Topic 8 Acids and Bases

Reactions of acids and bases

Acids react with a) metals to produce salts and Hydrogen gas

b) With bases to produce salt and water

c) With carbonates and hydrogen carbonates to produce salt + water + CO_2

Bases are chemicals that neutralise an acid ...so carbonates fit this description. Alkalis are soluble bases

Metal (ionic) oxides are bases, non-metal (covalent) oxides are acidic.

Examples of reactions of acids: a) $Mg + 2HCl - \rightarrow MgCl_2 + H_2$ bi) $MgO + 2HCl \rightarrow MgCl_2 + H_2O$ bii) $Mg(OH) + 2HCl \rightarrow MgCl_2 + 2H_2O$ c) $Na_2CO_3 + 2HCl - \rightarrow 2NaCl + CO_2 + H_2O$

The name of the salt typically comes from lopping off the -ic (or uric) from the acid name and adding -ate... carbonic acid produces carbonates; malonic makes malonates. Note HCl is different, since it forms chlorides. This is because when we remove the H⁺ from this acid, we are left with a simple negative ion, an -ide.

pH scale (8,4)

The way we typically note the acidity of a solution is by its pH , but what is pH? This term actually means " minus the log of the H^+ ion concentration"...but what does this mean? In pure water, there are a few molecules that break apart. They do not stay that way for long because they also recombine as well. This would be represented by the equation:

Or

$$H_2O \leftarrow -- \rightarrow H^+ + OH^{1-}$$

 $2H_2O \leftarrow -- \rightarrow H_3O^+ + OH^{1-}$

since H^+ is too small to exist on its own and as a result a number of waters will stick to it and in fact H_3O^+ is also a simplification! However we are allowed to use H^+ instead of the more awkward H_3O^+ or $H_5O_2^+$ or $H_7O_3^+$!

But according to this, the number of hydrogen ions and hydroxide ions must always be equal in pure water and scientists discovered that their concentration was 0.0000001 moles per liter at room temp...IN PURE WATER. The somewhat surprising thing was that whatever is added to the water, if you discovered the hydroxide and hydrogen ion concentration and multiplied them together you always ended up at the same answer...1 x 10^{-14} regardless. This is a modified equilibrium constant and is called K_w ...the dissociation constant for water. It is of course constant at a certain temp and this is at standard conditions, 298K.

Unfortunately these negative power numbers are not exactly user friendly, so it was decided to "negative log" them. When you do this you end up with a scale from zero to 14 for the possible H⁺ concentration of an aqueous solution. This is the pH scale that we use and the "p", which should never be capitalised, stands for "-log of".

In pure water the H⁺ concentration is $1 \ge 10^{-7}$. If you put this into your calculator and "log" it you get -7...and – times - is positive and so –log $1 \ge 10^{-7}$ is 7...the pH of pure water. As the concentration of hydrogen ions increases the pH falls...you can check this by negative logging progressively larger numbers. Note that because it is a log scale, a change of 1 pH unit is equal to a tenfold change in [H⁺] ... so if pH goes from 4 to 8, then the [H⁺] falls by a factor of 10^4 .

pН	1	4-6	7	8-10	14
acid/base	highly	medium	neutral	mild ->	highly
nature	acidic	mild acidic	2	medium	basic
				basic	
Universal	cherry	orange	green	aquamarine	blue
Indicator	Red	to yellow		to blue	purple

We use universal indicator to give us a quick guide to the pH of various solutions...but be warned...aqueous solutions only!

ACID / BASE THEORIES

(section 8.1)

The commonest acid/base theory is the Bronsted –Lowry theory. In this, an **acid is defined as an H⁺ donor and a base is an H⁺ acceptor**. What does this mean? Well it means that an acid will "lose" an H⁺ to the water it is placed in. In order for it to do that it must have an H in its molecule...AND the H must be weakly bonded to (preferably) an atom such as O, Cl or Br. What happens is: HCl -- \rightarrow H⁺ + Cl⁻. So when an acid is added to water, it releases H⁺ and thus the H⁺ concentration exceeds the OH⁻ and so the solution is acidic.

