## CHEMISTRY LEVEL 4C <br> (CHM415115)

## ACID - BASE EQUILIBRIUM

## THEORY SUMMARY

\&

## REVISION QUESTIONS

(CRITERIA 6 \& 8)

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## CHEMISTRY (LEVEL 4C) ACID ~ BASE EQUILIBRIUM

(CRITERIA 6 \& 8)

## INTRODUCTORY THEORY SUMMARY:

(FROM YEAR 11)

1. LOWRY-BRÖNSTED ACID.

This is a substance that can donate protons i.e. release hydrogen ions $\left(\mathrm{H}^{+}{ }_{(\mathrm{aq})}\right)$
e.g. $\mathrm{HCl}_{(\text {aqq })}, \mathrm{H}_{2} \mathrm{SO}_{4(\mathrm{aq})}, \mathrm{HNO}_{3(\mathrm{aq})} \ldots \ldots . . . . .$.

## 2. LOWRY-BRÖNSTED BASE.

This is a substance that can accept protons i.e. reacts with hydrogen ions $\left(\mathrm{H}^{+}{ }_{(a q)}\right)$
e.g. $\mathrm{NH}_{3(\mathrm{aq})}, \mathrm{NaOH}_{\text {(aq) }}$
3. HYDRONIUM IONS. $\left(\mathrm{H}_{3} \mathrm{O}^{+}{ }_{(\mathrm{aq})}\right)$

A hydronium ion can be thought of as equivalent to a hydrogen ion $\left(\mathrm{H}^{+}{ }_{(\mathrm{aq})}\right)$ in aqueous solution. i.e. $\quad \mathrm{H}^{+}{ }_{(\mathrm{aq})}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})} \quad \rightarrow \quad \mathrm{H}_{3} \mathrm{O}^{+}{ }_{(\mathrm{aq})}$
4. "WEAK" ACIDS \& BASES

These are acids or bases that don't dissociate (don't break up) fully into ions.

$$
\begin{array}{r}
\text { e.g. WEAK ACIDS }=\mathrm{CH}_{3} \mathrm{COOH}_{(\mathrm{aq})}, \mathrm{HNO}_{2(\mathrm{aq}),} \mathrm{H}_{2} \mathrm{CO}_{3(\mathrm{aq})} \ldots \ldots . . . . . . \\
\text { i.e. } \mathrm{H}_{2} \mathrm{CO}_{3(\mathrm{aq})} \rightleftharpoons \mathrm{H}_{(\mathrm{aq})}^{+}+\mathrm{HCO}_{3}^{-} \text {(aq) }
\end{array}
$$

e.g. WEAK BASES $=\mathrm{NH}_{4} \mathrm{OH}_{(\mathrm{aq})}$, ...........

$$
\text { i.e. } \mathrm{NH}_{4} \mathrm{OH}_{(\mathrm{aq})} \rightleftharpoons \mathrm{NH}_{4}^{+}{ }_{(\mathrm{aq})}+\mathrm{OH}_{(\mathrm{aq})}^{-}
$$

## 5. "STRONG" ACIDS \& BASES

These are acids or bases that dissociate (break up) fully into ions; i.e. $100 \%$ ionised

$$
\begin{aligned}
& \text { e.g. STRONG ACIDS }=\mathrm{HCl}_{(\mathrm{aq})}, \mathrm{H}_{2} \mathrm{SO}_{4(\mathrm{aq})}, \mathrm{HNO}_{3(\mathrm{aq})} \ldots \ldots \ldots \ldots . . \\
& \text { i.e. } \mathrm{HNO}_{3(\mathrm{aq})} \rightarrow \mathrm{H}_{(\mathrm{aq})}^{+}+\mathrm{NO}_{3}^{-}{ }_{(\mathrm{aq})} \\
& \text { e.g. } \text { STRONG BASES }^{+}=\mathrm{NaOH}_{(\mathrm{aq}),} \mathrm{KOH}_{(\mathrm{aq}),} \mathrm{Ca}(\mathrm{OH})_{2(\mathrm{aq}),}, \ldots \ldots \ldots . . \\
& \text { i.e. } \mathrm{NaOH}_{(\mathrm{aq})} \rightarrow \mathrm{Na}^{+}{ }_{(\mathrm{aq})}+\mathrm{OH}_{(\text {(aq })}^{-}
\end{aligned}
$$

## 6. "CONCENTRATED" \& "DILUTE" SOLUTIONS

These are terms used to indicate the relative molarity of solutions and has nothing to do with "strength" at all.
High molarity solutions are referred to as 'concentrated' solutions whereas low molarity solutions are described as 'dilute'.
e.g. $10 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{HCl}_{(\mathrm{aq})}$ is referred to as a concentrated hydrochloric acid solution.
$0.10 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{NaOH}_{(\mathrm{aq})}$ is referred to as a dilute sodium hydroxide solution.

## 7. MONOPROTIC ACID.

This is an acid capable of donating only one hydrogen ion $\left(\mathrm{H}^{+}{ }_{(a q)}\right)$ per molecule;
e.g. $\mathrm{HCl}_{(\mathrm{aq})}, \mathrm{HNO}_{3(\mathrm{aq})} \ldots . .$.

$$
\mathrm{HCl}_{(\mathrm{aq})} \rightleftharpoons \mathrm{H}_{(\mathrm{aq})}^{+}+\mathrm{Cl}_{(\mathrm{aq})}^{-}
$$

## 8. DIPROTIC ACID.

This is an acid capable of donating two hydrogen ions $\left(\mathrm{H}^{+}{ }_{(\mathrm{aq})}\right)$ per molecule;
e.g. $\mathrm{H}_{2} \mathrm{SO}_{4 \text { (aq) }} \mathrm{H}_{2} \mathrm{CO}_{3(\mathrm{aq}) \ldots \ldots .}$

NOTE The ionization for a diprotic acid occurs via two steps; e.g.

$$
\begin{aligned}
& \mathrm{H}_{2} \mathrm{CO}_{3(\mathrm{aq})} \rightleftharpoons \mathrm{H}_{(\mathrm{aq})}^{+} \quad+\quad \mathrm{HCO}_{3}^{-}(\mathrm{aq}) \\
& \mathrm{HCO}_{3}^{-}{ }_{(\mathrm{aq})} \rightleftharpoons \mathrm{H}_{(\mathrm{aq})}^{+} \quad+\quad \mathrm{CO}_{3}^{2-}{ }_{(\mathrm{aq})}
\end{aligned}
$$

## 9. TRIPROTIC ACID.

This is an acid capable of donating three hydrogen ions $\left(\mathrm{H}^{+}{ }_{(\mathrm{aq})}\right)$ per molecule; e.g. $\mathrm{H}_{3} \mathrm{PO}_{4(\mathrm{aq})}$..........
nOTE The ionization for a triprotic acid occurs via three steps; e.g.

$$
\begin{aligned}
& \mathrm{H}_{3} \mathrm{PO}_{4(\text { aq })} \rightleftharpoons \mathrm{H}_{(\mathrm{aq})}^{+}+\mathrm{H}_{2} \mathrm{PO}_{4}^{-}{ }_{(\mathrm{aq})} \\
& \mathrm{H}_{2} \mathrm{PO}_{4}^{-}{ }_{\text {(aq) }} \rightleftharpoons \mathrm{H}_{\text {(aq) }}^{+}+\mathrm{HPO}_{4}^{{ }^{2-}}{ }_{\text {(aq) }} \\
& \mathrm{HPO}_{4}{ }^{2-}{ }_{(\mathrm{aq})} \rightleftharpoons \mathrm{H}^{+}{ }_{(\mathrm{aq})}+\mathrm{PO}_{4}{ }^{3-}{ }_{(\mathrm{aq})}
\end{aligned}
$$

## 10. AMPHIPROTIC

This is a substance that is capable of being an acid in some circumstances and a base in others; e.g. $\mathrm{HSO}_{4}^{-}$(aq)

```
ACTING AS AN ACID: }\quad\mp@subsup{\textrm{HSO}}{4}{-}\mp@subsup{}{(aq)}{}->\mp@subsup{\textrm{H}}{(\mathrm{ (aq) }}{+}+\quad\mp@subsup{\textrm{SO}}{4}{2-}\mp@subsup{}{(aq)}{
ACTING AS A BASE: }\quad\mp@subsup{\textrm{HSO}}{4}{-}\mp@subsup{}{(\textrm{aq})}{}+\quad+\mp@subsup{\textrm{H}}{(\textrm{aq})}{+}->\mp@subsup{\textrm{H}}{2}{}\mp@subsup{\textrm{SO}}{4(aq)}{(a)
```


## 11. CONJUGATE BASE:

This is the species formed after the acid has donated the hydrogen ion $\left(\mathrm{H}^{+}{ }_{(\mathrm{aq})}\right)$. e.g. the conjugate base of nitric acid is the nitrate ion;

$$
\underset{\mathrm{ACID}}{\mathrm{HNO}_{3(\mathrm{aq})}} \rightleftharpoons \mathrm{H}_{(\mathrm{aq})}^{+} \stackrel{+}{\text { CONJUGATE BASE }}
$$

## 12. ALKALIS:

Aqueous solutions of bases are often referred to as ALKALIS and the solution described as ALKALINE.
e.g. $\mathrm{CaO}_{(\mathrm{s})}$ is a BASE but when it dissolves in water it forms an ALKALINE solution of $\mathrm{Ca}(\mathrm{OH})_{2(a q)}$. The terms 'alkali' and 'base' have very similar meanings.

