



Is the salt KCl acidic, basic or neutral?



Spectator  
(alkali ion)

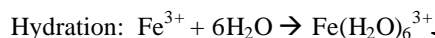
Spectator  
(top right of acid table)

- 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  $\text{H}_2\text{O}$  molecules

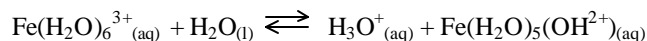
eg.)  $\text{Fe}^{3+}$  (iron (III) or ferric ion)



Called the  
**hexaaquoirron (III) ion**

This ion acts as a weak acid (see it ~ 13<sup>th</sup> down on the acid table.)

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



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

iron(III)  $\text{Fe}^{3+}$  forms  $\text{Fe}(\text{H}_2\text{O})_6^{3+}$  hexaaquoirron(III)  
 Chromium(III)  $\text{Cr}^{3+}$  forms  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  hexaaquochromium(III)  
 Aluminum  $\text{Al}^{3+}$  forms  $\text{Al}(\text{H}_2\text{O})_6^{3+}$  hexaaquoaluminum

Act as **weak acids**.

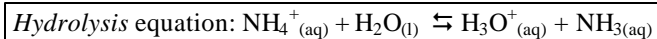
Can appear  
in either  
form in salts

Eg.)  $\text{AlCl}_3$  is the same as  $\text{Al}(\text{H}_2\text{O})_6\text{Cl}_3$

Another Acidic Cation



**Ammonium**



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

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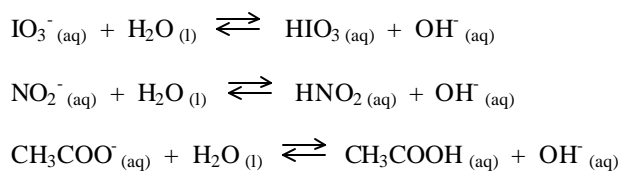
**ANIONS WHICH HYDROLYZE**

Looking on the RIGHT side of the ACID TABLE:

Base	K <sub>a</sub>	Strength of base
→ H <sup>+</sup> + ClO <sub>4</sub> <sup>-</sup> .....	very large	Weak ↓ Strong
→ H <sup>+</sup> + I <sup>-</sup> .....	very large	
→ H <sup>+</sup> + Br <sup>-</sup> .....	very large	
→ H <sup>+</sup> + Cl <sup>-</sup> .....	very large	
→ H <sup>+</sup> + NO <sub>3</sub> <sup>-</sup> .....	very large	
→ H <sup>+</sup> + HSO <sub>4</sub> <sup>-</sup> .....	very large	
→ H <sup>+</sup> + H <sub>2</sub> O .....	1.0	
→ H <sup>+</sup> + IO <sub>3</sub> <sup>-</sup> .....	1.7 x 10 <sup>-1</sup>	
→ H <sup>+</sup> + HOCCOO <sup>-</sup> .....	5.4 x 10 <sup>-2</sup>	
→ H <sup>+</sup> + HSO <sub>3</sub> <sup>-</sup> .....	1.7 x 10 <sup>-2</sup>	
.....	.....	All <i>ions</i> in this section can undergo <b>BASE HYDROLYSIS</b> . Most act as <b>weak bases</b> in water.
→ H <sup>+</sup> + PO <sub>4</sub> <sup>3-</sup> .....	4.4 x 10 <sup>-13</sup>	
.....	.....	
→ H <sup>+</sup> + OH <sup>-</sup> .....	1.0 x 10 <sup>-14</sup>	These 3 ions act as <b>STRONG BASES</b> . They undergo <b>100% hydrolysis</b> to form OH <sup>-</sup> ions
→ H <sup>+</sup> + O <sup>2-</sup> .....	very small	
→ H <sup>+</sup> + NH <sub>2</sub> <sup>-</sup> .....	very small	

All of the anions in this section from IO<sub>3</sub><sup>-</sup> down to S<sup>2-</sup> will undergo **base hydrolysis**. Anions that are NOT *amphiprotic* will act as **weak bases** in water. We will deal with amphiprotic anions (eg. HCOO<sup>-</sup>) later.

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



**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.

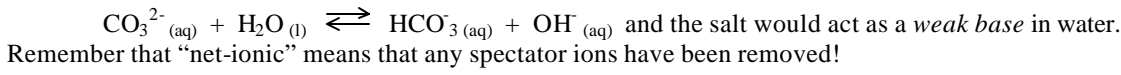
Eg.) Determine whether the salt sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) is acidic, basic or neutral in aqueous solution.

First dissociate the salt:  $\text{Na}_2\text{CO}_3 \rightarrow 2\text{Na}^+_{(\text{aq})} + \text{CO}_3^{2-}_{(\text{aq})}$

Spectator Cation  
Eliminate!

Hydrolyzing Anion(weak base)

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



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  $\text{NH}_4\text{NO}_2$  acidic, basic or neutral?

