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A PICTORIAL HISTORY OF CHEMISTRY

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By

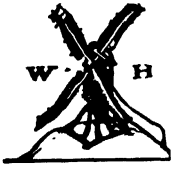
FRITZ FERCHL

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and

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PREFACE

In their Introduction to the original German edition, the authors wrote :

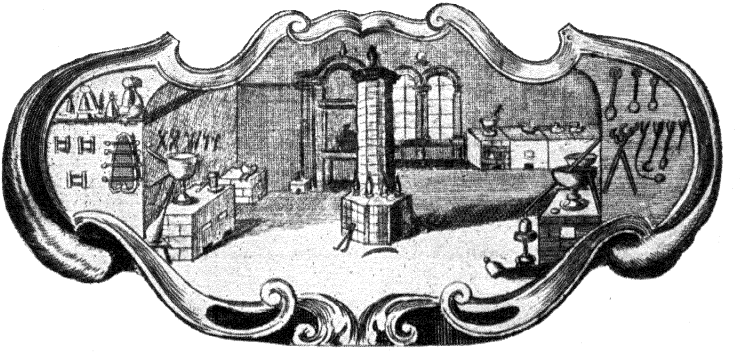
" The purpose of the present book is two-fold ; to arouse interest in the history of chemistry, and to give a brief general survey of the subject. The authors have made use to a great extent of the vivid and moving language of pictures. This plan has been carried so far that an interesting excursion into the chemical past can be made through the medium of the illustrations and their texts alone. This emphasis on illustrations has been intentionally exaggerated, since it is a remarkable fact that no other illustrated history of chemistry exists in the German language. The classical works of Gmelin and Kopp and the chemical histories of E. von Meyer made no attempt to enliven their texts by contemporary illustrations.

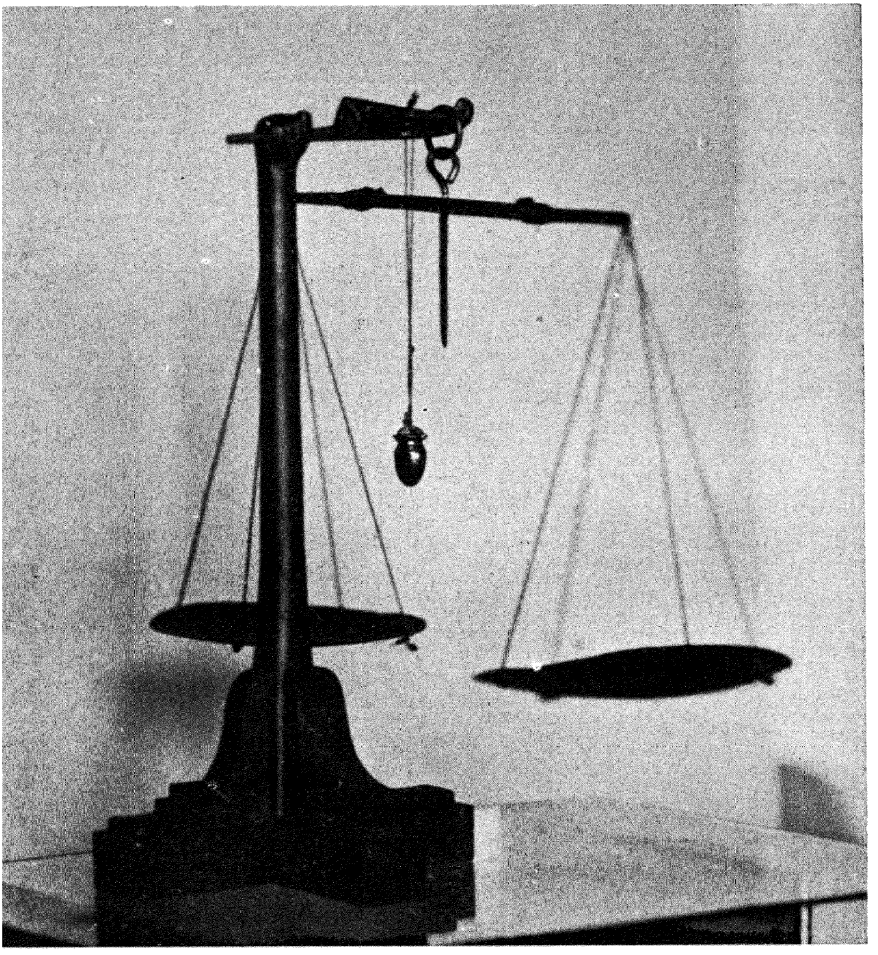
" The enormous power of pictures, which cannot be expressed in words, should facilitate this introduction to the history of chemistry. It is hoped that both research workers and teachers will make use of this book as a readily accessible storehouse of pictures."

The publishers, on the introduction of this work to their notice, appreciated that the remarkable collection of pictures provided in the German edition should be made available for English-speaking students and others. Throughout they have endeavoured to preserve the spirit of the original work, while modernising the text and securing expert advice on many controversial points raised therein. It has, unfortunately, proved impossible to remove from the German blocks certain inscriptions in that tongue, but in every case the information provided therein has been translated and placed in its proper setting. They wish to tender their thanks to all who have contributed to the task of preparing this translation and enabling the English-speaking peoples to enjoy this remarkable production.

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First picture of a balance with stops for the pans. (T. Leupold, 1726.)

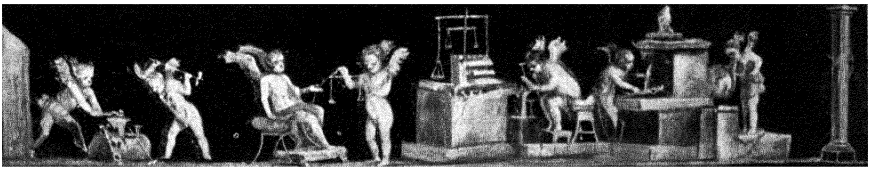


PLATE 1

Ancient goldsmiths' workshop. Casa dei Vettii, Pompeii.
Smelting furnace with bellows, remarkable balance with two beams.

PICTORIAL HISTORY OF CHEMISTRY

THE CHEMISTRY OF THE ANCIENTS

ALTHOUGH it is often stated that it is impossible to fix the beginning of chemistry, there is one great discovery which is unique in its effect upon the human race and may almost be described as the simultaneous beginning of chemistry and of civilisation. This is the *kindling of fire*, which is characteristic of all types of primeval man ; *Sinanthropus*, Neanderthal man and the early *Homo sapiens* of East Africa.

Any single man may have been the first to make fire artificially, or possibly two were needed, one to rub or spin a stick of hard wood on a piece of soft wood, and one to hold a suitable tinder. The man who struck sparks from two hard stones and thus ignited some inflammable material was a third and later pioneer, since all primitive peoples obtained fire first by friction and not by striking sparks. The first monument of chemical history should be erected to *Prometheus*, the fire-maker.

It must not be forgotten that this same Prometheus was also the discoverer of the *art of cooking:* an important branch of chemistry, since the cook brings about chemical changes in naturally occurring materials. Since the time of Prometheus mankind has been able to enjoy the savoury and appetising decomposition products of proteins and carbohydrates, broken down by the action of heat and enzymes. The scientific explanation of these processes has progressed very slowly and they are still only partly understood. However, they do represent the oldest chemical operation, and we shall not hesitate to award the second monument of primeval chemistry to the discoverer of *baking and roasting*.

The third pioneer of primeval chemistry lived in the stone age : he found how to bake clay and thus discovered the art of pottery. (The making of the earlier vessels which had not been treated by fire did not involve chemical

processes.) It was at this stage that *boiling* was introduced into cookery, and chemical changes could be brought about by heating liquids. Processes of fusion also became possible. At first these were restricted to melting out fats, but the manufacture of vessels was the first step towards rational metal work.

What materials were available to primeval man for chemical purposes? He could in fact use any naturally occurring object, either living or dead. Apart from any other sources, this includes all stones and minerals. Many things were used in a non-chemical manner, e.g. for tools, building, ornaments, painting. But his acquaintance with the materials used and his ability to distinguish them by their characteristic properties rank as scientific knowledge.

The same is true of the early use of the great variety of products offered by the vegetable and animal kingdoms. Here we must include not only foodstuffs (which have changed very little from that day to this), but also condiments, spices and medicaments which entered into cooking in an immense variety: roots, herbs, leaves, flowers, peels, woods, fruits, seeds and animal products, followed by resins, saps and flours. We can perhaps classify as chemical the artificial tapping of resins, rubber and saps from trees and shrubs, and a first step towards chemical operations may be seen in the extraction of plant juices and oils by pressing and in the grinding of seeds between two stones or (also in the stone age) in a kind of mill, or crushing them in a pestle and mortar. Of a truly chemical nature are the extraction of animal and vegetable materials by boiling, and the preparation of soups, mashes, glue and paste, in which chemical changes were brought about by boiling. Primitive man was familiar with the extraction of fats and animal oils, and he knew how to obtain dissolved substances by evaporating down solutions, since salt was known even in the stone age.

Fermentation took place spontaneously in fruit juices extracted by pressing, giving alcoholic drinks (fruit-wines). In the case of the complicated processes involved in brewing beer, nature again came to the assistance of chemical discovery. Grain which had germinated through bad storage was not thrown away, but was used to obtain sugar solutions which became alcoholic by spontaneous fermentation.

It is impossible to fix any limit in time for the first discovery of these processes or to the first production of acetic acid and lactic acid, and the same applies to the first use of animal and vegetable colouring matters (which were used to dye textiles in the stone age), or the first use of fragrant plant materials for perfumes or incense.

It should be added that the *use of metals* is much older than might be thought from the terms bronze age and iron age. These periods were characterised by the *general* use of these metals. In earlier times metals were found (more abundantly than now) native on the surface, especially gold (and occasionally platinum). Gold attracted men by its beauty, and because it was malleable. It could also be melted in a crucible, and a crucible is no more than a specially refractory cooking pot. Silver and copper also occasionally

occur native and have been shown to have been used (e.g. in America). Use has also been made from the earliest times of meteoric iron, which softens in the fire and can be worked by smiths.

These facts do not detract in the least from the importance of the greatest metallurgical discovery, that of how to *extract metals from their ores*. The first men to extract copper and iron in this way rank with the most important chemical discoverers, and may share the most eminent monuments of primitive chemistry with Prometheus, the first cook and the first potter.

The Metals

This discovery may have been made independently in a number of places, in fact anywhere where ores used as hearth stones came into contact with carbon.

The states of civilisation described as the *copper age*,[1] the *bronze age* and the *iron age* must not always be considered as following one another in that order. Even in the present age there are primitive peoples who know the smelting of iron, but not that of copper. It is not always that copper is more readily extracted from its ores than iron, in fact the reverse is often the case. Iron was probably not prized by some races who had not discovered steel. It should also be noted that iron corrodes if buried in the earth for thousands of years, so that we must not expect to find iron objects in very old excavations.

In any case, wrought iron was known in Egypt at the time of the Cheops pyramid (2700 B.C.). If the *discovery of iron* was made independently in Egypt, it may have happened when gold was being smelted from the Nubian magnetite sand of the Nile with the addition of substances containing carbon. It was certainly also known in East Asia, probably at a still earlier date. The Hittites (the present-day Armenians) had obtained *steel* by adding carbon to wrought iron (probably about 1400 B.C.): thus Rameses II used steel weapons. Unfortunately the identity of the great benefactor of humanity who discovered steel is lost in the darkness of history. The same is the case for the discoverers of the other metals. The ability to smelt copper from its ores must be dated back to 5000 B.C., while the corresponding dates for other metals are, silver at least 3000 B.C. (Egypt, Ægea), lead 4000 B.C., tin 3000 B.C., antimony about 2500 B.C., mercury 1500–1600 B.C. Arsenic was also known from very early times. The use of alloys is almost as old as that of pure metals. Copper-lead alloys came first, then bronze (copper-tin alloys of various compositions), and then brass and similar alloys made by adding other metals, especially zinc. Pure zinc was not known. Gold-silver and copper-arsenic alloys were also known, as well as amalgams of mercury with gold, silver, tin and lead. Soldering and tin-plating were also known.

If we consider how widely ancient armies (particularly those of the Romans) were provided with offensive and defensive weapons of iron and other metals, it is clear that there must have been a flourishing metal-industry at work.

[1] In early Babylon there was a copper age as well as a stone age. Copper was also mixed with lead in order to make it more fusible.

About 1300 B.C. the Iberian miners began to extract copper and tin in Britain. Almost all the ore deposits in the Rhineland were worked by the Romans. The magnitude of some of these undertakings cannot be doubted: thus there were 40,000 miners and founders in New Carthage during the Roman Empire. Further, copper alloys were used for vessels and technical articles to a far greater extent than to-day, which presupposes an active industry for extracting copper and tin. Large numbers of silver and gold coins were in circulation, and the same metals were used in considerable quantities for ornamental purposes. The production of the noble metals must therefore also have been at a high level.[1]

It was the widespread use of gold and silver which made necessary greater *analytical knowledge* in this direction.

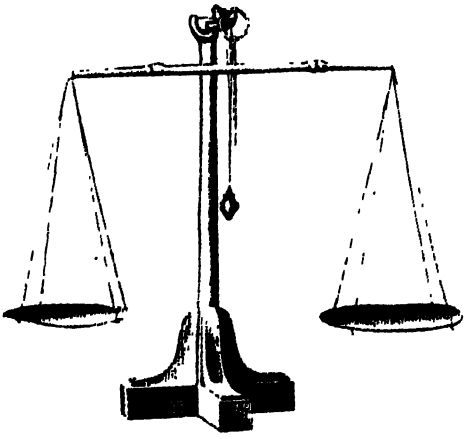


PLATE 2

Ancient Egyptian balance with two pans, in the Cairo Museum.

As regards metallurgical processes, the ancients were acquainted with assaying by the cupellation of gold and silver with lead.

They were also of course able to separate gold and silver. As they had neither nitric nor sulphuric acids, this separation was carried out by a so-called cementation process, i.e. igniting with common salt and clay, giving silver chloride, or with sulphur, giving silver sulphide. The goldsmiths' touchstone was in common use.

A mural painting in Pompeii shows a goldsmith's workshop, including a smelting-furnace with bellows which may have been used for gold testing, and which resembles furnaces used for this purpose right up to the beginning of the nineteenth century.

Trade in gold and silver made the use of *balances* necessary, since this is the only method for estimating the value of the noble metals. We know of a number of balances with either one or two pans from Egyptian or classical antiquity, of which the oldest date from several thousand years B.C. (from burial places and many pictures in Egypt).[2]

[1] The iron column of King Dhava in Delhi presents two unexplained chemical phenomena. In the first place no welding seam can be detected, and in the second place it appears to consist of non-rusting iron!

[2] Like the units of length and volume, the system of weights is of Babylonian origin. Before 2000 B.C. King Shulgi fixed the value of the mina (491·2 grams). This has remained the same through many centuries (Ptolemaic mina, Italian mina, Dutch and French pound, 489·5 grams). The Babylonian silver mina was 545·8 grams, which Darius raised to 560 grams. The Attic mina and the Roman mina were based on the Babylonian mina, being $\frac{5}{6}$ and $\frac{3}{4}$ of it respectively.

The Roman units of volume lasted for several centuries, *congius* (about 3 litres), *sextarius* (about $\frac{1}{2}$ litre), *hemina* ($\frac{1}{4}$ litre). Smaller measures were *cyathus*, *acetabulum*, *cochlear*.

A knowledge of the metals presupposes an acquaintance with their ores. The most important ones known and used were iron ores such as magnetite, hæmatite, brown iron ore, iron pyrites; copper pyrites and other copper ores such as carbonates (malachite, chalcocite); galena, tinstone, cinnabar, calamine, zinc-blende, pyrolusite, realgar, orpiment, stibnite, mispickel and many others.

Metallurgical processes led naturally to a *knowledge of metallic oxides*, such as iron oxide (yellow, red and black), cupric oxide, cuprous oxide, zinc oxide in different forms (flue dust, tutty), litharge, red lead, antimony oxide, white arsenic. Work with the ores and metals must have led to the observation of iron, copper, silver and lead slags, of lead matt and lead sulphide, cuprous and cupric sulphides, antimony sulphide, iron and copper hammer scale.

The following other compounds of the metals are of importance and interest: copper and iron sulphates (blue and green vitriol), white lead and lead sulphate, verdigris, verditer and copper silicate.

Other Inorganic Chemical Processes

The first lime burner and the first man to produce mortar were dealing with chemical facts of the greatest importance, although it is possible that the burning of lime is one of those which gradually obtruded itself upon human knowledge. *The burning and slaking of lime* take place wherever limestone is used as a hearthstone and then comes into contact with water. They have certainly been known for five thousand years. The use of lime for making cements is also very old: it was used mixed with volcanic rock at Puteoli and Baiae, at Santorin, and also at Andernach. Gypsum, plaster of Paris and their applications were also known to the ancients, as well as clays of all kinds (white, grey, yellow and red); other useful minerals such as talc, emery, asbestos, graphite, magnesite; salts such as common salt (rock-salt and sea-salt), soda (partly natural and partly from the ashes of seaweed), potash (lye from ashes, sometimes "sharpened" by added lime, and ignited tartar), alum (sometimes ignited), Epsom salt, borax (necessary for making *terra sigillata* ware), and probably calcium nitrate, which is formed spontaneously all over the world in suitable localities, though it may not have been observed. Ammonia and sulphur dioxide have been known for a very long time, and carbon dioxide is mentioned by Pliny. Of the inorganic elements the ancients were acquainted with sulphur (crystalline and flowers of sulphur) and carbon: soot, wood charcoal, graphite and diamonds, though the two last were not recognised as forms of carbon. It may of course be objected that many of these substances were not known in a pure state, but the same is true of our industrial chemical products to-day.

The palette of the painter of antiquity consisted partly of *natural mineral pigments*, such as white clay, chalk and other forms of calcium carbonate, yellow ochre (which was also used ignited), hæmatite and red ochre, pyrolusite,

glauconite, malachite, azurite, lapis lazuli, cinnabar, realgar, orpiment. It did, however, also include a number of artificial pigments: powdered *terra sigillata*, iron oxides (yellow, red, violet, *caput mortuum*), white lead, red lead, cinnabar, verdigris, artificial copper carbonate, artificial Babylonian lapis lazuli (Egyptian-blue, a lead glass coloured by copper oxide and sometimes cobalt oxide, the latter being unwittingly introduced by using materials containing cobalt), lampblack, bone-black, vine-black, and finally gold and silver as filings or leaf. Although the pigments of antiquity are known, the same is not true of the methods of painting used. In spite of much labour, the technique of the wonderful fresco painting and wax painting of the ancients still remains imperfectly understood.

The pottery of the ancients is also worthy of attention. Such pottery is usually valued for the incomparable beauty of its design, but purely from a chemical point of view the potter of antiquity has never since been equalled. Work like the black and red figured Attic vases could not be imitated to-day either in material or in design. The nature of the Roman *terra sigillata* ware (which was also made in Germany in the Palatinate) is gradually being cleared up, but it is not yet possible to equal it. The same is true for the black *terra sigillata* (Bucchero). A kind of stone ware was also known in Egypt.

The manufacture of glass in ancient times is worthy of special attention. There is a legend about the glazing of limestone standing in desert sands containing soda, though that is of course a later story.

It is certainly a fact that *glazing* was discovered first. In ancient Egypt there were glazed clay bricks and scarabs about 4000 B.C.

The oldest known glass vessel comes from Thebes and dates from about 3500 B.C. By 3000 B.C. it was possible to make blue and green glazes containing copper, as well as black beads. About 2800 B.C. there was colourless glass, green glass coloured with iron, and blue glass coloured with copper carbonate or silicate.

By 2000 B.C. the Babylonians certainly knew a variety of coloured glazes, e.g. light and dark blue, yellow and white, prepared by using copper, antimony and lead. By 1500 B.C. there were in Babylon (Tell-el-Amarna) a variety of small glass flasks, jugs, vases and cups (sometimes dark blue, which could be used as a pattern); glass imitations of cornelian, jasper, obsidian and lapis lazuli; yellow and red glass beads, dark red cups, and opaque white lines on glass made with zinc oxide. Iron ochre was used for colouring glass yellow, and additions of manganese and cobalt have been detected in blue and purple glass.

Glass-blowing with a tube is probably a Babylonian invention of later date. Coloured glass was widely used for imitating precious stones.

If we wished to erect a monument to the unknown *discoverers of glass* it would probably be to an Egyptian and a Babylonian jointly.

The Egyptians prepared glass from soda, wood ash (potash), marble or mussel shells, and quartz sand. Lead glass was also well known. Egyptian glass was coloured black with magnetite, yellow with iron, blue with copper

(or sometimes cobalt), red with cuprous oxide, purple and brown with pyrolusite and white (like enamel) with tin and lead. (It is sometimes incorrectly stated that tin glazes were not discovered until the Middle Ages.) Ruby glass coloured by gold was also known to the ancients.

Glass was originally shaped round a clay centre which could be removed afterwards, while later the glass was pressed on flat or concave moulds having raised or sunk relief. This developed later into the process of casting.

In Roman times the manufacture of glass was a flourishing concern. Blowing with a tube and into moulds was practised. Glass furnaces were known to the Romans (also in Roman Germany, e.g. at Trier), crucible furnaces and glass-makers' pots being used.

The range of technique was very wide. Thus there were glasses with thread decorations, with applied network, fluted glass, artificial iridescent glass, moulded dishes, striated glass, glasses made by pressing a solid centre into a mould. All kinds of grinding and engraving on glass were known. Glass mirrors coated with metal (sometimes deposited silver and gold) were used, glass window panes (Trier), and beautiful imitations of precious stones. Flashed glass was also known, and surface decoration by grinding. Even painting glass with colours to be burnt was not unknown to the Romans. Diamonds were used for cutting glass.

The zenith of Roman glass making is represented by the so-called myrrhine mosaic glass. Their *technique has been lost*, and in spite of much labour has never been rediscovered. High prices are paid for the few surviving pieces of this glass-work, or even for fragments.

These facts have been described in somewhat more detail in order to show the reader that in many fields the chemical technique of the ancients had reached an extraordinarily high level. In the fields of pottery and glass making it is particularly dangerous to despise the achievements of antiquity or to take pride in our present attainments. This fact may be readily seen by a walk through some of the museums of the world (e.g. for Roman glass the Walraf-Richartz Museum in Cologne).

Organic Substances

The number of organic substances known to the ancients was very great, including of course particularly those substances which occur naturally or may be easily prepared from naturally occurring materials. We may mention: petroleum, mineral wax, asphalt, natural gas, amber, resins from all conifers (pine, fir, larch, cedar, juniper), colophony, pitch, tar-oils (e.g. from pine, cedar and birch tar), turpentine (from terebinth), numerous *vegetable oils*, e.g. from olive, almond, bitter almond, sesame, castor-oil, walnut, palm, hemp, ben nuts, rape, turnip seeds, flax: animal fats, such as tallow and soft fats from many kinds of animals, wild and domestic, fish-oil, liver-oil, wool-grease (lanoline); soap, soap-solution and lead soap; [1] wax, crude and

[1] The manuscript of Galen *De simplicibus medicaminibus* (2nd century A.D.) clearly states that soap can be made from goat- or camel-tallow, ash-lye and lime.

bleached; starch from various kinds of grain, especially wheat; sugar substitutes: honey, manna, juice from liquorice, carrots, elecampane, palms. Contrary to Lippmann we believe that the Greeks had at least heard of cane-sugar, and we believe that his arguments against this supposition are not tenable. Besides the juice of sugar-cane, cane-sugar itself must have been known (at least in the countries of its origin). The process of obtaining sugar from the sugar-cane is so simple (pressing and evaporating down the juice) that it cannot fail to have been discovered wherever sugar-cane was available. The question as to whether or not Dioskurides had actually seen such sugar is of minor importance.

Varieties of gums, such as acacia (gum-arabic), cherry-tree, tragacanth. Vegetable mucilage (from orchids), and bird-lime from mistletoe. Vinegar from wine and beer, tartaric acid solution from unripe grapes, as well as tartar and juices containing malic, citric and oxalic acids.

Tanning substances, such as extracts of gall-nuts, oak-bark, pomegranate-bark, sumach, etc.

Resins for medicinal use, partly also as fumigatories, e.g. aloes, gum-ammoniac, asafœtida, bdellium, dragon's blood resin (also used as a pigment), euphorbium, galbanum, labdanum, gum mastic, myrrh, opoponax, scammony, gum-elemi, styrax, frankincense. Frankincense, myrrh, styrax and mastic were especially used as fumigatories, as well as benzoin in South Asia.

The true balsams (from the balsamodendron ?), which are not known to-day, were very costly even in ancient times.

From a chemical point of view especial importance attaches to the *colouring matters* of antiquity, particularly those used for *dyeing*. We may mention purple from the molluscs *purpura* and *murex*, madder, kermes, archil, alkanet, dragons' blood, pomegranate-flowers, indigo, woad, sepia, *Rhus cotinus*, nut-shells, myrobalan, acacia, broom, saffron, safflower, weld, *Diospyros lotus*, dyer's buckthorn (Avignon berries), sap green, gall-nuts. Alum, urine, vinegar, copper sulphate and other substances were used as mordants.

The most widely used writing materials were *India inks* and *ordinary iron-inks*. As to-day, India ink was made by mixing soot with gum or glue. It was kept as dry slabs and made up with water. The best varieties were made from vine-black, yeast-black or ivory-black; cheaper varieties from lamp-black, resin-black and pitch-black, while the worst was made from ordinary soot. Chinese ink was also used, coming into the market as *Atramentum indicum*. Vitruvius describes the manufacture of lampblack.

The gall-nut inks were prepared from extract of gall-nuts by adding gum and ferrous sulphate, just as to-day. Pliny describes a gall-nut test paper (of papyrus) for detecting the presence of ferrous sulphate (e.g. in verdigris).

Other animal organic substances which were probably known are egg-albumen, casein, gall, glue and gelatine (from bones and fishes), uric acid (from snake-excrement).

As stated above, the most important *fumigatory* was frankincense, to which must be added myrrh, mastic and styrax, and probably in South Asia

also sandal-wood and benzoin. Of the *compounded fumigatories*, the most important were those of the Egyptians. The most famous of all was *Kyphi*. According to the Osiris text from Dendera it contained twelve ingredients, while according to Plutarch there were sixteen, namely honey, wine, raisins, cyperus, resin, myrrh, aspalathus, melilot, mastic, bitumen, saffron, sorrel, juniper (two sorts), cardamom and calamus. It is possible, however, that some of the names have been incorrectly translated.

The substances used in Egypt for *embalming* corpses were of many kinds, in particular mastic, styrax, asphalt and resin from pine, juniper and cedar trees.

Ethereal oils were chiefly obtained by maceration with cold or lukewarm olive oil (or other oil), also in some cases by pressing. (We shall discuss later how far they were obtained by distillation.) In this way oils and mixtures of oils were obtained from aniseed, caraway, wormwood, cloves, iris, mustard, onion, chive, calamus, cherry-laurel, parsley, pennyroyal, lavender, mint, marjoram, thyme, myrtle, spikenard, narcissus, lily, rose, rue, cress, radish, rosemary, sage, mustard, juniper, cedar, cypress and cinnamon.

Of the costly *animal perfumes* the best known was castoreum, also used medicinally.

These perfumed oils were chiefly used for making *ointments*. Many of these were simple, but a number of them had very complicated compositions. Thus according to Dioskurides, ointment of Susa consisted of olive oil and the extract of a thousand lilies, spiced with calamus, myrrh, cardamom, saffron and cinnamon. According to the same author, narcissus-ointment consisted of oil with narcissus flowers and spices such as calamus and aspalathus, while oil for spikenard ointment contained Indian or Syrian spikenard (varieties of valerian), malobathrum oil, edible roots, amomum, beard grass, myrrh and real balsam.

Pliny mentions similar mixtures, of which the " augmented Mendesian balsam," the great balsam and the royal balsam must have been very costly. The last contained twenty-six ingredients.

Substances used as *cosmetics* (in addition to the ointments) were white lead, red lead and antimony sulphide (black), while blue and green face-pigments were also used. There were also hair-dyes to dye grey hair a dark colour and dark hair blonde or golden. We may further mention substances for blackening the eyebrows, hair-lotion, face-lotion, tooth-wash, remedies for odours of the breath and arm-pits, bleaching agents for the complexion, depilatories and hair-restoratives.

Medicines

The medicines of antiquity are worthy of particular attention. Most remedies were naturally of *vegetable* origin, but there were a number of an *animal, mineral* and *chemical* nature. Of the latter we may note especially alum, sulphur, copper oxide, copper sulphate and iron-rust.

It is quite impossible to enumerate all the *vegetable medicines*, although

all of them contain special chemical substances with characteristic properties. Thus the *Papyrus Ebers*, written between 1700 and 1200 B.C., mentions over a hundred medicinal plants. According to a list compiled by Tschirch, the medicine cupboard of the ancient Egyptians certainly contained one hundred and eighty drugs. Among these there were many worthy of note, such as aloes, calamus, hemp, henbane, mandragora, mint, wormwood, myrrh, frankincense, styrax, castor-oil, jujube, mustard, liquorice, fenugreek (*Trigonella purpurescens*), squill, strychnos, opium.

Among the animal medicines various animal fats, portions of entrails and kinds of blood are of special interest.

The knowledge of the *Babylonians* was probably quite similar. Many *Greek* authors from Homer onwards provide points of interest. Herodotus knew various medicines foreign to Greece (cinnamon, myrrh, frankincense, etc.), and a great deal of information is of course to be found in the writings of physicians. We shall not attempt to enumerate the hundreds of drugs mentioned in the *Corpus Hippocraticum*. Hippocrates the Great (probably 459–377 B.C.) and his school knew and mentioned numerous aperients, emetics, gargles, diuretics, sudorifics, astringents, sternutatories, corrosives, cooling remedies, hair-restoratives; also medicines for worms, ulcers, wounds, flatulence, female diseases, eye troubles, skin troubles, womb troubles (probably including ergot); medicines containing tanning principles, and poisons. Among the plant poisons of antiquity we may mention aconite, black and white hellebore, henbane, thorn-apple (stramonium), hemlock oleander, meadow saffron, varieties of mezereum, mandragora, belladonna (deadly nightshade), squill, dorcynium, strychnos, opium, hemp. Among the animal poisons were snake-venom, toad-venom, cantharides. Medicines were used in the form of decoctions, infusions (teas), extracts, electuaries, ointments, plasters and suppositories.

Theophrastos Eresios, the pupil of Aristotle (probably 371–286 B.C.) describes almost a hundred medicinal plants, among others *citrus medica*, varieties of pepper, male-fern, elemi, etc. However, by far the most important source for the drugs of antiquity is the great *Pharmacopœia of Pedanios Dioskurides*, A.D. 77 or 78. Dioskurides can hardly have known less than five hundred remedies, and he was justly the source of pharmaceutical knowledge for many centuries. All his successors right down to the sixteenth century are indebted to his knowledge.

A contemporary work is the natural history of *Caius Plinius Secundus* (A.D. 23–79) in thirty-seven volumes, which has preserved for us an immense amount of information about the knowledge of his time, including of course a great deal which is of interest to the historian of chemistry and pharmacy. Posterity has every reason to be grateful to him.

Of considerable interest for the history of medicine is the first-known *dispensatorium* by the Latin author *Scribonius Largus*, a collection of prescriptions entitled "Compositiones." This work gives an excellent idea of the complex medicines of antiquity. The author was a physician who wrote

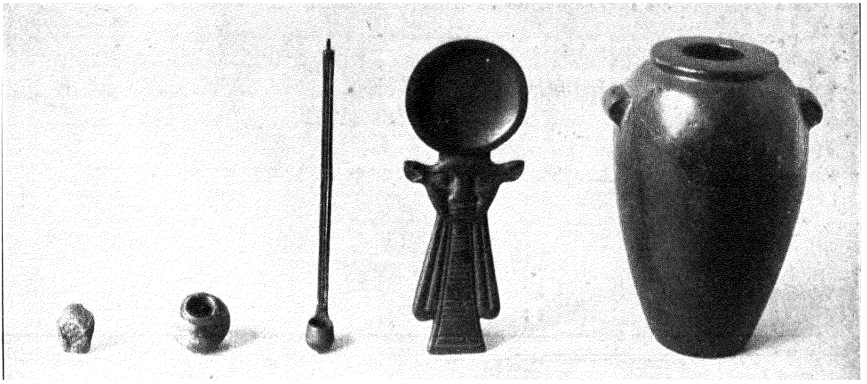


PLATE 3

Toilet articles of Queen Mentuhotep from her tomb at Thebes. About 1780 *B.C.* Originals in the Egyptian Museum, Berlin.

