MODULE 9.3: THE ACIDIC ENVIRONMENT

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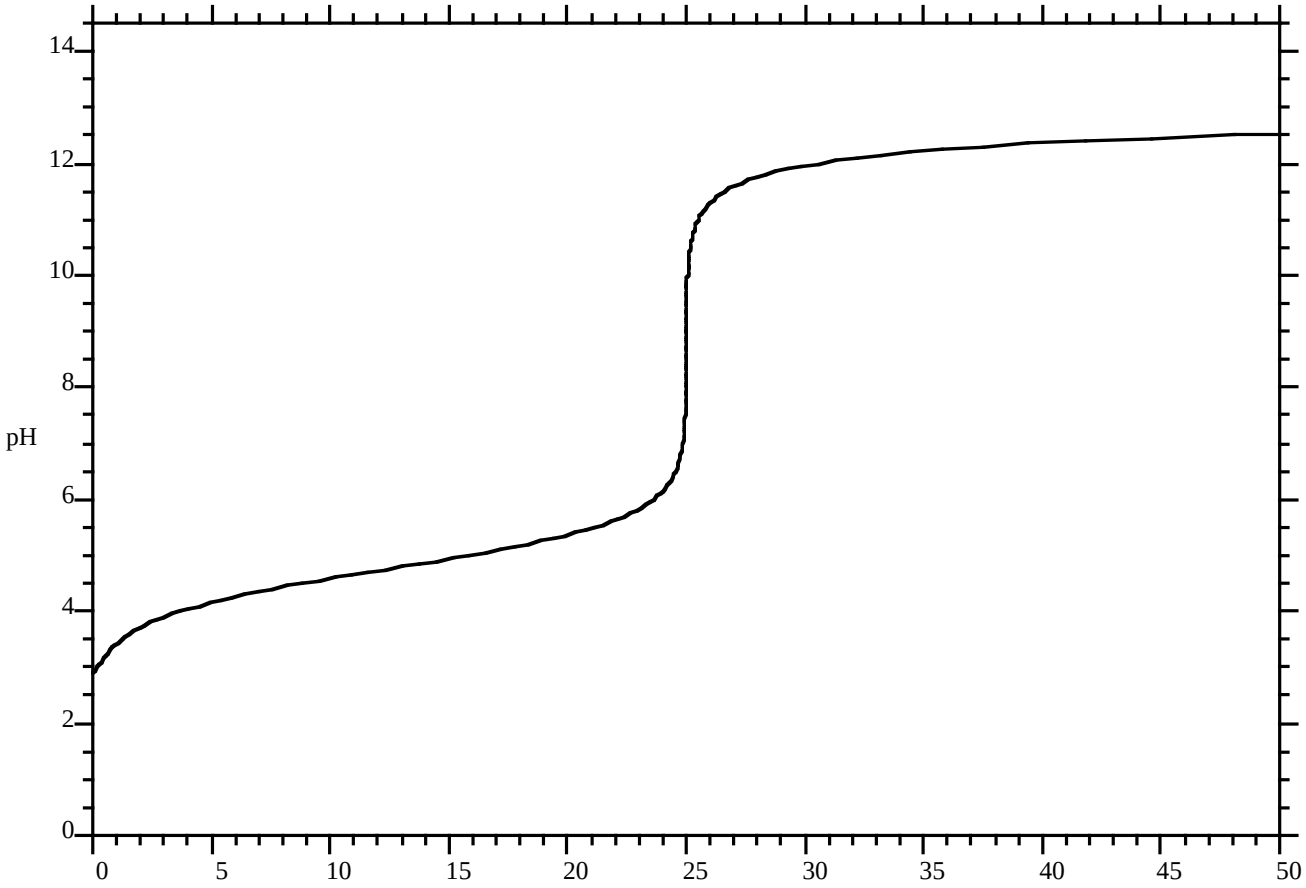


THE ACIDIC ENVIRONMENT

Overall content of this module:

Relate acid/base properties to proton transfer.
Identify the acidic oxides that are found in the atmosphere.
Recall the definitions of acids and bases, and place them into an historical context.
Compare the strengths of different acids.
Identify the relationships between conjugate acid/base pairs.
Identify neutralization reactions as a proton transfer reaction which is exothermic.
Discuss, and compare alkanols and alkanoic acids.
Esterification.

THE ACIDIC ENVIRONMENT

GENERAL CHEMISTRY CONCEPTS

Solutions and solubility

Electrolytic strength: Strong, weak and non-electrolytes

Acids as proton donors, bases as proton acceptors

Equilibrium concepts and Le Chatelier's Principle

Periodic trends of acid/base properties

$pH = -\log_{10}[H^+]$

H-bonding and dispersion forces in organic compounds: explaining physical (macro) properties based on interactions between molecules

Catalysis in organic chemistry, using esterification as an example

THE ACIDIC ENVIRONMENT

Relationship to the previous syllabus

The materials for The Acidic Environment were dispersed through the previous syllabus. Some of the material from the previous syllabus that is applicable to this topic can be found under these headings.