Of course we start out by *dissociating*:  $\text{NH}_4\text{NO}_2 \rightarrow \text{NH}_4^+(\text{aq}) + \text{NO}_2^-(\text{aq})$

On left of acid table: Weak acid

On right side of acid table 15<sup>th</sup> from top: Weak base

Remember that  $\text{NH}_4^+$  produces  $\text{H}_3\text{O}^+$  ( $\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{NH}_3$ ) (equation 1)  
And  $\text{NO}_2^-$  produces  $\text{OH}^-$  ( $\text{NO}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{HNO}_2 + \text{OH}^-$ ) (equation 2)

The  $K_a$  for  $\text{NH}_4^+$  tells how much  $\text{H}_3\text{O}^+$  it produces (The  $K_{\text{eq}}$  for equation 1 is the  $K_a$  of  $\text{NH}_4^+$ )  
The  $K_b$  for  $\text{NO}_2^-$  tells how much  $\text{OH}^-$  it produces (The  $K_{\text{eq}}$  for equation 2 is the  $K_b$  of  $\text{NO}_2^-$ )

The  $K_a$  for  $\text{NH}_4^+$  is  $5.6 \times 10^{-10}$  (look up  $\text{NH}_4^+$  on the left side of the table and its  $K_a$  is on the right)

The  $K_b$  for  $\text{NO}_2^-$  must be calculated:  $K_b(\text{NO}_2^-) = \frac{K_w}{K_a(\text{HNO}_2)} = \frac{1.0 \times 10^{-14}}{4.6 \times 10^{-4}} = \underline{2.2 \times 10^{-11}}$

Since the  $K_a$  of  $\text{NH}_4^+ > K_b$  of  $\text{NO}_2^-$

We can say that this salt is **ACIDIC**

$5.6 \times 10^{-10}$

$2.2 \times 10^{-11}$

So, in summary:

**If**

**Then the salt is:**

$K_a(\text{cation}) > K_b(\text{anion})$	<b>Acidic</b>
$K_b(\text{anion}) > K_a(\text{cation})$	<b>Basic</b>
$K_a(\text{cation}) = K_b(\text{anion})$	<b>Neutral</b>

Determine whether the salt  $\text{NH}_4\text{CN}$  (ammonium cyanide) is acidic, basic or neutral.

### Hydrolysis of Amphotropic Anions

Amphotropic Anions  $\rightarrow$  Start with “H” and have a “-“ charge.

Eg.  $\text{HSO}_4^-$ ,  $\text{HSO}_3^-$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$ ,  $\text{HS}^-$  etc.

Amphotropic Anions hydrolyze as *acids* to produce  $\text{H}_3\text{O}^+$  but they also hydrolyze as *bases* to produce  $\text{OH}^-$   
So, how can we tell whether they are acidic or basic or neutral? We need to determine the **predominant** hydrolysis. See the next page...

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

Find the  $K_b$  of the ion. (Look for the ion on the RIGHT SIDE of the table and use:

$$K_b = K_w / K_a(\text{conj. acid})$$

If	Then the predominant hydrolysis is:	And, in aqueous solution, the ion:
$K_a(\text{the ion}) > K_b(\text{the ion})$	<b>ACID HYDROLYSIS</b>	<b>Acts as an Acid</b>
$K_b(\text{the ion}) > K_a(\text{the ion})$	<b>BASE HYDROLYSIS</b>	<b>Acts as a Base</b>

Eg. Find the predominant hydrolysis of the hydrogen carbonate ion ( $\text{HCO}_3^-$ ) and write the net-ionic equation for it.

To find the  $K_a$  of  $\text{HCO}_3^-$ , look it up on the **left** side of table (6<sup>th</sup> from the bottom). It's  $K_a = 5.6 \times 10^{-11}$

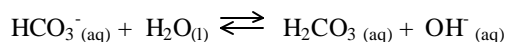
To find the  $K_b$  of  $\text{HCO}_3^-$ , look it up of the **right** side of table. (15<sup>th</sup> from the bottom)

(It's conjugate acid is  $\text{H}_2\text{CO}_3$  and the  $K_a$  of  $\text{H}_2\text{CO}_3 = 4.3 \times 10^{-7}$ )

So we calculate the  $K_b$  of  $\text{HCO}_3^-$  using:  $K_b(\text{HCO}_3^-) = \frac{K_w}{K_a(\text{H}_2\text{CO}_3)} = \frac{1.0 \times 10^{-14}}{4.3 \times 10^{-7}} = 2.3 \times 10^{-8}$

So, since  $K_b(\text{HCO}_3^-) > K_a(\text{HCO}_3^-)$ , the ion  $\text{HCO}_3^-$  predominantly undergoes **BASE HYDROLYSIS**.  
( $2.3 \times 10^{-8}$ )      ( $5.6 \times 10^{-11}$ )

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



Read p. 144 – 147 in SW & Do Ex. 69 (a-f) and Ex. 70 (a – j), 71, 72 & 73 on p. 148 SW.

Do Worksheet 4-5 (Hydrolysis) & Do Experiment 20-D (Hydrolysis)

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

Eg. Calculate the pH of 0.30 M  $\text{Na}_2\text{CO}_3$

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



Spectator

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

Step 2: Write HYDROLYSIS EQUATION ( Don't forget that  $\text{CO}_3^{2-}$  undergoes BASE hydrolysis!)  
And an ICE table underneath it:

$$\text{CO}_3^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HCO}_3^{-}(\text{aq}) + \text{OH}^{-}(\text{aq})$$

[I]	0.30		0	0
[C]	-x		+x	+x
[E]	0.30 - x		x	x

Step 3: Since  $\text{CO}_3^{2-}$  is a WEAK BASE, we need to calculate the value of  $K_b$  for  $\text{CO}_3^{2-}$ :

$$K_b(\text{CO}_3^{2-}) = \frac{K_w}{K_a(\text{HCO}_3^{-})} = \frac{1.0 \times 10^{-14}}{5.6 \times 10^{-11}} = 1.786 \times 10^{-4} \text{ (use unrounded value in the next calculation)}$$

Step 4: Write the  $K_b$  expression for the hydrolysis of  $\text{CO}_3^{2-}$ :

$$K_b = \frac{[\text{HCO}_3^{-}][\text{OH}^{-}]}{[\text{CO}_3^{2-}]}$$

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

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

Assume  
 $0.30 - x \cong 0.30$

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

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

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

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

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

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

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

Step 8: Convert to pH ( $\text{pH} = 14.00 - \text{pOH}$ ). Express in the correct # of SD's as justified by data:

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

Step 9: Make sure your answer makes sense.