## 13. THE pH SCALE

A scale based on powers of 10 used for measuring acidity or alkalinity.The lower the pH , the greater the solution's acidity. e.g. a pH of 3 means a $\mathbf{1 0}$ times more acidic solution than one with a pH of 4 .
A pH of 7.0 corresponds to a neutral solution at $25^{\circ} \mathrm{C}$. The scale extends from highly acidic solutions with a pH of approximately -1 through to highly alkaline solutions with a pH of around 15.
Acid solutions have a $\mathrm{pH}<7$ and basic(alkaline) solutions have a $\mathrm{pH}>7$

```
pH
    \leftarrowINCREASINGLY ACIDIC SOLNS. INCREASINGLY BASIC SOLNS. }
```


## 14. SOME COMMON REACTIONS OF ACIDS AND BASES:

You need to be familiar with about 6 types of reactions that are frequently encountered with acids and bases. These are:
(i) Reactive metal plus acid gives a salt plus hydrogen gas.

$$
\text { e.g. } \mathrm{Zn}_{(\mathrm{s})}+2 \mathrm{HCl}_{(\mathrm{aq})} \rightarrow \mathrm{ZnCl}_{2(\mathrm{aq})}+\mathrm{H}_{2(\mathrm{~g})}
$$

(ii) Acid plus base gives salt plus water ("neutralization").

$$
\text { e.g. } \mathrm{H}_{2} \mathrm{SO}_{4(\mathrm{aq})}+2 \mathrm{NaOH}_{(\mathrm{aq})} \rightarrow \mathrm{Na}_{2} \mathrm{SO}_{4(\mathrm{aq})}+2 \mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})}
$$

(iii) Acid plus carbonate gives salt plus water plus carbon dioxide gas.

$$
\text { e.g. } 2 \mathrm{HCl}_{(\mathrm{aq})}+\mathrm{Na}_{2} \mathrm{CO}_{3(\mathrm{aq})} \rightarrow 2 \mathrm{NaCl}_{(\mathrm{aq})}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})}+\mathrm{CO}_{2(\mathrm{~g})}
$$

(iv) Acid plus hydrogen carbonate gives salt plus water plus carbon dioxide gas.

$$
\text { e.g. } \mathrm{HCl}_{(\mathrm{aq})}+\mathrm{NaHCO}_{3(\mathrm{aq})} \rightarrow \mathrm{NaCl}_{(\mathrm{aq})}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})}+\mathrm{CO}_{2(\mathrm{~g})}
$$

(v) Acid plus sulfite gives salt plus water plus sulfur dioxide gas.

$$
\text { e.g. } 2 \mathrm{HCl}_{(\mathrm{aq})}+\mathrm{Na}_{2} \mathrm{SO}_{3(\mathrm{aq})} \rightarrow 2 \mathrm{NaCl}_{(\mathrm{aq})}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})}+\mathrm{SO}_{2(\mathrm{~g})}
$$

(vi) Acid plus sulfide gives salt plus hydrogen sulfide gas.

$$
\text { e.g. } 2 \mathrm{HCl}_{(\mathrm{aq})}+\mathrm{Na}_{2} \mathrm{~S}_{(\mathrm{aq})} \rightarrow \quad 2 \mathrm{NaCl}_{(\mathrm{aq})}+\mathrm{H}_{2} \mathrm{~S}_{(\mathrm{g})}
$$

## ACID ~ BASE STRENGTH

Q1. Suppose that you are presented with two solutions, one being $0.10 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{HA}_{(\mathrm{aq})}$ and the other is $0.10 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{HB}_{(\mathrm{aq})}$. You are told that one is a strong acid and the other is a weak acid. How could you identify by standard laboratory tests which one is the strong acid?

## ANSWER:

Note that this question involves solutions of the SAME molarity.

| LABORATORY TEST | IDENTIFICATION OF THE STRONGER ACID |
| :--- | :--- |
| Use a pH meter | Solution with the lower pH is the stronger acid. |
| React with zinc metal | Faster reaction rate occurs with the stronger acid |
| Electrical conductivity | Better conductor has more ions, and is the stronger acid. |
| Universal indicator paper | Solution with the lower pH is the stronger acid. |

Q2. A student makes the statement that " because $\mathrm{HX}_{(\mathrm{aq})}$ is a weak acid, this means that $\mathrm{HX}_{(\mathrm{aq})}$ must then be a strong base".
Correct this statement and explain your reasoning.

## ANSWER:

Because HX is a weak acid, it means that a very small \% of $\mathrm{HX}_{(\mathrm{aq})}$ molecules actually break up ("ionize") into ions when $\mathrm{HX}_{(\text {(aa) }}$ is in aqueous solution.

$$
\text { i.e. } \mathrm{HX}_{(\mathrm{aq}} \longrightarrow \mathrm{H}_{(\mathrm{aq})}^{+}+\mathrm{X}_{(\mathrm{aq})}^{-}
$$

Because the forward reaction has only a limited tendency to occur, it means that there is a high tendency for the back reaction to occur.

$$
\text { i.e. } \quad \mathrm{H}_{(\mathrm{aq})}^{+}+\mathrm{X}_{(\mathrm{aq})}^{-} \Rightarrow \mathrm{HX}_{(\mathrm{aq})}
$$

This means that $\mathrm{X}^{-}{ }_{(\mathrm{aq})}$ is a strong acceptor of protons $\left(\mathrm{H}^{+}\right)$making $\mathrm{X}^{-}$a strong base. We call $\mathrm{X}^{-}$the conjugate base of the acid $\mathrm{HX}_{(\mathrm{aq})}$.
The student's statement above thus needs to be reworded to say:
"Because $\mathrm{HX}_{(\text {(aq) }}$ is a weak acid, then this means that the conjugate base, $\mathrm{X}^{-}{ }_{(\mathrm{aq})}$ must necessarily be a strong base".

Q3. Given the equilibrium system:

$$
\mathrm{HA}_{(\mathrm{aq})}+\mathrm{X}_{(\mathrm{aq})}^{-} \rightleftharpoons \mathrm{HX}_{(\mathrm{aq})}+\mathrm{A}_{(\mathrm{aq})}^{-} \text {has a } \mathrm{K}_{\mathrm{c}} \text { value of } 10^{-4} \text { at }
$$

SLC, identify:
(i) the two species that are acids.
(ii) the two species that are bases.
(iii) the stronger of the two acids.
(iv) the stronger of the two bases.
$\left(\mathrm{HA}_{(\mathrm{aq})} \& \mathrm{HX}_{(\mathrm{aq})}\right)$
$\left(\mathrm{X}_{(\text {aq) }}^{-} \& \mathrm{~A}_{(\text {aqq })}^{-}\right)$
$\left(\mathrm{HX}_{(\mathrm{aq})}\right)$
( $\left.\mathrm{A}^{-}{ }_{(\mathrm{aq})}\right)$

## ACID ~ BASE EQUILIBRIA THE DISSOCIATION OF WATER.

The principal focus of our acid $\sim$ base equilibrium studies this year will be with regard to AQUEOUS solutions of acids and bases. Hence, unless told otherwise, assume that all solutions discussed will be ones involving water as the solvent and that conditions are SLC (1 atm and $25^{\circ} \mathrm{C}$ ).

Electrical conductivity experiments reveal that pure water is a very poor conductor of electricity; we describe water as a "weak electrolyte".
However, the important issue is that water dOES ionize to a slight extent.
i.e.

$$
\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})} \rightleftharpoons \mathrm{H}_{(\mathrm{aq})}^{+}+\mathrm{OH}_{(\mathrm{aq})}^{-}
$$

The equilibrium constant expression for this system is given by:

$$
\mathrm{K}_{\mathrm{c}}=\frac{\left[\mathrm{H}^{+}{ }_{(\mathrm{aq})}\right]\left[\mathrm{OH}^{-}{ }_{(\mathrm{aq})}\right]}{\left[\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})}\right]}
$$

Because such a tiny proportion of water molecules do actually ionize, the amount of water that is not ionized (i.e. stays as $\mathrm{H}_{2} \mathrm{O}_{(\mathrm{I})}$ ) is effectively constant and thus we can rewrite (*) to give:

$$
\mathrm{K}_{\mathrm{c}} \times\left[\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})}\right]=\left[\mathrm{H}_{(\mathrm{aq})}^{+}\right]\left[\mathrm{OH}_{(\mathrm{aq})}^{-}\right]
$$

As both $\mathrm{K}_{\mathrm{c}}$ and $\left[\mathrm{H}_{2} \mathrm{O}_{(\mathrm{I})}\right]$ are taken as constant numbers, their product will also be a constant and we assign it the symbol $K_{w}$ which is called the "dissociation constant" for water.

$$
\mathrm{K}_{\mathrm{w}}=\left[\mathrm{H}_{(\mathrm{aq})}^{+}\right]\left[\mathrm{OH}_{(\mathrm{aq})}^{-}\right]
$$

At $25^{\circ} \mathrm{C}$ the value of $\mathrm{K}_{\mathrm{w}}$ turns out to be:

$$
\mathrm{K}_{\mathrm{w}}=1.00 \times 10^{-14}
$$

There are three situations we need to consider with regard to aqueous solutions at $25^{\circ} \mathrm{C}$.

