Hydrolysis:

- Reaction between a **salt** (**ion** or **ions** in a salt) and **water** to produce an *acidic* or *basic* solution.

- Net ionic equations for ***hydrolysis***:

An ion + water → a molecule or ion + H_3O^+ or OH^-

SPECTATORS- ions which do **NOT** hydrolyze (need periodic table and acid table to find these)

Spectator **Cations** (look on per. table)

Group 1 (Alkali Metal ions) eg. Li^+, Na^+, K^+, Rb^+, Cs^+, Fr^+
Group 2 (Alkaline Earth ions) eg. Be^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Sr^{2+}, Ra^{2+}

Spectator **Anions** (look on acid table)

- Conjugate bases of strong acids.
- ***Top 5 ions on the right*** side of table.
- ClO_4^- I^- Br^- Cl^- NO_3^-

(HSO_4^- is not a spectator – it is amphiprotic – will be dealt with later

- **spectators are eliminated** in net ionic equations (NIE's) for hydrolysis!

Process – if given **salt** (dissociate → eliminate → evaluate)

1. Write **dissociation** equation
2. Eliminate **spectators**
3. Remaining ions → **left** side of table – undergo **acid** hydrolysis is –produce H_3O^+
   → **right** side of table – undergo **base** hydrolysis – produce OH^-
   → **amphiprotic** – determine $\mathbf{K_a}$ and $\mathbf{K_b}$ to find *dominant* hydrolysis.

Examples:

Determining A, B, or N

Is the salt NaF Acidic, basic or neutral in water?

Dissociation : NaF → $\cancel{Na^+}$ + F^-

Spectator
(alkali cation)

Found on **right** side of acid table-
forms a weak **base.**

- so NaF is **basic**

Is the salt NH_4 NO_3 acidic, basic or neutral in aqueous solution?

Dissociation: NH_4NO_3 → NH_4^+ + $\cancel{NO_3^-}$

Spectator top 5 on right side of table

Found on **left** side of table –
forms a weak **acid**

- so NH_4NO_3 is **acidic**.

Is the salt KCl acidic, basic or neutral?

Dissociation: $KCl \rightarrow \cancel{K^+} + \cancel{Cl^-}$

Spectator (alkali ion)

Spectator (top right of acid table)

- since **neither** ion undergoes hydrolysis, this salt is **NEUTRAL**.

Cations Which Hydrolyze

- **Hydrated cations**
  - metals from *center* of the periodic table (transition metals) are *smaller* ions and have *larger charges*
  - this attracts H_2O molecules

eg.) Fe^{3+} (iron (III) or ferric ion)

Hydration: $Fe^{3+} + 6H_2O \rightarrow Fe(H_2O)_6^{3+}$

Called the **hexaaquoiron (III) ion**

This ion acts as a *weak acid* (see it ~ 13th down on the acid table.)

The equation for the **hydrolysis** of *hexaaquoiron* or *ferric* ion is:

$$Fe(H_2O)_6^{3+}{}_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+{}_{(aq)} + Fe(H_2O)_5(OH^{2+})_{(aq)}$$

3 Common **Hydrated** cations (on ***left*** of acid chart):

iron(III) Fe^{3+} forms $Fe(H_2O)_6^{3+}$ hexaaquoiron(III)
Chromium(III) Cr^{3+} forms $Cr(H_2O)_6^{3+}$ hexaaquochromium(III)
Aluminum Al^{3+} forms $Al(H_2O)_6^{3+}$ hexaaquoaluminum

Act as **weak acids**.

Can appear in either form in salts

Eg.) $AlCl_3$ is the same as $Al(H_2O)_6Cl_3$

Another Acidic Cation
NH_4^+
Ammonium

Hydrolysis equation: $NH_4^+{}_{(aq)} + H_2O_{(l)} \leftrightarrows H_3O^+{}_{(aq)} + NH_{3(aq)}$

List the 4 *hydrolyzing* **cations** on the acid table:

____________________ _____________________ ____________________ ___________________

ANIONS WHICH HYDROLYZE

Looking on the RIGHT side of the ACID TABLE:

	Base	K_a	Strength of base
→	$H^+ + ClO_4^-$	very large	Weak
→	$H^+ + I^-$	very large	
→	$H^+ + Br^-$	very large	
→	$H^+ + Cl^-$	very large	
→	$H^+ + NO_3^-$	very large	
→	$H^+ + HSO_4^-$	very large	
→	$H^+ + H_2O$	1.0	
→	$H^+ + IO_3^-$	1.7×10^{-1}	
→	$H^+ + HOOCCOO^-$	5.4×10^{-2}	
→	$H^+ + HSO_3^-$	1.7×10^{-2}	
	⋮		
→	$H^+ + PO_4^{3-}$	4.4×10^{-13}	
→	$H^+ + OH^-$	1.0×10^{-14}	
→	$H^+ + O^{2-}$	very small	
→	$H^+ + NH_2^-$	very small	Strong

Remember: These five ions **DO NOT** hydrolyze. They are ***spectators***!

