

REACTIONS in AQUEOUS SOLUTION (Chapter 4)

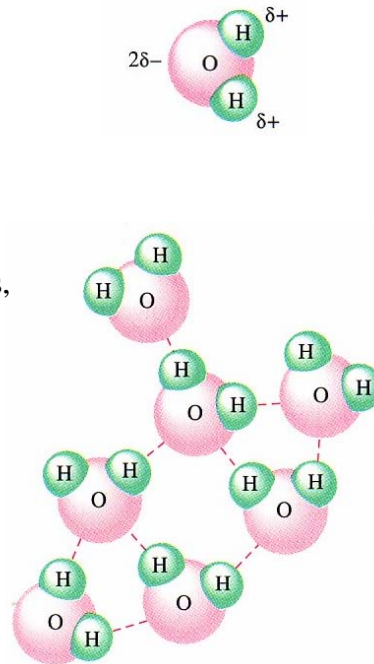
-Water often called 'universal solvent'

-All acid-alkali reactions, synthesis of salts, sugars,

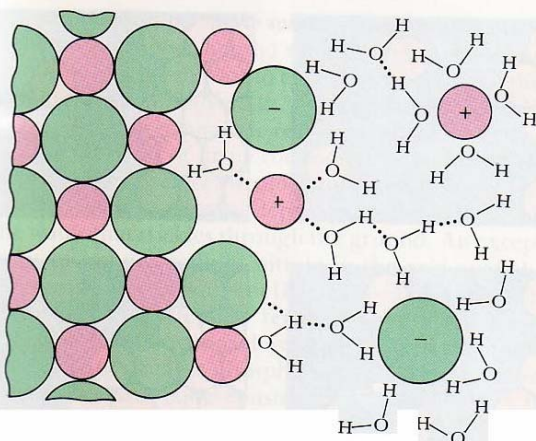
protein and biological reactions done in **aqueous** media

H₂O is a neutral but highly polar molecule

⇒ strong hydrogen bonding



Solvation of salt ions (p. 121)



Hydration of salt ions by water

-solvents dissolve salts by **solvation** of their **cations** and **anions**

- 'hydration' of ions is:

- an ion-dipole attraction.

- exothermic (stabilises ions, lowers energy of solution, prevents ion pair formation)

Classifying Aqueous Solutes (p. 121)

Most polar molecules dissolve in water but only some break apart into ions (**dissociate**)

Dissociating solutes are called **electrolytes**

electrolytes produce charge-carrying ions that allow solution to conduct electricity e.g. NaCl, Ca(OH)₂, HBr, CH₃COOH

Water is very weak conductor of electricity

Polar molecular compounds that dissolve in water (hydrogen bonding) but do not dissociate are **non-electrolytes** e.g.

sucrose (table sugar) **vitamin C** **urea** **glucose**



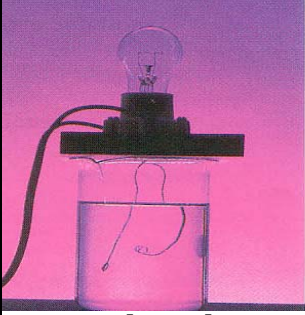
non-electrolyte

strong electrolyte

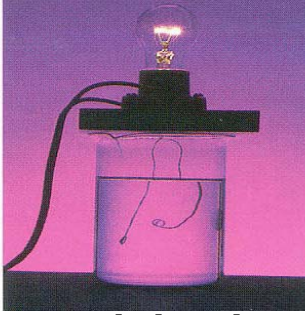
Electrolytes that completely dissociate are called **strong electrolytes**

salt NaBr	$\xrightarrow{\text{H}_2\text{O}}$	Na ⁺ (aq.) + Br ⁻ (aq.)
strong base Ba(OH) ₂	$\xrightarrow{\text{H}_2\text{O}}$	Ba ²⁺ (aq.) + 2OH ⁻ (aq.)
strong acid HCl	$\xrightarrow{\text{H}_2\text{O}}$	H ₃ O ⁺ (aq.) + Cl ⁻ (aq.)

