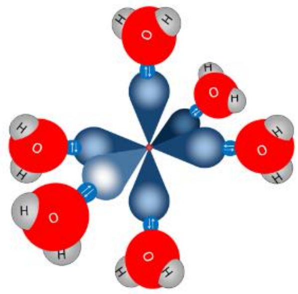
The Chemistry of Hyrdates



Introduction

You will be familiar from your GCSE days with some blue crystals called copper (II) sulfate. You probably made some of the crystals by reacting copper (II) carbonate or copper (II) oxide with sulfuric acid. After filtering the excess base from the neutralised acid, your blue solution will have been left to crystalise to produce some blue, approximately diamond shaped crystals.

Although we call this compound copper (II) sulfate, this is incorrect. The chemical formula of these dried crystals is **$CuSO_4 \cdot 5H_2O$.** The correct name for the compound is copper (II) sulfate **pentahydrate**.

The formula clearly indicates that there are five water molecules present for each 'copper (II) sulfate'.
This compound is a '***hydrated*** copper (II) sulfate'.

The water molecules that are present do not make the copper sulfate crystals wet. They will not leave a piece of filter paper looking damp. These water molecules are chemically bonded withing the structure. It isn't that they have simply been trapped inside the ionic lattice as the solution dried! These water molecules are known as the **water of crystallisation.**

Of course, at GCSE there would be no way of explaining this. Imagine being told at GCSE that oxygen atoms in water molecules have covalently bonded to a Cu^{2+} ion. On several levels, this would seem impossible to accept at GCSE. For example, you would probably not have been told that metal ions and atoms can form covalent bonds with non-metals, such as the oxygen in a water molecule. But this is actually a very common phenomenon and is responsible for the bonding of oxygen molecules to the Fe^{2+} ions in oxyhaemoglobin.

In the compound copper(II)sulfate **pentahydrate,** X-ray crystallographic studies show that water molecules are covalently bonded (dative) to the central Cu^{2+} ion in a highly organised way. The sulfate ions forms bridges between the copper ions. This creates a polymeric structure.

As with all covalent bonds, they are breakable with the input of energy. This can be done by strongly heating the hydrate. The heat energy breaks the bonds between the water molecules and the central Cu^{2+} ion. The water molecules are lost from the compound. When all the ***waters of crystallisation*** have been driven off, the compound is described as being the ***anhydrous salt***. In the case of copper(II)sulfate, the anhydrous salt is colourless (white). Addition of water to the white anhydrous copper(II)sulfate crystals produces a very exothermic reaction and the water molecules become bonded to the Cu^{2+} ion. This is a good example of a reversible reaction.

$$CuSO_{4(s)} + 5H_2O_{(l)} \rightarrow CuSO_4 \cdot 5H_2O_{(s)}$$

Once sufficient H_2O molecules have been added (5!), further addition of water causes the compound to become wet and eventually to dissolve.

Interestingly, in solution, the copper species present has the formula $[Cu(H_2O)_6]^{2+}_{(aq)}$. The Cu^{2+} is surrounded by 6 covalently bonded water molecules. This is a '***complex ion***' which will be discussed more during the study of transition metals.

$$CuSO_4 \cdot 5H_2O_{(s)} + H_2O_{(l)} \rightarrow [Cu(H_2O)_6]_{(aq)} + SO_4^{2-}{}_{(aq)}$$

Many salts of transition metals are hydrated. The number of water molecules that are in the formula varies between compounds. And some specific salts can have different extents of hydration. Here are some examples.

Note that most hydrates are formed with a **whole number of water molecules** and that this number is generally small, but not always! In some cases, the number is ½ (*hemi*) or 1½ (*sesqui*).

Formula of Hydrate	Chemical name	Old/Common Name
$CuSO_4 \cdot 5H_2O$	copper (II) sulfate **penta**hydrate	Blue vitriol
$Na_2CO_3 \cdot 10H_2O$	sodium carbonate **deca**hydrate	Washing soda
$MgSO_4 \cdot 7H_2O$	magnesium sulfate **hepta**hydrate	Epsom salts
$Fe(NO_3)_3 \cdot 9(H_2O)$.	iron (III) nitrate **nona**hydrate	
$CaSO_4 \cdot 2H_2O$	calcium sulfate **di**hydrate	Gypsum
$CaSO_4 \cdot ½ H_2O$	calcium sulfate **hemi**hydrate	Plaster of Paris

Finding the Formula of a Hydrate by Experiment.

Worked example:

Anhydrous **cobalt (II) chloride** has a chemical formula $CoCl_2$. It is blue in colour.

$CoCl_{2(s)}$

When left in moist air, it picks up water molecules and becomes a pink stable hydrate.

