- 2012 -

Chemistry 12

Unit IV – Acid/Base I

Key

I) Properties of Acids and Bases

Acids

1. Possess an H^+ in their structure.
2. Taste sour (see p. 111 Hebden)
3. Turn litmus paper RED
4. React with SOME metals to produce hydrogen gas.
   eg: $Mg + 2HCl \longrightarrow MgCl_2 + \boxed{H_2}$
5. a) Produce ELECTROLYTES (ions) in solution
   b) conduct electricity better than pure water.
6. React with BASES

Bases

1. Most possess OH^- in their structure.
2. Taste bitter
3. Turn litmus paper BLUE
4. Feel slippery to the touch (see p. 111 Hebden).
5. a) Produce electrolytes in solution.
   b) Conduct electricity better than pure water.
6. React with ACIDS.

II) Arrhenius Acids and Bases (1903)

Arrhenius Acid: a substance that releases H^+ in water.

Arrhenius Base: a substance that releases OH^- in water.

Salt: the neutralization product that results when a strong acid and a strong base react – made up of a METAL ION (CATION) and a NON-METAL ION (ANION).

e.g. $HCl_{(aq)} + NaOH_{(aq)} \Rightarrow H_2O_{(l)} + NaCl_{(aq)}$
str. acid + str. base = water + salt

e.g. $H_2SO_{4(aq)} + 2KOH_{(aq)} \Rightarrow 2H_2O_{(l)} + K_2SO_{4(aq)}$
str. acid + str. base = water + salt

Net Ionic Equation for a *strong acid/strong base* neutralization reaction: (net ionic equations display the true chemistry that is occurring – *spectator ions* are not included)

$$H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O_{(l)}$$

Assignment 1: Hebden p.110-112, Qs #1-4
Read pgs. 112-114 (Think about Qs 5-9 p.114)

III) Bronsted-Lowry Acids and Bases (1923)

Bronsted-Lowry Acid: A substance that donates a proton (H^+) to another substance.

Bronsted-Lowry Base: A substance that accepts a proton (H^+) from another substance.

Assignment 2: Label the acid reactant and the base reactant

1. $\underset{A}{HCl} + \underset{B}{H_2O} \Rightarrow H_3O^+ + Cl^-$

2. $\underset{B}{NH_3} + \underset{A}{H_2O} \Leftrightarrow NH_4^+ + OH^-$

3. $\underset{B}{CO_3^{2-}} + \underset{A}{H_2O} \Leftrightarrow HCO_3^- + OH^-$

4. $\underset{B}{HPO_4^{2-}} + \underset{A}{HBr} \Rightarrow H_2PO_4^- + Br^-$

5. $\underset{A}{HPO_4^{2-}} + \underset{B}{HS^-} \Leftrightarrow PO_4^{3-} + H_2S$

6. $\underset{B}{H_2PO_4^-} + \underset{A}{HF} \Leftrightarrow H_3PO_4 + F^-$

7. $\underset{A}{H_2PO_4^-} + \underset{B}{H_2O} \Leftrightarrow HPO_4^{2-} + H_3O^+$

Also do Hebden p.117 Q #11

IV) The Acid/Base Table

- acids are listed on the left from ***top (strongest) to bottom (weakest)***
- bases are listed on the right from ***bottom (strongest) to top (weakest)***
- the separate region at the top represents the **strong** acids (there are SIX), meaning they dissociate 100% (one-way arrow – no *equilibrium*)
- the separate region at the bottom represents the **strong** bases, meaning they dissociate 100% as well.
- Alkali metal hydroxides (eg. NaOH) and Alkaline Earth metal hydroxides (eg. $Ca(OH)_2$) are also strong bases, they are simply not listed on the table.
- Alkali metal hydroxides are very soluble salts (bases), whereas Alkaline Earth metal hydroxides are low soluble (except for $Sr(OH)_2$). Thus, even though Alkaline Earth metal hydroxides are deemed to be strong bases, their low solubility disallows them from generating a relatively high pH.
- Transition metal hydroxides, along with Aluminum hydroxide, are **weak** bases (Fe^{3+}, Cr^{3+}, and Al^{3+} shown on the table in the middle section).

- the section in the middle of the table represents the weak acids (left) and the weak bases (right). These substances form an equilibrium with water as their dissociation is defined as being <50% (most weak acids/bases, in the Chemistry 12 context, dissociate < 5%).
- therefore, weak acids are poorer conductors of electricity than strong acids (ie. they create less ions in solution than strong acids).
  *same with weak bases.

V) H^+ and H_3O^+

H^+ is simply a proton. Why? H^+ is missing an electron and its most common isotope is without a neutron.

When H^+ is created in water (due to the addition of acid), it immediately reacts with a water molecule to form the HYDRONIUM ion. Remember, a proton is an extremely concentrated positive charge and water's oxygen atom is partially negative in charge.

$$\underset{\text{proton}}{H^+} + \underset{\text{water}}{H_2O} \Rightarrow \underset{\text{hydronium ion}}{H_3O^+}$$

*thus, free protons do NOT exist in water!

Because this reaction is instantaneous, H^+ and H_3O^+ are used interchangeably (H^+ is used primarily for shorthand) . The dissociation of acid in water can be shown with or without water in the chemical equation:

i) $HCl_{(aq)} \Rightarrow H^+ + Cl^-$ shorthand

ii) $HCl + H_2O_{(l)} \Rightarrow H_3O^+ + Cl^-$ longhand (actual)

All of the reactions on the acid/base table are written in shorthand form. Each can be converted to type ii above by adding $H_2O_{(l)}$ to the left side and changing H^+ to H_3O^+ on the right side.

Change three equations from your table to include water.

$$HCOOH + H_2O \rightleftharpoons H_3O^+ + HCOO^-$$

$$HSO_3^- + H_2O \rightleftharpoons H_3O^+ + SO_3^{2-}$$

$$HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$$

An ACID can only act as an acid if it is in the presence of a BASE.
A BASE can only act as a base if it is in the presence of an ACID.
Water can act as either an acid or a base (it is *amphiprotic* in its nature).

VI) Further Definitions within Bronsted-Lowry Theory

Monoprotic Acid ($\overset{HX \text{ or}}{HA}$): an acid that can supply up to one proton only. eg: HCl, HCN, CH_3COOH etc.

Diprotic Acid (H_2A): an acid that can supply up to two protons. eg: H_2SO_4, H_2SO_3, H_2CO_3, H_2S etc.

Polyprotic Acid (H_xA): an acid that can supply up to many protons. eg: H_2SO_4, H_3PO_4, H_3BO_3, etc.
$x \geq 2$

Amphiprotic substance: A substance that has the ability to act as either an acid or a base (in water, an amphiprotic substance can act as both)
eg: H_2O, HCO_3^-, HSO_3^-

Look back at questions #4 and #5 in Assignment 2. What do you notice about HPO_4^{2-} and its behaviour in either question?

in Q 4 it's a base and in Q5 it's an acid

What can be concluded, then, about HPO_4^{2-}?

It must be AMPHIPROTIC

H_2O is amphiprotic as well, but it's a special case; see #3 of Assignment 3.

Generally, amphiprotic substances (except for H_2O) are polyatomic groups that contain at least one proton and are negatively charged.

HSO_3^-, HPO_4^{2-}, $H_2PO_4^-$

Exceptions to this rule?

H_2O, OH^-, NH_2^-, HSO_4^-

How can you tell if a substance is amphiprotic using the acid/base table?

If it is observed in both columns.

RULE: In a reaction between two amphiprotic substances, the stronger acid (higher on the left side of the table) will act as the acid and be the proton donor.

Assignment 3: Determine the products

1. $\underset{B}{HCO_3^-} + \underset{A}{H_2PO_4^-} \Leftrightarrow HPO_4^{2-} + H_2CO_3$

2. $\underset{B}{HPO_4^{2-}} + \underset{A}{HSO_4^-} \Leftrightarrow H_2PO_4^- + SO_4^{2-}$

3. $\underset{B}{H_2O} + \underset{A}{HSO_3^-} \Leftrightarrow H_3O^+ + SO_3^{2-}$

#3: Water is a special-case amphiprotic as it is the Weakest weak acid AND the weakest weak base. Thus, any other amphiprotic species will *hydrolyze* both acidically AND basically in water, but one will predominate.
↳ "react with water"

4. $\underset{B}{HCO_3^-} + \underset{A}{HSO_4^-} \Leftrightarrow H_2CO_3 + SO_4^{2-}$

Also do Q12 p.117 and Qs 13-14 p.119.