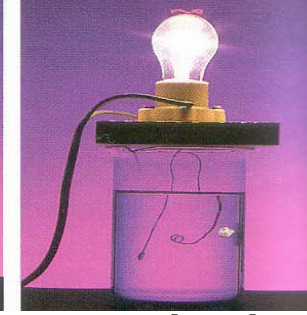
Classifying Aqueous Solutes



non-electrolyte



weak electrolyte

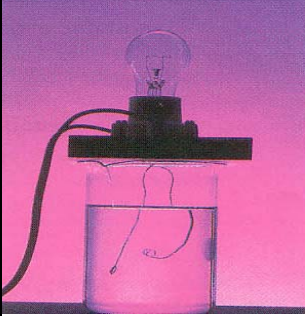


strong electrolyte

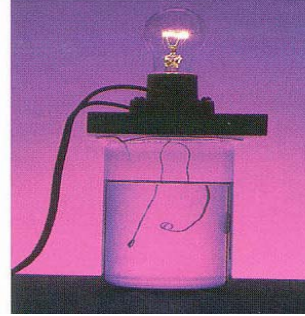
Electrolytes that only partially dissociate are called **weak electrolytes**

weak acid	CH_3COOH	$\xrightleftharpoons{\text{H}_2\text{O}}$	$\text{CH}_3\text{COO}^- (\text{aq.}) +$	$\text{H}_3\text{O}^+ (\text{aq.})$
weak base	NH_3	$\xrightleftharpoons{\text{H}_2\text{O}}$	$\text{NH}_4^+ (\text{aq.}) +$	$\text{OH}^- (\text{aq.})$
weak acid	HF	$\xrightleftharpoons{\text{H}_2\text{O}}$	$\text{H}_3\text{O}^+ (\text{aq.}) +$	$\text{F}^- (\text{aq.})$

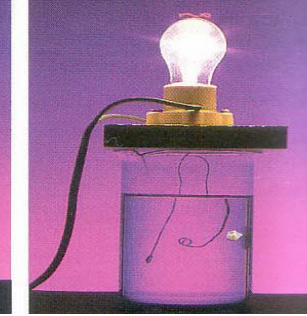
Classifying Aqueous Solutes



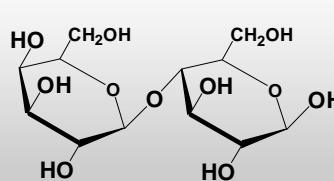
non-electrolyte



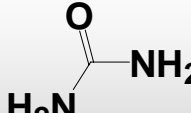
weak electrolyte



strong electrolyte

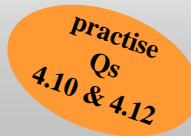


Lactose



Urea

These covalent molecular solids are non electrolytes



Classifying Reactions

Several ways to classify countless combinations of reactions

1) by arrangement of reactants and products:

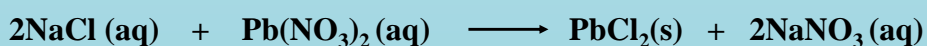
Combination (or Synthesis) reaction – molecule is formed from simpler reagents ('two become one') e.g.



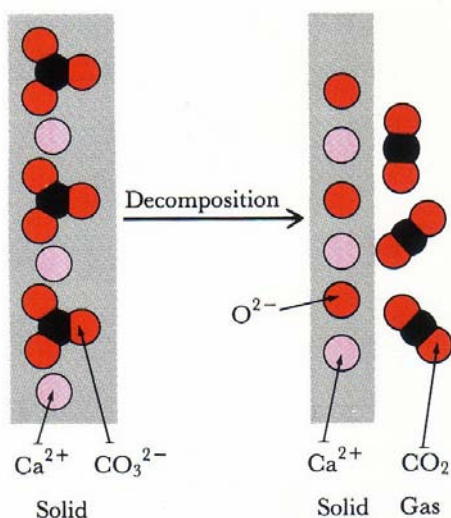
Displacement - atom or ion is replaced by that of another element



Double replacement – molecules or ions swap partners e.g.



Decomposition – molecule breaks apart into simpler components e.g.

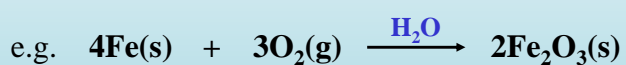


Solid calcium carbonate (an ionic compound) decomposes into calcium oxide (another ionic compound) and carbon dioxide (a gas). In a decomposition reaction a substance changes into less complex substances, which may be either elements or other compounds. In this case, the solid compound CaCO₃ decomposes into two compounds, the solid CaO and the gas CO₂.

Combustion – a rapid exothermic reaction of a substance with oxygen. Products usually gaseous.



