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THE EXTRAORDINARY WORLD OF SULPHUR PART 1

Abstract: Sulphur is a highly reactive element, and is therefore able to enter into a great variety of chemical combinations, resulting in the formation of compounds of widely differing properties. Reactions involving sulphur, and the compounds which they produce, have stimulated and inspired people throughout the ages. Sulphur has always been associated with volcanoes, fires and smells. However, its story goes much further. Sulphur is present in thousands of products of the chemical industry, which are in everyday use. These include car batteries, car tyres, matches, paints, paper, textiles, food, detergents and pharmaceuticals. In part 1 of this essay, the evolution of the role of sulphur in the history of markind is explained, through the eyes of etymology, geology, literature, art, and chemistry. In part 2 the role of sulphur in biochemistry and chemical technology is reviewed. In so doing, a case is established, to show that sulphur is the most extraordinary substance known to Man.

Keywords: sulphur, sulphuric acid, sulphur dioxide, alchemy, chemistry, technology

Introduction

From the wonderful experience of a giant pyrotechnic display, to the joy of riding a bicycle, to the exhilaration of soaring high above a rocky mountain valley on a hang glider, from the simple satisfaction of washing dishes, to the euphoria of being cured from an illness, or the delight of looking at a freshly hand painted wooden floor and the inspiration to handwrite a poem with brown ink on a white sheet of textured cartridge paper, sulphur has been at hand since the dawn of time to stimulate the human imagination. No other substance on earth could possibly have been involved in so many different ways, and done so much for humanity.

Sulphur's role in history is examined with a particular focus on its chemistry, thus presenting the case that sulphur is, the most remarkable substance ever known.

Etymology

Evidence of the knowledge of sulphur in ancient times arises from references in early languages, the oldest of which is Sanskrit. This was an Indo-European language of India, and the sacred language of Hindu scriptures. According to the eminent teacher, author and scholar Eric Holmyard [1], the word *sulphur* is the Latin derivative of the Sanskrit word *sulvari*, which means *enemy of copper* [2]. Thus not only did the Hindus know of sulphur some 5000 years ago, they also knew the reaction of its vapour with hot copper.

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Today we can easily reproduce this reaction in a school chemistry laboratory. Figure 1 shows a sample of copper foil being strongly heated in boiling sulphur vapour. The red glow shows the reaction. Figure 2 shows the resultant black brittle solid (copper(I)sulphide), alongside a piece of unreacted copper foil. It is possible to see from this reaction, why sulphur might be described as the enemy of copper.



Fig. 1. Copper meets its "enemy"



Fig. 2. Copper, before and after "destruction"

Another word which is synonymous with sulphur is the now obsolete term *brimstone*. This originates from the old English *brynstan*, which is similar to the old German

brennstein, both of which meant "burning stone". Figure 3 shows a lump of roll sulphur burning in a pool of burning molten sulphur. The characteristic blue flame is barely visible in daylight - the only sign of combustion is the slow but continuous stream of acrid sulphur dioxide fumes.



Fig. 3. Burning sulphur, or Brimstone

From Ancient Greek, in which sulphur was *theion*, the prefix *thio* has been derived, to denote some sulphur containing compounds, such as sodium thiosulphate or sodium tetrathionate.

Various discussions have taken place to decide on a consistent spelling of sulphur in the English language. In 1990 the International Union of Pure and Applied Chemistry (IUPAC) adopted *sulfur* as the preferred spelling, although the spelling *sulphur* continues to be widely used. The reason for this change was that the word 'sulphur' does not originate from Ancient Greek, in which the letters "ph" are derived from "phi" [Φ], but rather the Latin 'sulfur' (3rd century AD). Interestingly, the letter 'f ' has been accepted in other European languages e.g. *azufre* (Spanish), *schwefel* (German), *soufre* (French) and *zolfo* (Italian) [3].

The symbols for sulphur have also undergone many changes throughout the ages. Two of several different symbols for sulphur are given here, both from the same source [4]. Figure 4 shows the alchemists' symbol for sulphur, which is listed among a variety of substances, whereas Figure 5 gives a completely different symbol, which is based on its inclusion with combustible elements. The context within which the symbols are given reflect the difficulty which early chemists experienced, in classifying substances.



Fig. 4. Alchemists' symbol for sulphur

Hidrogen bstances comm mbustible Simp Sulphur NS10110CON Phosphorus

Fig. 5. Haffenfratz and Adet's symbol for sulphur

In 1808, the English chemist, physicist and meteorologist John Dalton [1766-1844] published a substantial work (560 pages), in which he summarised all chemical knowledge, which was still just possible in those times [5]! The quintessential part of his new philosophy was his Atomic Theory, which was to play a key role in the development of chemical theory. In conjunction with this theory, he proposed a set of symbols to represent atoms of each element. Sulphur was represented as a circle with a cross, and the elements

were arranged in order of increasing atomic weight, the concept of which had only recently been established. Figure 6 shows a table of symbols for his elements, which are taken from his great work. This table was used by him for teaching purposes and sulphur is represented as the element with atomic weight 13.

Fig. 6. Dalton's symbols for elements

It was not until the modern system of symbols was devised by the Swedish chemist Jacob Berzelius [1779-1848] in 1813, the today's symbol for sulphur, S, was adopted, and not until the modern classification of the elements - the Periodic Table - had been established by Mendeleev in 1869, that all the elements were put into a systematic classification. This was initially based on chemical properties and atomic weights, but subsequently, in the first decades of the 20th century, confirmed on the basis of atomic structure.

Geology

Sulphur is the 5th most abundant element on Earth (2.9 %), 10th most abundant in the universe, and the 16th most abundant element in the Earth's crust. Much of the Earth's sulphur is found in its crust and mantle, which explains the huge quantities of sulphureous

fumes (sulphur dioxide and/or hydrogen sulphide) which are associated with volcanic regions, in which molten magma comes to the earth's surface. Frequently these fumes condense or combine to form sulphur which is found in the rims of active volcanoes, of which the volcano complex Ijen in east Java in Indonesia, and Grimsvotn in Iceland are examples.

Small quantities of native sulphur are widely distributed as thin strata throughout the Earth's crust. Figure 7 shows a map of the world with its principal regions of volcanic activity, shown by dotted lines, which are also the locations of sulphur deposits [6].



Fig. 7. Volcanic regions and sulphur deposits



Fig. 8. Sulphur deposits in Lousiana, USA

The sulphur deposits are usually interspersed/mixed with other minerals such as limestone. In some regions such as Canada, Japan, Mexico, Poland, Sicily, USA (Louisiana and Texas) large underground deposits of almost pure sulphur occur. These deposits, which can be found in salt domes at depths of 60 to 600 metres, are generally associated with

sedimentary rocks: limestone (calcium carbonate) and anhydrite and gypsum (calcium sulphate). No other element occurs in such large deposits in such a pure state. Figure 8 shows a schematic diagram of the location of sulphur deposits in Louisiana, USA [7].