Root, small basin of green pottery, small ladle with a movable rod in the centre, hand mirror with the head of Hathor (goddess of love), upright vessel of serpentine.

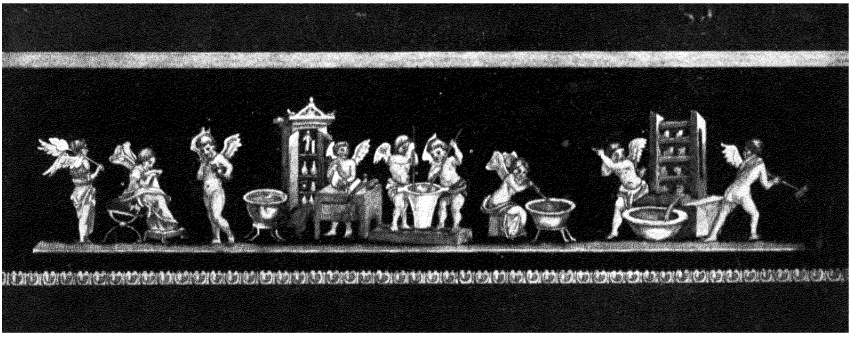


PLATE 4

Ancient workshop for preparing ointments. (Wall painting in the Casa dei Vettii, Pompeii.)

1. Delivery of ointments.
2. Ointment cupboard.
3. Table with scales and roll of prescriptions.
4. Mortar with pestles.
5. Tripod cauldron.
6. Oil press : the expressed liquid runs into a bowl.
7. The vertical plates of the press were not fixed together by means of screws, but by hitting with heavy hammers.

about A.D. 47. He used in his prescriptions about two hundred and fifty vegetable and twenty-nine animal ingredients. Many of the complex remedies must have been very laborious to prepare. We shall mention a few of the most famous.

The *panacea of Heras* contained the following ingredients: chamæpitys (probably *Ajuga iva*), comfrey, chamælaia (*Daphne Gnidium*, or another species), marrubium (*M. Pseudodictamnus*), pennyroyal (*Mentha Pulegium*), lesser centaury (*Erythræa Centaurium*), helenium (*elecampane*), aristolochia, frankincense, myrrh, aloes, galbanum, olive oil, honey, propolis, amianthus,



PLATE 5

Dioskurides with mandrake. At his feet a dog doubled up with pain. From the Codex constantinopolitanus of Dioskurides (A.D. 512), now in Vienna, which contains the oldest pictures of herbs extant.

turpentine, green vitriol, bitumen, *Terra ampelitidis*, silver-slag, gall-nuts and orris-root.

A particularly fragrant medicine was the *ambrosia of Zopyros* (180 B.C.): the root of *Costus Arabicus*, frankincense, pepper, *Flores Junci* (perhaps *Andropogon Schœnanthus*), cinnamon, cassia, saffron, myrrh, Indian spikenard: these ingredients were mixed with powdered wax and wine.

The *antidote of Philo* consisted of saffron, pyrethrum (probably *Anacyclus Pyrethrum*), euphorbium resin, spikenard, white pepper, henbane, opium, and honey.

The most complex medicines of antiquity are probably the *antidote of Mithridates* and the *Theriac of Andromachus* (about A.D. 54). We shall only describe the latter, which contained the following ingredients:

Pastilles of vipers' flesh, pastilles of scilla bulbs (which were coated with flour and baked), opium, Magma Hedychroi (an ointment prepared from asarum, aspalathus, calamus, Valeriana Phu, schœnanthus, balsam wood and sap, cinnamon, myrrh, malobathrum, Indian spikenard, cassia, saffron, mastic and Falernian wine), orris-root, rose-petals, liquorice-juice, turnip seeds, scordium (*Teucrium Scordium*), Syrian balsam, cinnamon, agaricus (purging agaric), myrrh, root of *Costus Arabicus*, saffron, cassia, frankincense, schœnanthus (*Andropogon*), spikenard, white and black pepper, Pontic rhubarb, stœchas (*Lavandula Stœchas*), marrubium (*Pseudodictamnus*), apium (probably parsley), calamintha, turpentine, quinquifolium (*Potentilla reptans*), ginger, pennyroyal (*Mentha Pulegium*), chamæpitys (*Ajuga iva*), amomum, styrax, seeds of the Cretan Gamander, Valeriana Phu, Lemnian earth (clay), malobathrum leaves (patchouli ?), calcined green vitriol (*Caput mortuum*), gentian, aniseed, the juice of *Cytinus Hypocistis*, gum-arabic, seseli (a plant of the *Umbelliferæ* genus), cardamom, fennel fruits, acacia, thlaspi, hypericum, ammi, sagapenum, castor plant, aristolochia, carrot seeds, bitumen, opoponax, centaurium (lesser centaury), galbanum, old wine and Attic honey.

Many more recipes are given in the writings of the Roman physicians Aulus Cornelius Celsus (about A.D. 20–50) and especially Claudius Galenus (about A.D. 130–210).

Finally, as regards *beverages*, even the Babylonians knew a number of varieties of both beer and wine. Emmer wheat and barley were used to brew mixed beers, black beer, red beer, small beer and spiced beers. Apart from the use of hops (which apparently was not known to the ancients), spiced beers are no longer made in Germany. To this day beer is made in Egypt by methods very similar to those of the ancient Egyptians. Mead, made from fermented honey-water, was known to a number of races. Honey-water was often added to the beer-mash in order to increase the alcoholic content.

The Chemical Apparatus and Appliances of Antiquity

The Papyrus Ebers shows that even in its days (1600 B.C.) the production of medicinally active substances involved the operations of boiling, infusion, maceration, extraction, filtration, percolation, expressing, powdering with grindstones, pestles and mortars. It need hardly be pointed out that all kitchen utensils could be used for chemical purposes when suitable. The most important of these was smelting. The relatively extensive industrial activity of antiquity must undoubtedly have required the establishment of correspondingly large furnaces.

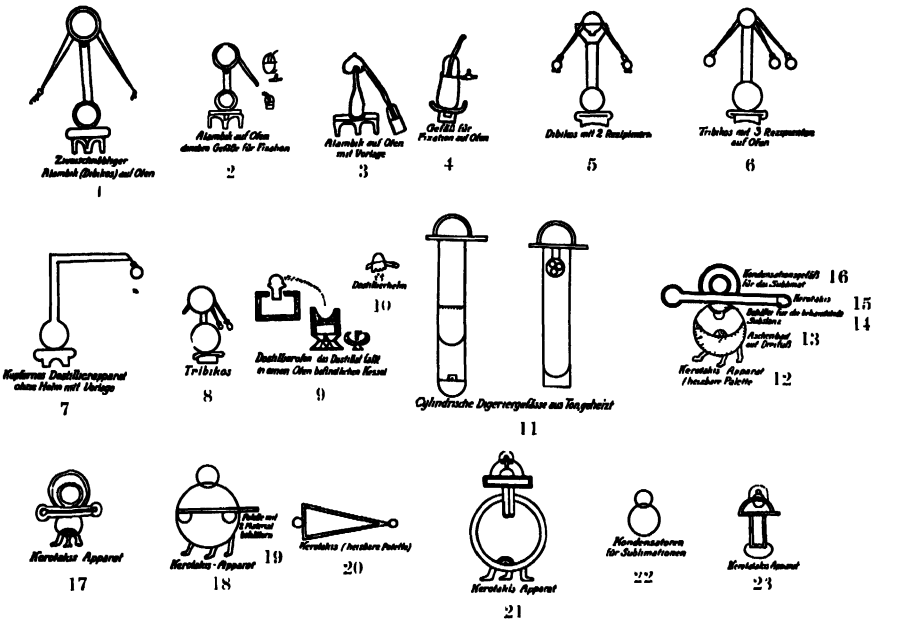


PLATE 6

Illustrations of Alexandrian chemical apparatus.

The pictures are taken from a manuscript of the tenth or eleventh century, written in Greek, with numerous explanatory illustrations. It is kept in St. Mark's library at Venice and reproduces, among many other alchemical texts, the work of an Egyptian alchemist named Cleopatra on making gold ("Chrysopoeia"), perhaps of the second century A.D. The drawings from this and other MSS. were first published by the French chemist M. Berthelot in his *Introduction à l'étude de la chimie des anciens et du moyen âge*, Paris, 1889.

1. Alembic with two delivery tubes (dibikos) on a furnace.
2. Alembic on furnace : vessels for fixation.
3. Alembic on furnace, with receiver.
4. Vessel for fixation, on furnace.
5. Dibikos with two receivers.
6. Tribikos on furnace, with two receivers.
7. Copper distillation apparatus and receiver : no still-head.
8. Tribikos.
9. Distilling furnace. The distillate falls into a heated cauldron.
10. Still-head.
11. Cylindrical digestion vessels of earthenware, heated.
12. Kerotakis apparatus (heated palette).
13. Ash-bath on tripod.
14. Container for the substance to be treated.
15. Kerotakis.
16. Condensation vessel for the sublimate.
17. Kerotakis apparatus.
18. Kerotakis apparatus.
19. Palette with two containers for substances.
20. Kerotakis (heated palette).
21. Kerotakis apparatus.
22. Condensers for sublimation.
23. Kerotakis apparatus.

The extraction of copper, iron, tin and lead from their ores demanded reduction furnaces fitted with bellows. Tempering furnaces must have been

used for the production of steel, and cupellation furnaces were a necessity for refining silver. The extraction of mercury involves some kind of distillation

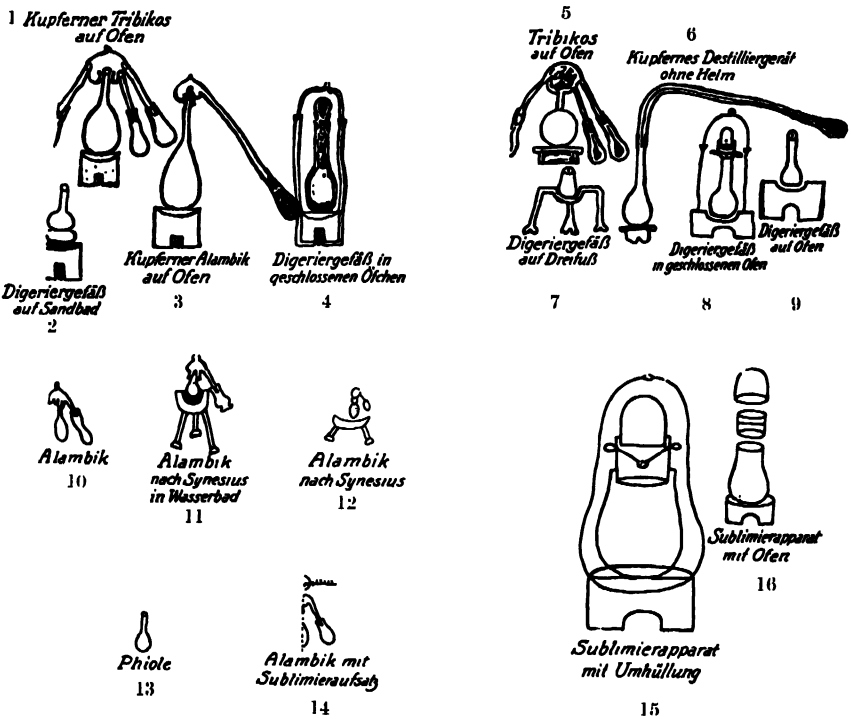


PLATE 7

Illustrations of Alexandrian chemical apparatus.

Manuscripts 2325 and 2327 in the National Library, Paris. Taken from *Introduction à l'étude de la chimie des anciens et du moyen âge*, M. Berthelot, Paris, 1889.

1. Copper tribikos on furnace.
2. Digestion-vessel on sand-bath.
3. Copper alembic on furnace.
4. Digestion-vessel in closed furnace.
5. Tribikos on furnace.
6. Copper distilling-vessel without still-head.
7. Digestion-vessel on tripod.
8. Digestion-vessel in closed furnace.
9. Digestion-vessel on furnace.
10. Alembic.
11. Alembic on water- or ash-bath (Synesius).
12. Alembic (Synesius).
13. Phial.
14. Alembic with sublimation attachment.
15. Sublimation apparatus with jacket.
16. Sublimation apparatus on furnace.

apparatus. In order to smelt metals, crucibles and crucible furnaces were necessary, while cast iron was also known. The production of mortar and plaster of Paris presupposes kilns for ignited lime and gypsum. The manu-

facture of bricks and pottery took place in kilns, of which a number have been found, and glass manufacture took place in glass furnaces with refractory pots.

Especial interest attaches to *distillation vessels*. Distillation was carried out even in antiquity. Even when we have no direct evidence of this, it is reasonable to suppose that such a simple fact could not have been unknown. The lid of a boiling saucepan would illustrate the process to anyone with the slightest power of observation. If the saucepan lid is provided with an outlet or some arrangement for draining, then the distillation vessel is complete. Aristotle confirms the knowledge of this principle. He says : " If a mixture of liquid and solid components is evaporated, a vapour is formed which can be condensed to liquid, while the solid components remain behind." The principle of distillation could hardly be more clearly expressed. In another place he says that sea-water can be made potable by distillation.

The process of charcoal-burning also illustrates a type of distillation process which was very well known to the ancients. The depression in the hearthstone to collect the non-volatile products together with the delivery pipe and the trap for tar constitute a distillation apparatus. Tar from all kinds of conifers, pitch and pitch oil were known, and were produced particularly in Colophon, Gaul and Pityusa. Further, the slow combustion of conifer wood in its own kiln constituted a kind of *distillatio per descensum*. In the product of soot by a kind of destructive sublimation, Dioskurides recommends water cooling for the cover, which he calls *ambix*. It is impossible to obtain mercury from cinnabar without distillation, and the production of zinc oxide in the chimneys of smelting furnaces belongs to the same category.

We must also mention the type of distillation described by Pliny and Dioskurides, in which sheep's wool was used to catch the oil distilling over (in the preparation of oil from cedar, juniper, or resin).[1]

P. Ch. Ray has described some Indian apparatus used in the late Middle Ages which probably resembles the apparatus of the ancients. It includes sublimation vessels, two pots placed one above the other, apparatus with bellows for *distillatio per descensum*, and distillation apparatus with delivery tubes and primitive cooled receivers.

No pre-Christian drawings of distillation vessels have come down to us. It was only after the third century A.D. that manuscripts dealing with chemical subjects were illustrated. A manuscript in the Library of St. Mark, Venice, contains texts by various authors, notably Zosimos of Panopolis ; in this are illustrated numerous vessels which undoubtedly must have been used for the purpose of distillation. A manuscript in the National Library at Paris also shows illustrations of a large variety of chemical appliances. The apparatus at the disposal of the chemist at the close of ancient times and the beginning of the Middle Ages is very well illustrated. There were small portable furnaces, while oil lamps and candles were also used for heating. Distillation was carried out on an ash-bath or on

[1] In this connection we may mention that both Aristotle and Pliny knew that strong wines give off inflammable vapours (alcohol) on heating.

a water-bath (Isis bath, or bain marie); both these methods were known much earlier. The distillation vessels were of copper or glass. They consisted of a flask (or phial) surmounted by a still-head, which was later known as an alembic (from the Greek word *ambix*, which was also used to describe a still-head). The evaporating liquid condensed in the head, which could be fitted with an enlarged rim in which the condensed liquid collected. By means of a delivery tube fitting into this rim the liquid was led into a flask (receiver or receptaculum). In place of one delivery tube there might be two or three, each with its receiver: the apparatus was then called *dibikos* or *tribikos*. It may be noted that copper distillation vessels with two necks are used to the present day in the spirit-distilling industry.

There were of course digestion vessels (e.g. for dissolution) and also the so-called circulating vessels, the action of which may be compared with that

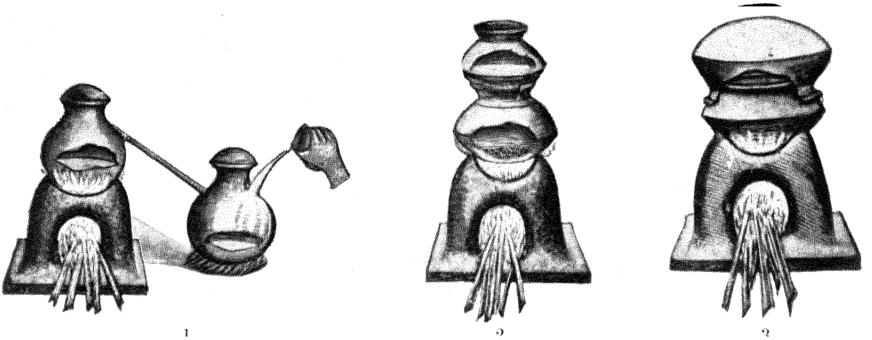


PLATE 8

Mediæval Indian chemical apparatus (Ray).

1. Distilling apparatus with very simple cooling for the receiver.
2. Sublimatory: the upper dish is filled with cold water.
3. Sublimatory.

of reflux condensers. There were vessels for calcination (oxidation of metals) and distillation vessels somewhat resembling the retorts still used to-day. A piece of apparatus in the St. Mark's manuscript may be a "Moor's head," i.e. a water-cooled still-head. (The cooling vessel surrounding the still-head has been compared to a turban.) There were also sublimation vessels, which are of course only a variant of distillation vessels.

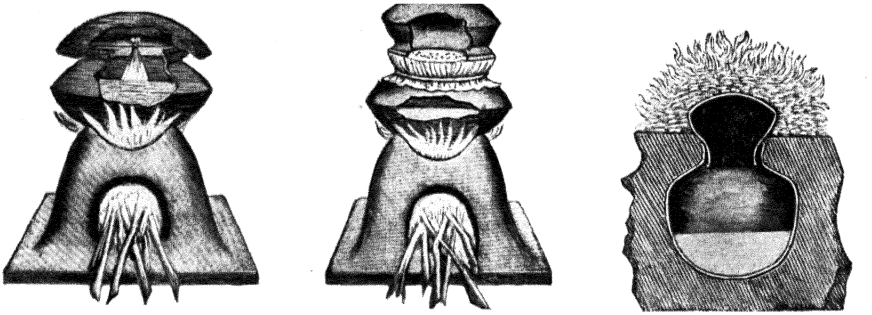
Especial interest attaches to the so-called kerotakis or palette apparatus. This was probably similar to the construction described by the Indian Ray, in which a perforated plate is fixed between an upper and a lower jar. The substance below can volatilise through the perforations and sublime into the upper vessel, or alternatively a substance can be placed on the perforated plate, where it is extracted, dissolved or otherwise acted upon by the vapours coming from below.

Only a little actual chemical apparatus has been preserved from ancient times. There are of course many earthenware jugs and glass bottles and phials,

which may or may not have been used for chemical purposes. Many of them have been found in tombs and were never used at all. However, vessels for oil, ointment and balsam are well known in large numbers in any collection of antiquities : aryballos, alabastron, balsamaries. They were made of earthenware, glass, alabaster and bronze. There are also cosmetic vessels of many kinds, mortars of marble and other sorts of stone, also a few vessels used by apothecaries. Earthenware vessels with filters are not rare, including beer-filters and jugs with a filter in place of a lid (for making infusions).

The incense burners, censers and incense-spoons which have been found are of a ceremonial nature.

Of numerous varieties of cooking appliances, special mention may be made of funnels and siphons of glass and metal.



1 2 3

PLATE 9

Mediæval Indian chemical apparatus (Ray).

1. Extraction apparatus.
2. Apparatus resembling kerotakis.
3. Descensory.

Smelting-crucibles and pots for glass-making belong to the field of technical chemistry.

It is important to note that *balances* (with one or two pans) are often found, and still more often *weights*, of which there are complete sets in museums and private collections. We may also mention the existence of actual measures for measuring the volume of liquids.

Two supposed glass retorts are known, one at Aliscamps in France and the other, originally found in Syria, in the Deutsche Museum in Munich. These so-called retorts are probably only faulty or unfinished phials.

As regards the most important *manuscript sources* for the chemistry of the ancients, we have in addition to those dealing with medicine (particularly Pliny : see above) the papyri of Leyden and of Stockholm. These are from the third century A.D. and deal especially with the falsification of metals, precious stones and costly dyes.

Material is also available in the agricultural and technical writers of antiquity (Vitruvius : the cookery book of Apicius).

The Egyptians appear to have known the fundamental principles of practical chemical manipulation, in fact the word " chemistry " (or alchemy) may have originally meant " Egyptian learning." However, the Greek philosophers and physicians also carried out experiments, especially Aristotle, who, among other things, carried out researches in what we should to-day term colloid chemistry.

He grasped in a remarkable way the action of the male sex hormone, realising that " small changes acting on the principle of a thing can effect large and manifold changes at the periphery, just as a small movement of the rudder can bring about a large change in the direction of the ship." This is a most penetrating and modern enunciation.

The Theoretical Chemistry of Antiquity

Special interest attaches to the *concept of elements*. This was quite different to the conception which was held right up to present times, a conception which in turn has given way to the idea of electrons, positrons, neutrons (and photons), which can hardly be termed " chemical " entities.

We can hardly expect that the scientific concepts of the ancients should be lasting and unchanged by further work. It is quite unjustifiable to belittle the concept of elements founded by Empedocles and Aristotle without considering under what circumstances it was produced. The idea that there were substances which could not be subdivided further must have appeared illogical to any philosopher, and we cannot suppose that an Aristotle would entertain such an absurd contradiction to experience.

Aristotle taught that there are four elements, *earth*, *air*, *fire* and *water*. It did not occur to numerous chemists of the past era that these names were only symbols for the solid, gaseous, incandescent and liquid states. Thus if it is stated that a substance contains the element air, it means that it can be converted into the gaseous state. If wood is stated to contain " earth " and " air," it means merely that it can be transformed to solid (ash, charcoal) and gaseous substances. Considered in this light, Aristotle's conception of elements has a reasonable interpretation.

The elements are closely connected with the principles of heat, cold, dryness and moisture. When Aristotle says that the properties of substances can be explained on the basis of these four principles, he is not so far from the truth. He states for example that the form of matter is regulated by the principles of heat and cold, which is completely correct, as is also the statement that even their specific weights depend on these two principles. Aristotle's theory of elements must be interpreted as an attempt to refer the properties of substances, i.e. all that is known about them to a small number of principles (*fundamental properties*), which is a fundamentally sound line of attack.

As regards the theory of chemical processes, the attitude of the chemists of antiquity to the atomistic theories of Democritus and Epicurus was certainly not the one which we are inclined to attribute to them in the light of present

PLATE 10

From the Syriac alchemical manuscript in the British Museum

knowledge. A large number of chemical processes were known, but these were as a rule regarded as *subtle processes of blending or separation*, and were not in any way connected with an atomistic conception. The idea that all chemical substances are mixtures must not be lightly dismissed, since it is in fact the truth.

The idea associated with the word *transmutation* was not that one substance could be transformed into another by some wonderful or magical process, but merely that (just as in marriage) two substances could unite to produce a new substance. The *conceptions of alchemy* may be in part due to this idea.

As regards weights and proportions in chemical processes, Empedocles is of the opinion that the differences between substances depend ultimately upon differences in their *quantitative compositions*. Like Aristotle, he states quite clearly the law of conservation of matter, a law which is to some extent abandoned in present-day chemistry, but which has stood as a fundamental chemical principle since the time of Lavoisier. The fact that the weight of matter remains constant in combustion (proved experimentally by Lavoisier) is quite unequivocally stated by Lucian.

The oldest known *chemical symbols* belong to the close of antiquity or the beginning of the Middle Ages.

The manuscript of St. Mark (Venice) dealing with the knowledge of the Alexandrines identifies the seven metals with the seven planets: the sun with gold, the moon with silver, Kronos (Saturn) with lead, Zeus (Jupiter) not (as was the case later) with tin, but with electrum: this is of course the gold-silver alloy of that name and not the similarly named amber. Ares (Mars) was assigned to iron, Aphrodite to bronze (copper), and Hermes to tin; not (as later) to mercury. The signs used for these metals are obviously the signs of the planets. The chemical symbol for gold was a circle with rays, which were omitted later. The signs for silver, lead, iron and copper are approximately the same as those used subsequently. The sign for Hermes (tin) is the same as that used later for mercury, while mercury was represented by a waning moon and silver by a waxing one. The other symbols bear very little resemblance to those used later by the alchemists. However, the list of signs shows that the Alexandrian chemist was aware of the presence of copper, tin, silver, lead, etc., in the ores and compounds of these metals: thus the presence of iron in iron oxide is shown by the use of the symbol for metallic iron in the sign for iron oxide. In view of the doctrine of transmutation (which also existed at that time), this recognition is of the *greatest importance*, and gives a direct link between the Alexandrians and present-day chemistry.

The identification of the metals with the planets is certainly not due to the Alexandrian Olympiodoros, to whom it is often ascribed, but is undoubtedly very much older, and most probably represents a part of the Babylonian star religion.

An early mediæval manuscript from Syria in the British Museum also contains a list of chemical signs, which however show very little agreement

with those used later. Almost the only ones to correspond are those for gold, silver and iron. The sun represents gold and fire, the moon silver and water, Zeus is air, Ares is iron, Hermes is mercury and Kronos is lead. The table shows clearly that in most cases the signs used were in no way invariable.

The fact that signs were used at all is partly due to the secrecy with which chemistry was surrounded (an important factor in all periods), while they were also used as a convenient and rapid method of recording chemical facts.



PLATE 11

End plate of the index of the Rösslin herbal.

CHEMISTRY IN THE MIDDLE AGES

THE centuries of racial migration did a great deal of harm to human culture, including both the theory and practice of chemistry. A number of countries which were less affected by the disturbances of migration (particularly Byzantium and the Orient) were harmed by the spread of Mohammedanism, with its opposition to culture. However, in the near East and the whole of the Orient a considerable portion of the knowledge and technique of the ancients was preserved, particularly in Constantinople, Syria, Egypt and Persia. Under a veneer of Mohammedanism the culture of antiquity continued triumphantly. There were at first several centuries of wearisome salvage work, during which much was irrevocably lost. Then about the thirteenth century the stream of development again began to flow smoothly, and a great new movement in the field of chemistry dates from this period. The often repeated phrases which depict the Middle Ages as a period of the deepest ignorance and impotence can no longer be accepted. If applied to the field of chemistry they can definitely be described as falsehoods, since the Middle Ages produced discoveries of the very highest importance, which are *quite on a level with any subsequent chemical discoveries*, and which stand higher than most of them. In the last centuries of the Middle Ages chemistry was in full flower, both technically as an art or trade and scientifically in its theories and philosophy, while great explorations had begun to widen its horizons still further.

In the first few centuries of the Middle Ages chemistry was still dependent on the work of antiquity. Thus in the Compendium of Isidorus of Seville (560–636) there is hardly any chemical information which was not known to the Romans. The same is true of Rhabanus Maurus, the German Benedictine (776–856). The work of the latter does, however, show that the technical chemical arts of the ancient Romans were gradually springing up again in Germany, e.g. he gives illustrations of a workshop for glass-blowing and a dye-works. The manufacture of glass in Germany appears to have died out completely between the fifth and seventh centuries.

The Carolingian manuscript *Compositiones ad tingenda* dates from the end of the eighth or the beginning of the ninth century, but is probably derived from a Greek original. Many technical chemical processes are described. especially in connection with the manufacture of dyes and dyed materials.

It describes the tinting of glass, the colouring and gilding of mosaic. the

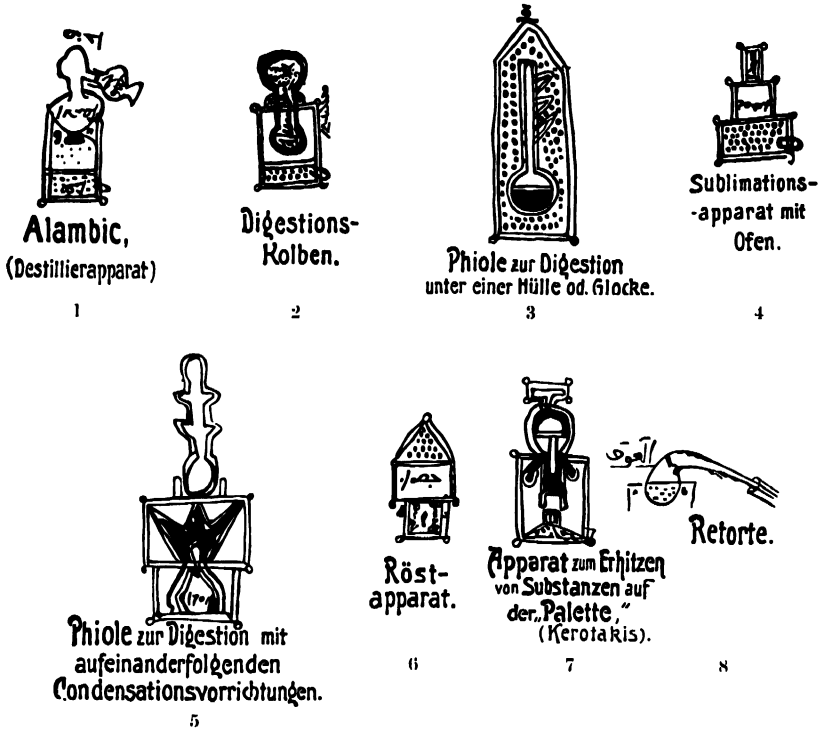


PLATE 12

Illustrations of chemical appliances from an early mediæval Syrian manuscript, after Berthelot.

1. Alembic (distillation apparatus).
2. Digestion-flasks.
3. Phials for digestion (under a bell-jar).
4. Sublimation apparatus with furnace.
5. Phials for digestion with successive attachments for condensation.
6. Roasting apparatus.
7. Apparatus for heating substances on a " palette " (kerotakis).
8. Retort.

colouring of metals (preparation of alloys), dyeing of textiles and leather, the preparation of white lead and artificial cinnabar, as well as many other things. The general impression, however, is that nothing is described which was not known to the ancients. Other manuscripts of uncertain date exist, e.g. the *Book of Heraclius* on the arts of the Romans (i.e. the Byzantines). The dyes mentioned by this author were all known to the ancients. He introduces a

few new names, e.g. brazil-wood (red sandal-wood), but this was certainly used as a dye in southern Asia, even in ancient times.[1]

A similar book, *Mappæ clavicula* (key to painting), is of more interest to the painter than to the chemist.[2]

The carmine described in this book was probably prepared from the cochineal insect, and appears not to have been known to the ancients (as was the kermes dye).

Schedula diversarum artium was written by *Theophilus Presbyter*, a Byzantine monk who migrated to Cologne about 950 and took the name of Rogerus. It is a book on the art of painting, and describes the knowledge and technique of the Byzantines. A list of pigments is given, containing dyes from certain berries (whortleberries, cranberries, elderberries), which of course, were known from primitive times: also carmine and red lacquer, probably from the Indian stick-lac.[3]

Theophilus' work contains particularly good directions for making glass, both plate-glass and glass vessels. He describes glass-furnaces, glass-pots, annealing furnaces, flattening furnaces, tools; the melting, colouring and flashing of glass: painting glass and burning in colours (with furnaces for the latter): ornamentation, glass-cutting and glass-repairing. The book also deals with the preparation of enamels, niello technique, inlaying and goldsmiths' work.