A base has got to "take on" an H^+ . In order for it to do this, it would be beneficial if it was a negative ion, or, if it is not, then it will have to have an atom with a slightly negative charge on it AND a lone pair of electrons for the H^+ to bond on to.

Here are two examples: $CO_3^{2-} + H^+ - \rightarrow HCO_3^{1-} + NH_3 + H^+ - \rightarrow NH_4^+$.

The second example is of the weak base ammonia, which accepts an H^+ to form the ammonium ion. The molecule of ammonia looks like this:

The N is a stronger non-metal than H and so it pulls the shared electron pair closer to it, making it negative. Note the "lone electron pair" on top of the N...that's where the H⁺ ends up. When added to water these chemicals remove H⁺ and so there are less H⁺ than OH⁻ and so the solution is basic.

Thus any species that has an H in it could act as a B-L acid, but most will not as the H is too strongly attached...example : CH_4 . Further example: The acid CH_3COOH has only one acidic H, the one at the end. This is because that is weakly bonded onto the O whereas the other H's are more strongly bonded to the C*.

Likewise any species that has a lone pair could act as a B-L base, but in reality, only –ve ions and very electronegative atoms will do this easily. (see examples above) So H_2S has a couple of lone pairs on the S and so in theory it could accept an H^+ , but in reality it rarely would do this.

Conjugate pairs of acid /base.

The conjugate of a B-L acid or base is the species that is formed when it acts as an acid or a base.

So the conjugate acid of NH_3 is NH_4^+ and turning the whole thing round, the conjugate base of NH_4^+ is NH_3 . So if you want to form the conjugate acid of a species, simply add H^+ to it and if you want to find the conjugate base, remove H^+ .

Determine the conjugate acid and base of the following amphoterics

a) H_2O b) OH^{1-} c) $H_2 PO_4^{-1-}$ c) C_2H_5OH d) $[Al(H_2O)_3(OH)_3]$

d is the nasty amphoteric hydrated aluminium oxide as a complex ion

*This is a bit of a lie. The thing is because the O pulls the bonded electrons towards it, H^+ is likely to break off. However with the C – H bond, when that breaks, the H is likely to take an electron with it...so it won't form H^+ but rather atomic H!

Bond strengths show the O – H is over 10% stronger than a C – H bond (464 compared to 413kJ/mol)

LEWIS ACID - BASE THEORY

Problem : the B-L theory, which is the one most often used, does not adequately explain all acid-base reactions.

Example : $CaO + SO_3 - --- \rightarrow CaSO_4$.

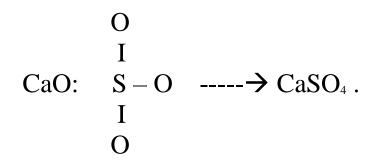
Here we have a base (metal oxide) neutralized by an acid (non-metal oxide) and yet the B-L theory cannot account for it.

So Lewis came up with another theory, which sounds totally different:

An acid is a lone electron pair taker and a base is a lone electron pair donor.

Using the above equation, we can see that the O in CaO bonds on to the S in sulfur trioxide with a DATIVE (or co-ordinate) covalent bond. The use of

curved arrows in the equation below highlights the movement of the electron pair, and you will need to use this concept quite often in organic chemistry



Now most B-L acid base reactions fit into this theory as well, as the H^+ accepts the lone pair of a base such as NH₃. In fact the reaction in water is Lewis acid/base as well because the abbreviation we use for acid [H⁺], is in reality H_3O^+ , where a water molecule has acted as a Lewis base by donating a lone pair to the H⁺.

Summary

Almost all B-L acids fit into the Lewis theory...one classic exception is NH_4^+ since this has no space to accept a lone pair...N cannot have 5 electron pairs around it since it is in period 2...the latter $\frac{1}{2}$ of period 3 might be able to use the 3d orbitals for this

ALL B-L bases fit the Lewis theory, since they all need to have a lone pair for the H^+ to attach on to.

While most Lewis acids are B-L acids, there is a whole range of species that are not B-L acids.