Corrosion – depletion of a metal by slow reaction with oxygen



2) Can also classify reactions by the type of chemistry involved:

PRECIPITATION reactions – solid drops out of solution

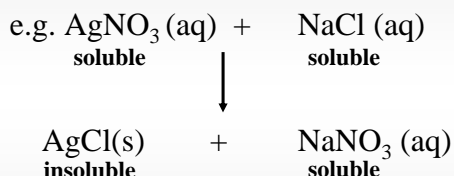
ACID-BASE reactions – product forms with water (neutralisation)

REDOX reactions – atom(s) of each reagent change **oxidation state**

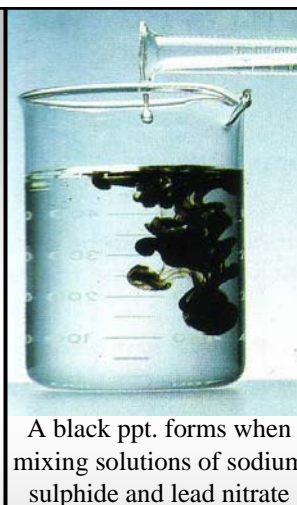
PRECIPITATION REACTIONS (p. 122)

-formation of a solid suspension in a solution

-typically ionic compounds (salts)



(also a double replacement reaction)

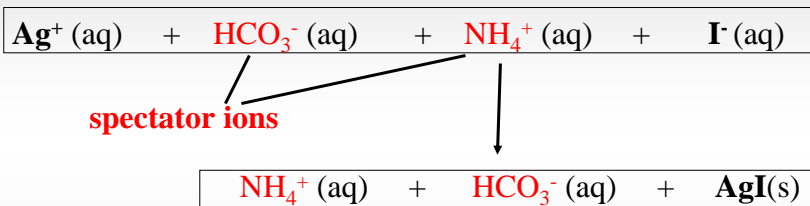


Silver halides always water-insoluble so form whenever Ag^+ and X^- ions come together in solution e.g.



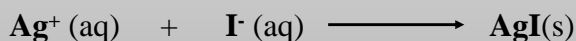
Ionic Equations (p. 124)

-more accurate description involves listing all the ions that are involved:



n.b. bicarbonate and ammonium ions do not take part in the reaction – they are **spectator ions**

-Can write the **net ionic reaction** as:



-by checking the solubility rules for different salts:

Solubility of ionic compounds

Classes of soluble compounds	Classes of insoluble compounds
compounds of Group I elements ammonium (NH_4^+) compounds chlorides (Cl^-), bromides (Br^-), and iodides (I^-), EXCEPT Ag^+ , Hg_2^{2+} , Pb^{2+}	carbonates (CO_3^{2-}), phosphates (PO_4^{3-}), oxalates ($\text{C}_2\text{O}_4^{2-}$), and chromates (CrO_4^{2-}), EXCEPT Group I elements and NH_4^+ sulfides (S^{2-}), EXCEPT Group I elements, Group II elements, and NH_4^+
nitrates (NO_3^-), chlorates (ClO_3^-), perchlorates (ClO_4^-), acetates (CH_3CO_2^-)	hydroxides (OH^-) and oxides (O^{2-}), EXCEPT Group I elements and Group II elements*
sulfates (SO_4^{2-}), EXCEPT Sr^{2+} , Ba^{2+} , Pb^{2+}	

* $\text{Ca}(\text{OH})_2$ and $\text{Sr}(\text{OH})_2$ are sparingly (slightly) soluble; $\text{Mg}(\text{OH})_2$ is only very slightly soluble.

We can:

i) determine which salts are soluble

e.g. CuSO_4 = soluble

BaSO_4 = insoluble

*practise
Ex 4.1, Q 4.20*

-by checking the solubility rules for different salts:

Solubility of ionic compounds

Classes of soluble compounds	Classes of insoluble compounds
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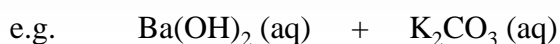
ii) synthesise most insoluble metal salts by mixing together the appropriate solutions

e.g. if we wanted to prepare **barium carbonate** (BaCO_3).....

