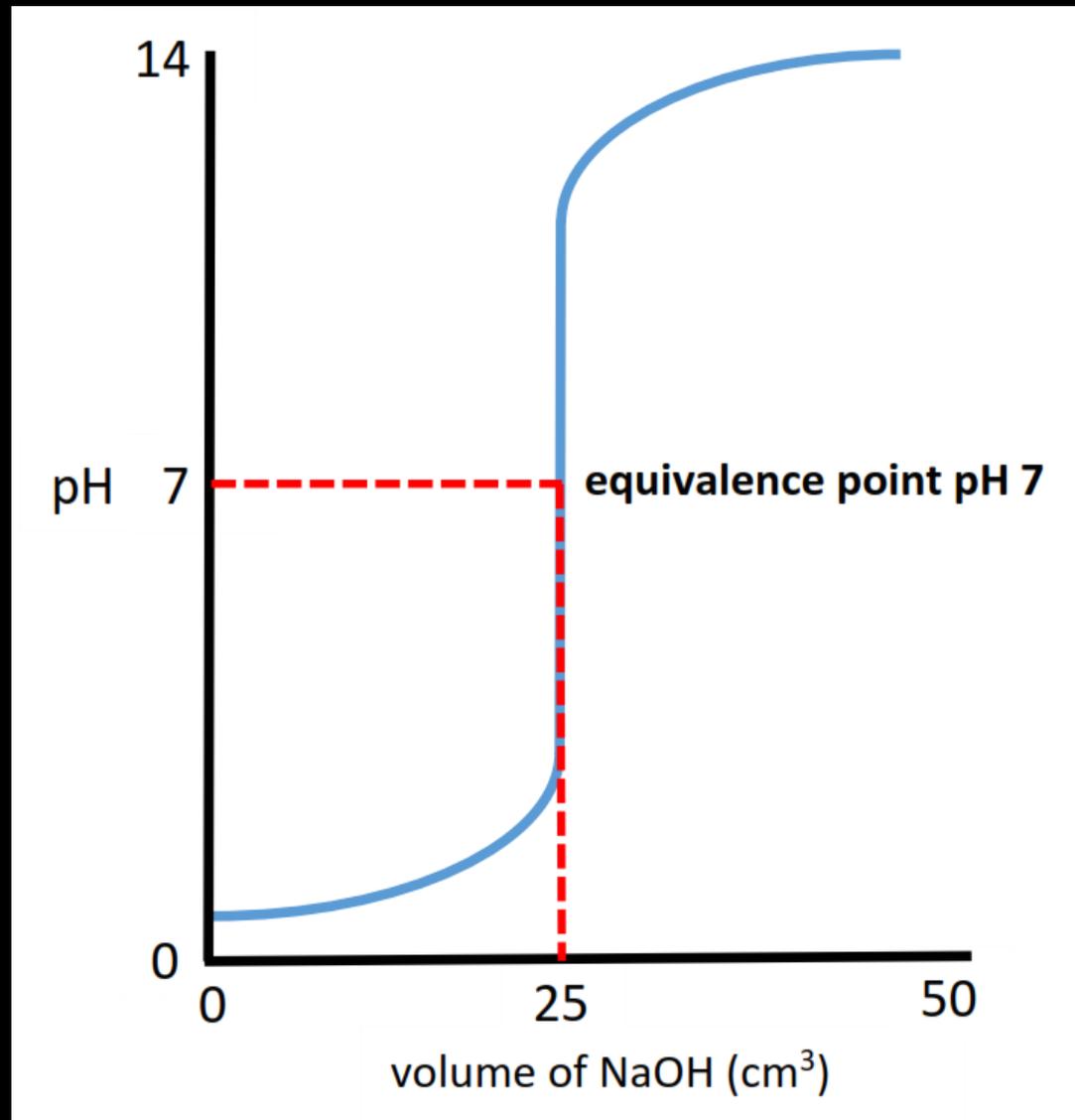
Pure water is still neutral at lower and higher temperatures as the $[H^+] = [OH^-]$.

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pH curves

pH curves



**Strong acid and strong base
(HCl + NaOH)**

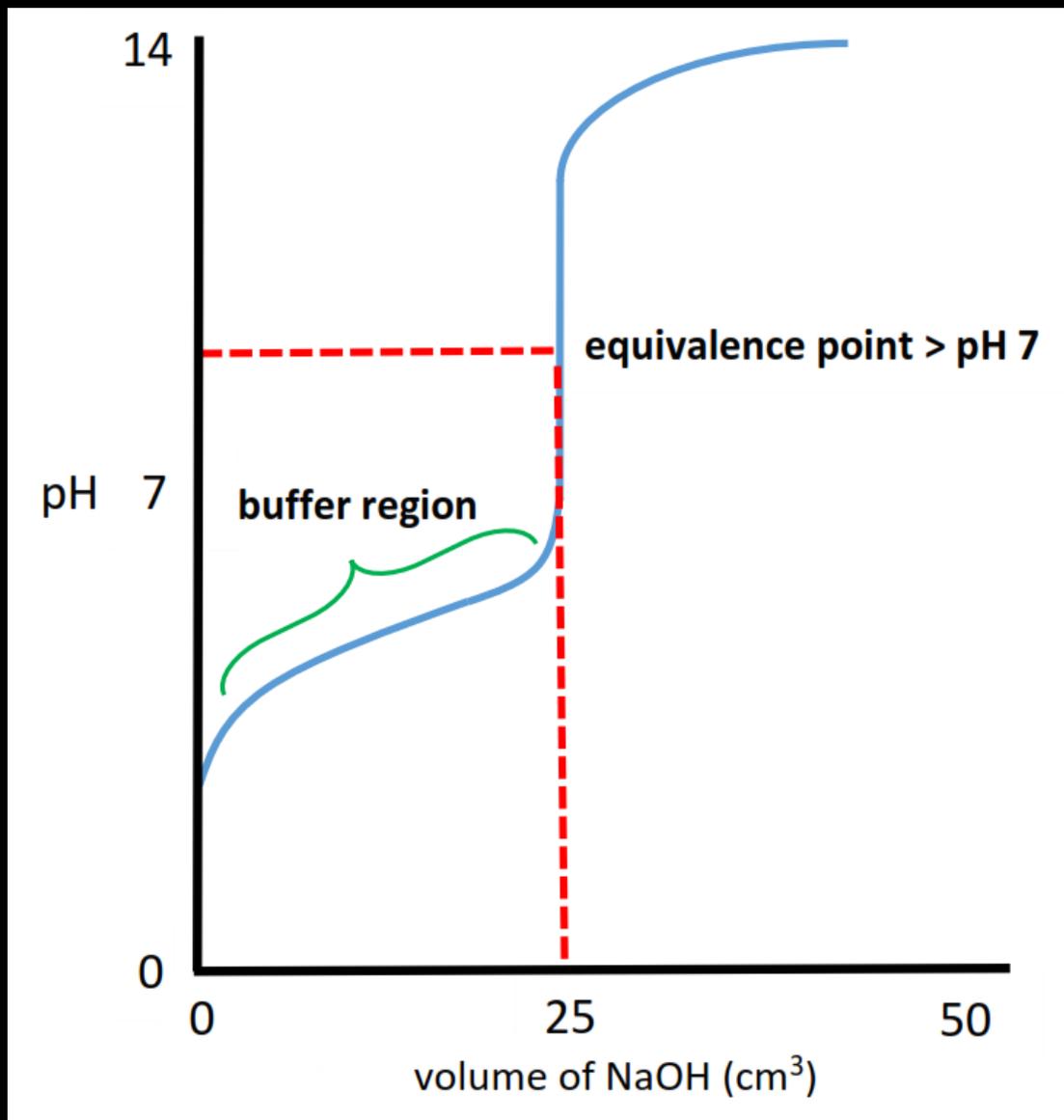
Initial pH low (strong acid)