Core 6 water is weakly ionized

Core 8 H-bonding, dispersion forces and their relationship to physical properties; solubility

Core 9 write K_a for a given acid; K_a value can be interpreted in terms of acid strength

Core 10 acids and bases; strengths of acids can be compared by the extent of their proton transfer to water forming aqueous hydrogen ions; the pH scale; importance of pH in many natural systems — qualitative description of buffers only

Elective 4 Chemistry and the Environment —— the atmosphere

RELATIONSHIP TO OTHER MODULES

The acidic environment uses concepts from the following:

earth	
metal	
water	dissociation of water
energy	enthalpy of reaction
materials	
monitoring	Lewis diagrams (electron dot formulae)

THE ACIDIC ENVIRONMENT

General perspective on the content of the acidic environment:

Many industrial processes involve acids and bases,
eg. the manufacture of detergents involves addition of acid followed by addition of an appropriate base;
in plating metals the metal is often pickled in an acid solution to ensure that the surface of the metal is free of any oxide layer;
acid is added to many processed foods to prevent spoilage.

THE ACIDIC ENVIRONMENT

Many biochemical processes are extremely sensitive to changes in pH.

eg. oxygen transfer in blood is sensitive to pH;

digestion of food requires that the pH of the stomach be maintained at a very low level, and the pH is increased as the food moves into the small intestine, to ensure that the enzymatic processes that occur in the stomach and in the small intestine can occur;

THE ACIDIC ENVIRONMENT

Many biological compounds are acids or esters that can be formed by the reaction of an acid with an alkanol.

vinegar is acetic (ethanoic) acid

citric acid is 2-hydroxypropane-1,2,3-tricarboxylic acid

vitamin C is L-ascorbic acid

fats are triglycerides formed from the esterification of 1,2,3-propanetriol with organic acids

THE ACIDIC ENVIRONMENT

The atmosphere contains acidic oxides of carbon, nitrogen and and sulfur. The release of these gases into the atmosphere can have profound effects on the environment.

eg. acid rain;

the greenhouse effect;

the equilibrium between atmospheric and oceanic levels of carbon dioxide and the consequences of disturbances to this natural equilibrium.

1

Indicators were first identified with the observation that the colour of some flowers depends on the soil composition.

Fig. 19.4 Silberberg, Chemistry 2nd ed 2000, McGraw

THE ACIDIC ENVIRONMENT

The classic case is the colour of hydrangea which depends on the pH of the soil.

The pH of these agents could be tested by using universal indicator solutions.

Generally, the fertility of soil is closely related to its pH (see Table 1).

THE ACIDIC ENVIRONMENT

Table 1

Under natural conditions hydrogen ions from rain, plant roots, biological decay and microbial activity can displace calcium and other metal ions from soil. The soil becomes more acidic and the fertility of the soil is reduced. The accompanying table shows the pH values below which plant growth is restricted.

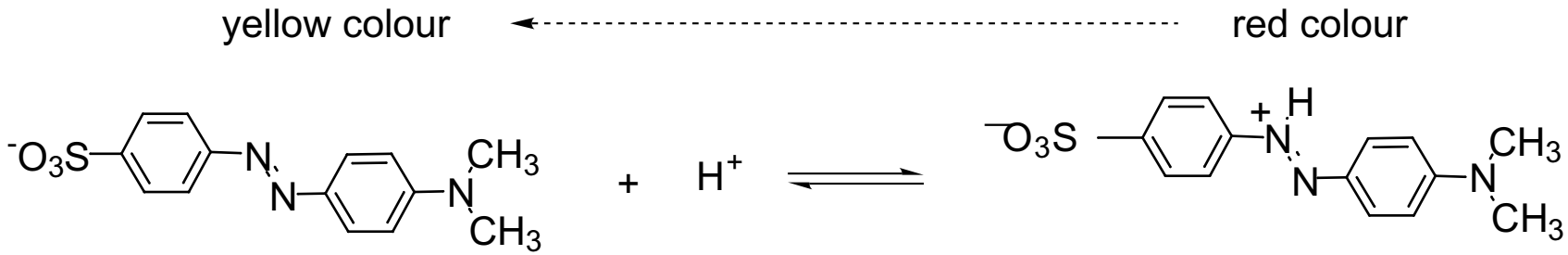
Crop	pH
potatoes	4.9
apples	5.0
oats	5.3
cabbages	5.4
wheat	5.5
blackcurrants	6.0
beans	6.0
lettuces	6.1

THE ACIDIC ENVIRONMENT

Classify common substances as acidic, basic or neutral (see Table 2)

Identify that indicator colour changes can be used to determine the acidic or basic nature of a material.

methyl orange will be yellow in basic solution



methyl orange will be red in acidic solution

Table 18.1, Silberberg, Chemistry 2nd, 2000, McGraw

THE ACIDIC ENVIRONMENT

Table 2 pH value of some common substances

substance	pH	substance	pH	substance	pH
stomach acid	1.7				
lemon juice	2.3	vinegar	2.8	soft drinks	2.9
apples	3.2	orange	3.5		
grapes	4.0	juice	4.2		
bread	5.6	tomatoes			
urine	6.0		6.4	rain water	6.5
pure water	7.0	milk	7.4		
sea water	8.5	human			
milk of magnesia	10.5	blood			

2

While we usually think of the air around us as neutral, the atmosphere naturally contains acidic oxides of carbon, nitrogen and sulfur. The concentrations of these acidic oxides have been increasing since the industrial revolution.