.....we need to introduce carbonate ion (CO_3^{2-}) and barium ion (Ba^{2+}) in soluble form:

most Ba^{2+} salts are soluble e.g. can use BaBr_2 , $\text{Ba}(\text{NO}_3)_2$, $\text{Ba}(\text{OH})_2$, BaS

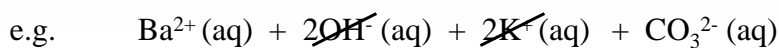
BUT few carbonates are soluble \Rightarrow must choose NH_4 or alkali metal
e.g. K_2CO_3 , $(\text{NH}_4)_2\text{CO}_3$



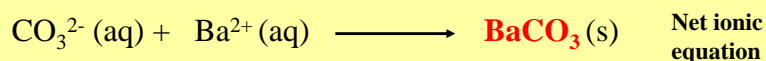
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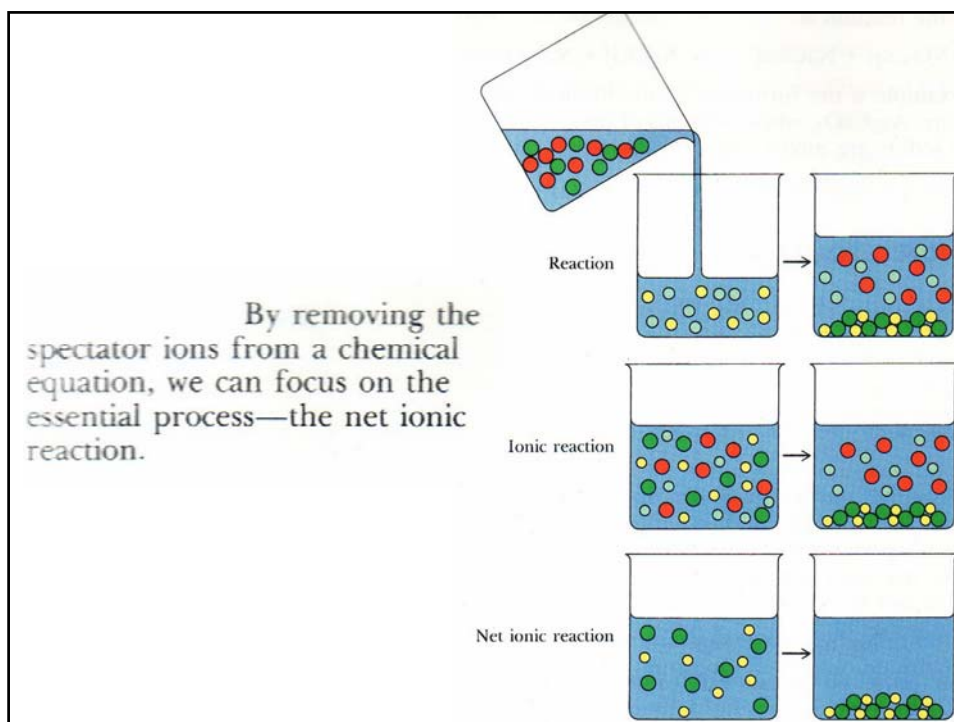
BUT few carbonates are soluble \Rightarrow must choose NH_4 or alkali metal
e.g. K_2CO_3 , $(\text{NH}_4)_2\text{CO}_3$



cancel spectator ions to give net ionic equation:



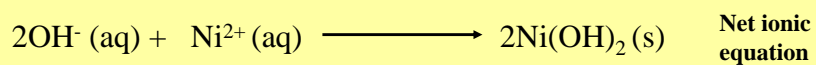
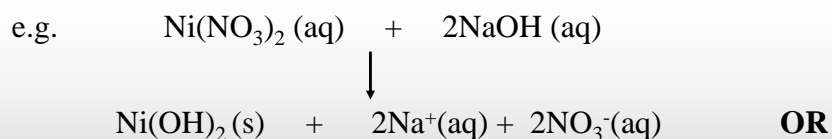
desired BaCO_3 precipitate is then collected by filtration



Q: Will precipitation result on mixing solutions of nickel (II) nitrate and sodium hydroxide? Write the net ionic equation.

A: Consider the possible products of double replacement i.e. sodium nitrate and nickel (II) hydroxide.

All nitrates are soluble but hydroxides such as nickel (II) hydroxide are insoluble (\Rightarrow we expect $\text{Ni}(\text{OH})_2$ to precipitate).



Q: Will precipitation result on mixing solutions of silver perchlorate and caesium nitrate? Write the net ionic equation.

A: Consider the possible products of double replacement i.e. silver nitrate and caesium perchlorate.

