

Chemistry in your cupboard: Cillit Bang

Introduction

Dirt and stains can be categorised according to their constituents into water-soluble, particulate, fats/oils, proteins/carbohydrates and oxidisable components, although the majority of cases will contain a mixture of these. There is no one product that can remove all dirt; the Cillit Bang brand covers a wide range of cleaners which use a variety of chemical methods to remove dirt and stains.

Links to the curriculum

This section contains information relevant to the following areas of your chemistry curriculum:

- Group 1 elements
- Bonding
- Weak acids

CILLIT BANG

Not all dirt is the same, so removing different types of dirt will require a range of different types of cleaners. The Cillit Bang family of cleaners uses a variety of chemical methods to remove dirt and stains. Table 1 shows examples of a number of types of dirt and stains.

Water-soluble	Particulate	Fats/oils	Proteins/ Carbohydrates	Oxidizable
Inorganic salts	Metal oxides	Vegetable oil	Blood	Fruits
Sugar	Clays	Animal fat	Egg	Vegetables
Urea	Carbon	Human sebum	Milk	Wine
		Waxes	Starches	Coffee/Tea

Table 1: Types of dirt and stains

*Cillit Bang is a registered trade mark of the Reckitt Benckiser group of companies.
Last reviewed by Reckitt Benckiser in 2013.*

Some types of cleaning agents are listed below.

- bleaches
- detergents (surfactants)
- solvents
- acids

Cillit Bang is a brand rather than a single product. It includes a range of cleaners for different types of dirt. The brand is marketed throughout the world and there are different formulations for different types of cleaning, Figure 1. The products also differ in different countries to fit people's cleaning habits and local regulations as to what components can be included.



Figure 1: Part of the Cillit Bang range of products

It would be impossible to cover every member of the Cillit Bang family here so we will look at a representative range of the different types.

The Cillit Bang range can be broken down into three main types of product

- 'Lime and Grime' range of cleaners based on acids
- Toilet cleaners – based on bleaches
- Degreasers – alkaline, based on detergents and solvents

Acid-based cleaners

Limescale is a deposit that may form around taps (particularly hot taps).

Question 1

Give two reasons why the calcium carbonate deposit forms more readily on the hot tap of a sink rather than the cold one.

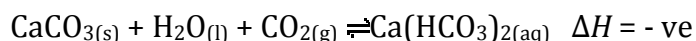
*Cillit Bang is a registered trade mark of the Reckitt Benckiser group of companies.
Last reviewed by Reckitt Benckiser in 2013.*



Figure 2: Formation of limescale deposit around leaking valves

It is composed of calcium carbonate, which is insoluble in water. It originates from dissolved calcium hydrogencarbonate, which is one of the components of hard water (see Calgon).

The hydrogencarbonate is formed when rain, naturally acidic due to dissolved carbon dioxide, dissolves calcium carbonate (limestone) as it seeps through the ground before being collected in a reservoir, for example.



When drops of hard water are left on a surface, the water evaporates and the above equilibrium moves to the left to leave insoluble calcium carbonate - a whitish deposit.

Calcium carbonate is virtually insoluble in water but it is soluble in acids (as we have seen when limestone rock dissolves in acidic rain). Strictly, the calcium carbonate is not dissolving, it is reacting with the acid. So, an acid-based product will be effective in dissolving limescale.

Cillit Bang Lime and Grime (1 of 2)

This family of cleaners is based around a formulation containing acids including the following

- Sulfamic acid (HOSO_2NH_2) $pK_a = 0.99$
- Formic acid (HCOOH) $pK_a = 3.8$
- Phosphoric acid (H_3PO_4) $pK_{a1} = 2.1$; $pK_{a2} = 7.20$; $pK_{a3} = 12.38$

They are all weak acids and the equations for their dissociations are shown in Figure 3.