THE ACIDIC ENVIRONMENT

Identify oxides of non-metals which act as acids and describe the conditions under which they act as acids

There are many criteria that can be used to classify elements into the three broad categories of metals, non-metals and semi-metals (or metalloids).

Categorising the elements based on the acid/base properties is one of the most useful.

In general, the oxides, hydroxides, oxo-hydroxo compounds of non-metals are acidic.

The easiest oxide to test is carbon dioxide.

THE ACIDIC ENVIRONMENT

Carbon dioxide is acidic.

Demonstrations:

Students blow through a straw into a very dilute solution of sodium hydroxide.

For example, add a few drops of 0.100 M NaOH to a 100 mL of water. Add 1-3 drops of phenolphthalein to this solution. It should be faintly pink. After blowing through the solution, the pink colour will fade and a colourless solution will remain.

THE ACIDIC ENVIRONMENT

Alternatively, dry ice (carbon dioxide) is great fun.

To a 500 mL measuring cylinder add about half a litre of 0.05 M NaOH solution with a few drops of universal indicator. Note the colour of the solution.

Add a few pellets of dry ice (caution, wear a pair of gloves), note and give reasons for the colour changes

THE ACIDIC ENVIRONMENT

Phosphorus(V) oxide (P_4O_{10}) is perhaps the only other acidic oxide that can be readily obtained. Whilst phosphorus(V) oxide is a hazardous material, the risk to students can be minimised either by ensuring that only small amounts of the material are presented to the students (that is that the laboratory staff, prepare sample tubes that contain only a small amount of material, say 0.05 to 0.10 g) or that the reaction between phosphorus(V) oxide and water is performed as a demonstration and the resulting solution is distributed to amongst the students for subsequent tests.

(Dick Alliband suggested an alternative: burn red phosphorus in a gas jar. Add water to the oxide. Test the resultant solution.)

** Note: burn the phosphorus in the fume cupboard. Exercise caution.*

THE ACIDIC ENVIRONMENT

Analyse the position of these non-metals in the Periodic table and generalize about the relationship between position of the elements in the Periodic table and acidity/basicity of oxides

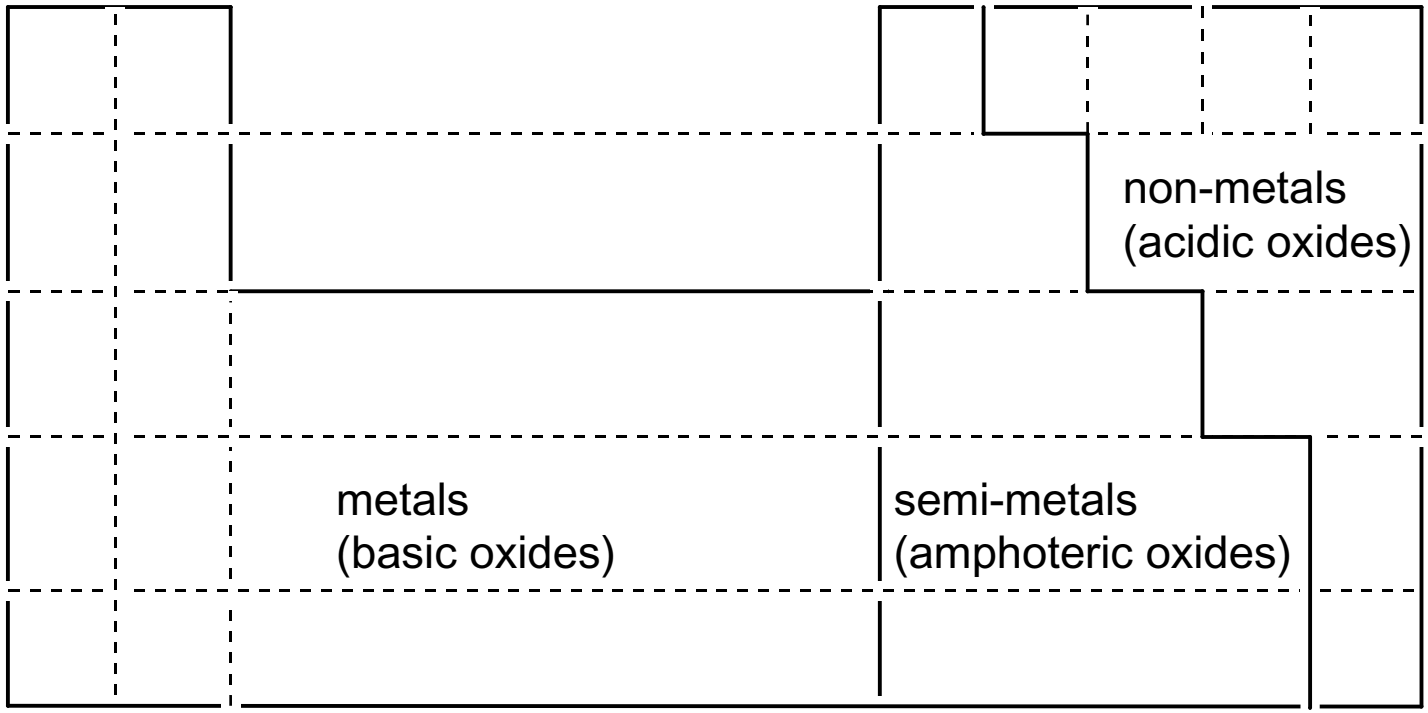
Categorising the elements based on the acid/base properties is one of the most useful. It can be shown that the oxides, hydroxides, oxo-hydroxo compounds of metals are basic.