The salt was a WEAK BASE, so a pH of 11.86 is reasonable!

Both the 0.30 M and the  $K_a$  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!

Now it's your turn!

**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 <sub>2</sub>			
Aqueous NO <sub>2</sub>			
Aqueous SO <sub>2</sub>			

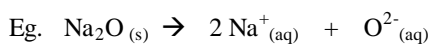
Conclusions:

Metal oxides act as (*acids/bases*) \_\_\_\_\_ in aqueous solution.

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

Explanation:

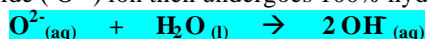
Group 1 and Group 2 Oxides are **ionic**. They dissociate to form the oxide ion (O<sup>2-</sup>)



Spectator

STRONG BASE (2<sup>nd</sup> 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)

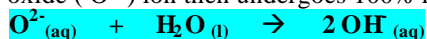


Another example:  $BaO_{(s)} \rightarrow Ba^{2+}_{(aq)} + O^{2-}_{(aq)}$

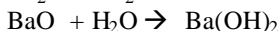
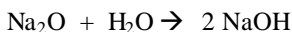
Spectator

STRONG BASE (2<sup>nd</sup> 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)



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



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

Calcium oxide: \_\_\_\_\_

Lithium oxide: \_\_\_\_\_

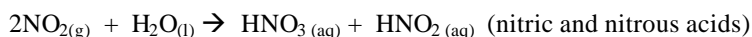
### Non-Metal Oxides act as ACIDS in aqueous solution:

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

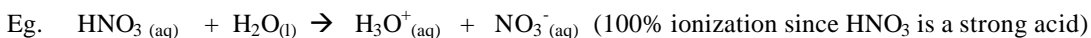
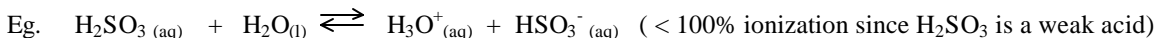
These compounds react with water to form **ACIDS**.

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

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



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



### 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

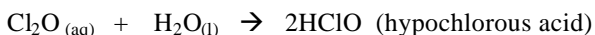
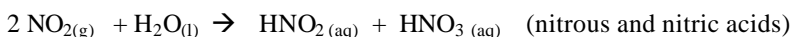
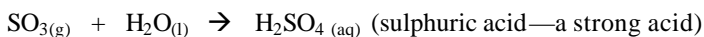
Oxide compounds that react **as** acids or bases in aqueous solution are also called **Anhydrides**. (an-hydride translates to “without water”) These are compounds that react **WITH** water to form acidic or basic solutions.

**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<sub>2</sub> , SO<sub>3</sub> , Cl<sub>2</sub>O etc.

And some of their reactions with water are:



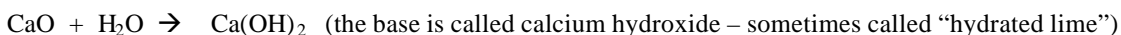
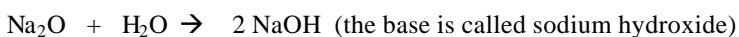
**(NOTE:** You should KNOW these equations!)

**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<sub>2</sub>O , CaO , MgO , CaO ...etc.

Formula equations for some Basic Anhydrides reacting with water:

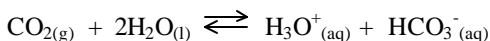


Read p. 184-185 in SW.

Do Ex. 144-145 on p. 185 of SW.

## Acid Rain

Since our atmosphere naturally contains CO<sub>2</sub> (an acidic anhydride), some of this reacts with water (rain) to make the rain slightly acidic:



So natural rainwater (unaffected by human activities) can have a pH as low as 5.6 (due to the CO<sub>2</sub> in air)

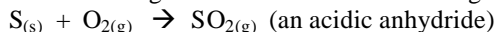
If rain has a **pH < 5.6** it is called **ACID RAIN**.