*Cillit Bang is a registered trade mark of the Reckitt Benckiser group of companies.
Last reviewed by Reckitt Benckiser in 2013.*

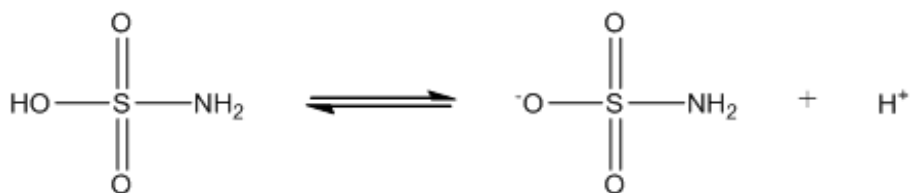


Figure 3a: Dissociation of sulfamic acid

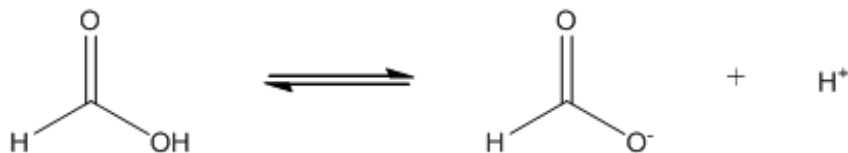


Figure 3b: Dissociation of formic acid

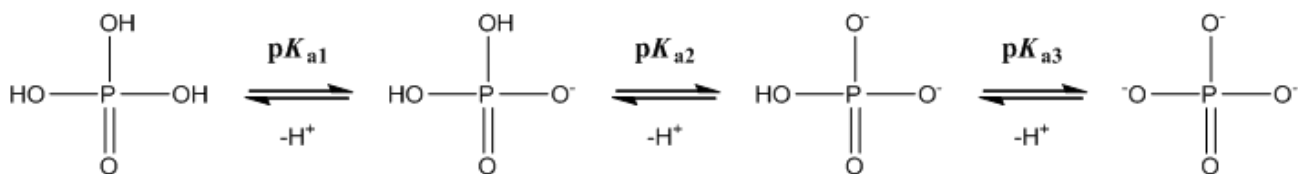


Figure 3c: Dissociation of phosphoric acid

The pK_a value is a measure of the strength of an acid (how easily a H^+ ion is lost). The larger the pK_a value, the *weaker* the acid.

Question 2

Sulfamic, formic and phosphoric acids are all weak acids. Explain the difference between a weak acid and a strong acid.

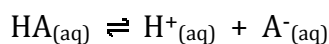
Question 3

What is the systematic name of formic acid?

Cillit Bang Lime and Grime (2 of 2)

Weak acids

Imagine a weak acid, HA, which dissociates



The equilibrium constant is given by:

$$K_c = \frac{[H^+_{(aq)}]_{eqm} [A^-_{(aq)}]_{eqm}}{[HA_{(aq)}]_{eqm}}$$

For a weak acid, this is usually given the symbol K_a and called the acid dissociation constant.

$$K_a = \frac{[H^+_{(aq)}]_{eqm} [A^-_{(aq)}]_{eqm}}{[HA_{(aq)}]_{eqm}}$$

$$pK_a = -\log_{10}K_a$$

(This is analogous with $\text{pH} = -\log_{10}[\text{H}^+]$)

The larger the value of K_a , the stronger the acid and the greater the concentration of H^+ it produces on dissociation. However, because of the negative sign in the expression above, the larger the value of pK_a , the *weaker* the acid.

Phosphoric acid has three acidic hydrogens (ones which can be lost as H^+ ions or protons).

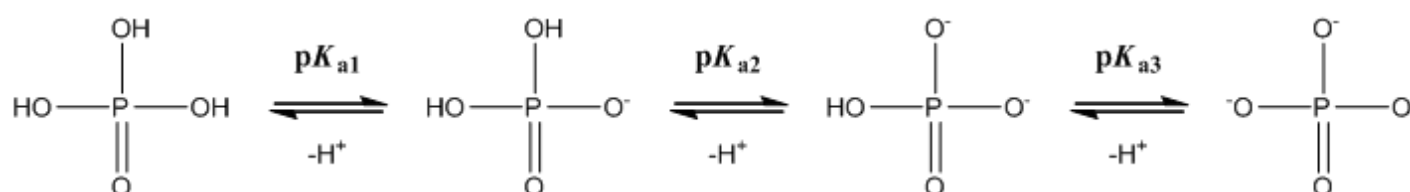


Figure 4: Dissociations of phosphoric acid

Question 4

Explain why the pK_a values get larger for the second and third dissociations of phosphoric acid.