- QUIZ 1 -

VII) Conjugate Acid-Base Pairs

Conjugate acid/base pairs are molecules or ions that differ only by a PROTON (H^+).

A base has one less proton than its conjugate acid, and an acid has one more proton than its conjugate base.

Remember to **adjust the charge** when writing the conjugate.
(Gain proton => less - / more +; Lose proton => more - / less +)

What is the conjugate base of each of the following acids?

$HClO_4$ / ClO_4^-
CH_3COOH / CH_3COO^-
H_2CO_3 / HCO_3^-
PH_4^+ / PH_3
HNO_2 / NO_2^-
$HC_2O_4^-$ / $C_2O_4^{2-}$

What is the conjugate acid of each of the following bases?

CN^- / HCN
HSO_3^- / H_2SO_3
NH_3 / NH_4^+
$H_2PO_3^-$ / H_3PO_3
F^- / HF
$HCOO^-$ / $HCOOH$

<u>Acid/Base Equations</u>

Complete the following equation and identify the conjugate acid-base pairs.

$$\underset{B}{HCO_3^-} + \underset{A}{H_2PO_4^-} \Leftrightarrow \underset{A}{H_2CO_3} + \underset{B}{HPO_4^{2-}}$$

Assignment 4: Complete the equation and identify conjugate acid-base pairs

1. $\underset{A}{HSO_4^-} + \underset{B}{H_2O} \Leftrightarrow \underset{B}{SO_4^{2-}} + \underset{A}{H_3O^+}$
2. $\underset{B}{H_2O} + \underset{A}{HNO_2} \Leftrightarrow \underset{A}{H_3O^+} + \underset{B}{NO_2^-}$
3. $\underset{A}{HIO_3} + \underset{B}{NH_3} \Leftrightarrow \underset{B}{IO_3^-} + \underset{A}{NH_4^+}$
4. $\underset{B}{CO_3^{2-}} + \underset{A}{HF} \Leftrightarrow \underset{A}{HCO_3^-} + \underset{B}{F^-}$
5. $\underset{B}{HS^-} + \underset{A}{H_3PO_4} \Leftrightarrow \underset{A}{H_2S} + \underset{B}{H_2PO_4^-}$
6. $\underset{A}{HCO_3^-} + \underset{B}{CN^-} \Leftrightarrow \underset{B}{CO_3^{2-}} + \underset{A}{HCN}$
7. $\underset{A}{H_3BO_3} + \underset{B}{HO_2^-} \Leftrightarrow \underset{B}{H_2BO_3^-} + \underset{A}{H_2O_2}$
8. $\underset{B}{C_2O_4^{2-}} + \underset{A}{H_2O} \Leftrightarrow \underset{A}{HC_2O_4^-} + \underset{B}{OH^-}$
9. $\underset{B}{H_2O} + \underset{A}{H_2SO_3} \Leftrightarrow \underset{A}{H_3O^+} + \underset{B}{HSO_3^-}$

Assignment 5: Hebden p. 121 #16-19

VIII) Strong and Weak Acids and Bases

Strong acids and bases are 100% ionized (dissociated) in solution. Thus, they react to completion and do not form an equilibrium (see table).

e.g. $\underset{0\%}{HCl} + H_2O_{(l)} \underset{\text{one way}}{\Rightarrow} \underset{100\%}{H_3O^+} + \underset{100\%}{Cl^-}$

Weak acids and bases are not 100% ionized in solution (in fact, by definition, they dissociate <50% -- in Chem 12, the general assumption is that they dissociate <5%). They create an equilibrium with reactants heavily favoured (ie. [R] >> [P] → therefore, $K_{eq} \underline{<} 1$)

e.g. $HF + H_2O \Leftrightarrow H_3O^+ + F^-$

95% 5% 5%

Only weak acids and bases are in equilibrium with their conjugate pairs. Strong acids (such as HCl) have a conjugate base (Cl^-), but they are unable to form an equilibrium because conjugate bases of strong acids cannot act as a base (see table). The same idea pertains to strong bases and their non-functional conjugate acids.

*It is important to mention that the terms **strong** and **weak** differ from the terms **concentrated** and **dilute**.

6M KOH is STRONG and CONCENTRATED.

0.0001M KOH is STRONG and DILUTE.

6M CH_3COOH is WEAK and CONCENTRATED

0.0001M CH_3COOH is WEAK and DILUTE.

So, to summarize:

In order to determine if an acid/base is strong or weak, one must determine the Species.

In order to determine if the same chemical is concentrated or dilute, one must know the molarity.

Leveling Effect

All of the strong acids listed at the top of the acid-base table ionize (dissociate) 100% in solution. Therefore, each of the six are **level** in strength. The same goes for strong bases.

Thus, H_3O^+ is the 'strongest' acid that can exist in water (aqueous solution) because H_3O^+ is the result of adding a STRONG acid to water…similarly with bases → OH^- is the 'strongest' base that can exist in water (aqueous solution) because OH^- is the result of adding a STRONG base to water.

Question: Why are 1M HCl and 1M H_2SO_4 *level* in strength if one species is monoprotic and the other is diprotic?

1 M HCl : $\underset{1M}{HCl} + H_2O \longrightarrow \underset{1M}{H_3O^+} + \underset{1M}{Cl^-}$

1 M H_2SO_4 : $\underset{1M}{H_2SO_4} + H_2O \longrightarrow \underset{1M}{H_3O^+} + \underset{1M}{HSO_4^-}$ * only first proton dissociates 100%

but… HSO_4^- is a weak acid; however, it cannot act as such in the presence of a high $[H_3O^+]$.

IX) Determining Whether Reactants or Products are Favoured in an Acid/Base Reaction

Note: All Bronsted-Lowry reactions involve the transfer of 1 proton unless one or both species are STRONG. → unless, of course, water is the other reactant

$$\underset{B}{\overset{weak}{HCO_3^-}} + \underset{A}{\overset{weak}{HF}} \Leftrightarrow \underset{A}{H_2CO_3} + \underset{B}{F^-}$$

There is a 'competition' between the two acids HF and H_2CO_3 to donate a proton. The stronger acid 'wins out' and will give a proton to a greater extent. Since HF is the stronger acid in this equilibrium, the FORWARD reaction is favoured (in terms of possessing a lower E_a) and therefore PRODUCTS are favoured (ie. at equilibrium, [P] $>$ [R]).

RULE: The side of the reaction with the WEAKER acid is always favoured.
REASON: The stronger acid donates a proton more readily, causing the other side (weaker side) to be greater in concentration.
So…if products are favoured: $K_{eq} > 1$; if reactants favoured: $K_{eq} < 1$.

Assignment 6: Label conjugate acid-base pairs and state whether reactants or products are favoured.

1. $\underset{A}{NH_4^+} + \underset{B}{H_2O} \Leftrightarrow \underset{B}{NH_3} + \underset{A}{H_3O^+}$ Reactants since H_3O^+ stronger than NH_4^+
2. $\underset{A}{H_2S} + \underset{B}{NH_3} \Leftrightarrow \underset{B}{HS^-} + \underset{A}{NH_4^+}$ Products since H_2S stronger than NH_4^+
3. $\underset{A}{H_2PO_4^-} + \underset{B}{HS^-} \Leftrightarrow \underset{B}{HPO_4^{2-}} + \underset{A}{H_2S}$ Reactants since H_2S stronger than $H_2PO_4^-$
4. $\underset{A}{H_2O_2} + \underset{B}{SO_3^{2-}} \Leftrightarrow \underset{B}{HO_2^-} + \underset{A}{HSO_3^-}$ Reactants since HSO_3^- stronger than H_2O_2
4. $\underset{A}{CH_3COOH} + \underset{B}{PO_4^{3-}} \Leftrightarrow \underset{B}{CH_3COO^-} + \underset{A}{HPO_4^{2-}}$ Products since CH_3COOH stronger than HPO_4^{2-}
6. $\underset{A}{H_2PO_4^-} + \underset{B}{C_2O_4^{2-}} \Leftrightarrow \underset{B}{HPO_4^{2-}} + \underset{A}{HC_2O_4^-}$ Reactants since $HC_2O_4^-$ stronger than $H_2PO_4^-$
7. $\underset{A}{H_2SO_3} + \underset{B}{SO_4^{2-}} \Leftrightarrow \underset{B}{HSO_3^-} + \underset{A}{HSO_4^-}$ Products since H_2SO_3 stronger than HSO_4^-

Assignment 7: Review Questions

1. Will the K_{eq} be greater or less than 1 for the following equilibrium? Why?

$$\underset{A}{HSO_4^-} + \underset{B}{NH_3} \Leftrightarrow \underset{B}{SO_4^{2-}} + \underset{A}{NH_4^+}$$

HSO_4^- is a stronger acid than NH_4^+, thus products are favoured $\Rightarrow [P] > [R] \Rightarrow \boxed{K_{eq} > 1}$

2. Which acid has the higher $[H_3O^+]$ when reacting with water, HCN or CH_3COOH? Why?

CH_3COOH because it is the stronger acid.
* of course, it is assumed that their original concentrat^{n}s are the same, unless otherwise stated.