These include a) non-metal oxides when reacting out of solution...example : SO_2 .

b) A lot of triangular planar species that exist in violation of the octet rule...example BF_3 .

c) Transition metal ions when they form complex ions

Again most Lewis bases are also B-L bases, EXCEPT when a proton (H^+) is not involved

Example $BF_3 + F^{1-} - - - \rightarrow [BF_4]^{1-}$.

In the above , the fluoride ion is the Lewis base and since it is not bonding to a hydrogen ion, it is not acting as a B-L base. BF_3 is a Lewis acid, but not a B-L acid since no protons are involved

Section 8.3

Strong acids

There are three common strong acids and these are hydrochloric, sulfuric and nitric acids which are HCl, H_2SO_4 and HNO_3 respectively. A strong acid is defined as a good H⁺ donor and will "lose" all its acidic hydrogens very quickly when placed in water...it ionises totally or you could say it dissociates completely in solution

. Thus when I make an HCl solution I have NO HCl molecules left...they have all split up (ionised) into H^+ and Cl^- . The bonds attaching the H's to the rest of the molecule are all very weak indeed.

 $HX \dashrightarrow H^+ + X^{1-}$

Weak acids

There are many weak acids and most of them are organic in nature...ie they are produced by living things. Examples would include citric acid (lemons), lactic acid (sour milk) and ethanoic acid (vinegar). These are weaker H⁺ donors than strong acids and so will not make a solution that acidic...its pH will not be too low, but will usually be somewhere between 3 and 7.

The reason these acids are weak is that their acidic H is more tightly bonded to the molecule and so will not break off so easily. If we use HX as the formula of the weak acid, we would show this as:

 $\mathrm{HX} \leftarrow -- \rightarrow \mathrm{H}^{+} + \mathrm{X}^{-} .$

This means that in solution we have mostly HX molecules and only a few H⁺ and X⁻ ions. Since there is not so much H⁺, then the pH is not so low. Note that there will still be some additional H⁺ because of the acid and so $H^+ >> OH^-$ and we have an acidic solution. We say that the acid only partially dissociates.

When we add things like Mg to a weak and a strong acid, then if we control concentration, volume and metal mass, then the weak acid will react much slower than the strong acid BUT it will react for LONGER and it will produce the same amount of hydrogen gas. The point is that if we have (say) 1000 molecules of HCl and HX and we add each to a certain volume of

water then we would end up with ZERO HCl and 1000 H⁺ and Cl⁻ because it all splits up. However we would have probably around 990 HX's and only a few of its component ions because so little breaks up. Hence HCl reacts more violently...but as the H⁺ 's are removed by the Mg they cannot be replaced in the HCl solution and they are replaced in the HX solution. We call the reaction HX< \leftarrow -> H⁺ + X⁻ an equilibrium..the reaction goes both ways. Now as the Mg reacts with the H⁺, then naturally the amount of H⁺ falls..so there is less to react with X⁻ and so the equilibrium reaction left is being slowed down. However HX is still splitting up at the same rate as before, so the H⁺ is replaced. The simple point is that I can get 1000 H⁺ from HCl quickly and I can get 1000 H⁺ from HX, but slower!

Question: Draw a sketch graph of volume of hydrogen produced (y) against time (x) and sketch the results you would expect for a) HCl and b) HX (where all variables are controlled) on the same graph.

As a result of the above many people dismiss weak acids as not dangerous. However their effect over a prolonged timespan can be devastating. Example acid decay of limestone buildings. Also since most weak acids can produce solutions below pH 4, they can kill most life forms, particularly aquatic ones, but the effects of acid rain on delicate flowers is still nasty. You will know quickly when you get a strong acid on your skin, but a weak acids effect may be delayed several hours!

Strong bases

One would expect the definition to be "a good H⁺ acceptor", however the commonest strong base we use is NaOH and that is a strong base for a different reason. When you add that to water it releases its component ions into solution...Na⁺ and OH⁻ and so the hydroxide ion concentration rises rapidly...of course the hydroxide ion is a very powerful H⁺ acceptor and if added to a supply of these ions, then they would neutralise them very quickly. All group 1 hydroxides and barium hydroxide are considered to be strong bases,

Weak bases

Just like weak acids, then one could say they do not "fully ionise", but in reality, things are a little different. These are classic H⁺ acceptors and so when added to water, they remove the H⁺ and so there is an excess of OH^{1-} left behind and so pH is > 7. Classic weak base is ammonia.