The pK_a values for the dissociations show that it gets successively harder to lose the second and third H^+ ions.

Question 5

- Explain why, when formic acid dissociates, the hydrogen atom bonded to an oxygen atom is the one lost as a H^+ ion rather than the one bonded to the carbon atom.
- The pK_a of formic acid is 3.8, what is the value of K_a ? Give the correct units.
- Write an expression for K_a of formic acid (represent the acid as HCOOH).
- Calculate the pH of a 1 mol dm^{-3} solution of formic acid.
- Compare your answer for the pH of formic acid with that of 1 mol dm^{-3} hydrochloric acid (HCl), a strong acid.

Rust

Rust is not a single compound. It is an everyday term for a mixture of iron oxides and hydroxides formed by the oxidation of iron by oxygen in the air, usually when water is present. Probably the most important constituent is iron(III) oxide with various amounts of hydration ($\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$) but there will also be hydroxides such as iron(III) hydroxide ($\text{Fe}(\text{OH})_3$).

Question 6

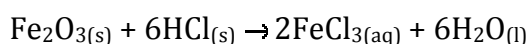
Iron also forms iron(II) oxide and iron(II) hydroxide. Give the formulae of these compounds and suggest why they are less likely to be found in rust than the corresponding iron(III) compounds.

Rust stains are common because many everyday items are made from iron. They are unsightly because iron(III) compounds are brown.



Figure 5: Example of a rust stain on fabric

Because metal oxides are basic, acid-based cleaners are used to dissolve rust stains. For example hydrochloric acid:



Notice that the starting material is solid and the product forms an aqueous solution, thus removing it from the surface.

Question 7

Write a balanced symbol equation for the reaction of iron(III) hydroxide with hydrochloric acid.

Detergents and surfactants

Acid-based cleaners also contain surfactants to lower the surface tension of water and allow them to spread more effectively over dirty surfaces.

We use surfactants to get water and grease to mix. They are molecules that are 'tadpole shaped' in that they have a non-polar 'tail' and a polar or ionic 'head'. The 'tail' can form van der Waals bonds with non-polar grease molecules whilst the 'head' can form hydrogen bonds with water. This is an example of the 'like dissolves like' rule.

There are essentially three types of surfactants - anionic, cationic and non-ionic.

*Cillit Bang is a registered trade mark of the Reckitt Benckiser group of companies.
Last reviewed by Reckitt Benckiser in 2013.*

Anionic surfactants have a negatively charged head. Common types include soaps, Figure 6, and alkylbenzene sulfonates, Figure 7.