**Acid Rain** is caused by Acidic Anhydrides (not counting  $\text{CO}_2$ ) in the air.

The main human sources of **acid rain** are:

1. Burning fuels containing sulphur.
2. Car exhaust

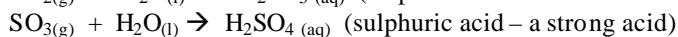
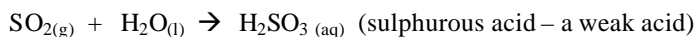
1. When burning coal or other fuels containing sulphur, the sulphur burns too forming sulphur dioxide:



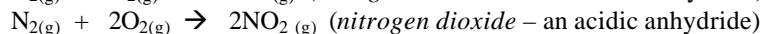
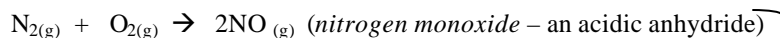
In the atmosphere further oxidation can occur producing sulphur trioxide:



In rainwater or cloud droplets two reactions can then occur:

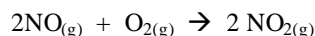


2. In the hot cylinders in an internal combustion engine,  $\text{N}_2$  from the air and  $\text{O}_2$  from the air react to form nitrogen oxides:

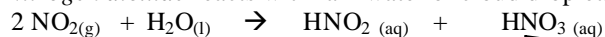


Oxides of nitrogen are collectively called:  $\text{NO}_x$

*Nitrogen monoxide* can further oxidize in the air to produce *nitrogen dioxide*:



*Nitrogen dioxide* reacts with rain water or cloud droplets to produce both *nitrous* and *nitric* acids:



Nitrous acid  
(a weak acid)

Nitric acid  
(a strong acid)

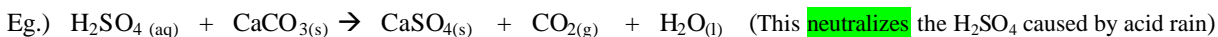
### Some natural sources of Acid Rain

**Volcanoes** can produce  $\text{SO}_2$  into the atmosphere (which produces both  $\text{H}_2\text{SO}_3$  and  $\text{H}_2\text{SO}_4$ )

**Lightning** can provide enough energy to cause nitrogen and oxygen in the air to react and form  $\text{NO}_2$  (which produces  $\text{HNO}_2$  and  $\text{HNO}_3$ ).

### Natural Protection

Some areas are **not as sensitive** to acid rain as others—even when there are major sources of acid rain present! This is because these areas have rocks and soils that are high in “carbonates” or compounds containing carbonate ( $\text{CO}_3^{2-}$ ). The  $\text{CO}_3^{2-}$  acts as a **weak base** and neutralizes the acid rain to a certain extent:



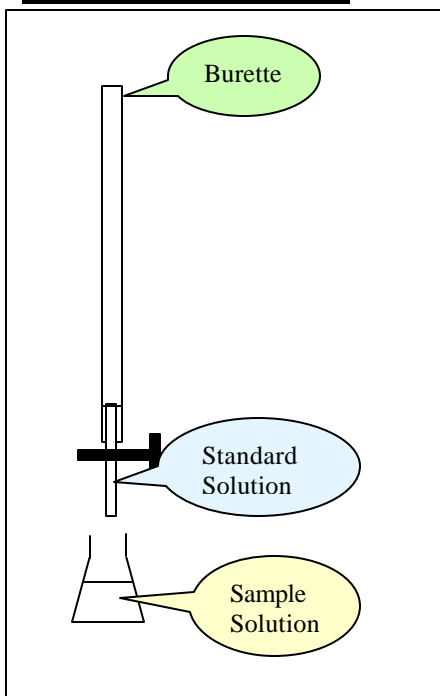
In some cases, powdered limestone ( $\text{CaCO}_3 \text{ (s)}$ ) is dumped onto lakes that are too acidic and this helps neutralize the acid rain. But the process is expensive.

**Problems Associated with Acid Rain** (see p. 187-188 in SW.)

- Aquatic life is affected (from bottom of food chain up)
- Forests weakened and killed (Quebec, Germany, Scandinavia)
- Minerals are leached out of the topsoil to lower levels.  $\text{Al}^{3+}$  ions are released which are very toxic to fish (mucous in gills) and plants (prevents uptake of other important minerals)
- Metal and stone buildings and statues (especially marble ( $\text{CaCO}_3$ )) are damaged.
- Acid Rain is carried over large distances (due to high smoke stacks) –can cross international borders

**Possible Solutions to the Problem**

- International conferences and agreements to limit sulphur in fuels and  $\text{NO}_x$  in car exhaust.
- Alternate, less polluting energy sources being used. (geothermal, solar, wind etc.)
- Industrial processes are being modernized (eg. new process for pulp mills involving  $\text{H}_2\text{O}_2$  instead of sulphites.)
- Devices to remove gases like  $\text{SO}_3$  from smoke stacks. (scrubbers).  $\text{SO}_3 + \text{CaO} \rightarrow \text{CaSO}_{4(s)}$ . The  $\text{CaSO}_4$  is removed by electrostatic precipitation.
- Recycling

**Review of Titrations**

TITRATIONS	
STANDARD	SAMPLE
Conc. & Volume → moles or Mass → moles	moles → Conc. or Volume
mol = M x L or: grams x $\frac{1 \text{ mol}}{\text{MM g}} = \text{mol}$	M = mol/L or L = mol/M

The “heart” of titrations is (*moles in the middle*):

Moles of <i>standard</i>	$\xrightarrow{\text{Coefficient ratio}}$	Moles of <i>sample</i>
--------------------------	--	------------------------

The *moles of standard* can be calculated by knowing the *concentration* of the standard and by measuring the *volume used* in the titration. Then the equation: **mol = M x L** can then be used.

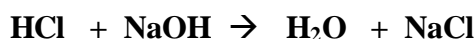
The *coefficient ratio in the balanced equation* can then be used to calculate the *moles of sample* in the flask.