All nitrates are soluble....

.....and all perchlorates are soluble

⇒ no precipitate

read
Ex 4.2 & Q 4.22

Q: How could we separate an aqueous mixture of K^+ from Ag^+ ?

A: Find anion X such that KX and AgX have different solubilities

⇒ K salts typically more soluble than Ag

⇒ need KX to be soluble and AgX to be insoluble

⇒ could add Cl^- ions ⇒ $KCl(aq) + AgCl(s)$

.....or could add OH^- ions ⇒ $KOH(aq) + AgOH(s)$

.....or could add CO_3^{2-} ions ⇒ $K_2CO_3(aq) + AgCO_3(s)$

(remove ppt of silver salt by filtration)

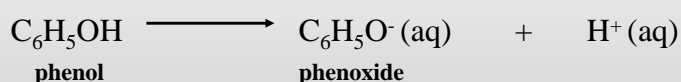
try
Q 4.24 b)-d)

ACID-BASE REACTIONS (p. 127)

Arrhenius described i) **acids** as molecules that released H^+ ions in water

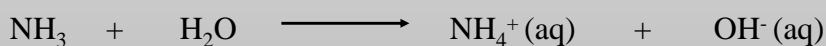
e.g. HCl (hydrochloric acid)

CH_3COOH (acetic acid)



...and ii) **bases** as those that gave rise to OH^- ions in aqueous solution

e.g. NaOH and



bases that dissolve in water are **alkalis**

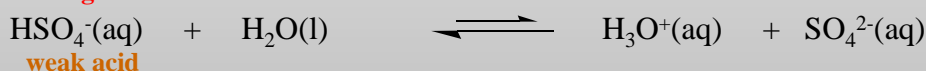
Acid Equivalentents (p. 128)

- some acids have only one proton to donate per molecule e.g. HCl



-we say HCl is **monoprotic** or monobasic (because it is neutralised by one equivalent of NaOH)

sulphuric acid is **diprotic**:



HSO_4^- anion is only weakly acidic \Rightarrow second proton loss written as equilibrium

Neutralisation (p. 130)

- when an acid H^+X^- and a base M^+OH^- come together, a neutral salt M^+X^- is formed e.g.



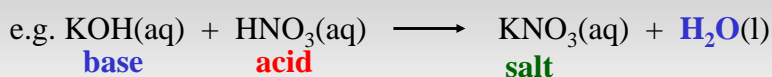
since M^+ and X^- are typically soluble they are **spectator ions**

-the net ionic reaction obtained by cancelling out the spectator ions:

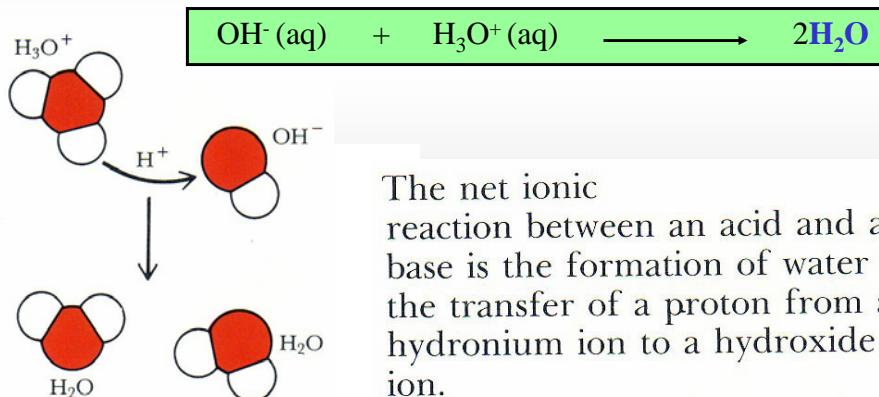


net ionic reaction of neutralisation is the formation of water

Neutralisation (p. 130)



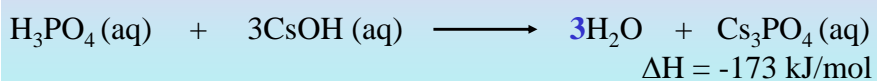
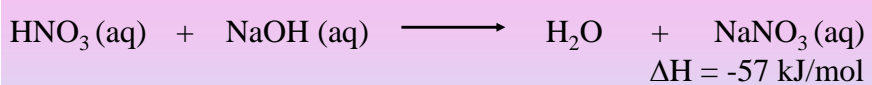
but K^+ and NO_3^- are spectator ions. Again, the net ionic equation is:



⇒ mixing is **exothermic** (no bonds need be broken *and* strong O-H bonds form)

neutralisation involves formation of water from hydrogen and hydroxide ions

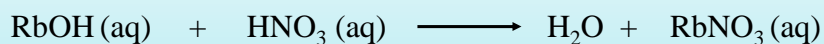
-heat evolved is same (per mole of water formed) for all neutralisations:



Q: What acids and bases could be used to prepare a rubidium nitrate solution?