3. Will a reaction occur between NH_2^- and $C_2O_4^{2-}$? Explain why or why not.

No, because neither species has the ability to act as an acid.

4. Write an equation to show the reaction between NH_2^- and water to form a basic solution (containing OH^-), and explain why products are favoured.

$$\underset{B}{NH_2^-} + \underset{A}{H_2O} \longrightarrow \underset{A}{NH_3} + \underset{B}{OH^-}$$

ONE WAY, since NH_2^- is a STRONG base.

cannot act as an acid!

$\boxed{[P] > [R] \Rightarrow \text{PRODUCTS FAVOURED}}$

Assignment 8: Hebden p. 125-126 #21-27, p. 133 #38-46

- QUIZ 2 -

X) Ionization of Water

Water is amphiprotic, meaning it can act as an ACID in certain situations, and a BASE in others. Water reacts with itself to a very small extent, with one water molecule being the acid and donating a proton and the other a base and accepting a proton.

$$2H_2O_{(l)} + 59kJ \Leftrightarrow H_3O^+_{(aq)} + OH^-_{(aq)}$$

does not affect SIGFIGS.

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 25°C$$

K_w = equilibrium constant for water

Pure water is neutral (in pH) and since $[H_3O^+][OH^-] = 1.0 \times 10^{-14}$, then

$[H_3O^+]$ = 1.0×10^{-7} M and $[OH^-]$ = 1.0×10^{-7} M

$[H_3O^+] = [OH^-]$, therefore they 'cancel each other out.'

Approx. One in every 10 million water molecules dissociates at 25^0 C, or approx 2 in every 20 million water molecules react with each other which is what really happens! * it takes two to tango!

Shorthand water dissociation reaction equation:

$$H_2O_{(l)} + \boxed{E} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$

Longhand (actual) version:

$$2H_2O_{(l)} + \boxed{E} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$

$[H_3O^+] = [OH^-]$ because every reaction between two water molecules produces one hydronium ion and one hydroxide ion. In any solution where $[H_3O^+] = [OH^-]$, the solution is considered to be NEUTRAL in pH. Water reacting with an acid will produce more H_3O^+ ions, thereby creating an ACIDIC solution. Water reacting with a base will produce more OH^- ions, thereby creating a BASIC solution.

Regardless of the chemicals, if water is the 'arena'(ie. reaction takes place in aqueous solution), then the K_w remains constant at 1.0×10^{-14} (since a temperature change is the only stress that can alter a K_{eq} value). Therefore, if one of the hydronium ion or hydroxide ion increases, the other must decrease in concentration (by the same proportion) in order to satisfy the K_w equation.

Water dissociation equation: $2H_2O_{(l)} + 59kJ \Leftrightarrow H_3O^+_{(aq)} + OH^-_{(aq)}$

Scenarios:

ADD ACID (incr. $[H_3O^+]$): shift Ⓛ

$[H_3O^+]: \uparrow\downarrow = \uparrow$ $[OH^-]: - \downarrow = \downarrow$

In acid: $[H_3O^+]$ > 1.0×10^{-7}M and $[OH^-]$ < 1.0×10^{-7}M

* Still OH^- present, since K_w equilibrium still exists even though it shifted. (**there will NEVER be 0 M hydronium or hydroxide in an aqueous sol'n).

ADD BASE (incr. $[OH^-]$): shift Ⓛ

$[H_3O^+]: - \downarrow = \downarrow$ $[OH^-]: \uparrow\downarrow = \uparrow$

In base: $[H_3O^+]$ < 1.0×10^{-7}M and $[OH^-]$ > 1.0×10^{-7}M

* Still H_3O^+ present, since K_w equilibrium still exists even though it shifted.

Assignment 9: K_w Exercises

1. Calculate the $[OH^-]$ in a solution in which $[H_3O^+]$ is 1.0×10^{-12}M. Is the solution neutral, acidic, or basic?

$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1 \times 10^{-14}}{1.0 \times 10^{-12} M} = \boxed{1.0 \times 10^{-2} M}$ $\boxed{\text{BASIC}}$

2. Calculate the $[H_3O^+]$ in a solution in which $[OH^-]$ is 1.0×10^{-8}M.

$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1 \times 10^{-14}}{1.0 \times 10^{-8} M} = \boxed{1.0 \times 10^{-6} M}$ $\boxed{\text{ACIDIC}}$

3. Calculate the $[OH^-]$ for solutions with the given $[H_3O^+]$. Is each solution acidic, basic, or neutral?

a. $[H_3O^+] = 1.0 \times 10^{-3}$M $[OH^-] = 1.0 \times 10^{-11} M$ ACIDIC
b. $[H_3O^+] = 2.6 \times 10^{-10}$M $[OH^-] = 3.8 \times 10^{-5} M$ BASIC
c. $[H_3O^+] = 8.7 \times 10^{-7}$M $[OH^-] = 1.1 \times 10^{-8} M$ ACIDIC

4. Calculate the $[H_3O^+]$ for solutions with the given $[OH^-]$. Is each solution acidic, basic, or neutral?

a. $[OH^-] = 1.0 \times 10^{-2}$M $[H_3O^+] = 1.0 \times 10^{-12} M$ BASIC
b. $[OH^-] = 3.4 \times 10^{-6}$M $[H_3O^+] = 2.9 \times 10^{-9} M$ BASIC
c. $[OH^-] = 9.2 \times 10^{-9}$M $[H_3O^+] = 1.1 \times 10^{-6} M$ ACIDIC

5. What is the $[H_3O^+]$ and $[OH^-]$ in 0.0010M HCl?

$\underset{0.0010 M}{HCl} + H_2O \longrightarrow \underset{\boxed{0.0010 M}}{H_3O^+} + \underset{0.0010 M}{Cl^-}$ $\boxed{[OH^-] = 1.0 \times 10^{-11} M}$

6. What is the $[H_3O^+]$ and $[OH^-]$ in 0.00345M NaOH?

$\underset{0.00345 M}{NaOH} \longrightarrow Na^+ + \underset{\boxed{0.00345 M}}{OH^-}$ $\boxed{[H_3O^+] = 2.90 \times 10^{-12} M}$

7. Calculate the $[H_3O^+]$ and $[OH^-]$ in

a. 2.5×10^{-4}M HNO_3 $[H_3O^+] = 2.5 \times 10^{-4} M$; $[OH^-] = 4.0 \times 10^{-11} M$
b. 5.0M HCl $[H_3O^+] = 5.0 M$; $[OH^-] = 2.0 \times 10^{-15} M$
c. 6.00×10^{-3}M $Ca(OH)_2$ $[H_3O^+] = 8.33 \times 10^{-13} M$; $[OH^-] = 1.20 \times 10^{-2} M$

Effect of Temperature on K_w

$$2H_2O_{(l)} + 59kJ \Leftrightarrow H_3O^+_{(aq)} + OH^-_{(aq)}$$

This reaction is ENDOTHERMIC in the forward direction and EXOTHERMIC in the reverse direction. Increasing the temperature will shift the equilibrium to the RIGHT. This causes an increase in $[H_3O^+]$ and $[OH^-]$, and an increase in the value of K_w. Similarly, decreasing the temperature causes a shift to the LEFT, thereby decreasing the $[H_3O^+]$ and $[OH^-]$, and causing K_w to decrease.

Even though $[H_3O^+]$ and $[OH^-]$ change due to a temperature change, they are still equal to one another, so water at any temperature is still neutral in pH.

Assignment 10: Hebden: Read pp. 126-127; Do Qs 28-29.

XI) pH (Potential Hydrogen Ion)

pH is a measure of the $[H^+]$ or $[H_3O^+]$ in a solution using logarithms (log).

The pH scale is 0-14 at 25°C, however pH values below 0 and above 14 are possible.