Knowing the *volume* of the sample and using the *moles* from the last step, one can then calculate the *concentration* of the sample: **M = mol/L**

**Equivalence Point (Stoichiometric Point)**

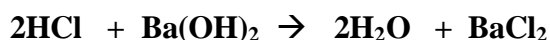
The point at where the **actual mole ratio** of Sample/Standard is the same as the **coefficient ratio** in the balanced equation.

Eg. Using the following reaction for a titration:



At **equivalence point** : moles of NaOH / moles of HCl = 1/1 (or mol NaOH = mol HCl)

Using the following reaction for a titration:



At **equivalence point** : moles of Ba(OH)<sub>2</sub> / moles of HCl = 1/2 (or mol HCl = 2 x mol Ba(OH)<sub>2</sub>)

In the most common type of titration question, we calculate: mol of standard → mol of sample → conc. of sample

Here's an example:

A solution of HCl of unknown concentration was titrated with 0.150 M Ba(OH)<sub>2</sub>. The equivalence point is reached when 14.83 mL of Ba(OH)<sub>2</sub> is added to 50.00 mL of the HCl solution. Find the [HCl] in the original sample.

(The **standard** solution is the one of known concentration → in this case the 0.150 M Ba(OH)<sub>2</sub>.)

1. **Moles of Ba(OH)<sub>2</sub>** = 0.150 M x 0.01483 L = 0.0022245 mol Ba(OH)<sub>2</sub>

2. **Moles of HCl:**

Using the balanced equation:  $2\text{HCl} + \text{Ba}(\text{OH})_2 \rightarrow 2\text{H}_2\text{O} + \text{BaCl}_2$

$$0.0022245 \text{ mol Ba}(\text{OH})_2 \times \frac{2 \text{ mol HCl}}{1 \text{ mol Ba}(\text{OH})_2} = 0.004449 \text{ mol HCl}$$

3. **[HCl]** =  $\frac{0.004449 \text{ mol HCl}}{0.05000 \text{ L HCl}} = \mathbf{0.0890 \text{ M}}$

Round to 3 SD's according to the data.

From the 50.00 mL of the original HCl solution.

**Don't forget**, if a series of volume readings for different "Trials" are given, you may have to discard a reading that is more than 0.02 or so mL different from the rest of them. This ability to discard "far off" volume readings and then to calculate the "best average" volume will be tested!

**Also** markers always seem to use titration questions to test your ability to handle **Significant Digits**. Remember, when subtracting (or adding) use decimal places and when multiplying or dividing, use # of SD's!

Here's a question for you to try:

0.200 M NaOH is used to titrate 3 separate 50.0 mL samples of a solution of  $\text{H}_2\text{SO}_4$  of unknown concentration. The NaOH is in the burette. Use the following data table to calculate the  $[\text{H}_2\text{SO}_4]$  in the original  $\text{H}_2\text{SO}_4$  solution. Show all of your steps clearly, including the balanced formula equation for the reaction.

	<b>Trial 1</b>	<b>Trial 2</b>	<b>Trial 3</b>
Initial Burette Reading (mL)	0.00	9.02	17.95
Final Burette Reading (mL)	9.02	17.95	26.89

Read "Experimental Note" on the bottom of page 157 of SW.  
Do Ex. 94 – 97 on p. 158 of SW.

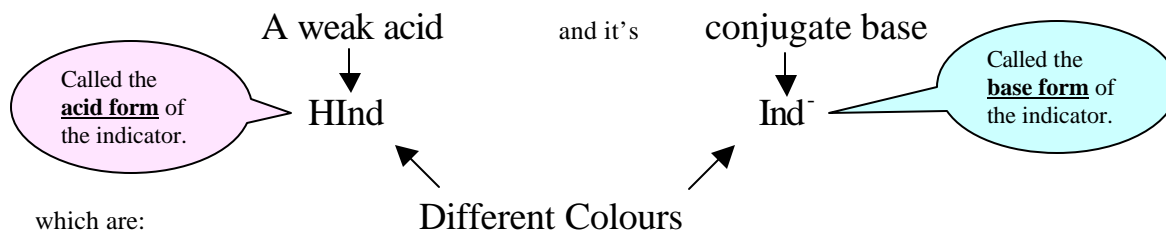
NOTE: If you check your answers on p. 291 of SW, you'll notice, he uses "mmol's" (millimoles) in his work. See p. 154 – 155 of doing these using mmols. You don't have to use mmols. You can if you like. Just be careful with your units.

Do Worksheet 4-6

## Indicators

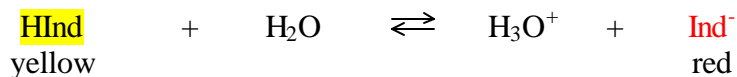
- See demonstration of some indicators and their colours in acid and base solutions.

Acid-Base Indicators consist of equilibrium mixtures of:



Eg. ) An indicator HInd has a yellow acid form (HInd) and a red base form (Ind<sup>-</sup>).

The **equilibrium equation** representing this indicator is :



If **reactants** are favoured (equilibrium shifts to the **LEFT**), then:  $[\text{HInd}] > [\text{Ind}^-]$   
 So: yellow is much greater than red.

And the solution will be **YELLOW**

If **products** are favoured (equilibrium shifts to the **RIGHT**), then:  $[\text{Ind}^-] > [\text{HInd}]$   
 So: red is much greater than yellow.