**Very sharp increase in pH
from pH 3 to pH 11**

**Curve flattens out at high pH
(pH of strong base)**

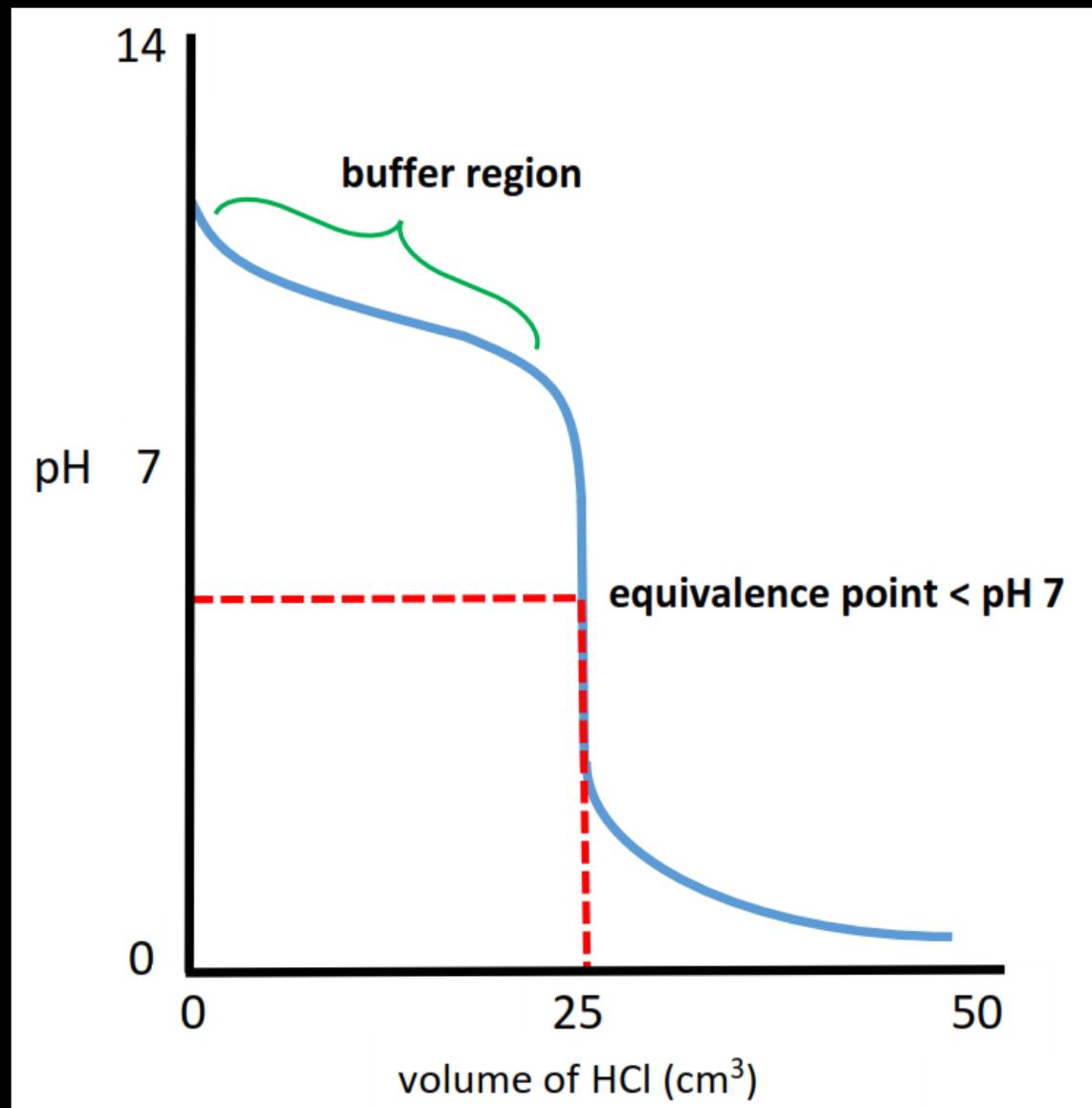
pH at equivalence point = 7

pH curves



**Weak acid and strong base
($\text{CH}_3\text{COOH} + \text{NaOH}$)**
Initial pH quite low (weak acid)
**pH stays relatively constant
(buffer region)**
**Sharp increase in pH from pH 7
to pH 11**
**Curve flattens out at high pH
(pH of strong base)**
pH at equivalence point > 7

pH curves



Strong acid and weak base
(HCl + NH₃)