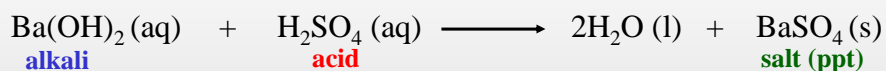
A: base provides metal cation Rb^+use RbOH

acid provides anion NO_3^- use HNO_3



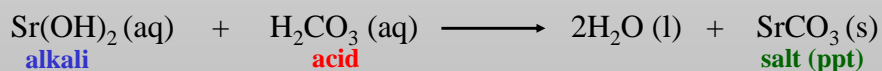
Salt precipitation from neutralisation

n.b. neutralisation reactions can also be precipitation reaction if salt product is insoluble e.g.



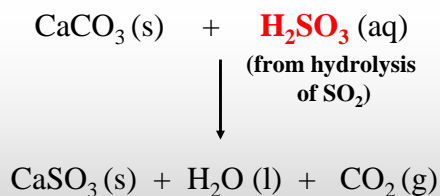
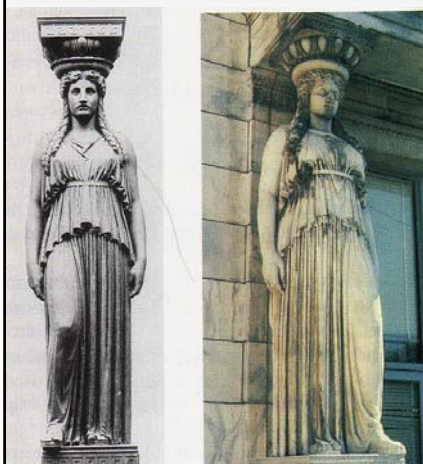
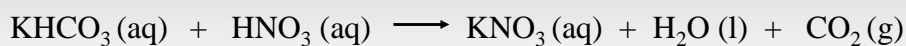
Q: How could we prepare a precipitate of strontium carbonate (SrCO_3)

A: Metal must be provided by base \Rightarrow use Sr(OH)_2
anion must be provided by acid \Rightarrow use H_2CO_3



Acids and CO_2 release (p. 127 & 131)

-acids dissolve carbonates and bicarbonates to liberate CO_2 e.g.



Acid rain dissolves limestone statues (p. 767)

Acids and CO₂ release (p. 127 & 131)

Q: The rock dolomite (MgCO₃) dissolves and effervesces when immersed in a solution of the triprotic acid phosphoric acid (H₃PO₄) leaving a white precipitate. Write a balanced equation for the reaction.

A: carbonate + acid \Rightarrow gas must be CO₂
white ppt = magnesium phosphate

imbalanced equation:



balanced equation:

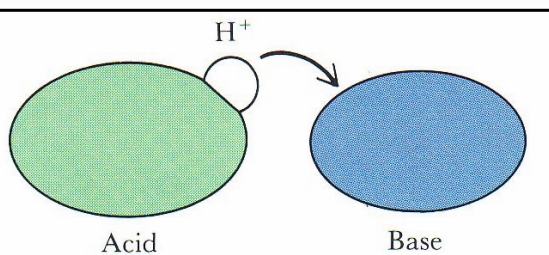


Bronsted Acid-Base theory (p. 128)

Proposed in 1920s

A **Bronsted acid** is a proton donor

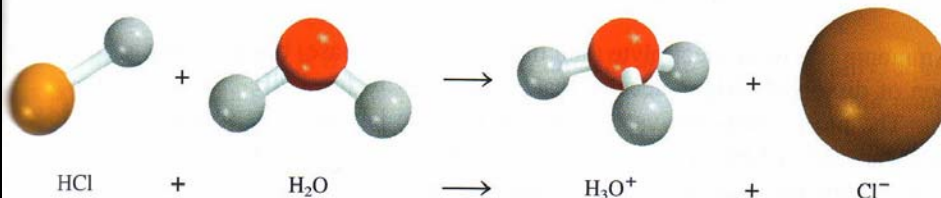
A **Bronsted base** is a proton acceptor



proton simply refers to hydrogen cation, H⁺

A Brønsted acid is a proton donor; a Brønsted base is a proton acceptor.