As regards pharmaceutical knowledge, the Western world depended completely on the lore of antiquity for the first few centuries of the Middle Ages. For the purposes of this book we shall take account only of new drugs (not of new applications of old ones), and from this point of view there is little to be said about this epoch. As sources we may mention *Lucius Apuleius* and his "Herbarius" (first half of the fifth century): *Aetius Amydenos* (about 540), who, as an Asiatic, was particularly acquainted with drugs from Asia, e.g. camphor, galangal, zedoary, anacardia, myrobalan, cloves, etc.: the physician *Alexander Trallianus* (born 525), who was probably the first to mention rhubarb (although the plant was used domestically long before): the physician *Paulos Aeginetes* (first half of the seventh century): and finally *Simon Sethos* (eleventh century) who knew nutmeg and hashish, and used camphor, ambergris and musk medicinally. These substances must have been known long previously in India. Musk had already been mentioned by Aretæus and by St. Jerome.

It is sometimes said that the physician Paulos Aeginetes (about 640) was the first to introduce mercury and antimony (antimony sulphide) into medicine, but this is a matter more of medical than of chemical interest. (Preparations of lead and zinc were used by the ancients.)

[1] We shall not discuss here how far the painting materials he describes (e.g. drying oils, white and yolk of eggs) were in use at an earlier date.

[2] It contains the technique of using wax, glue and white of egg, and instructions on wall painting, varnishes, the miscibility of different pigments, etc.

[3] We must again ignore the question of how far the painting technique described (in particular oil-painting with linseed oil, preparation of varnish, translucent painting, etc.) involved fresh discoveries.

We may say that there is nothing new for the chemist in the central European prescription books of the early Middle Ages, e.g. the book of Bamberg or the two of St. Gallen.

The introduction of important spices and herbs into Germany was valued so highly by the Benedictine monasteries that the Carolingian *Capitulare de villis* (Ludwig the pious) bears the official stamp : this has, however, only an indirect bearing on chemistry.

The so-called *Greek or Median fire* was an early Byzantine discovery (about 671), due to the technician *Kallinikos* from Heliopolis in Syria. It appears to have been a spontaneously inflammable liquid which by means of pumps could be sprayed on to the enemy's ships. It is a fact that by this method the Arab ships were destroyed off Kyzikos in the year 678, and also the Russian fleet off Byzantium in 941.

The solution is to be found in the term " Median " fire. History relates that it consisted of a mixture of Median petroleum, sulphur, pitch and salt (?), in which finely divided quicklime was suspended. The mixture ignited on coming into contact with water. Since crude petroleum would hardly have ignited, the mixture must have contained a distillate from petroleum, the preparation of which would have been possible at any period. The word ' salt " has aroused some speculation, since the presence of ordinary salt would have been purposeless, if not harmful. Saltpetre cannot be intended, since according to experts it was not known at that time. The point is worthy of further consideration.

We now come to the subject of Arabic chemistry. Of prime importance is the famous *Djābir. b. Haiyān*,[1] who, under the name Geber, was considered right through the Middle Ages and later (up to the time of Berthelot) to be the founder not only of Arabic chemistry, but of all truly scientific chemistry. He was probably a Persian from Khorasan. His father appears to have been a druggist and a martyr of the Shi'ite Mohammedanism. His teacher was the famous Dja'far al-Sādik, who was not however a chemist. It has now been shown that the Latin texts of Western origin under the name of " Geber " cannot be attributed to Djabir, and do not correspond to any Arabic originals. The true Djabir texts have meanwhile been discovered in the libraries of Cairo and Constantinople. They show that although Djabir was the agency by which the knowledge of the Greeks and the Hellenised culture of the Persian age was conveyed to the Mohammedans, he was not the great discoverer he was at one time taken for. Only a portion of his works deal with chemistry, e.g. the Book of the Seventy, the Book of Poisons, and the Book of Specific Properties.

His works contain much which is of chemical interest, in particular antidotes for poisons, soporifics and sedatives, cosmetic preparations (e.g. for removing hair and for tattooing), pigments, varnishes, inks, artificial precious stones, and talismans. These are, however, subjects which for the most part

[1] Here and throughout, the spelling of Arabic names is that of the *Encyclopædia of Islam*. Leyden and London, 1913.

occur (or might be expected to occur) in late chemical manuscripts of the antique age. The Latin Geber manuscripts do not contain any chemical knowledge far in advance of the ancients, except the recognition of sal-ammoniac and salts of hartshorn (ammonium carbonate).

From our knowledge of religious history, the "genuine" writings of Djabir must be dated before 860. By 950 Djabir was considered a great authority by his countrymen. Since Djabir lived in the eighth century, the



PLATE 13

Ancient Arabic distillation apparatus for preparing rose water.

1. Glass flasks heated by steam.
2. Glazed flasks heated directly.
3. Tin apparatus.
4. Apparatus for steam distillation (Greek).

question arises as to how far various pupils of the Ismailian sects may have united their work and that of their circle, and produced the resulting works under the name of Djabir. From the point of view of chemical history this is not of so much importance as the question of how much Djabir (whoever he may have been) actually contributed in advancing chemical knowledge beyond that of the ancients. As far as can be ascertained, his chief claim to fame is that he (like other Mohammedans of Persian, Syrian, Egyptian and Spanish origin) contributed to the salvage of the science of antiquity.[1]

[1] Thus when it is emphasised that he had some conception of quantitative proportions in chemical processes (in the combination of lead oxide and vinegar), it should be remembered that this idea had also been put forward by the philosophers of antiquity.

What we have said of Djabir is true also of the chemical knowledge of the " Arabian " physicians contemporary with him and following immediately after him, most of whom were not Arabians at all. We may mention *Mesue the Elder* (Yahyā ibn Māsawaih), supposed to have been the Messiah (died 857); the Persian *Rhazes* (Razes, Abū Bakr Muhammad b. Zakarīyā al-Rāzī, 850–923 or 932); *Serapion* the elder (Janus Damascenus) (Yahya ibn Sarāfyūn) in the ninth or tenth century; and even the great *Avicenna* or *Ibn Sina* (Abu 'Alī al-Husain Ibn 'Abd Allāh Ibn Sīnā, 980–1037), a Persian whose *Canon Medicinæ* represents the summit of Mohammedan medical knowledge. The new applications of medicines were probably largely due to the new and improved means of transport, whereby drugs could be obtained from Southern and Eastern Asia and from Africa. For the greater part the work of these Mohammedan physicians is based on the knowledge of antiquity, and the work of Avicenna shows clearly the influence of Dioskurides. The newly introduced drugs must in all probability have been known much earlier in the countries of their origin. Among others we may mention tamarind, purging cassia, kamala, sagapenum, senna, flores cinæ. The last three appear to have been first mentioned by Serapion, while the fourteenth-century explorer Ibn Battuta is supposed to be the first to describe gum benzoin (?).

Mention must be made of sal-ammoniac. Known to Djabir, it found more extended application in the thirteenth century. It probably came from Central Asia and Persia, where it occurred naturally as a product of volcanic eruption; this is stated by al-Dimashki, who also mentions the artificial production of sal-ammoniac by the Egyptians. The discovery of the distinction between potash and soda has been ascribed to the Arabs, but it must in some cases have been known to the glass makers of antiquity. Sugar and syrups were widely and extensively used. Combustible spirits of wine (i.e. liquids containing a high percentage of alcohol) do not appear to have been known to the Mohammedans.

Much more important chemical discoveries were at one time attributed to Avicenna; this is because a number of chemical writings bearing his name were believed to be genuine, but have subsequently proved to be later productions, mostly fourteenth century or later. The real *Chemical Renaissance* began *after* all these Mohammedans.

It began with the *discovery of saltpetre* and of the mineral acids.

Unfortunately the discoverers are completely unknown. The home of *the discoverer of saltpetre* was probably Central Asia or China. The mineral acids, *sulphuric acid* and *nitric acid*, were most probably discovered in Southern Europe (possibly in Italy), hardly before 1200.[1]

We should be much nearer a solution of the problem if we knew the author of the *Latin Geber manuscripts*, which for hundreds of years led students of mediæval chemistry on a false trail. The work of Berthelot was the first to

[1] al-Kazwīnī (died 1283) knew that on heating vitriol thick fumes were given off which endangered health and produced great heat on coming into contact with water. However, this was probably also known to the ancients.

clear up the position. The Geber manuscripts date from the beginning of the thirteenth century. Hardly any of the internal evidence as to his place of origin points to Southern Europe, and it is possible that he may have been a German. Philological experts might be able to decide whether the Latin used by Geber is that of a southern or a northern European ; this would be a further step towards the solution of the enigma. His chief work, *Summa perfectionis magisterii*, is the most important in this connection.

What new facts were known to Geber ? Most important is his acquaintance with the acids, *sulphuric acid* (obtained by distilling green vitriol), *nitric acid* and *aqua regia*. He obtained nitric acid by distilling saltpetre with copper sulphate and alum, or saltpetre and copper sulphate alone. Aqua regia was made by distilling saltpetre, copper sulphate and sal-ammoniac.

Further data are given by other writers of the period. Vitalis de Furno (died 1327) probably lived somewhat later than Geber, but gives some of the earliest accounts of acids. His starting materials were saltpetre and blue vitriol. Just as in the case of Geber, it is impossible to establish whether his prescriptions are of earlier origin. A Pseudo-Albertus prepared aqua regia by heating saltpetre with calcined alum and ferrous sulphate, or saltpetre with alum, ferrous sulphate and common salt (from his work *Compositum de compositis*). Odomar in 1350 also gives saltpetre, ferrous sulphate and common salt as starting materials. A Byzantine recipe of the fourteenth century uses saltpetre with Rocca alum and ferrous sulphate, or saltpetre and copper sulphate.

A detailed description of all these methods was first given by Biringuccio in the sixteenth century. He uses saltpetre with alum, brickdust or sand, and uses a receiver containing water and silver to remove hydrochloric acid. (Water must always have been necessary, but is not mentioned previously.) If sal-ammoniac was added to the above mixture, aqua regia was obtained. Both Biringuccio and before him Geber used quantities which correspond roughly to the stoichiometric ratios. According to Walden the agreement is satisfactory.

There are a number of points of interest in these preparations. When the ancients prepared *Caput mortuum* by heating green vitriol, fumes of sulphur trioxide must have been evident. Further (as shown by Walden), the experiments described above also lead to the formation of potassium sulphate, nitrogen peroxide, hydrochloric acid and chlorine. All these substances must easily have been observed. (Other substances which were formed but which probably escaped detection are nitric oxide, nitrogen and nitrosyl chloride.) Other phenomena which must have been noticed are the formation of hydrogen by the action of dilute acids on metals, and the formation of hydrogen sulphide by the action of dilute acids on sulphides.

Geber knew that aqua regia will dissolve gold, and also the preparation of concentrated acetic acid by distilling verdigris or vinegar. A number of new substances could be prepared by means of acids, e.g. silver nitrate, silver sulphate, gold chloride, lead acetate, and the chlorides and sulphates of mercury.

Silver chloride must have been known to the ancients, as they separated gold from silver by a cementation process.

Mention should also be made of ammonia, sal-ammoniac, microcosmic salt (from urine), the preparation of caustic lyes from soda and potash (thus even in the time of Charlemagne soap-boiling was an independent trade), liver of sulphur, milk of sulphur precipitated by acids, the separation of gold and silver from copper, tin and lead by cupellation (as in antiquity), and the recovery of mercury from amalgams by distillation.

A study of Geber's works gives the definite impression that he was *a man of wide practical experience*, and that his writings are not a mere repetition of the work of others, but deal with facts of his own experience. *The work of Geber demonstrates clearly the incorrectness of the statement that no experimental work was done in the Middle Ages.* All his writings deal with experiments. We may go so far as to say that it would be of interest, even to-day, to repeat some of the experiments described by Geber. It is quite possible that new discoveries might be made by using methods very different from modern ones. It should also be noted that Geber knew that calcined (i.e. oxidised) lead, tin and mercury could be reconverted to metal, i.e. reduced. He also mentions the change of weight in these processes.[1]

Of the notable Western scholars of the thirteenth century whose names are known, by far the most important is the truly great *Albertus Magnus* (1193–1284, Albert von Bollstädt, Lauingen). He collected and expounded chemical lore, especially in his book *De Mineralibus*. Although he can hardly be termed a chemical *discoverer*, he knew a great deal about the subject, and certainly also carried out experiments. He knew of the separation of gold and silver by means of nitric acid, and found that all metals (iron, copper, lead, tin, mercury, silver) except gold would combine with sulphur.

Albertus tested saltpetre for the presence of potash by adding vinegar and observing whether effervescence took place. Saltpetre from dung heaps consists largely of calcium nitrate and had first to be "broken," i.e. the lime was precipitated by adding potash solution and then filtered off.

Such work is obviously evidence of much practical knowledge. The same applies to the English Franciscan *Roger Bacon* (1217 (?) to 1294), though he was more a physicist and a technician than a chemist. He knew mixtures resembling gunpowder.

We thus came to an event of world-wide importance, the *discovery of gunpowder*.

The recognition or discovery of saltpetre led on the one hand to the discovery of nitric acid, and on the other hand to observations of *the properties of mixtures of saltpetre with combustible substances*.

Saltpetre appears to have been first recognised in China. Explosives containing saltpetre are not however mentioned until the middle of the twelfth

[1] Walden has found that the change of weight undergone by metals on oxidation is mentioned by Conrad von Megenberg (1350) for the use of lead-lead oxide, and by Eck von Sulzbach (1489) for mercury-mercuric oxide. These dates may, however, be incorrect, as the latter manuscript is probably wrongly dated, and is actually of later origin.

century. The first use of mixtures resembling gunpowder to discharge rockets for military purposes seems to have been in 1164. A more detailed account dates from 1232, when incendiary mixtures were propelled from bamboo canes by charges of powder.

An Arabic book on fireworks dating from 1200 still makes no mention of saltpetre. It was first known to the Persians (as "Chinese salt") at the beginning of the thirteenth century. The oldest Mohammedan writers to



PLATE 14

Filtration of saltpetre lye.

Picture manuscript of the fifteenth century from the H K. Royal Museum, Vienna.

mention saltpetre are Ibn Abī Usaibi'a (1203–1269) and Ibn al-Baitār (1197–1248), although they knew nothing of its use for military purposes. The former mentions its use in freezing mixtures, and the latter its value as a medicine. On the other hand, al-Hasan al Rammāh (1275–1295) gives saltpetre as the basis of fireworks. He was acquainted with its preparation from potash. He describes the preparation of rockets (Chinese arrows), crackers, squibs, and Bengal fire. He knew of percussive and explosive effects, but he describes no *firearms*. The same is true of Shams al-dín Muhammad in 1350.

The Fire book of Marcus Graecus (1250) indicates a similar knowledge,

and the same is true of Roger Bacon and Albertus Magnus, who wrote later than Marcus.

It appears that the idea of using saltpetre to discharge stones from a pot or a mortar first occurred *after* 1250. Unfortunately, owing to the lack of contemporary sources it cannot be stated with certainty when and where the

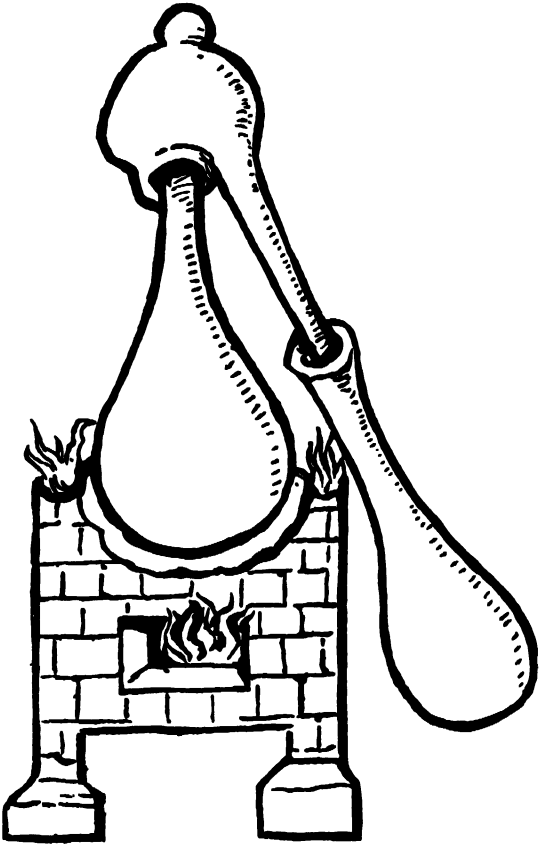


PLATE 15

Alembic on a sand-bath furnace, for making nitric acid.

The receiver contains some water and silver for removing chlorine. From a chemical manuscript, 1414-1418, dedicated to Count Friedrich I von Brandenburg. German National Museum, Nürnberg.

discovery was made. There is a tradition (first committed to writing in the fourteenth century) that *shooting was invented in Freiburg (Breisgau) by Brother Berthold the Black*, whose real name was Constantin Anklitzen. An explosion in a mortar is supposed to have suggested the invention. It seems certain that *the inventor was a German*, and many facts indicate *Freiburg as the scene of the discovery*. A Breisgau manuscript of the year 1371 states that shooting was

generally practised when Freiburg cathedral was completed (1296), and in 1416 Freiburg manufactured firearms for the larger towns Strassburg and Basle. Italian, French and even Byzantine sources describe gunpowder as a German discovery. The oldest recipe extant for making gunpowder dates from 1330.

The amount of saltpetre available from manure heaps and latrines was insufficient, and saltpetre plantations had to be set up. They were first described by the artillerist Conrad Keyser (1398–1405), and flourished chiefly in the south of France. Much could be collected from natural sources, and a large amount appears to have been imported from India.

Some centuries after the discovery of saltpetre in China, the same country

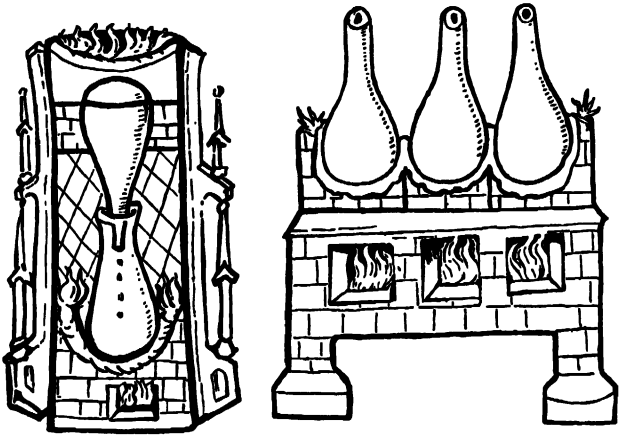


PLATE 16

Left: Vessels in a furnace with bellows, used for sublimation or distillation per descensum. *Right:* Three flasks in sand-baths on a cupelling furnace. From a chemical manuscript, 1414–1418, dedicated to Count Friedrich I von Brandenburg. German National Museum, Nürnberg.

produced the first *porcelain*, probably in the seventh century. This involves a knowledge of the raw materials and the use of elutriation, moulds and glazing. Chinese porcelain could not be imitated until the seventeenth century in Japan, and the eighteenth century in the Occident. Chinese porcelain first reached Europe in the thirteenth century. The manufacture of pottery also flourished in mediæval China and Korea.

The *European ceramic industry* produced glazed pottery in Byzantium and in the island of Majorca (majolica). Tin glazes and majolica ware were produced in Italy (Faenza, Siena, Urbino, Castel Durante) in the fourteenth century and later, and were sometimes coloured yellow, blue, green or black. A glaze rich in tin was used by Lucca delle Robbia (Florence, 1438), also with red and purple tints. Ruby red glaze was discovered by G. Andreoti in Florence (1498).

The fifteenth century saw the beginnings of the *German* ceramic industry,

which reached its zenith in the sixteenth century (Cologne, Frechen, Nassau, Siegburg) and in the seventeenth century (Kreassen).

The *Venetian glass industry* has flourished since the thirteenth century. Among other types of glass they made filigree, aventurine and mottled glass.

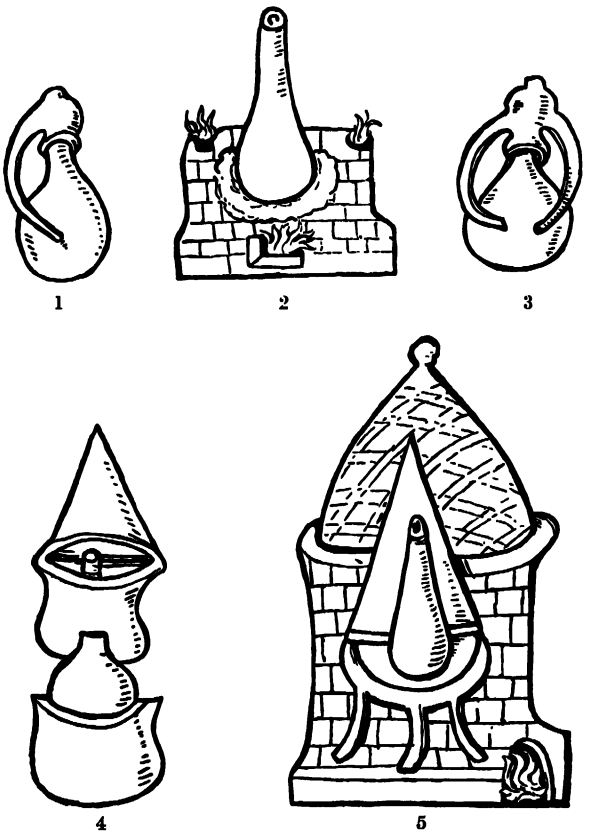


PLATE 17

1 and 3 Circulating vessels (pelicans) with one and two tubes. 2 Bellows furnace with flasks in a sand-bath. 4 Digestion vessel in a dung-bath with a domed top to retain the liquid evaporating. 5 Digestion-furnace with a similar vessel on a tripod, for heating with a lamp or a fire. From a chemical manuscript, 1414-1418, dedicated to Count Friedrich I von Brandenburg. German National Museum, Nürnberg.

while they used burnt-in colours for tinting and gilding. The manufacture of glass in Germany also increased during this period.

The manufacture of true *stained glass* (e.g. for windows) began in the tenth century with copper oxide shading in Tegemsee, Rheims and Limoges. The use of silver yellow for stained glass has been known since the fourteenth century.

Mirrors with tin amalgam (including concave and convex mirrors) have also been made since the fourteenth century.

We now come to the *knowledge of metals in the Middle Ages*. The metal zinc was new, being first prepared pure in Persia in the sixteenth century:

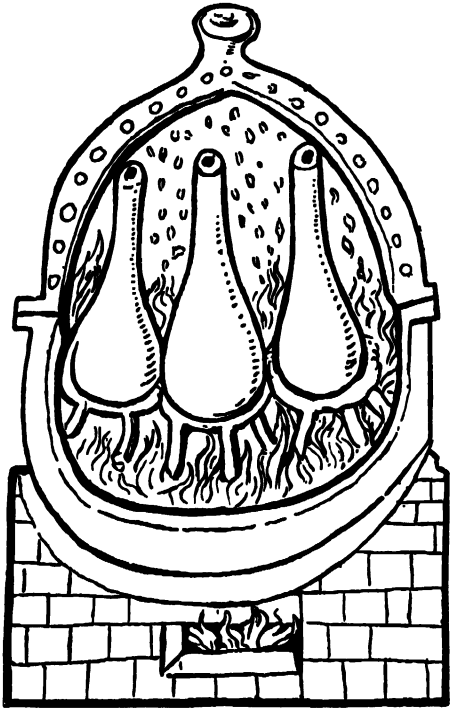


PLATE 18

Digestion-furnace with three small flasks on tripods.

From a chemical manuscript, 1414–1418, dedicated to Count Friedrich I von Brandenburg. German National Museum, Nurnberg.

it was probably known in China earlier than in Europe. The metal bismuth was first used in Germany in the fifteenth century. It appears to have been used by the early printers as a constituent of type metal. More important in this connection is antimony, which has been used increasingly since the middle of the fifteenth century. Cobalt and nickel ores were certainly known in the fourteenth century: there is Venetian glass of this date coloured with cobalt.

Metallurgical Technique in the Middle Ages

After the upheavals of racial migration, the Roman metal industry in western Germany appears to have gradually come into action again. Some of



PLATE 19

Mediæval silver mining and smelting works at Kuttenberg.

the places concerned were Sleiermark and Kärnten in the eighth century; Franken in the ninth century; the Harz (Goslar) and Amberg in the tenth century; Schwarzwald and other districts in the eleventh century; Freiberg, Mansfeld, Minden, Siegerland, Salzburg, Kärnten, Tirol, Sleiermark in the twelfth century; Upper and Lower Schlesvig and the Erzgebirge in the thirteenth century. The fifteenth century saw the beginning of the famous silver mines of Schneeberg (1471) and Annaberg (1492), gold mining in the Fichtelgebirge and tin mining in Altenberg. The fifteenth century was the zenith of the German metallurgical industry. There was copper and silver mining in Tirol; silver, copper and lead mining in the Harz; mercury mining in Idria (1497): and numerous other undertakings which cannot be considered here.

The extraction of iron also progressed very greatly in the fifteenth century. This was partly connected with the use of water-power for producing a blast in smelting. In this way the smelting furnaces could be made much larger, often up to eight metres.

It was also possible to make crude liquid iron (cast iron) and to convert it by means of a refining furnace into either wrought iron or steel. In Siegerland and in Amberg all the direct process furnaces had disappeared by 1500, being replaced by refining furnaces.

The production of brass also took place on a very large scale in fifteenth-century Germany. The export of brass articles from the Lower Rhine and from Nürnberg was greater than that of any other country. Germany was also the chief source of bronze even in the fifteenth century. Tinplate was produced from the fourteenth century onwards.

Part of our information about mediæval metallurgy comes from the so-called *Family Book* of the royal Waldburg-Wolfegg family (1480). This contains many excellent metallurgical illustrations, especially to do with copper, many of which are better than the later pictures of Agricola. The unknown author was acquainted with the colouring of flames by metals. He describes the preparation of caustic potash from potash and lime, the manufacture of alum, the luting of flasks for preparing nitric acid, the testing of ores with stibnite, the precipitation of gold by antimony, the preparation of saltpetre and gunpowder, and he gives the oldest known picture of a refining furnace with an iron cap and bellows.

In addition to those mentioned in connection with Geber, the following substances were known in this period: ammonium carbonate, lead nitrate, mercury nitrate, white precipitate, zinc sulphate, potassium acetate, iron acetate, ammonium acetate (Gilbertus Anglicus, end of the thirteenth century), zinc acetate (Geber). Among minerals of interest, fluorspar was known. Giacomo de Dondis (1298) describes the production of salts from mineral waters.

Organic Substances

Among organic substances, *combustible spirits of wine* was the most important. The preparation of spirits containing a high percentage of alcohol

was closely connected with the perfection of distillation apparatus ; in particular, spirits could only be profitably made if water cooling was used. Cooling the delivery tube by means of a cooling jacket is shown in an apparatus of Joh. Wenod de veteri Castro, who prepared spirits from beer. However, this apparatus dates from the year 1420, when spirits of wine had been known for a long time. (We have stated above that spirits of wine were known to Rhazes. He may, however, have been dealing with an alcoholic fermentation product of sugar.) They were probably discovered in Italy in the eleventh



PLATE 20

The seal of "Lintfried in der Apotheck." Augsburg, 1302. State archives, *München.*

century. Vitalis de Furno knew spirits of wine, and a distillation apparatus is described by Thaddäus Alderotti (1223–1303). Arnald of Villanova (thirteenth century) knew similar liquids (distilled wine, acqua di vita or Acqua vite). It is obvious that the discovery of spirits would follow almost automatically from the discovery of an efficient still.

Of the *colouring matters of the Middle Ages* we may mention Dutch pink, gamboge, catechu, myrobalan (the fruits of various species of Terminalia), carmine, red lac, litmus, red sandalwood, vaccinium berries, saw-wort, oak bark. It is, however, probable that most (if not all) of these had already been used by the ancients.

With the introduction of good distilling apparatus it became possible to prepare the *ethereal oils* from herbs by steam-distillation. This took place in the Mohammedan Orient and also in Southern Europe. A large number of such oils were known by the end of the fifteenth century, among which were probably the essential oils of the following: rose, violet, jasmine, water lily, gillyflower, orange blossom, spike, lavender, rosemary, rue, hyssop, mint, pennyroyal, savory, thyme, marjoram, origanum, camomile, tansy, juniper (wood and berries), cade, savin, birch, peppermint, spearmint, wormwood,

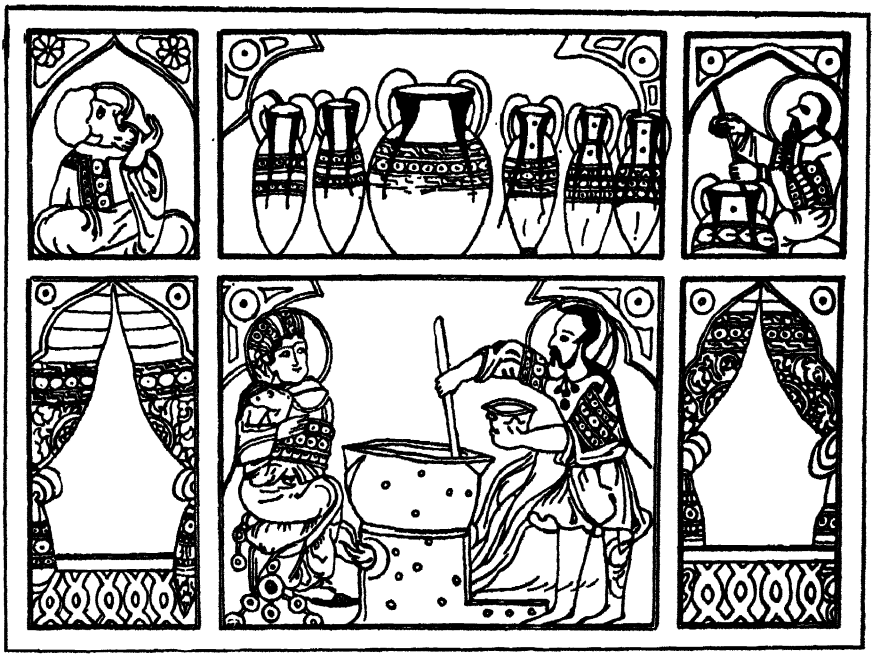


PLATE 21

Ancient Persian chemist's shop.

From a Dioskurides manuscript, after Martin, 1222.

sage, box, rosewood, aniseed, caraway, fennel, dill, coriander, black caraway, parsley, calamus, valerian, angelica, cinnamon, clove, mace, nutmeg, cardamom, bay, pepper, zedoary, orange peel and lemon peel. Camphor was also mentioned. Besides the essential oils, the process of steam-distillation produced scented water, which was also used.

The best information as to the *medicines* of the Mohammedan civilisation is provided by the work of the Persian *Alhervi* (Abu Mansur Mowaffaq ben Ali al Harawi) in the tenth century. He mentions about five hundred remedies, mostly vegetable but some of animal origin. It is impossible to enumerate them here. Avicenna's writings mention a similar number of medicines.