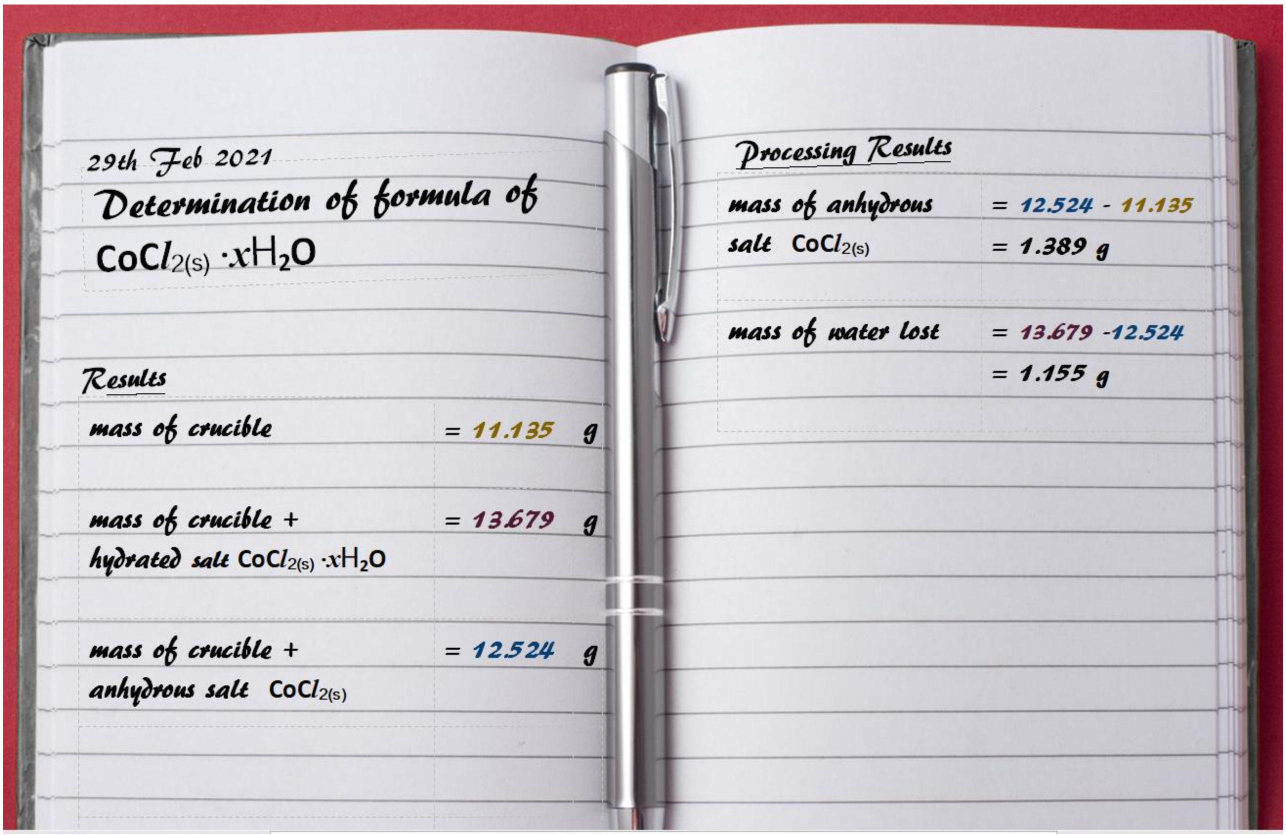
$CoCl_2 \cdot xH_2O_{(s)}$

We describe compounds that readily pick up water from the atmosphere as **hygroscopic** or **deliquescent**.
We need to find the chemical formula of the pink hydrate. In other words, we need to find the value of x in the xH_2O.

A traditional method for doing this involves the following:

1. Accurately weigh a crucible (or crystallising dish). Record the mass.
2. Place a sample of the hydrated compound into the crucible and reweigh the crucible **plus** hydrate. Record the mass.
3. Heat the open crucible on a pipeclay triangle over a blue Bunsen flame.
4. After several minutes, allow the sample to cool enough for you to weigh the crucible plus contents. Record the mass.
5. Repeat step 4. Record the mass.
6. If the mass recorded in step 5 is lower than the mass recorded in step 4, then repeat step 4.
7. Once consecutive masses are the same, then then compound has not dehydrated any further and so you no longer need heat the compound. We say that we have ***heated to constant mass***.
8. You can now calculate the mass lost between the original hydrate mass and the dehydrated form. This mass lost is the ***water of crystallisation*** and will allow you to calculate $\boldsymbol{x}$ in the $\boldsymbol{x}H_2O$.

Sample results:



We have found the mass of anhydrous $CoCl_{2(s)}$ =1.389g

We can calculate the moles of anhydrous $CoCl_{2(s)}$ $= \frac{1.389g}{MM(CoCl_2)} = \frac{1.389g}{129.8\ g/mol} = 0.01069$ mol

We have found the mass of water lost =1.155g

We can calculate the moles of water lost $= \frac{1.155g}{MM(H_2O)} = \frac{1.155g}{18.0\ g/mol} = 0.06416$ mol

The amount of water is the xH_2O.