The vast majority of the earth's sulphur occurs in minerals, in which it is combined with metals in the form of sulphides or sulphates. Examples of these minerals, which have been known and exploited since ancient times, include: iron pyrites FeS_2 (by far the most common, sometimes referred to as "Fool's Gold" on account of its golden lustre), copper pyrites (chalcopyrite) Cu₂S.Fe₂S₃, galena PbS, cinnabar HgS, sphalerite (zinc blende) ZnS, realgar As₂S₂, and orpiment As₂S₃. Figure 9 shows pyrite crystals, which have a beautiful cubic structure.



Fig. 9. Pyrite crystals

An example of a sulphate mineral in gypsum, CaSO₄.2H₂O. Sulphur bearing minerals are distributed in small amounts in a wide variety of geochemical environments throughout the earth. They are metamorphic rocks, having been formed in the earth's crust through the action of intense heat and pressure.

Sulphide minerals are also found in meteorites, on Mars, and have been recently found on the moon [8]. Tiny amounts of gaseous sulphur compounds are found in the Vesuvian atmosphere, and sulphur has recently been reported on exoplanets [9].

Thermal springs have been popularly used since ancient times for curative purposes. They have a specific odour which arises from the very low concentrations of hydrogen sulphide which are found in the spring waters. These springs exist in many places throughout the world, e.g. Australia, Brazil, Canada, Costa Rica, China, Hungary, Italy, Iceland, India, Iran, Japan, New Zealand, Peru, Slovakia, Taiwan, Turkey, USA. The water in these springs is geothermally heated, the heat being generated from the decay of radioactive elements in the earth's mantle. Recent research has suggested that 90 % of the earth's sulphur is present in its core [10].

Sulphur is present in small variable quantities, in compounds which are found in the fossil fuels: coal \approx (1-2) % S natural gas \approx 0.2 % S and oil \approx 0.5 % S. Coal deposits, which were formed during the carboniferous period between 300 and 360 million years ago, constitute sedimentary rocks, and are widely dispersed at various depths in the Earth's crust. The sulphur in coal can be divided into 2 categories: inorganic (pyrites and sulphates)

and organic (mercaptans, sulphides (thioethers), disulphides, sulphones, thiophenes etc.). The sulphur containing compounds in crude oil include mercaptans, hydrogen sulphide, and thiophene derivatives. In natural gas the sulphur bearing components are mercaptans and hydrogen sulphide.

Mercaptans are a class of organic compounds which contain an -SH group attached to a hydrocarbon chain. They are the sulphur equivalent of alcohols, and are also referred to as thiols. They have exceedingly unpleasant odours resembling rotten eggs or garlic. The simplest mercaptan is CH₃SH which is known as methanethiol or methyl mercaptan. Humans can detect the smell of mercaptans at a concentration of 10 ppbillion, and hydrogen sulphide at a concentration of 30 ppbillion. Thiophene, C₄H₄S, consists of cyclic 5 membered ring molecules, resembling benzene. Sulphones have a general formula $R-S(=O)_2-R^1$, and sulphides (thioethers) have general formula $R-S-R^1$. Disulphides are of two kinds: symmetrical, which are encountered in organo sulphur chemistry, and which have general formulae R-S-S-R, and unsymmetric sulphides, R-S-S-R¹, which are encountered in nature.

In a surprising development during the past few decades, fossil fuels have become the main source of elemental sulphur for the chemical industry.

Literature and art

On account of its strong association with volcanoes, fire, destruction, and deep steamy foul smelling chasms, sulphur has long been associated with evil, demons, death, eternal damnation, and hell.

The Bible is divided into the Old and New Testaments. The Old Testament was written in Hebrew over a period of several centuries some 3000 years ago. It consists of numerous chapters which are presented in 46 books and treats on the history of Israeli tribes. The New Testament, which was inspired by the life and death of Jesus Christ, consists of 27 books, divided into 4 sections - the Gospel, Acts of the Apostles, Letters to the Apostles and Revelations - was written over a period of some 40 years.

One of the key recurring themes throughout the Bible is morality and its interpretation and implementation in the behaviour of humans. The tensions between the opposites such as: good and evil, right and wrong, just and unjust, austere and luxurious, wealthy and poor, suffering and pleasure, pride and humility, generous and mean, reward and punishment are key elements of the Bible. It is in the domain of divine retribution, or punishment, that sulphur makes its several appearances, of which three examples are given. The first is from the Old Testament, and the second and third are from the New Testament, written some 2000 years later.

The first book of the Old Testament is entitled Genesis, in which are described the story of the earth's formation by God and the history of the early tribes of Israel. In Chapter 19, we learn of the extremely immoral lives of the inhabitants of two cities, Sodom and Gomorrah. They were punished severely.

"Then the LORD rained on Sodom and Gomorrah sulphur and fire from the LORD out of heaven; and he overthrew these cities, and all the Plain, and all the inhabitants of the cities, and what grew on the ground" [11].

The fourth book of the New Testament, the Revelations, provides the reader with an apocalyptic description of the intervention of God, in the case of evil doing. In Chapter 8, seven angels from heaven, with seven trumpets, announce severe punishments for sinners.

The author, John, described the scene once the sixth angel had blown his trumpet to unleash the fury of God, in the form of horses, upon the multitudes of wrongdoers:

"And this was how I saw the horses in my vision: the riders wore breastplates the colour of fire and of sapphire and of sulphur; the heads of the horses were like lions' heads, and fire and sulphur and smoke came out of their mouths. By these three plagues a third of humankind was killed, by the fire and smoke and sulphur coming out of their mouths" [12].

In a subsequent verse of the Revelations, entitled *The Beast and Its Armies Defeated*, we read:

"Then I saw the beast and the kings of the earth with their armies gathered to make war against the rider on the horse and against his army. And the beast was captured, and with it the false prophet who had performed in its presence the signs by which he deceived those who had received the mark of the beast and those who worshipped its image. These two were thrown into the lake of fire that burns with sulphur" [13].

Sulphur's role in connection with evil, sins and eternal damnation also featured vividly in the huge outpouring of artistic creativity in Europe. Two examples are given.



Fig. 10. Lot and his daughters (from a print in the author's collection)

One of Poland's best known legends is: *Smok Wawelski* or the *Dragon of Wawel*. During the 13th century, Krakow was the proud capital of Poland, and its castle Wawel stood on a steep bank on the river Vistula. A dragon which breathed fire and terrorised the people of Krakow, is baited by a boy shepherd, with a sheep which is stuffed with sulphur. As the hungry fire breathing dragon consumes the bait, it catches fire and dies a horrific death, consumed in flames of burning sulphur.