This can be demonstrated by showing that calcium oxide is slightly soluble in water.

It would be interesting to go further and demonstrate that the oxides, hydroxides, oxo-hydroxo compounds compounds of the semi-metals are amphoteric.

THE ACIDIC ENVIRONMENT

The acidity or basicity of the oxides of the elements can be related to the position of the element in the periodic table as shown below:



THE ACIDIC ENVIRONMENT

Definite Le Chatelier s principle

If a chemical system at equilibrium is disturbed by an external stress, the reaction will shift to minimize the stress so as to restore equilibrium.

Identify factors which can affect the equilibrium in a reversible reaction

Possible to change the ratio of products to reactants by changing the external conditions.

1. Adding or removing a product.
2. Changing the volume of the system (associated with a change in pressure)
3. Changing the temperature

THE ACIDIC ENVIRONMENT

Describe the solubility of carbon dioxide in water under various conditions as an equilibrium process and relate this to Le Chatelier s principle

A saturated solution of carbon dioxide in water at 1 atm and 298K contains about 0.034 mol $L^{-1} CO_2$.

Only approximately one out of every 400 CO_2 molecules reacts with water to give carbonic acid.

Carbonic acid is a weak acid that dissociates to give hydrogen ion and hydrogencarbonate ion. The equilibria that are involved are shown below:

THE ACIDIC ENVIRONMENT

$CO_2(g) \rightleftharpoons CO_2(aq) \qquad \Delta H = -19 \text{ kJ mol}^{-1}$

Solubility of a gas is directly proportional to the partial pressure of the gas above the solution

$S_{gas} = k_H \times P_{gas}$

where k_H for CO_2 at 298K is 3.3×10^{-2} mol L^{-1} atm

THE ACIDIC ENVIRONMENT

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

$$K = \frac{[H_2CO_3]}{[CO_2]} = \frac{1}{400} = 2.5 \times 10^{-3}$$

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

$$K_{a1} = \frac{[H^+]\,[HCO_3^-]}{[H_2CO_3]} = 4.5 \times 10^{-7}$$

THE ACIDIC ENVIRONMENT

Identify natural and industrial sources of sulfur dioxide and oxides of nitrogen

Natural:

sulfur dioxide, SO_2. Colourless, choking gas formed in volcanoes or whenever a sulfur containing compound (coal, oil, sulfide ores) is burned.

nitric oxide, NO. Colourless gas; biochemical messenger.

nitrogen dioxide, NO_2. Orange-brown gas.

Industrial:

oxidation of SO_2 to SO_3 by the contact process.

oxidation of NH_3 to NO and NO to NO_2.

THE ACIDIC ENVIRONMENT

Describe, using equations, examples of chemical reactions which release sulfur dioxide and chemical reactions which release oxides of nitrogen

$H_2S(g) + 2\ O_2(g) \longrightarrow SO_2(g) + S(g) + 2\ H_2O(g)$

$S(s) + O_2(g) \longrightarrow SO_2(g)$

$N_2(g) + O_2(g) \longrightarrow 2\ NO(g)$ (car engine)

$2\ NO(g) + O_2(g) \longrightarrow 2\ NO_2(g)$

$3\ NO(g) \longrightarrow N_2O(g) + NO_2(g)$

$2\ NH_3(g) + 5\ O_2(g) \longrightarrow 4\ NO(g) + 2\ H_2O(g)$

THE ACIDIC ENVIRONMENT

Assess the evidence which indicates increases in atmospheric concentration of oxides of sulfur and nitrogen

Calculate volumes of gases given masses of some substances in reactions, and calculate masses of substances given gaseous volumes, in reactions involving gases at $0^{o}C$ and 101.3 kPa or $25^{o}C$ and 101.3 kPa

The relationship between the volume of gas and the mass of gas can be obtained by considering the relationship between mass and number of moles and volume of gas and number of moles

Molar volume of gas = 22.44 L at 273K and 101.3 kPa
= 24.45 L at 298K and 101.3 kPa

$$\text{mol of gas} = \frac{\text{mass of gas A}}{\text{molar mass of gas A}} = \frac{\text{volume of gas A}}{\text{molar volume of gas A}}$$

THE ACIDIC ENVIRONMENT

Explain the formation and effects of acid rain

1. Sulfurous acid

   SO_2, formed from burning high-sulfur coal, comes in contact with water

2. Sulfuric acid

   SO_3, from the atmospheric oxidation of SO_2 by ozone or oxygen, comes in contact with water

3. Nitric acid

   nitrogen oxides (NO_x). NO, formed by combustion (car engines), and it forms NO_2 in air. Rain water converts NO_x to HNO_2 and HNO_3.

   Rain water is acidic, due to the dissolved carbon dioxide, has a pH value of about 5.6. Acid rain has been known to have a pH value of between 1.6 -1.8.