1. $\left[\mathrm{H}_{(\mathrm{aq})}^{+}\right]>\left[\mathrm{OH}^{-}{ }_{(\mathrm{aq})}\right] \quad \rightarrow \quad$ THE SOLUTION IS ACIDIC
2. $\left[\mathrm{H}^{+}{ }_{(\mathrm{aq})}\right]<\left[\mathrm{OH}^{-}{ }_{(\mathrm{aq})}\right] \quad \rightarrow \quad$ THE SOLUTION IS BASIC (ALKALINE)
3. $\left[\mathrm{H}^{+}{ }_{(\mathrm{aq})}\right]=\left[\mathrm{OH}^{-}{ }_{(\mathrm{aq})}\right] \quad \rightarrow \quad$ THE SOLUTION IS NEUTRAL

In a neutral solution $\left[\mathrm{H}^{+}{ }_{(\mathrm{aq})}\right]=\left[\mathrm{OH}_{(\mathrm{aq})}\right]=1.00 \times 10^{-7} \mathrm{~mol} \mathrm{~L}{ }^{-1}$
In an acidic solution $\left[\mathrm{H}^{+}{ }_{(\mathrm{aq})}\right]>1.00 \times 10^{-7} \mathrm{~mol} \mathrm{~L}^{-1}$
In an alkaline solution $\left[\mathrm{OH}^{-}{ }_{(\mathrm{aq})}\right]>1.00 \times 10^{-7} \mathrm{~mol} \mathrm{~L}^{-1}$

## THE pH SCALE

The pH scale is a logarithmic scale to base 10 where the LOWER the pH the GREATER the acidity of the solution.
pH is defined as:

$$
\mathrm{pH}=-\log _{10}\left[\mathrm{H}_{(\mathrm{aq})}^{+}\right]
$$

The inverse function is:

$$
\left[\mathrm{H}_{(\mathrm{aq})}^{+}\right]=10^{-\mathrm{pH}}
$$

| pH | -1 | 1 | 3 | 5 | 7 | 9 | 11 | 13 | 15 |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\left[\mathrm{H}^{+}{ }_{(\mathrm{aq})}\right]$ <br> $\mathrm{mol} / \mathrm{L}$ | $10^{1}$ | $10^{-1}$ | $10^{-3}$ | $10^{-5}$ | $10^{-7}$ | $10^{-9}$ | $10^{-11}$ | $10^{-13}$ | $10^{-15}$ |
| $\left[\mathrm{OH}^{-}(\mathrm{aq})\right.$ <br> $\mathrm{mol} / \mathrm{L}$ | $10^{-15}$ | $10^{-13}$ | $10^{-11}$ | $10^{-9}$ | $10^{-7}$ | $10^{-5}$ | $10^{-3}$ | $10^{-1}$ | $10^{1}$ |

The table above shows the inter-relation between $\left[\mathrm{H}^{+}(\mathrm{aq})\right]$ and $\left[\mathrm{OH}^{-}\right.$(aq) $]$and we see that no matter what the solution is, whether it be acidic or basic, there are both species present and that their product is always $1.00 \times 10^{-14}$ at $25^{\circ} \mathrm{C}$.

Acidic solutions have $\mathrm{pH}<7$ and thus have high $\left[\mathrm{H}^{+}{ }_{(\mathrm{aq})}\right]$ and lower $\left[\mathrm{OH}^{-}{ }_{(\mathrm{aq})}\right]$.
Basic solutions have $\mathrm{pH}>7$ and thus have high $\left[\mathrm{OH}^{-}(\mathrm{aq})\right]$ and lower $\left[\mathrm{H}_{(\mathrm{aq})}\right]$.

## pH CALCULATIONS

## SAMPLE QUESTION 1.

What is the pH of neutral water at $25^{\circ} \mathrm{C}$ ?

$$
\text { ANS. } \quad \begin{aligned}
{\left[\mathrm{H}_{(\mathrm{aq})}^{+}\right] } & =\left[\mathrm{OH}^{-}(\mathrm{aq})\right]=\mathrm{X} \mathrm{~mol} / \mathrm{L} \\
\text { Thus } \mathrm{X}^{2} & =1.00 \times 10^{-14} \\
\therefore \mathrm{X} & =1.00 \times 10^{-7} \mathrm{~mol} \mathrm{~L}^{-1} \\
\therefore \mathrm{pH} & =-\log \left(1.00 \times 10^{-7}\right) \\
& =7.00
\end{aligned}
$$

## SAMPLE QUESTION 2.

What is the pH of $0.0024 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{H}_{2} \mathrm{SO}_{4(\mathrm{aq})}$ assuming it is $100 \%$ ionised at $25^{\circ} \mathrm{C}$ ?
ANS. Sulfuric acid is diprotic: $\quad \mathrm{H}_{2} \mathrm{SO}_{4(\mathrm{aq})} \rightarrow 2 \mathrm{H}^{+}{ }_{(\mathrm{aq})}+\mathrm{SO}_{4}{ }^{2-}{ }_{(\mathrm{aq})}$

$$
\begin{aligned}
& {\left[\mathrm{H}^{+}(\text {aq) })\right]=2 \times 0.0024 \mathrm{~mol} \mathrm{~L}^{-1}} \\
& {\left[\mathrm{H}^{+}(\mathrm{aq})\right]=0.0048 \mathrm{~mol} \mathrm{~L}^{-1}} \\
& \therefore \mathrm{pH}=-\log (0.0048)=2.3
\end{aligned}
$$

## EXERCISES IN pH CALCULATIONS

Q4. What is the pH of a solution that has a hydrogen ion $\left[\mathrm{H}^{+}(\mathrm{aq})\right]$ concentration of:
(i) $0.0365 \mathrm{~mol} \mathrm{~L}^{-1}$ ?
(ii) $4.78 \times 10^{-4} \mathrm{~mol} \mathrm{~L}^{-1}$ ?
(iii) $3.09 \times 10^{-12} \mathrm{~mol} \mathrm{~L}^{-1}$ ?
(iv) $5.60 \mathrm{~mol} \mathrm{~L}^{-1}$ ?
(v) $6.00 \times 10^{-14} \mathrm{~mol} \mathrm{~L}^{-1}$ ?
(vi) $1.00 \times 10^{-7} \mathrm{~mol} \mathrm{~L}^{-1}$ ?
(vii) $0.0100 \mathrm{~mol} \mathrm{~L}^{-1}$ ?
(viii) $1.00 \mathrm{~mol} \mathrm{~L}^{-1}$ ?

Q5. For each of the following pH values, give the corresponding hydrogen ion $\left[\mathrm{H}^{+}{ }_{(\mathrm{aq})}\right]$ concentration?
(i) $\mathrm{pH}=3.00$
$\left(1.00 \times 10^{-3} \mathrm{~mol} \mathrm{~L}^{-1}\right)$
(ii) $\mathrm{pH}=12.0$
$\left(1.00 \times 10^{-12} \mathrm{~mol} \mathrm{~L}^{-1}\right)$
$\mathrm{pH}=4.62$
$\left(2.40 \times 10^{-5} \mathrm{~mol} \mathrm{~L}^{-1}\right)$
(iv) $\mathrm{pH}=6.87$
$\left(1.35 \times 10^{-7} \mathrm{~mol} \mathrm{~L}^{-1}\right)$
(v) $\mathrm{pH}=0.50$
$\left(0.32 \mathrm{~mol} \mathrm{~L}^{-1}\right)$
(vi) $\mathrm{pH}=14.8$
$\left(1.58 \times 10^{-15} \mathrm{~mol} \mathrm{~L}^{-1}\right)$
(iii)

Q6. For each of the following pH values, give the corresponding hydroxide ion $\left[\mathrm{OH}^{-}{ }_{(\mathrm{aq})}\right]$ concentration?
(i) $\mathrm{pH}=12.0$
$\left(1.00 \times 10^{-2} \mathrm{~mol} \mathrm{~L}^{-1}\right.$
(ii) $\mathrm{pH}=14.0$
$\left(1.00 \mathrm{~mol} \mathrm{~L}^{-1}\right)$
(iii) $\mathrm{pH}=11.7$
$\left(5.01 \times 10^{-3} \mathrm{~mol} \mathrm{~L}^{-1}\right)$
(iv) $\mathrm{pH}=9.87$
$\left(7.41 \times 10^{-5} \mathrm{~mol} \mathrm{~L}^{-1}\right)$

Q7. Consider a $0.00562 \mathrm{~mol} \mathrm{~L}^{-1}$ solution of $\mathrm{NaOH}_{(\mathrm{aq})}$, a strong base.
(a) What is the hydroxyl ion concentration $\left[\mathrm{OH}^{-}(\mathrm{aq})\right]$ ?
$\left(0.00562 \mathrm{~mol} \mathrm{~L}^{-1}\right)$
(b) What is the hydrogen ion concentration $\left.\left[\mathrm{H}^{+}{ }_{(\text {aq }}\right)\right]$ ?
$\left(1.78 \times 10^{-12} \mathrm{~mol} \mathrm{~L}^{-1}\right)$
(c) What is the pH of this $\mathrm{NaOH}_{(\mathrm{aq})}$ solution?