And the solution will be **RED**

If **there are equal amounts of reactant and products** (equilibrium favours neither reactants nor products), then:

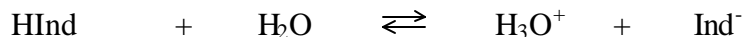
$[\text{HInd}] = [\text{Ind}^-]$   
 So: there is an equal mixture of yellow and red.

And the solution will be **ORANGE**

Make sure you read the material above a few times and make sure you understand how the shifts affect the colours of the solution in each case. This understanding is VERY important in dealing with indicators!

### Finding Colours of Acid and Base forms of indicators experimentally

Looking at the equilibrium equation representing any indicator:

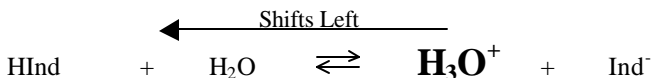


Adding any **strong acid** (eg. 1 M HCl) to an indicator (mixture of HInd and Ind<sup>-</sup>) will:

- Increase the  $[\text{H}_3\text{O}^+]$
- Cause the equilibrium to shift to the LEFT
- Make  $[\text{HInd}] > [\text{Ind}^-]$
- Cause the solution to turn the colour of HInd.

Go over those last 4 points while looking at the equilibrium equation and make sure you understand them. (Remember Le Chatelier's Principle!)

So when HCl is added to an indicator (mixture of HInd and Ind<sup>-</sup>), it increases  $[\text{H}_3\text{O}^+]$  causing the equilibrium:

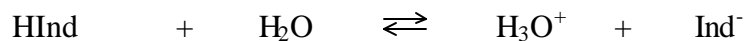


To shift LEFT so  $[\text{HInd}] > [\text{Ind}^-]$  and **the colour of HInd predominates**

In summary: If you add any strong acid (eg. HCl) to an indicator, it will turn the colour of the ACID FORM (HInd).

What about the Base Form ( $\text{Ind}^-$ )?

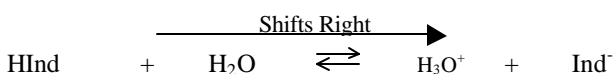
Looking at the equilibrium equation representing any indicator:



Adding any **strong base** (eg. 1 M NaOH) to an indicator (mixture of HInd and  $\text{Ind}^-$ ) will:

- **Decrease** the  $[\text{H}_3\text{O}^+]$  (because the OH<sup>-</sup> neutralizes  $\text{H}_3\text{O}^+$  to form  $\text{H}_2\text{O}$ :  $\text{H}_3\text{O}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$ )
- Cause the equilibrium to shift to the **RIGHT**
- Make  $[\text{Ind}^-] > [\text{HInd}]$
- Cause the solution to turn the colour of  $\text{Ind}^-$ .

So when NaOH is added to an indicator (mixture of HInd and  $\text{Ind}^-$ ), it decreases  $[\text{H}_3\text{O}^+]$  causing the equilibrium:



To shift **RIGHT** so  $[\text{Ind}^-] > [\text{HInd}]$  and **the colour of  $\text{Ind}^-$  predominates**

In summary: If you add any strong base (eg. NaOH) to an indicator, it will turn the color of the **BASE FORM ( $\text{Ind}^-$ )**.

**Question:** When a drop of 0.1M HCl is added to the indicator bromcresol green, the colour is yellow. When a drop of 0.10M NaOH is added to the indicator, the colour is blue.

- a. What colour is the acid form of bromcresol green (HInd)? \_\_\_\_\_
- b. What colour is the base form of bromcresol green ( $\text{Ind}^-$ )? \_\_\_\_\_
- c. What would the colour be if  $[\text{HInd}] = [\text{Ind}^-]$  for bromcresol green? \_\_\_\_\_

### **Transition Point**

The **Transition Point** for an indicator is reached when  $[\text{HInd}] = [\text{Ind}^-]$

This is where you have equal amounts of the colour of HInd and the colour of  $\text{Ind}^-$ .

(See the next page...)

Eg.) Looking on the “Acid-Base Indicators” Table (on the back of your Acid Table):

The two colours on the right side of the table for each indicator lists the colour of the ACID FORM first and then the colour of the BASE FORM.

So the Acid Form of methyl violet (HInd) is YELLOW and the Base Form of methyl violet (Ind<sup>-</sup>) is BLUE.

The colour at the TRANSITION POINT of

Methyl violet would be \_\_\_\_\_

The colour at the TRANSITION POINT of

Bromcresol green would be \_\_\_\_\_

The colour at the TRANSITION POINT of

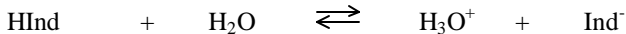
Indigo carmine would be \_\_\_\_\_

ACID-BASE INDICATORS

Indicator	pH Range in Which Colour Change Occurs	Colour Change as pH Increases
Methyl violet	0.0 – 1.6	yellow to blue
Thymol blue	1.2 – 2.8	red to yellow
Orange IV	1.4 – 2.8	red to yellow
Methyl orange	3.2 – 4.4	red to yellow
Bromcresol green	3.8 – 5.4	yellow to blue
Methyl red	4.8 – 6.0	red to yellow
Chlorophenol red	5.2 – 6.8	yellow to red
Bromthymol blue	6.0 – 7.6	yellow to blue
Phenol red	6.6 – 8.0	yellow to red
Neutral red	6.8 – 8.0	red to amber
Thymol blue	8.0 – 9.6	yellow to blue
Phenolphthalein	8.2 – 10.0	colourless to pink
Thymolphthalein	9.4 – 10.6	colourless to blue
Alizarin yellow	10.1 – 12.0	yellow to red
Indigo carmine	11.4 – 13.0	blue to yellow