THE ACIDIC ENVIRONMENT

Effects of acid rain

- most fishes and shell-fishes die at pH values between 4.5-5.0
- the acid rain removes the protective waxes from leaves surfaces
- acid rain dissolves the calcium carbonate from marble and limestone of building and monuments
- acid rain causes ion exchange with the soil

Fig 19.B, Silberberg, Chemistry 2nd, 2000, McGraw

3

Acids occur in many foods, drinks and even within our stomach

General discussion of acids in society and in the environment.
Mention that many foods have either acetic acid (ethanoic acid), citric acid or benzoic acid (food acid) added as preservative.
Illustration—manyfresh fruits are preserved by lemon juice (citric acid).

THE ACIDIC ENVIRONMENT

Define acids as proton donors and describe the ionization of acids in water

Arrhenius

Acids species that increase proton concentrati on in water.

$$HA + H_2O \rightleftharpoons \underset{\text{hydronium ion}}{H_3O^+} + A^-$$

THE ACIDIC ENVIRONMENT

Identify acids such as acetic acid (ethanoic acid), citric acid (2-hydroxypropane-1,2,3-tricarboxylic acid), vitamin C and hydrochloric acid as naturally occurring acids, and acids such as sulfuric acid and hydrobromic acids as manufactured acids

THE ACIDIC ENVIRONMENT

Describe the use of the pH scale in comparing the concentrations of acids and alkalis

pH scale

Defined as $pH = - \log_{10} [H^+]$

pH scale ranges from 1-14

For pure water

$pH = - \log_{10} [10^{-7}] = 7.0$ defined as being ***neutral***.

Fig 18.6, Silberberg, Chemistry 2nd, 2000, McGraw

THE ACIDIC ENVIRONMENT

Describe acids and their solutions with the appropriate use of the terms strong, weak, concentrated and dilute

Students will need to be aware of the common strong acids and the common weak acids. The best preparation is that they "learn by rote" the names and formulae of the strong acids. The five strong acids that have appeared most commonly in previous HSC examinations are:

nitric acid (HNO_3), sulfuric acid (H_2SO_4), hydrochloric acid (HCl), hydrobromic acid (HBr) and hydriodic acid (HI).

THE ACIDIC ENVIRONMENT

Strong acids are acids that are essentially completely dissociated in aqueous solution. These acids are not involved in an equilibrium with hydrogen ion.

$$HNO_3(aq) \longrightarrow H^+(aq) + NO_3^-(aq)$$

All other acids that are encountered can be considered to be weak acids, and hence be involved in an equilibrium process:

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

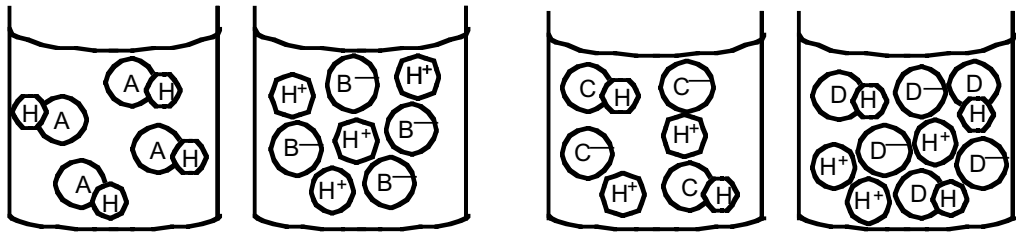


Fig 18.3, Silberberg, Chemistry 2nd, 2000, McGraw

THE ACIDIC ENVIRONMENT

Identify pH as - $\log_{10}[H^+]$ and explain that a change in pH of 1 means a ten-fold change in $[H^+]$

THE ACIDIC ENVIRONMENT

Compare the relative strengths of equal concentrations of citric, acetic and hydrochloric acids and relate this to the degree of ionization of their molecules

This could be difficult.

Not sure how much equilibrium the students have completed.

Can be done as an experiment, or as a classroom demonstration. Simply take a solution of each acid and measure the pH.

Students are also expected to plan and perform a first hand investigation to measure the pH of identical concentrations of strong and weak acids.

THE ACIDIC ENVIRONMENT

The degree of ionisation is dependent on the concentration of each weak acid. The stronger the acid the greater the degree of ionisation.

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

$$K_a = \frac{[H^+]\,[A^-]}{[HA]_{initial}}$$

$$\text{Degree of ionization} = \frac{[H^+]}{[HA]_{initial}}$$

THE ACIDIC ENVIRONMENT

acid	pK_a	degree of dissociation (of 0.50 M acid solution)
acetic acid (ethanoic acid)	weak acid 4.76	$\frac{0.030}{0.50} = 0.0060$
hydrochloric acid	strong acid no pK_a	$\frac{0.50}{0.50} = 1.0$

THE ACIDIC ENVIRONMENT

Describe the difference between a strong and a weak acid in terms of an equilibrium between the intact molecule and its ions

4

Because of the prevalence and importance of acids, they have been used and studied for hundreds of years. Over time, the definitions of acid and base have been refined

THE ACIDIC ENVIRONMENT

Outline the historical development of ideas about acids including those of

Arrhenius	acids are compounds that in aqueous solutions increase the concentration of hydrogen ions
Lavoisier	acids contain oxygen. Oxygen means "sharp forming", a reference to the sharp taste of acids.
Davy	demonstrated that oxymuriatic acid (hydrochloric acid) did not contain oxygen and thus Lavosier's definition of acids must be incorrect
Liebig	argued that some acid did not contain hydrogen.

THE ACIDIC ENVIRONMENT

Outline the Bronsted-Lowry theory of acids and bases

More general

Acids species that donate a proton.

