Chem Factsheet

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Brønsted - Lowry Bases in 'A' level Chemistry

The use of the word "base" as a substance that reacts with an acid was first used in 1754 by Rouelle. The term base superseded the word alkali (from the Arabic for "calcined ashes") as meaning the opposite of an acid.

Table 1 Three Acid-Base Definitions and Examples

	A **BASE** is a species which:	An **ACID** is a species which:
1883 Arrhenius	produces hydroxide ions in water. e.g. $NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$	produces hydrogen ions in water. e.g. $HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$
Neutralisation	$NaOH(aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(l)$ Arrhenius base + Arrhenius acid ⟶ salt + water The *ionic equation* for all Arrhenius neutralisations is: $H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$	
1923 Brønsted – Lowry (BL)	is a **proton (H^+) acceptor**. A BL base has an atom with a non-bonded pair (lone pair) of electrons. They form a dative bond with a H^+ from a BL acid.	is a **proton (H^+) donor**. A BL acid has a covalently bonded hydrogen atom which is lost as a proton.
Neutralisation	$NH_3(aq) + CH_3COOH(aq) \longrightarrow NH_4^+(aq) + CH_3COO^-(aq)$ i.e. BL base 2 + BL acid 1 ⟶ BL acid 2 + BL base 1 NH_4^+ is $[_3HN{\rightarrow}H]^+$. The arrow → showing that a dative bond is formed between the N and the H atoms and that both electrons of this bond are being donated by the N atom.	
1923 Lewis	is an **electron pair donor**. A Lewis base has a suitable electron pair which forms a dative bond by entering a vacant orbital in a Lewis acid.	is an **electron pair acceptor**. A Lewis acid has a vacant orbital which accepts the electron pair from a Lewis base.
"Their reaction together"	$NH_3(g) + BF_3(g) \rightleftharpoons H_3N{\rightarrow}BF_3(s)$ i.e. Base + Acid = Lewis adduct / Lewis acid-base complex. The arrow → represents the dative bond. The tail shows the electron pair is **donated by the N atom** and the head shows it is **donated to the B atom**.	

Note A change of shape occurs when a base accepts a proton since a non-bonded electron pair becomes a bonded pair and electron pair repulsions change. The shape of an ammonia molecule ($:NH_3$), with three bond pairs and one lone pair, is a trigonal pyramid and that of an ammonium ion (NH_4^+), with four bond pairs but no lone pairs, is tetrahedral.

Brønsted – Lowry Acids and Bases

The definition of a base as a proton acceptor enabled many different species to be classified as bases including molecules such as ammonia, amines and negative ions such as hydroxide ions, alkanoate ions (e.g. ethanoate ions, CH_3COO^-) and anions of oxyacids (e.g. chlorate(I) ions $[ClO^-]$ and chromate(VI) ions $[CrO_4^{2-}]$).

(a) Conjugate Acid-Base Pairs

Using B for a base and HA for an acid the general equation for an acid-base reaction is:

$$B + HA \rightleftharpoons BH^+ + A^-$$

B	HA	BH^+	A^-
Base 2	Acid 1	Acid 2	Base 1
Conjugate base of acid 2	Conjugate acid of base 1	Conjugate acid of base 2	Conjugate base of acid 1

B and BH^+ are one conjugate pair while HA and A^- are another conjugate pair. **The members of a conjugate acid base pair are related to each other by the presence or absence of a proton (H^+).** Above, base 2 accepts a proton from acid 1 to form its conjugate acid (BH^+) and the conjugate base (A^-) of HA respectively. Similarly, in the reverse reaction, base 1 accepts a proton from acid 2 to form their conjugates.

e.g. $H_2O + HClO \rightleftharpoons H_3O^+ + ClO^-$.

H_2O	$HClO$	H_3O^+	ClO^-
Base 2	Acid 1	Acid 2	Base 1

H_2O and H_3O^+ are an acid-base conjugate pair and HClO and ClO^- are also an acid-base conjugate pair.