$[H_3O^+]$ (M)	$>10^0$	10^0	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}	10^{-10}	10^{-11}	10^{-12}	10^{-13}	10^{-14}	$<10^{-14}$
pH	<0	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	>14

Sigfigs??? See p.16 (booklet) or Hebden p.139 for explanation…

Essentially, only digits AFTER the decimal are significant in pH values.

Each unit change in pH represents a 10x change in $[H_3O^+]$ and $[OH^-]$.

Remember that $[H_3O^+]$ and $[OH^-]$ are inversely related (as one goes up, the other goes down), in order to maintain K_w. Thus, a high $[H_3O^+]$ in a solution corresponds to a low $[OH^-]$, since their product must always equal 1.0×10^{-14} at 25°C.

** When doing pH problems, **assume 25° C unless otherwise stated.**

When $[H_3O^+] = 1.0 \times 10^{-7}M$, what is the pH and what is $[OH^-]$?

pH = 7.00 (see table) ; $[OH^-] = \frac{K_w}{1.0\times10^{-7}M} = \boxed{1.0\times10^{-7}M}$

Conclusion:

Since $[H_3O^+] = [OH^-]$, a pH of 7 is considered NEUTRAL.

If $[H_3O^+] > 1.0 \times 10^{-7}M$, such as $1.0 \times 10^{-4}M$, what is the pH? What is $[OH^-]$?

pH = 4.00 (table) ; $[OH^-] = \frac{K_w}{1.0\times10^{-4}M} = \boxed{1.0\times10^{-10}M}$

Conclusion: A low pH (less than 7) corresponds to an ACIDIC solution. $[H_3O^+] > [OH^-]$

If $[H_3O^+] < 1.0 \times 10^{-7}M$, such as $1.0 \times 10^{-11}M$, what is the pH and the $[OH^-]$?

pH = 11.00 (table) ; $[OH^-] = \frac{K_w}{1.0\times10^{-11}M} = \boxed{1.0\times10^{-3}M}$

Conclusion: A high pH (greater than 7) corresponds to a BASIC solution. $[H_3O^+] < [OH^-]$

What if the concentration values are 'in between' those that are given in the table above (ie. coefficients other than 1, 1.0, 1.00, etc…)?

pH can be calculated from $[H_3O^+]$ by the following:

$$pH = -\log [H_3O^+]$$

$[H_3O^+]$ can be calculated from pH by the following:

$$[H_3O^+] = \text{inv log}(-pH) = 10^{(-pH)}$$

Fill in the blanks in the following table (use proper sigfigs!):

$[H_3O^+]$ (M)	2.1×10^{-2}	2.74×10^{-5}	9×10^{-9}	6×10^{-14}	5.09×10^{-13}	4.8×10^{-8}
pH	1.68	4.562	8.0	13.2	12.293	7.32

pOH

pOH is a measure of hydroxide ion concentration using logarithms.

$$pOH = -\log [OH^-] \qquad [OH^-] = \text{inv log}(-pOH)$$

If pOH < 7; solution is basic If pOH > 7; solution is acidic.

Assignment 11: pH/pOH Exercises

1. Find the pH of
   a) 1.0×10^{-5}M H_3O^+. pH = 5.00
   b) 2.6×10^{-7}M H_3O^+. pH = 6.59
   c) 6.7×10^{-12}M H_3O^+. pH = 11.17

2. Find the $[H_3O^+]$ for each
   a) pH = 2.35 $[H_3O^+] = 4.5 \times 10^{-3}$ M
   b) pH = 6.456 $[H_3O^+] = 3.50 \times 10^{-7}$ M
   c) pH = 10.76 $[H_3O^+] = 1.7 \times 10^{-11}$ M

3. Find the pOH of each in #1. Hint: use $K_w = [H_3O^+] [OH^-]$
   a) 9.00 b) 7.41 c) 2.83
4. Find the pOH of each in #2.
   a) 11.65 b) 7.544 c) 3.24
5. Find the $[OH^-]$ for each
   a) pOH = 2.34 $[OH^-] = 4.6 \times 10^{-3}$ M
   b) pOH = 12.59 $[OH^-] = 2.6 \times 10^{-13}$ M
   c) pOH = 7.10 $[OH^-] = 7.9 \times 10^{-8}$ M

6. Add the pH and pOH for each of a, b, and c in #1 and 3. What do you notice?
   $pH + pOH = \boxed{14}$

Upper limit of pH scale at 25°C (lower limit always 0)

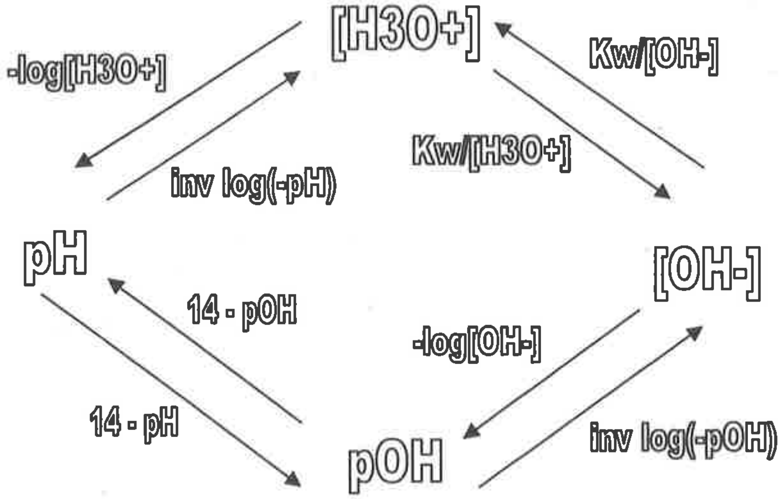
pK_w (Helps to derive the upper limit of pH scale)

$pK_w = -\log K_w$ at 25°C = $-\log(1 \times 10^{-14})$ = 14

Since $K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$,
Then $pK_w = pH + pOH$ and
$14 = pH + pOH$ (at 25°C)

* important so that we know NEUTRAL (halfway point).

Conversion "Road-Map":



Assignment 12: More pH/pOH Exercises:

1. Calculate pH and pOH of (with proper sigfigs)

a) 1.2×10^{-2}M H_3O^+ pH = 1.92 pOH = 12.08

b) 3.54×10^{-8}M OH^- pH = 6.549 pOH = 7.451

c) 8.77×10^{-10}M H_3O^+ pH = 9.057 pOH = 4.943

d) 6.5×10^{-1}M OH^- pH = 13.81 pOH = 0.19

2. Calculate $[H_3O^+]$ and $[OH^-]$ for (with proper sigfigs)

a) pH = 3.45 $[H_3O^+] = 3.5 \times 10^{-4} M$ $[OH^-] = 2.8 \times 10^{-11} M$

b) pH = 12.54 $[H_3O^+] = 2.9 \times 10^{-13} M$ $[OH^-] = 3.5 \times 10^{-2} M$

c) pOH = 2.335 $[H_3O^+] = 2.16 \times 10^{-12} M$ $[OH^-] = 4.62 \times 10^{-3} M$

d) pOH = 13.22 $[H_3O^+] = 1.7 \times 10^{-1} M$ $[OH^-] = 6.0 \times 10^{-14} M$

Outside the pH scale

At 25⁰ C, very concentrated acidic solutions may have pH values less than 0 and very concentrated basic solutions may have pH values greater than 14.

Examples: Find the pH of

a) 2.0M HBr

$HBr + H_2O \longrightarrow H_3O^+ + Br^-$

2.0 M 2.0M

$pH = -\log(2.0) = \boxed{-0.30}$

b) 10.0M KOH

$KOH \longrightarrow K^+ + OH^-$

10.0 M 10.0 M

$pOH = -\log(10.0) = -1.000$

$pH = \boxed{15.000}$

c) 1.5M $Sr(OH)_2$

$Sr(OH)_2 \longrightarrow Sr^{2+} + 2OH^-$

1.5 M 3.0 M

$pOH = -\log(3.0) = -0.48$

$pH = \boxed{14.48}$

d) 1.5 moles $Mg(OH)_2$ placed into 1L of water *teehee…

$Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$

x $2x$

$K_{sp} = 5.6 \times 10^{-12}$

$K_{sp} = 4x^3$

$5.6 \times 10^{-12} = 4x^3$

$x = [Mg(OH)_2] = 1.1187 \times 10^{-4} M$

$[OH^-] = 2.\underline{2}374 \times 10^{-4} M$

$pOH = -\log(2.2374 \times 10^{-4})$

$= 3.6\underline{5}03$

$\boxed{pH = 10.35}$

Assignment 13: Hebden p. 139 #49, 50, 53 & p. 141 #55, 57

MORE EXAMPLES:

Eg 1: Find the pH of a 0.0020M solution of HNO_3.

$$HNO_3 + H_2O \longrightarrow H_3O^+ + NO_3^-$$

0.0020 M 0.0020 M

$$pH = -\log(0.0020\,M) = \boxed{2.70}$$

Eg 2: Calculate the pH of a 0.010M NaOH solution.

$$NaOH \longrightarrow Na^+ + OH^-$$

0.010 M 0.010 M

$$pOH = -\log(0.010\,M) = 2.00 \quad \boxed{pH = 12.00}$$

Eg 3: If the pH is decreased from 5.0 to 2.0, what happens to the $[H_3O^+]$ and $[OH^-]$?