Q8. Consider a $0.0252 \mathrm{~mol} \mathrm{~L}^{-1}$ solution of $\mathrm{Ba}(\mathrm{OH})_{2(\mathrm{aq})}$, a strong base.
(a) What is the hydroxyl ion concentration $\left[\mathrm{OH}^{-}{ }_{(\mathrm{aq})}\right]$ ?
$\left(0.0504 \mathrm{~mol} \mathrm{~L}^{-1}\right)$
(b) What is the hydrogen ion concentration $\left[\mathrm{H}^{+}{ }_{(\mathrm{aq})}\right]$ ?
$\left(1.98 \times 10^{-13} \mathrm{~mol} \mathrm{~L}^{-1}\right)$
(c) What is the pH of this $\mathrm{Ba}(\mathrm{OH})_{2(\text { aq) }}$ solution?

Q9. Consider a $0.0600 \mathrm{~mol} \mathrm{~L}^{-1}$ solution of the weak acid $\mathrm{HNO}_{2(\mathrm{aq})}$ which is known to be only 21.0\% ionised.
(a) What is the hydrogen ion concentration $\left[\mathrm{H}^{+}{ }_{(\mathrm{aq})}\right]$ ? $\quad\left(0.0126 \mathrm{~mol} \mathrm{~L}^{-1}\right)$
(b) What is the pH of this $\mathrm{HNO}_{2(\mathrm{aq})}$ solution?

Q10. Consider a $0.000742 \mathrm{~mol} \mathrm{~L}^{-1}$ solution of the weak monoprotic acid $\mathrm{CH}_{3} \mathrm{COOH}_{(\text {aq })}$ which is only $15.3 \%$ ionized.
(a) What is the hydrogen ion concentration $\left[\mathrm{H}^{+}{ }_{(\mathrm{aq})}\right]$ ?
$\left(1.14 \times 10^{-4} \mathrm{~mol} \mathrm{~L}^{-1}\right)$
(b) What is the pH of this $\mathrm{CH}_{3} \mathrm{COOH}_{(\mathrm{aq})}$ solution?
3.94)

Q11. If a $0.00346 \mathrm{~mol} \mathrm{~L}^{-1}$ solution of the monoprotic acid $\mathrm{HX}_{(\mathrm{aq})}$ has a pH of 3.78 , what is the $\%$ dissociation of this acid? Is it strong or weak?
( $4.80 \%$ ionized $=$ weak $)$

Q12. If a $0.0846 \mathrm{~mol} \mathrm{~L}^{-1}$ solution of the base $\mathrm{NH}_{4} \mathrm{OH}_{(\mathrm{aq})}$ has a pH of 11.4 , what is the $\%$ dissociation of this base? Is it strong or weak? (2.97\% ionized $=$ weak $)$

Q13. What is the molarity of an aqueous solution of the monoprotic acid acetic acid $\left(\mathrm{HX}_{(\mathrm{aq})}\right)$ which is only $3.15 \%$ dissociated and gives a pH of 3.32 ?

$$
\left(0.0152 \mathrm{~mol} \mathrm{~L}^{-1}\right)
$$

Q14. A solution of the strong acid $\mathrm{HCl}_{(\mathrm{aq})}$ has a pH of 2.76 at $25^{\circ} \mathrm{C}$. A sample of this solution is diluted 10 times with pure distilled water. What is the pH of the new diluted solution of hydrochloric acid?

Q15. $\mathrm{Ba}(\mathrm{OH})_{2(\mathrm{~s})}$ is a strong base and you are required to prepare 150 mL of a solution that has a pH of 12.5
What mass of $\mathrm{Ba}(\mathrm{OH})_{2(\mathrm{~s})}$ needs to be dissolved in the 150 mL of solution?
$\left(\mathrm{M}\left(\mathrm{Ba}(\mathrm{OH})_{2}\right)=171 \mathrm{~g} \mathrm{~mol}^{-1}\right)$

Q16. If 50.0 mL of $0.0252 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{HCl}_{(\mathrm{aq})}$ is mixed with 150 mL of $0.00675 \mathrm{~mol} \mathrm{~L}^{-1}$ $\mathrm{H}_{2} \mathrm{SO}_{4(\mathrm{aq})}$ what is the pH of the resulting solution, assuming $100 \%$ dissociation of both acids?

Q17. Prove that at $25^{\circ} \mathrm{C}, \quad \mathrm{pH}+\mathrm{pOH}=14.00$ where $\mathrm{pOH}=-\log \left[\mathrm{OH}^{-}{ }_{(\mathrm{aq})}\right]$

Q18. What is the $\%$ dissociation of the acid $\mathrm{HX}_{(\text {aq })}$ given that a $0.200 \mathrm{~mol} \mathrm{~L}^{-1}$ solution of $\mathrm{HX}_{(\mathrm{aq})}$ has a pH of 2.10 ? Is this acid strong or is it a weak acid? Explain briefly.

ANS.

$$
\begin{aligned}
\mathrm{pH} & =2.10 \\
\therefore\left[\mathrm{H}_{(\mathrm{aq})}^{+}\right] & =7.94 \times 10^{-3} \mathrm{~mol} \mathrm{~L}^{-1}
\end{aligned}
$$

Thus \% dissociation $=\left\{\frac{\left(7.94 \times 10^{-3}\right)}{0.200} \times \frac{100}{1}\right\} \%$
$=3.97 \%$
This very low \% dissociation suggests that $\mathrm{HX}_{(a \mathrm{aq}}$ is very definitiely a WEAK acid.
*Q19. Consider the following two acidic solutions:

> | SOLUTION \#1 is a solution of acid $\mathrm{HA}_{(\mathrm{aq})}$ and has a pH of 4.0 |
| :--- |
| SOLUTION \#2 is a solution of acid $\mathrm{HB}_{(\mathrm{aq})}$ and has a pH of 1.0 |

Why is it NOT correct to say that on the basis of this information alone, acid HB is stronger than acid HA?

## ANSWER:

Solution \#1 could possibly be a $1.0 \times 10^{-4} \mathrm{~mol} \mathrm{~L}^{-1}$ solution of $\mathrm{HA}_{(\mathrm{aq})}$ which is $100 \%$ ionised and thus has $\left[\mathrm{H}_{(\mathrm{aq})}^{+}\right]=1.0 \times 10^{-4} \mathrm{~mol} \mathrm{~L}^{-1}$ giving it a pH of 4.0 and being $100 \%$ ionised it would be a strong acid.
Solution \#1 could also possibly be a $1.0 \mathrm{~mol} \mathrm{~L}^{-1}$ solution of $\mathrm{HA}_{(\mathrm{aq})}$ and it is only $0.010 \%$ ionised and thus has $\left[\mathrm{H}^{+}\right.$(aq) $]=1.0 \times 10^{-4} \mathrm{~mol} \mathrm{~L}^{-1}$ giving it a pH of 4.0
Being $0.010 \%$ ionised would make an extremely weak acid.
Alternatively:
Solution \#2 could be a $10 \mathrm{~mol} \mathrm{~L}^{-1}$ solution of $\mathrm{HB}_{(\mathrm{aq})}$ and it is only $1.0 \%$ ionised and thus has $\left[\mathrm{H}^{+}(\right.$aq) $\left.)\right]=1.0 \times 10^{-1} \mathrm{~mol} \mathrm{~L}^{-1}$ giving it a pH of 1.0
Solution \#2 could also be a $0.10 \mathrm{~mol} \mathrm{~L}^{-1}$ solution of $\mathrm{HB}_{(\text {(aq) }}$ which is $100 \%$ ionised and thus has $\left[\mathrm{H}^{+}(\mathrm{aq})\right]=1.0 \times 10^{-1} \mathrm{~mol} \mathrm{~L}^{-1}$ giving it a pH of 1.0

Thus, comparisons of acid strength need to be made on the basis of the pH values of solutions that have the SAME molarity!
Without having this information, a comparison of strength is not possible.