Initial pH is quite high (weak base)

pH stays relatively constant (buffer region)

Sharp decrease in pH from pH 7 to pH 3

Curve flattens out at low pH (pH of strong acid)

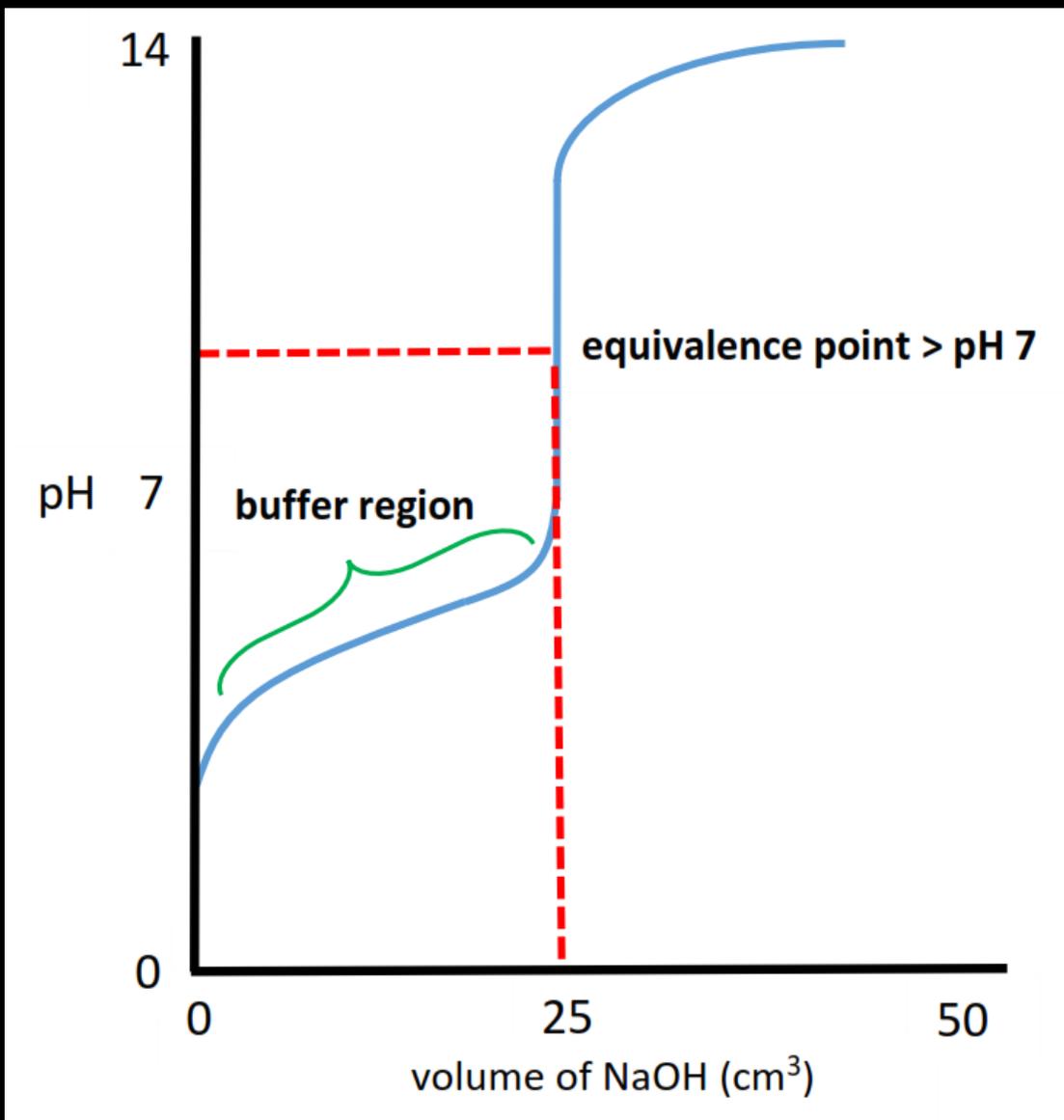
pH at equivalence point < 7

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**Buffer region and half-
equivalence point**