### Transition Point and Ka of Indicator

The equilibrium equation for an indicator (HInd) is, as you know:



So the acid form (HInd) can be thought of as a weak acid. And weak acids, as you know, have a “Ka”. The Ka expression for the weak acid HInd would be:

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

If we look back to the definition of transition point:

The **Transition Point** for an indicator is reached when  $[\text{HInd}] = [\text{Ind}^-]$

Since  $[\text{HInd}] = [\text{Ind}^-]$  at the transition point, we can cancel them out in the Ka expression:

$$\text{So AT THE TRANSITION POINT: } K_a = \frac{[\text{H}_3\text{O}^+][\text{Ind}^-]}{[\text{HInd}]}$$

or AT THE TRANSITION POINT:  $K_a = [\text{H}_3\text{O}^+]$

Now, I'd like to throw in another definition. It's a quantity called “pKa”:

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



Going back to the  $K_a$  at transition point:

$$\text{AT THE TRANSITION POINT: } K_a = [\text{H}_3\text{O}^+]$$

We take the  $-\log$  of both sides:  $-\log K_a = -\log [\text{H}_3\text{O}^+]$  or as we know from definitions:

$$\text{AT THE TRANSITION POINT: } \mathbf{pK_a = pH}$$

Remember, this is **ONLY true at the TRANSITION POINT** of the indicator. (When  $[\text{HInd}] = [\text{Ind}^-]$  and the two colours are equal)

So now, we can summarize FOUR things we know to be true at the Transition Point:

### AT THE TRANSITION POINT

- $[\text{HInd}] = [\text{Ind}^-]$
- $K_a (\text{indicator}) = [\text{H}_3\text{O}^+]$
- $\mathbf{pK_a = pH}$
- **The colour is a 50/50 mixture of the acid and base colours**

You need to remember all that really well to understand the next material!

### Transition Range and Transition Point

If you look at the Indicator Table on the back of the Acid Table, there is a column entitled “pH Range in which Colour Change Occurs”.

As the pH is gradually raised, the colour does not instantaneously change from acid colour to base colour. There is a gradual change over a range of pH's.

For example:

Indicator	pH Range in Which Colour Change Occurs	Colour Change as pH Increases
Methyl violet	0.0 – 1.6	yellow to blue
Thymol blue	1.2 – 2.8	red to yellow
Orange IV	1.4 – 2.8	red to yellow

It says that Methyl Violet gradually changes from yellow to blue in the pH range of 0.0 – 1.6.

This means when pH is at or below 0.0, the colour of methyl violet is yellow.

When pH is 1.6 or above, the colour of methyl violet is blue. But what about between?

Between pH of 0.0 and 1.6, there is a mixture of the yellow and the blue form of methyl violet, so the colour is GREEN. We can refine it even further by saying that between pH of 0.0 and 0.8, the colour is more of a yellow green and between pH 0.8 and 1.6, it is more of a blue green. At a pH of 0.8 (half way between 0.0 and 1.6), the colour would be simply Green! See if you can fill these colours in the table on the next page...

pH	Indicator	
	Thymol Blue	Orange IV
0.8		
2.0		
3.5		

### Finding the Ka of an Indicator

To find the pH at Transition Point:

1. Look on the Indicator table
2. Find the midpoint of the pH range by adding the two numbers and dividing by two.

Remember from the last page:

**pKa = pH at the Transition Point.**

Since  $pK_a = -\log K_a$

**Ka = antilog (-pKa)**

Let's do an example. Find the Ka of Phenol Red:

Indicator	pH Range in Which Colour Change Occurs	Colour Change as pH Increases
Phenol red	6.6 – 8.0	yellow to red

The pH at the Transition Point is:  $\frac{6.6 + 8.0}{2} = 7.3$

Since pH at TP = pKa, then  $pK_a = 7.3$

$K_a = \text{antilog}(-7.3) = 5 \times 10^{-8}$

Answer to 1 SD

pH's are only 1 decimal place which means 1 SD

Find the Ka of Alizarin Yellow:

### Thymol Blue (A diprotic Indicator)

You'll notice that Thymol Blue appears twice on the Indicator Table:

Indicator	pH Range in Which Colour Change Occurs	Colour Change as pH Increases
Thymol blue	1.2 – 2.8	red to yellow
Thymol blue	8.0 – 9.6	yellow to blue

First ionization

Second ionization

This is because Thymol Blue is a diprotic acid. Each time it loses a proton, it goes through a color change.