An excellent example of a work of art is found in the painting, by an unknown Dutch master c. 1530, which is entitled *Lot and his Daughters*. It shows the destruction of Sodom and Gomorrah, with Lot and his two daughters in the foreground. Figure 10 shows this painting, in which burning sulphur pours from heaven, resembling a meteorite shower.

William Shakespeare [1564-1616] is widely regarded as the greatest and most influential English playwright and poet. His works have been translated into every language in the world, and they continue to be performed, studied and reinterpreted. The play *Othello* (written in 1603-1604 and published in 1622) is a tragedy in which *Othello*, who was an African general in the Venetian army, murders his wife for her perceived betrayal of him. Having found out that she was innocent, he kills himself. The fragment below is from his speech upon having discovered that he has unjustly murdered his own wife. It brilliantly illustrates the great drama, passion and emotions of which humans are capable.

"O! cursed, cursed slave. Whip me ye devils, From the possession of this heavenly sight! Blow me about in winds! Roast me in sulphur! Wash me in steep-down gulfs of liquid fire! O Desdemona! Desdemona! dead! Oh! oh! oh!" [14]

John Milton [1608-1674] was an English poet and philosopher. He became inspired by the teachings of the Bible, and was particularly moved by his observation of the huge amount of ill doing in his times. In his youth he conceived of an epic tale, which would be a discourse on Man's creation and his fall from grace, as described in the Bible. *Paradise Lost* was written during the years 1658 and 1665 when he was blind. Today it is considered by many to be the greatest epic poem in the English language. It consists of 12 books and is written in plain verse, using beautiful and powerful descriptive language to express grand ideas. In the first section of the second book, the struggle against Satan, the Torturer, is described:

"Turning our tortures into horrid arms Against the tort'rer; when to meet the noise Of his almighty engine he shall hear Infernal thunder; and for lightning, see Black fire and horrour shot with equal rage Among his angels; and his throne itself Mix'd with Tartarean sulphur, and strange fire His own invented torments. But perhaps The way seems difficult and steep to scale With upright wing against a higher foe" [15]

(The word *Tartarean*, which is derived from the deep abyss of Tartarus in ancient Greek mythology, means hellish.)

Today, scholars from across various disciplines of learning have become fascinated by the use of sulphur in connection with fire, eternal damnation and hell. In this field of study, a noteworthy contribution of the issues involved, has been made by the Dutch geologist Salomon Kroonenberg. As a geologist, Professor Kroonenberg combined his research into mythology with geology, to examine the evidence, both geological and mythological, for the connection between sulphur and hell. As part of this research, he turned to one of the great masterpieces of Western literature, Dante's *Divine Comedy*, which was first published in 1300. Dante Alghieri [1291?-1361] was an Italian poet, writer and philosopher. *The Divine Comedy* is an allegorical work, which can be interpreted as the story of Man's descent into sin. Hell is depicted in 9 circles, descending deeper underground, in which sinners are subjected to fire and horrendous tortures. Surprisingly, there is no reference to sulphur.

However, recent scholarship has shown that the subject matter of the *Divine Comedy*, including ideas of layers of hell, was derived from earlier Islamic sources, which contained references to sulphur. In the Isra' and Mi'aj, which is the story of the prophet Mohammet's allegorical journey to heaven, mention is made of several lands of hell. "The fifth land, Malca, is full of sulphur stones from hell. "These are the stones of which Allah speaks in the Koran when he says: "We shall prepare stones to burn and torture the sinners" [16]. Other authors have suggested that the idea of a layered hell may have had even earlier origins. Kroonenberg thus writes: "…there may be even deeper roots in Iranian and Indian mythology" [17].



Fig. 11. Administering brimstone and treacle medicine

Charles Dickens is widely regarded as one of the greatest authors of the Victorian period. He had a remarkable talent for creating extraordinary fictional characters, which frequently represented archetypes of people. In the novel *Nicholas Nickleby*, published in 1839, Nickleby was assigned to a poor boys' boarding school, Dotheboys, for teacher training. The headmaster's wife Mrs Squeers, used brimstone as a component [sulphur has an action as a mild laxative] of a nasty medicinal mixture. Its purpose was to show Nickleby, how to save money in the running of the school:

"They have brimstone and treacle, partly because if they hadn't something or other in the way of medicine they'd be always ailing and giving a world of trouble, and partly because it spoils their appetites and comes cheaper than breakfast or dinner. So, it does them good and us good at the same time, and that's fair enough, I'm sure" [18].

Figure 11 shows an illustration by Halbot K. Browne ("Phiz"), depicting the agony on the boys faces, at the prospect of consuming brimstone and treacle medicine.

Who would have thought that sulphur, otherwise known as brimstone, a yellow harmless looking solid, could have had such evil and terrifying connotations?

Alchemy

The eyes of the alchemists saw a very different world from the one that we see today. Their view was based on a philosophy of Nature that had its roots in a different set of axioms from those of modern science. These axioms stemmed from ancient philosophies of nature e.g. Chinese, Hindu, Egyptian. Common to all of them was the quest for finding the ultimate constituents of all matter. The Greek philosopher Empedocles [c. 494 - c. 434 BC] constructed the first coherent theory of the "roots" matter, which were: earth, fire, air and water. Two forces - attraction and repulsion, joined and separated these "roots". Plato [427-347 BC] was the first to introduce the term "element" to denote a formless matter from which substances are made.



Fig. 12. Aristotle's elements

Aristotle [384-322 BC] improved on Plato's ideas. On the basis of his long term observations of natural phenomena such as: volcanoes, flames, weather patterns,

reproduction and growth in plants and animals, corrosion of metals, Aristotle introduced the four properties - hot, cold, wet and dry. Figure 12 shows a diagrammatic representation of this system.

Aristotles's system of the elements became widely accepted and was to underpin alchemical philosophy for many centuries. In his world view, all matter was alive (this was the idea of panvitalism) and filled all space i.e. a vacuum could not exist, and changes in matter occurred as it flowed into another form. Thus arose the idea of transmutation, which was perceived as the act of changing from one form into another. Furthermore, there were three kinds of body: animals, plants and minerals. Animals were the most complex and lived the shortest whereas minerals were the simplest and lived the longest. Thus mother Earth gave to birth to rocks, minerals and metals. This philosophical system inspired a multitude of operations and experiments, whose aims were to improve Man's life on Earth, through a better understanding of how substances interact with one another.

With such a vague, yet universal philosophy, it was possible to interpret natural changes and processes in a vast number of ways. Since sulphur had been known for millennia, it and its compounds were to play a key role in both the philosophical speculations of the alchemists, and in the development of early chemical and metallurgical technologies.