 $NH_3 + H_2O \leftarrow -- \rightarrow NH_4^+ + OH^{1-}$

The salts of weak acids are basic in solution. We can appreciate this best when we reverse the equation for the ionisation of the weak acid:

 $X^{1-} + H^+ \iff HX$

Now we have said that HX is a poor H⁺ donor and thus we are in effect also saying that X^{1-} is an H⁺ acceptor...it is a base. So when we dissolve a salt of HX..say NaX, then we get Na⁺_(aq) and X¹⁻_(aq) in solution...we have the base in solution and so pH rises.

X is a base and so it is an H acceptor and water is the victim:

 $X^{1-} + H_2O \dashrightarrow \rightarrow HX + OH^{1-}.$

So the $[OH^{1-}]$ rises and so the pH is above 7.

For comparison, lets see what happens with the salts of strong acids. We have the equation HCl $--\rightarrow$ H⁺ + Cl¹⁻. The one directional arrow says that the chloride ion WILL NOT ACCEPT H⁺ and so it is not a base..or to be correct, it is a pathetic base and almost unwilling to accept H⁺ ions. So the salts of strong acids are not basic.

Strength and concentration

Acid strength depends upon the degree of ionization, while concentration is a measure of # of moles per dm³. Thus you can have a concentrated weak acid solution...a weak acid with a high # of moles per dm³.

Q Is it possible to have a weak acid solution with a lower pH than a solution of a strong acid?

Answer: YES...if you have a concentrated weak acid and a VERY dilute strong acid, but if they have the same molarity, then by definition, the pH of the strong must be lower

The common weak base that we use in the lab is ammonia, NH_3 . Neutralisation

A neutral solution has a pH of 7and at normal temps $[H^+] = [OH^-]$. An acid neutralises a base (or vice versa) because if you have an excess of OH⁻ ions and add H⁺, then they react together to produce water. In fact, if you think about it, anything that reacts with an acid will neutralise it eventually, as the reaction will steadily use up all the excess H⁺. Of course the problem with many neutralisation reactions is that you can add an excess of the base and thus go beyond the point of neutralisation.

Common misconception explained

a) It DOES NOT take more base to neutralize a strong acid than it does an equal volume of equally concentrated weak acid. The weak acid is in equilibrium and as you add hydroxide ions, eqm is shifted right:

 $\mathrm{HX} \xleftarrow{} - - \xleftarrow{} \mathrm{H}^{\scriptscriptstyle +} + \mathrm{X}^{\mathrm{1-}} \, .$

As hydroxide is added, the H^+ ions are removed and so eventually all HX is used up. So if you started with (say) 100 HX molecules, the NaOH is going to have to neutralize 100 H^+ 's ... exactly the same # as if you started with 100 HCl's

Tests to distinguish between strong and weak acids

Firstly you must start with the same molarity of both and then a) Physical :

The pH of the strong acid will be lower

The color of universal indicator may show brighter red with the strong acid, whereas the weak acid may be orange/yellow.

The electrical conductivity of the strong acid will be higher since it has more ions in solution.

b) Chemical

The classic reactions of acids are a) they react with (relatively) strong metals to produce salts + hydrogen gas + heat b) they react with bases to produce salt + water + heat and c) They react with carbonates and hydrogen carbonates to produce salts + water + CO_2 .

The strong acid will react more violently with a fairly strong metal such as Mg or Zn and produce a faster bubbling and more heat The stronger metal will react more violently with a carbonate or hydrogen carbonate, producing bubbles of CO_2 faster than the weak acid

Both of the above are due to the higher H⁺ conc of the strong acid

YOU CANNOT DISTINGUISH BY TITRATION

With bases you can use the same physical tests described above, but the pH of the strong base will be higher; the color with UI will be more purple and the conductivity will be higher.