(b) Calculating the pH of Aqueous Solutions of Bases

By definition, $pH = -\log_{10}[H^+]$ and $pOH = -\log_{10}[OH^-]$

Also, the ionic product of water $K_w = 1 \times 10^{-14} = [H^+].[^-OH]$ mol^2dm^{-6} at 298K.

$\therefore$ $[H^+] = 1 \times 10^{-14} / [^-OH]$

Taking $-\log_{10}$ of both sides

$\therefore$ $pH = 14 - pOH$

(i) Strong Bases

Such bases are **fully ionised** in aqueous solution so $[^-OH]$ is obtained directly from the molarity of the solution allowing for the number of moles of ^-OH produced per mole of base.

e.g.1 pH of 1.5×10^{-2} M NaOH?

$\therefore$ $[^-OH] = 1.5 \times 10^{-2}$ moldm^{-3}.

$\therefore$ $pOH = -\log_{10}[OH^-] = -\log_{10}[1.5 \times 10^{-2}] = 0.82$

$\therefore$ $pH = 14 - 0.82 = 12.18$

e.g.2 pH of 1.5×10^{-2} M $Ba(OH)_2$?

$\therefore$ $[^-OH] = 2(1.5 \times 10^{-2}) = 3.0 \times 10^{-2}$ moldm^{-3}.

$\therefore$ $pOH = -\log_{10}[OH^-] = -\log_{10}[3.0 \times 10^{-2}] = 0.52$

$\therefore$ $pH = 14 - 0.52 = 12.48$

(ii) Weak Bases

Such bases are **partially (usually only slightly) ionised** in aqueous solution so $[^-OH] << [\text{weak base}]$. This means the pH cannot be calculated directly. Instead, K_a of the conjugate acid or K_b for the weak base is needed to allow calculation.

Consider 0.1 mol dm^{-3} ammonia solution.
The following dynamic equilibrium exists in a closed system at constant temperature:

$NH_3 + H_2O \rightleftharpoons NH_4^+ + {}^-OH$ (State symbols left out)

An equilibrium constant, called a base dissociation constant (symbol K_b), is given by the expression:

$$K_b = \frac{[NH_4^+]_{eqm}\,[OH^-]_{eqm}}{[NH_3]_{eqm}} = 1.8 \times 10^{-5} \text{ mol dm}^{-3} \text{ at } 298K$$

$$\therefore K_b \approx \frac{[^-OH]^2}{[NH_3]_{initial}}$$

$$\therefore [^-OH] = \sqrt{K_b \times [NH_3]_{initial}} = \sqrt{1.8 \times 10^{-5} \times 0.1}$$
$$= 1.34 \times 10^{-3} \text{ mol dm}^{-3}$$

$\therefore$ $pOH = -\log_{10}[OH^-] = -\log_{10}[1.34 \times 10^{-3}] = 2.87$

$pH = 14 - pH = 14 - 2.87 = 11.13$

Note If K_a for the conjugate acid is given, (i.e. K_a of NH_4^+ = 5.6×10^{-10} mol dm^{-3}), since $K_w = K_a \times K_b$ then K_b can be calculated using $K_b = K_w / K_a$ and the pH of the weak base found as above.

The small value of the equilibrium constant (1.8×10^{-5} mol dm^{-3}) shows the equilibrium lies well to the left.

Hence, $[NH_3] >> [^-OH]$, since the base ^-OH is much stronger than the base NH_3. Similarly, NH_4^+ is a stronger acid than H_2O.

This demonstrates a general relationship between conjugate acids and bases. i.e. **the stronger a base is, then the weaker is its conjugate acid**.

(c) A Comparison of the Base Strengths of Ammonia and Ammonia Derivatives in Aqueous Solutions

		K_b/mol dm^{-3}
Phenylamine	$C_6H_5NH_2$	4.3×10^{-10}
Ammonia	NH_3	1.8×10^{-5}
Methylamine	CH_3NH_2	3.7×10^{-4}

The base strength depends on several factors including how readily the proton is accepted by the lone pair on the N atom. Any feature of the base that alters the electron density of the lone pair will change the base strength relative to ammonia.