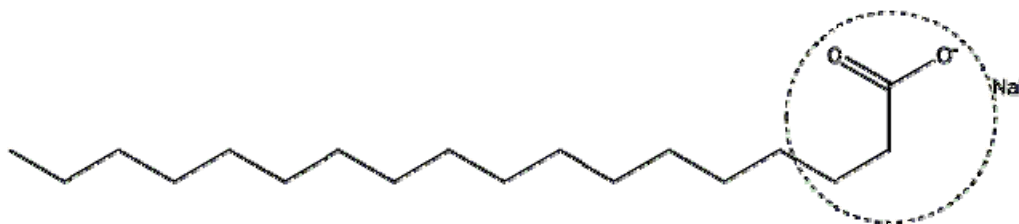


Figure 6: Sodium stearate (a soap) – an anionic surfactant

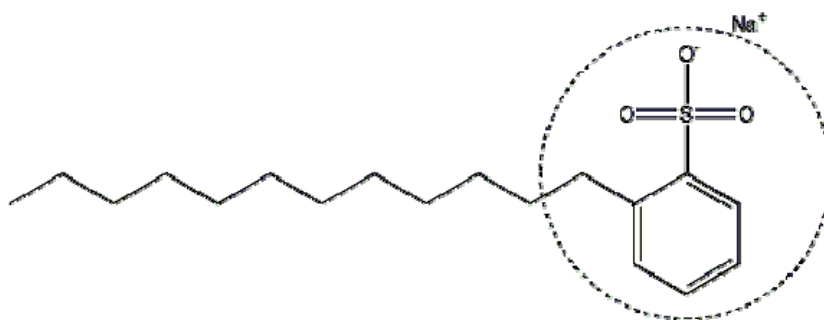


Figure 7: Sodium dodecylbenzene sulfonate – an anionic surfactant

Cationic surfactants have a positively charged head. Common types include alkyl ammonium chlorides.

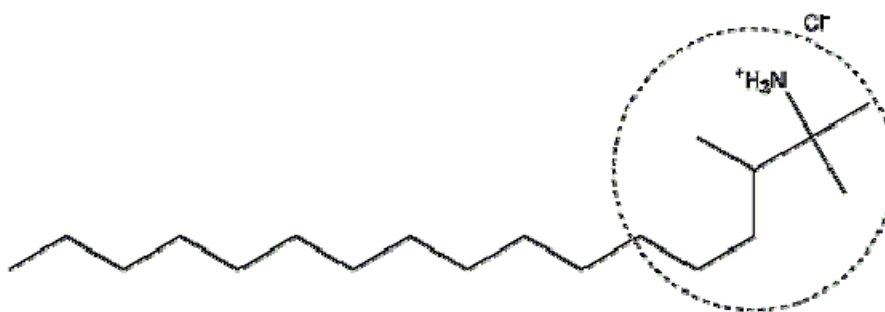


Figure 8: Trimethylhexadecyl ammonium chloride – a cationic surfactant

Non ionic surfactants have a polar, but uncharged, head. Common types include polyethylene ethoxylates.

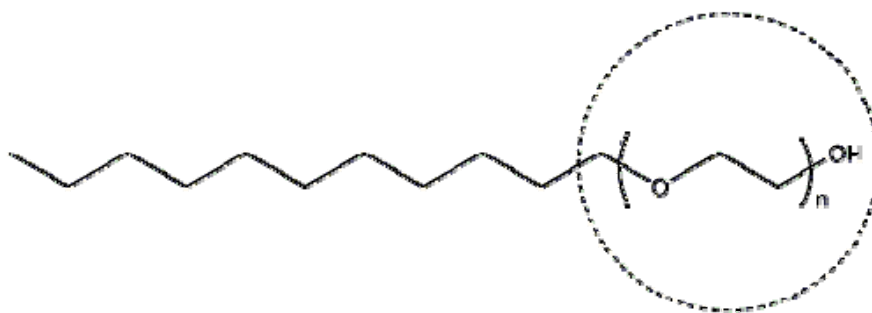


Figure 9: A polyethylene ethoxylate – a nonionic detergent

When dissolved in water, surfactants tend to cluster at the surface (hence the name), so that their non-polar tails can stick out of the water.

Question 8

Look at the molecules in Figures 6-9. Explain why the heads are polar and the tails non polar.

Cillit Bang toilet cleaners

These cleaners work by bleaching stains. They are based around a formulation containing sodium hypochlorite (NaClO) and sodium hydroxide (an alkali).

Question 9

What is the systematic name for sodium hypochlorite? Hint, work out the oxidation number (oxidation state) of the chlorine atom.

+1 is an unusually high oxidation state for chlorine - it is normally -1 in its compounds. This means that it can act as an oxidising agent, oxidising other species as it itself drops in oxidation state. This is how it bleaches and kills germs.