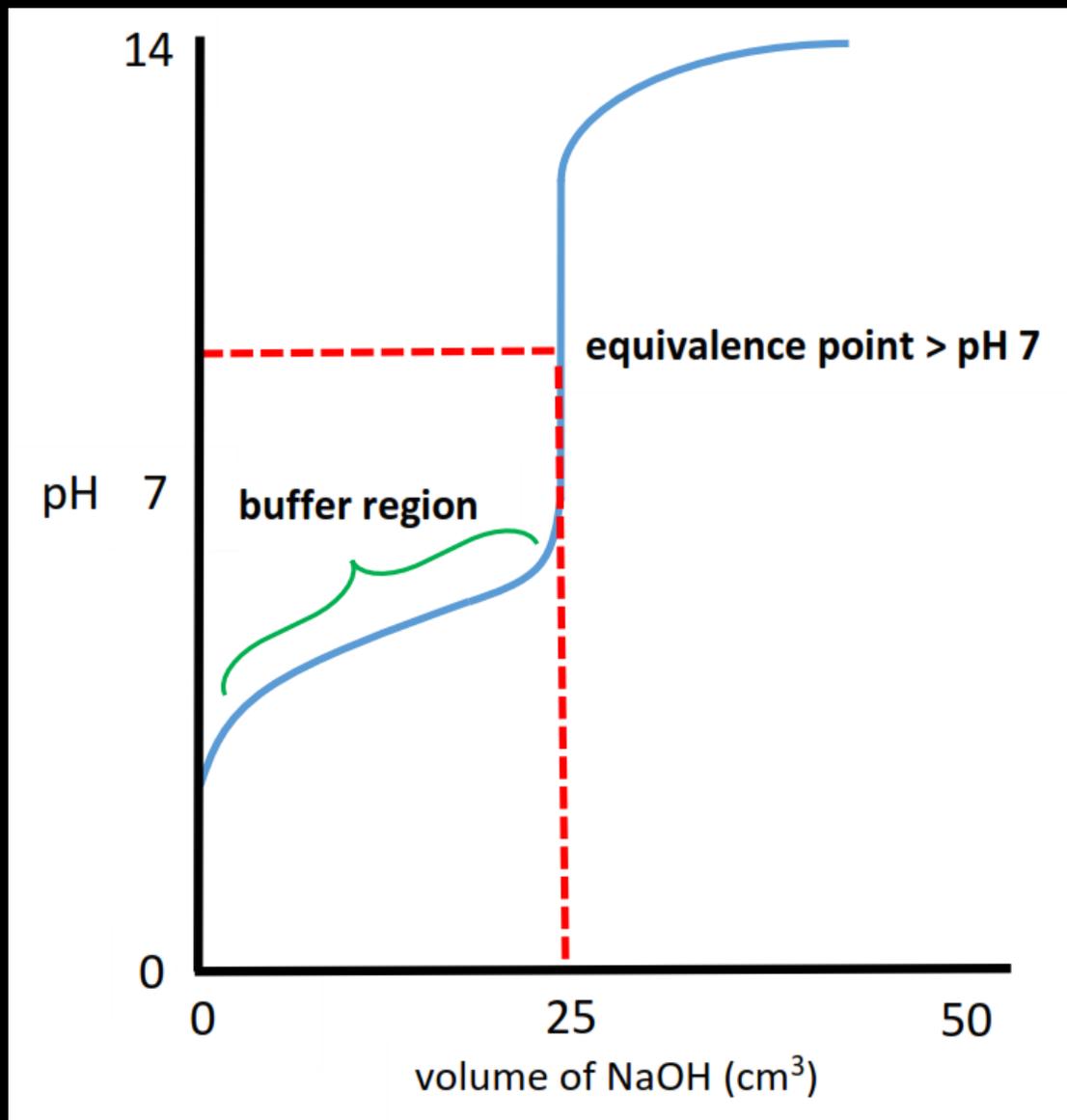
Equivalence point



The equivalence point occurs when stoichiometrically equivalent amounts of acids and bases have reacted (the solution contains only salt and water).

The pH of the equivalence point depends on whether the salt produced is acidic or basic (salt hydrolysis).

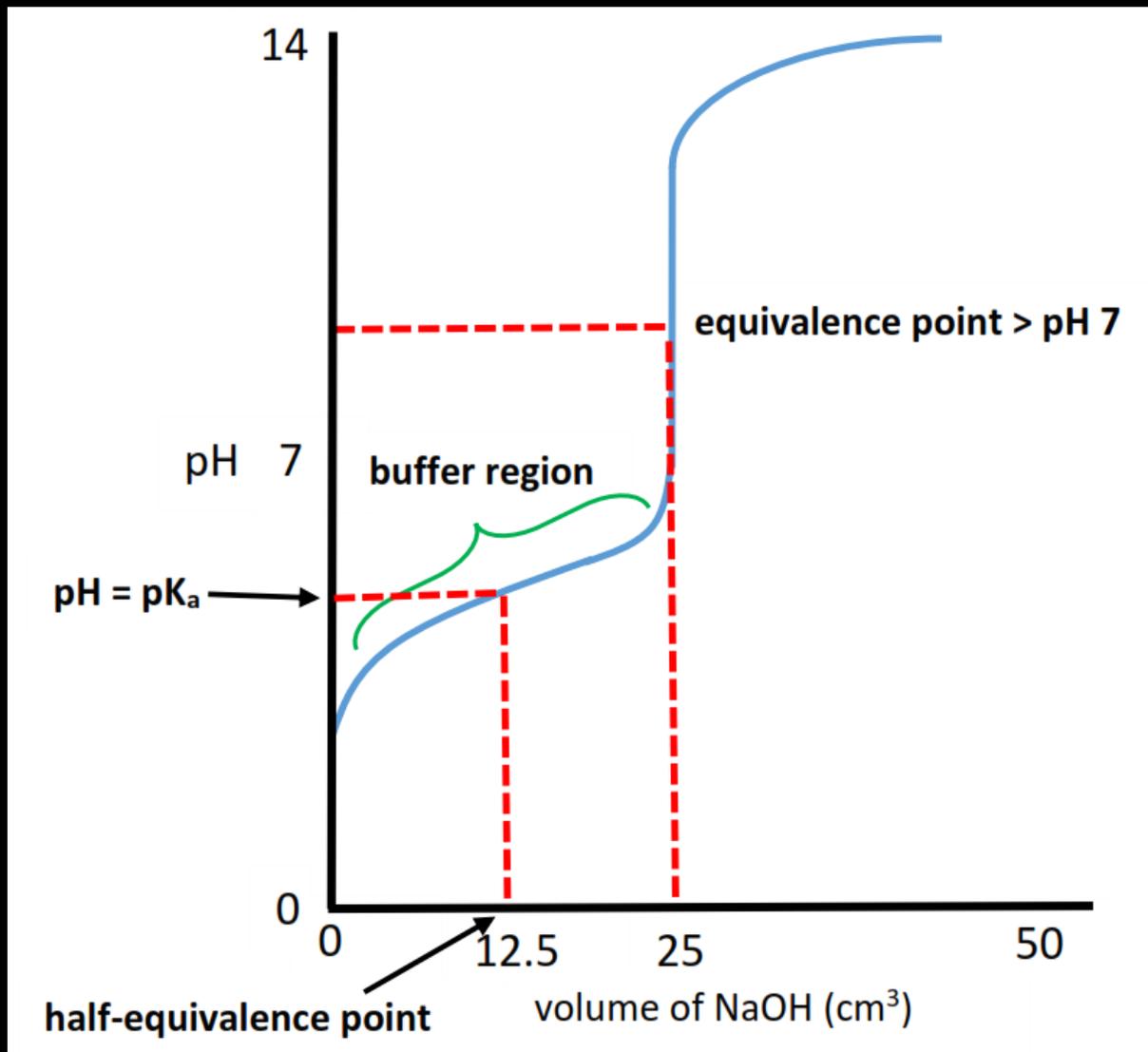
Buffer region



A buffer solution resists a change in pH when small amounts of acid or base are added.