Most of these were known to Dioskurides and Galenus, but there are some additions, particularly of drugs from Persia, India and China. The mithri-

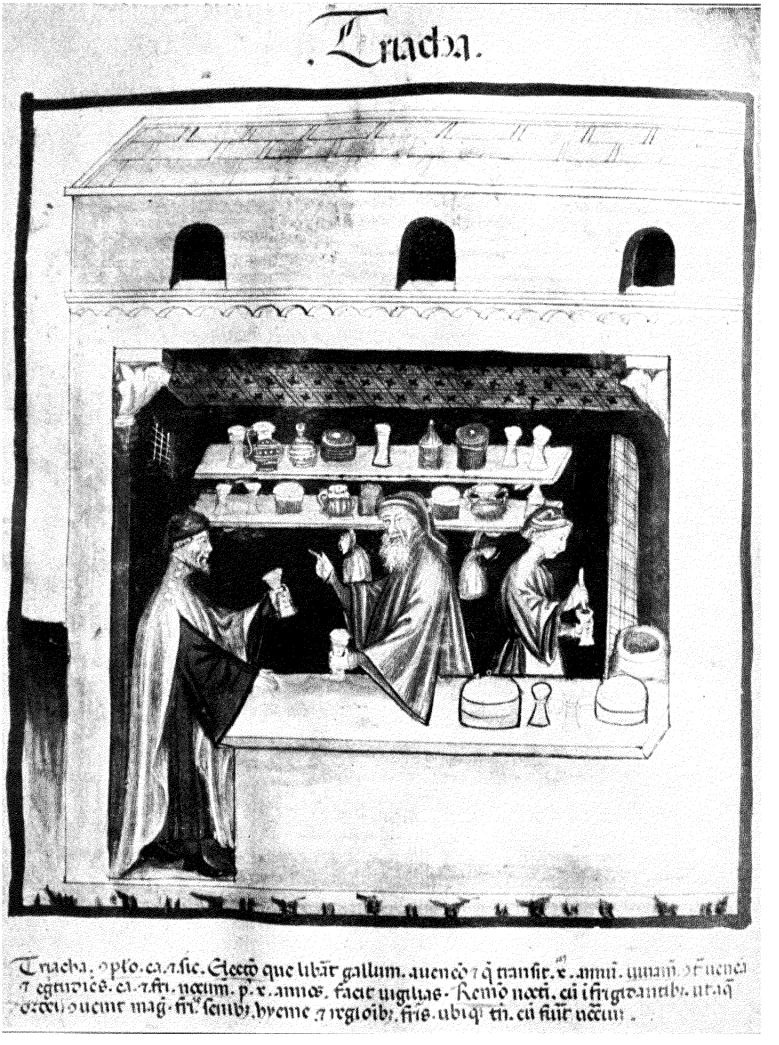


PLATE 22

Mediæval chemist's shop, fourteenth century or end of the thirteenth century.
From "Tacuinum sanitatis," Vienna Royal Museum.

date described by Avicenna consists of fifty-seven ingredients, and his theriac of sixty-three. There is also a list of remedies purporting to be due to one Serapion the younger. This is, however, almost certainly not the case,

and they probably represent a Spanish work of the twelfth or thirteenth century.

The best of the Mohammedan pharmacists was probably Ibn al-Baitār from Spain (Abū Muhammad 'Abd Allah b. Ahmad Diyā ' al-Dīn Ibn al-Baitār al Mālakī), died 1248. This work is entitled *A Summary of the Properties of well-known Simple Medicines and Foods*, and depends to a great extent on first-hand knowledge rather than book learning. He mentions about fourteen hundred drugs, including about two hundred vegetable preparations not

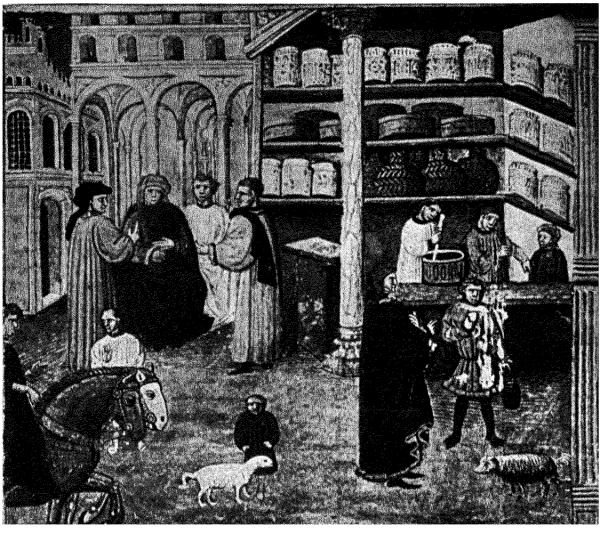


PLATE 23

Chemist's shop, after a fourteenth-century Avicenna manuscript.
University Library, Bologna.

previously reported. It is not certain how far he may have taken some of his material from the Spanish doctor Ahmed al Ġhâfiqî.[1]

A curious case is that of the so-called *Mesue* the younger. It is probable that no such person ever existed, and that his name conceals one or more twelfth-century Italian doctors from Bologna or Padua. The *Antidotarium* and two other writings bearing his name were of considerable importance up to 1600.

A review of medical knowledge in mediæval Europe is provided in the following works by Italian authors: *Practica Brevis* by *Johannes Platearius* (ca. 1050), the *Antidotarium* by *Nicolaus Præpositus* (ca. 1140),[2] and *De*

[1] These doctors knew various forms for administering drugs, e.g. pills, pastilles, candied drugs and medicinal syrups.

[2] According to Sudhoff, this work is based on older sources.

Simplici Medicina or *Circa instans* by *Matthæus Platearius* (about 1140). The so-called *Alphita*, purporting to be the work of one Maroncio (thirteenth century), contains a list of no fewer than six hundred and forty-five drugs, which we cannot reproduce here. It gives a general survey of the medicines (simplicia) of the Middle Ages.

The first real pharmacopœia in the modern sense (i.e. distinguishing

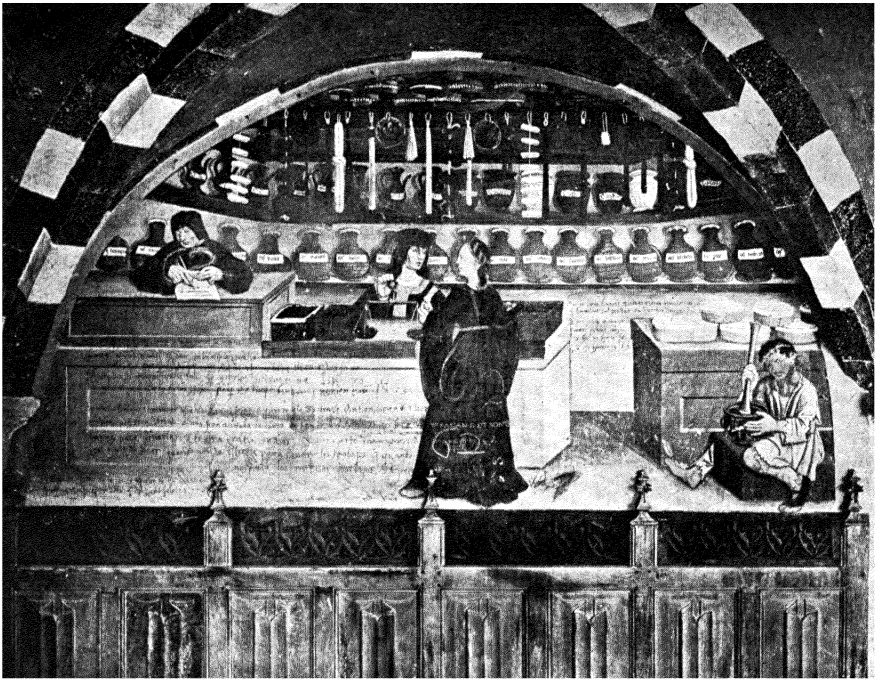


PLATE 24

Interior of an Italian chemist's shop, late fifteenth century.
Late Gothic wall painting from the Issogne Castle, about 1490.

between the functions of the pharmacist and those of the doctor) is the *Compendium aromatariorum* of *Saladin of Ascoli*, written about 1450.

The *Ricettario Fiorentino* is the *first official pharmacopœia*, introduced in Florence in 1498. It served as a model for the later German pharmacopœias. The second official pharmacopœia appeared in Spain in 1535.

These books naturally do not contain any new chemical discoveries, but they contain a great deal of chemical information.

In connection with these pharmacopœias it is convenient to consider here some of the *pharmaceutical and chemical expressions* which were used in



PLATE 25

Title page of the 1567 edition of the Ricettario Fiorentino.

This is the oldest official pharmacopœia, and first appeared in 1498. The above plate is a magnificent example of the work of the Italian Renaissance. Between the mortar and distillation apparatus (attended by cherubs) are the arms of the Medici with the six pills.

books of the Middle Ages and of succeeding centuries, in some cases right up to the present day. Many of them are of *considerable chemical interest.* It is not important in this connection that some forms and expressions did not

appear until the sixteenth century and that there are variations in their use at different times. It would be difficult to establish this with certainty.

Aquæ destillatæ are distillates from drugs covered with water. If wine was used in place of water, *Spiritus* was obtained ; if only one drug was used it was



PLATE 26

Preparation of theriak about 1500, *Hieronymus Brunschwyk.*

The raw materials were exhibited, and the theriak was prepared publicly in presence of the doctor. The two Venetian banners indicate that the most important ingredients came from Venice.

termed *Spiritus simplex*, while the distillate from several drugs was *Spiritus compositus*.

Extracta are extracts of drugs with water or wine, while *Infusiones* and *Decocta* were infusions and decoctions with water.

Extracts made with spirits were also called *tinctures*.

Aceta are extracts of drugs with vinegar, and distillations with vinegar were also known.

Solutiones referred almost exclusively to solutions of inorganic substances in vinegar or other acids.

Elixirs are spirituous extracts with the addition of sugar or syrup. If ethereal oils were also added, they were termed *Essentia*.

Sales solubiles are salts prepared by evaporating down solutions, and are hence chiefly inorganic.

Sales volatiles are sublimates obtained by dry distillation.

Sales vegetabiles (per incinerationem) are salts obtained by incinerating plants, extracting the ashes and crystallising.

Sales essentiales are salts crystallised from expressed plant juices.

Succi liquidi are expressed plant juices.

Succi inspissati are the same juices concentrated by evaporation.

Rob are concentrated expressed fruit juices.

Spiritus per retortam eliciti and *Olea per retortam* or *per descensum* are liquids obtained by dry distillation (destructive distillation).

Olea ex mineralibus are inorganic substances of an oily nature prepared by *Deliquium* (deliquescence), solution or distillation (e.g. oil of vitriol).

Magisteria are precipitates from solutions of inorganic substances (metallic salts, minerals) or resins.



PLATE 27

Five sages in a chemist's shop.

From "Hortus Sanitatis," Augsburg. Hans Schönsperger, 1496. The assistant is in the background by the counter, with a mortar.

Olea destillata aromatica was the term used for ethereal oils.

Balsams are fats containing one or more ethereal oils.

Elæosacchara are sugars containing ethereal oils.

Syrups are sugar solutions with juices or infusions.

Juleps are syrups made up with *Aquis destillatis.*

Mel is honey containing drugs.

Oxymel is honey and vinegar with drugs.

Oxysacchara were made by extracting vegetable matter with vinegar or other acid and thickening with sugar.

Pulpæ are fruit pulps boiled with or without sugar. The one prepared from quinces was called Diacitonium.

Potus are spiced and sweetened wines.

There were also the *Confectiones*, e.g. *Electuaria* and *Lohoch*, i.e. jam-like syrups containing drugs ; *Conservæ* (Pulveres or Species cum saccharo) ; solid medicines, such as *Morsuli* (rectangular), *Tabulæ* (square), *Rotundæ* (spherical), *Trochisci* (lozenge-shaped), and *Candita* (candied fruits).

Finally, there were also *Pillulæ* (pills), *Emplastra* (plasters), *Cerota* (powdered drugs with wax or fat), *Unguenta* (ointments), *Cataplasmata* (compresses), etc.

It must not be forgotten that two of the *most important human beverages* go right back to the Middle Ages. *Coffee* came to Arabia from Abyssinia at the beginning of the fifteenth century, but did not reach Europe until the seventeenth century.

Tea was known in China in the fourth century A.D., and was in general use after the seventh century. It reached Europe (as a drug) in 1610.

The *beer* of the Middle Ages was made with hops as a flavouring. It is not clear which nation was the first to use hops, and all statements which have been made on the subject are speculations without any foundation. It is, however, a fact that King Pipin had a hop garden, and such gardens existed in Freising in the ninth century.

The monasteries of the early Middle Ages appear to have brewed their beer more from oats than from barley. We do not know what the first of these tasted like.

The best mediæval beer seems to have been brewed in northern Germany, particularly in lower Saxony (Einbeck). Strong beers (sometimes spiced) were also known (Braunschweiger Mumme, 1492), and beer from wheat was in use in the later Middle Ages.

Chemical Appliances

The apparatus of the Middle Ages descended directly from that of antiquity. Distillation was usually carried out in apparatus with still-heads (alembics). Arabic pictures show whole galleries of retorts, e.g. for distilling attar of roses.

Rhazes (Razes) knew large and small furnaces, crucibles for fusion, flasks, still-heads, apparatus for distillation *per descensum*, receivers, closed flasks for digestion, aludels (singly and in series) for sublimation, phials, beakers, mortars, bellows, water-baths and ash-baths. This, however, hardly represents any advance on the apparatus of the Alexandrians.

The *Latin Geber* knew fusion, crystallisation, heating in ash-baths, sand-baths and dung-baths; aludels for sublimation, filtration (through bags), *Destillatio per filtrum* (i.e., the use of pieces of fabric to siphon off liquid, thus purifying it), digestion vessels, vessels for calcining metals, *Destillatio per*

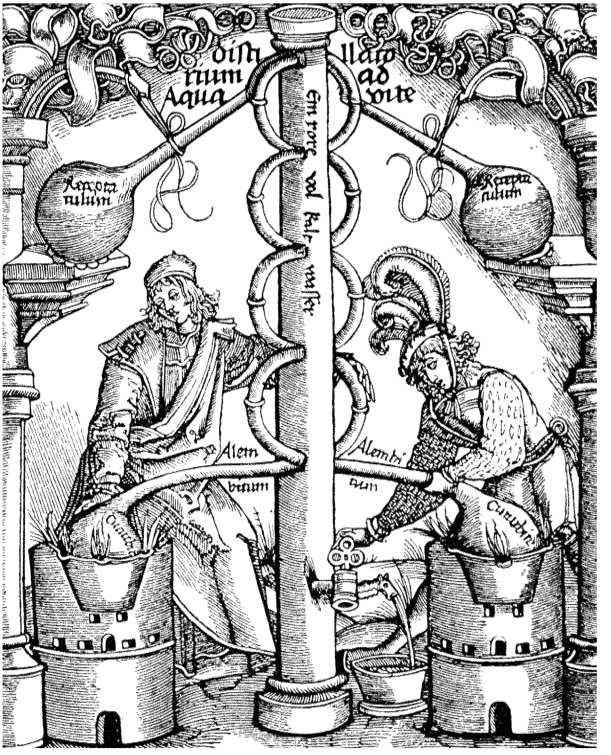


PLATE 28

Distillation apparatus with a condenser pointing upwards.

Woodcut from the book "Liber de arte destillandi," by Hieronymus Brunschwyk, Strassburg, 1500.

The column is supposed to be hollow and filled with water. This is probably a design which was never actually carried out in practice.

descensum, and distillation vessels (alembics) of glass and earthenware.

His manuscripts are sometimes accompanied by illustrations, in which we can recognise alembics on furnaces, sublimation vessels (aludels with a testing rod), vessels for distillation *per descensum*, arrangements for decantation, calcining vessels with spatulæ, calcining furnaces, apparatus for mercury calcination, digestion apparatus with sand- and ash-baths.



PLATE 29

Alchemist's laboratory.

From Petrarka, Trostspiegel. "of the great folly of the alchemists." Hans Weiditz: Alchemist's workshop, about 1500.

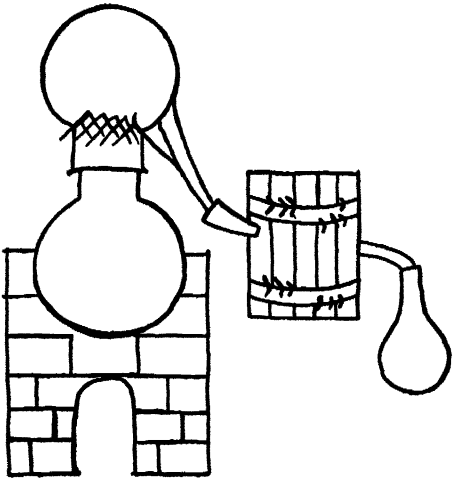


PLATE 30

Distillation apparatus—Joh. Wenod de veteri castro, 1420.

Preparation of spirits of wine from beer. Probably the oldest illustration of water cooling with a water-jacket. Furnace with alembic, cooling jacket, receiver.

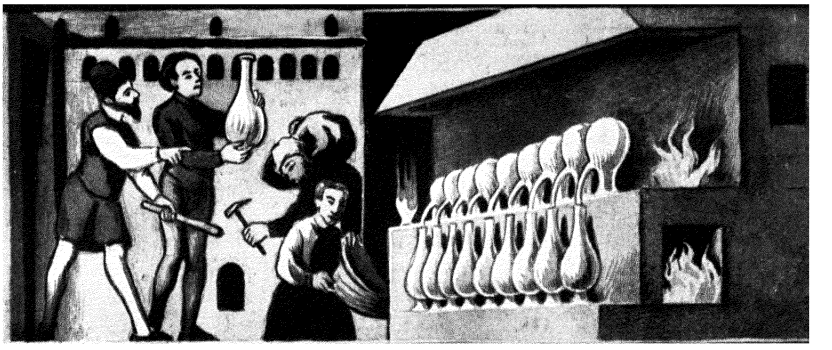


PLATE 31

Ancient Italian distillation apparatus with still-heads.

From a mediæval fresco. Probably the oldest illustration of a chemical still.

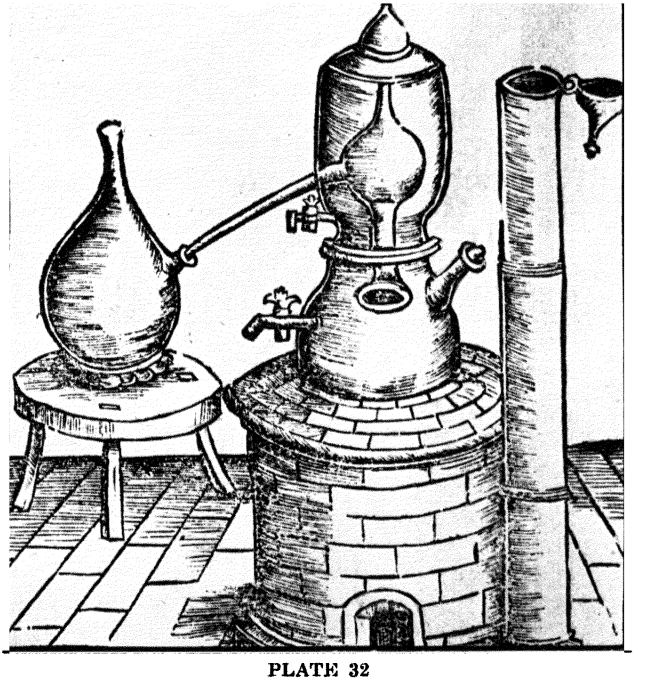


PLATE 32

"Moor's head" distillation apparatus—Hieronymus Brunschwyk, about 1500.

The still-head is here surrounded completely by the cooling water, and not (as was usual) left uncovered at the top.

The illustrations added to the later printed editions of Geber express the spirit of the sixteenth century.

Drawings in another Paris manuscript from about 1300 show similar arrangements: sublimation apparatus for sal-ammoniac, mercury compounds and arsenic: apparatus for distillation *per descensum;* alembics; solution vessels in water-baths.

The introduction of a *delivery tube cooled by a water jacket* was certainly *the most important advance* in chemical apparatus. It probably belongs to the fourteenth century.

An apparatus described by Albini de Mente Calerio in the fourteenth century shows an arrangement for *fractionating* the distillate (without water cooling).

A mediæval Italian multiple distillation apparatus is fitted with large still-heads.

Hieronymus Brunschwyk (Brunsvig, Brunschwygk) in his distillation



PLATE 33

Filtration through a bag, about 1505.

book of 1500 shows a tall cooling column, serving two distillation apparatuses, from which the cooling water could be emptied. This arrangement does not occur anywhere else, and is probably only an ingenious suggestion.

The "*Moor's Head*" *cooling arrangement* and the digestion vessels called *pelicans* probably both belong to the fifteenth century, as they are described by Brunschwyk. He was not, however, their inventor, but merely gave an account of them. The alchemist in Sebastian Brand's "Ship of Fools" (1494) used retorts of the modern shape.

Continuously burning furnaces with a tower for filling in fuel were used a great deal in the sixteenth century and probably also in the fifteenth (cf. Brunschwyk, 1500).

A picture of an alchemist's laboratory in the fifteenth century shows many of the small appliances used in a metallurgical laboratory, e.g. smelting furnaces with bellows and poker, crucibles of all sizes, crucible tongs, cupels, anvil and hammer, files, pliers, spatulæ, measures, gravers, chisels, gimlets, tools of all kinds, glass flasks, still-heads, all used in metallurgical operations.

A text-book devoted directly to the distillation of spirits was first prepared by Michael Puff (of Schrick) in the year 1474.

The mortars used in mediæval times and by the ancients were made of

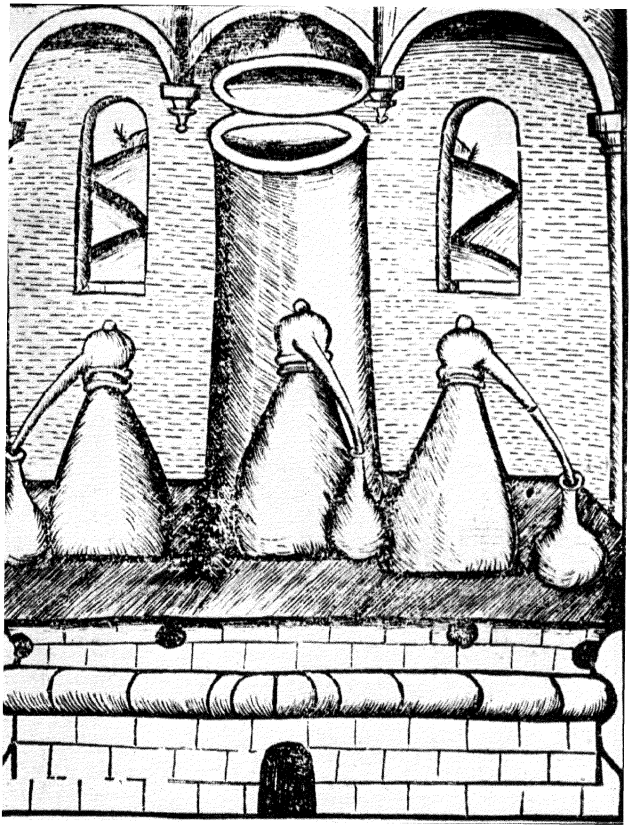


PLATE 34

Continuously burning distillation furnace, with tower for filling up with fuel. Hieronymus Brunschwyk, about 1500.

granite, sandstone, marble, serpentine, agate, bronze, brass, iron, earthenware and wood. Porcelain mortars were first made in the eighteenth century.

Theoretical Ideas

Mediæval chemists, e.g. Geber, assumed the existence of two elements besides those of Aristotle, namely :

Sulphur, the principle of combustion.

Mercury, the principle of volatility and metallic character. Later there

was also the idea of a fire-resisting and incombustible (but soluble) principle termed *sal* or *earth*.

It is clear that this point of view regards the metals as being composite. Since most of them can be burnt (calcined), they must contain the element sulphur, while their metallic character is attributed to the element mercury.



PLATE 35

Title page of the pamphlet "Von den gebranuten Wassern," by Michael Puff, Schrick, 1474. Early text-book of distillery.

(Distillation with alembic.)

The volatility of the metals (e.g. mercury, zinc, antimony, arsenic) was also known.

It is not, however, altogether correct to describe the Middle Ages as the alchemistic age of chemistry, since these ideas flourished much more in the succeeding age. The alchemistic standpoint is not characteristic of the Middle Ages, which might better be described as *a mineral acid and saltpetre age*.

The concept of elements held by the chemists of this period is by no means as absurd as is often supposed. Thus the special characteristics of metals

must, in fact, have a common cause, which is present in all metals and may be given the name of mercury.

The concept of the element sulphur is the same as the later, more lucid phlogiston theory. This theory was held by such unusually wise men as Scheele and Cavendish. It is certainly not very absurd, and it served a useful purpose in its time. It is quite unreasonable to despise the essentially practical mediæval chemists on account of their theoretical ideas.



PLATE 36

Vignette from the writings of Biringuccio, 1540.
(Distillation with alembics and still-heads.)

THE SIXTEENTH CENTURY AND THE FIRST HALF OF THE SEVENTEENTH CENTURY

THIS period is not characterised by any great developments in chemistry. It was occupied chiefly with extending the improvements of the Middle Ages, though there were some discoveries of new preparations and appliances, and progress was made in reaching a better understanding of the processes taking place. This is in particular true of *metallurgy*.

This age has often been characterised as the age of iatro-chemistry, but this is by no means justified. The basis for such a characterisation is to be found in the work of the doctor *Theophrastus Bombast von Hohenheim*, otherwise known as *Paracelsus*, 1493–1541. Like other doctors of his time, Hohenheim had considerable knowledge of chemical matters. Between 1510 and 1520 he worked in the laboratory of the important Schwazer mines (Tirol). He transferred the chemical ideas thus acquired to the functions of the human body, though (as we should express it to-day) in a vitalistic and not a materialistic sense. It was no part of Hohenheim's ideas to explain vital processes as purely chemical in nature. If the term " iatro-chemical " age is to be used at all, it actually applies best to the second half of the nineteenth century. The introduction of minerals and chemicals into medicine began long before the time of Hohenheim. Thus Roger Bacon wrote quite clearly of the medical problems of chemistry. The extended use of chemicals in medicine developed very slowly, in spite of the activity of Paracelsus. Very little was known of pure organic substances (which are best adapted to the human organism), and the attempt to extend the use of inorganic preparations from external to internal application met with little success. Probably not more than a dozen of the inorganic substances known at that time are used internally in medicine to-day. It will easily be understood that the experts of those days opposed iatro-chemistry, in spite of the efforts of Paracelsus.

Hohenheim is supposed to have used the following preparations medicinally: gold chloride, silver nitrate, the nitrates and chlorides of iron, copper, tin and lead; stannic acid, mercuric chloride, mercuric ammonium chloride

EFFIGIES PHILIPPI
THEOPHRASTI AB HO
HENHEIM: ÆTATIS SUÆ. XLVII



PHILIPPUS
THEOPHRASTUS
BOMBAST

PLATE 37

Wood-cut of Theophrastus von Hohenheim, known as Paracelsus, born 1493 at Einsiedeln, died 1541 at Salzburg. The wood-cut is taken from "Chirurgischen Büchern und Schriften . . . an tag geben durch Joh. Huserum," Strassburg, 1618, and is printed from the cut by Tob. Stimmer: it is thus a mirror image of the well-known sketch by Augustin Hirschvogel.

(alembroth), basic mercurous sulphate (Turpethum minerale), the sulphates of iron and copper, various antimony preparations such as the trichloride and oxychloride (algaroth), arsenic acid, colloidal gold and silver.

These preparations were not discovered by Hohenheim, but were available owing to the flourishing metallurgical technique of the period. It may be

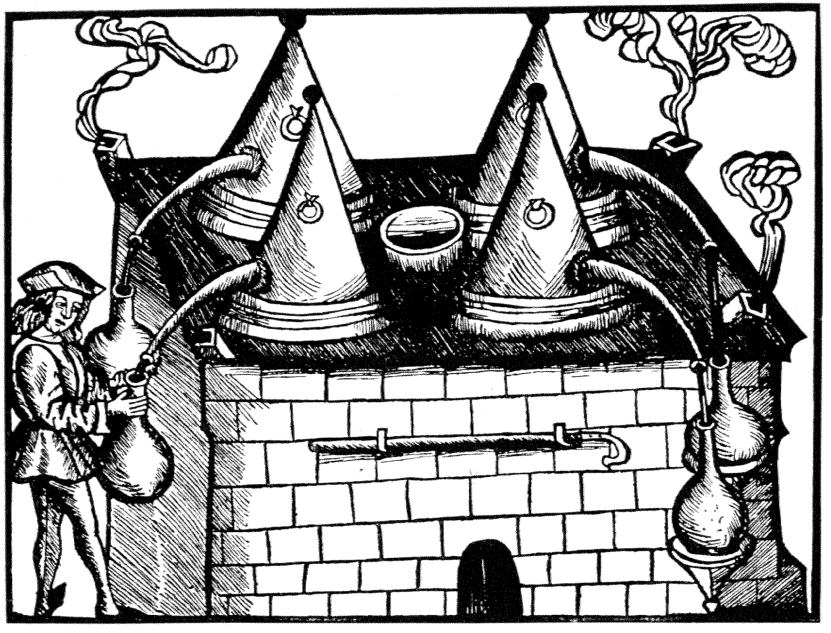


PLATE 38

Stove with "hooded" distillation apparatus, from Hieronymus Brunschwyk, about 1500.

The lower vessel containing the substance to be distilled is surmounted by a hood of glazed earthenware or tinned copper. Inside the hood is a rim for collecting the condensed liquid. Especially used for preparing aquae destillatae.

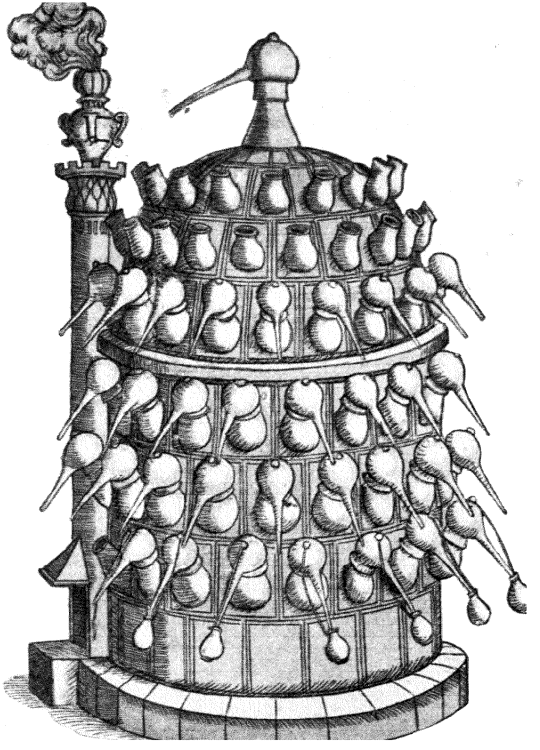


PLATE 39

Stove-like distillation apparatus, Italian, sixteenth century.

Each opening contains an earthenware distillation vessel fitted with a glass still-head.

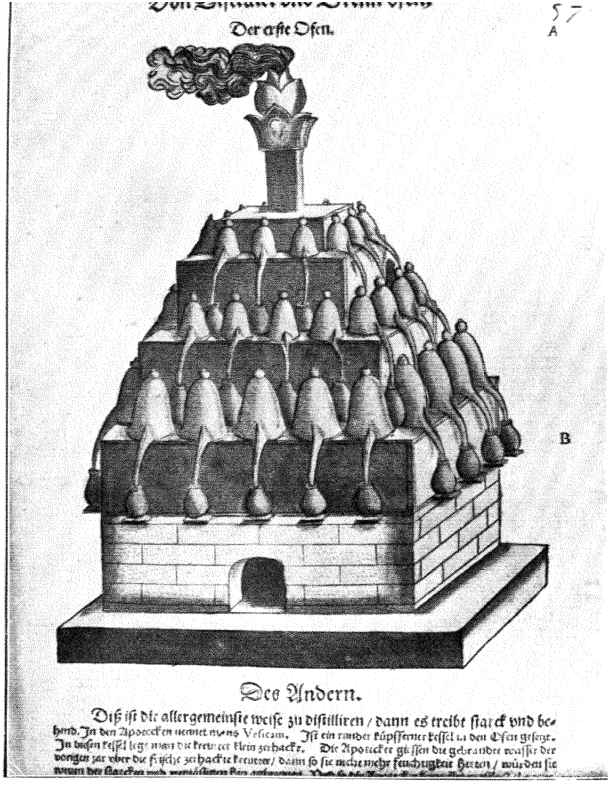


PLATE 40

Furnace for the simultaneous distillation of a large number of drugs. P. Matthiolus, sixteenth century.