Divine water

Alexandria, which was founded in 331 BC by Alexander the Great [356-323 BC] became a melting pot of people of different cultures - Greeks, Syrians, Egyptians and Jews. It was here that alchemical experimentation began, and the first writings were recorded. Among the earliest written records of these processes were the relatively recently [in 1828] discovered Chemical Papyri [19], in which detailed descriptions are given for a large number of chemical processes. Of particular interest were processes in which gold could be made. On account of its inertness and beautiful lustre, gold was considered to be the symbol of perfection and eternal life. It became a focus of alchemical philosophy and experimentation. Any substance which could turn base metals into gold acquired a special and miraculous significance - it became known as the "stone of the philosophers".

In this respect, the "divine water" whose preparation was carefully described by Zosimos in one of Chemical Papyri, was very special. Zosimos of Panapolis [c. 270-340 AD] is widely regarded as one of the founders of alchemy. He described a wide range of chemical processes and gave a large number of recipes. One of these was "divine water", also known as "bile of the serpent". Zosimos recognised that he was not describing a transmuting agent for changing base metals into gold, but a process for colouring, or tinging a metal with gold. His water was made by a series of reactions involving the boiling of sulphur with milk of lime (calcium hydroxide suspension) and urine or vinegar. The product, essentially calcium polysulphide, had a foul smell, which we recognise today as that of hydrogen sulphide. Using his "divine water", Zosimos was able to tinge silver with gold. Lawrence Principe has experimentally investigated this procedure and has achieved a spectacular success. He was able to change the appearance of a silver cent coin to a gold cent coin. Naturally, the gold appearance was due not to gold, but to an ultra-thin coating of silver sulphide [20].

Sulphur-mercury theory of metals

The origins of this, the most famous philosophical legacy of the alchemists, is shrouded in mystery. It was an unsolved puzzle for generations of chemical historians, but recent research has suggested a very plausible answer. I will first present the historical background, then the theory itself, the rationale behind the theory, and finally its assessment in the light of today's knowledge.

With the fall of the Roman Empire in the 5th century AD, and Alexandria in 641 AD, Arabic culture gradually spread through southern Europe. New alchemical trends thus evolved. The Arabs developed new apparatus, improved many chemical processes, developed a classification system for substances, and made significant contributions to alchemical theory. From the 11th century onwards, when alchemical practice became widespread in Europe, Latin became the main alchemical language. Until the 15th century knowledge was disseminated by handwritten documents, which were frequently beautifully and ornately illustrated, and re-written by scores of copyists. With the invention of the printing press in 1440 by Johannes Guttenberg [c. 1400-1468], the spread of knowledge became much faster. Many Arabic works were translated into Latin.

Independently of epoch, nationality, subject matter, occupation or language, the authors of new research were frequently secretive. On account of the perceived potential impact of their work, e.g. which could lead to great wealth or to eternal life, or to imprisonment as a heretic, and death, alchemists were especially secretive. They frequently camouflaged their work, which was often written in an obscure style, with pseudonyms or with complete anonymity.

The sulphur-mercury theory of metals was a theory whose author, or populariser, seemed to desire anonymity. For centuries, its conception was accredited to Jabir ibn-Hayyan, or Geber as he was known by his latinised name, about whom little was known. Today it is believed that this theory was developed in the 9th century by Balinus, and subsequently popularised by Geber. Of the many authors of the 3000 works in the Jabirian corpus, the popularisation of the sulphur-mercury theory in latinised Europe is attributed to Paul of Taranto, a 13th century Italian Franciscan friar [21].

The theory postulated that all metals were composed of two elements: mercury and sulphur. Gold, which was the most perfect of the 7 metals which were then known, was composed of an optimum ratio of pure sulphur to pure mercury. Less optimum ratios or less pure elements gave rise to different metals. Based on the alchemical way of thinking, which involved analogies and correspondences, this made good sense, since sulphur is yellow and mercury is silver in colour. Thus by combining sulphur and mercury in the right manner, gold could be formed. Furthermore, in the alchemists' view, sulphur and mercury were not only interpreted as the yellow solid and shiny silver dense liquid, by which we recognise them today. They saw them as Aristotelian opposites: "fire" was linked to "sulphur", and "water" was linked to "mercury". As an extension of the doctrine of opposites, the additional attributes of masculinity and femininity were assigned to both sulphur and mercury. For alchemists, the terms "sulphur " and "mercury" thus embodied both the physical and spiritual qualities with which those elements were associated.

The sulphur-mercury theory had a profound effect on people's imaginations, and was quoted and interpreted by various authors over a period of several centuries. The medieval English philosopher Roger Bacon [c. 1220-c. 1292], also known as *Doctor Mirabilis*, gave an interpretation, which gives a superb insight into the thinking of his times:

"The natural principles in the mynes, are Argent Vive [Mercury], and Sulphur. All metals and minerals, whereof there be sundrie and divers kinds, are begotten of these two: but I must tel you, that nature always intendeth and striveth to the perfection of Gold: but many accidents coming between, change the metals... For according to the puritie and impuritie of the two aforesaid principles, *Argent-vive*, and *Sulphur*, pure and impure metals are ingendred" [22].

Paracelsus and the Tria Prima

The outspoken Swiss iatrochemist and physician Paracelsus [1493-1541] incorporated the sulphur-mercury theory into his new system of elements. On the basis of his own experiments and observations, he added salt to sulphur and mercury, thus creating a *tria prima*: SALT, SULPHUR, MERCURY in his own philosophical system. The Paracelsian system was also to play a significant role in the evolution of the alchemical world view. This was summarised succinctly in Poisson's *Theories & Symboles des Alchymistes* (Paris, 1891, p.17). Figure 13 shows Read's diagrammatic representation of Poisson's synthesis [23].



Fig. 13. Alchemical theory after Paracelsus

Typically for alchemical times, substances have qualities associated with them, which are spiritual, and not related to chemical or physical properties of matter.

Sendivogius and his Treatise on sulphur

Several centuries after the theory had been formulated, it was clearly playing a major role in alchemical philosophy. The secretive Polish alchemist Michael Sendivogius [1566-1636] included a treatise on sulphur in his own epoch making work, *Novum Lumen Chymicum* (A New Light on Alchymy), which was first published anonymously in Prague in 1604 [24]. In the opening statement, he emphasises the importance of sulphur:

"Sulphur is not the last amongst the Principles, because it is a part of the Metall; yea and the principall part of the Philosophers Stone: and many wise men have left in writing divers, and very true things of Sulphur" [25].