$10^{5.0-2.0} = 10^{3.0} = \underline{1}000\times$ more acidic (less basic)

$$\boxed{[H_3O^+] \uparrow 1000\times \quad ; \quad [OH^-] \downarrow 1000\times}$$

Eg 4: If pH is increased from 7.25 to 8.93, what happens to the $[H_3O^+]$?

$10^{8.93-7.25} = 10^{1.68} = 4\underline{7}.86 = 48\times$ more basic (less acidic

$$\boxed{[H_3O^+] \downarrow 48\times}$$

Eg 5: Calculate the pH of the final solution if 100.0mL of a strong acid at pH = 4.500 is diluted by adding 50.0mL of water.

$$[H_3O^+]_i = \text{inv}\log(-4.500) = 3.1\underline{6}23 \times 10^{-5}\,M$$

$$[H_3O^+]_f = \frac{M_iV_i}{V_f} = \frac{(3.1\underline{6}23 \times 10^{-5}\,M)(0.1000\,L)}{(0.1500\,L)} = 2.1\underline{0}82 \times 10^{-5}\,M$$

$$pH = -\log(2.1\underline{08}2 \times 10^{-5}\,M) = \boxed{4.676}$$

Eg 6: By how many pH units does the pH change if 80.0mL of 0.0200M HCl is diluted to a final volume of 160.0mL?

$$[H_3O^+]_i = 0.0200\,M \qquad pH_i = -\log(0.0200\,M) = 1.69\underline{8}97$$

$$[H_3O^+]_f = \frac{M_iV_i}{V_f} = \frac{(0.0200\,M)(0.0800\,L)}{0.1600\,L} = 0.0100\,M$$

$$pH = -\log(0.0100\,M) = 2.00\underline{0}$$

Change in pH: $2.00\underline{0} - 1.69\underline{8}97 = 0.30\underline{1}03$

$$\boxed{\text{Increase of } 0.301}$$

Assignment 14: More pH Exercises

0. Hebden p.141 #56.

See Answers in back of text.

1. Calculate the pH, pOH and [OH⁻] of a 0.00100M solution of HNO_3.

$HNO_3 + H_2O \longrightarrow H_3O^+ + NO_3^-$

$0.00100\,M \qquad 0.00100\,M$

$pH = -\log(0.00100M) = \boxed{3.000} \quad pOH = \boxed{11.000} \quad [OH^-] = \text{inv}\log(-11.000) = \boxed{1.00 \times 10^{-11} M}$

2. Calculate the pOH, pH, and [H_3O^+] of a 2.34 x 10⁻⁴M solution of $Ca(OH)_2$. Assume 2.34 x 10⁻⁴ M is low enough to allow $Ca(OH)_2$ to fully dissociate

$Ca(OH)_2 \longrightarrow Ca^{2+} + 2OH^-$

$2.34 \times 10^{-4} M \qquad 4.68 \times 10^{-4} M$

$pOH = -\log(4.68 \times 10^{-4} M) = \boxed{3.330} \quad \boxed{pH = 10.670}$

$[H_3O^+] = \text{inv}\log(-10.67\underline{0}25) = \boxed{2.14 \times 10^{-11} M}$

3. If the pH is increased from 1 to 6, what happens to the [H_3O^+] and [OH⁻] ?

$10^{6-1} = 10^5 = 100\,000 \times$ more basic

*technically, zero sigfigs ⟹ so, we'll say <u>one</u> sigfig

$\boxed{[OH^-] \uparrow 100000 \times \; ; \; [H_3O^+] \downarrow 100\,000 \times}$

4. If the pH decreases from 9.3 to 6.5, what happens to the [H_3O^+]?

$10^{9.3-6.5} = 10^{2.8} = \underline{6}31 \times = \underline{6}00 \times$ more acidic

$\boxed{[H_3O^+] \uparrow 600 \times}$

5. What is the pH of the final solution if 35.00mL of a strong acid at pH 3.56 is diluted by adding 100.0mL of water?

$[H_3O^+]_i = \text{inv}\log(-3.56) = 2.\underline{7}542 \times 10^{-4} M$

$[H_3O^+]_f = \dfrac{M_iV_i}{V_f} = \dfrac{(2.\underline{7}542 \times 10^{-4} M)(0.03500 L)}{0.1350 L} = 7.\underline{1}405 \times 10^{-5} M$

$pH_f = -\log(7.\underline{1}405 \times 10^{-5} M)$ $\boxed{= 4.15}$

6. You have 50.00mL of a 0.00345M solution of $HClO_4$. How does the pH change if you dilute the solution to a final volume of 175.0mL?

$HClO_4 + H_2O \longrightarrow H_3O^+ + ClO_4^-$

$0.00345\,M \qquad 0.00345\,M$

$pH_i = -\log(0.00345M) = 2.46\underline{2}18$

$pH_f: \; [H_3O^+]_f = \dfrac{M_iV_i}{V_f} = \dfrac{(0.00345 M)(0.05000 L)}{0.1750 L} = 9.8\underline{5}71 \times 10^{-4} M$

$pH_f = -\log(9.8\underline{5}71 \times 10^{-4} M) = 3.00\underline{6}25$

$\Delta pH = 3.00\underline{6}25 - 2.46\underline{2}18 = \boxed{0.544 \text{ INCREASE}}$

Temperature and pH

At 25°C: $2H_2O_{(l)} + 59kJ \Leftrightarrow H_3O^+_{(aq)} + OH^-_{(aq)}$

$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$, so $pK_w = 14$

remember: (pK_w = upper limit of pH scale)

Therefore, the pH scale (at 25⁰ C) is 0-14

If the temperature is increased, what happens to the above equilibrium and the resulting K_w? What will happen to the pH scale? Will the pH be acidic, basic, or neutral? $\uparrow$ temp → $\uparrow$ both rates → $\uparrow$ endo- more → shift Ⓡ → $\uparrow [H_3O^+][OH^-] \rightarrow \boxed{\uparrow K_w} \rightarrow \downarrow pK_w \rightarrow$ $\boxed{\text{pH scale narrows}}$; $\boxed{\text{NEUTRAL}}$

Answer the same questions for when the temperature is decreased.

$\downarrow$ temp. → $\downarrow$ both rates → endo $\downarrow$ more → shift Ⓛ → $\downarrow [H_3O^+][OH^-] \rightarrow \boxed{\downarrow K_w} \rightarrow \uparrow pK_w \rightarrow$ $\boxed{\text{pH scale widens}}$; $\boxed{\text{NEUTRAL}}$

An increase in temperature to 50°C results in a K_w of 5.48×10^{-14}. Calculate the pH, pOH, $[H_3O^+]$, and $[OH^-]$ in water.

$pK_w = -\log(5.48 \times 10^{-14}) = 13.26122$ (UPPER-LIMIT of pH SCALE)

So... since water is neutral, $pH_{water} = pOH_{water} = \frac{13.26122}{2} = \boxed{6.631}$

$[H_3O^+] = [OH^-] = \text{invlog}(-6.63061) = \boxed{2.34 \times 10^{-7}\ M}$

A sample of distilled, pure water has a pH of 7.50. Is the temperature greater than or less than 25°C? Explain.