The actual active ingredient is chloric(I) acid (HOCl) and is formed by the reaction

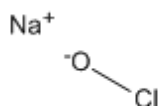
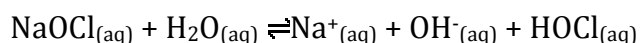
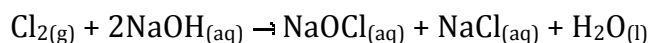


Figure 10a: Structure of sodium chlorate(I), NaClO

Sodium chlorate(I) is formed by the reaction of chlorine with sodium hydroxide



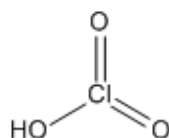
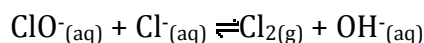


Figure 10b: Structure of chloric(I) acid, HOCl

The OH⁻ ions from the sodium hydroxide will also break down the proteins in hair, for example, (which often blocks the drains in baths and wash basins).

Limescale is often found in toilets and drains and it is tempting to add an acid-based cleaner to a bleach-based one. However, the following equilibrium exists in a bleach- and sodium hydroxide-based cleaner.



Added acid will react with the OH⁻ ions to form water and, by Le Chatelier's principle, the equilibrium will move to the right to restore the concentration of OH⁻, with the consequent formation of poisonous chlorine gas. Not a good idea!

Bleach-based cleaners also contain surfactants to lower the surface tension of water and allow them to spread more effectively over dirty surfaces (see previous page). Other bleaching systems include ones based on percarbonates (see Finish).

Cillit Bang degreasers (1 of 3)

Grease essentially consists of fats. Fats are triglycerides, that is they are esters of the triol glycerol (propane-1,2,3-triol) and three long chain fatty acids (RCOOH), where R is a hydrocarbon chain of around 15 carbon atoms, see Figure 11.

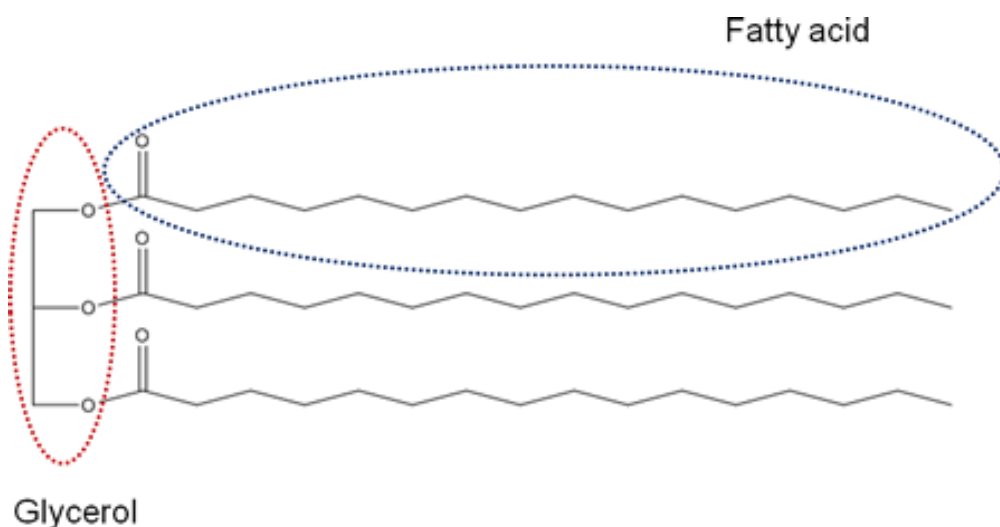


Figure 11: Fats are esters of glycerol

*Cillit Bang is a registered trade mark of the Reckitt Benckiser group of companies.
Last reviewed by Reckitt Benckiser in 2013.*

They are relatively non-polar and therefore do not mix well with water which is what makes them difficult to remove.

Degreasing cleaners, for greasy stains and baked on dirt, are based on detergents and surfactants as well as solvents. They are generally formulated to be alkaline. Grease is **saponified** under alkaline conditions - a process that itself removes grease and produces soaps that help any remaining grease to mix with water.