In subsequent passages, using language which sounds quite unscientific to the modern ear, and which seems to make no sense at all, Sendivogius, in the form of "The Voice, or Master", extolls on the spiritual significance of sulphur and mercury:

"If you understand that the Mercury of the Sages contains within itself its own good Sulphur, digested and matured by Nature, you can accomplish the whole process by means of Mercury alone; but if you know how to add the supplement which our Art requires to the natural proportions of substances, to double the Mercury and to triple the Sulphur, you will all the more quickly produce, first the good, then the better, and finally the best - though only one Sulphur appears, and two Mercuries... . It is really unnecessary to describe the matter of the Mercury and the Sulphur of the Sages, as it has already been plainly delineated by the Ancients as is consistent with our vow. We do not altogether say that the Mercury of the Philosophers is a common thing, or that they have openly called it by its name, and that the matter from which Mercury and Sulphur are philosophically extracted has been plainly pointed out. For the Mercury itself is not found above ground, but is extracted by an artifice from Sulphur and Mercury conjoined. In short, Sulphur and Mercury are the ore of our quicksilver, and this quicksilver has power to dissolve, mortify, and revive metals, which power it has received from the Sulphur" [26].

Further on, in a dialogue between the Alchemist and a Voice, the Voice informs the Alchemist on the true nature of sulphur:

"For the blood of Sulphur is that inward virtue and dryness which congeals quicksilver into gold and imparts health and perfection to all bodies" [27].



Fig. 14. The sulphur-mercury theory (Courtesy of the Wellcome Institute Library)

Riddled language indeed, but this was the world of the alchemists, and it helps us to understand and marvel at how modern science has evolved from such complex roots. Yet sulphur, clearly, was very important!

An imaginative pictorial representation of the sulphur-mercury theory appears in an engraving from Daniel Stolcius' *Viridarium Chymicum* (the chemical garden) [28]. This is shown in Figure 14.

This is from a set of engravings, which show 12 of the greatest alchemical philosophers, which include Michael Sendivogius (depicted as Sarmata Anonymus). Thomas Aquinas [1225-1274] is shown in this engraving, pointing to the pictorial depiction of the sulphur-mercury theory. At the bottom of the pit, exhalations of mercury and sulphur (denoted by their alchemical symbols) are rising from inside the earth. These vapours exit through a vent at the top, where the alchemist is waiting to combine them to make gold. The diagram resembles a cross section of a volcano.

The sulphur-mercury theory from today's viewpoint

The incredulous and sceptical modern reader might be inclined to ask, what were the grounds for such a theory to be developed?

It has been known since ancient times, that metals were frequently associated with sulphur in minerals. The inspiration for this theory came from two minerals: cinnabar and pyrites. Pyrites has the superficial appearance of gold, and decomposes when heated to yield yellow sulphur and a solid black residue of Fe_3S_4 . Cinnabar decomposes when heated, to yield mercury in the form of a dense silver liquid, and sulphur as a yellow solid. Both of these processes were well known in ancient times, especially in China, where artificially created rivers of mercury flowed underground for ornamental purposes. It was also well known that cinnabar did not decompose to give gold, yet the theory was accepted. Undoubtedly the very special natures of mercury, as a silver coloured dense liquid, and sulphur, as a yellow solid that burnt, enabled the link to be established between them and gold. Gold's special attributes, of course, were its beautiful permanent shiny lustre, inertness, ductility and rarity. It represented a special kind of perfection.

Lawrence Principe has succinctly summarised the success of the sulphur-mercury theory of metals: "The mercury-sulphur theory proved astonishingly long-lived. It was accepted... until the eighteenth century, almost a thousand years after it was first proposed" [29].

Chemistry

Sulphur was first recognised as an element by Lavoisier [1743-1794] in 1778, yet its elemental nature continued to be debated until the first decade of the 19th century. At this time, idea of particles, atoms and molecules became well established, in addition to simple ideas on chemical affinity. The laws of chemical combination were also established. Chemists were thus able to understand the nature of substances, classify them as elements, compounds or mixtures, to assign formulae to compounds, and to elucidate their chemical and physical properties. Many compounds of sulphur were identified and characterised e.g. sulphur dioxide in 1774 (Joseph Priestley [1733-1804]), hydrogen sulphide in 1777 (Carl Wilhelm Scheele [1742-1786]) and carbon disulphide in 1796 by Wilhelm August Lampadius [1772-1842]. These all have pungent smells (resembling rotten eggs (H₂S) or rotten cabbages (CS₂)) and are highly toxic, like many other compounds of sulphur.

Sulphur has atomic number 16 and is in group 6, also known as the Chalcogens or "ore formers" of the Periodic Table. Its chemistry is non-metallic, typically exhibiting oxidation states of -2 (sulphides and organosulphur compounds), -1 (disulphides, S_2^{2-}), +4 (sulphites) and +6 (sulphates) in its compounds. On account of the exceptionally interesting reactions of sulphur and its compounds, by the middle of the 19th century its chemistry had become incorporated into school teaching programmes. Below are described some aspects of the chemistry of sulphur, which can be used for teaching purposes in schools.

Physical properties

Sulphur has a melting point of 115 °C and boils at 445 °C. It has more allotropic forms than any other element, but the two most common forms are rhombic (diamond shaped) and monoclinic (needle shaped). Both of these can be readily prepared: rhombic sulphur by crystallisation from its solution in carbon disulphide, and monoclinic sulphur by allowing molten sulphur to solidify, or to crystallise from its hot solution in toluene (methylbenzene). The transition temperature for the allotropes is 96 °C. Above this temperature, monoclinic sulphur is more stable, below 96 °C, rhombic sulphur is more stable. Figures 15 and 16 show these two allotropes of sulphur.



Fig. 15. Monoclinic sulphur



Fig. 16. Rhombic sulphur

When sulphur is heated, it undergoes a remarkable series of changes: from a yellow solid at room temperature, to an amber mobile liquid at 115 °C. At about 200 °C its viscosity suddenly increases due to the rupture of S_8 molecules and their subsequent polymerisation. Figure 17 shows diagrammatic representations of the S_8 molecule - this is described as a puckered ring.



Fig. 17. S₈ molecule



Fig. 18. Plastic sulphur

When sulphur boils, it turns to a dark brown vapour which is spontaneously flammable in air. If molten sulphur is poured into cold water, it forms plastic sulphur, which is metastable. After a few days it loses its plasticity, and gradually hardens to form a microcrystalline structure of rhombic sulphur. Figure 18 shows freshly formed plastic sulphur in a beaker of water.

Chemical properties

Preparation and properties of sulphur dioxide using copper and sulphuric acid

This experiment, in which copper is reacted with concentrated sulphuric acid to form SO_2 , was one of the great classics of the teaching repertoire for 150 years, until its removal from school teaching programs in the late 20^{th} century [30]. It is an outstanding example of a demonstration experiment. Many references to practical details have been provided in the past [31-37]. Figure 19, taken from a school textbook, shows the experimental setup for the preparation of sulphur dioxide [38].



Fig. 19. Preparation of sulphur dioxide

The diagram is drawn and labelled to a high standard, enabling it to be easily interpreted. When conducting this experiment, care should be taken throughout its duration, to minimise the risk of SO_2 inhalation. This is an irritating gas with a choking smell. The experiment is thus best done with an assistant and in a well ventilated laboratory or fume cupboard. As with all demonstration experiments, it must be practised and well-rehearsed, before showing it to students.