7.50 > 7, so $pH_{water} \uparrow$ → pH scale widened → $pK_w \uparrow$ → $K_w \downarrow$ → $[H_3O^+][OH^-] \downarrow$ → shift Ⓛ → rev. faster → endo- slower → $\boxed{\text{temp.} \downarrow}$ so $\boxed{\text{Temp.} < 25^\circ C}$

Assignment 15: Hebden p. 139 #51, 52, + question 1 below

1. Water at a certain temperature has a K_w of 4.4×10^{-15}.
   a) Is the water at a temperature above or below 25° C ? BELOW
   b) What is the pK_w ? 14.36
   c) What would the pH scale be at this temperature? 0 - 14.36
   d) Find the $[H_3O^+]$ and $[OH^-]$. $[H_3O^+] = [OH^-] = 6.6 \times 10^{-8}$ M
   e) Find the pH and pOH. pH = pOH = 7.18
   f) Is water at this temperature acidic, basic, or neutral? NEUTRAL

- QUIZ 3 -

XII) Mixtures of Strong Acids and Bases – a Quantitative Approach

Mixing an acid with a base produces a solution that can be
ACIDIC, BASIC, or NEUTRAL
depending on the *moles* of H_3O^+ compared to the *moles* of OH^- mixed. Hebden uses a *molarity* method; I teach a *moles* method. Either may be used, but sigfigs could differ. The moles method allows one to better understand the 'true' chemistry at work.

1. Calculate the pH of a solution obtained by adding 50.0mL of 0.10M HCl to 80.0mL of 0.15M NaOH.

$HCl + H_2O \rightarrow H_3O^+ + Cl^-$

$NaOH \rightarrow Na^+ + OH^-$

$$HCl + NaOH \longrightarrow H_2O + NaCl$$

mol H_3O^+ added (= mol HCl added) $= MV = (0.10M)(0.0500L) = 0.005\underline{0}$ mol H_3O^+

mol OH^- added (= mol NaOH added) $= MV = (0.15M)(0.0800L) = 0.01\underline{2}0$ mol OH^-

mol excess OH^- $= 0.01\underline{2}0$ mol OH^- $- 0.005\underline{0}$ mol H_3O^+

$= 0.00\underline{7}$ mol OH^- remaining

$$[OH^-]_f = \frac{mol}{V_f} = \frac{0.007\ mol}{0.1300\ L} = 0.0\underline{5}3846\ M\ OH^-$$

$$pOH = -\log(0.053846\ M) = 1.\underline{2}69 \qquad pH = 14 - 1.\underline{2}69 = \boxed{12.7}$$

Some important information:
- monoprotic acids dissociate into hydronium at a one-to-one ratio;
- diprotic acids dissociate into hydronium at a one-to-two ratio;
- triprotic acids dissociate into hydronium at a one-to-three ratio;
- etc…

When in the presence of an in-excess, strong counterpart.

- 'Diprotic' (or 'polyprotic') Arrhenius bases that are low soluble will dissociate to their fullest extent when in the presence of an in-excess strong acid.

2. Calculate the pH of a solution obtained by adding 30.00g of LiOH to 650.0mL of 0.400M H_2SO_4.

$$H_2SO_4 + 2LiOH \longrightarrow Li_2SO_4 + 2H_2O$$

$$H_2SO_4 + H_2O \longrightarrow 2H_3O^+ + SO_4^{2-} \qquad LiOH \longrightarrow Li^+ + OH^-$$

* in presence of strong base

mol LiOH added = mol OH^- added = $\dfrac{30.00g \mid 1 \text{ mol LiOH}}{\mid 23.9g \text{ LiOH}} = 1.2552$ mol OH^-

mol H_2SO_4 added = $MV = (0.400M)(0.6500L) = 0.260$ mol H_2SO_4

$$\frac{0.260 \text{ mol } H_2SO_4 \mid 2 \text{ mol } H_3O^+}{\mid 1 \text{ mol } H_2SO_4} = 0.520 \text{ mol } H_3O^+ \text{ added}$$

mol excess OH^- = 1.2552 mol OH^- − 0.520 mol H_3O^+ = 0.73523 mol OH^-

$[OH^-]_f = \dfrac{mol}{V_f} = \dfrac{0.73523 \text{ mol}}{0.6500L} = 1.13112$ M OH^-

pOH = − log (1.13112 M)

= −0.05351

$\boxed{pH = 14.05}$

3. What mass of NaOH would have to be added to 500.0mL of 0.100M $HClO_4$ in order to produce a solution with a pH of 3.200.

$$HClO_4 + NaOH \longrightarrow NaClO_4 + H_2O$$

mol $HClO_{4\,i}$ = mol $H_3O^+_i$ = $MV = (0.100M)(0.5000L) = 0.0500$ mol $H_3O^+_i$

$$HClO_4 + H_2O \longrightarrow H_3O^+ + ClO_4^-$$

mol $H_3O^+_f$: $[H_3O^+]_f$ = invlog (−3.200) = 6.30957×10^{-4} M

mol $H_3O^+_f$ = $MV = (6.30957 \times 10^{-4} M)(0.5000L)$

$= 3.1548 \times 10^{-4}$ mol $H_3O^+_f$

$$NaOH \longrightarrow Na^+ + OH^-$$

mol NaOH added = mol OH^- added = mol H_3O^+ consumed = mol $H_3O^+_i$ − mol $H_3O^+_f$

= 0.0500 mol − 0.00031548 mol = 0.049685 mol NaOH added

$$\frac{0.049685 \text{ mol NaOH} \mid 40.0g \text{ NaOH}}{\mid 1 \text{ mol NaOH}} = \boxed{1.99 \text{ g NaOH}}$$

4. How many moles of HCl must be added to 40.0 mL of 0.180 M $Ca(OH)_2$ to produce a solution having a pH of 7.00? (Assume that there is NO change in volume when the HCl is added).

*some trivial, but useful, information: most pure acids are gases (HCl included); pure sulfuric acid is a liquid. Acids become aqueous when they are mixed into water. Thus, there is no change in volume in #4 because the HCl must have been added in gaseous form.

$$2HCl + Ca(OH)_2 \longrightarrow CaCl_2 + 2H_2O$$

$$Ca(OH)_2 \longrightarrow Ca^{2+} + 2OH^- \qquad HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$

* solubility ↑ in presence of strong acid

$$\text{mol } Ca(OH)_{2\,i} = MV = (0.180\text{ M})(0.0400\text{L}) = 0.00720 \text{ mol}$$

$$\frac{0.00720 \text{ mol } Ca(OH)_2 \;\Big|\; 2 \text{ mol } OH^-}{\;\Big|\; 1 \text{ mol } Ca(OH)_2} = 0.0144 \text{ mol } OH^-_i$$

pH 7.00 means those existing 0.0144 mol OH^- get neutralized.

So, mol H_3O^+ added = 0.0144 mol

$$\text{mol HCl added} = \boxed{0.014 \text{ mol}}$$

See pH w/ 2 sigfigs

Assignment 16: Hebden p. 143 # 58-68 (Change question 60 to 400.0 mL of HCl – new answer: pH of 2.197)

- QUIZ 4 -

XIII) Titrations

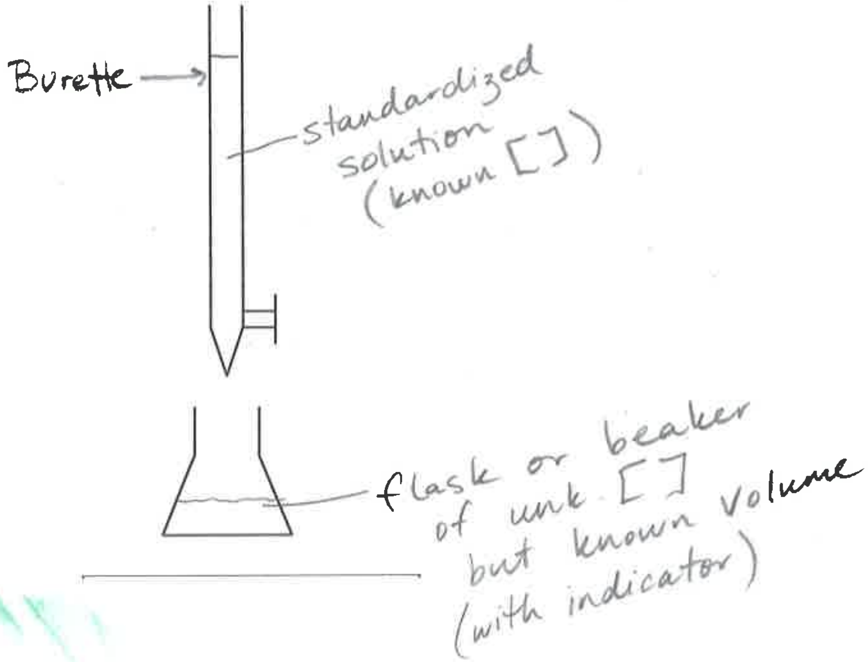
Scenario: You are a public school teacher and you enter the chemical room looking for some HCl of a particular molarity. You see a container marked HCl but the concentration has been rubbed off the bottle. Since money is tight, you want to avoid dumping the solution, but in order to use the acid productively, you'll need to know the concentration. A TITRATION can be performed in order to determine the unknown concentration.