The buffer region on a pH curve represents the region where small additions of acid or base result in little or no change in pH.

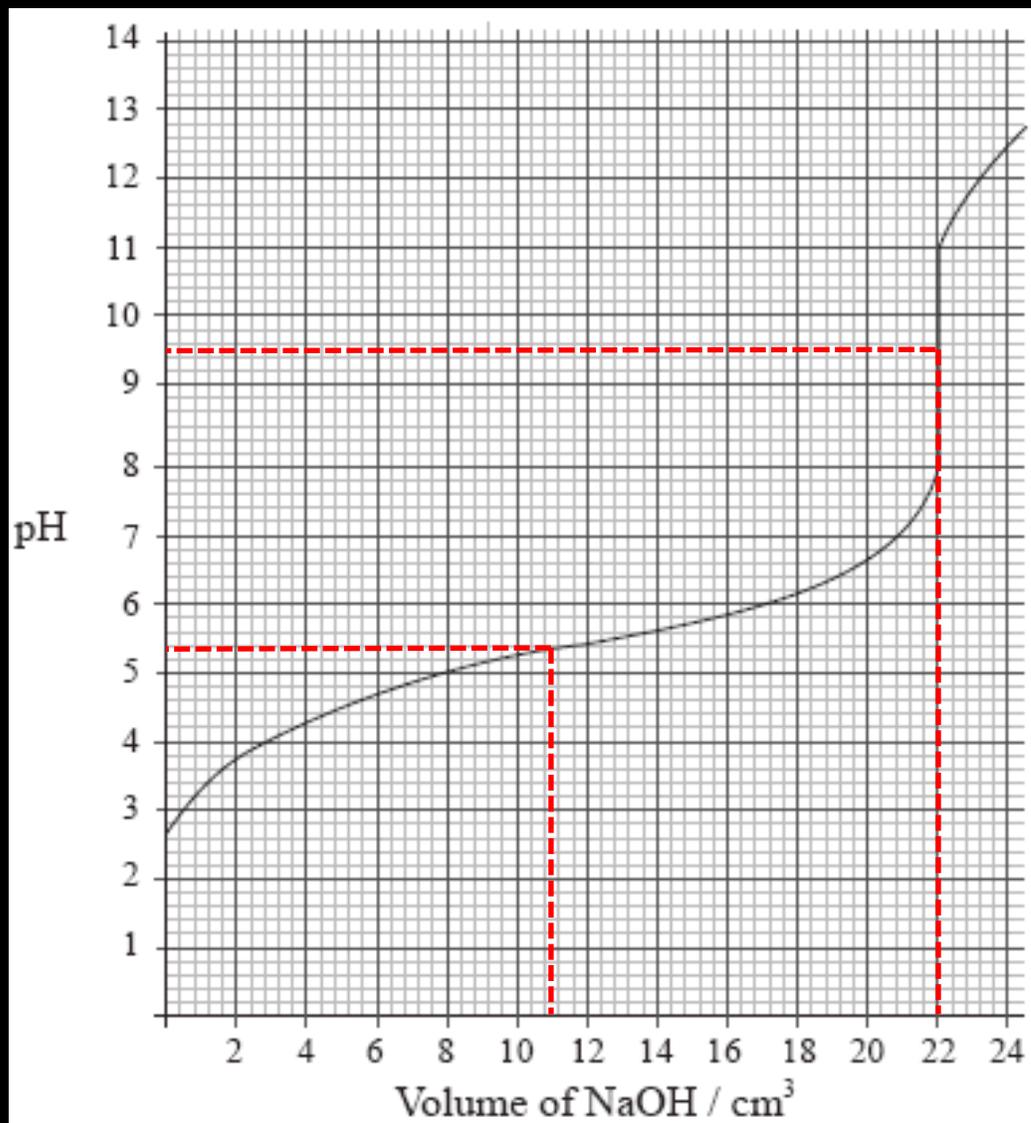
Half-equivalence point



The half-equivalence point is the point where half the acid has been neutralised by base and converted into salt.

At the half-equivalence point, the pH is equal to the pK_a

Half-equivalence point



volume of NaOH added at
equivalence point = 22 cm³
pH at equivalence point = 9.5
At half-equivalence point,
pH = pK_a
pH = 5.4, pK_a = 5.4

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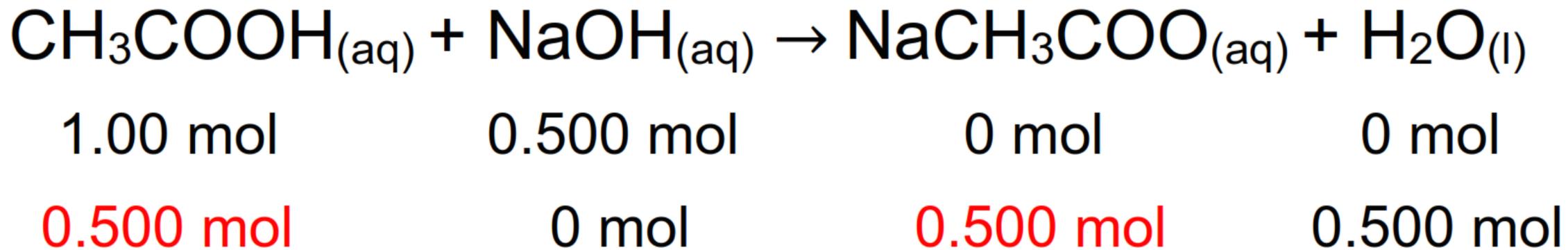
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Buffer solutions

Buffer solutions

Buffer solutions resist a change in pH when small amounts of acid or base are added.

A buffer solution can be prepared by reacting a weak acid with a strong base.



