Titrations

An important analytical technique, titrations are used to determine the concentration of a substance in solution by comparing it to a solution of a known concentration; called a **standard**

The reaction between the unknown and the standard is allowed to proceed until mole ratios like those in the balanced chemical equation are reached.

This stoichiometric point (sometimes called the equivalence point or end point) is determined using some sort of chemical indicator

Often these reactions are used with acids/bases, for acid/base titrations the end point is reached when:

Moles of OH⁻ from the base= moles of H⁺ from the acid Titrations consist of several trials; the first is an estimate, usually done quickly to get an approximate endpoint, almost always the first trial will be over the endpoint (overshot) The average volume of the second and subsequent trials are used in calculations:

Steps to follow

- 1) Write the balanced equation (as always you can't go wrong with this)
- 2) Calculate the moles of standard used $(n = M \times V)$
- 3) Determine the moles of unknown using the mole ratio
- 4) Calculate the unknown concentration (M = n/V)

Ex. If 10.0mL of HCl is titrated with 20.0mL of 0.40M NaOH, what is [HCl]?

NaOH $_{(aq)}$ + HCl $_{(aq)}$ \rightarrow H₂O $_{(I)}$ + NaCl $_{(aq)}$

Moles of standard (in this case NaOH) = 0.40 M x 0.0200 L = 8.0×10^{-3}

Moles of unknown (HCI) =

- Some acids or bases produce two (or more) H^+ or OH^- for each formula unit ($H_3PO_4 \rightarrow 3 H^+ + PO_4^{3-}$)

Ex. An average volume of 24.90mL of 0.100 M NaOH was required to neutralize 15.00mL of H_2SO_4 . What is the concentration of the acid?

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2 NaOH _{(aq)} + H<sub>2</sub>SO<sub>4 (aq)</sub> \rightarrow 2 H<sub>2</sub>O<sub>(I)</sub> + Na<sub>2</sub>SO<sub>4 (aq)</sub>
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Moles of standard (NaOH) =

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Moles of unknown (HCI) =
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[HCI] =

Salt Hydrolysis (reacting with water)

Dissolving salts in water sometimes yields a change in pH, as some anions and cations can interact with water and produce H⁺ and/or OH⁻.

<u>Cations</u>

Most **cations** are spectator ions, with 4 exceptions (there **are** more than 4 but we'll just do these 4 for Chemistry 12) – These **cations** act as **acids** in solution

NH₄⁺ donates H⁺, the metal ions Fe³⁺, Cr³⁺, Al³⁺, all form hexahydrates that can act as Brønsted-Lowry acids:

$$NH_{4}^{+}{}_{(aq)} + H_{2}O \rightarrow NH_{3(aq)} + H_{3}O^{+}{}_{(aq)}$$

$$Fe^{3+}{}_{(aq)} + 6H_{2}O \rightarrow Fe(H_{2}O)_{6}^{3+} \rightarrow Fe(H_{2}O)_{5}(OH)^{2+} + H^{+}{}_{(aq)}$$

$$Cr^{3+}{}_{(aq)} + 6H_{2}O \rightarrow Cr(H_{2}O)_{6}^{3+} \rightarrow Cr(H_{2}O)_{5}(OH)^{2+} + H^{+}{}_{(aq)}$$

$$Al^{3+}{}_{(aq)} + 6H_{2}O \rightarrow Al(H_{2}O)_{6}^{3+} \rightarrow Al(H_{2}O)_{5}(OH)^{2+} + H^{+}{}_{(aq)}$$

<u>Anions</u>

Most **anions** undergo hydrolysis as **bases**, grabbing an H^+ from water, with 6 exceptions = the conjugate bases of strong acids

No hydrolysis with Cl⁻, Br⁻, l⁻, ClO₄⁻, HSO₄⁻, NO₃⁻

 $HS_{(aq)} + H_2O_{(I)} \rightarrow H_2S_{(aq)} + OH_{(aq)}$

 $\text{CO}_3^{2^-}_{(aq)} + \text{H}_2\text{O}_{(I)} \rightarrow \text{HCO}_3^-_{(aq)} + \text{OH}^-_{(aq)}$

Ex. What is the pH of a 0.100M solution of NaF?

 $NaF \rightarrow Na^+ + F^-$

 $F_{(aq)} + H_2O_{(I)} \rightarrow HF_{(aq)} + OH_{(aq)}$

Reaction	F ⁻	+ H ₂ O	≓ HF	+	OH⁻
[Initial]					
Change					
[Equilibirum]					

Ex. Two solutions contain fluoride: 1.0M KF and 1.0M HF, which has higher conductivity?

HF only partially dissociates (1/10000) so HF is present in solution 10,000 times more than H^+ and F^- . HF is not very conductive.

With KF, K⁺ dissociates 100% because it's a spectator ion, where F⁻ reacts with water producing almost as much OH^- so KF is much more conductive.

Amphiprotic hydrolysis

Amphiprotic ions can both donate and accept protons, so when they hydrolyze it's not always obvious as to whether a basic or acidic solution will arise.

Have to compare the $K_{\rm a}$ and the $K_{\rm b}.$ Whichever constant is larger that's what reaction occurs.

Ex. NaHCO₃ is dissolved in water, is the resulting solution acidic, basic or neutral?

 $NaHCO_3 \rightarrow Na^+ + HCO_3^-$

 Na^+ is a spectator, so we're left with HCO_3^- . The questions is will the HCO_3^- behave as an acid or a base?