The furnace contains small earthenware flasks which are provided with glass still-heads and glass receivers.



PLATE 41

Page from the "Giblom Apotheck."

Section through a distilling furnace. The fire is in the centre of the cone and the temperature can be regulated by lateral flues. The earthenware slots serve to hold the alembics.

(From the *Ricettario Fiorentino*, 1567.)

noted that he used Pliny's test (with tincture of gall-nuts) for detecting iron in mineral waters.

To confirm the statement that the sixteenth century was not actually a period of iatro-chemistry, the following facts may be quoted. If we examine the pharmacopœias of the sixteenth century, e.g. the excellent Cologne pharmacopœia of 1565, we find altogether only about two dozen inorganic

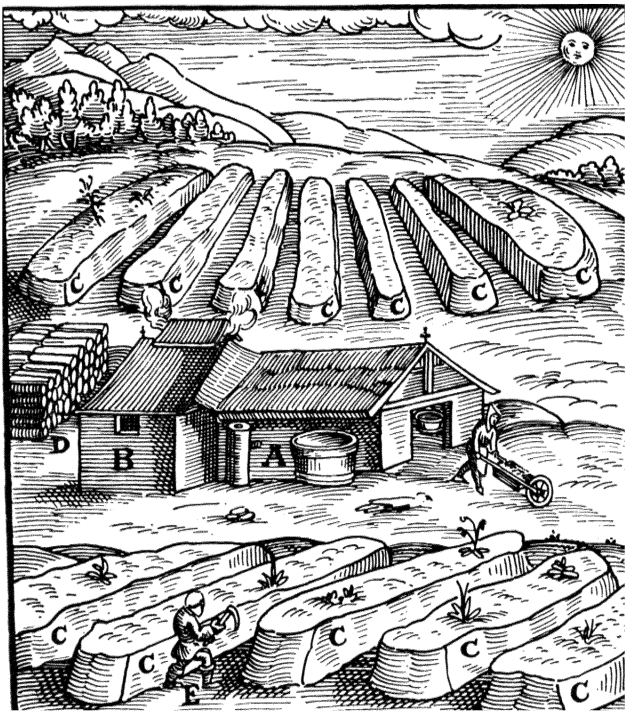


PLATE 42

Manufacture of saltpetre: Lazarus Ercker, 1574. Saltpetre plantation.

A Hut containing the lye vats. B Hut containing the boiler. C The old workings from which the saltpetre is scraped. D Wood. E Workman scraping off the saltpetre.

remedies. Similarly, the inventory of the chemist's shop at Udberg (1589) contains about twenty-eight chemical remedies, and it should be remembered that this is a true inventory of products in actual use, unlike the older pharmacopœias. In face of such facts, it is misleading to speak of an iatro-chemical age, and it can only be assumed that earlier writers on the history of chemistry were not sufficiently acquainted with pharmacology. If it is wished to have a name to describe this period, it would be more correct to describe the *fifteenth and sixteenth centuries together* as a *metallurgical-chemical period.* From a *chemical* point of view the true greatness of the period lies in this direction,

and not in the work of Paracelsus. The attempt to magnify the *chemical* achievements of Paracelsus appears again in Lieben's *History of Physiological Chemistry*, where he is described as the "father of physiological chemistry."

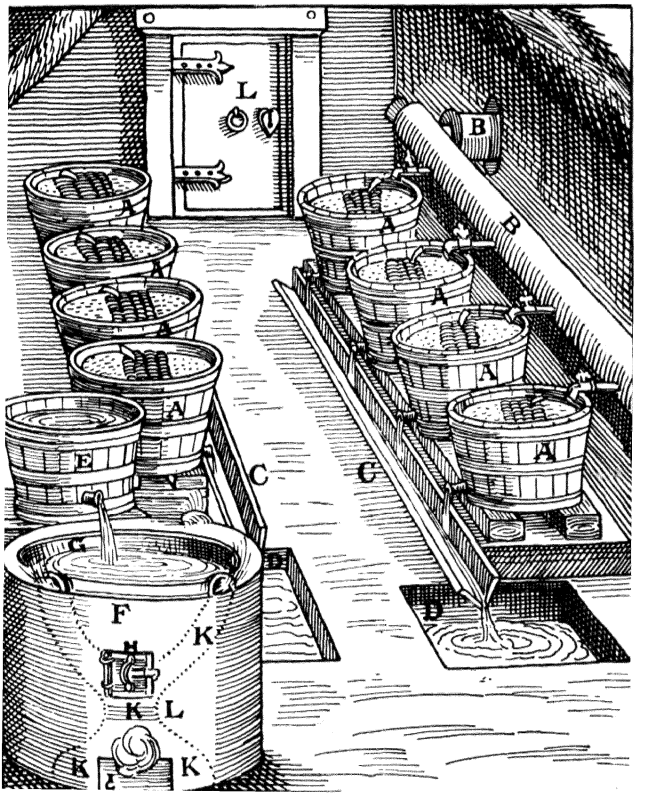


PLATE 43

Manufacture of saltpetre : Lazarus Ercker, 1574.

Extraction and boiling.

A The lye vats in which the earth is extracted. B The pipes through which the water flows. C The gutters along which the lye flows into the storage tank. D The storage tanks in which the lye is collected. E Small vats, from which the lye runs into the boiler. F The furnace. G The boiler. H Iron door for fuelling with wood. J The flue. K The shape of the furnace. L Iron grating.

This is also misleading, as the name is much more deservedly applied to the great physicians of antiquity.

The iatro-chemists of modern times have attempted to claim this great eccentric as one of themselves, but this is unjustifiable, as he was no materialist.

Metallurgical chemistry is described in a large number of writings. There is a series of small books on mining, testing and metalwork. A book of tests

from 1518 is a summary of the analytical chemistry of the period. It describes the testing of gold and silver by means of touch needles, a method which occurs from ancient times right up to the present day. There were sixteen needles for silver (1–16 loths) alloyed with copper, twenty-four needles for gold



PLATE 44

Manufacture of saltpetre : Lazarus Ercker, 1574.

Crystallisation.

A Tall narrow vat in which the boiling liquid cools. B The furnace in which the boiler stands. C The master, who boils the liquid, removes the salt with a ladle, and places it on the movable grating so that the excess of strong lye runs back into the boiler. D The movable grating. E Small vats from which strong lye runs into the boiler. F Moulds in which the crude saltpetre crystallises out. G Four vessels let into the ground, in which crude saltpetre separates out. H Strong vat in which the lye drains off the crystals.

(1–24 carats) also alloyed with copper, the black touchstone (slate or basalt), and nitric acid for testing gold. There were also analytical weights for gold (mark, 24 carats, 12 grains) and for silver (mark, 12 loths).

It gives also the testing of gold and silver by heating with lead, cupellation (practised in antiquity), appliances, such as assay furnaces, muffles, cupels of

ash or bone-ash. Other processes mentioned are fusion of samples with iron filings and salt, which removes sulphur from ores containing sulphur or arsenic; the separation of gold and silver by means of stibnite (silver sulphide forms a liquid slag with antimony sulphide leaving gold antimonide, from which the latter can be removed by burning to oxide); the separation of gold and silver by means of nitric acid; the separation of gold and copper by heating with sulphur and saltpetre (the sulphur being enclosed in wax to prevent it from burning too soon); the recovery of silver from its solution in nitric acid by means of salt, the silver chloride being then cupelled with lead and potassium sulphite; and finally the separation of gold and silver by cementation, known also in ancient times.

Another writing, *The Correct Use of Alchemy* (1531), gives recipes for gold-plating, silver-plating, manufacture of pigments (cinnabar, white lead, red lead, azurite, verdigris), the separation of the noble metals from copper and iron, the calcination of copper and tin, the preparation of solutions of alkalies, the preparation of sal-ammoniac, etc. A small book published in 1535 describes the hardening and softening of steel, the preparation of inks and of dyes, the removal of stains, and (for the first time) the production of mosaic gold (stannic sulphide) from tin amalgam by the action of sulphur and sal-ammoniac. It also gives a recipe for the so-called brick oil, i.e. oil distilled over pieces of red-hot brick.



PLATE 45

Manufacture of saltpetre : Lazarus Ercker, 1574.

The tester (i.e., the chemist) of the works.

A The small vessel in which a sample of the saltpetre earth is extracted. B The container into which the lye runs. C The balance. D The chemist who tests the lye. E The foil, on the end of which the sample is placed in a small dish. F The candle with which the sample is boiled.

A large proportion of the knowledge of this period is collected in the *Pirotechnia* of *Venoccio Biringuccio* (1480–1538). This work first appeared in 1540. Biringuccio was for a time director of smelting works, and also made two journeys to the German smelting works for the purpose of study. He gives an account of practically all the chemical technology of his time, and must be

considered further. We find the smelting of gold, silver, copper, lead, tin and iron ores; pre-treatment of the ore, shaft and reverberatory furnaces; with special detail the extraction of silver from its ores, the extraction of silver and gold from copper, silver refining, description of cupels, the re-conversion of oxidised lead into the metal and the extraction of any silver still present in it; the conversion of copper matte into copper, the production of steel, and the production of brass from calamine or tutty. Biringuccio deseribes the production of mercury in the old earthenware sublimation pots, and also in the newer conical distilling vessels with delivery tubes. He also describes the use of the latter apparatus for obtaining sulphur, and the production of roll sulphur. He

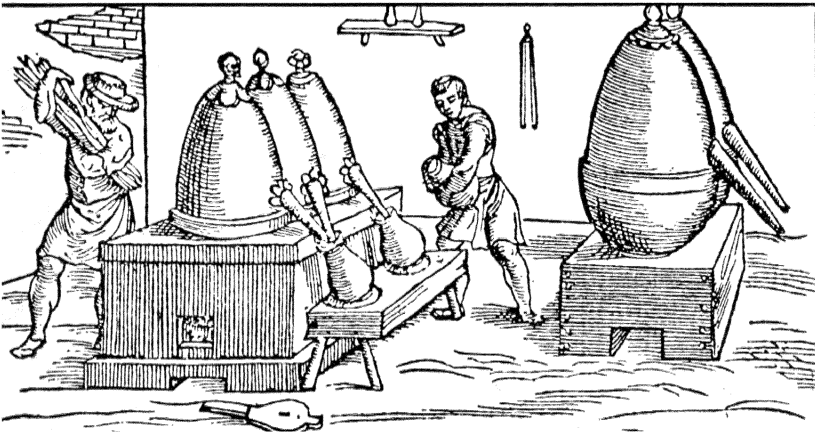


PLATE 46

Manufacture of mercury: Biringuccio, 1540.

Vessels fitted with still-heads having a channel for collecting the mercury, which then runs out through the delivery tube. The lower part of the vessels contains pulverised cinnabar with various additions.

treats stibnite, pyrites, anglesite, alunite, alum, orpiment, realgar, and the relation of the last two to white arsenic.

There follows the technology of rock salt and sea salt, mineral and vegetable soda, and the production of saltpetre and sal-ammoniac (the latter also from urine).

One chapter describes zaffre (cobalt ore) and the production of smalt by heating it with quartz. Smalt was used for colouring glass and pottery blue. Biringuccio knew pyrolusite and its use for decolorising greenish or yellowish glass, and also for producing purple colours in glass and pottery. He refers to magnetite, ochre, bole, emery, borax and sal-ammoniac. He appears not to have distinguished properly between the last two, an error in which he was followed by Agricola. Other substances mentioned are lapis lazuli, azurite, malachite, rock crystal and precious stones.

There is a valuable account of glass, glass furnaces and glass manufacture in general, staining and decoration of glass, and glazing of pottery.

The section on the analysis of ores is especially important from a chemical point of view. Biringuccio states quite rightly that the testing of ores is equivalent to carrying out the smelting process on a small scale, using an analytical balance. This is a very sound statement, and it is to be wished that our chemical students were taught methods of this kind at an early stage: this would give them a better introduction to industrial work than the

Der Heintzen Thurn A
Die Nebenöfen B
Der fürgelegte erdene Krug C
Der erdene Helm D
Der blinde Helm, mit dem ober Schneuzlein, darein das Wasser gegossen kann werden E
Der Anquicker F
Der das Quecksilber durchs Leder druckt G
Des eisern Krugs unter Theil H
Das ober Theil darauf K
Ein lederner Beutel zum Durchdrucken L
Der das Gold für dem Gebläs zusammen giehst M



PLATE 47

Extraction of gold: Lazarus Ercker, 1574.

Preparation of gold amalgam. Furnace with two side stoves for regaining the mercury from the amalgam, using a closed alembic and an alembic with delivery tube. The mercury is purified by means of leather. Large smelting furnace with bellows for melting down the gold.

analytical methods commonly used at present, which bear no relation to actual smelting processes. Analysis for gold and silver had (according to Biringuccio) to be especially accurate. He recommends that samples of ore as pure as possible should first be fused alone. If this was not found possible, additions were made, e.g. marble, glass, lead, hammer scale, borax, saltpetre, etc. The sample was next treated with mercury and then with lead, followed by cupellation in a cupel made of bone or horn ash. The sample of metal obtained was weighed. The most sensitive balances were even then kept in a protecting case (first picture in the Augsburg booklet on analysis (1510); also in the works of

Agricola and Ercker). The balances could be clamped and released by means of a lever.

An important process for the analyst is the separation of gold and silver on a small scale by means of nitric acid in a flask. Biringuccio describes how to recover the silver from solution.

The separation of gold and silver on a large scale necessitates the manu-



PLATE 48

Extraction of sulphur from pyrites by distillation.

Georg Agricola (1494–1555).

A Distilling vessel. B Receiver. C Lid. Since native sulphur does not occur in Germany, it was prepared by heating iron pyrites.

facture of nitric acid. Biringuccio describes the construction of a furnace for nitric acid manufacture, distilling flasks (which must be luted), dishes for ash- or sand-baths, and the recovery of silver from the solution. He gives good hints which reveal him as a true practical expert.

He also describes the separation of gold and silver by means of sulphur (also known to the ancients, e.g. Theophilus), and the separation using

antimony first described in the *House Book*. Finally he gives the separation by cementation with salt, on a small scale in an assay furnace and on a large scale in a blast furnace. Among the alloys mentioned by Biringuccio are those of

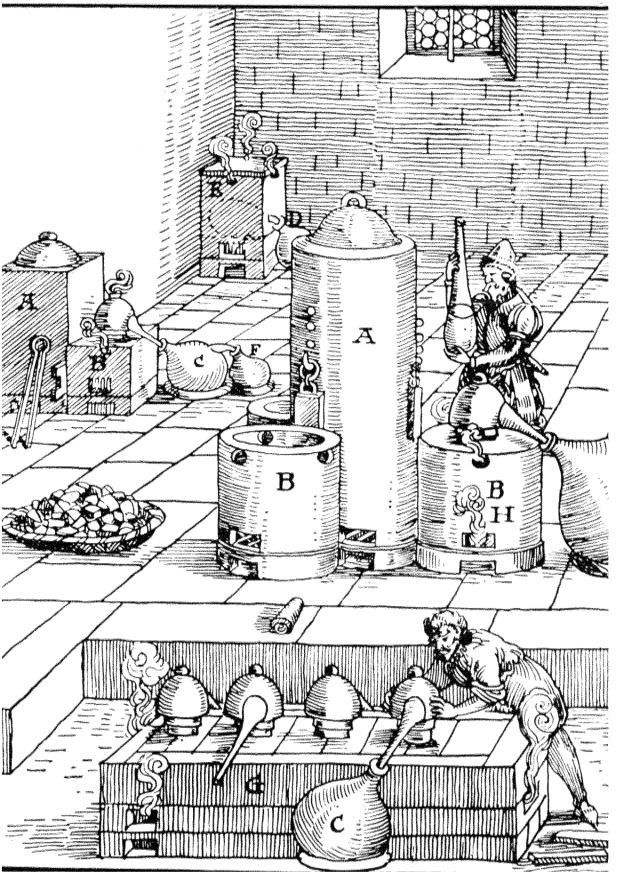


PLATE 49

Manufacture of nitric acid : Lazarus Ercker, 1574.

Athanor with dampers and three side stoves. Long furnace with several glass alembics. Small furnace with tower for fuelling and double receiver. Retort furnace in the left-hand corner.

gold with silver and copper, silver with copper, copper with tin, and lead with tin. (The sections on casting are not of interest here.)

An account is also given of the removal of gold from gilded objects by hot mercury, from which the gold could be recovered after pressing through a leather bag. Also the solution of gold in *aqua regia*, and the recovery of gold on

a large scale from sludges and slags by amalgamation with mercury in an amalgamation mill, followed by recovery of the mercury by distillation.

Other chapters describe pottery, the manufacture of crucibles and dishes, ceramic glazes from tin and lead, lime burning, brick making, and finally pyrotechnics, including the production of saltpetre, gunpowder and fireworks. (The section on guns is not of interest here.)

Biringuccio's work has been dealt with in some detail so as to give the

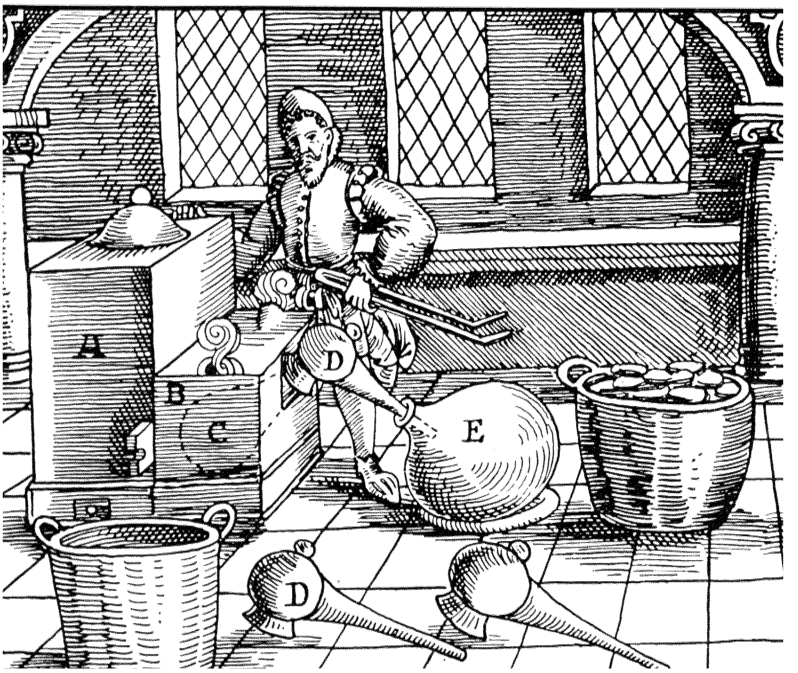


PLATE 50

Apparatus for preparing acids : Lazarus Ercker, 1574.

Small athanor with side stove and distilling apparatus (alembic, glass still-head and receiver).

reader a true idea of the *chemical technology of the sixteenth century*, and to remove the widespread impression that technical chemistry is a subject of recent growth. It will also serve to show that it is this subject which is truly characteristic of the century, and not the exaggerated use of a few chemical remedies for internal administration.

The German counterpart to Biringuccio's work is that of the Saxon philologist and physician, *Georg Bauer*, also known as *Agricola*, who out of love for the subject also became an important expert on mining and smelting. Agricola was familiar with antiquity, and probably for that very reason was no

stranger to the present. Even up to the present day there is in the German tongue no general book on mining and smelting which can in any way compare with Agricola's for general grasp and depiction of the subject.

Agricola studied philosophy, medicine and science in Padua and Bologna, where he obtained a doctor's degree. It is of interest that he acted as a proof-reader in the famous printing works of Aldus Manutius in Venice. He settled down as a doctor in Joachimstal, which was right in the centre of new mining

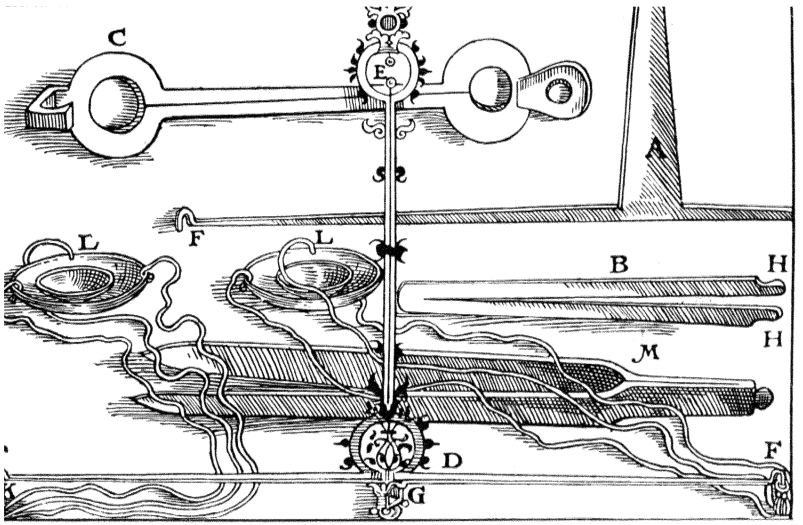


PLATE 51

Assay balance of Lazarus Ercker, 1574.

A Balance beam, forged. B Small tweezers, roughly forged. C Tweezers, forged. D Assay balance, filed. E Beads. F Suspension. G Bearing. K Small beam on which the threads hang. L Scale-pans. M Forceps.

discoveries, and might almost be compared with California in the nineteenth century. Joachimstal was founded in 1516, and as early as 1520 was declared a free city (Marienberg 1521, Gottesgab 1532).[1]

The mining town of Freiberg then had thirty thousand inhabitants. (For comparison it may be noted that Cologne, then the largest town in Germany,

[1] Some figures may be given to illustrate the flourishing state of the German metallurgical industry in the sixteenth century. During the years 1520–1626 the metal works at Annaberg and Schneeberg produced twenty-four tons of gold, besides enormous quantities of silver, lead and copper. Rammelsberg and Andreasberg in the Harz were at their zenith, and the Mansfeld copper works produced twenty to thirty thousand hundredweight of copper per annum. Joachimstal produced in one year (1523) 13,498 marks of silver. The works in Alpine districts (Falkenstein, Kitzbühel, Ittertal, Brixental, Gastein, Rauris) were also at the height of their prosperity. Idria produced annually three to six hundredweight of mercury. Between 1532 and 1536 Tamowitz produced two hundred and eleven thousand hundredweight of lead, as well as large quantities of zinc, and the tin mines of Saxony during the period 1577–1599 produced no less than ninety-six thousand hundredweight of tin.

had thirty-seven thousand, Frankfurt ten thousand, and Annaberg twelve thousand.) In 1525 the annual metallurgical production in Germany was worth two million gold gulden, and more than a hundred thousand men were employed.

Agricola lived in the midst of all this activity and was thus able to report a



PLATE 52

Andreas Libau.

Born 1540 at Halle; died 1616 at Koburg.

Engraving by Fennitzer, portrait collection of the National Library of Vienna.

One of the most important figures of the Renaissance period is Andreas Libau (Latin form, Libavius) born at Halle. He studied medicine and chemistry in his home city, and later history and languages at Jena. He was a school-teacher at Rothenburg, and finally director of the school at Koburg. He ranged over the whole field of chemistry, in theory, apparatus, technology, medicine and alchemy. His chief work "Alchymia" appeared first at Frankfurt in 1595, and again in 1597, 1606 and 1613. As an excellent work on the science of chemistry its influence extended for several centuries.

great deal of the knowledge which the practical workers were unable or unwilling to commit to writing.

It is clear from his excellent descriptions of minerals that he was familiar with a large proportion of the important minerals occurring in Germany, in particular ores of silver and copper. His work *De natura fossilium* is a handbook

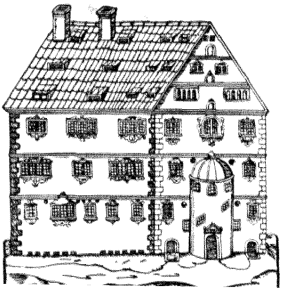
of mineralogy. *De re metallica* describes the extraction of gold, silver, copper, lead, iron, steel, mercury, antimony, bismuth, cobalt and tungsten. He also deals with salt, soda, saltpetre, alum, ferrous sulphate, sulphur, arsenic, mineral pigments and bitumen. In general his knowledge is equal to that of Biringuccio (whom he knew), e.g. in dealing with nitric acid. In many cases he gives more detailed information than Biringuccio, e.g. about the estimation of copper and lead. He also describes tests for tin, mercury and iron. It appears that Agricola was the first to mention potassium silicate.

Agricola seems to have been a sincere and capable man of great energy (he was an expert in three different occupations) and strong character. His book remained the gospel of mining and smelting in Germany for two centuries.

A few other individuals from this period must also be mentioned. Agricola's learned successor was the royal director of mines in Bohemia, *Lazarus Ercker*, who in 1574 published a compendium of metallurgical and analytical chemistry which was of importance for the next hundred and fifty years. The book is provided with magnificent pictures which illustrate the text clearly. Special mention may be made of the excellent laboratory pictures of the preparation of acids and the production of saltpetre. His descriptions indicate that the author had in many respects brought the subject to a state of greater clarity than had his predecessors. From a purely chemical point of view he advanced considerably beyond Biringuccio and Agricola.

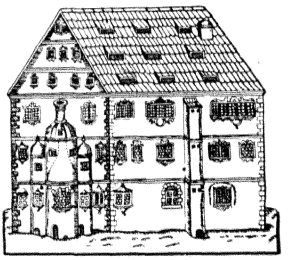
The *Alchymia* of *Andreas Libavius* (Libau) (died 1616) gives a summary of a great deal of chemical knowledge. Together with its supplementary writings it represents the first real *international chemical text book*, a fact which is worthy of note. Libavius had full command over the theoretical side of his material, but he must also have known something about the practical side of the subject. This is shown by his designs for a complete chemical institute, which although never executed are so excellent that they could only have been produced by a man of practical experience. Few later chemical institutes will bear comparison with these plans. They include a main laboratory, an analytical laboratory and a private laboratory for the director. Further, there was a chemical store, a preparation room with benches and fittings, a crystallising room with vats, storerooms, cellars, a wine cellar, a wood store and a room for the assistants. The laboratory had water laid on and charcoal stoves, also bathroom and steam bath. Among the larger installations were the following: large furnace, furnace with sand- or ash-baths, water-baths, distillation with and without cooling arrangements, distillation *per descensum*, sublimation, reverberatory furnace, large bellows, distillation *per lacinias* (i.e. purification by a series of fabric strips acting as siphons), dung baths. In the analytical room we see assay furnaces, and in the private laboratory the " philosophical " furnace, which (like all the other contrivances) is illustrated elsewhere in his works. Outside the building there is a large pond, and plots for making saltpetre, ferrous sulphate and alum. The upper storey contains living quarters, study rooms and library.

The following advances in practical chemistry are attributed to Libau.



Südostfront

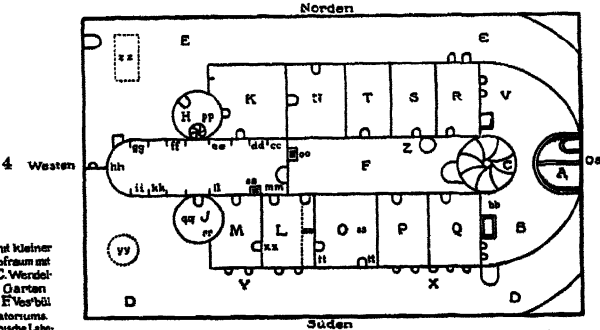
1



Nordostfront
(mit Hauptlaboratoriums Kamin)

2

3



A. Ostter mit kleiner Pforte. B. Hofraum mit Galerien. C. Wendeltreppe. D. Garten. E. Umgang. F. Vestibül des Laboratoriums. G. Das chemische Laboratorium. H. Oechemielaboratorium mit Wendeltreppe zum Studierzimmer. J. Türmchen mit Probierkabinett (analytisches Laboratorium). K. Chemische Apotheke. L. Präparierraum. M. Schlafraum des Laboranten. N. Vorratsraum. O. Krystallisierraum (Coagulatotorium). P. Holzraum. Q. Südliches Gewölbe. R. Obstkammer. S. Badezimmer. T. Aphodeuterium (Abort). V. Gemüsekeller. X. Weinkeller. Y. Laboratoriumskeller. Z. Wasserleitung.

7

aa Türe zum Keller des Laboratoriums. bb Eingang zum Weinkeller. cc Dampfbad. dd Aschenbadofen. ee Wasserbad. ff Destillatorium für Abwärtsdestillation. gg Sublimierapparat. hh Gewöhnliche Feuerstelle. ii Reverbe rierofen. kk. Destillierapparat. ll Destillierapparat mit Kühlschlange. mm Mistbad. nn Blasbalg, der auch ins Laboratorium verbracht werden kann. oo Kohlengewölbe. pp Philosoph. Ofen des Oekonomiebaumeisters. qq Probierröhren. rr Analytische Wäge in Gehäuse. ss Wannen und Rufen. tt Destillation per lacinias (Tisch mit Gefässen). uu Presse. xx Geräte und Tische zum Präparieren. yy Wasserbecken. zz Platz für das Salpeter-, Alaun- und Vitriolgewinnung.

8

PLATE 53

The chemical institute of Libau, 1606.

The institute contains a main laboratory with furnaces for water-baths, ash-baths, and steam-baths: distillation apparatus for upward and downward distillation, with and without cooling: sublimation apparatus, fireplace, reverberatory furnace and large bellows. The analytical laboratory contains assay furnaces and analytical balances, some in cases. The private laboratory contains a "philosopher's furnace." There are also in the institute a preparation room with press, a pharmacy, a crystallisation room, etc. The laboratory has water laid on, and in the open air there are facilities for making alum and vitriol, and a saltpetre plantation.

1. South-east front.
2. North-east front (with the chimney-stack of the main laboratory).
3. North. 4. West. 5. East. 6. South.
7. A East entrance with small door. B Main room with galleries. C Spiral staircase. D Garden. E Drive. F Vestibule of the laboratory. G Chemical laboratory. H Private laboratory with spiral stairs to the study. J Small analytical laboratory. K Chemical pharmacy. L Preparation room. M Bedroom for the laboratory assistant. N Store room. O Crystallisation room (coagulatotorium). P Wood store. Q South store room. R Fruit store. S Bathroom. T Aphodeuterium (closet). V Vegetable cellar. X Wine cellar. Y Laboratory cellar. Z Water supply.
8. *a a* Doors to the laboratory cellar. *b b* Entrance to the wine cellar. *c c* Steam-bath. *d d* Ash-bath furnace. *e e* Water-bath. *f f* Distillation apparatus for upward distillation. *g g* Sublimation apparatus. *h h* Ordinary fireplace. *i i* Reverboratory furnace. *k k* Distillation apparatus. *l l* Distillation apparatus with spiral condenser. *m m* Dung bath. *n n* Bellows, which can also be brought into the laboratory. *o o* Coal store. *p p* Philosophers' furnace in the private laboratory. *q q* Assay furnaces. *r r* Analytical balances in cases. *s s* Tubs and vats. *t t* Distillation "per lacinias" (table with vessels). *x x* Equipment and benches for preparations. *y y* Water tanks. *z z* Space for preparing saltpetre, alum and vitriol.