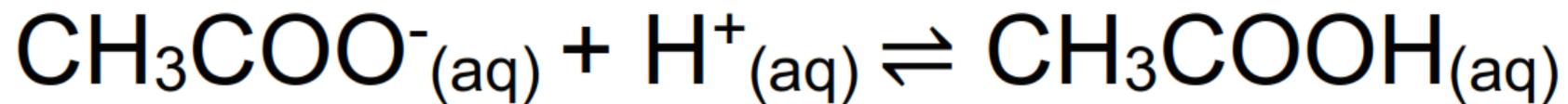
The final solution has equal amounts of weak acid and the salt of the weak acid and strong base (buffer solution).

Buffer solutions

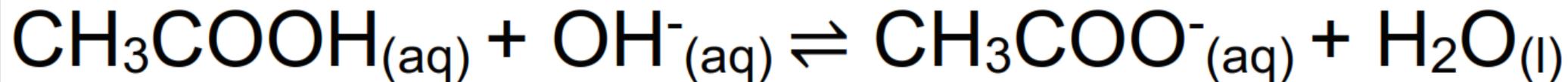
An acidic buffer can be made by mixing together a weak acid and the salt of the weak acid and a strong base.



Response to added acid $\text{H}^+_{(\text{aq})}$

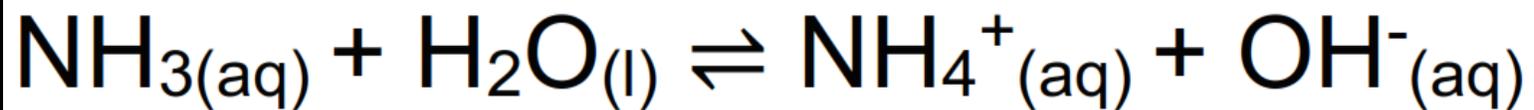


Response to added base $\text{OH}^-_{(\text{aq})}$

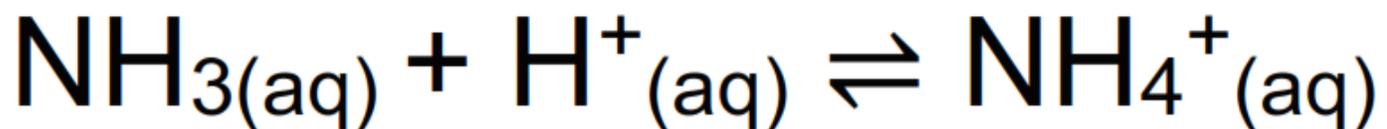


Buffer solutions

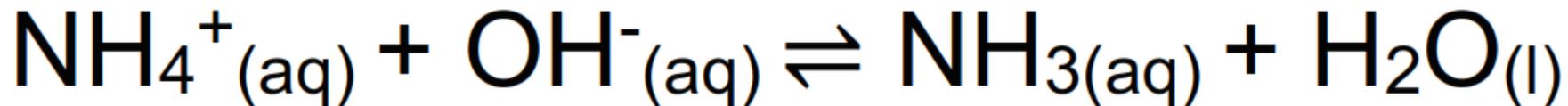
A basic buffer can be made by mixing together a weak base and the salt of the weak base and a strong acid.



Response to added acid $\text{H}^+(\text{aq})$



Response to added base $\text{OH}^-(\text{aq})$



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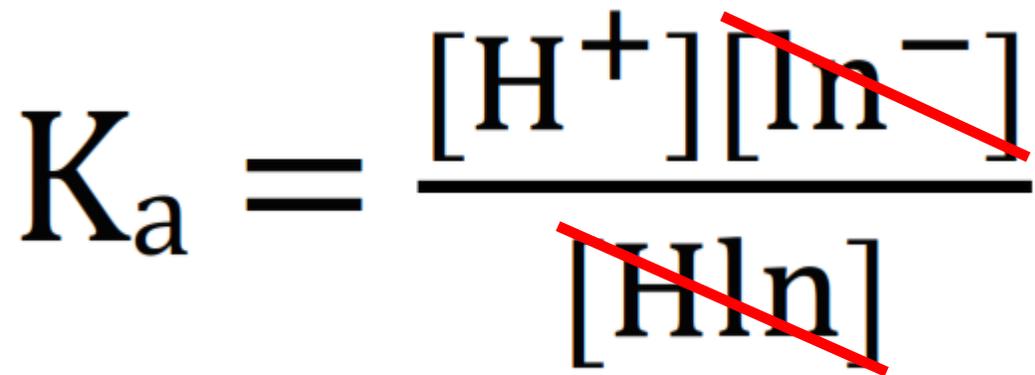
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Acid-base indicators

Acid-base indicators

The end point of an indicator is the pH at which it changes colour.