K_b shows phenylamine is a much weaker base than ammonia. The **phenyl group is electron attracting** because the lone pair on the nitrogen is in a p-orbital which overlaps with the pi-orbital of the benzene ring reducing the electron density on the N atom. Therefore the N lone pair less readily attracts and gains a proton. Therefore the pH is lower than ammonia for the same concentration.

K_b shows methylamine is a stronger base than ammonia. The **methyl group is electron releasing** – a so-called **inductive effect**. This increases the electron density on the N atom so a proton is more strongly attracted and accepted. Therefore the pH of methylamine > pH of ammonia or the same concentration.

(d) Period 3 Oxides that Behave as Bases

Na_2O, MgO and Al_2O_3 have giant ionic structures containing metal cations and oxide anions (O^{2-}).
The oxide ions have lone pairs of electrons which allow them to be Brønsted - Lowry bases and accept protons.

(i) With acids

$O^{2-} + H^+ \rightarrow {}^-OH$; followed by $^-OH + H^+ \rightarrow H_2O$ as the hydroxide ion is also a base.

Overall: $O^{2-} + 2H^+ \rightarrow H_2O$.

The "full" equation with magnesium oxide and hydrochloric acid is:
$MgO + 2HCl \rightarrow MgCl_2 + 2H_2O$.

(ii) With water

The oxide ion has a high charge density (high charge and small volume) and in aqueous solution readily polarises a water molecule to remove a proton from that water molecule to produce two hydroxide ions and hence an alkaline solution.

$O^{2-}(aq) + H_2O(l) \rightarrow 2\,{}^-OH(aq)$

The pH produced when equal moles of Na_2O, MgO and Al_2O_3 are added to water depends upon the solubility of the oxide. Once dissolved the oxide ions immediately polarise water molecules – there are no $O^{2-}(aq)$ ions! (Table 2)

Table 2

	Na_2O	MgO	Al_2O_3
Solubility of oxide	Very high	Very low	Insoluble
Equation with water	$Na_2O(s) + H_2O(l) \rightarrow 2Na^+(aq) + 2\,{}^-OH(aq)$	$MgO(s) + H_2O(l) \rightarrow Mg(OH)_2(s)$ $Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\,{}^-OH(aq)$	No reaction
pH of solution	14	10 (only 12 mgdm^{-3} $Mg(OH)_2$ dissolves)	Stays at 7

(e) Reactions of Bases with $[M(H_2O)_6]^{2+}$ and with $[M(H_2O)_6]^{3+}$, where M is a Transition Metal ion or Al^{3+}

Note. Sometimes alternative equations can be written for some of the equations written below.

The ions $[M(H_2O)_6]^{2+}$ and $[M(H_2O)_6]^{3+}$ (abbreviated M^{2+} (aq) and M^{3+} (aq)) are **hydrolysed** in water and the following equilibria occur.

Table 3

	$[M(H_2O)_6]^{2+}$	$[M(H_2O)_6]^{3+}$
Water	$[M(H_2O)_6]^{2+} + H_2O \rightleftharpoons [M(H_2O)_5OH]^{+} + H_3O^+$	$[M(H_2O)_6]^{3+} + H_2O \rightleftharpoons [M(H_2O)_5OH]^{2+} + H_3O^+$
	The **$[M(H_2O)_6]^{2+/3+}$ acid** donates protons to **solvent water molecules which act as bases**. M^{3+} has a much greater charge density than M^{2+}. So M^{3+} more strongly polarises the ligand water molecules resulting in the loss of more protons to solvent water molecules and hence a lower pH.	
Acidity	Very weakly acidic. pH ≈ 6	Weakly acid. pH ≈ 3

Since the hydrated metal ions are acting as acids, what happens if bases of different strengths are added?

(i) Addition of a little Sodium Hydroxide Solution or a little Ammonia Solution

A coloured or white precipitate occurs with M^{3+} (aq) and most M^{2+} (aq) when 3 or 2 H^+ ions respectively have been removed by the added base. This is often called **deprotonation** of the aqueous metal ion.