All ***ions*** in this section can undergo **BASE HYDROLYSIS**. Most act as **weak bases** in water.

These 3 ions act as **STRONG BASES**. They undergo **100% hydrolysis** to form OH^- ions

All of the anions in this section from IO_3^- down to S^{2-} will undergo **base hydrolysis**. Anions that are NOT *amphiprotic* will act as **weak bases** in water. We will deal with amphiprotic anions (eg. $HCOO^-$) later.

Some examples of **net-ionic** ***hydrolysis equations*** for these would be:

$$IO_3^-{}_{(aq)} + H_2O_{(l)} \rightleftharpoons HIO_{3\,(aq)} + OH^-{}_{(aq)}$$

$$NO_2^-{}_{(aq)} + H_2O_{(l)} \rightleftharpoons HNO_{2\,(aq)} + OH^-{}_{(aq)}$$

$$CH_3COO^-{}_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COOH_{(aq)} + OH^-{}_{(aq)}$$

Salts which contain these anions may also be ***basic*** (depending on the cation).
When you get a salt, you must *dissociate* it, *eliminate spectators* and then look for *hydrolysis* of any remaining ions.

Eg.) Determine whether the salt sodium carbonate (Na_2CO_3) is acidic, basic or neutral in aqueous solution.

First dissociate the salt: $Na_2CO_3 \rightarrow 2\,\cancel{Na^+}_{(aq)} + CO_3^{2-}{}_{(aq)}$

Spectator Cation Eliminate!

Hydrolyzing Anion(weak base)

The **net-ionic equation** for the ***hydrolysis*** taking place in this salt would be:

$CO_3^{2-}{}_{(aq)} + H_2O_{(l)} \rightleftharpoons HCO_3^-{}_{(aq)} + OH^-{}_{(aq)}$ and the salt would act as a *weak base* in water.
Remember that "net-ionic" means that any spectator ions have been removed!

Write the **net-ionic equation** for the ***hydrolysis*** taking place in aqueous magnesium sulphate:

____

Hydrolysis When BOTH Cation and Anion hydrolyze

Eg. Is the salt ammonium nitrite NH_4NO_2 acidic, basic or neutral?

Of course we start out by *dissociating*: $NH_4NO_2 \rightarrow NH_4^+{}_{(aq)} + NO_2^-{}_{(aq)}$

On left of acid table: *Weak acid*

On right side of acid table 15th from top: *Weak base*

Remember that NH_4^+ produces H_3O^+ ($NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3$) (equation 1)
And NO_2^- produces OH^- ($NO_2^- + H_2O \rightleftharpoons HNO_2 + OH^-$) (equation 2)

The Ka for NH_4^+ tells how much H_3O^+ it produces (The K_{eq} for equation 1 is the Ka of NH_4^+)
The Kb for NO_2^- tells how much OH^- it produces (The K_{eq} for equation 2 is the Kb of NO_2^-)

The Ka for NH_4^+ is $\underline{5.6 \times 10^{-10}}$ (look up NH_4^+ on the left side of the table and it's Ka is on the right)

The Kb for NO_2^- must be calculated: $Kb\,(NO_2) = \dfrac{Kw}{Ka\,(HNO_2)} = \dfrac{1.0 \times 10^{-14}}{4.6 \times 10^{-4}} = \underline{2.2 \times 10^{-11}}$

Since the Ka of NH_4^+ > Kb of NO_2^- We can say that this salt is **ACIDIC**

5.6×10^{-10} 2.2×10^{-11}

So, in summary :

If	Then the salt is:
Ka (cation) > Kb (anion)	***Acidic***
Kb (anion) > Ka (cation)	***Basic***
Ka (cation) = Kb (anion)	***Neutral***

Determine whether the salt NH_4CN (ammonium cyanide) is acidic, basic or neutral.

Hydrolysis of Amphiprotic Anions

Amphiprotic Anions → Start with "H" and have a "**-**" charge.

Eg. HSO_4^- , HSO_3^- , $H_2PO_4^-$ HPO_4^{2-} HS^- etc.

Amphiprotic Anions hydrolyze as *acids* to produce H_3O^+ but they also hydrolyze as *bases* to produce OH^-
So, how can we tell whether they are acidic or basic or neutral? We need to determine the ***predominant*** hydrolysis.

Find the Ka of the ion. (Look for ion on the LEFT SIDE of the acid table, read Ka on the right.)