We can call Thymol Blue (Tb) a weak acid  $\text{H}_2\text{Tb}$

The equilibrium equation for the **first ionization** is:  $\text{H}_2\text{Tb} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HTb}^-$

Using the table above, fill in the colours: \_\_\_\_\_

The equilibrium equation for the **second ionization** is:  $\text{HTb}^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{Tb}^{2-}$

Using the table below, fill in the colours: \_\_\_\_\_

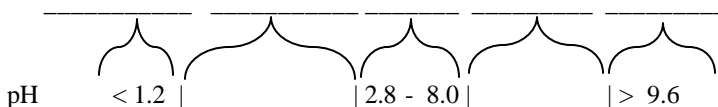
Indicator	pH Range in Which Colour Change Occurs	Colour Change as pH Increases
Thymol blue	1.2 – 2.8	red to yellow
Thymol blue	8.0 – 9.6	yellow to blue

Looking at the pH ranges above, try to fill in the following information:

pH	Form(s) which predominate(s) ( $\text{H}_2\text{Tb}$ , $\text{HTb}^-$ or $\text{Tb}^{2-}$ )	Approximate Colour
1.0		
2.0	& are equal	
3.0		
7.0		
8.8	& are equal	
10.0		

Also, fill in the colours on the following diagram:

Colours of Thymol Blue:



Find the pH's and the colours of the given indicators in the following solutions (assume temp. = 25°C):

Solution	pH	Colour in Thymol Blue	Colour in Methyl Red	Colour in Alizarin Yellow
0.2 M HCl				
0.01 M HCl				
0.0005 M HCl				
Pure water				
0.0001 M NaOH				
0.2 M NaOH				

A variety of indicators can also be used to narrow the known pH range for a solution and help identify the solution:

For example, a solution displays the following colours in the indicators shown. See if you can narrow the pH down to a range:

Indicator	Colour of Solution	Approximate pH Range
Bromthymol blue	Blue	
Thymol blue	Yellow	
Phenolphthalein	Colourless	
Approximate pH range of the solution using all information:		

Let's try another one:

For example, a solution displays the following colours in the indicators shown. See if you can narrow the pH down to a range:

Indicator	Colour of Solution	Approximate pH Range
Orange IV	Yellow	
Methyl red	Red	
Methyl Orange	Red	
Approximate pH range of the solution using all information:		

For example, a solution displays the following colours in the indicators shown. See if you can narrow the pH down to a range:

Indicator	Colour of Solution	Approximate pH Range
Methyl Orange	Yellow	
Alizarin Yellow	Yellow	
Thymol Blue	Green	
Approximate pH range of the solution using all information:		

Universal Indicators – Give a variety of colours over a larger pH range

If several indicators are mixed, the combinations of colours can lead to many different colours as we move from one pH to another. Study the 3 tables given on page 162 of SW to give you an idea of how universal indicators can be made. The second table is somewhat simplified as it does not include the colours of indicators in their transition ranges. The third table is more precise.

Read p. 159 – 162 in SW.

Do Ex. 108 – 112 and 114 – 120 on p. 162 – 163 of SW

### Using Indicators to Rank Weak Acids in Order of Strengths

To understand this section, recall that equilibrium always favours the side with the WEAKER acid (or weaker base)

Let's say an indicator HInd is **Red** in 0.1M HCl and **Blue** in 0.1M NaOH

Give the equilibrium equation for this indicator and write the colour of each form(HInd) and (Ind<sup>-</sup>) underneath it:

A few drops of this indicator (a mixture of HInd and Ind<sup>-</sup>) is added to a weak acid called HA<sub>1</sub> and the colour is **blue**. Which is the stronger acid, HA<sub>1</sub> or HInd?

To find out, we write an equilibrium equation (NOT with H<sub>2</sub>O this time!). For reactants, we use the weak acid HA<sub>1</sub> and the **base** form of the indicator, Ind<sup>-</sup>. (two acids are not written on the same side of equilibrium equations!) I'm sure you can fill in the two products: Write the colours of Ind<sup>-</sup> and HInd right underneath each one.



Since the colour of the indicator was **blue**, it means that the form of the indicator (*HInd or Ind<sup>-</sup>*) \_\_\_\_\_ is predominating (favoured by the equilibrium). So the (*reactants/products*) \_\_\_\_\_ of the equation above are favoured, meaning (*HA<sub>1</sub>/HInd*) \_\_\_\_\_ is the Weaker acid or

(*HA<sub>1</sub>/HInd*) \_\_\_\_\_ is the Stronger Acid.

Now let's look at another experiment involving the same indicator and a different weak acid HA<sub>2</sub>.

A few drops of this indicator (a mixture of HInd and Ind<sup>-</sup>) is added to a weak acid called HA<sub>2</sub> and the colour is **red**. Which is the stronger acid, HA<sub>2</sub> or HInd?

To find out, we write an equilibrium equation (NOT with H<sub>2</sub>O this time!). For reactants, we use the weak acid HA<sub>2</sub> and the **base** form of the indicator, Ind<sup>-</sup>. (two acids are not written on the same side of equilibrium equations!) I'm sure you can fill in the two products: Write the colours of Ind<sup>-</sup> and HInd right underneath each one.



Since the colour of the indicator was **red**, it means that the form of the indicator (*HInd or Ind<sup>-</sup>*) \_\_\_\_\_ is predominating (favoured by the equilibrium). So the (*reactants/products*) \_\_\_\_\_ of the equation above are favoured, meaning (*HA<sub>2</sub>/HInd*) \_\_\_\_\_ is the Weaker acid or

(*HA<sub>2</sub>/HInd*) \_\_\_\_\_ is the Stronger Acid.

So, to summarize the results of both experiments: Experiment 1: \_\_\_\_\_ > \_\_\_\_\_

Experiment 2: \_\_\_\_\_ > \_\_\_\_\_

So, in comparing strengths of HA<sub>1</sub> and HA<sub>2</sub>, we can say that \_\_\_\_\_ > \_\_\_\_\_