We can now calculate the ratio of anhydrous salt to water molecules to obtain a value for x

$$\frac{n(H_2O)\ \text{in hydrate}}{n(\text{anhydrous compound})} = \frac{0.06416\ \text{mol}}{0.01069\ \text{mol}} = 6.002$$

So, there are 6 H_2O molecules for every $CoCl_2$. The formula of the hydrate is **$CoCl_2 \cdot 6H_2O$**

Its name is **cobalt(II)chloride hexahydrate**.

A simplified example for you to try:

A mass of 1.881g of hydrated nickel(II) chloride $NiCl_2 \cdot xH_2O$ is heated repeatedly until a constant mass is obtained.

After heating, the mass of the anhydrous salt that remains is 1.025g.

What is the formula of the hydrate? What is the name of the hydrate?

Answer:

We have found the mass of anhydrous $NiCl_{2(s)}$ =1.025g

We can calculate the **moles of anhydrous** $NiCl_{2(s)}$ $= \frac{1.025g}{MM(NiCl_2)} = \frac{1.025g}{129.6\ g/mol} = 7.90 \times 10^{-3}$ mol

We have found the mass of water lost =1.881g − 1.025g = 0.856g

We can calculate the **moles of water** lost $= \frac{0.856g}{MM(H_2O)} = \frac{0.856g}{18.0\ g/mol} = 0.0476$ mol

The amount of water is the x H_2O.

We can now calculate the ratio of anhydrous salt to water molecule to obtain a value for x

$$\frac{n\ H_2O\ \text{in hydrate}}{n\ \text{anhydrous compound}} = \frac{0.0476\ \text{mol}}{7.90 \times 10^{-3}\ \text{mol}} = 6.002$$

This is called nickel (II) chloride hexahydrate. Another hexahydrate!

You can now practise calculations by having a go at the Module 2 Hydrates quiz on chemistry.cramnow.com

Some Further Reading

Plaster of Paris

The compound is a well-known material and has been used for centuries to form casts.

Until recently, a runny paste made from Plaster of Paris was used to coat bandages with so that a plaster cast could be formed around broken limbs. It was often referred to as a 'pot'.

The chemistry involved the conversion for the ***hemihydrate*** into the ***dihydrate*** .

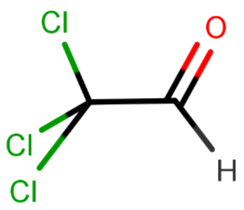
$$CaSO_4 \cdot \frac{1}{2} H_2O_{(s)} + 1\frac{1}{2}H_2O_{(l)} \rightarrow CaSO_4 \cdot 2H_2O_{(s)}$$

This reaction produces a very tough compound which sets hard around the bandage. The runny paste can also be poured into moulds where is sets.

The reaction is pretty exothermic! Special precautions need to be followed to ensure that the heat produced by the hydration process does not cause burns to the limb receiving the cast.

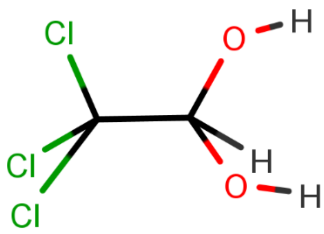
There are other examples of hydrates in the world of chemistry.

For example, there are compounds that have been made by chemically adding water molecules to larger molecules. Chloral is an organic molecule with the following structure:



chloral

Reacting chloral with water produces chloral hydrate with the following structure. It has 2 extra hydrogen atoms and an extra oxygen atom:



chloral hydrate:

This molecule has been used extensively for over a century as a sedative drug. It is no longer used due to concerns about its toxicity. It has been used illegally and is linked to robberies of people having has their drinks laced with chloral hydrate. The most famous example was where patrons of a Chicago bar had their drinks spiked by the bartender, Michael '*Mickey*' Finn. He would then rob them and dump their unconscious bodies outside the bar. They had no recollection of what happened. The term '*slip them a Mickey Finn'* is still used today.

Clathrates

There are some very unusual hydrates that can form at low temperatures and high pressures. It is possible for methane to form an association with water molecules under some quite extreme condition. These conditions can be found in deep cold oceans. They can also be found in permafrost. The '*clathrate*' is a methane hydrate.

The chemical formula of this odd material is CH_4•5¾ H_2O

The water molecules are not actually bonded to the methane molecules. Instead, the water molecules entrap the methane molecules in a crystalline structure that resembles regular ice. They become very unstable at higher temperatures and lower pressures.

H_2O molecules form a cage around the methane molecule which is at the

It is anticipated that there are greater fuel reserves of methane in deep sea clathrates and permafrost than there are all of the coal, oil and traditional natural gas reserves on Earth! The existence and spontaneous release and ignition of these reserves is thought to be behind the stories told by ancient mariners when they came home from voyages in the north oceans. They told stories of the oceans being on fire. Their tales were put down to too many weeks at sea and to rum.

Methane clathrate 'ice' on fire.

Methane clathrate's potential spontaneous release of methane, in large quantities, poses a threat to the climate due to the potency of methane as a greenhouse gas.