To prepare a few gas jars of sulphur dioxide, 10g. copper turnings are heated with 50 cm³ of concentrated sulphuric acid. After about 5 minutes, fumes of sulphur dioxide, frequently discernible by a fine mist of sulphur trioxide impurity, are observed. About 8 gas jars of SO_2 are collected. The gas is collected by downward delivery, since it is quite soluble in water and much denser than air. To test whether a jar is full, a burning splint, inserted into the mouth of the jar, is quickly extinguished. After the jars have been filled, and the reaction has subsided, the delivery tube can be connected to an absorption tower filled with soda lime, which neutralises excess SO_2 . The following properties of SO_2 can be easily demonstrated:

i. Solubility in water and effect on indicator. If water, coloured green with universal indicator, is poured into a jar of SO₂, it immediately turns red and subsequently becomes pale orange. This is due to the reaction of water with SO₂, which results in the formation of sulphurous [sulphuric(IV)] acid, which also has bleaching properties.

$$H_2O(l) + SO_2(g) \rightarrow H_2SO_3(aq) \Leftrightarrow 2H^+(aq) + SO_3^{2-}(aq)$$

where: (l) - liquid, (g) - gas, (aq) - aqueous.

Sulphurous acid is a weak acid, being only partially ionised.

- ii. If a red rose is placed into a jar of SO_2 , its petals lose their colour within a few minutes. The SO_2 acts as a reducing agent, removing oxygen from the petal pigment. On subsequent exposure to air, the petal colour is restored: thus the bleaching action of SO_2 is reversible.
- iii. A dilute solution (about 0.001 M) of purple potassium permanganate is immediately decolourised when poured into a jar of SO_2 . This is a striking example of a redox reaction.

$$2MnO_4^{-}(aq) + 5SO_2(g) + 2H_2O(l) \rightarrow 2Mn^{2+}(aq) + 5SO_4^{2-}(aq) + 4H^{+}(aq)$$

The oxidation state of manganese changes from +7 to +2 (reduction), whereas the oxidation state of sulphur increases from +4 to +6 (oxidation).

iv. If a dilute (0.1 M) solution of acidified potassium dichromate solution is poured into a jar of SO₂, its colour changes dramatically from orange to green. This is another example of a redox reaction.

$$Cr_2O_7^{2-}(aq) + 3SO_2(g) + 2H^+(aq) \rightarrow 3SO_4^{2-}(aq) + 2Cr^{3+}(aq) + H_2O(l)$$

The oxidation state of chromium changes from +6 to +3 (reduction), whereas that of sulphur changes from +4 to +6 (oxidation).

Both of the above reactions are additionally of interest from the standpoint of transition metal compounds, in which coloured ions, variable oxidation states and complex ions are characteristic features. Figures 20 and 21 show these two reactions.

v. When a gas jar of hydrogen sulphide is allowed to mix with SO_2 in the presence of a few drops of water, a yellow deposit of sulphur forms on the sides of the jars.

$$2H_2S(g) + SO_2(g) \rightarrow 2H_2O(l) + 3S(s)$$

where (s) - solid.



Fig. 20. Permanganate into SO₂



Fig. 21. Dichromate into SO₂

For several reasons, this is a remarkable reaction: (a) two gases react to form a solid and a liquid, (b) two very toxic substances react to form nontoxic substances, (c) this is a disproportionation reaction in which the S in H_2S is oxidised and the S in SO_2 is reduced and (d) an element is formed spontaneously from two gases in which it is combined.

- vi. If a dilute (0.1 M) solution of iodine is poured into a jar of SO₂, it is immediately decolourised to form iodide ions. The sulphur in SO₂ is oxidised to the +6 oxidation state in sulphate ions. Iodine is reduced from an oxidation state of 0 to -1. This is another example of a redox reaction.
- vii. If a piece of burning magnesium ribbon is lowered into a gas jar of SO_2 , it continues to burn with a bright white light. This is because the temperature of the burning magnesium is sufficiently high to break the covalent S-O bonds in SO_2 .

$$2Mg(s) + SO_2(g) \rightarrow 2MgO(s) + S(s)$$

In this reaction the SO_2 acts as an oxidising agent. Figures 22a and 22b show the magnesium burning in, and the products of the reaction - magnesium oxide (white) and sulphur (yellow).



Fig. 22 a) Magnesium burning in SO₂, b) Products of the reaction

What happens to the copper during its reaction with hot concentrated sulphuric acid? If sulphur is reduced from the +6 oxidation state in H_2SO_4 , then it follows that copper should be oxidised. And so it is - it changes from the 0 oxidation state in elemental copper to the +2 oxidation state. Examination of the residue of this reaction shows that it is a black solid. Copper(II)oxide is the only easily recognisable compound of copper, which is black. This however cannot be formed in sulphuric acid, since it reacts to form copper(II) sulphate solution, which is blue. And indeed, on dilution of the liquid product of this reaction, and filtering it, a pale blue solution is obtained, which gives an intense deep blue colour of the copper tetramine complex ion, upon addition of ammonia solution. But an insoluble black solid persists as the main reaction product of copper. After much debate in the past, this has been shown to be a mixture of copper(II) sulphide and copper(I) sulphide. Furthermore, these two sulphides react differently with sulphuric acid, depending on the temperature of the reaction. Only a complex series of procedures, as described by Fowles, proves that the product contains a sulphide [39]. Partington offers a more extensive discussion on this reaction, and his suggested equations for it are given in Figure 23 [40].

$$\begin{aligned} 5\mathrm{Cu}_2\mathrm{SO}_4 + 4\mathrm{H}_2\mathrm{SO}_4 &= \mathrm{Cu}_2\mathrm{S} + 8\mathrm{Cu}\mathrm{SO}_4 + 4\mathrm{H}_2\mathrm{O} \ ; \\ \mathrm{Cu}_2\mathrm{S} + 2\mathrm{H}_2\mathrm{SO}_4 &= \mathrm{Cu}\mathrm{S} + \mathrm{Cu}\mathrm{SO}_4 + 2\mathrm{H}_2\mathrm{O} + \mathrm{SO}_2 \ ; \\ \mathrm{Cu}_2\mathrm{S} + 6\mathrm{H}_2\mathrm{SO}_4 &= 2\mathrm{Cu}\mathrm{SO}_4 + 5\mathrm{SO}_2 + 6\mathrm{H}_2\mathrm{O} \ ; \\ \mathrm{Cu}\mathrm{S} + 4\mathrm{H}_2\mathrm{SO}_4 &= \mathrm{Cu}\mathrm{SO}_4 + 4\mathrm{SO}_2 + 4\mathrm{H}_2\mathrm{O} . \end{aligned}$$

Fig. 23. Partington's equations for the copper/sulphuric acid reaction

So what appears to be a relatively straightforward reaction between copper and concentrated sulphuric acid, and which is commonly described by the equation:

$$Cu + 2H_2SO_4 \rightarrow CuSO_4 + 2H_2O + SO_2$$

is actually far more complex. It also brings to attention the much wider issue of the fascinating chemistry and metallurgy of the sulphides (and oxides) of copper (and of iron), of which there are far more than might be expected!