## ACID DISSOCIATION CONSTANTS $\left(K_{A}\right.$ ов $\left.K_{a}\right)$

In this section we will consider the equilibrium system associated with the dissociation of a monoprotic acid such as the general one represented by $\mathrm{HX}_{(\mathrm{aq})}$.

$$
\mathrm{HX}_{(\mathrm{aq})} \rightleftharpoons \mathrm{H}_{(\mathrm{aq})}^{+}+\mathrm{X}_{(\mathrm{aq})}^{-}
$$

The equilibrium constant for this and any other "acid dissociation" system is represented by the symbol $\mathrm{K}_{\mathrm{A}}$ and has the format:

$$
\mathrm{K}_{\mathrm{A}}=\frac{\left[\mathrm{H}_{(\mathrm{aq})}^{+}\right]\left[\mathrm{X}_{(\mathrm{aq})}^{-}\right]}{\left[\mathrm{HX}_{(\mathrm{aq})}\right]}
$$

## NOTES:

(i) The units for $\mathrm{K}_{\mathrm{A}}$ are in this case, $\mathrm{mol} \mathrm{L}^{-1}$ but in most cases, the units are omitted.
(ii) If HX is a very strong acid it will have almost totally dissociated into ions and this will mean that there are practically no molecules of $\mathrm{HX}_{(\mathrm{aq})}$ left in solution as all will have broken up into ions. Thus, $\left[\mathrm{HX}_{(\mathrm{aq})}\right]=$ approx zero; making $\mathrm{K}_{\mathrm{A}}=$ a very large number.

$$
\text { e.g. } \quad \operatorname{HBr}_{(\mathrm{aq})}=\text { very strong acid: } \quad \mathrm{K}_{\mathrm{A}}\left(\operatorname{HBr}_{(\mathrm{aq})}\right)=10^{9} \quad \text { (at SLC) }
$$

(iii) If HX is a very weak acid it will have hardly dissociated into any ions and this means that $\left[\mathrm{H}^{+}(\mathrm{aq})\right]$ and $\left[\mathrm{X}^{-}{ }_{(\mathrm{aq})}\right]=$ approx zero; making $\mathrm{K}_{\mathrm{A}}=$ approx. zero.

$$
\text { e.g. } \left.\quad \mathrm{HNO}_{2(\mathrm{aq})}=\text { very weak acid: } \quad \mathrm{K}_{\mathrm{A}}\left(\mathrm{HNO}_{2(\mathrm{aq})}\right)=5.1 \times 10^{-4} \quad \text { (at SLC }\right)
$$

Q20.
A $0.500 \mathrm{~mol} \mathrm{~L}^{-1}$ solution of the weak acid $\mathrm{HB}_{(\text {(aq) }}$ has a pH of 1.90 at $25^{\circ} \mathrm{C}$. What is $\mathrm{K}_{\mathrm{A}}$ for $\mathrm{HB}_{(\mathrm{aq})}$ at $25^{\circ} \mathrm{C}$ ?

$$
\mathrm{pH}=1.90 \quad \rightarrow \quad\left[\mathrm{H}_{(\mathrm{aq})}^{+}\right]=10^{-1.90}
$$

$$
=0.0126 \mathrm{~mol} \mathrm{~L}^{-1}
$$

Drawing up an "ICE" diagram:

| mole L $^{-1}$ | $\mathrm{HB}_{(\mathrm{aq})}$ | $\rightleftharpoons$ | $\mathrm{H}^{+}{ }_{(\mathrm{aq})}$ |
| :--- | :---: | :---: | :---: |
|  | + | $\mathrm{B}_{(\mathrm{aq})}^{-}$ |  |
| INITIAL | 0.500 | 0 | 0 |
| CHANGE | -0.0126 |  | +0.0126 |
| EQUILIBRIUM | 0.487 |  | 0.0126 |

Now, substituting the EQUILIBRIUM values into Ka gives:

$$
\begin{gathered}
\mathrm{K}_{\mathrm{A}}=\frac{\left[\mathrm{H}_{(\mathrm{aq})}^{+}\right]\left[\mathrm{B}_{(\mathrm{aq})}^{-}\right]}{\left[\mathrm{HB}_{(\mathrm{aq})}\right]}=\frac{(0.0126)(0.0126)}{0.487} \\
\text { i.e. } \quad \mathrm{K}_{\mathrm{A}}(\mathrm{HB})=3.25 \times 10^{-4}
\end{gathered}
$$

Q21. If a $0.100 \mathrm{~mol} \mathrm{~L}^{-1}$ solution of the monoprotic acid hydrocyanic acid $\mathrm{HCN}_{(\mathrm{aq})}$ has a pH of 5.08 at $25^{\circ} \mathrm{C}$, determine $\mathrm{K}_{\mathrm{A}}\left(\mathrm{HCN}_{(\mathrm{aq})}\right)$ at $25^{\circ} \mathrm{C}$.
( $6.92 \times 10^{-10}$ )
Q22. What is the pH of a $0.250 \mathrm{~mol} \mathrm{~L}^{-1}$ solution of the monoprotic acid acetic acid given that it has a $\mathrm{K}_{\mathrm{A}}\left(\mathrm{CH}_{3} \mathrm{COOH}_{(\mathrm{aq})}\right)=1.80 \times 10^{-5}$ (at SLC)

## ANSWER

| mole L $^{-1}$ | $\mathrm{CH}_{3} \mathrm{COOH}_{(\mathrm{aq})}$ | $\rightleftharpoons$ | $\mathrm{H}_{(\mathrm{aq})}$ |
| :--- | :---: | :---: | :---: |
| INITIAL | 0.250 | 0 | $\mathrm{CH}_{3} \mathrm{COO}^{-}{ }_{(\mathrm{aq})}$ |
| CHANGE | -x | +x | 0 |
| EQUILIBRIUM | $(0.250-\mathrm{x})$ | x | +x |

(let x mole $\mathrm{L}^{-1}$ of the original acid dissociate)
Now susbtitute the EQUILIBRIUM concentrations into the expression for $\mathrm{K}_{\mathrm{A}}$
i.e.

$$
\mathrm{K}_{\mathrm{A}}=\frac{\left[\mathrm{H}_{(\mathrm{qq})}^{+}\right]\left[\mathrm{CH}_{3} \mathrm{COO}_{(\mathrm{aq})}^{-}\right]}{\left[\mathrm{CH}_{3} \mathrm{COOH}_{(\mathrm{aqq}}\right]}=\frac{(\mathrm{x})(\mathrm{x})}{(0.250-\mathrm{x})}=1.80 \times 10^{-5}
$$

Because this is a weak acid as shown by its $\mathrm{K}_{\mathrm{A}}$ value being $1.80 \times 10^{-5}$ we can regard the amount of dissociation ( x ) as being so small that $(0.250-\mathrm{x}$ ) will be very nearly 0.250 . Thus the $\mathrm{K}_{\mathrm{A}}$ equation now becomes: $\mathrm{x}^{2} / 0.250=1.80 \times 10^{-5}$

$$
\begin{aligned}
& \mathrm{x}^{2}=\left(1.80 \times 10^{-5}\right)(0.250) \\
& \mathrm{x}=\sqrt{ }\left(4.50 \times 10^{-6}\right) \\
& \mathrm{x}=2.12 \times 10^{-3} \mathrm{~mol} \mathrm{~L}^{-1}
\end{aligned}
$$

But $\mathrm{x}=\left[\mathrm{H}^{+}{ }_{(\mathrm{aq})}\right]=2.12 \times 10^{-3} \mathrm{~mol} \mathrm{~L}^{-1}$
Thus; $\quad \mathrm{pH} \stackrel{-l}{=}-\log \left(2.12 \times 10^{-3}\right)$

$$
=2.67
$$

Q23. What is the pH of a $0.250 \mathrm{~mol} \mathrm{~L}^{-1}$ solution of the monoprotic acid, benzoic acid given that $\left.\mathrm{K}_{\mathrm{A}}(\mathrm{HBz})_{(\mathrm{aq})}\right)=6.62 \times 10^{-5} \quad\left(\right.$ at $\left.25^{\circ} \mathrm{C}\right) \quad(\mathrm{pH}=2.4)$

Q24. If a $0.100 \mathrm{~mol} \mathrm{~L}^{-1}$ solution of cyanic acid $\mathrm{HCNO}_{(\text {(aq })}$ has a pH of 3.02 at $25^{\circ} \mathrm{C}$, determine $\mathrm{K}_{\mathrm{A}}\left(\mathrm{HCNO}_{(\mathrm{aq}}\right)$ at $25^{\circ} \mathrm{C}$.

Q25. The $\mathrm{K}_{\mathrm{A}}$ for hypoiodous acid $\left(\mathrm{HOI}_{(\mathrm{qq})}\right)$ is $2.50 \times 10^{-11}$ at $25^{\circ} \mathrm{C}$. What is the pH of:
(i) a $0.10 \mathrm{~mol} \mathrm{~L}^{-1}$ solution of hypoiodous acid at $25^{\circ} \mathrm{C}$ ?
$(\mathrm{pH}=5.80)$
(ii) a $0.20 \mathrm{~mol} \mathrm{~L}^{-1}$ solution of hypoiodous acid at $25^{\circ} \mathrm{C}$ ? $(\mathrm{pH}=5.65)$
(iii) a $0.300 \mathrm{~mol} \mathrm{~L}^{-1}$ solution of hypoiodous acid at $25^{\circ} \mathrm{C}$ ? $(\mathrm{pH}=5.56)$

## ACID ~ BASE INDICATORS

Most acid $\sim$ base indicators are themselves weak acids with one important characteristic and that is the weak acid and its conjugate base have different colours.
For example, consider the weak acid, bromothymol blue (" $\mathrm{HBb}_{(\mathrm{aq})}$ ") which has a $\mathrm{K}_{\mathrm{A}}$ value of $7.94 \times 10^{-8}$ at room temperature. (N.B. bromothymol blue is a complex organic compound but we will use the formula " HBb " for simplification.)