Bases species that accept a proton.

Neutralization transfer of proton.

Conjugate acid/base pair HA and A^-

$$HA \rightleftharpoons H^+ + A^-$$

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

conjugate acid — hydronium ion — conjugate base

THE ACIDIC ENVIRONMENT

Describe the relationship between an acid and its conjugate base and a base and its conjugate acid

The statement that the conjugate acid of a weak base a strong acid is not true.
The conjugate acid of the weak base, ammonia, is ammonium ion.
Ammonium ion is a weak acid.
The statement that the conjugate base of a weak acid is a strong base is not true.
The conjugate base of the weak acid, carbonic acid, is hydrogencarbonate ion. Hydrogencarbonate ion is a weak base.

Fig 18.9, Silberberg, Chemistry 2nd, 2000, McGraw

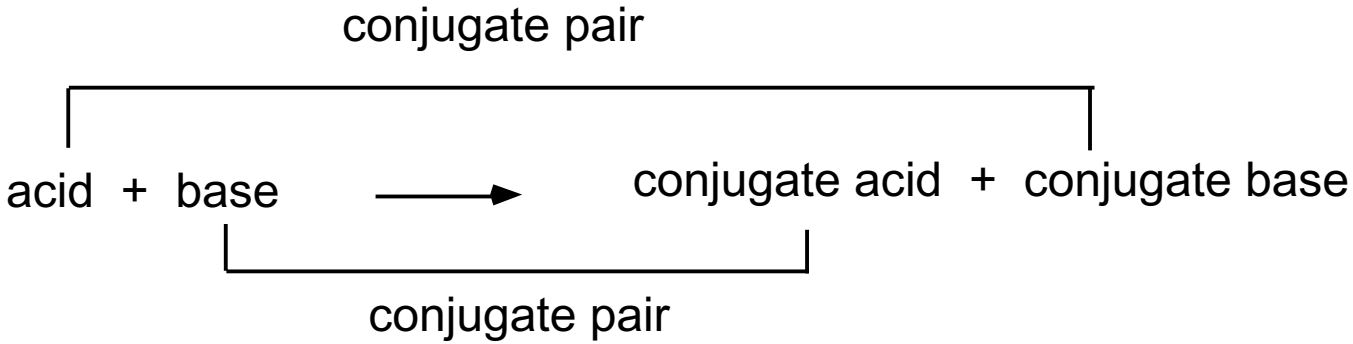
THE ACIDIC ENVIRONMENT

Identify a range of salts which forms acidic, basic, or neutral solutions and explain their acidic, neutral or basic nature

NaCl	neutral
NH_4Cl	acidic
NaF	basic

THE ACIDIC ENVIRONMENT

Identify conjugate acid/base pairs



THE ACIDIC ENVIRONMENT

Identify amphiprotic substances and write equations to describe their behaviour in acidic and basic solution

$HCO_3^-(aq)$

$H^+(aq) + HCO_3^-(aq) \rightleftharpoons H_2CO_3(aq)$

$OH^-(aq) + HCO_3^-(aq) \rightleftharpoons CO_3^{2-}(aq) + H_2O(l)$

THE ACIDIC ENVIRONMENT

Outline the Lewis definition of an acid

Acids electron pair acceptors

Bases electron pair donors

Neutralization formation of a covalent bond.

$BF_3 + :NH_3 \longrightarrow BF_3: NH_3$

Al^{3+} is another Lewis acids

THE ACIDIC ENVIRONMENT

Assess the importance of each definition in terms of understanding

Lavoisier

Davy

Arrhenius

Bronsted

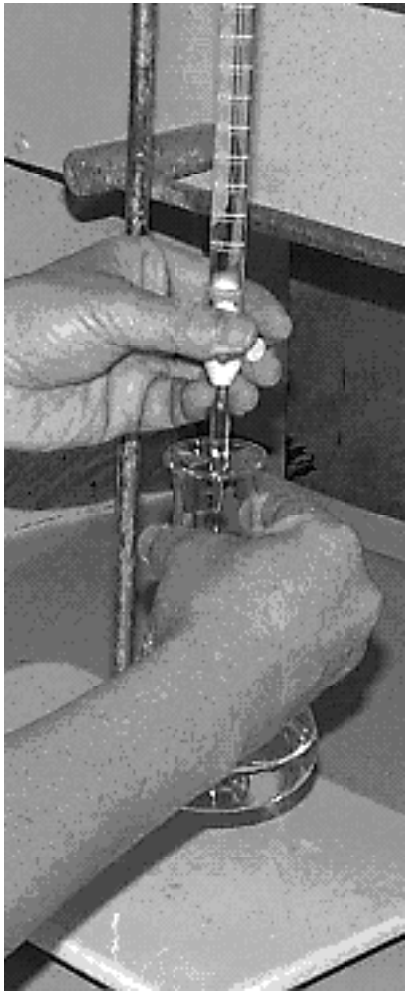
Lewis

THE ACIDIC ENVIRONMENT

Identify neutralization as a proton transfer reaction which is exothermic

THE ACIDIC ENVIRONMENT

Describe the correct technique for conducting titrations and preparation of standard solutions