Hydroxide ions react with the molecules of grease and break them up into salts of fatty acids and glycerol. The reaction is shown in Figure 12 and is the same as that for making soap from fats and oils - saponification. The resulting sodium salts of fatty acids are themselves soaps and aid cleaning.

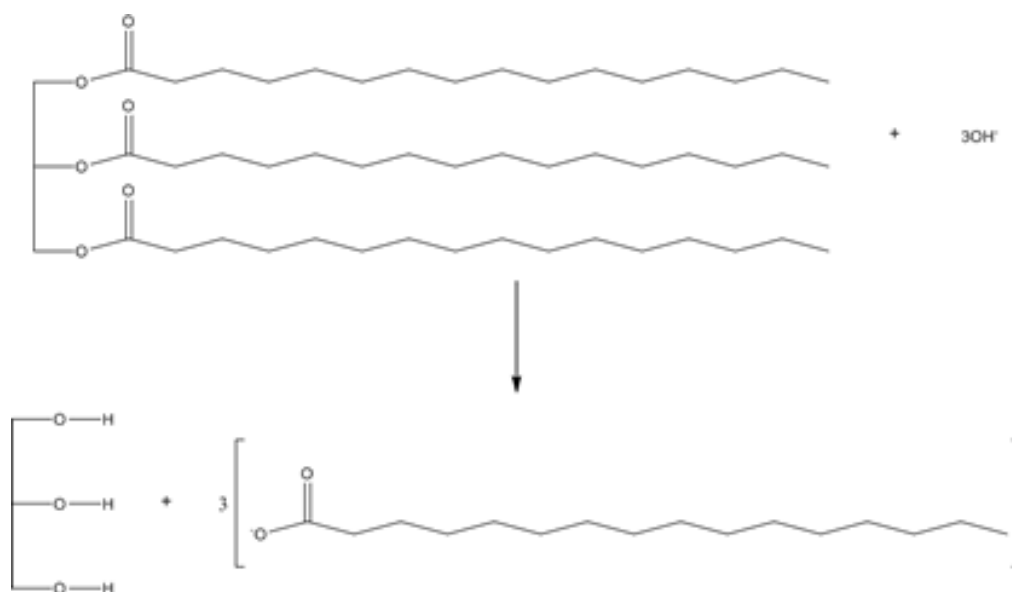


Figure 12: The saponification of grease

Cillit Bang degreasers (2 of 3)

One formulation of Cillit Bang degreaser includes the following active ingredients (the names are non-systematic):

- A long-chain amine oxide
- Ethanolamine
- Glycol ethers

Perfume and, sometimes, dye is also added to make the product more attractive to the consumer.

We'll look briefly at the chemistry and functions of these below.

Amine oxides

Amine oxides, Figure 13, are surfactants - they have the classic 'tadpole-shaped' molecule with a polar head and a non-polar tail (see Detergents and surfactants). The

tail can mix with non-polar grease molecules and the head with polar water molecules thus promoting mixing of grease and water. It also reduces the surface tension of water and allows water to 'wet' surfaces more effectively, that is to spread over them.

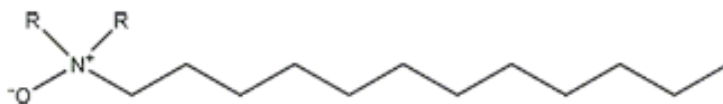


Figure 13: Structure of an amine oxide – the length of the hydrocarbon chain may vary

Ethanolamine

Ethanolamine is a solvent. It has the formula shown in Figure 14.

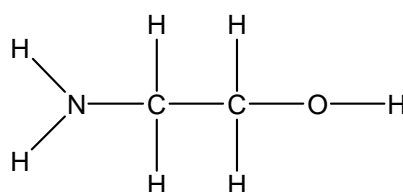


Figure 14: Structure of ethanolamine

Question 10

What is the systematic name of ethanolamine?