The undissociated acid, $\mathrm{HBb}_{(\mathrm{aq})}$ is YELLOW in colour.
When dissociated, the conjugate base, $\mathrm{Bb}^{-}{ }_{(\mathrm{aq})}$ is BLUE in colour.

$$
\underset{\text { YELLOW }}{\mathrm{HBb}_{(\mathrm{aq})}} \rightleftharpoons \mathrm{H}_{(\mathrm{aq})}^{+}+\underset{\text { BLUE }^{(\mathrm{Bq})}}{\mathrm{Bb}^{-}}
$$

Applying Le Chatelier's Principle, we see that the colour of the indicator will vary as we alter the acid/base properties of the indicator's environment; i.e.

1. Increasing $\left[\mathrm{H}^{+}{ }_{(\mathrm{aq})}\right]$ means the system adjusts so as to remove $\mathrm{H}^{+}{ }_{(\mathrm{aq})}$ and this drives the equilibrium position to the left. Thus the dominant colour will be yellow. Thus, bromothymol blue is yellow in acidic solutions.
2. Adding a base will remove $\mathrm{H}^{+}{ }_{\text {(aq) }}$ and so the equilibrium position moves to replace the $\mathrm{H}^{+}{ }_{\text {(aq) }}$ and this drives the position to the right. Thus the dominant colour will be blue. Thus, bromothymol blue is blue in basic solutions.

The indicator HBb will be neither blue nor yellow but a greenish colour if there are approximately equal concentrations of the two coloured species.
When does this 'intermediate' green colour occur? Consider the $\mathrm{K}_{\mathrm{A}}(\mathrm{HBb})$

$$
\mathrm{K}_{\mathrm{A}}=\frac{\left[\mathrm{H}_{(\mathrm{aq})}^{+}\right]\left[\mathrm{Bb}_{(\mathrm{aq})}^{-}\right]}{\left[\mathrm{HBb}_{(\mathrm{aq})}\right]}=7.94 \times 10^{-8} \quad\left(\text { at } 25^{\circ} \mathrm{C}\right)
$$

Now the intermediate colour is going to occur when the amount of yellow molecules is about the same as the amount of blue ions.
i.e. The intermediate colour occurs when: $\left[\mathrm{HBb}_{(\mathrm{aq})}\right] \approx\left[\mathrm{Bb}^{-}{ }_{(\mathrm{aq})}\right]$ and so as these two concentration numbers are equal we can cancel them out in the $\mathrm{K}_{\mathrm{A}}$ expression above and get:

$$
\left[\mathrm{H}^{+}(\mathrm{aq})\right] \approx 7.94 \times 10^{-8}
$$

i.e. The intermediate colour for HBb occurs when the $\left[\mathrm{H}^{+}{ }_{(\mathrm{aq})}\right] \approx 7.94 \times 10^{-8}$ or when the pH is about 7.1 In fact the colour change from yellow $\leftrightarrow$ blue occurs across a range of pH values of $7.1 \pm 0.7$ i.e from about $6.4 \leftrightarrow 7.8$
We say bromothymol blue is colour sensitive in the pH range $6.4 \leftrightarrow 7.8$
As each acid/base indicator has its own $\mathrm{K}_{\mathrm{A}}$ value, they each have their own pH range in which they are colour sensitive. The colour sensitive range is usually about $\mathrm{pK} \mathrm{A}_{\mathrm{A}} \pm \mathrm{X}$ where $\mathrm{pK}_{\mathrm{A}}=$ $-\log _{10} \mathrm{~K}_{\mathrm{A}}$ and X is about 0.7 , but it varies because the acid and base colours are not usuallly of the same colour intensity.

Q26. The acid $\sim$ base indicator methyl yellow is a monoprotic organic acid with a dissociation constant $\mathrm{K}_{\mathrm{A}}=5.0 \times 10^{-4}$ at room temperature. We can express the complex organic molecule as "HMy" and you are given that HMy is red whereas My" is yellow.
(i) what colour will methyl yellow indicator be in an acidic solution?
(ii) what colour will methyl yellow indicator be in a basic solution?
(yellow)
(iii) what will be the intermediate colour for methyl yellow indicator? (orange)
(iv) in what pH range will methyl yellow indicator be colour sensitive?

## SOME COMMON ACID~BASE INDICATORS COLOUR CHANGES \& pH RANGES

| INDICATOR | pH RANGE | ACID <br> COLOUR | BASE <br> COLOUR | K <br> INDICATOR |
| :---: | :---: | :---: | :---: | :---: |
| acid cresol red | $0.2-1.8$ | red | yellow | - |
| thymol blue | $1.2-2.8$ | red | yellow | $2.0 \times 10^{-2}$ |
| bromophenol <br> blue | $3.0-4.6$ | yellow | blue | $7.9 \times 10^{-5}$ |
| methyl yellow | $2.9-4.0$ | red | yellow | $5.0 \times 10^{-4}$ |
| methyl orange | $3.1-4.4$ | red | yellow | $2.0 \times 10^{-4}$ |
| congo red | $3.0-5.0$ | violet | red | - |
| bromocresol <br> green | $3.8-5.4$ | yellow | blue | $2.0 \times 10^{-5}$ |
| methyl red | $4.2-6.3$ | red | yellow | $1.0 \times 10^{-5}$ |
| bromocresol <br> purple | $5.2-6.8$ | yellow | purple | $7.9 \times 10^{-7}$ |
| bromophenol <br> red | $5.2-6.8$ | yellow | red | - |
| litmus | $5.0-8.0$ | red | blue | $1 \times 10^{-7}$ |
| bromothymol <br> blue | $6.0-7.6$ | yellow | blue | $7.9 \times 10^{-8}$ |
| phenol red <br> cresol red | $6.8-8.4$ | yellow | red | $1.6 \times 10^{-8}$ |
| m-cresol purple | $7.2-8.8$ | yellow | red | $6.3 \times 10^{-9}$ |
| phenolphthalein | $8.3-10.0$ | yellow | purple | - |
| colourless | pink | $2.5 \times 10^{-10}$ |  |  |
| indigo yellow | $10.1-12.0$ | yellow | red | - |
| tropaeolin | $11.6-13.0$ | blue | yellow | - |
| nitramine | $11.1-12.7$ | yellow | orange | - |

## ACID ~ BASE TITRATIONS

Acid $\sim$ base titrations involve volumetric analysis where the chemical reaction under investigation is neutralization; i.e.

$$
\begin{aligned}
& \text { ACID }+ \text { BASE } \rightarrow \text { SALT }+ \text { WATER } \\
& \text { e.g. } \quad \mathrm{H}_{2} \mathrm{SO}_{4(\text { aq })}+2 \mathrm{NaOH}_{(\mathrm{aq})} \rightarrow \mathrm{Na}_{2} \mathrm{SO}_{4(\mathrm{aq})}+2 \mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})}
\end{aligned}
$$

Although the term 'neutralization' suggests that a theoretical end-point (called the equivalence point) pH of 7.0 will be achieved, the real situation is determined by the relative strengths of the acid and base undergoing the reaction. The salt produced is not neutral because of 'HYDROLYSIS" and if the:
parent acid is stronger than the parent base, the salt will be ACIDIC
parent acid is weaker than the parent base, the salt will be BASIC (ALKALINE)

## pH OF SALT SOLUTIONS

|  | STRONG PARENT BASE <br> e.g. $\mathrm{NaOH}, \mathrm{KOH}$, | WEAK PARENT BASE e.g. $\mathrm{NH}_{4} \mathrm{OH}$, AMINES.. |
| :---: | :---: | :---: |
| STRONG PARENT ACID e.g. $\mathrm{HCl}, \mathrm{HNO}_{3}$, | $\begin{gathered} \mathbf{p H}=7 \\ \left(\mathbf{N a C l}, \mathrm{KNO}_{3}\right) \end{gathered}$ | $\begin{gathered} \mathrm{pH}<7 \\ \left(\mathrm{NH}_{4} \mathrm{Cl}, \mathrm{NH}_{4} \mathrm{NO}_{3}\right) \end{gathered}$ |
| WEAK PARENT ACID <br> e.g. $\mathrm{CH}_{3} \mathbf{C O O H}, \mathrm{HNO}_{2}$, | $\begin{gathered} \mathrm{pH}>7 \\ \left(\mathrm{CH}_{3} \mathrm{COONa}, \mathrm{KNO}_{2}\right) \end{gathered}$ | $\begin{gathered} \mathrm{pH} \approx 7 \\ \left(\mathrm{CH}_{3} \mathrm{COONH}_{4}\right) \end{gathered}$ |

This enables us to see which indicators are suitable for detecting the end-point of an acid/base titration. We need to select an indicator that will be colour sensitive in the pH region around the end-point (equivalence point)
i.e.

| PARENT ACID | PARENT BASE | pH AT EQUIVALENCE POINT | SUITABLE INDICATOR |
| :---: | :---: | :---: | :---: |
| STRONG | STRONG | 7 | MOST |
| STRONG | WEAK | $<7$ | METHYL ORANGE |
| WEAK | STRONG | $>7$ | PHENOL PHTHALEIN |
| WEAK | WEAK | $?$ | NONE |

The titration curves on the next pages show this more effectively.