The equations can be written as acid-base reactions or as ionic precipitations.

e.g. Cu^{2+} (aq) forms a pale blue precipitate and Cr^{3+} (aq) forms a green ppte.

Acid-base: $[Cu(H_2O)_6]^{2+} + 2\,^-OH \rightarrow [Cu(H_2O)_4(OH)_2] + 2H_2O$.

or ionic precipitation: $Cu^{2+}(aq) + 2\,^-OH(aq) \rightarrow Cu(OH)_2(s)$

Acid-base: $[Cr(H_2O)_6]^{3+} + 3NH_3 \rightarrow [Cr(H_2O)_3(OH)_3] + 3NH_4^+$.

or ionic precipitation: $Cr^{3+}(aq) + 3\,^-OH(aq) \rightarrow Cr(OH)_3(s)$

Note Ammonia solution is alkaline and provides OH- ions because of the equilibrium:

$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + {}^-OH(aq)$

Remember: In a balanced equation the sum of the atoms **and the sums of charges are equal** on both sides.

(ii) Addition of excess Sodium Hydroxide Solution or Dilute Acid (e.g. HCl(aq)) - (Amphoteric Nature)

The hydroxides of Zn^{2+}, Al^{3+} and Cr^{3+} act as Brønsted - Lowry acids with sodium hydroxide **and** as Brønsted - Lowry bases with dilute acids, e.g. hydrochloric acid. Hence, these metal hydroxides are **amphoteric**.

As an acid: $[Cr(H_2O)_3(OH)_3](s) + 3\,^-OH(aq) \rightarrow [Cr(OH)_6]^{3-}(aq) + 3H_2O(l)$.
A green solution forms.

$[Zn(H_2O)_4(OH)_2](s) + 4\,^-OH(aq) \rightarrow [Zn(OH)_6]^{4-}(aq) + 4H_2O(l)$.
A colourless solution forms.

$[Al(H_2O)_3(OH)_3](s) + 3\,^-OH(aq) \rightarrow [Al(OH)_6]^{3-}(aq) + 3H_2O(l)$.
A colourless solution forms.

Ligand water molecules donate protons to lone pairs on O of ^-OH (aq).

As a base: $[Cr(H_2O)_3(OH)_3](s) + 3H_3O^+(aq) \rightarrow [Cr(H_2O)_6]^{3+}(aq) + 3H_2O(l)$.
A green solution forms.

H_3O^+ ions donate protons to lone pairs on the ^-OH ligands producing water molecule ligands.

These reactions can also be seen as **complete deprotonation** of all six original water ligand molecules. This is only possible using the strong base OH^-. It does not occur for weaker bases such as ammonia.

(iii) Addition of Excess Ammonia Solution

Some metal hydroxides dissolve forming ammine complexes.

e.g. $[Cr(H_2O)_3(OH)_3](s) + 6NH_3(aq) \rightarrow [Cr(NH_3)_6]^{3+}(aq) + 3H_2O_{(l)} + 3\,^-OH(aq)$
Purple solution forms.

e.g. $[Co(H_2O)_4(OH)_2](s) + 6NH_3(aq) \rightarrow [Co(NH_3)_6]^{2+}(aq) + 4H_2O(l) + 4\,^-OH(aq)$
Pale yellow solution forms.

The **ammonia molecules act as Lewis bases** since they provide an electron pair to be shared with the metal ion. These reactions are also referred to as **ligand exchanges** or **ligand substitutions**.

Note. The equation can be written from the hydrate ion:

e.g. $[Cr(H_2O)_6]^{3+}(aq) + 6NH_3(aq) \rightarrow [Cr(NH_3)_6]^{3+}(aq) + 6H_2O(l)$

(iv) Addition of Sodium Carbonate Solution

The carbonate ion is such a weak BL base that it does not take protons from the water ligands in M^{2+} complexes. The latter is only very weakly acidic because of the low charge density of M^{2+} ions.