Question 11

- What two functional groups does ethanolamine have?
- Which of these groups is significantly basic?

As well as acting as a solvent, ethanolamine raises the pH of the product, making it more alkaline.

Question 12

- Write an equation for the reaction of ethanolamine with water to show how ethanolamine makes the product more alkaline.
- What feature of the ethanolamine molecule makes this reaction possible?

Question 13

The oxygen atom of ethanolamine also has a lone pair of electrons. Explain why it is the lone pair of electrons on the nitrogen atom rather than that on the oxygen atom that is donated to a proton.

Cillit Bang degreasers (3 of 3)

Glycol ethers

Glycol phenyl ethers are water soluble solvents. They penetrate grease. A typical structure is shown in Figure 15.

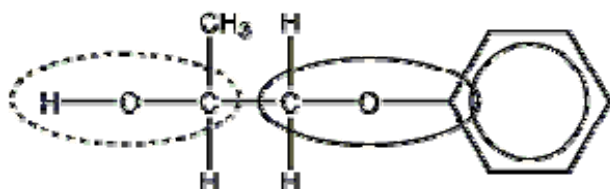


Figure 15: Typical structure of a glycol ether. This one is a glycol phenyl ether as it has a benzene ring. The alcohol functional group is shown in the dotted oval and the ether in the solid oval

To do this, they should ideally be non-polar, because grease molecules are essentially non-polar. However, they must also mix with water as Cillit Bang degreasers are dispersed in aqueous solution. So the compounds chosen must be sufficiently polar to mix with water.

Glycol ethers, which have both an alcohol (R-O-H) and an ether (R-O-R) group, have the right degree of polarity to do both. These considerations are similar to those that apply to surfactants described above. They must also, of course, have no damaging effects on the surfaces on which they will be used.



Figure 16: Cillit Bang Power Cleaner Degreaser

*Cillit Bang is a registered trade mark of the Reckitt Benckiser group of companies.
Last reviewed by Reckitt Benckiser in 2013.*

Further information

The Cillit Bang family of cleaners are sold by Reckitt Benckiser (www.cillitbang.co.uk). Cillit Bang is a registered Trade Mark of Reckitt Benckiser NV. There are other branded products which work in a similar way.

Acknowledgements

The Royal Society of Chemistry wishes to thank Chris Jones, Candice Taylor, Ed Cooney and Farid Nekmard of Reckitt Benckiser for help in preparing this material.

The Royal Society of Chemistry gratefully acknowledges that this project was initially supported by Reckitt Benckiser in 2007. Reckitt Benckiser conducted a final review in 2013 so please note that certain information may be out of date.

QUESTIONS AND ANSWERS

Question 1

Give two reasons why the calcium carbonate deposit forms more readily on the hot tap of a sink rather than the cold one.

The heat evaporates the water. In hot conditions, Le Chatelier's principle predicts that the equilibrium moves to the left, the direction in which ΔH is positive, *ie* the reaction is absorbing heat and cooling the surroundings.

Question 2

Sulfamic, formic and phosphoric acids are all weak acids. Explain the difference between a weak acid and a strong acid.

Weak acids are only partially dissociated in solution. Strong acids are completely dissociated in solution.

Question 3

What is the systematic name of formic acid?

Methanoic acid

Question 4

Explain why the pK_a values get larger for the second and third dissociations of phosphoric acid.

The pK_a values are a measure of the strength of the acids (how easily a H^+ ion is lost). The bigger the pK_a value, the weaker the acid. It is harder to lose the second proton than the first because it is being lost from a singly negatively charged ion rather than a neutral molecule. It is harder to lose the third proton than the second because it is being lost from a doubly negatively charged ion rather than a singly charged one.

Question 5

a) Explain why, when formic acid dissociates, the hydrogen atom bonded to an oxygen atom is the one lost as a H^+ ion rather than the one bonded to the carbon atom.