What is required?

- A measured volume of a standardized solution (a reactant of known molarity).
- A small, but known volume of the unknown molarity chemical (in our case for this scenario, HCl).
- An acid/base **indicator**.

*if the unknown molarity solution is an acid (like our scenario), then the standardized solution will be a base; if the unknown molarity solution is a base, then the standardized solution will be an acid.

The SET-UP:



Suppose the flask contains the HCl of unknown concentration and the burette contains a standardized base. At some point during the titration, the moles of OH^- added from the burette will equal the moles of H_3O^+ in the flask. This is called the EQUIVALENCE POINT (aka the STOICHIOMETRIC POINT).

Equivalence Point: mol H_3O^+ = mol OH^-

Strong Acid vs. Strong Base Titration → pH at equiv. pt. is 7.

An INDICATOR is used to help visually determine when the equivalence point has been reached (due to a colour change). The volume of standardized base is determined using the gradations on the burette, and is used to calculate the concentration of the acid.

A 10.00mL sample of HCl of unknown concentration is titrated using 23.62mL of 0.100M NaOH (the standardized solution). Determine [HCl].

$$HCl + NaOH \rightarrow NaCl + H_2O$$

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$

$$NaOH \longrightarrow Na^+ + OH^-$$

mol NaOH added = mol OH^- added = $MV = (0.100M)(0.02362L)$

$= 0.0023\underline{6}2$ mol OH^-

$= 0.0023\underline{6}2$ mol H_3O^+ in flask = $0.0023\underline{6}2$ mol HCl
(def'n of EQUIV. PT.)

$$[HCl] = \frac{mol}{V_i} = \frac{0.0023\underline{6}2\ mol}{0.0100\underline{0}\ L} = \boxed{0.236\ M}$$

initial volume in flask

Primary Standards (pp. 164-165)

Pure and dry acids or bases are very uncommon as the majority of acids and bases (such as NaOH) absorb water vapour very easily; they are **hygroscopic** (ie. they become hydrates). In order to prepare a standardized solution of, say, NaOH, NaOH would have to be weighed on a scale. However, an unknown percentage of the mass would be due to the absorption of water, and therefore calculating an accurate molarity of the resulting solution would not be possible by simple quantitative methods. A primary standard acid would be required to standardize the standardized solution (ie. 'standardize the standard').

Acids and bases that are non-hygroscopic are known as __PRIMARY__ __STANDARDS__. An accurate molarity (concentration) of primary standard solutions can be found by direct calculation, since none of their mass can be attributed in any way to water vapour acquisition.

Example of a Primary Standard Base: sodium carbonate (Na_2CO_3) – solid.

Examples of Primary Standard Acids: potassium hydrogen phthalate ($C_8H_5KO_4$) – solid, and oxalic acid ($H_2C_2O_4$) – solid.

Once a primary standard of known concentration is prepared, it can be used to **standardize** any other acid or base solution. For example, oxalic acid is used to standardize NaOH through titration. Then, that same NaOH, whose concentration is now accurately known, can be used to titrate our unknown concentration of HCl. Likewise, if we have an unknown concentration of base in our lab, we can use sodium carbonate as a primary standard to standardize a hygroscopic acid like HBr, so that we may use the HBr as a standardized solution to titrate our unknown base.

Why wouldn't a chemist simply use primary standards as standardized solutions and, in the process, save time and energy?

Primary standards are much more expensive!

Titration Calculations

Remember: A STRONG base will fully neutralize (dissociate) a weak and/or polyprotic acid and vice versa.

37.86mL of 0.250M NaOH was required to neutralize a 20.0mL sample of HF. Calculate the [HF]. $HF + NaOH \longrightarrow NaF + H_2O$

$HF + H_2O \longrightarrow H_3O^+ + F^-$ $\quad NaOH \longrightarrow Na^+ + OH^-$

full dissoc. w/ str. base!

mol NaOH added = mol OH^- added = $MV = (0.250M)(0.03786\,L) = 0.0094\underline{6}5$ mol

= $0.0094\underline{6}5$ mol H_3O^+ in flask = $0.0094\underline{6}5$ mol HF

$$[HF] = \frac{mol}{V_i} = \frac{0.0094\underline{6}5\ mol}{0.0200\ L} = \boxed{0.473\ M}$$

A 15.0mL sample of unknown [KOH] was titrated using 18.56mL of 0.350M HNO_3. Find [KOH]. $HNO_3 + KOH \longrightarrow KNO_3 + H_2O$

$HNO_3 + H_2O \longrightarrow H_3O^+ + NO_3^-$ $\quad KOH \longrightarrow K^+ + OH^-$

mol HNO_3 added = mol H_3O^+ added = mol OH^- in flask

= mol KOH = $MV = (0.350M)(0.01856\,L) = 0.0064\underline{9}6$ mol

$$[KOH] = \frac{mol}{V_i} = \frac{0.0064\underline{9}6\ mol}{0.0150\ L} = \boxed{0.433\ M}$$

50.0mL of 0.100M $Sr(OH)_2$ was required to neutralize a 30.0mL sample of HBr. Determine the [HBr].

$2HBr + Sr(OH)_2 \longrightarrow SrBr_2 + 2H_2O$

$HBr + H_2O \longrightarrow H_3O^+ + Br^-$ $\quad Sr(OH)_2 \longrightarrow Sr^{2+} + 2OH^-$

mol $Sr(OH)_2$ added = $MV = (0.100M)(0.0500L) = 0.00500$ mol $Sr(OH)_2$

$$\frac{0.00500\ mol\ Sr(OH_2)}{} \left| \frac{2\ mol\ OH^-}{1\ mol\ Sr(OH)_2} \right. = 0.010\underline{0}\ mol\ OH^-\ added = 0.010\underline{0}\ mol\ H_3O^+\ in\ flask$$

= $0.010\underline{0}$ mol HBr

$$[HBr] = \frac{mol}{V_i} = \frac{0.010\underline{0}\ mol}{0.0300\ L} = \boxed{0.333M}$$

* talk about # 103 p.158 (Hebden)

Assignment 17: Titration Exercises

1. Find the concentration of an HCl solution if 25.00mL is titrated with 28.46mL of a 0.105M standardized solution of NaOH.

$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$ $\quad$ $NaOH \longrightarrow Na^+ + OH^-$

mol NaOH added = mol OH^- added = mol H_3O^+ in flask = mol HCl

$= MV = (0.105M)(0.02846L) = 0.0029\underline{8}83$ mol HCl

$$[HCl] = \frac{mol}{V_i} = \frac{0.0029883\ mol}{0.02500\ L} = \boxed{0.120M}$$

2. You titrated a 30.0mL solution of HNO_3 with 23.75mL of a 0.25M standardized solution of KOH. What is the $[HNO_3]$?

$HNO_3 + H_2O \longrightarrow H_3O^+ + NO_3^-$ $\quad$ $KOH \longrightarrow K^+ + OH^-$

mol KOH added = mol OH^- added = mol H_3O^+ in flask = mol HNO_3

$= MV = (0.25M)(0.02375L) = 0.005\underline{9}375$ mol HNO_3

$$[HNO_3] = \frac{mol}{V_i} = \frac{0.0059375\ mol}{0.0300L} = \boxed{0.20M}$$

3. A 35.00mL unknown solution of LiOH is titrated with 17.67mL of 0.200M HI. What is the [LiOH]?

$HI + H_2O \longrightarrow H_3O^+ + I^-$ $\quad$ $LiOH \longrightarrow Li^+ + OH^-$

mol HI added = mol H_3O^+ added = mol OH^- in flask = mol LiOH

$= MV = (0.200M)(0.01767L) = 0.0035\underline{3}4$ mol LiOH

$$[LiOH] = \frac{mol}{V_i} = \frac{0.003534\ mol}{0.03500\ L} = \boxed{0.101\ M}$$

4. A 24.00mL sample of H_2SO_4 is titrated with 32.43mL of 0.150M NaOH solution. Find $[H_2SO_4]$.

$H_2SO_4 + H_2O \longrightarrow 2H_3O^+ + SO_4^{2-}$ $\quad$ $NaOH \longrightarrow Na^+ + OH^-$

* in presence of str. base!