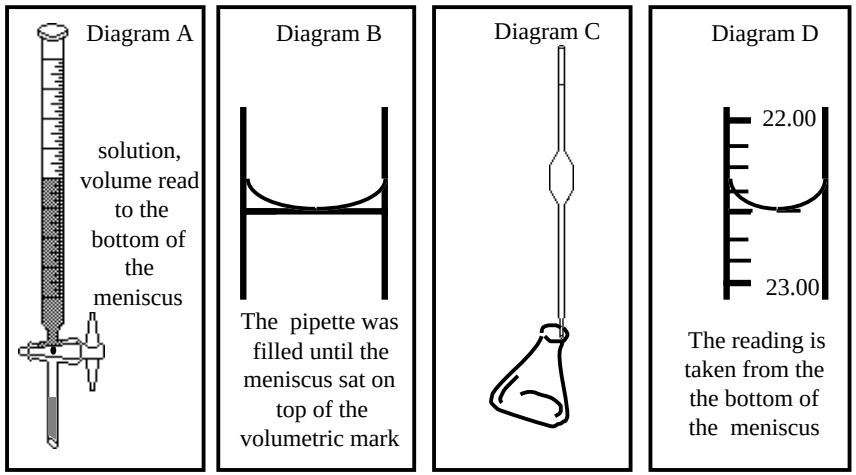
THE ACIDIC ENVIRONMENT

Titrations

equipment

correct choice of indicators

end point vs equivalence point



THE ACIDIC ENVIRONMENT

Qualitative describe the effect of buffers with reference to specific examples in a natural system

buffers resist changes in pH

blood

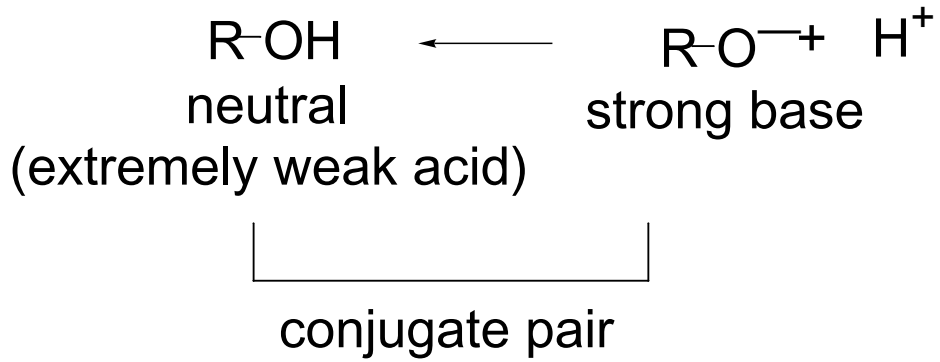
5

Esterification is a naturally occurring process which can be modelled in the laboratory

THE ACIDIC ENVIRONMENT

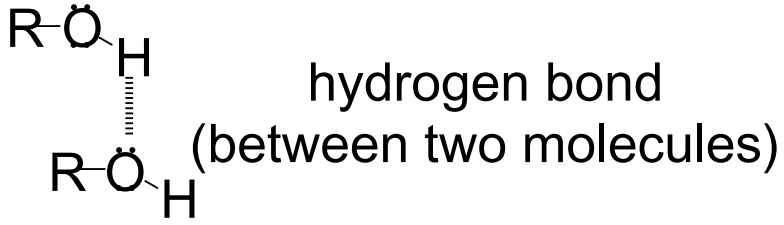
Describe the differences between the alkanol and alkanoic acid functional groups in carbon compounds

The functional group present in alkanols is the hydroxyl group (—OH).
Alkanols form neutral solutions with water, (alkanols are hydroxo compounds of carbon).



THE ACIDIC ENVIRONMENT

The presence of the highly polarised oxygen to hydrogen bond in alkanols means that alkanols can form hydrogen bonds.

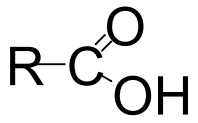


Thus alkanols have a higher boiling (or melting) point than the corresponding alkanes.

Small chain alkanols are soluble in water, long chain alkanols are insoluble in water.

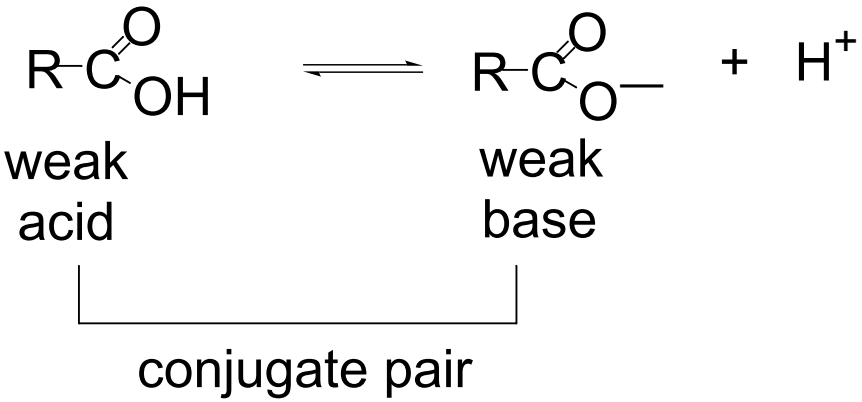
THE ACIDIC ENVIRONMENT

The functional group present in alkanoic acids is the the -COOH group



or R–COOH

Alkanoic acids are weak acids (as they are the oxo-hydroxo compounds of carbon).