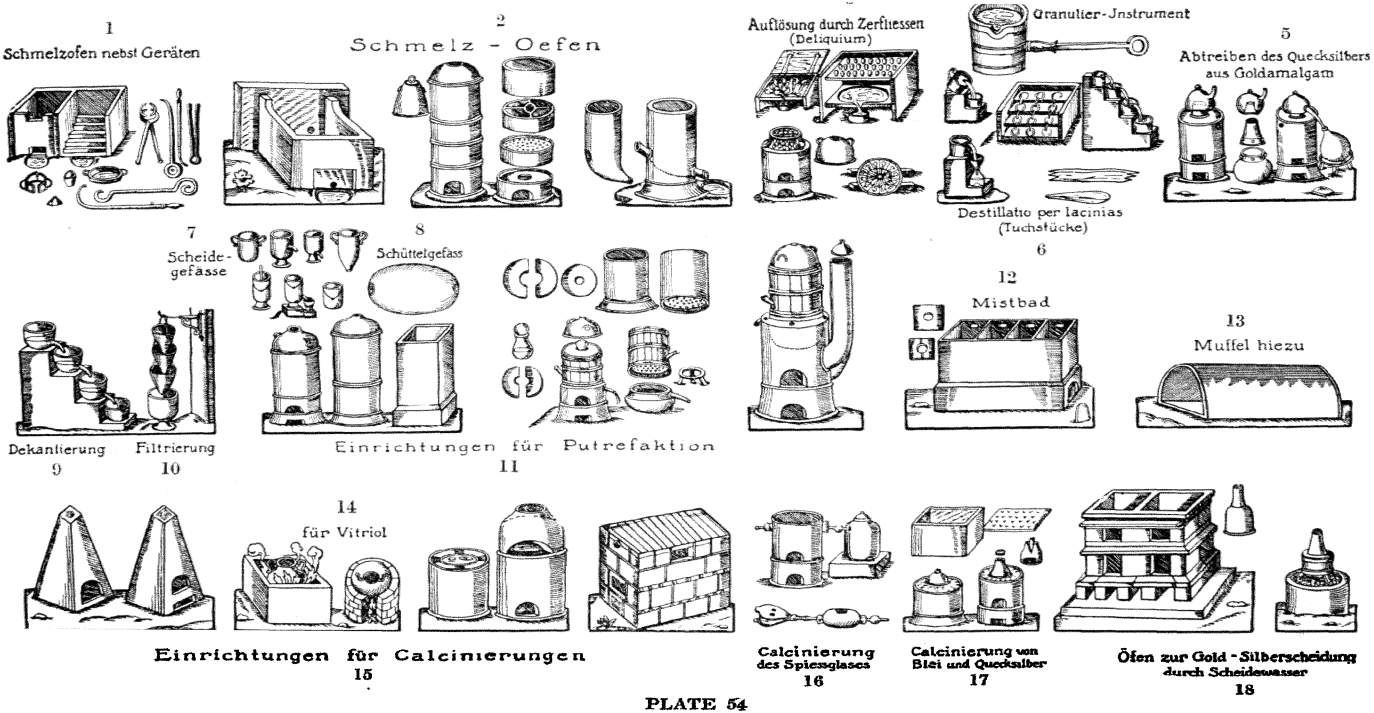


PLATE 54

Apparatus for analysis and separation : A. Libau, 1606.

1. **Smelting furnace with tools.**
2. **Smelting furnace.**
3. **Solution by deliquescence (deliquium).**
4. **Granulating instrument.**
5. **Removal of mercury from gold amalgam.**
6. **Destillatio per lacinias (cloth strips).**
7. **Analysis vessels.**
8. **Vessel for shaking.**
9. **Decantation.**
10. **Filtration.**
11. **Arrangements for putrefaction.**
12. **Dung bath.**
13. **Muffle for dung bath.**
14. **For vitriol.**
15. **Arrangements for calcination.**
16. **Calcination of antimony.**
17. **Calcination of lead and mercury.**
18. **Furnace for separating gold and silver by means of nitric acid.**

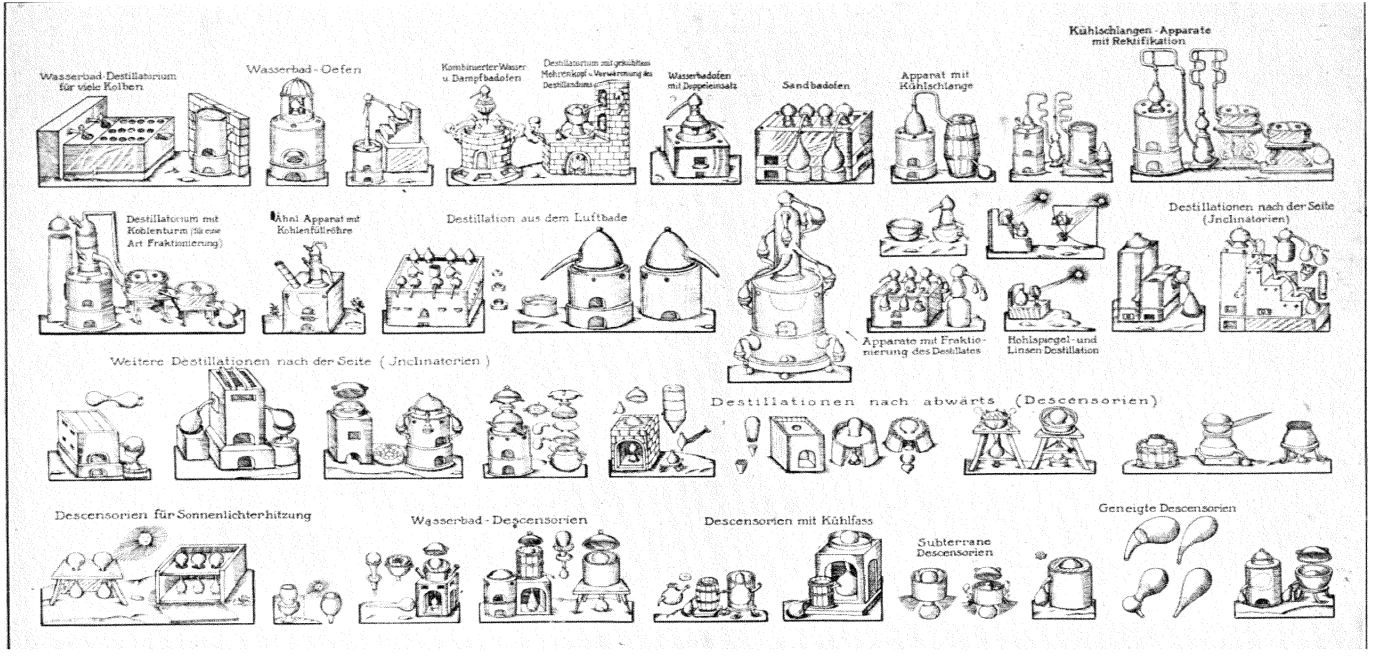


PLATE 55

Apparatus for distillation : *A. Libau*, 1606.

1. Water-bath distillation apparatus for several flasks.
2. Water-bath furnace.
3. Combined water-bath and steam-bath.
4. Distillation apparatus with cooled still-head and pre-heating of the liquid to be distilled.
5. Water-bath furnace.
6. Sand-bath furnace.
7. Apparatus with spiral condenser.
8. Apparatus with spiral condensers and rectification.
9. Distillation apparatus with fuel tower (for a sort of fractionation).
10. Similar apparatus with opening for fuelling.
11. Distillation from air-baths.
12. Apparatus for fractionating the distillate.
13. Distillation by means of a concave mirror and a lens.
14. Distillation to the side (inclinatorium).
15. Further apparatus for distillation to the side (inclinatorium).
16. Downward distillation (descensorium).
17. Descensorium for heating by sunlight.
18. Water-bath descensorium.
19. Descensorium with cooling vessel.
20. Subterranean descensorium.
21. Inclined descensorium.

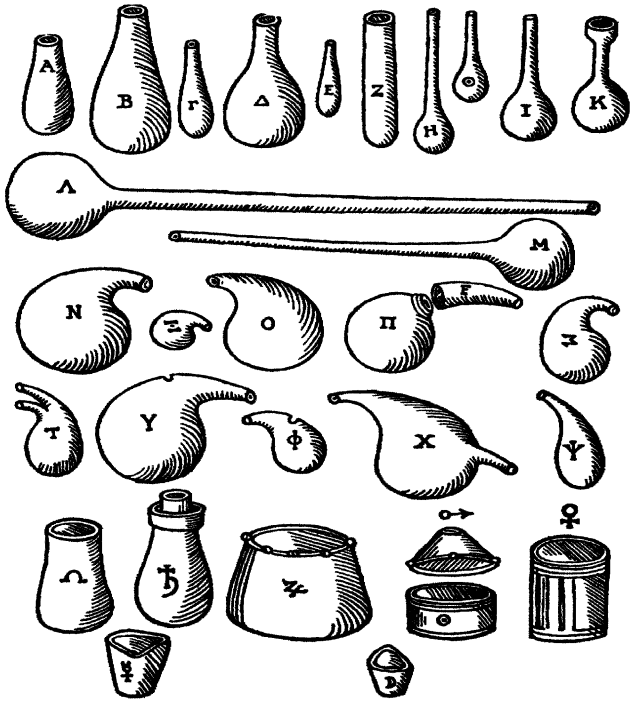


PLATE 56

Chemical utensils : Andreas Libau, about 1600.

ABΓE Cucurbita. Δ Ampulla. Z Glass tube. H Crane's bill. ΘIAM Phials. K Phial with fitting for alembic. NΞOΣΨ Retorts (horn of Hermes). Π Metal retort with fitting. TTΦX Retorts with tubus or second opening. Ω Matula (test-tube). ♑ Sublimation vessel, earthenware. ♃♂ Iron pots for strong acids. ♀ Cementation box. ☿☽ Crucibles.

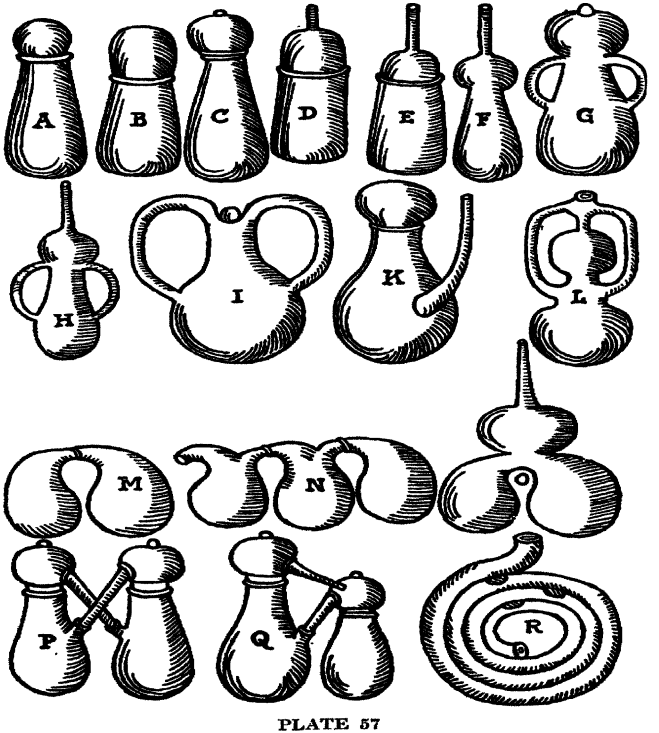


PLATE 57

Vessels for digestion and circulation : Andreas Libau, about 1600.

A, B Cucurbita closed with a round flask. C The same with a closed alembic. D, E, F digestion vessels with exit tubes. G Pelican. H Pelican with tubes. I Circulation apparatus with side tubes. L The same (reflux condenser). K "Jubilans." M "Bocia contra bociam" (double retort "columbissanter"). N "Tripudianter." O "Crumena" (double retort with a common tubulated head). "Aquilæ" (eagle). Q "Vultures" (vulture). R Snake or serpent.

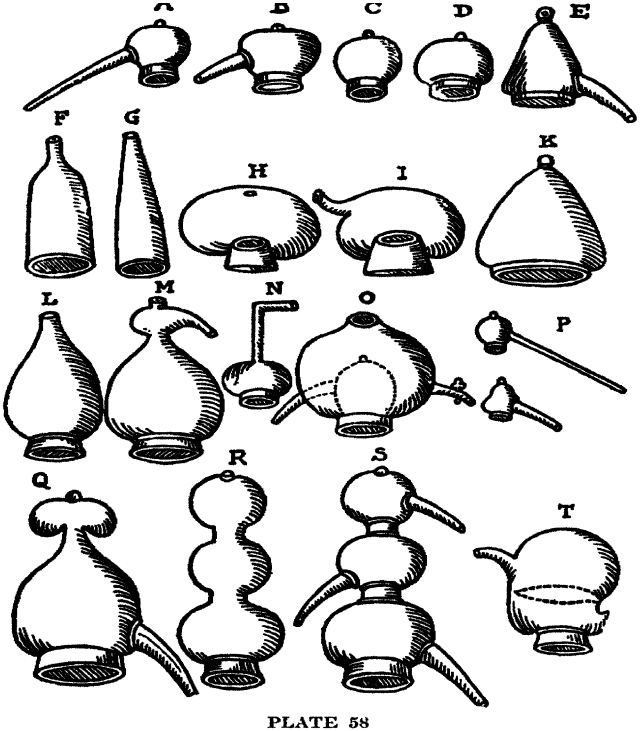


PLATE 58

Still-heads : Andreas Libau, about 1600.

A Alembic with long delivery tube. B Alembic with short delivery tube. C, D, H Closed alembics. E Tin alembic. F, G Sublimation heads. J, T Closed alembics with tubus. K Bell-shaped head. L Elongated alembic. M Tin alembic with delivery tube in the apex. N Alembic with exit tube. O Alembic with arrangement for cooling. P Miniature alembics. Q Closed alembic with delivery tube. R Triple closed alembic. S Alembic with three delivery tubes.

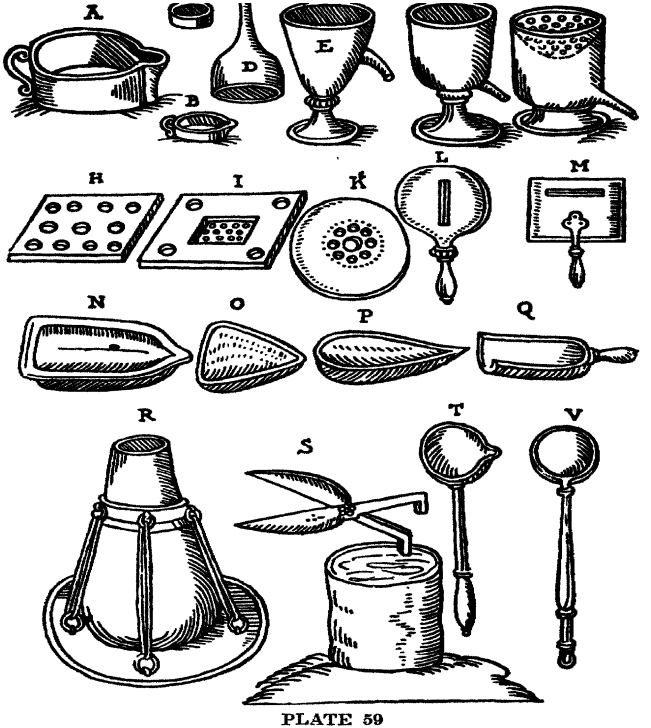


PLATE 59

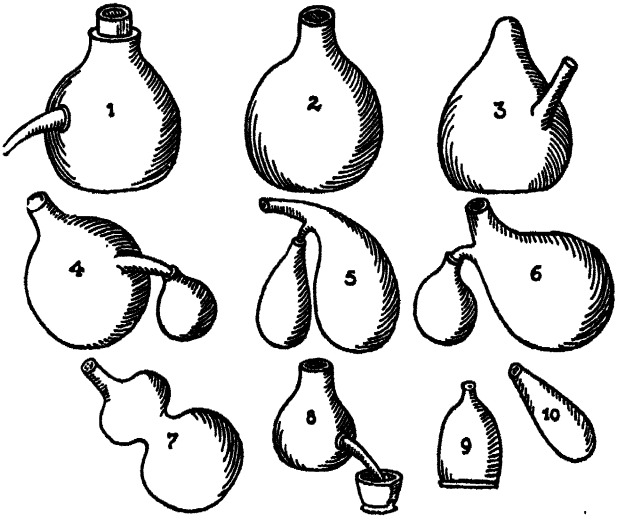
Other chemical utensils : Andreas Libau, about 1600.

A Crystallising dish. B Small dishes for the quartation of gold. C Small dishes of gold and glass. D Glass funnel. E Vessel for separating oils heavier than water. F Vessel for separating oils lighter than water. G Filtering vessel. H Casting mould. I, K Gratings. L, M Diopters (for protecting the eyes). N, O, P, Q Troughs for gold-washing. R Flask stand with lead ring. S Metal shears. T, V Casting ladles.

PLATE 60

Receivers: Andreas Libau, about 1600.

1. Large tubulated ampulla, of iron or pottery.
2. Simple bulbous ampulla.
3. Closed receiver.
4, 5, 6. Twin receivers.
7. Receiver with two bulbs.
8. " Thieve's " receiver.
9. Ordinary receiver.
10. Cucurbita receiver.



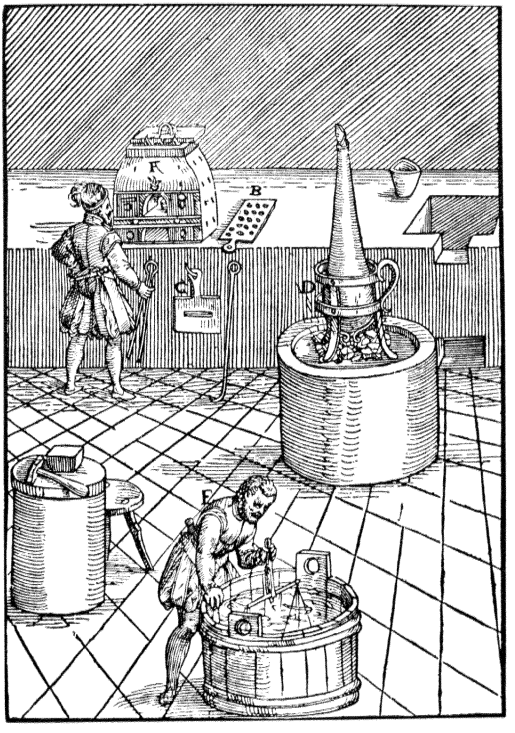


PLATE 61

Analytical laboratory: L. Ercker.

Second half of the sixteenth century.

A. Assay furnace.
B. Iron plate on to which the sample being tested was poured.
C. Wooden instrument with slit for observing the fire in the assay furnace (eye guard).
D. Flask on tripod for parting the sample of gold.
E. Weighing the gold-silver alloy in water.

He was the first to recognise the presence of carbon dioxide in certain mineral waters, and to determine their specific gravity and the residue left on evaporating down. He discovered liquid stannic chloride (Spiritus fumans Libavii), bismuth oxide and nitrate, the preparation of (impure) acetone and of camphoric acid. He also describes sulphur dioxide and sulphuric acid. His descriptions of different kinds of chemical apparatus are the most complete which occur in any handbook on this subject.

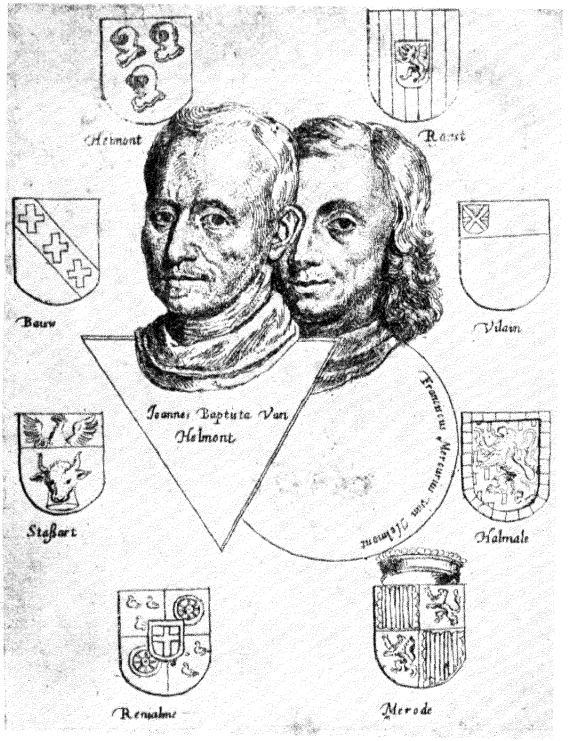


PLATE 62

J. B. van Helmont (1577–1644).

A nobleman of Brabant.

In addition to J. B. van Helmont the picture shows his son, Franciscus Mercurius van Helmont.

Other important works of this period are the writings of the so-called *Basilius Valentinus*. In several respects they constitute an obscure chapter in the history of chemistry. It is impossible to understand how serious historical writers can have entertained even for a moment the mediæval view of the Basilius writings, when we consider their language, outlook and content.

It is usually assumed that Basilius Valentinus was the pseudonym of the salt-maker, Johannes Thölde, of Frankenhausen, who also made hydrometers.[1]

This assumption is, however, by no means as certain as has been supposed. The earliest edition of the works of Valentinus was *not* produced by Thölde, but comes from Rorschach on Lake Constance. It contains the writings *Von dem grossen Stein der Uralten* and the *Zwölf Schlüssel*, and appeared in 1600 as the third part of the *Aureum Vellus*, a well-known alchemistic treatise which was also produced at Rorschach (1598). The question can only be

[1] Hydrometers are mentioned by Pappos of Alexandria (A.D. 290), Synesios, in *Carmen de ponderibus* (fifth century), Al-Chazini (1121), French writers of the sixteenth century, and Schwenter (1636).

considered as settled if it can be shown that Thölde had something to do with this earliest edition.[1]

The author of the *Aureum Vellus* was certainly not Thölde, and the author of the Valentinus writings was clearly not a Benedictine. Whoever he may have been, he was a gifted practical worker with a specially good knowledge of antimony. It cannot, however, be assumed that he actually discovered any fresh substances. This supposition is based upon inaccurate chronology. Thus among other substances Basilius mentions antimony trichloride, potassium antimonate, kermes mineral, ammonium sulphide, ethyl nitrate, ethyl chloride and fulminating gold, all of which were demonstrably known by 1600.[2]

The first German university professor who taught chemistry was Johann Hartmann from Amberg (1568–1631), professor at Marburg.

The Belgian, *Johann Baptist van Helmont* (1577–1644), may be regarded as the *founder of gas chemistry*, being well known as the inventor of the word "gas." He recognised hydrogen (which



PLATE 63

Johann Rudolf Glauber.

Born 1604 at Karlstadt; died 1670 at Amsterdam.

[1] A 1599 edition from Eisleben is also mentioned.

[2] We may mention here a work of P. Antonio Neri, which gives an excellent description of contemporary glass manufacture, though it must be presumed that the Venetian glass workers knew still more than P. Neri. The work is entitled: *L'arte vetraria distinta*, and appeared in 1612.

Neri was acquainted with lead glass containing no alkali, and he gives a recipe for gold ruby glass which is correct, according to the later specifications of Kunckel. (Libau had also heard of gold glass, which was also prepared by Cassius long before Kunckel. It was, in fact, known to the ancients, as is shown both by writers and by specimens of glass.)

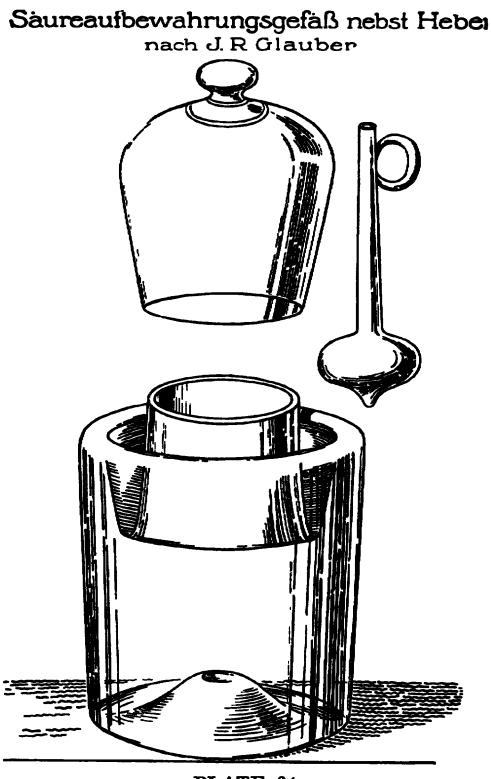


PLATE 64

Vessel for storing acid, with sampler : J. R. Glauber.

The groove is to be filled with mercury. Sampler on the right.

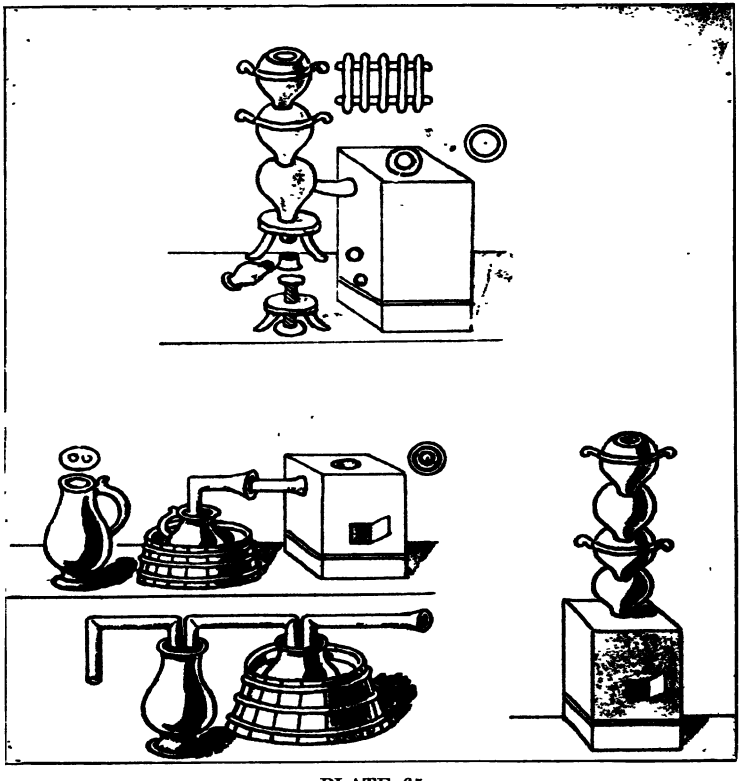


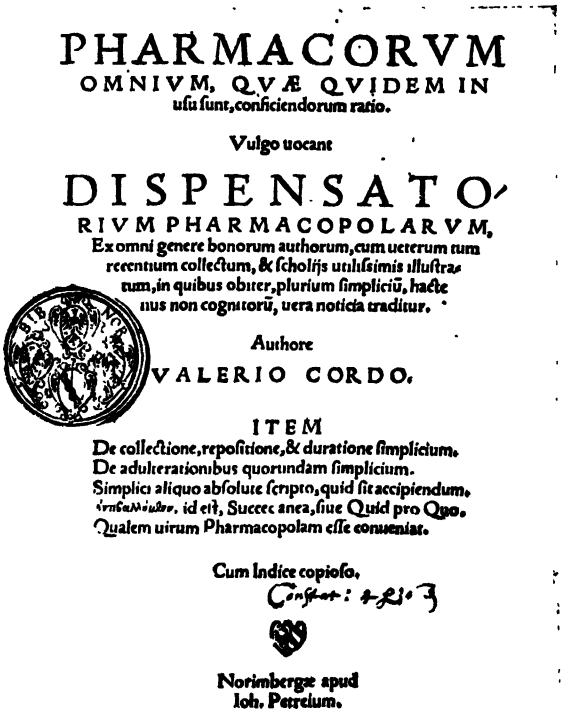
PLATE 65

Chemical apparatus : J. R. Glauber, 1661.

Above : preparation of sulphuric acid.
Below, left : distillation apparatus for obtaining "Spiritus et Flores." *right :* sublimation apparatus.

had, of course, been previously observed as a separate combustible gas), also hydrogen sulphide (to which the same applies) and the fire-extinguishing carbon dioxide, which he termed "gas sylvestre." He found the last-named gas in the mineral waters of Spa. He also knew of silicic acid and had some conception of chemical physiological processes (e.g. gastric acid and gall).

The last great chemist of this period was the outstanding technician, *Rudolf Glauber*, of Karlstadt (1604–1670). His importance is often underestimated, as he was a man without any academic training. However, he had remarkable practical skill, and his activities covered a very wide range. He is best known for his improved methods for preparing hydrochloric and nitric acids (1648). He knew and practised the older methods, in which hydrochloric acid was obtained from common salt and green vitriol or alum, and nitric acid from saltpetre and vitriol, alum or clay. In his own method hydrochloric acid was obtained from salt and sulphuric acid, and nitric acid from saltpetre and sulphuric acid. It should, however, be noted that these processes were probably known before Glauber's time, but were not used in technical practice on account of the high price of sulphuric acid. According to Walden, the proportions of the materials employed by Glauber are the correct ones.[1]


PHARMACORVM
OMNIVM, QVÆ QVIDEM IN
usu sunt, conficiendorum ratio.

Vulgo uocant

DISPENSATO-
RIVM PHARMACOPOLARVM,
Ex omni genere bonorum authorum, cum ueterum tum
recentium collectum, & scholijs utilissimis illustra-
tum, in quibus obiter, plurium simpliciū, hactenus non cognitorū, uera notitia traditur.

Authore
VALERIO CORDO.

ITEM
De collectione, repositione, & durationc simplicium.
De adulterationibus quorundam simplicium.
Simplici aliquo absolute scripto, quid sit accipiendum.
Qualem uirum Pharmacopolam esse conueniat.

Cum Indice copioso.

Norimbergæ apud
Ioh. Petreium.

PLATE 66

Title page of the Dispensatorium of Valerius Cordus, 1546.

Glauber used hydrochloric acid for the preparation and study of chlorides,

[1] Agricola apparently did not know Glauber's methods. He obtained hydrochloric acid from salt by heating with loam or terra sigillata. The same applies to Beguin (1615). The so-called Basilius Valentinus prepared aqua regia from saltpetre, sal-ammoniac and powdered flint, while he obtained hydrochloric acid from common salt and green vitriol. The preparation of nitric acid from saltpetre and sulphuric acid does, however, appear to have been known to Angelus Sala.

of which the best known were zinc chloride and arsenic chloride. It may be noted that Glauber mentions saltpetre as a good manure which he had tested himself. Glauber's work in the field of explosives is of great importance. He discovered ammonium nitrate, prepared potassium picrate from wool, nitric acid and potash, and improved the preparation of fulminating gold. He occupied himself with the problem of poison gases and gas shells, actually completing some of the latter. He mentions their use in the war against the Turks, and predicted (1661) chemical warfare. Glauber prepared colloidal gold from gold chloride and lemon juice, improved the preparation of tartar emetic (1648), and knew the manufacture of ruby glass.



PLATE 67

Title engraving of the Antwerp edition of the first German pharmacopœia of Valerius Cordus, Nürnberg.

Published in Antwerp by the pharmacist Peter Coudenberg, who founded in 1548 the Antwerp botanical garden (shown in the picture).

It can hardly be doubted that Glauber was acquainted with chlorine and potassium chlorate. He observed the *mineral chamæleon* (permanganate, manganate), gives directions for obtaining antimony pentasulphide from antimonic acid, and cast antimony vessels for drinking. He recommends copper tartrate in place of verdigris, and obtained acetic acid from crude wood-vinegar (which had long been known). He distilled coal, obtaining benzene and probably also carbolic acid, prepared fairly pure grape-sugar (1660) and malt extract (1657). He knew that fuming nitric acid would ignite turpentine and other ethereal oils. He also obtained ethyl chloride (1648),

acetone and acrolein. In 1654 he indicated the method of obtaining the alkaloid bases strychnine, brucine and morphine.

Glauber also made contributions to theoretical chemistry. He had a good conception of the nature of chemical reactions, and knew the change: acid + base = salt. He was probably the first to grasp the nature of double decompositions. His example of this kind of reaction is: corrosive sublimate + antimony sulphide gives antimony trichloride + mercuric sulphide.

The world of German chemistry (and in particular German chemical industry) owes a great deal to Glauber. It is incredible that there is yet no memorial in his native country (Germany) to such a great man. As a non-academic worker he was always looked down upon, especially since he maintained that as a skilled practical worker he could learn nothing from the universities. This statement of his actually hits the nail on the head, since at that time real practical chemists could only be trained in metallurgical works or pharmacies.