## pH RANGE FOR SOME INDICATORS



Colour changes through the pH range for various indicators.

## ACID - BASE TITRATION CURVES

Graph 1 shows how the pH changes for a reaction between a strong base and a strong acid ( 20.0 mL of $0.10 \mathrm{~mol} / \mathrm{L} \mathrm{NaOH}$ and $0.10 \mathrm{~mol} / \mathrm{L} \mathrm{HCl})$. The equivalence-point for this reaction occurs at pH 7 because here the solution contains sodium and chloride ions, both of which are neutral.


Strong acid - strong base.

Because the pH at the equivalence point changes dramatically from $\mathrm{pH}-11$ down to $\mathrm{pH}-3$, just about any acid-base indicator can be used for detecting the end-point.

## ACID - BASE TITRATION CURVES



Graph 2 shows the pH titration curve for the reaction between a strong base (eg. NaOH ) and a weak acid (eg. acetic acid). The equivalence point for this reaction. occurs at around $\mathrm{pH}-9$ because sodium ions are neutral but aqueous acetate ions are slightly basic. A suitable indicator for this titration would be phenolphthalein or alizarin yellow.


Graph 3 shows the pH titration curve for the reaction between a strong acid (eg. HCl ) and a weak base (eg. ammonia). The equivalence point for this reaction occurs at around $\mathrm{pH}-5$ because chloride ions are neutral but aqueous ammonium ions are slightly acidic. A suitable indicator for this titration would be methyl orange.


Graph 4 shows the pH titration curve for the reaction between a weak acid (eg. acetic acid) and a weak base (eg. ammonia). The equivalence point for this reaction does not occur at a sharply determined pH value and consequently no indicator is suitable for this titration.

## QUESTIONS ON ACID/BASE TITRATIONS

Q27. For the acid/base neutralization reaction;

$$
\mathrm{H}_{2} \mathrm{SO}_{4(\mathrm{aq})}+2 \mathrm{NaOH}_{(\mathrm{aq})} \rightarrow \mathrm{Na}_{2} \mathrm{SO}_{4(\mathrm{aq})}+2 \mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})}
$$

(i) what volume of $0.125 \mathrm{~mol} \mathrm{~L}^{-1}$ sulfuric acid $\left(\mathrm{H}_{2} \mathrm{SO}_{4(\mathrm{aq})}\right)$ is needed to just react with 35.0 mL of $0.160 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{NaOH}_{(\text {aq) }}$ ?
$(22.4 \mathrm{~mL})$
(ii) what will be the pH at the equivalence point?
( $\mathrm{pH}=7$ )
(iii) what would be a suitable acid/base indicator for this titration?

Q28. Nitric acid is to be titrated against potassium hydroxide solution; i.e.

$$
\mathrm{HNO}_{3(\mathrm{aq})}+\mathrm{KOH}_{(\mathrm{aq})} \rightarrow \mathrm{KNO}_{3(\mathrm{aq})}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})}
$$

If a 20.0 mL aliquot of $\mathrm{HNO}_{3(\mathrm{aq})}$ is neutralized by 25.6 mL of $0.204 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{KOH}_{(\mathrm{aq})}$ what is the $\left[\mathrm{HNO}_{3(\mathrm{aq})}\right]$ ?
( $0.261 \mathrm{~mol} \mathrm{~L}^{-1}$ )
Q29. Acetic acid is a weak acid and a titration is to be carried out using sodium hydroxide, a strong base, to determine its concentration in a sample of vinegar. The neutralization reaction is:

$$
\mathrm{CH}_{3} \mathrm{COOH}_{(\mathrm{aq})}+\mathrm{NaOH}_{(\mathrm{aq})} \rightarrow \mathrm{CH}_{3} \mathrm{COONa}_{(\mathrm{aq})}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})}
$$

Step 1: This involved diluting the vinegar 10 times with distilled water.
Step 2: This involved titrating 20.0 mL aliquots of the diluted vinegar solution against 0.107 $\mathrm{mol} \mathrm{L}^{-1} \mathrm{NaOH}_{(\mathrm{aq})}$. The average end-point occurred with the addition of 35.3 mL of $\mathrm{NaOH}_{(\text {aq) }}$.
(i) What is the concentration of $\mathrm{CH}_{3} \mathrm{COOH}_{(\mathrm{aq})}$ in the diluted vinegar?
( $0.189 \mathrm{~mol} \mathrm{~L}^{-1}$ )
(ii) What is the concentration of $\mathrm{CH}_{3} \mathrm{COOH}_{(\text {aq })}$ in the original undiluted vinegar?
$\left(1.89 \mathrm{~mol} \mathrm{~L}^{-1}\right)$
(iii) If 1.00 L of vinegar has a mass of 1150 g what is the $\%$ by mass of acetic acid in vinegar?
(9.85 \%)
(iv) Suggest an indicator that would have been appropriate for this titration?
(phenolphthalein)

Q30. Vitamin C (ascorbic acid $=$ "HAsc")) is to be titrated against sodium hydroxide solution; i.e.

$$
\mathrm{HAsc}_{(\mathrm{aq})}+\mathrm{NaOH}_{(\mathrm{aq})} \rightarrow \mathrm{NaAsc}_{(\mathrm{aq})}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})}
$$

If a 20.0 mL aliquot of $\mathrm{HAsc}_{(\mathrm{aq})}$ is neutralized by 18.2 mL of $0.155 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{NaOH}_{(\mathrm{aq})}$ what is the concentration of the ascorbic acid?
( $0.141 \mathrm{~mol} \mathrm{~L}^{-1}$ )

Q31. A 20.0 mL sample of the weak base, household ammonia $\left(\mathrm{NH}_{4} \mathrm{OH}_{(\text {aq })}\right)$ is analysed by titrating against $0.300 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{H}_{2} \mathrm{SO}_{4(\mathrm{aq})}$. The end-point occurred when 18.2 mL of $\mathrm{H}_{2} \mathrm{SO}_{4(\mathrm{aq})}$ had been added. The reaction equation is:

$$
\mathrm{H}_{2} \mathrm{SO}_{4(\mathrm{aq})}+2 \mathrm{NH}_{4} \mathrm{OH}_{(\mathrm{aq})} \rightarrow\left(\mathrm{NH}_{4}\right)_{2} \mathrm{SO}_{4(a q)}+2 \mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})}
$$

(a) What is the molarity of the ammonia solution?
( $0.546 \mathrm{~mol} \mathrm{~L}^{-1}$ )
(b) Suggest an indicator that would have been appropriate for this titration?
(methyl orange)
(c) What would have been the problem if the ammonia had been titrated against a weak acid such as acetic acid $\left(\mathrm{CH}_{3} \mathrm{COOH}_{(\mathrm{aq})}\right)$ ?
(See Titration Graph 4 - page 18)
Q32. A titration is carried out between 20.0 mL of $0.100 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{HCl}_{(\mathrm{aq})}$ and $0.100 \mathrm{~mol} \mathrm{~L}^{-1}$ $\mathrm{NaOH}_{(\mathrm{aq})}$. The equivalence point will occur at 20.0 mL of $\mathrm{NaOH}_{(\mathrm{aq})}$.
(i) What is the pH when 15.00 mL of $\mathrm{NaOH}_{(\mathrm{aq})}$ has been added?

ANSWER:
At this point there will be 5.00 mL of $0.100 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{HCl}_{(\mathrm{aq})}$ in excess, now diluted to a total volume of $(20.0+15.0)=35.0 \mathrm{~mL}$

$$
\begin{aligned}
\therefore\left[\mathrm{H}_{(\mathrm{aq})}^{+}\right]=0.100 \times(5.00 / 35.0) & =0.0143 \mathrm{~mol} \mathrm{~L}^{-1} . \\
\rightarrow \mathrm{pH} & =1.85
\end{aligned}
$$

(ii) What would be the pH if 25.00 mL of $\mathrm{NaOH}_{(\text {aq })}$ had been added?