An indicator changes colour when the pH is equal to its pK_a



$$K_a = [H^+]$$

$$pK_a = pH$$

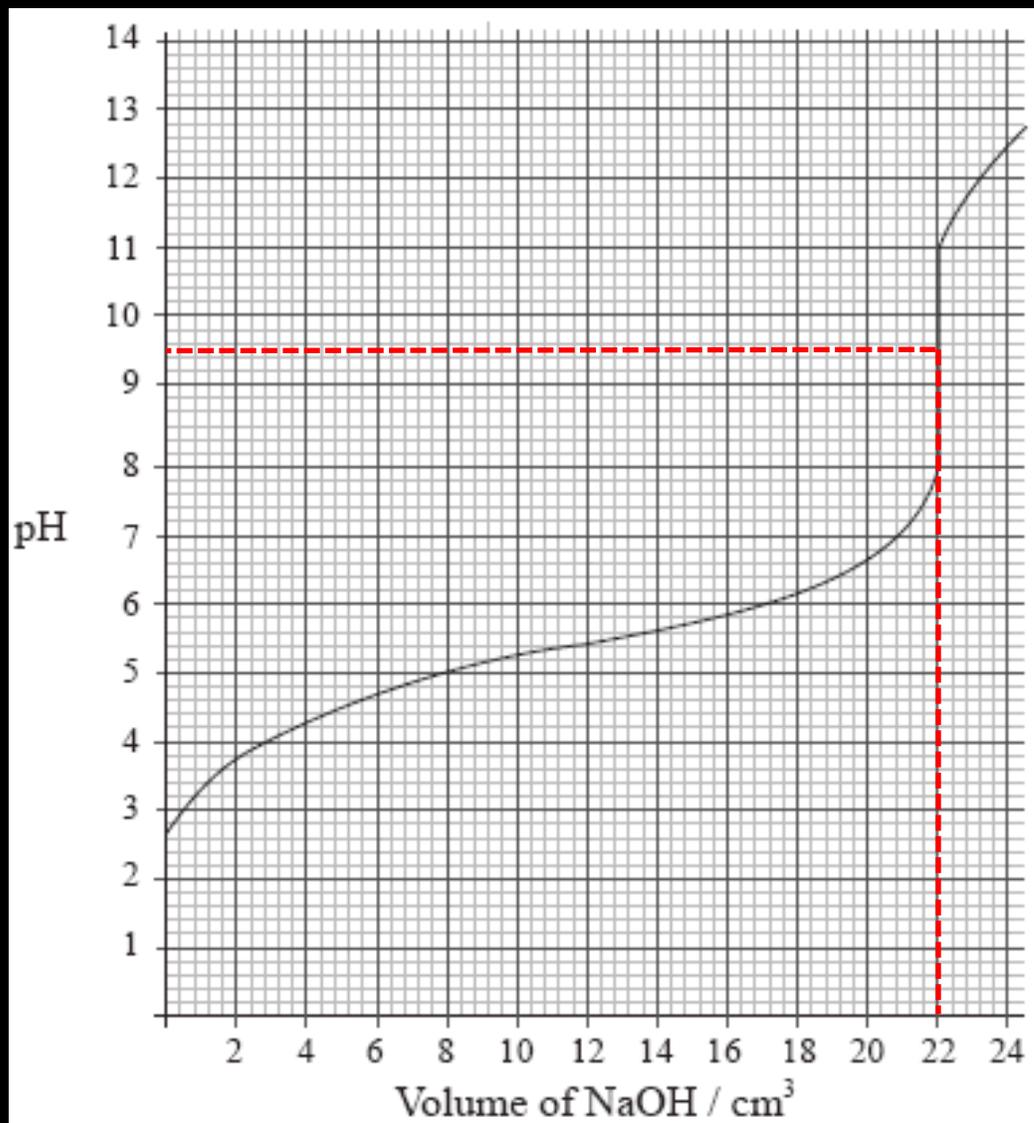
Acid-base indicators

Table 22 of the data booklet has a list of acid-base indicators, the pK_a values and the pH range over which they change colour. The colour change can be considered to take place over a range of $pK_a \pm 1$

22. Acid-base indicators

Indicator	pK_a	pH range	Colour change	
			Acid	Alkali
methyl orange	3.7	3.1–4.4	red	yellow
bromophenol blue	4.2	3.0–4.6	yellow	blue
bromocresol green	4.7	3.8–5.4	yellow	blue
methyl red	5.1	4.4–6.2	red	yellow
bromothymol blue	7.0	6.0–7.6	yellow	blue
phenol red	7.9	6.8–8.4	yellow	red
phenolphthalein	9.6	8.3–10.0	colourless	pink

Acid-base indicators



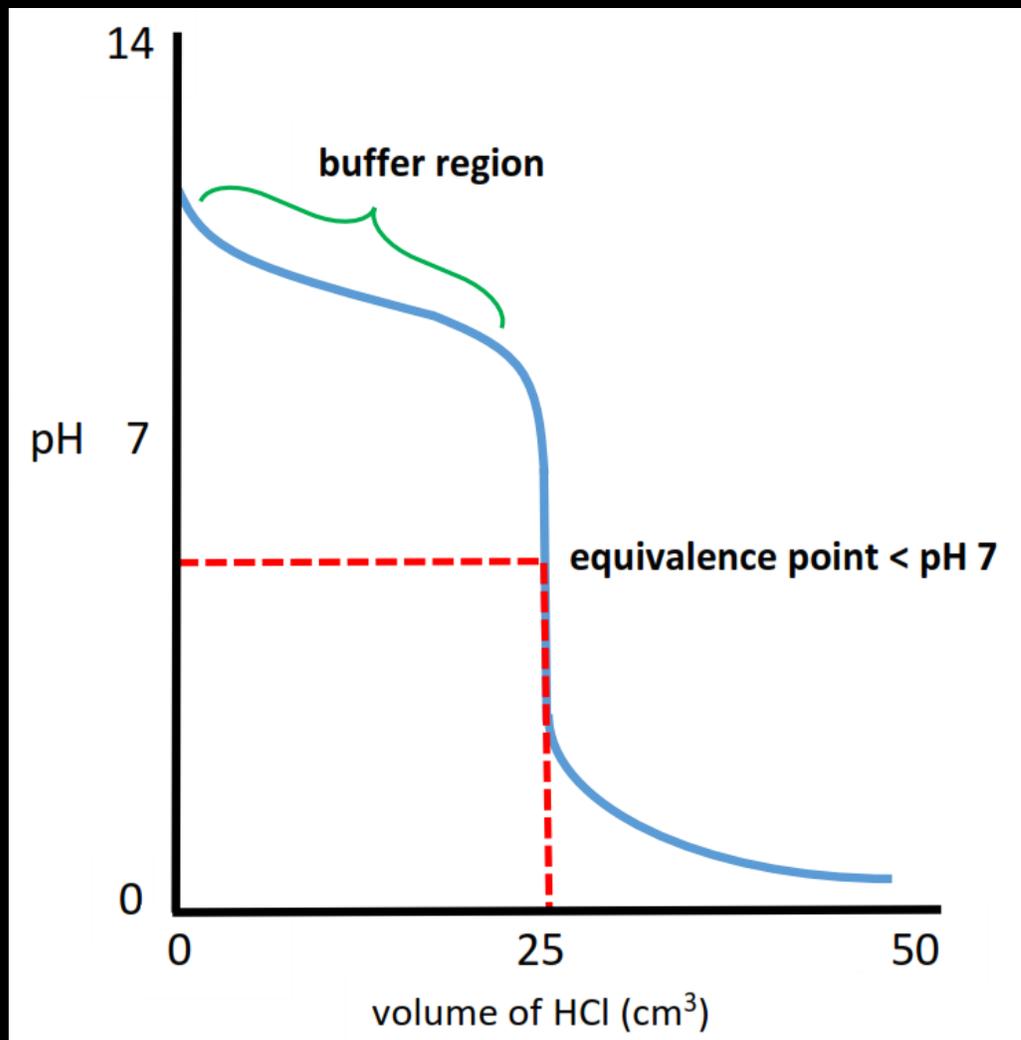
Titration of a weak acid and a strong base.