THE ACIDIC ENVIRONMENT

Explain the difference in melting point and boiling point caused by the alkanoic acid and alkanol functional groups

mainly due to the strength of the intermolecular forces of attraction

hydrogen bonding

THE ACIDIC ENVIRONMENT

Identify esterification as the reaction between an acid and an alkanol and describe, using equations, examples of esterification

THE ACIDIC ENVIRONMENT

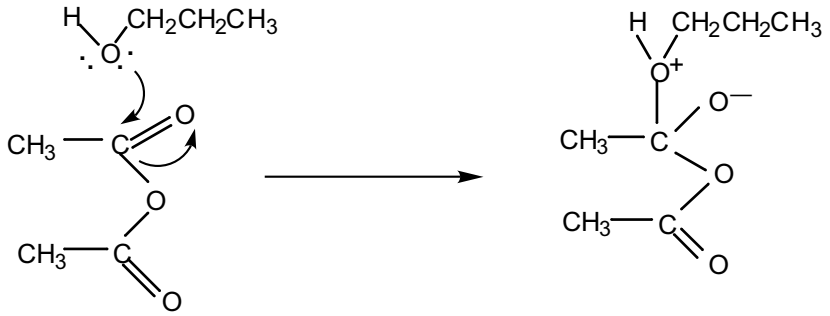
Describe the purpose of using concentrated sulfuric acid in esterification for catalysis and absorption of water

Sulfuric acid is used as a catalyst in the esterification reaction.

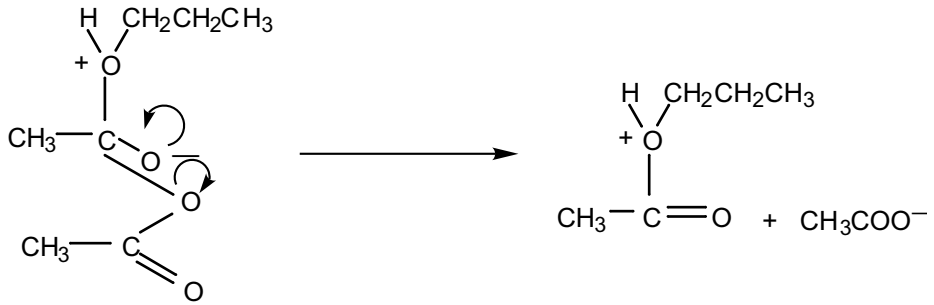
If sufficient sulfuric acid is added to absorb significant quantities of water, then the alkanol will dehydrate to give the alkene (alkanol plus concentrated acid gives alkene plus water) or the ether will form.

If sulfuric acid is replaced by any other reagent capable of absorbing water (say anhydrous copper(II) sulfate) no reaction is observed. The idea that sulfuric acid absorbs water is wrong, as only catalytic amounts of sulfuric acid should be added.

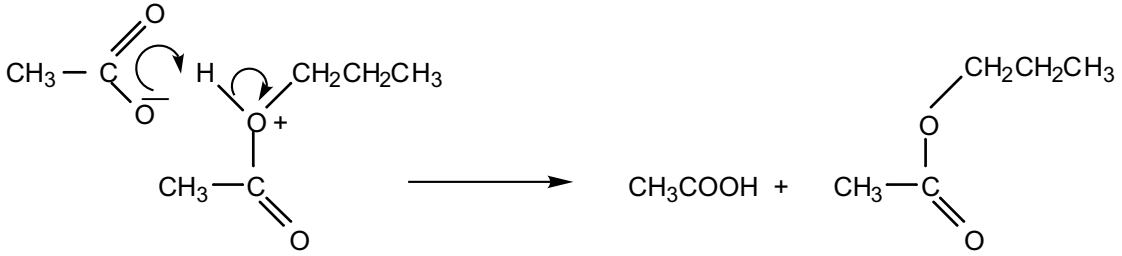
The mechanism by which the reaction occurs is believed to involve initial attack by the alcohol at one of the unsaturated carbon atoms:



This intermediate can then decompose with loss of CH_3COO^-:



Finally, loss of proton can occur to give the final ester:



THE ACIDIC ENVIRONMENT

Explain the need for heating under reflux during esterification

Reactions are heated under reflux conditions as this allow the maximum temperature to be reached (the boiling point of the mixture) and ensures that the vapours produced on boiling are condensed and returned to the flask, rather than escaping into the laboratory. Students should be reminded that the reaction rate of all reactions is increased by temperature (from energy module).

THE ACIDIC ENVIRONMENT

Outline some examples of the occurrence, production and uses of esters

Alkanoate (esters) are important for their use as polymers, adhesives, flavouring compounds, industrial solvents. They are prepared from the reaction between alkanoic acids and alkanols. Esters are named as derivatives of alkanoic acids, in much the same way as inorganic derivatives. Consider the methyl ester of ethanoic acid and the sodium salt of ethanoic acid.

CH_3CO_2Na sodium ethanoate

The anion name is formed by dropping the ic acid and adding oate ie., ethanoic acid forms ethanoate ion

$CH_3CO_2CH_3$ methyl ethanoate

whilst an anion is not formed, the same nomenclature is used.
A very important class of naturally occurring esters are fats (the long term store of energy for most animals and plants). Fats are triesters of 1,2,3-propanetriol.