Chemical tests for bases are more awkward. They do form precipitates with most metal ions except Gp I and Ba, but this is will not distinguish weak from strong. The common weak bases will (when in XS, form deeply colored complex ions with things like Cu²⁺ while strong bases only form a precipitate.

 Δ H for neutralization:

Would ΔH for neutralization be the same for strong and weak acids? Answer NO....with strong acids, we are simply bond making $H^+ + OH^{1-} \rightarrow H_2O$

However with weak acids we will have to break the X-H bond before we do the above and so the reaction is (slightly) less exothermic.

Investigating pH changes upon adding an acid to a basic solution

This simple lab can be done in several different ways.

- 1) Place about 2 cm³ of base (NaOH solution) in a test tube and add some drops of universal indicator. Record the color of the solution. Now add acid (HCl) dropwise and after the addition of every drop, swirl the tube and record the color. Continue until you get a cherry red color. If we use the approximation that blue is pH 10 + and that aquamarine = pH 8; mid green = pH7; lime green = pH 6 yellow = pH 5; orange = pH 4 and red = less than pH 4, construct a sketch graph to show pH changes upon adding acid to base. pH should be on the y axis and drops of acid on the x axis.
- 2) The process can be repeated using larger volumes and a more accurate measurement of pH... a pH meter. Place 10 cm of base(NaOH) into a small flask. Get a dropper and a small measuring cylinder and use the two to determine how much liquid needs to be in the dropper to deliver 1 cm portions. Now add 1 cm portions of HCl and swirl the flask and record the new pH. Continue until the pH falls below 2. Construct an accurate graph for pH change when acid is added to base.

pH changes

 $pH = -log[H^+]$

This means that it is a LOG scale and so if the $[H^+] = 0.1 \text{ moldm}^{-3}$, then the pH is 1 and if it is 0.001 moldm^{-3} , the pH is 3. So we should notice that the more acidic a solution is the lower the pH and that a 1 unit change in pH means a ten fold change in the $[H^+]$ and so pH 1 has $[H^+] 100$ times that of pH 3

When the pH gets to (say) 4, then the $[H^+]$ is incredibly low

(0.0001moldm⁻³), and so the addition of a small amount of 1.0molar NaOH contains enough hydroxide ions to massively reduce the [H] and so the pH rises rapidly. This sudden rise in pH is the endpoint of a titration and allows us to calculate the concentration of the acid.

It is quite difficult to get strong acids to have a pH in the 3-7 range due to this...when you did your lab, you should have suddenly got the pH to change from 1 to 12. Weak acids start with a higher pH...say around 3 and this gradually rises as NaOH is added up to perhaps around 5.5 and then it suddenly jumps to 11 or 12.

Thus around pH 7 many solutions will suddenly change their pH markedly when small amounts of acid or base are added. This is a real problem in biological systems, but the answer is next.

BUFFERS

A buffer is defined as a solution that resists pH change upon addition of SMALL amounts of acid or base according to the IB. They need to add "in moderate pH ranges".

We can note that the strong acid/base mixes mentioned above cannot do this, but the weak acid could at around pH 4. A buffer is a weak acid (or base) in the presence of its salt:

CH₃COOH/ CH₃COONa or NH₃ /NH₄Cl

You do not need to worry about the "other part" of the salt...the Na⁺ or the Cl^{1-} above. What we have is an equilibrium For the weak acid HX and its salt X^{1-} .

$$\mathrm{HX} \bigstar \mathbf{H}^{+} + \mathrm{X}^{-}$$

Review Notes

9.1

A neutral solution has $[H^+] = [OH^-]$ an acid solution has $[H^+] > [OH^-]$ and a basic solution has the opposite

Acids react with a) metals to produce salts and Hydrogen gas

b) With bases to produce salt and water

c) With carbonates and hydrogen carbonates to produce salt + water + CO_2

Bases are chemicals that neutralise an acid ...so carbonates fir this description. Alkalis are soluble bases metal oxides are bases, non-metal oxides are acidic.