Metal sulphides

Many metals combine directly with sulphur to form metal sulphides. The reactions are highly exothermic. The reaction between iron filings and flowers of sulphur, and an investigation of the properties of the two elements, their mixture, and compound (FeS), is used by schoolchildren to experimentally distinguish between elements, mixtures and compounds.

The reaction between zinc and sulphur is less well known. If stoichiometric proportions (2:1 by mass) of zinc and sulphur are heated in a boiling tube, they react in much the same way as iron and sulphur, to synthesise zinc sulphide. However, if the ratio of zinc to sulphur is increased to 6:1 by mass, and the mixture is ignited by a delayed action fuse, a spectacular explosive reaction occurs. This pyrotechnic effect was demonstrated during a meeting of Chemistry Club at Highgate School in 1978. This is illustrated in Figure 24.



Fig. 24. Reaction between sulphur and excess zinc



Fig. 25. Insoluble metal sulphides

Needless to say, the room was vacated for two hours after the experiment, in order to allow the fumes of sulphur dioxide to disperse. The reason for this effect is that zinc sulphide, initially formed in the reaction, burns in the oxygen of the air to form sulphur dioxide and zinc oxide. At the high temperature of the reaction, the SO_2 undergoes a huge increase in volume due to thermal expansion. Equations for the reactions are given below:

$$Zn + S \rightarrow ZnS$$
 $2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$

All metals form sulphides, but the majority of metal sulphides are insoluble in water. Indeed, lead sulphide is one of the least soluble substances known, having a solubility product of $4 \cdot 10^{-28}$ mol²dm⁻⁶ at 25 °C. These sulphides can be precipitated from solution in striking reactions, by adding sodium sulphide solution to solutions of metal salts. Figure 25 shows the metal sulphides of tin(II), mercury(II), copper(II), iron(III), lead(II) and antimony(III). They have been precipitated by adding a few drops of sodium sulphide solution to solutions of salts of the metals.

The chemistry of metal sulphides is complex, and Linus Pauling has provided some interesting further insights into this topic [41].

Sulphuric acid

Sulphuric acid is a colourless oily liquid of specific gravity 1.83, freezing point 10 °C and boiling point 337 °C. It is exceedingly corrosive, being a powerful dehydrating agent which reacts violently and exothermically with water, and also a powerful oxidising agent. When diluting this acid, it must always be added to water, and stirred continuously. This procedure must be carried out in a well-ventilated laboratory or in a fume cupboard. The chemical properties of the dilute acid and concentrated acid are quite different.

Dilute sulphuric acid behaves as a typical acid, producing hydrogen gas and salts from metals, and forming salts and water on its reaction with bases. These reactions can be illustrated by means of simple equations:

$$\begin{split} &Zn(s) + H_2SO_4(aq) \rightarrow H_2(g) + ZnSO_4(aq) \\ &CuO(s) + H_2SO_4(aq) \rightarrow CuSO_4(aq) + H_2O(l) \end{split}$$

In each type of reaction, beautiful crystals of the salts can be obtained by crystallisation from solution. Figure 26 shows crystals of blue vitriol (copper(II) sulphate pentahydrate, $CuSO_4 \cdot 5H_2O$) and green vitriol (iron(II) sulphate heptahydrate, $FeSO_4 \cdot 7H_2O$).



Fig. 26. Blue vitriol and green vitriol

Three experiments can be conducted with concentrated sulphuric acid, which illustrate its dehydrating action:

- i. If 10 mL of the acid are poured over 5 g copper(II)sulphate pentahydrate in a dry evaporating basin, the crystals turn in colour from blue to off-white as they are dehydrated.
- ii. If 30 mL of the acid are poured over 80 g sucrose in a 100 mL beaker, the sugar gradually turns yellow, then brown and finally black. The mixture becomes very hot as the reaction proceeds, and is accompanied by the evolution of clouds of steam and some sulphur dioxide. The SO_2 is formed by the reducing action of carbon from the sucrose on the sulphuric acid. During this reaction, which lasts about 5 minutes, a black solid frothy mass of carbon arises from the beaker. Thus it is sometimes referred to as the "black monster" experiment by children. The effect is shown in Figures 27a-d at 1-4 minutes after adding sulphuric acid to sugar. The solid residue of this reaction is a spongy mass of carbon, also known as sugar carbon



Fig. 27. The "black monster" experiment: a) 1 minute, b) 2 minutes, c) 3 minutes, d) 4 minutes

iii. When concentrated sulphuric acid is added to sodium formate (methanoate), carbon monoxide is released as a gaseous product. This is because the sodium formate initially makes formic acid by substitution of Na with H, and formic acid is chemically dehydrated in accordance with the equations:

 $HCOONa + H_2SO_4 \rightarrow HCOOH + NaHSO_4$

 $HCOOH \rightarrow CO + H_2O$ The H_2O is removed by the concentrated sulphuric acid.

The carbon monoxide can be ignited, and burns with a beautiful flame at the mouth of the flask. Figure 28 shows carbon monoxide burning at the mouth of a 500 mL flask, in which 50 mL concentrated sulphuric acid have been added to 30 g of sodium formate. This experiment is conveniently and safely brought to an end by filling the flask slowly with water.

Sulphuric acid is also a strong oxidising agent, as has been shown above (preparation and properties of sulphur dioxide) in its reaction with copper. It undergoes similar reactions with other metals e.g. mercury, silver and the non-metals carbon, and sulphur. In each of these reactions, sulphur dioxide is produced as a gaseous product. It also undergoes an unusual reaction with potassium chlorate, in which the chlorine atom of the chlorate (+5 oxidation state) disproportionates into chlorine (+7) in perchlorate, and chlorine (+4) in chlorine dioxide, which are formed:

 $3KClO_3 + 3H_2SO_4 \rightarrow 3KHSO_4 + HClO_4 + 2ClO_2 + H_2O_4$



Fig. 28. Carbon monoxide flame

Chlorine dioxide is unstable, and decomposes explosively when warmed. If a drop of concentrated sulphuric acid is added to a mixture of finely powdered sucrose (icing sugar), the mixture spontaneously ignites by the decomposing chlorine dioxide, and burns with a lilac smoky flame. Figures 29 a, b and c show the progress of the reaction after adding one drop of concentrated sulphuric acid to a mixture containing 17 g of icing sugar and 7 g of potassium chlorate. The end product is another "black monster", consisting of unburnt carbon.