Oxygen is significantly more electronegative than hydrogen (3.5 as opposed to 2.1). So the O-H bond is polarised $O^{\delta-}-H^{\delta+}$ making loss of the hydrogen as H^+ easy. Carbon's

electronegativity is similar to that of hydrogen (2.5 to 2.1) so the C-H bond is relatively non-polar and there is little tendency for the H atom to acquire a positive charge.

b) The pK_a of formic acid is 3.8, what is the value of K_a ? Give the correct units.

$$pK_a = -\log_{10}K_a \text{ so } K_a = 1.6 \times 10^{-3} \text{ mol dm}^{-3}$$

c) Write an expression for K_a of formic acid (represent the acid as HCOOH).

$$K_a = \frac{[H^+_{(aq)}]_{eqm}[HCOO^-_{(aq)}]_{eqm}}{[HCOOH_{(aq)}]_{eqm}}$$

d) Calculate the pH of a 1 mol dm⁻³ solution of formic acid.

$$[HCOO^-_{(aq)}]_{eqm} = [H^+_{(aq)}]_{eqm}$$

$$[HCOOH_{(aq)}]_{eqm} = 1 - [H^+_{(aq)}]_{eqm} \approx 1 \text{ (we can safely make this assumption for a weak acid)}$$

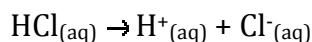
$$\text{So } 1.6 \times 10^{-3} = \frac{[H^+_{(aq)}]_{eqm}^2}{1}$$

$$[H^+_{(aq)}]_{eqm} = \sqrt{(1.6 \times 10^{-3})} = 0.04 \text{ mol dm}^{-3}$$

$$pH = -\log_{10} [H^+_{(aq)}]_{eqm} = 1.4$$

e) Compare your answer for the pH of formic acid with that of 1 mol dm⁻³ hydrochloric acid (HCl), a strong acid.

Hydrochloric acid dissociates completely in solution



$$\text{So } [H^+]_{eqm} = 1 \text{ mol dm}^{-3}$$

$$pH = -\log_{10} [H^+_{(aq)}]_{eqm} = 0$$

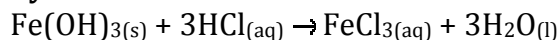
Question 6

Iron also forms iron(II) oxide and iron(II) hydroxide. Give the formulae of these compounds and suggest why they are less likely to be found in rust than the corresponding iron(III) compounds.

FeO; Fe(OH)₂. Oxygen in the air can oxidise iron(II) to iron(III).

Question 7

Write a balanced symbol equation for the reaction of iron(III) hydroxide with hydrochloric acid.



Question 8

Look at the molecules in Figures 6-9. Explain why the heads are polar and the tails non polar.

In each case, the head contains electronegative atoms which can participate in hydrogen bonding with water. In the first three cases, the heads have ionic charges. The tails consist of hydrocarbon chains which cannot form hydrogen bonds.

Question 9

What is the systematic name for sodium hypochlorite? Hint, work out the oxidation number (oxidation state) of the chlorine atom.

Sodium chlorate(I). The oxidation number of the sodium is +1 and that of the oxygen is -2. So to keep the sum of the oxidation numbers in a neutral compound equal to zero, that of the chlorine must be +1. Hint 'ate' in a chemical name usually means 'and oxygen as well'.

Question 10

What is the systematic name of ethanolamine?

2-aminoethanol.

Question 11

a) What two functional groups does ethanolamine have?

Primary amine and primary alcohol.

b) Which of these groups is significantly basic?

Primary amine.

Question 12

a) Write an equation for the reaction of ethanolamine with water to show how ethanolamine makes the product more alkaline.



b) What feature of the ethanolamine molecule makes this reaction possible?

A lone pair of electrons on the nitrogen atom.

Question 13

The oxygen atom of ethanolamine also has a lone pair of electrons. Explain why it is the lone pair of electrons on the nitrogen atom rather than that on the oxygen atom that is donated to a proton.

Nitrogen is less electronegative than oxygen (it has one less proton in its nucleus) so its lone pair is less strongly held and more easily donated to a proton.