pH at equivalence point = 9.5

A suitable indicator for the titration of a weak acid and a strong base is

phenolphthalein (pH range 8.3-10.0)

Acid-base indicators



Titration of a weak base and a strong acid.
pH at equivalence point = 5.0
A suitable indicator for the titration of a weak base and a strong acid is methyl red (pH range of 4.4-6.2)

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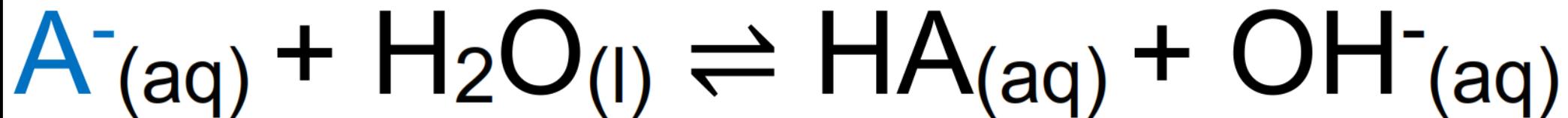
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Salt hydrolysis

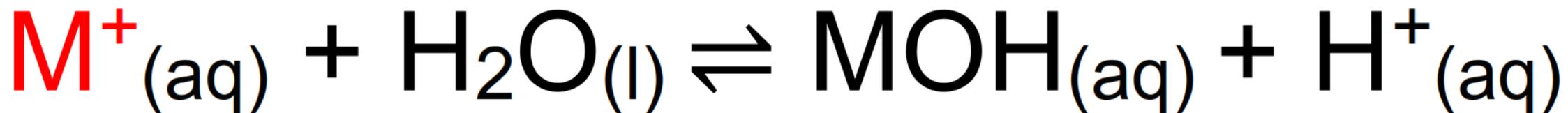
Salt hydrolysis

Salt hydrolysis refers to the reaction of a cation or an anion with water which ionizes the water molecule into H^+ and OH^-

Anion hydrolysis ($\text{pH} > 7$ at 298 K)

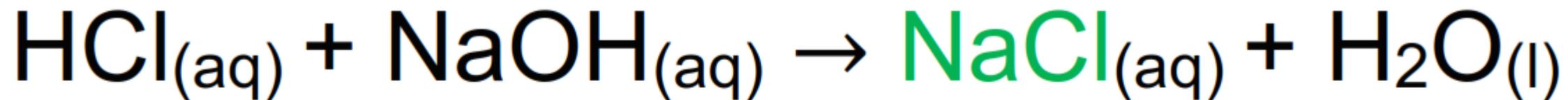


Cation hydrolysis ($\text{pH} < 7$ at 298 K)



Salt hydrolysis

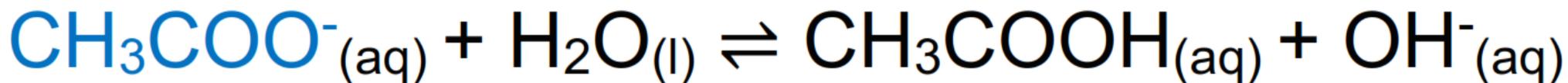
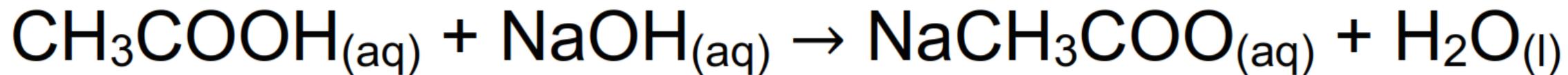
Salt of a strong acid and strong base



The salt formed from a strong acid and a strong base (NaCl) has a pH of approximately 7 at 298 K (neither ion hydrolyses).

Salt hydrolysis

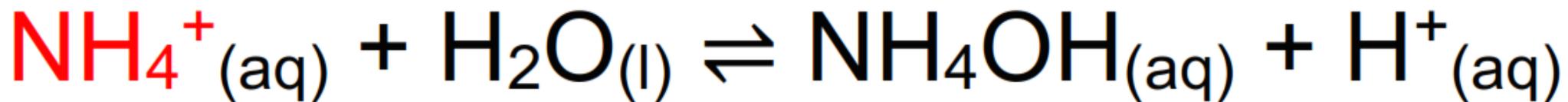
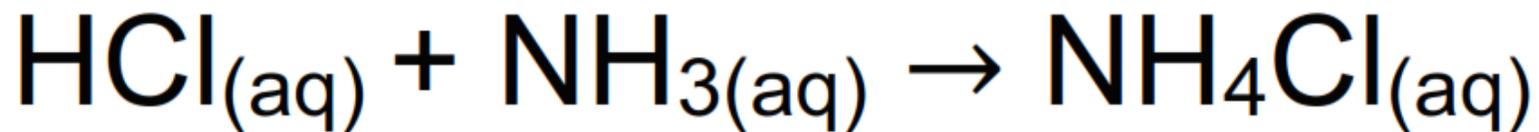
Salt of a weak acid and strong base



The salt formed from a weak acid and a strong base has a pH of > 7 at 298 K (the anion hydrolyses).

Salt hydrolysis

Salt of a strong acid and weak base



The salt formed from a strong acid and a weak base has a pH of < 7 at 298 K (the cation hydrolyses).