Find the Kb of the ion. (Look for the ion on the RIGHT SIDE of the table and use:
Kb = Kw/ Ka(conj. acid)

If	Then the predominant hydrolysis is:	And, in aqueous solution, the ion:
Ka (the ion) > Kb (the ion)	***ACID HYDROLYSIS***	***Acts as an Acid***
Kb (the ion) > Ka (the ion)	***BASE HYDROLYSIS***	***Acts as a Base***

Eg. Find the predominant hydrolysis of the hydrogen carbonate ion (HCO_3^-) and write the net-ionic equation for it.

To find the Ka of HCO_3^-, look it up on the **left** side of table (6th from the bottom) . It's Ka = 5.6×10^{-11}

To find the Kb of HCO_3^-, look it up of the **right** side of table. (15th from the bottom)

(It's conjugate acid is H_2CO_3 and the Ka of $H_2CO_3 = 4.3 \times 10^{-7}$)

So we calculate the Kb of HCO_3^- using : $Kb(HCO_3^-) = \dfrac{Kw}{Ka(H_2CO_3)} = \dfrac{1.0 \times 10^{-14}}{4.3 \times 10^{-7}} = 2.3 \times 10^{-8}$

So, since Kb (HCO_3^-) > Ka (HCO_3^-) , the ion HCO_3^- predominantly undergoes BASE HYDROLYSIS.
(2.3×10^{-8}) (5.6×10^{-11})

And the net-ionic equation for the ***predominant*** ***hydrolysis*** is:

$HCO_{3\,(aq)}^- + H_2O_{(l)} \rightleftharpoons H_2CO_{3\,(aq)} + OH^-_{(aq)}$

Putting it all Together—Finding the pH in a Salt Solution

Eg. Calculate the pH of 0.30 M Na_2CO_3

Step 1: Dissociate and Eliminate any spectators. Identify any ions left as *weak acids* or *weak bases*.

$Na_2CO_3 \rightarrow \cancel{2Na^+} + CO_3^{2-}$

Spectator

Found on RIGHT side of acid table 6th from the bottom. Undergoes BASE HYDROLYSIS

Step 2: Write HYDROLYSIS EQUATION (Don't forget that CO_3^{2-} undergoes BASE hydrolysis!) And an ICE table underneath it:

	$CO_{3\,(aq)}^{2-}$	+ $H_2O_{(l)}$ ⇌	$HCO_{3\,(aq)}^-$	+ $OH^-_{(aq)}$
[I]	0.30		0	0
[C]	- x		+ x	+ x
[E]	*0.30 - x*		x	*x*

Step 3: Since CO_3^{2-} is a WEAK BASE, we need to calculate the value of Kb for CO_3^{2-}:

$Kb(CO_3^{2-}) = \dfrac{Kw}{Ka(HCO_3^-)} = \dfrac{1.0 \times 10^{-14}}{5.6 \times 10^{-11}} = 1.786 \times 10^{-4}$ (use unrounded value in the next calculation)

Step 4: Write the Kb expression for the hydrolysis of CO_3^{2-}:

$$Kb = \frac{[HCO_3^-]\,[OH^-]}{[CO_3^{2-}]}$$

Step 5: Insert equilibrium concentration [E] values from the ICE table into the Kb expression. State any valid

assumptions:

Assume
$0.30\text{-}x \cong 0.30$

$$Kb = \frac{x^2}{(0.30 - x)}$$

Step 6: Calculate the value of x. Remember in the ICE table, that $x = [OH^-]$

$$Kb \cong \frac{x^2}{0.30}$$

$$1.786 \times 10^{-4} = \frac{x^2}{0.30}$$

$$x^2 = 0.30\,(1.786 \times 10^{-4})$$

$$[OH^-] = x = \sqrt{0.30\,(1.786 \times 10^{-4})} = 7.319 \times 10^{-3}\text{ M}$$

Step 7: Calculate pOH ($pOH = -\log [OH^-]$)

$$pOH = -\log(7.319 \times 10^{-3}) = 2.1355$$

Step 8: Convert to pH (pH = 14.00 – pOH). Express in the correct # of SD's as justified by data:

$$pH = 14.00 - 2.1355 = \mathbf{11.86}$$

Both the 0.30 M and the Ka used were 2 SD's, so our answer cannot have more than 2 SD's. Remember: In a pH SD's are AFTER the decimal!

Step 9: Make sure your answer makes sense.
The salt was a WEAK BASE, so a pH of 11.86 is reasonable!

Question: Calculate the pH of a 0.24 M solution of the salt aluminum nitrate. Show all your steps. State any assumptions used.

Metal, Non-metal and Metalloid Oxides (also called Anhydrides)

Demonstration of the pH's of metal and non-metal oxides.