A coloured or white carbonate precipitate occurs with M^{2+} (aq).

e.g. $Co^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CoCO_3(s)$ Pink recipitate forms.

However, because of increased polarization (see earlier) M^{3+} aqueous ions are sufficiently acidic to donate H^+ to the very weakly basic carbonate ions. A coloured or white hydroxide precipitate occurs with $M^{3+}{}_{(aq)}$ plus fizzing as the carbonate ions accept protons to form water and carbon dioxide gas.

Acid-base:

$2[Fe(H_2O)_6]^{3+} + 3CO_3^{2-} \rightarrow 2[Fe(H_2O)_3(OH)_3] + 3CO_2 + 3H_2O$

(Note: LHS 2(3+) and 3(2-); RHS: 0 charge)

(f) The Elimination Reaction of Halogenoalkanes with Hot Concentrated Potassium Hydroxide in Ethanol.

The hydroxide ion is the Brønsted - Lowry base as it accepts a proton from the haloalkane – the acid.

e.g. $CH_3CH_2Br + {}^-OH \rightarrow CH_2{=}CH_2 + H_2O + Br^-$

This is also called an elimination reaction because HBr is eliminated.

(g) Amino Acids and Zwitterions as Bases

Amino acids have amino groups ($-NH_2$) and Zwitterions have carboxylate groups ($-CO_2^-$). These groups can accept protons and hence they are Brønsted - Lowry bases.

The lone pair on the N of the amino acid accepts a proton forming its conjugate acid:

$HOOCCH(R)NH_2 + H^+ \rightarrow HOOCCH(R)N^+H_3$

The lone pair on the O of the Zwitterion accepts a proton forming its conjugate acid:

${}^-OOCCH(R)^+NH_3 + H^+ \rightarrow HOOCCH(R)N^+H_3$

(h) Buffer Solutions

Acidic buffer: e.g. ethanoic acid + (sodium) ethanoate.

Alkaline buffer: e.g. ammonia + ammonium (chloride).

Hence they are both mixtures of BL conjugate acids and bases.

Buffer solutions have high concentrations of these conjugate acid-base pairs. Hence the base present can remove small amounts of added acid and thus keep the pH almost constant. The acid present can remove small amounts of added alkali and thus keep the pH almost constant.

Removal of acid by the base:

For an acidic buffer: $CH_3COO^- + H^+ \rightarrow CH_3COOH$

and for an alkaline buffer: $NH_3 + H^+ \rightarrow NH_4^+$.

Removal of alkali by the conjugate acid:

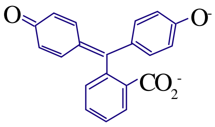
For an acidic buffer: $CH_3COOH + {}^-OH \rightarrow CH_3COO^- + H_2O$

and for an alkaline buffer: $NH_4^+ + {}^-OH \rightarrow NH_3 + H_2O$.

Practice Questions

1. (a) Give two reasons why the reaction:
   $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$ is **not** an Arrhenius acid-base reaction.
   (b) Why is the same reaction a Brønsted – Lowry acid-base reaction and state the conjugate acid-base pairs.

2. The structure of the acid-base indicator phenolphthalein at pH 8.2 to 12 is shown below.



   Suggest and explain, in terms of the Brønsted – Lowry theory, a change to the structure that could occur when dilute HCl(aq) is added. What colour change occurs?

3. The solubility of sodium oxide at room temperature is about 109g per 100 cm^3 of solution.
   Calculate the pH of the solution.

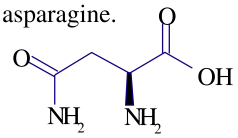
4. Explain why the hydrolysis reactions shown below are Brønsted – Lowry acid-base reactions.
   $[Cr(H_2O)_6]^{3+} + H_2O \rightarrow [Cr(H_2O)_5(OH)]^{2+} + H_3O^+$
   and $[Cr(H_2O)_6]^{2+} + H_2O \rightarrow [Cr(H_2O)_5(OH)]^+ + H_3O^+$.
   Explain which reaction leads to a lower pH.