mol NaOH added = mol OH^- added = mol H_3O^+ in flask = MV

$= (0.150M)(0.03243L) = 0.0048\underline{6}45\ mol\ H_3O^+ \left| \dfrac{1\ mol\ H_2SO_4}{2\ mol\ H_3O^+} \right. = 0.0024\underline{3}225\ mol\ H_2SO_4$

$$[H_2SO_4] = \frac{mol}{V_i} = \frac{0.00243225\ mol}{0.02400L} = \boxed{0.101M}$$

5. A 40.00mL sample of $Ca(OH)_2$ is titrated with 16.55mL of 0.100M HCl. Find $[Ca(OH)_2]$.

$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$ $\quad$ $Ca(OH)_2 \longrightarrow Ca^{2+} + 2OH^-$

in presence of str. acid!

mol HCl added = mol H_3O^+ added = mol OH^- in flask = MV

$$= (0.100\,M)(0.01655\,L) = \frac{0.001655 \text{ mol } OH^-}{} \left| \frac{1 \text{ mol } Ca(OH)_2}{2 \text{ mol } OH^-} \right. = 0.0008275 \text{ mol } Ca(OH)_2$$

$$[Ca(OH)_2] = \frac{\text{mol}}{V_i} = \frac{0.0008275 \text{ mol}}{0.04000\,L} = \boxed{0.0207\,M}$$

*6. A 20.00mL sample of H_3PO_4 is titrated with 25.76 mL of a 0.100M $Sr(OH)_2$ solution. Find $[H_3PO_4]$.

$H_3PO_4 + H_2O \longrightarrow 3H_3O^+ + PO_4^{3-}$ $\quad$ $Sr(OH)_2 \longrightarrow Sr^{2+} + 2OH^-$

* in presence of str. base!

mol $Sr(OH)_2$ added = $MV = (0.100\,M)(0.02576\,L) = 0.002576$ mol

$$\frac{0.002576 \text{ mol } Sr(OH)_2}{} \left| \frac{2 \text{ mol } OH^-}{1 \text{ mol } Sr(OH)_2} \right. = 0.005152 \text{ mol } OH^- \text{ added}$$

$$= \frac{0.005152 \text{ mol } H_3O^+ \text{ in flask}}{} \left| \frac{1 \text{ mol } H_3PO_4}{3 \text{ mol } H_3O^+} \right. = 0.0017173 \text{ mol } H_3PO_4$$

$$[H_3PO_4] = \frac{\text{mol}}{V_i} = \frac{0.0017173 \text{ mol}}{0.02000\,L} = \boxed{0.0859\,M}$$

Calculating Volumes

What volume of 0.0350M $Ba(OH)_2$ will be required to neutralize 50.0mL of 0.0275M HCl?

$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$ $Ba(OH)_2 \longrightarrow Ba^{2+} + 2OH^-$

* in presence of str. acid!

mol HCl in flask = mol H_3O^+ in flask = mol OH^- added

$$= MV = (0.0275M)(0.0500L) = 0.0013\underline{7}5 \text{ mol } OH^- \times \frac{1 \text{ mol } Ba(OH)_2}{2 \text{ mol } OH^-}$$

$$= 0.00068\underline{7}5 \text{ mol } Ba(OH)_2$$

$$V_i = \frac{mol}{M} = \frac{0.0006875 \text{ mol}}{0.0350 M} = 0.0196 \text{ L} = \boxed{19.6 \text{ mL}}$$

Determining Percent Purity

A 0.74g sample of impure $NaCH_3COO$ is diluted in a volume of 25.0mL. The solution is titrated using 30.0mL of 0.100M HCl. Calculate the % purity of the $NaCH_3COO$. $NaCH_3COO \longrightarrow Na^+ + CH_3COO^-$

weak base!

$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$

$CH_3COO^- + H_2O \longrightarrow OH^- + CH_3COOH$

* in presence of str. acid!

mol HCl added = mol H_3O^+ added = mol OH^- in flask = mol CH_3COO^- in flask

= mol $NaCH_3COO$ (pure) in flask = $MV = (0.100M)(0.0300L)$

$= 0.0030\underline{0}$ mol pure $NaCH_3COO$

$$0.00300 \text{ mol } NaCH_3COO \times \frac{82.0 \text{ g } NaCH_3COO}{1 \text{ mol } NaCH_3COO} = 0.246 \text{ g pure } NaCH_3COO$$

$$\% \text{ PURITY} = \frac{\text{pure mass}}{\text{impure mass}} = \frac{0.246 \text{ g}}{0.74 \text{ g}} = 0.33 = \boxed{33\%}$$

Molar Mass Determination

A 0.49g sample of unknown monoprotic acid HA is diluted to 40.0mL. The solution is titrated using 12.0mL of 0.100M NaOH. Calculate the molar mass of the acid.

$HA + H_2O \longrightarrow H_3O^+ + A^-$ $NaOH \longrightarrow Na^+ + OH^-$

* in presence of str. base!

mol NaOH added = mol OH^- added = mol H_3O^+ in flask = mol HA

$= MV = (0.100M)(0.0120 L) = 0.00120$ mol HA

$\Rightarrow$ 0.00120 mol HA has a mass of 0.49 g

$$\text{Molar mass} = \frac{\text{mass}}{\text{mol}} = \frac{0.49\,g}{0.0012\underline{0}\,\text{mol}} = 408.3\ g/\text{mol}$$

$$\boxed{= 410\ g/\text{mol}}$$

Chloride Ion (Cl^-) Titrations – Sol'n Chem. -- Read pp. 99-100 as a class. Main point – Equivalence point is reached when moles Ag^+ added = moles Cl^- in flask. Like acid/base titrations, this is a one-to-one ratio, making the math easier than if the ratio was not one-to-one.

eg1: In order to find the [Cl^-] in a sea water sample, a 25.0 mL sample was titrated with a 0.500M $AgNO_3$ solution, using sodium chromate as an indicator. At the equivalence point, 26.8 mL of $AgNO_3$ solution had been added. What was the [Cl^-] in the sea water?

$AgNO_3 \longrightarrow Ag^+ + NO_3^-$ def'n of equiv. pt.

mol $AgNO_3$ added = mol Ag^+ added = mol Cl^- in flask

$= MV = (0.500\,M)(0.0268\,L) = 0.013\underline{4}$ mol Cl^-

$$[Cl^-] = \frac{\text{mol}}{V_i} = \frac{0.013\underline{4}\ \text{mol}}{0.0250\,L} = \boxed{0.536\ M}$$

eg2: What volume of 0.125M silver nitrate will be required to titrate 50.0 mL of 0.0550 M Cl^- solution, using a sodium chromate indicator?

$Ag(NO_3) \longrightarrow Ag^+ + NO_3^-$

mol Cl^- in flask = mol Ag^+ added = mol $AgNO_3$ added

$= MV = (0.0550\ M)(0.0500\ L) = 0.0027\underline{5}$ mol $AgNO_3$

$$V_i = \frac{mol}{M} = \frac{0.00275\ mol}{0.125\ M} = 0.0220\ L = \boxed{22.0\ mL}$$

eg3. A 5.29g sample of impure NaCl was dissolved and diluted to a total volume of 250.0 mL. If 25.0 mL of the NaCl solution required 28.5 mL of 0.300M silver nitrate solution to reach the equivalence point, using chromate indicator, what was the percentage purity of the original sodium chloride sample?

$NaCl \longrightarrow Na^+ + Cl^-$

$AgNO_3 \longrightarrow Ag^+ + NO_3^-$

mol $AgNO_3$ added = mol Ag^+ added = mol Cl^- (pure) in flask

= mol NaCl (pure) = $MV = (0.300\ M)(0.0285\ L) = 0.0085\underline{5}$ mol NaCl (pure)

$$\frac{0.0085\underline{5}\ mol\ NaCl \mid 58.5\ g\ NaCl}{\mid 1\ mol\ NaCl} = 0.50\underline{0}175\ g\ pure\ NaCl$$

25.0 mL is $\frac{1}{10}$ of 250.0 mL, so $\frac{5.29\ g}{10} = 0.529\ g$ impure NaCl

$$\%\ PURITY = \frac{pure\ mass}{impure\ mass} = \frac{0.50\underline{0}195\ g}{0.529\ g} = \boxed{94.6\%}$$

Assignment 18: Hebden p. 158 #94-97, 102-103, 105, 106; p. 165 #121-122. Also read pp. 99-101; do #70-72, 74-75 (Cl^- titrations)

- QUIZ 5 -