 $HCO_3^{-}(aq) + H_2O_{(I)} \rightarrow H_2CO_{3(aq)} + OH^{-}(aq)$

Or

 $HCO_{3^{-}(aq)} + H_2O_{(I)} \rightarrow CO_{3^{2^{-}}(aq)} + H_3O^{+}_{(aq)}$

Compare K_a and K_b

$$K_a = 5.6 \ge 10^{-11}$$

NOTICE THAT THE K_a used is for the CONJUGATE ACID! $K_b > K_a$ \therefore acts AS A BASE! **Ex.** NH_4F is dissolved in water, is the resulting solution acidic, basic or neutral?

 NH_4^+ (acting as an acid) and F^- (acting as a base)

Indicators

An indicator is a weak acid/base where the acid form as a different colour from the base form.

For the example above, blue/yellow, this is a common indicator called bromthymol blue.

Excess of strong acid (H^+) will shift equilibrium left, forming more of the 'acid form' - protonated (yellow) whereas excess base (OH^-) will shift right producing more of the 'base form' - deprotonated (blue).

End Point

End Point \equiv the point where $[H^+] = [OH^-]$ (acid = base)

For an indicator... if $[H^+] = [OH^-]$ then **[HIn] = [In^-]**

Ex. Bromthymol blue [yellow] = [blue] → green!

$$K_{a}(In) = \frac{[In^{-}][H^{+}]}{[HIn]}$$

So @ Endpoint, b/c [HIn] = [In⁻] \therefore K_a = [H⁺]

→ pKa (at end point) = pH (of indicator) Based on data booklet: can choose appropriate indicators for different acid/base reactions. **Ex.** Some indicator is green in its acid form, and red in its base form. Its pKa = 4.2 what colour is it in a 0.010 M HCN?

 $K_a =$

Reaction	HCN	4	H^+	+	CN⁻
[Initial]					
Change	-				
[Equilibirum]					

Assume X is small

pH =

So if indicator pKa =

So it's Red

Hebden pg 162/3 #110-120

Oxides

<u>Metal Oxides</u>

- solids @ room temperature
- solutions >7 pH (Basic)
- Soluble oxides → strong bases

Ex.

 $\begin{array}{l} \mathsf{CaO}_{(s)} + \mathsf{H}_2\mathsf{O}_{(l)} \rightarrow \mathsf{Ca}(\mathsf{OH})_{2(\mathsf{aq})} \\ \mathsf{MgO}_{(s)} + \mathsf{H}_2\mathsf{O}_{(l)} \rightarrow \mathsf{Mg}(\mathsf{OH})_{2(\mathsf{aq})} \\ \mathsf{Na}_2\mathsf{O}_{(s)} + \mathsf{H}_2\mathsf{O}_{(l)} \rightarrow \mathsf{2NaOH}_{(\mathsf{aq})} \end{array}$

<u>Non-metal oxides</u>

- Gases @ room temp.
- Solutions <7 pH (acidic)
- Major contributors to acid rain

Ex.

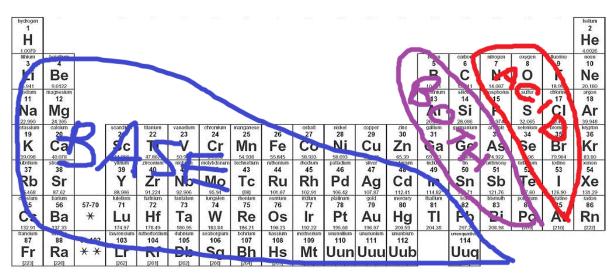
 $\begin{array}{l} SO_{2(g)} + H_2O_{(I)} \rightarrow H_2SO_{3(aq)} \\ 2NO_{2(g)} + H_2O_{(I)} \rightarrow HNO_{3(aq)} + HNO_{2(aq)} \end{array}$

<u>Semi-metal oxides</u>

- Usually solids at room temp.
- Can be basic OR acidic
- Amphiprotic

Ex.

 $\begin{array}{l} \mathsf{AI}_2\mathsf{O}_{3(s)} + 3\mathsf{H}_2\mathsf{O}_{(l)} \rightarrow 2 \ \mathsf{AI}(\mathsf{OH})_{3(aq)} - \mathsf{Base} \\ \mathsf{AI}_2\mathsf{O}_{3(s)} + 3\mathsf{H}_2\mathsf{O}_{(l)} \rightarrow 2 \ \mathsf{H}_3\mathsf{AIO}_{3(aq)} - \mathsf{Acid} \end{array}$



Anhydride reactions

Just as acids react with bases to produce water and salt. So too can oxides react to produce a salt – but NO WATER!!!

Ex Na₂O_(s) + CO_{2(g)} → Na₂CO_{3(aq)} CaO_(s) + SO_{3(g)} → CaSO_{4(aq)}

 $\begin{array}{l} \mathsf{AI}_2\mathsf{O}_{3(s)} + \mathsf{SO}_{3(g)} \rightarrow \mathsf{AI}_2(\mathsf{SO}_4)_{3(aq)} \\ \mathsf{AI}_2\mathsf{O}_{3(s)} + \mathsf{3K}_2\mathsf{O} \rightarrow \mathsf{2K}_3\mathsf{AIO}_{3(aq)} \end{array}$