5. Explain the terms amphiprotic and amphoteric. Illustrate your answer by writing suitable equations using the hydrogencarbonate ion (HCO_3^-).

6. One buffer system in the blood consists of the ions $H_2PO_4^-$ and HPO_4^{2-}. Which ion is a Brønsted – Lowry base? Write an equation for the removal of hydrogen ions by this buffer system.

7. Write i) "full" equations and ii) ionic equations (using H^+) for the reactions that occur when hydrochloric acid is added to the following (a) magnesium hydroxide, (b) iron(III) oxide and (c) sodium carbonate.

8. This is the amino acid, asparagine.



   Write the structures of the particles produced when asparagine is added to i) HCl(aq), ii) KOH(aq). Explain why asparagine is amphoteric. Note. Amides are not basic.

Answers

1. (a) NH_3 has no hydroxide ions so cannot be an Arrhenius base and gaseous HCl has no hydrogen ions so cannot be an Arrhenius acid. Also Arrhenius definitions are limited to aqueous solutions.
   (b) NH_3 is a B-L base since it accepts a proton from HCl. HCl is a B-L acid since it donates a proton to NH_3.
   Conjugate acid-base pairs are NH_4^+ / NH_3 and HCl / Cl^-.

2. O^- becomes OH and CO_2^- becomes COOH and C=O becomes $C{=}O^+H$. The O atom has a lone pair of electrons so is a B-L base when it accepts a proton from the HCl / H_3O^+, the B – L acid. Pink to colourless.

3. $Na_2O(s) + H_2O(l) \rightarrow 2Na^+(aq) + 2{}^-OH(aq)$
   $Na_2O = 1090/62 = 17.6$ mol dm^{-3}.
   $[{}^-OH] = 2 \times 17.6 = 35.2$ mol dm^{-3}.
   pH = pKw – pOH = 14 – (-1.5) = 15.5.

4. $[Cr(H_2O)_6]^{3+}$ and $[Cr(H_2O)_6]^{2+}$ are both Brønsted – Lowry acids since they donate protons to water, the Brønsted – Lowry base.
   Cr^{3+} has a higher charge density than Cr^{2+}. So it more strongly polarises the water ligands so they lose more protons and hence the pH is lower.

5. Amphiprotic - means that the species can both donate and receive a proton.
   Amphoteric - means that the species can act as an acid or as a base. (Note: Brønsted – Lowry or Lewis)
   Receiving a proton so acting as a Brønsted – Lowry base:
   e.g. $HCO_3^- + H_3O^+ \rightarrow 2H_2O + CO_2$
   Donating a proton so acting as a Brønsted – Lowry acid:
   e.g. $HCO_3^- + {}^-OH \rightarrow CO_3^{2-} + H_2O$.

6. HPO_4^{2-}. $HPO_4^{2-} + H^+ \rightarrow H_2PO_4^-$
   or $HPO_4^{2-} + H_3O^+ \rightarrow H_2PO_4^- + H_2O$

7. (i) (a) $Mg(OH)_2 + 2HCl \rightarrow MgCl_2 + 2H_2O$.
   (b) $Fe_2O_3 + 6HCl \rightarrow 2FeCl_3 + 3H_2O$.
   (c) $Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$
   (ii) (a) ${}^-OH + H^+ \rightarrow H_2O$.
   (b) $O^{2-} + 2H^+ \rightarrow H_2O$ or $O^{2-} + H^+ \rightarrow {}^-OH$
   and ${}^-OH + H^+ \rightarrow H_2O$.
   (c) $CO_3^- + 2H^+ \rightarrow H_2O + CO_2$ or $CO_3^- + H^+ \rightarrow HCO_3^-$
   and $HCO_3^- + H^+ \rightarrow H_2O + CO_2$

8. (i) The $-NH_2$ groups both become $-N^+H_3$.
   (ii) The –COOH becomes $-COO^-$.
   Asparagine is amphoteric since it has reacted as a base with HCl(aq) and as an acid with KOH(aq).

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