Examples of reactions of acids: a) $Mg + 2HCl - \rightarrow MgCl_2 + H$ bi) $MgO + 2HCl \rightarrow MgCl_2 + H_2O$ bii) $Mg(OH) + 2HCl \rightarrow MgCl_2 + 2H_2O$ c) $Na_2CO_3 + 2HCl - \rightarrow 2NaCl + CO_2 + H_2O$

The name of the salt typically comes from lopping off the -ic (or uric) from the acid name and adding -ate... carbonic acid produces carbonates; malonic makes malonates. Note HCl is different, since it forms chlorides. This is because when we remove the H⁺ from this acid, we are left with a simple negative ion, an -ide.

9.2

Strong acids are good H+ donors and are fully dissociated into ions in dilute solutions

 $HCl ---- \rightarrow H^+ + Cl^-$

Note here that you can put water into the equation, as the above is a simplification:

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

Weak acids are only slightly dissociated : $HX < \leftarrow --- \rightarrow H^+ + X^-$

. In this case we show an equilibrium, but please note that I am showing that there are lot more reactants than products, suggesting that few acid molecules break apart and the K value is small...probably smaller than 1 x 10⁻⁵.

As a result of this, strongly acidic solutions contain more ions and thus are good conductors of electricity

Strong acids are HCl, HNO₃ and H_2SO_4 (know their names and formulae). Weak acids are ethanoic acid (CH₃COOH) and carbonic acid (H₂CO₃, dissolved CO₂). If you have two acids and need to know which is strong and which is weak, first titrate to find molarity, then obtain a weak and a strong acid of IDENTICAL molarity, then compare rate of reaction with a metal such as Zn or a carbonate. Or you could test pHthe strong acid will have a lower pH than a weak acid OF THE SAME MOLARITY.

9.4

Universal indicator colour range

	Red	orange	yellow	green	blue	violet
σH	[1	4	6	7	9	12 +
I			Ū	,	,	12
acid/base	strong acid		weak acid	neutral	mild base	strong base

pH is a log scale and so a 1 unit difference = a tenfold change in conc.....0.1M HCl has a pH of 1, but 0.01 M HCl has a pH of 2 and 0.0001M HCl has a pH of 4. You get the pH from log [H⁺] and then ignoring the – sign, since the little p means "-log of" The pH scale comes from the fact that when water dissociates it does this : $H_2O \leftarrow --- \rightarrow H^+ + OH^-$ and we can see that it is in equilibrium. There is a K_c value for this of 1 x 10⁻¹⁴ and so $[H^+] x[OH^-] = 1 x 10^{-14}$ and so pH + pOH = 14 and if $[H^+] = [OH^-] = 1 x 10^{-7} = pH7$. We note that as $K_c = [H^+] x$ [OH⁻] then as the conc of H⁺ rises, so the conc of OH⁻ falls.

9.4 Buffers

A buffer solution is a solution that resists pH change upon addition of small amounts of acid or base. If a small amount of HCl is added to a bucket of water, the pH would plummet.....if a small amount of HCl is added to a bucket of water containing a buffer, the pH would hardly change. A buffer is made up of a weak acid or base in the presence of its conjugate.....ie ethanoic acid + sodium ethanoateor ammonia and ammonium chloride. However, watch out because a partly neutralized weak acid or base is also a buffer solution. The logic here is that if you have (say) 0.50 moles of ethanoic acid and you adda lesser #of moles of NaOH, you will have some ethanoic acid over AND you will have produced some ethanoate.

Buffers work like this:

$CH_{3}COOH \leftarrow -- \rightarrow CH_{3}COO^{-} + H^{+}$

This is an equilibrium and if acid is added (H^+) then eqm shifts left and the H^+ is removed...if base is added, then H^+ reacts with the OH⁻ and thus LOWERS the [H+] and this shifts the eqm right, so more H^+ is generated. Obviously the amount of H^+ that can be absorbed/ released depends on how much weak acid and conjugate base you have.

9.5

When a titration is performed with a strong acid and base, a graph of pH against volume of base added would look like this:

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Volume of strong base added

We can see that initially there is little change in pH and then as the end point is neared, there is a massive change. Then there is hardly any more change as more base is added.