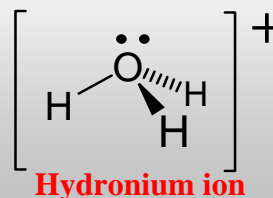
When HCl dissolves in water:



HCl is Bronsted acid and water the Bronsted base (accepts proton)

H₃O⁺ is hydrated proton,

isoelectronic with ammonium ion, NH₄⁺



-all HCl molecules ionise in water ⇒ HCl is a **strong** Bronsted acid

most Bronsted acids are weak (partially ionise) e.g. CH₃COOH (5% ionised at room tempertaure)

Salts containing OH⁻ or O²⁻ ions are strong Bronsted bases

e.g. KOH - completely dissociates into ions

oxides salts are also strongly basic as the O²⁻ ion accepts proton:

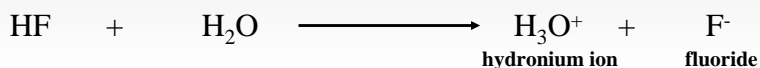


(100% of oxide ions are converted to hydroxide)

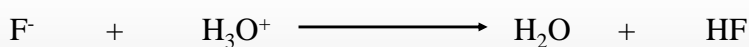
Weak acids and bases: Bronsted Acid-Base Equilibria (p. 129)

Dissociation of **weak acids** is an equilibrium:

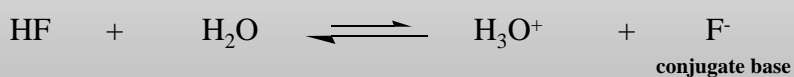
e.g. HF is Bronsted acidic:



But fluoride ion is slightly basic:

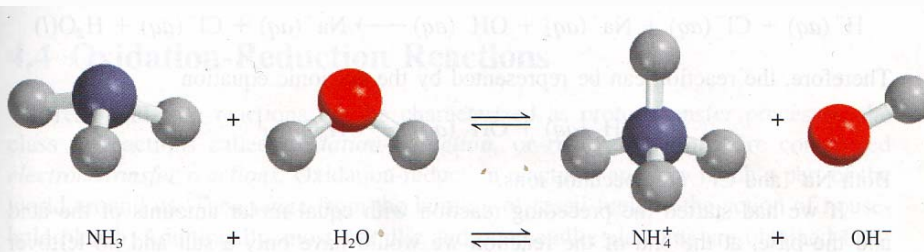
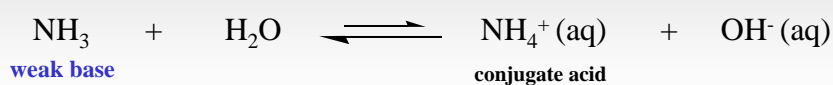


Both forward and backward reactions occur at same rate – equilibrium is reached:



Weak acids and bases: Bronsted Acid-Base Equilibria (p. 129)

-methylamine and ammonia are **weak bases** - only a small fraction of molecules accept proton

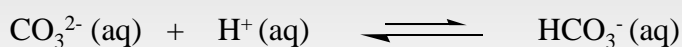


Q: Classify the following as Bronsted acid or bases or both:

- a) CO_3^{2-} b) H_2SO_3 c) H_2PO_4^-

A:

- a) CO_3^{2-} - has no protons so cannot be Bronsted acid
- can accept proton to become bicarbonate (HCO_3^-) ion



carbonate ion is a **Bronsted base**

bicarbonate is weakly acid

⇒ write with equilibrium arrow

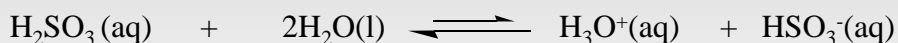
practise
Ex 4.3, Q 4.32

Q: Classify the following as Bronsted acid or bases or both:

- a) CO_3^{2-} b) H_2SO_3 c) H_2PO_4^-

A:

- b) H_2SO_3 - has two protons so likely to be Bronsted acid



sulphurous acid (H_2SO_3) is a **Bronsted acid**

hydrogen sulphite (HSO_3^-) ion is weakly basic

⇒ write with equilibrium arrow

practise
Ex 4.3, Q 4.32

Q: Classify the following as Bronsted acid or bases or both:

- a) CO_3^{2-} b) H_2SO_3 c) H_2PO_4^-

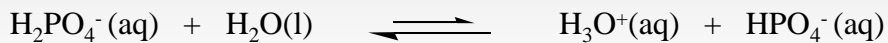
practise
Ex 4.3, Q 4.32

A:

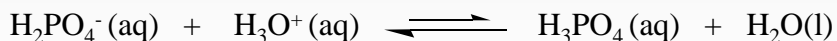
- c) H_2PO_4^- - has protons so likely to be Bronsted acid
 - is an oxo**anion** so likely to be able to be protonated

dihydrogen phosphate ion:

-can act as a Bronsted acid:



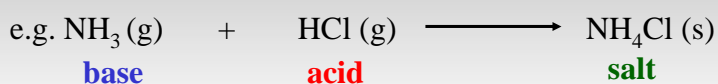
or as a Bronsted base:



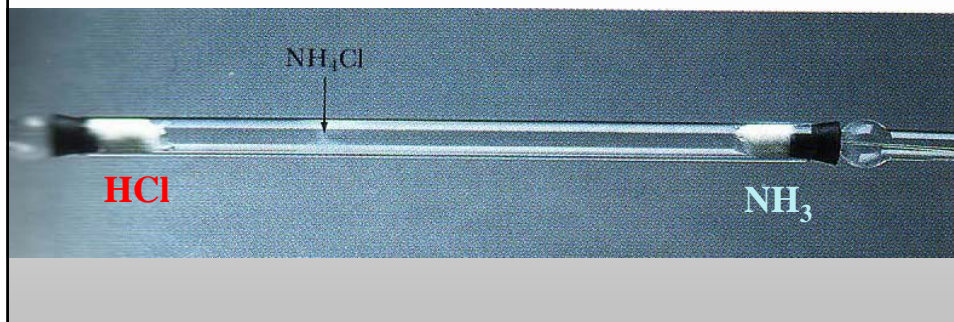
dihydrogen phosphate ion is both a **Bronsted base**

.....and a **Bronsted acid**

-Bronsted theory also account for acid-base neutralisations in anhydrous media:



(neutralisation but no water involved)



Conjugate acids: Bronsted Acid-Base Equilibria (p. 652-56)

-position of equilibrium is determined by extent of ionisation



K_a is the acid dissociation constant

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}][\text{H}_2\text{O}]}$$

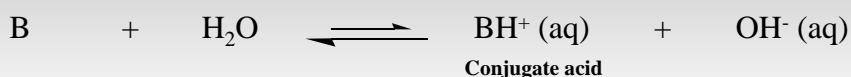
$= > 1$ for strong acids e.g. HCl
 $= 3 \times 10^{-4}$ for HF
 $= 2 \times 10^{-5}$ for acetic acid
 $= 10^{-10}$ for phenol

-Stronger acids have weak conjugate bases (i.e. conjugate base is a poor attractor of protons) \Rightarrow F^- is poor base, Cl^- is non-basic

-Weaker acids have stronger conjugate bases (i.e. conjugate bases that are relatively strong proton acceptors) \Rightarrow acetate is rel. basic

Conjugate acids: Bronsted Acid-Base Equilibria (p. 652-56)

Likewise for weak bases:



-Stronger bases have weak conjugate acids (i.e. conjugate acid is a poor proton donor)

-Weaker bases have strong conjugate acids (i.e. conjugate acid is a strong proton donor)

-Base strength usually indicated by the acid dissociation constant of the conjugate acid e.g.

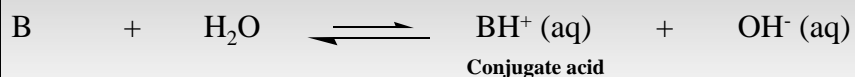
-Ammonium (NH_4^+) $K_a = 5 \times 10^{-10}$

-Pyridinium ($\text{C}_5\text{H}_5\text{NH}^+$) $K_a = 5 \times 10^{-6}$

-Pyridinium stronger acid – therefore pyridine weaker base than NH_3

Conjugate acids: Bronsted Acid-Base Equilibria (p. 652-56)

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