Compound	Metal or Non-metal Oxide	Colour in Universal Indicator	Approximate pH
Aqueous MgO			
Aqueous CaO			
Aqueous ZnO			
Aqueous CO_2			
Aqueous NO_2			
Aqueous SO_2			

Conclusions:

Metal oxides act as *(acids/bases)*__________ in aqueous solution.
Non-Metal oxides act as *(acids/bases)*__________ in aqueous solution.

Explanation:

Group 1 and Group 2 Oxides are **ionic**. They dissociate to form the oxide ion (O^{2-})

Eg. $Na_2O_{(s)} \rightarrow 2\,Na^+_{(aq)} + O^{2-}_{(aq)}$

Spectator

STRONG BASE (2nd from the bottom on the right side of Acid table.)

The oxide (O^{2-}) ion then undergoes 100% hydrolysis (because it's a strong base)

$$\mathbf{O^{2-}_{(aq)} + H_2O_{(l)} \rightarrow 2\,OH^-_{(aq)}}$$

Another example: $BaO_{(s)} \rightarrow Ba^{2+}_{(aq)} + O^{2-}_{(aq)}$

Spectator

STRONG BASE (2nd from the bottom on the right side of Acid table.)

The oxide (O^{2-}) ion then undergoes 100% hydrolysis (because it's a strong base)

$$\mathbf{O^{2-}_{(aq)} + H_2O_{(l)} \rightarrow 2\,OH^-_{(aq)}}$$

We can also summarize the reactions of group 1 and group 2 metals with water in the form of **formula equations**:

$Na_2O + H_2O \rightarrow 2\,NaOH$
$BaO + H_2O \rightarrow Ba(OH)_2$

Write a balanced **formula equation** for the **overall reactions** of the following oxides with water:

Calcium oxide: ____

Lithium oxide: ____

Non-Metal Oxides act as ACIDS in aqueous solution:

Some common examples of **non-metal oxides**: NO_2 , N_2O_5 , SO_2 , SO_3 , CO_2 , Cl_2O

Don't get these confused with the IONS: NO_2^- (nitrite) and SO_3^{2-}(sulphite)! They are covalent compounds, not ions!

These compounds react with water to form ACIDS.

The **formula equations** for some of these are:

$SO_{2(g)} + H_2O_{(l)} \rightarrow H_2SO_{3\,(aq)}$ (sulphurous acid)

$2NO_{2(g)} + H_2O_{(l)} \rightarrow HNO_{3\,(aq)} + HNO_{2\,(aq)}$ (nitric and nitrous acids)

Once these acids are formed, they can ionize (strong ones 100%, weak ones < 100%) to form H_3O^+ ions.

Eg. $H_2SO_{3\,(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + HSO_3^-{}_{(aq)}$ (< 100% ionization since H_2SO_3 is a weak acid)

Eg. $HNO_{3\,(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + NO_3^-{}_{(aq)}$ (100% ionization since HNO_3 is a strong acid)

Metalloid Oxides (by staircase)

Eg. Al_2O_3 , Ga_2O_3 , GeO_2 These compounds usually have LOW solubility so not many ions are freed to undergo hydrolysis. So very little hydrolysis occurs so they do not act AS acids or bases.

These compounds can react WITH acids or bases. Compounds that can do this are called **amphoteric**.

Anhydrides

Oxide compounds that react **as** acids or bases in aqueous solution are also called **Anhydrides**. (an-hydride translates to "without water") These are compounds that react WITH water to form acidic or basic solutions.

Acidic Anhydride—An oxide ("O" containing) compound which reacts with water to form an ACIDIC SOLUTION.

Acidic anhydrides are oxides of elements on the **RIGHT** side of the periodic table.

Some examples of *acidic anhydrides* are: SO_2 , SO_3 , Cl_2O etc.

And some of their reactions with water are:

$SO_{3(g)} + H_2O_{(l)} \rightarrow H_2SO_{4\,(aq)}$ (sulphuric acid—a strong acid)

$2\,NO_{2(g)} + H_2O_{(l)} \rightarrow HNO_{2\,(aq)} + HNO_{3\,(aq)}$ (nitrous and nitric acids)

$Cl_2O_{(aq)} + H_2O_{(l)} \rightarrow 2HClO$ (hypochlorous acid)

(NOTE: You should KNOW these equations!)

Basic Anhydride—An oxide ("O" containing) compound which reacts with water to form a BASIC SOLUTION.

NOTE: **Basic Anhydrides** are METAL (LEFT side of Periodic Table) oxides.

Some examples are: Na_2O , CaO , MgO , CaO ….etc.

Formula equations for some Basic Anhydrides reacting with water:

$Na_2O + H_2O \rightarrow 2\,NaOH$ (the base is called sodium hydroxide)

$CaO + H_2O \rightarrow Ca(OH)_2$ (the base is called calcium hydroxide – sometimes called "hydrated lime")