Reactions of sodium thiosulphate

Sodium thiosulphate is a colourless translucent crystalline solid with formula $Na_2S_2O_3.5H_2O$. It undergoes several interesting reactions, partly on account of the somewhat unusual bonding of sulphur atoms, and partly on account of the fact that it can readily form a supersaturated solution. A simple calculation of the oxidation number of sulphur in the thiosulphate ion reveals it to be +2. On examination of the bonding in the thiosulphate ion, $S_2O_3^{2-}$, it is clear that the two sulphur atoms are in different chemical environments. Thus they have different oxidation numbers of +6, and -2. The structure of this ion is shown in Figure 30.



Fig. 29. The spontaneous combustion of a sucrose/chlorate mixture: a) 30 seconds, b) 1.5 minutes, c) 3 minutes



Fig. 30. Thiosulphate ion

Supersaturated solution of sodium thiosulphate

If 10 g of hydrated sodium thiosulphate crystals are heated in a boiling tube, they dissolve in their own water of crystallisation to form a supersaturated solution. Supersaturated solutions are unstable, since they contain more dissolved solute than

a saturated solution, at a given temperature. If a cold supersaturated solution of sodium thiosulphate is thus seeded with a small crystal of sodium thiosulphate, the solution rapidly crystallises. This reaction is exothermic and a temperature rise of some 30 °C can be measured. This reaction can be used to illustrate the concept of a reversible reaction in conjunction with exothermic (crystallisation, or solidification) and endothermic (the formation of a supersaturated solution through the action of heat) processes.

Reaction of thiosulphate with acids

If dilute acid (e.g. hydrochloric) is added to a solution of thiosulphate, a disproportionation reaction occurs, in which sulphur dioxide and sulphur are produced.

$$S_2O_3^{2-}(aq) + 2H^+(aq) \rightarrow SO_2(aq) + S(s) + H_2O(l)$$

As the reaction proceeds, so the opacity of the mixture increases, due to the formation of a suspension of sulphur particles. This reaction is eminently suited for elementary chemical kinetics experiments [42]. Depending on the relative concentrations of the acid and thiosulphate, the precipitate of sulphur forms at different rates, leading to an opaque appearance of the reacting mixture. The time taken for the solution to become completely opaque can thus be used to measure the rate of reaction. This can be done by observing a black cross on a piece of paper (for example) through the reacting mixture, and timing how long it takes for the cross to be obscured by the growing sulphur particles. By measuring the time taken for the cross to disappear for differing relative concentrations of acid and thiosulphate at a given temperature, the rate of reaction can be easily determined.

This reaction is also suited for demonstrating a most interesting physical phenomenon, the scattering of white light. The experiment was developed by the Irish physicist John Tyndall [1820-1893], who was an outstanding populariser of science through his lectures (1853-1887) at the Royal Institution in London. Figure 31 shows the effect.



Fig. 31. Scattering of light by colloidal sulphur (courtesy of Andres Tretiakov)

In the experiment shown above, 100 mL of 1 M hydrochloric acid were added to 6 litres of a 0.02 M solution of sodium thiosulphate. Within about 2 minutes, the scattering of a beam of white light occurs, which is shown by the appearance of a blue colour. Simultaneously, the transmitted beam starts to turn yellow. This effect is due to the interaction of the light with tiny sulphur particles which are evenly dispersed throughout the mixture, forming a sol. Blue light, with wavelength of about 450 nm interacts with the sol particles, whose size is of the same order, and is scattered. Yellow/orange light, whose

waves have a longer wavelength, do not interact with the sol particles, and are thus transmitted. The phenomenon of light scattering occurs in the earth's atmosphere, where light from the sun is scattered by tiny airborne solid particles of ice and dust, to make the sky appear to be blue.

Reaction of thiosulphate with halogens

Chlorine, bromine and iodine all react in aqueous solution with thiosulphate ions. These are all redox reactions, in which the halogen element is reduced to a halide ion. Sulphur is correspondingly oxidised. With iodine, which has a brown colour in aqueous solution, the reaction is particularly spectacular on account of the dramatic colour change which occurs. This colour change can be enhanced by the addition of starch indicator, which gives an intense blue colour (starch-iodine complex) even at very small concentrations of iodine. This reaction is thus eminently suited for quantitative analysis, using titrimetric methods. The equation for the reaction with iodine is:

 $\begin{array}{l} I_2(aq) + 2S_2O_3^{\ 2^-}\!(aq) \rightarrow 2I^-\!(aq) + S_4O_6^{\ 2^-}\!(aq) \\ brown \qquad \qquad colourless \end{array}$

The oxidation numbers of the sulphur atoms in the tetrathionate ion are 0 for the inner sulphur atoms, and +5 for the outer sulphur atoms. The structure of this ion is shown in Figure 32.



Fig. 32. Tetrathionate ion

The reaction described above can be used to slow down the oxidation of iodide to iodine with acidified peroxide. The equation is given below:

$$2I^{-}(aq) + H_2O_2(aq) + 2H^{+}(aq) \rightarrow I_2(aq) + 2H_2O(l)$$

colourless brown

Thus if a solution containing acidified peroxide is added to a mixture containing iodide and thiosulphate, the acidified peroxide will start to react with the iodide to make iodine. In the presence of a limited amount of thiosulphate however, the iodine is initially converted back to iodide. When the thiosulphate is used up, iodine suddenly appears, and the solution turns a golden brown. If starch indicator solution has been added, a spectacular and sudden colour change from colourless (iodide) to blue-black (starch-iodine complex) occurs in the reacting mixture. Today, this reaction is popularly called a "clock reaction", and it is widely employed by magicians and in school teaching programs, where its kinetics can easily be investigated.

A simple procedure for this reaction is to mix together 100 mL of 0.01 M potassium iodide solution with 100 mL 0.01 M sodium thiosulphate solution and a few drops of freshly made starch solution. Upon addition of 100 mL of a mixture which is 1 M with respect to hydrochloric acid (H⁺ ions) and 1.5% hydrogen peroxide solution at about 20 °C, and subsequent stirring, the mixture suddenly turns a deep blue-black from colourless, after about 45 seconds. Figures 33 show the changing colour in a mixture which was not stirred.



Fig. 33. Iodine clock reaction, showing the gradual appearance after of the blue-black colour in an unstirred iodine clock reaction mixture: a) 20 seconds, b) 30 seconds, c) 45 seconds

The short selection of chemical experiments, as detailed above, shows how wonderfully suited the compounds of sulphur are, for both entertainment and educational purposes.

Summary

Sulphur has been discussed as a most interesting and inspiring substance in a multitude of contexts, ranging from etymology, where it was known and recognised 5,000 years ago, to geology, literature, art, alchemy, and chemistry.

The scene has been set for two final episodes from the life of this element - its roles in biochemistry and chemical technology. These chapters will conclude the remarkable story of sulphur.

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