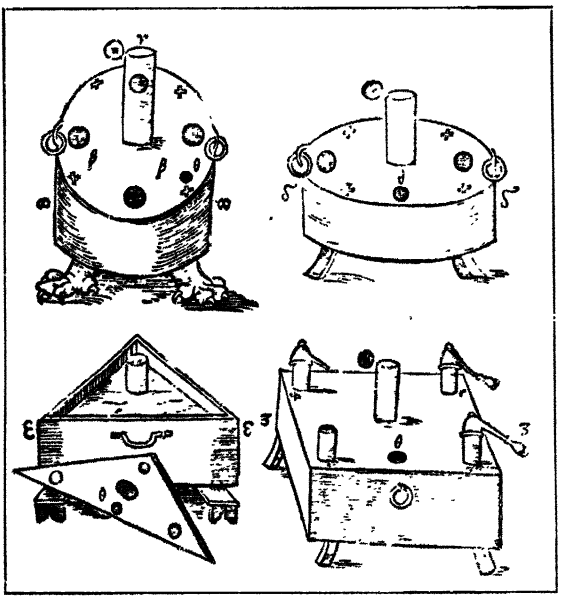


PLATE 68

Water-baths.

From the *Antidotarium generale* of Joh. Jac. Wecker, Basle, 1585.

Various metal containers for hot water with heating tubes.

We must now describe the *medicinal knowledge* of the period.

In the first place we must again deal with Paracelsus. Tschirch and von Lippmann describe him as a Neo-Platonist with a strong tendency to mysticism, who attempted to destroy the Galenic doctrine without ever succeeding in doing so. Hohenheim believed that every vegetable or animal remedy contained one particularly effective substance, the true aim of pharmacy being to obtain this substance by chemical means. We know to-day that this idea has only been slowly realised in practice since the nineteenth century, and the most recent investigations seem to show that it is erroneous in its most general form, since the most effective remedies are rarely individual pure substances, being more often mixtures. The extracts or tinctures recommended by von Hohenheim (which were used widely both before and after his time) are of course

mixtures. Inorganic chemical remedies, on the other hand, were generally only used for external applications (as in earlier periods—see above).

The sixteenth century saw the rise of *records of pharmaceutical knowledge* in various countries, after the model of the *Ricettario Fiorentino*. This often took the form of local pharmacopœias sanctioned by the municipal or state authorities.

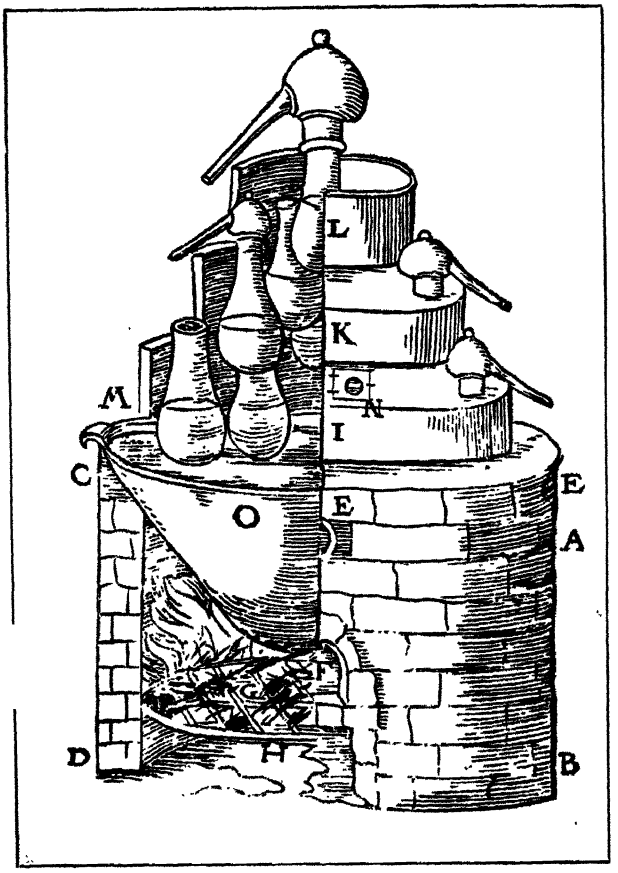


PLATE 69

Apparatus for carrying out distillation in steam.

J. Wecker, 1574.

The flasks do not stand in the water, but are surrounded by the hot steam. This kind of distillation is mediæval, and the picture is probably taken from a late edition of the Ricettario Fiorentino.

The *first German pharmacopœia* was the *Dispensatorium* of *Valerius Cordus*, compiled in 1546 for the town of Nürnberg.[1] The importance of this should not be underestimated because it was based on earlier works, as it is the function of pharmacopœias to preserve existing knowledge. The *Dispensatorium* of Cordus contains nearly four hundred Composita, requiring for their preparation seven hundred and twelve Simplicia, some of which are mineral or chemical. To-day the extreme complexity of many of the remedies causes astonishment and doubt as to whether this complexity serves any useful purpose. It should, however, be remembered that the plant drugs and animal products

[1] A facsimile edition appeared in 1934 with a commentary by Dr. Ludwig Winkler, Innsbruck, published for the *Gesellschaft für Geschichte der Pharmazie* (Berlin) by Arthur Nemayer, Mittenwald.

provided by nature are usually very complex. Thus a glass of wine contains dozens of chemical substances, and such simple products as essence of peppermint or attar of roses contain more than forty chemical individuals. It is therefore wise to reserve judgment on this question, especially as to-day we have no practical experience with Composita containing many components.

Municipal pharmacopœias were published shortly afterwards in the towns of Lyon (1546), Mantua (1559), Antwerp (1560), Augsburg (1564), Cologne (1565), Bologna (1574), Bergamo (1580), Venice (1617), London (1618), and Frankfurt-on-Maine (1624 and 1626).[1]

Valerius Cordus (1515–1544) was also an able chemist. He was the discoverer of ethyl ether, which he prepared from spirits of wine and sulphuric acid. He also prepared a whole series of ethereal oils, of which we may mention cinnamon, clove, cubeb, cardamom, mace, nutmeg, pepper, angelica, celery, parsley, fennel, dill, parsnip, caraway and aniseed. He also observed anethol in aniseed oil. His vessel for preparing volatile essential oils is of interest: it consists of an alembic with a



PLATE 70

Laboratory for extracting chemical substances from plants : Barlet, 1657.

1. Assistant preparing an extract from plants.
2. Water-bath on tripod with flask, still-head and receiver (under a large draught-hood).
3. Refrigeratorium with small furnace and receiver (under a large draught-hood).
4. Chemist, separating the vegetable essences or spirits from the water.
5. Furnace with ash-bath.
6. Calcining basket for obtaining salts from plants.

[1] There were also large numbers of unofficial pharmacopœias, e.g. the *Dispensatorium* of Joh. Bretschneider (Placotomus) at Münnerstadt, 1560 (which contains the first example of the word "pharmacopœia"), the *Antidotarium* of Joh. Jak. Wecker, 1585, the Thesaurus pharmaceuticus of Caspar Schwenckfeldt, the *Pharmacopœia* of Jos. Quercetanus (J. du Chesne), 1603, the *Thesaurus et Armamentarium* of Adrian Seumenicht (Mynsicht), 1631, Joh. Schröder's famous *Pharmacopœia medico-chymica*, 1641, J. Zwelffer's *Pharmacopœia regia*, 1675 (which appeared in many editions in Germany up to the middle of the eighteenth century), and finally the valuable *Pharmacopée* of the Parisian pharmacist M. Charas, 1676.

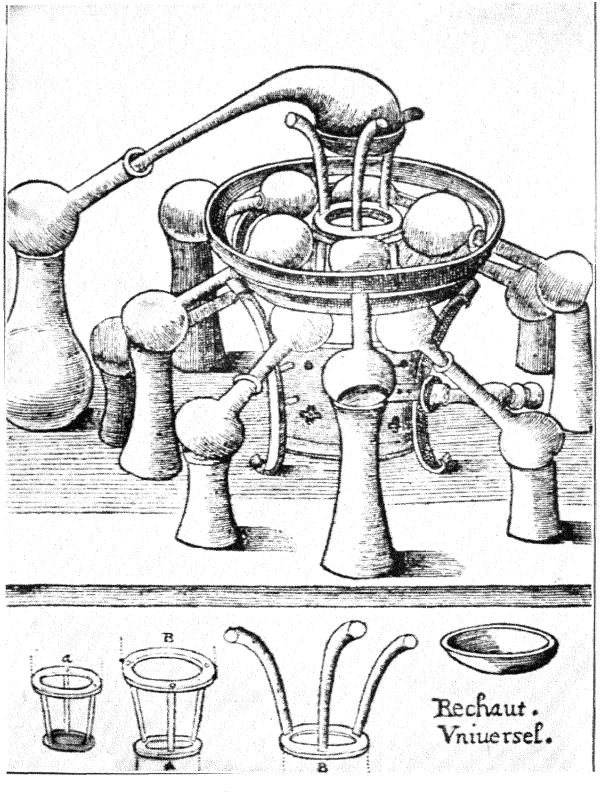


PLATE 71

Distillation apparatus : Barlet, seventeenth century.

For the simultaneous distillation of nine products.

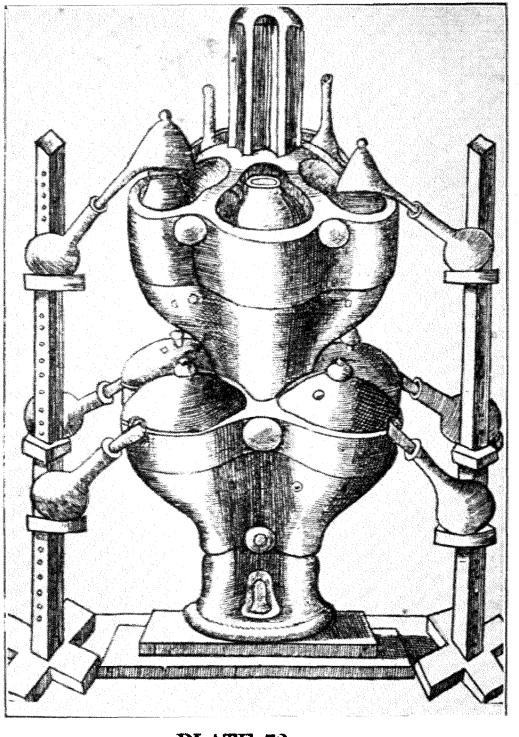


PLATE 72

Furnace in tiers, for distillation : Barlet, 1657.

This apparatus appears to have been used for the distillation of small quantities. Note the stands.

fused-on head and a tubulated flask, thus allowing for filling and refilling. Cordus brought the spirit of chemistry into pharmacology, and he sought to prepare pure extracts in the same sense as Paracelsus. However, as stated above, solutions, extracts and tinctures prepared from vegetable or animal sources can hardly be regarded as chemical individuals, but rather as complicated mixtures. The same of course applies to the many "waters" and essences prepared by distillation. Brunschwyk mentions (among others) the oils of angelica, blessed-thistle, linden flowers, lavender, camomile, aniseed, primula farinosa, juniper wood and rosemary. W. Ryff prepared ethereal oils from practically all the pharmaceutical gums, e.g. myrrh, styrax,



PLATE 73

Alchemical laboratory.

Engraving from "Vom philosoph. Steine ein kurtzes Tractätlein," by H. C. D., Frankfurt. Published 1625, Luca Jennis. In the foreground snakes are being treated. In the back of the picture, a fine water-bath. This is apparently the research laboratory of a church dignitary.

mastic, opoponax, benzoin, and also from cloves, cinnamon, mace, saffron and other spices. J. Porta did the same with wormwood, lavender, primula farinosa, camomile and lemon peel.

The products of dry distillation of vegetable and animal products are all mixtures: this includes animal charcoal from various sources such as ivory, fungi and animal oils, also tars and tar oils. Still less chemical individuals are the many liquids obtained by pressing various fresh vegetable products. Oils were also obtained by pressing from many seeds and fruits, and could be rendered much more aromatic by the addition of ethereal oils. Many kinds of animal fats were also used, derived from dozens of different animals, e.g. all domestic animals (including dogs and cats), all kinds of poultry, all mammals and birds which could be hunted, adders, vipers and fish. The fat of executed

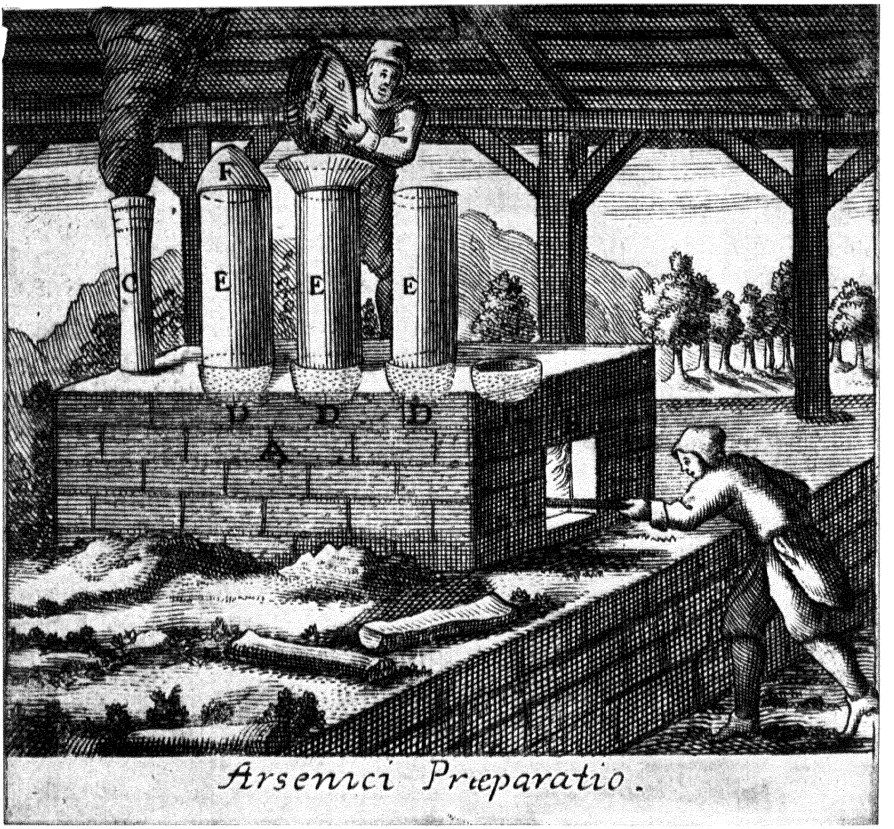


PLATE 74

Preparation of arsenic : M. B. Valentini, 1704.

Fumes of white arsenic were produced by roasting cobalt ores or metallic arsenic, and were resublimed from the cupels D. White arsenic is deposited as a thick layer in the iron tubes E, with lids E.

human beings was a much sought and expensive medicament. (Even Saladin's compendium contains sixteen different fats.) In later periods the tendency has been to laugh at this arsenal of fats, and to be content with lard and lanoline. It may be, however, that the ancients were wise and the moderns foolish, since fats differ to a great extent in their chemical composition (ergosterol, etc.).

We may note the use of hormone and enzyme preparations, e.g. the liver of various animals, lungs, spleen, brain, marrow, blood (of different kinds), gastric membrane, and gall (Saladin's compendium contains eight different kinds of animal gall). The medicinal effect of toad poison was also used, and was re-discovered at a much later date. Particularly noteworthy is the intro-

duction of *new remedies from the newly discovered American continent*, which later also influenced the field of chemistry. It would occupy too much space



PLATE 75

Franz de le Boë Sylvius (1614-1672).

Born in Hanau, worked as a university teacher in Leydon and Amsterdam.

to enumerate all these remedies, but we shall mention a few of them : tobacco (and the distillate prepared from it), cinchona bark, coca leaves, guaiacum wood and resin, quassia, sassafras, ipecacuanha, sarsaparilla root, senega root ; copaiva, Peruvian and tolu balsams ; jalap, sabadilla seeds, cocoa and cocoa

butter; spices such as vanilla, canella, pimento and Spanish pepper: dyestuffs like Brazil wood, campeachy wood, and cochineal insects. The last-named were used as a source of carmine dye, which gave an excellent shade of red with stannic chloride, as described by Drebbel (1643). This list represents a most valuable collection of materials.

In the seventeenth century China tea and Abyssinian coffee began to spread to the West to a considerable extent.

We shall now give a *list of substances* containing some products which have not already been mentioned.

(*a*) *Inorganic.* The so-called "Hollandus" knew calcium chloride. Vinzentius Casciarolus found heavy spar (in 1603 or later) and prepared from it phosphorescent barium sulphide. He states that it is very difficult to reduce this mineral to a metal, and in this way discovered the phosphorescent material. Joseph du Chesne (Quercetanus), 1521–1609, a Paracelsian physician, used calomel (mercurous chloride) and golden antimony pentasulphide. We cannot, however, suppose that he discovered these substances.[1]

Angelus Sala, a doctor of the first half of the seventeenth century, knew of the precipitation of copper from solution by means of iron. The metallurgical works at Neusohl made copper-plated iron vessels in this way, and sold them as examples of the transmutation of metals; actually, of course, a galvanic process is involved.

Otto Tachenius, middle of the seventeenth century, gives some methods for analysis in the wet way. He used tincture of gall-nuts for detecting not only iron, but also copper, lead, mercury and gold in solution. He also used lunar caustic for recognising salts in solution, and *vice versâ*.

Franz de le Boë (also known as Sylvius), the famous iatro-chemist and professor of medicine (1614–1672), mentions and uses potassium chloride. He attempted to develop a chemical theory of physiology, and recognised respiration as a process of combustion.

(*b*) *Organic.*

Succinic acid, Agricola 1540, Libau 1595.
Very pure alcohol, Cardanus 1554.
Benzoic acid, Nostradamus 1556, Ruscelli 1557, Blaise de Vigenére 1580.
Grape sugar from honey, Olivier de Serres 1600.
Pure bone oil, Turquet de Mayerne 1608.
Anhydrous potassium acetate, Th. Müller 1610.
Ammonium acetate, Raymund Minderer 1613.
Milk sugar, Fabrizio Bartoletti 1615; Thurneysser 1583.
Tartar emetic, Adrian Semmenicht (Mynsicht) 1630.
Potassium oxalate, Angelus Sala 1647.
Mustard oil, N. le Fèbre 1660.

[1] Konrad Gesner was the first to mention graphite lead pencil (1563), and gives an illustration of a shaped rod of graphite in a case. The discovery was probably made by the English, though the early manuscript of Theophilus Presbyter (see above) is written with a graphite pencil.

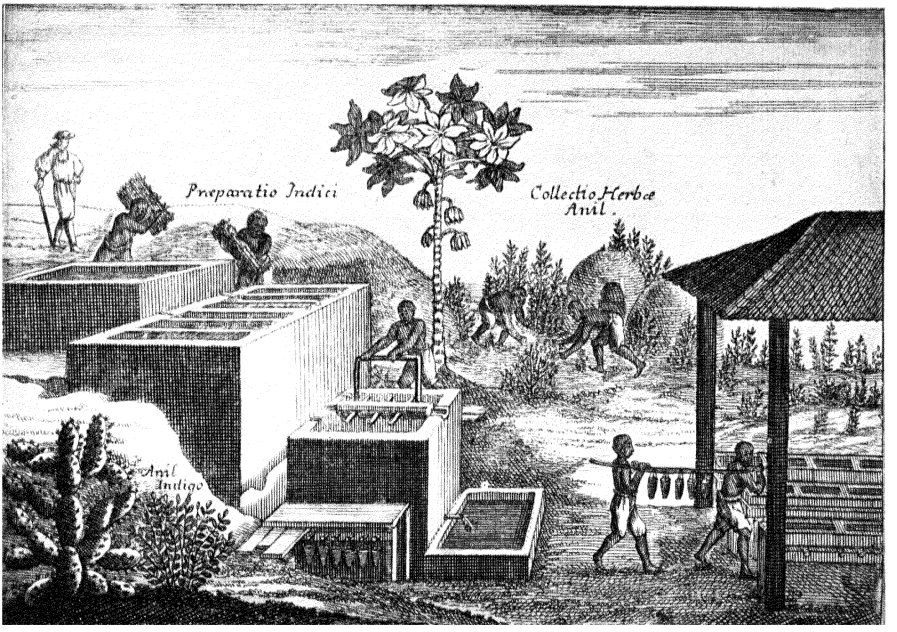


PLATE 76

The extraction of indiyo in India.

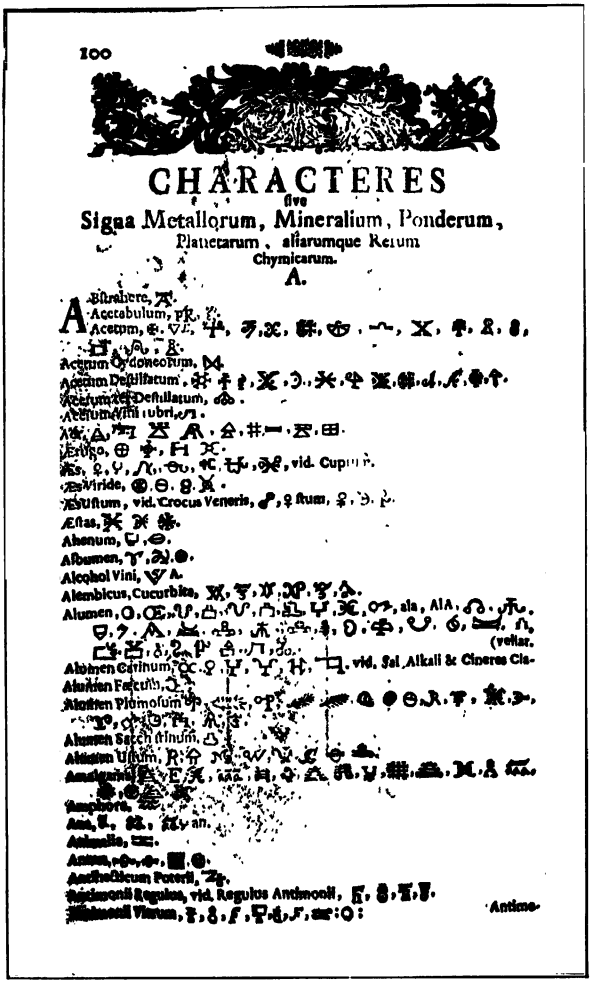
From Museum Museorum, by M. B. Valentini, Frankfurt, 1704. The indigo plants were extracted with water, thus dissolving the indican. This solution was agitated in the second vat, when oxidation took place and indigo separated out: this was then filtered off and dried.

Theoretical Chemistry

The concept of elements described in a previous section did not change appreciably in this period. The element "sulphur" gradually acquired the character of phlogiston. Biringuccio states that sulphur is more "combusted" than stibnite, and later the term "richer in phlogiston" was used (see below). *Chemical symbols* remained essentially the same, though practically every author has some special signs of his own. The Cologne pharmacopœia of 1628 gives a table which probably represents wide usage. The number and diversity of the symbols (some of which were used as secret signs) is well illustrated by the lexicon of the apothecary *Johann Christoph Sommerhoff*, which was first printed in 1701 but which deals chiefly with the literature of the sixteenth and seventeenth centuries.

The law of constant proportions by weight was taken into account by all the practical chemists of this period. This is true of the authors of many booklets on assaying, and also of Biringuccio, who states directly in his *Pirotechnia* that in chemical operations the quantities of the substances taken

must correspond correctly to one another. Biringuccio also knew that in chemical processes the nature and quantity of the substances involved remained unchanged. Thus he says that when silver is dissolved in nitric acid, although it appears to be completely destroyed, the full weight of it can be recovered without loss.


100

CHARACTERES
five
Signa Metallorum, Mineralium, Ponderum,
Planetarum, aliarumque Rerum
Chymicarum.

A.

Bituhere, A.
Accetabulum,
Acetum,
Acetum Cydoneorum,
Acetum Destillatum,
Acetum Destillatum,
Acetum Vini rubri,
Æthiops,
Æs, vid. Cuprum.
Æs Viride,
Æsutum, vid. Crocus Veneris,
Æstas,
Abenum,
Albumen,
Alcohol Vini,
Alembicus, Cucurbita,
Alumen,
Alumen Catinum,
Alumen Facutii,
Alumen Plumosum,
Alumen Sacchariuum,
Alumen Usium,
Amalgama,
Amphora,
Anima,
Animalia,
Anthos,
Antimonium Potorii,
Antimonii Regulus, vid. Regulus Antimonii,
Antimonii Vitrum,

PLATE 77

From Sommerhoff.

At the end of Sommerhoff's pharmaceutical-chemical lexicon there are fifteen pages (in alphabetical order) containing the abbreviations and secret symbols used in the sixteenth, seventeenth and eighteenth centuries for the most important chemical and pharmaceutical substances, appliances, weights, times and manipulations.

The investigator *Cardanus* (1554) states the increase to be one part in thirteen, which also agrees well. He also gives an explanation of the phenomenon which presupposes the phlogiston theory. Cardanus should therefore really be regarded as the founder of the phlogiston theory instead of Stahl.

Cæsalpinus (1596) describes the same facts and gives a completely untenable explanation.

H. Popp found the same behaviour in the calcination of antimony by means of a burning glass. *J. Beguin* (1616) investigated the same phenomenon

Biringuccio was also the first to give numerical data on the increase of weight accompanying the calcination (oxidation) of metals. He states that lead increases in weight by 8 to 10% when calcined. According to Walden the correct values are 7·7% (litharge) and 10·2% (red lead), so that the agreement is good.

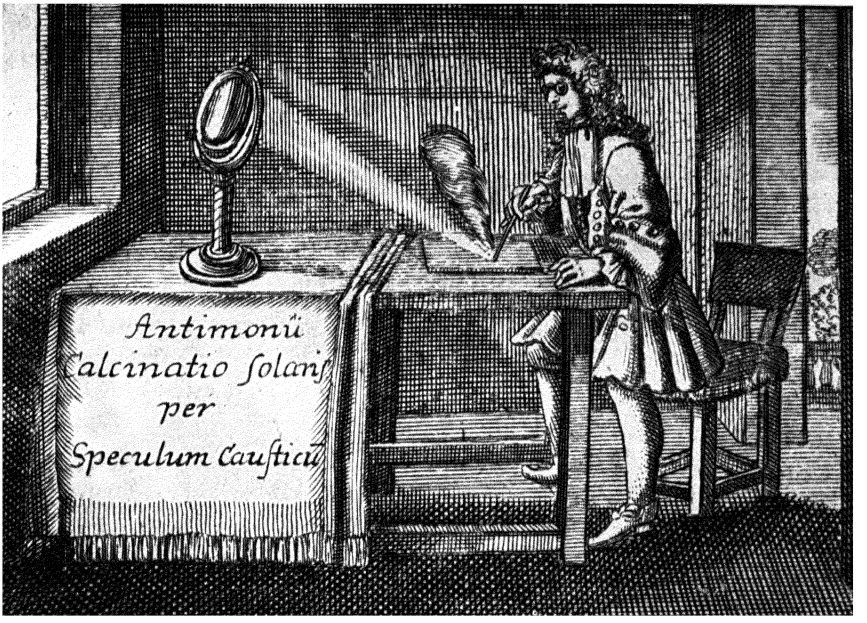


PLATE 78

Burning of antimony by the sun's rays : M. B. Valentini, 1704.

in the oxidation of iron in the wet way, and obtained the fairly accurate ratio 1 : 1·43 (instead of 1·5).

It is thus completely untenable and in contradiction to the facts to maintain that quantitative methods in chemistry were only used after Lavoisier's time, and that the proper use of the balance in chemistry was not understood before Lavoisier. In *Glauber's* relics there are three balances : a balance for gold, a carat balance for precious stones, and a rapid balance for tests. The scale-pans and the set of weights were of silver.[1]

The French doctor *Jean Rey* (died 1645) stated correctly in 1630 that *the increase of weight on calcination comes from the air*. He observed this phenomenon for tin and lead.

Sennert (1572–1637) taught that the particles of elements persisted in compounds. *Joachim Jungius* (1587–1657) was of the opinion that chemical processes could be investigated by means of the balance.

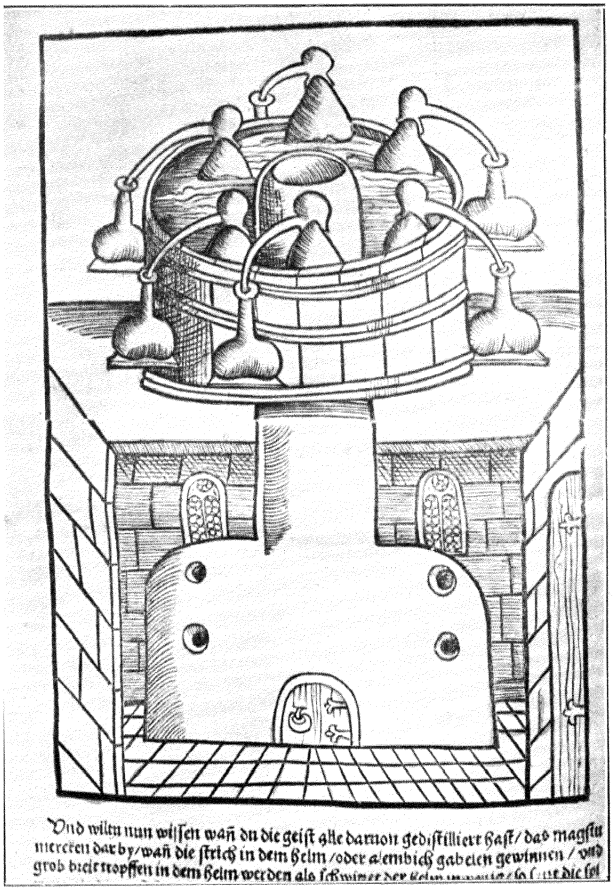
Johann Baptist van Helmont (1587–1657) knew that gold remains gold and lead remains lead, whatever is done to them.

[1] Upright balances with a pointer pointing downwards appear to have come into use after the seventeenth century, and balances with a scale for showing the deflection of the pointer were rarely used until the eighteenth century. The first-known balance with an arrangement for arresting the pans was made by T. Leopold in 1726 from a French description. No comprehensive book appears to have been written on the history of the balance.

He also knew (1648) *that when a candle burns in a bell-jar sealed by means of water, the amount of air decreases and the water rises.*

Van Helmont also mentions the conservation of matter in the combustion of carbon, provided that it takes place in a closed vessel. Boyle gives an incorrect account of this experiment.

The fact that later chemists have not paid sufficient attention to these excellent statements of fact in no way detracts from their excellence.



Vnd wiltu nun wiſſen wañ du die geiſt alle darvon gedeſtilliert haſt/ das magiſte nierẽden darby/wañ die ſtrich in dem helm/oder alembich gabelen gewinnen/ vnd grob dicke tropffen in dem helm werden als ſchwitzer der leib [illegible] die ſel

PLATE 79

Large water-bath for distillation.

Brunschwyk, sixteenth century.

The wooden casing contains a heating dome of copper.

Chemical Apparatus

There is an abundance of material for establishing the history of chemical apparatus in this period, especially in the so-called "distilling books," of which that written by Hieronymus Brunschwyk (Brunschwyg). His descriptions really belong to the Middle Ages, since the book appeared in 1500 (or 1505) and the appliances described are those of the fifteenth century. Some of them have already been mentioned.

Other distilling books of the period are those of Philipp Ulstad, 1526, Piesandrea Matthioli, 1544, Walther Hermann Ryff (Reif, Rivius), 1545, Konrad Gesner (Euonymus Philiatrus), 1552, Adam Lonicer (Lonitzer), 1557. We may mention the glass vessels used by Brunschwyk for digestion and circulation, the latter of which may be said to act like a reflux condenser. The

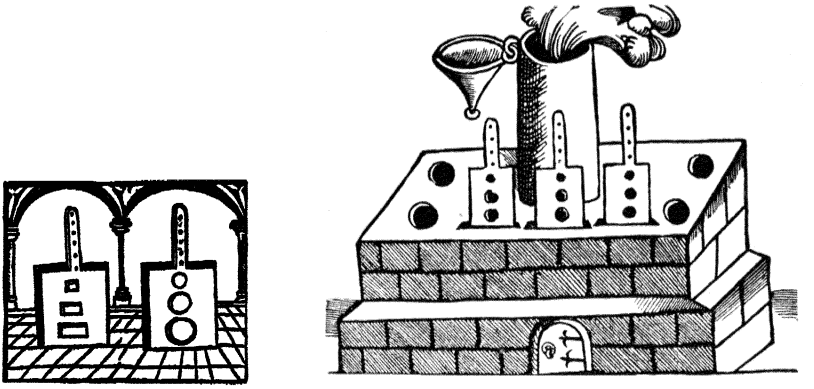


PLATE 80

Stove with fuelling tower and dampers.