ANSWER:
At this point there would be 5.00 mL of $0.100 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{NaOH}_{(\mathrm{aq})}$ in excess, now diluted to a total volume of $(20.0+25.0)=45.0 \mathrm{~mL}$

$$
\begin{aligned}
\therefore\left[\mathrm{OH}_{(\mathrm{aq})}\right] & =0.100 \times(5.00 / 45.0)=0.0111 \mathrm{~mol} \mathrm{~L}^{-1} . \\
\therefore\left[\mathrm{H}_{(\mathrm{aq})}\right] & =\left(1.00 \times 10^{-14}\right) /(0.0111) \\
& =9.00 \times 10^{-13} \mathrm{~mol} \mathrm{~L} \\
& \rightarrow \mathrm{pH}=12.0
\end{aligned}
$$

Q33. A titration is carried out between 20.0 mL of $0.100 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{HCl}_{(\mathrm{aq})}$ and 0.100 mol $\mathrm{L}^{-1} \mathrm{NaOH}_{(\mathrm{aq})}$. The equivalence point will occur at 20.0 mL of $\mathrm{NaOH}_{(\mathrm{aq})}$.
(HINT: For each of the following parts, use the 'excess' technique as in Q6. above)
(a) What is the pH when 19.90 mL of $\mathrm{NaOH}_{(\mathrm{aq})}$ has been added?

$$
(\mathrm{pH}=3.6)
$$

(b) What is the pH when 19.95 mL of $\mathrm{NaOH}_{(\mathrm{aq})}$ has been added?
( $\mathrm{pH}=3.9$ )
(c) What is the pH when 19.99 mL of $\mathrm{NaOH}_{(\text {aq) }}$ has been added?
( $\mathrm{pH}=4.6$ )
(d) What is the pH when 20.00 mL of $\mathrm{NaOH}_{(\mathrm{aq})}$ has been added?
( $\mathrm{pH}=7.0$ )
(e) What is the pH when 20.01 mL of $\mathrm{NaOH}_{(2 q)}$ has been added?
( $\mathrm{pH}=9.4$ )
(f) What is the pH when 20.05 mL of $\mathrm{NaOH}_{(\mathrm{aq})}$ has been added?
( $\mathrm{pH}=10.1$ )
(g) What is the pH when 20.10 mL of $\mathrm{NaOH}_{(\mathrm{qq})}$ has been added?

Q34. Combining your answers from Q32. and Q33. above, sketch a graph of pH versus volume of $\mathrm{NaOH}_{\text {(aq) }}$ added.
(have 'volume' on the horizontal axis and range from $15 \mathrm{~mL} \leftrightarrow 25 \mathrm{~mL}$.)

NAME

## CHEMISTRY (LEVEL3C) ACID-BASE CHEMISTRY TEST

Q1. Suggest four different properties that are characteristics of an ACID.
(i) $\qquad$ (ii)
(iii)
(iv) $\qquad$ (2 marks)
Q2. Consider the following chemical equation which may be considered to describe a reversible reaction:

$$
\mathrm{HBrO}_{3(\mathrm{aq})}+\mathrm{NH}_{3(\mathrm{aq})} \rightleftharpoons \mathrm{BrO}_{3}^{-}{ }_{(\mathrm{aq})}+\mathrm{NH}_{4}^{+}{ }_{(\mathrm{aq})}
$$

In accordance with the Brönsted-Lowry definitions, which two species are behaving as BASES?
(i)
(ii)
(2 marks)

Q3. What is the meaning of the statement that $\mathrm{HNO}_{3(\mathrm{aq})}$ is a STRONG acid?

Q4.Categorise the following solutions under the headings: concentrated/dilute, strong/weak and acid/base. The first example has been done for you.

$$
\text { CONCENTR }^{\mathrm{N}} \text {. STRENGTH }
$$

(i) $0.10 \mathrm{~mol} / \mathrm{L} \mathrm{HCl} \mathrm{Haq}_{\text {(aq) }} \quad=$ dilute strong acid
(ii) $8.0 \mathrm{~mol} / \mathrm{L} \quad \mathrm{NaOH}_{\text {(aq) }}$
(iii) $0.40 \mathrm{~mol} / \mathrm{L} \mathrm{CH}_{3} \mathrm{COOH}_{(\mathrm{aq})}=$
(iv) $15 \mathrm{~mol} / \mathrm{L} \quad \mathrm{NH}_{4} \mathrm{OH}_{(\text {aq })} \quad=$
(v) $12.0 \mathrm{~mol} / \mathrm{L} \quad \mathrm{H}_{2} \mathrm{SO}_{4(\mathrm{aq})} \quad=$
(4 marks)
Q5. Give the chemical formula for one example of each of the following:
(i) a MONOPROTIC acid: $\qquad$ (ii) a DIPROTIC acid:
$\qquad$
(iii) a TRIPROTIC acid: $\qquad$ (iv) an AMPHIPROTIC ion $\qquad$ (2 marks)
Q6. You are presented with two aqueous solutions of acids:
(a) $0.10 \mathrm{~mole} / \mathrm{L}$ solution of acid " $\mathrm{HA}^{\prime}$
(b) $0.10 \mathrm{~mole} / \mathrm{L}$ solution of acid " HB "

One of the two acids is known to be a STRONG acid and the other is a WEAK acid. Suggest briefly, THREE different laboratory tests that you could use to identify which one was the stronger acid.
(i)
(ii)
(iii) $\qquad$

Q7. Coca Cola has a pH of 3 and black coffee has a pH of 5 .
(i) Which is the more acidic?
(ii) How many times more acidic?

## (2 marks)

Q8. What is the pH of the following solutions (at $25^{\circ} \mathrm{C}$ ) given that they have the following aqueous ionic concentrations? (assume $\left[\mathrm{H}^{+}\right]=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$)
(i) $\left[\mathrm{H}^{+}\right]=10^{-2} \mathrm{~mol} \mathrm{~L}^{-1}$ $\qquad$ (ii) $\left[\mathrm{H}^{+}\right]=10^{-5} \mathrm{~mol} \mathrm{~L}{ }^{-1}$
(iii) $\left[\mathrm{OH}^{-}\right]=10^{-3} \mathrm{~mol} \mathrm{~L}^{-1}$ $\qquad$ (iv) $\left[\mathrm{OH}^{-}\right]=10^{-1} \mathrm{~mol} \mathrm{~L}^{-1}$ (2 marks)
Q9. What volume of $10.0 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{HCl}_{(\mathrm{aq})}$ is needed to prepare 600 mL of $0.400 \mathrm{~mol} \mathrm{~L}^{-1}$ $\mathrm{HCl}_{\text {(aq) }}$ ?

Q10. Consider a $0.125 \mathrm{~mol} \mathrm{~L}^{-1}$ solution of $\mathrm{Ca}(\mathrm{OH})_{2 \text { (aq) }}$ at $25^{\circ} \mathrm{C}$ and assume it is fully ionised, i.e. completely dissociated into ions.
(i) What is the $\left[\mathrm{OH}^{-}\right]$for this solution in $\mathrm{mol} \mathrm{L}^{-1}$ ?
(ii) What is the $\left[\mathrm{H}^{+}\right]$for this solution in $\mathrm{mol} \mathrm{L}^{-1}$ ?
(iii) What is the pH of this solution? $\qquad$ (3 marks)

Q11. For the acid/base neutralization reaction:

$$
3 \mathrm{HNO}_{2(a q)}+\mathrm{Al}(\mathrm{OH})_{3(\mathrm{aq})} \rightarrow \mathrm{Al}\left(\mathrm{NO}_{2}\right)_{3(a q)}+3 \mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})}
$$

(i) What volume of $0.125 \mathrm{~mol} \mathrm{~L}^{-1}$ nitrous acid $\left(\mathrm{HNO}_{2 \text { (aq) }}=\right.$ a weak acid) is needed to just react with 35.0 mL of $0.160 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{Al}(\mathrm{OH})_{3(\text { aq) }}$ which is a strong base?
(ii) What will be the pH at the equivalence point?
(iii) What would be a suitable acid/base indicator for this titration?

## (4 marks)

Q12. What is the pH of a $0.505 \mathrm{~mol} \mathrm{~L}^{-1}$ solution of the monoprotic acid, benzoic acid given that $\left.\mathrm{K}_{\mathrm{A}}(\mathrm{HBz})_{(\mathrm{aq})}\right)=6.62 \times 10^{-5} \quad\left(\right.$ at $\left.25^{\circ} \mathrm{C}\right)$

(iii) a TRRPRoric acid. $\mathrm{H}_{3} \mathrm{PO}$ (ive an amphiprotic ion $\mathrm{HSO}_{4 \mathrm{~m}}$ - ( 2 marks)
Q6. You are presented with two aqueous solutions of acids:
(a) 0.10 mole/ solution of acid "HA"
(i) a MONOPROTIC acid: $\mathrm{HCl}_{\mathrm{mp}}$ - (ii) a DPRRTIC acid: $\mathrm{H}_{2} \mathrm{SO}_{4}$ -
(iii) a TRIPROTIC acid: $\mathrm{H}_{3} \mathrm{HO}_{4}$ (iv) an AMPRIPROTIC ion $\mathrm{HSO}_{4}$ (2 marks) Q5. Give the chemical formula for one example of each of the following



(00) 1 IOH
hionsuls Nainzono

 In accordance with the Bronsted Lowry definitions, which two species are behaving as
BAESS? $\mathrm{NH}_{\text {a }}$
$\begin{array}{lll}\text { (i) } & \text { (ii) } \mathrm{BrO}_{3}^{-} & \text {(2 marks) }\end{array}$
 (iii) $\mathrm{PH}<7$ (iv) neviralizes Lases ( 2 marks) Q1. Suggest four different properties that are chanacteristics of an ACID.
$\begin{array}{ll}\text { (i) donates. } H^{+} \text {(aan) } & \text { (ii) Emans. blue litmus ted }\end{array}$ ACID-BASE CHEMISTRY TEST (כعTHATH) ХHLSIWTHD Sป马MSNV 3wvN
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2

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& \bar{z} \\
& \hline
\end{aligned}
$$

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