Philipp Uhlstadt. 1536 (continously burning adjustable stove).

most interesting of these is the pelican (the best preserved example is one of Italian origin in the Deutsches Museum at Munich, while there is a damaged specimen in the Germanic Museum at Nuremberg). Double circulating vessels consisted of pairs of retorts or alembics with heads fused on, the delivery tube of each opening into the tubes of the other. Tapering vessels with an opening at the side are characteristic of this period (originals in the Munich and Nuremberg museums).

One of the most important is the so-called "Moor's head" distillation apparatus. One of these illustrated in Brunschwyk's book shows the whole distillation head immersed in the cooling water, but in most cases the cooling vessel only surrounds the distillation head, rather like a turban. The liquid to be distilled was pre-heated, and the cooling water was renewed when it became warm, and probably ran continuously when possible. The same points are shown by

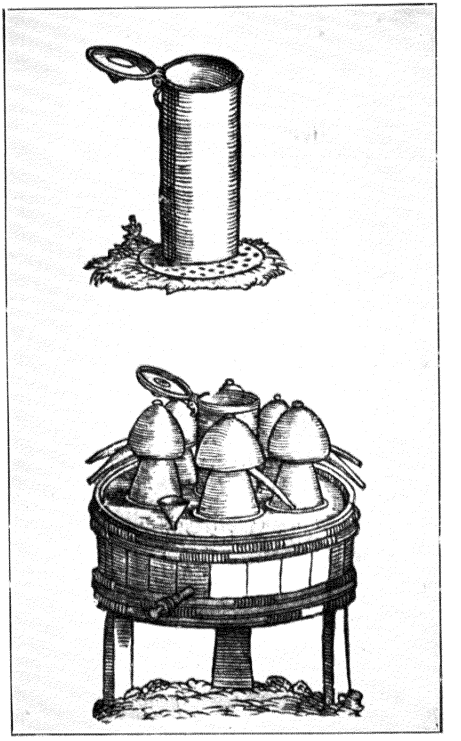


PLATE 81

Balneum Mariæ.

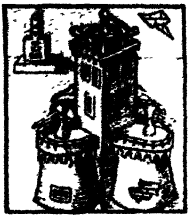
With arrangement for fuelling.
From the distilling book of Gualtherius Ryff, Frankfurt, sixteenth century.

Franc. Calciolaio (about 1550), Cl. Dariot (1553–1594) and a "Moor's head" with spiral condenser is shown by Donato d'Eremita (1624) and Ferrara (1625). The fractionating effect of the distillation head does not of course exclude the condensing action of the spiral condenser.

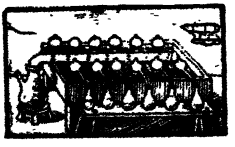
Complete utilisation of the material being extracted was often ensured by cohobation, i.e. the distillate was allowed to run back on to the material. Repeated redistillation of the distillate served to purify or refine it. This gradually became unnecessary as distillation apparatus with a rectifying action was introduced. Lonicer (1573) shows an apparatus with a second flask inserted between the distilling vessel and the condenser, but it is uncertain whether this had any rectifying effect. This was, however, certainly the case with the arrangements illustrated by Euonymus Philiatrus (K. Gesner), and still more those of Libavius (1606). Apparatuses effecting a fractional distillation into two or more receivers are given by Ryff (middle of the sixteenth century), Libavius, Porta (1609) and Donato d'Eremita. Distillation in steam with a separate vessel for generating the steam is described by Lonicer, Dariot, and others.



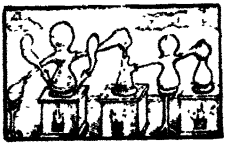
1. Balneum Mariæ.



2. Athanor with side stoves: Biringuccio.



3. Dung bath and steam-bath: Biringuccio.



4. Complicated apparatus for distilling and rectifying.

The apparatus illustrated here is one of the earliest apparatuses for rectification.

PLATE 82

Chemical apparatus from Euonymus Philiatrus, 1525; i.e. Konrad Gesner (1516–1565).

We have already referred to the continuously burning stove with a tower for replenishing the fuel, and a similar stove is illustrated by Leonardo da Vinci, 1500. Interest attaches to an apparatus of Brunschwyk for water-bath distillation on a large scale, in which a large wooden vessel is heated by means of a copper dome let into it.

O. Ryff (middle of the sixteenth century) describes simpler but obviously practical apparatuses, e.g. dibikos (distillation head with two delivery tubes), spiral condensers, and wooden water-baths with metal let in for heating.

Illustrations are often found of *large-scale distillation apparatuses* out of doors in herbal gardens. The earliest picture of a herb garden with distillation apparatus (Brunschwyk, 1500) contains only simple arrangements. Other illustrations give a very instructive picture of the preparation and treatment of fresh drugs. The stove often contained dozens of alembics of glazed pottery with glass heads. Specially fine illustrations of distillation apparatuses are

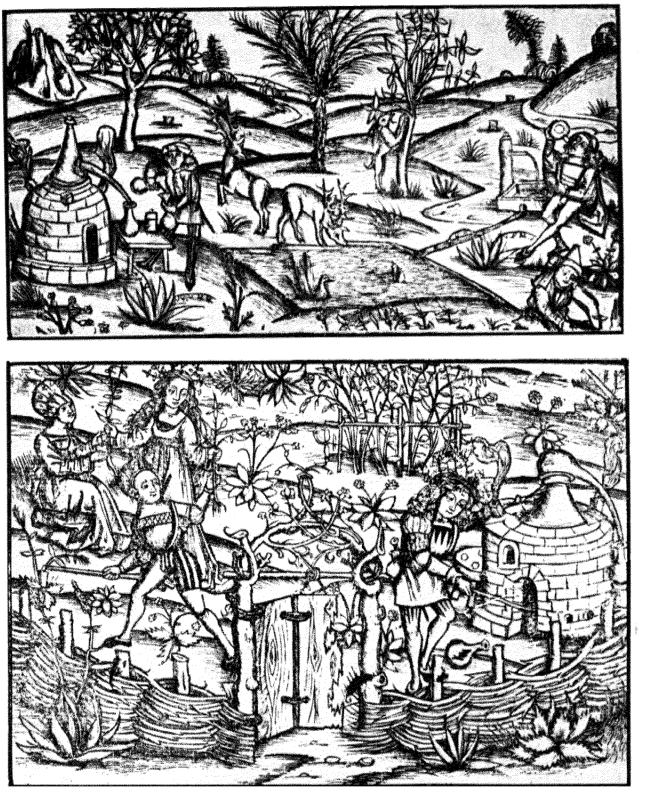


PLATE 83

The earliest picture of a herbal garden with distillation apparatus (alembic and still-head): Hieronymus Brunschwyk, about 1500.

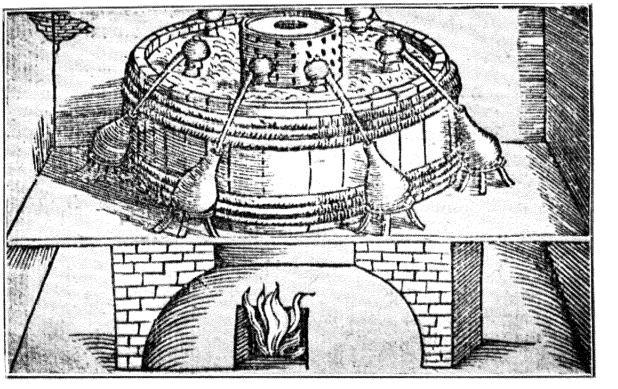


PLATE 84

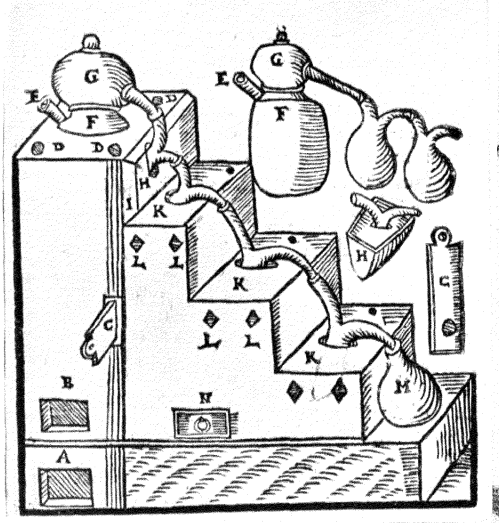
Large water-bath : Biringuccio, Pirotechnia, Venice, 1540.

The furnace which heats the water-bath is at ground level. The water-bath itself is in the first floor of a house, and is of wood with metal let in for heating.

PLATE 85

Distillation apparatus with rectification.

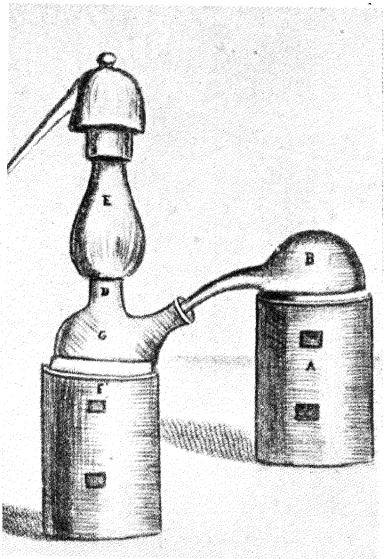
The condensate is again boiled in order to increase its percentage content.



Distillation system with redistillation and fractional condensation.

(Libavius, Alchymia, Frankfurt, 1606.)

We see the distilling vessel F, placed in direct contact with the fire. The distillate formed in the alembic G passes down through several fractional condensers K K K, which are heated by the fire by means of the adjustable smoke deflector C. According to Libau the condensate in the first receiver is of a "material" nature, while subsequent condensates are "spirituous," and the purest, most volatile product collects in the final receiver M.



Redistillation apparatus.

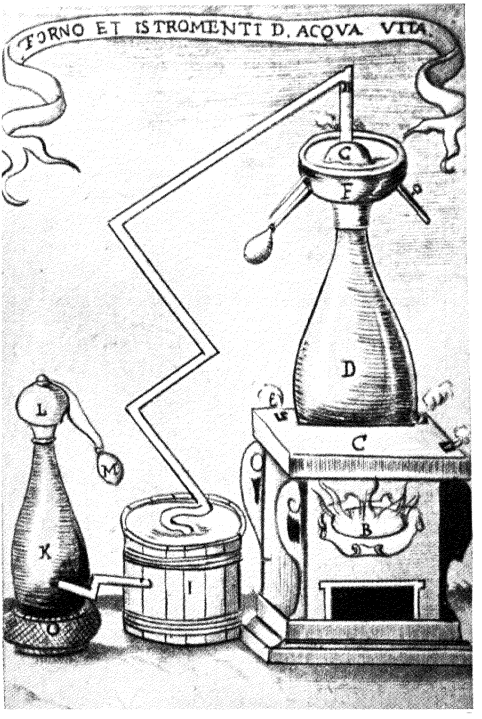
(Valentine, Triumphal Chariot of Antimony, London, 1655.)

A Furnace, B Retort, C Receiver. D Open tube of moderate width on which the alembic fits. The furnace F redistils what condenses in the receiver and the alembic E.

given by Lonicer and in the herbal of Tabernæmontus. In these cases we are dealing chiefly with the steam distillation of ethereal oils.

As in many other things, we can learn much from *Biringuccio* in the construction of apparatus. He describes distillation from bell-shaped vessels of copper tinned internally, or of glass. They had a delivery tube and rested on a suitable dish. They were used for making distilled water. According to B., the ordinary distilling flasks and heads could be made of glass, pottery or tin-plated copper. The glazed flasks for preparing nitric acid were covered with clay and could then be heated by a direct flame. B. also distilled from the water-bath, which could be a copper cauldron or a wooden vat heated from below by a piece of copper plate let into it. The dung-bath consisted of chopped straw mixed with horse-dung. It could be still better heated by passing steam through a metal pipe immersed in it. B. was also acquainted with distillation by means of a concave mirror, as were Lonicer and Libau after him.

PLATE 86



Combined air and water cooling.
Donato d'Eremita dell' Elixir Vitæ, Naples, 1624.



"Moor's head" and spiral condenser.
Ferrara, Chirurgiæ, Frankfurt, 1625.
The "Moor's head" is continuously filled.

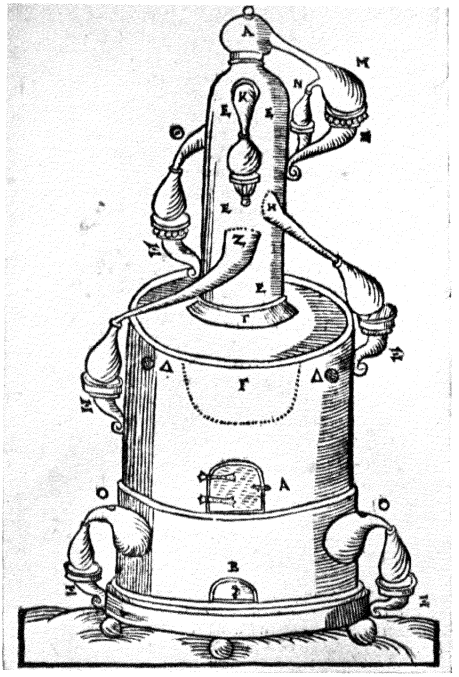
The left-hand picture shows a large boiler D, which is subjected to considerable air cooling on account of its large surface. Above this is a still-head G, surrounded by cooling water in a container F. From G a small portion of the distillate is fractionated into a small receiver on the left-hand side. The greater part passes into an air-cooled spiral, and then through the cooling vessel I, into the container K. The remaining vapour condenses in the still-head L, and is collected in the receiver M.

According to Biringuccio the best apparatus for preparing spirits of wine consists of a tinned copper boiler with a vertical tube fitted with extensions. At a height of four to six yards (!) there is a trough of copper or wood through which the tube passes spirally and is cooled. Above this there is a still-head with receiver. (Illustration from Biringuccio, German translation by O. Johannsen, p. 413.) It is not quite clear whether the extensions represent attachments for fractionation. (The preparation of spirit from grain was carried out on a large scale in 1629 in Wernigerode and other places.)

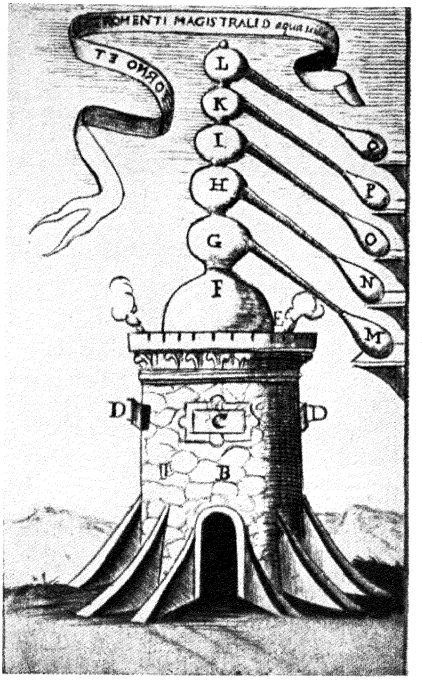
B. also describes the preparation of spirits of wine using elongated bell-shaped vessels (*per campanam*), the delivery tube passing spirally through the vessel with cooling water. One distillation was not, however, sufficient, and re-distillation had to be carried out.

PLATE 87

Distillation apparatus with fractionation.



Column for obtaining five fractions.
(Libavius, Alchymia, Frankfurt, 1606.)



Fractionating column.
(Donato d'Eremita, dell' Elixir Vitæ, Naples, 1624.)

A knowledge of fractional distillation is met with in the work of the greatest sixteenth and seventeenth century writers on distillation, and is clearly illustrated by pictures. The right-hand drawing shows a bulbous fractionating column for obtaining five fractions. The left-hand apparatus also provides the possibility of separating the distillate into five fractions of different specific weights. At the bottom of the furnace there are two small flasks for the purpose of redistillation.

According to B. less volatile distillates (oils) are better obtained by using retorts, which can be placed directly in the fire provided they are covered with clay. This method was used for oil of vitriol and resin oils. B. also burnt sulphur under an open bell-jar which served to retain the vapours: these condensed and ran out into a receiver. This process is the forerunner of the lead chamber method for obtaining sulphuric acid (cf. Biringuccio, plate LXIX, p. 418 of the German translation). Downward distillation was employed in the distillation of wood: the earthenware vessel had a sieve-like bottom, with wood shavings above it and the receiver beneath. B. carried out sublimation both upwards and downwards, using flasks of glass or glazed earthenware. If glass was coated with clay it could be heated directly in the flame without

an ash-bath. In this way he obtained corrosive sublimate, white arsenic and cinnabar. Besides the ordinary furnaces (with or without bellows), B. mentions *tower furnaces* (athanors). These had small furnaches at the side which were



PLATE 88

Various forms of distillation furnace, sixteenth century, from the herbal of Roesslin (1535 edition).

In order to provide for a large number of distillation vessels in one furnace the latter was built in several tiers (the furnace being round, square or straight), or sometimes in the form of a zig-zag or spiral staircase. They were used chiefly for obtaining ethereal oils. Each flask contained a different product, which explains the large number. According to Biringuccio these furnaces are not to be specially recommended.

used for distillation, e.g. on sand-baths. The side furnaces were fitted with adjustable flues for regulation. These tower furnaces could also be combined with drying apparatus, water-baths and dung-baths. A. Libavius and L. Ercker give many illustrations of these furnaces, with details of their construction.



PLATE 89

Chemical laboratory : Joh. Stradanus, sixteenth century.

In the centre a large water-bath with alembic. On the right a hood-shaped distillation apparatus in action, and a second not in action : also a mortar with the pestle on an elastic rod. In the right background is a press and in the left background an athanor with distillation apparatus, in front of which is a stand for filtering.



PLATE 90

Witches' kitchen : Peter Brueghel, sixteenth century.

This grotesque picture is of great interest, since the small chemical appliances are depicted very realistically, showing details which are absent from books.

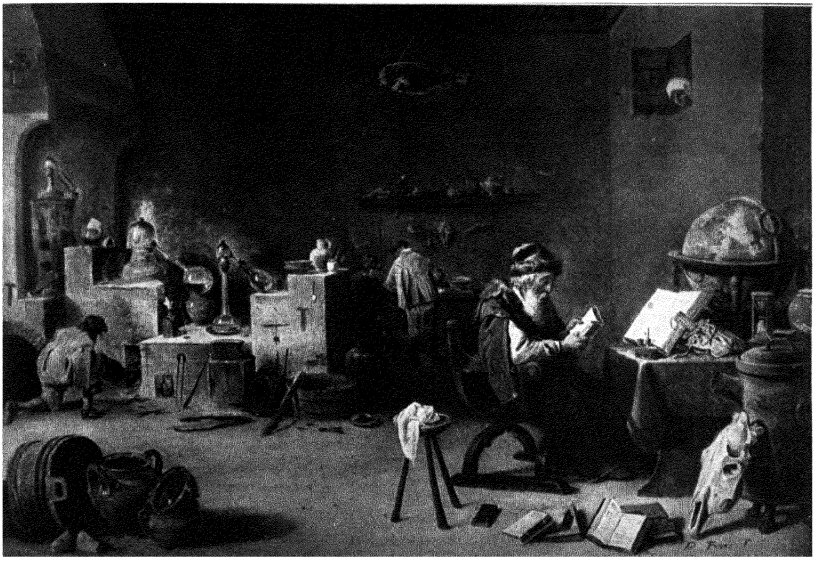


PLATE 91

Chemical laboratory, painted by D. Teniers, seventeenth century.

Fine group of furnaces with distilling vessels : still-heads of greenish glass.

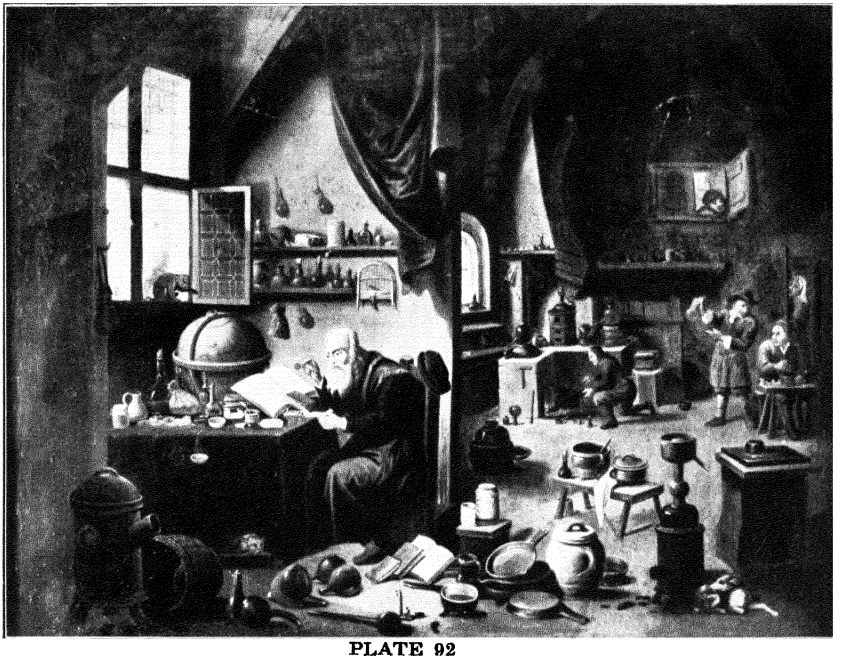


PLATE 92

Chemical laboratory, painted by D. Teniers, seventeenth century.

Fine furnace with draught-hood and various stills. In the foreground phials, still-heads, retorts, grindstone, and many other appliances.

Finally there were also tall furnaces resembling domestic stoves, in the tiles of which were inserted small glass distilling flasks with glass still-heads, often as many as six tiers above one another. They were used for the simultaneous distillation of several sorts of ethereal oils. Biringuccio does not recommend this type of furnace, since the heat is different in the different tiers. Excellent illustrations of them are given by Matthiolus and in the later editions of the Florentine pharmacopœia. Such apparatuses were actually

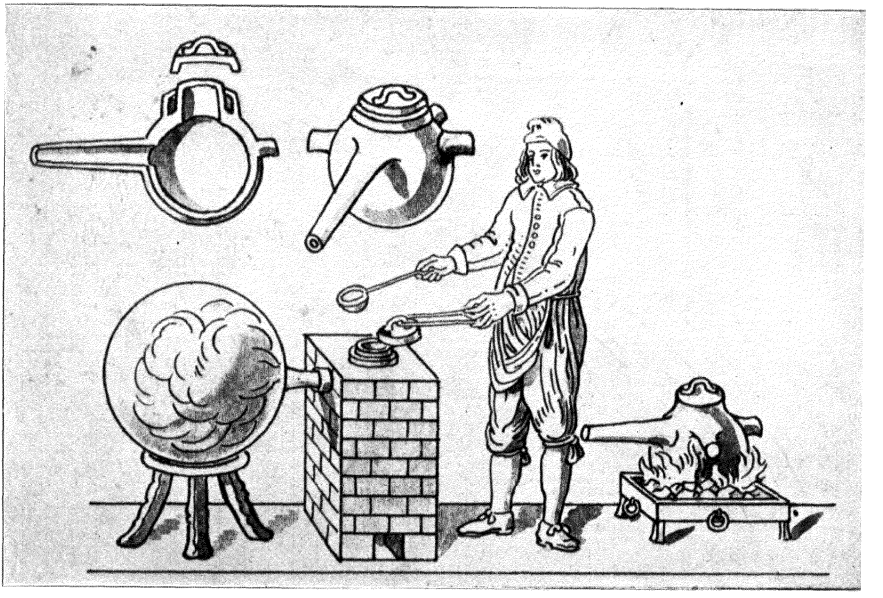


PLATE 93

Distilling furnace: Glauber.

From "Furni novi Philosophici," Amsterdam, 1648.

Furnace with an iron distilling vessel surrounded by masonry. The vessel is a retort with a lid and the receiver is of glass. At the top of the picture is a section of the still and a view from above. On the right the distilling vessel is shown standing on an open fire.

Apparatus for obtaining hydrochloric acid from common salt and sulphuric acid.

used, since they occur in contemporary pictures of an Italian pharmacy.

Ercker (1547) used retorts in an open furnace for obtaining sulphuric acid, and gives pictures of them.

The most complete review of chemical apparatus is given in the chemical treatise of Libavius, where practically all contemporary apparatus is not only mentioned but also illustrated. In this respect later authors are far inferior, even in the case of the treatises of Thénard or Berzelius. There is no corresponding book at all in modern times. Libavius classifies the apparatus into groups, e.g. digestion and circulation vessels, still-heads, flasks and retorts, crucibles and cupels, auxiliary instruments of all kinds, vessels for testing and

separating gold, an enormous variety of vessels for distillation, sublimation, deliquescence, crystallisation, separation, filtration, " destillatio per lacinias," arrangements for calcination, and furnaces of all, especially of the continuously burning type.

Among the apparatus of Rudolf Glauber, his arrangement for preparing hydrochloric acid is worthy of special note. It consists of a closed iron retort placed directly in the furnace and fitted with a large glass globe covered with water. Glauber's vessel for storing acids, using a mercury seal, is also noteworthy. He also employed mechanical stirrers.[1]

There are many fine laboratory pictures from this period, especially those by Ercker, of which a laboratory for making acids and an analytical laboratory are the most interesting subjects. The great artists have also immortalised chemical laboratories in several instances, and although these pictures usually represent alchemists' laboratories, the usual chemical equipment is portrayed.

We may mention the paintings of David Teniers the younger, at the Hague, Dresden and Braunschweig, the latter being the best from the technological point of view. There are also paintings by Adrian van Ostade in London, and by Th. Wyck in Dresden, Braunschweig and Karlsruhe. There are still further examples, Teniers in particular having produced a number of other laboratory pictures.

Finally we shall give a *general review of the apparatus and equipment of the chemist in the seventeenth century:* this review was prepared by the sage Athanasius Kircher, and shows clearly *what the chemist of this period really did, and what he worked with.*

THE EQUIPMENT OF CHEMISTS IN THE SIXTEENTH AND SEVENTEENTH CENTURIES

I. *Apparatus*

A. *Furnaces:*
- (*a*) open
  1. *Assay furnaces*
  2. Bellows furnaces
     Cementation furnaces
     Reverberatory furnaces
     Dissolving furnaces
     for upward distillation and sublimation,
     dry: *furnace with distilling flask or sand-bath*
     wet: furnace with water-bath
     for downward distillation
- (*b*) covered
  1. simple: *athanors*
  2. compound: furnace with auxiliaries.

[1] Dialysis (purification of salts using an ox-bladder) was practised as early as 1529.

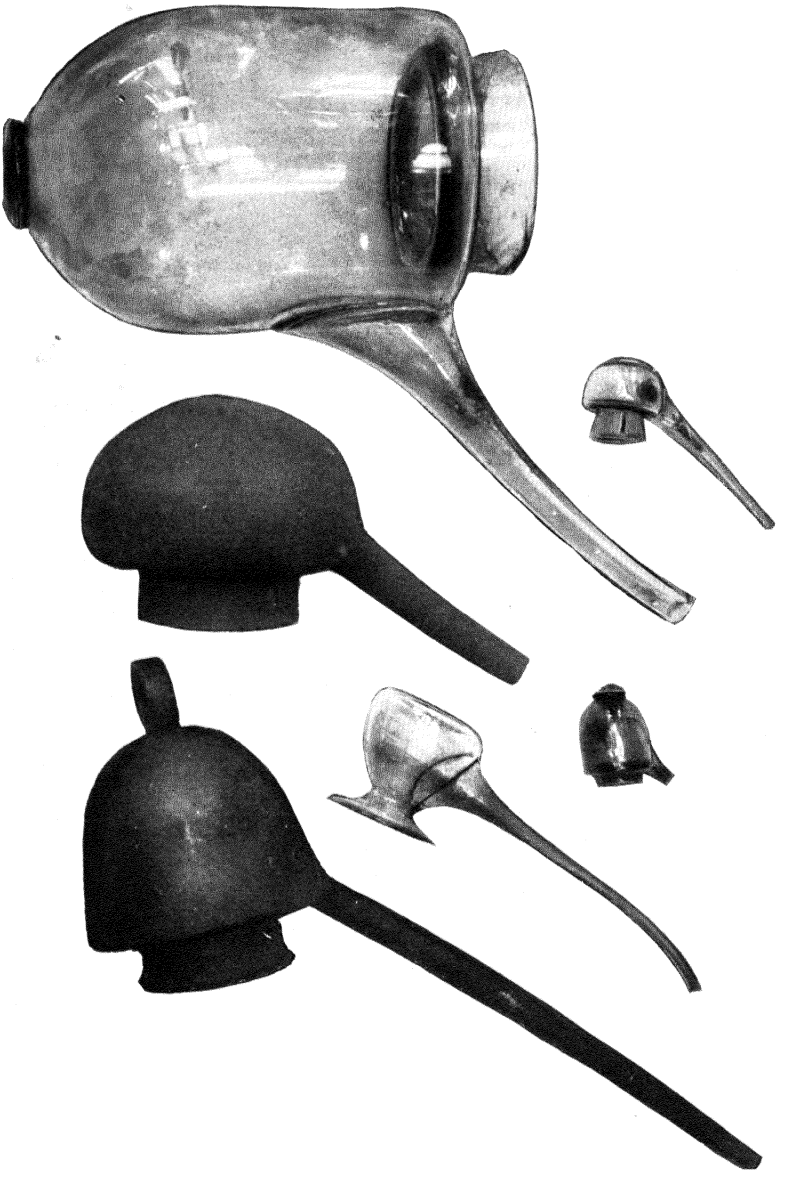


PLATE 94

Still-heads (alembics).

From the Henrici collection, Halle.

At the top a large alembic of greenish glass from the pharmacy at Halle. Below this, one of pottery from Eisenberg, and at the bottom an alembic made of tin (with ring) from Bruneck. The two small alembics of clear glass on the right are from Zwickau, and the smallest (with broken delivery tube) from Roda.

25. Forceps.
32. Sigill Hermetis: Sigillare Herm, for closing up a glass vessel by fusion. An earthenware pot with a hole in the bottom through which the neck of the vessel passes. This is surrounded by a fire until the glass becomes soft, when it is pressed together with pincers.
49. Separatorium. Separating funnel (glass).
41. Pyramis. Iron mould for casting a regulus.
17. Crucibulum. Goldsmiths' crucible made from special clay.
37. Phiolo. Phial for rectifying spirits of wine.
59. Volsella. Coal tongs.
62. Vas Cupreum Balneo Mariæ dicatum. Copper vessel for use as water-bath.
52. Syphon. Siphon of sheet metal.
54. Tegula. Earthenware muffle.
21. Excipulum. Glass receiver for use in distilling spirit.
11. Circulatorium. Circulating vessel.
14. Concha. Glass dishes.
6. Arcula. Small wooden box for keeping dry substances.
61. Vasa dicata secretioni aquarum ab oleis por Ellychnium. Vessels for separating water and oil by means of cotton. The oil is extracted from the main vessel by means of cotton wick and runs into a small flask attached to the neck of the large one.
30. Mola Chalybea. Steel mills for pulverising.
57. Tritorium. Funnel.
4. Alembicus cœcus. Closed still-head without delivery tube.
3. Alembicus. Still-head with delivery tube, for fitting on flasks.

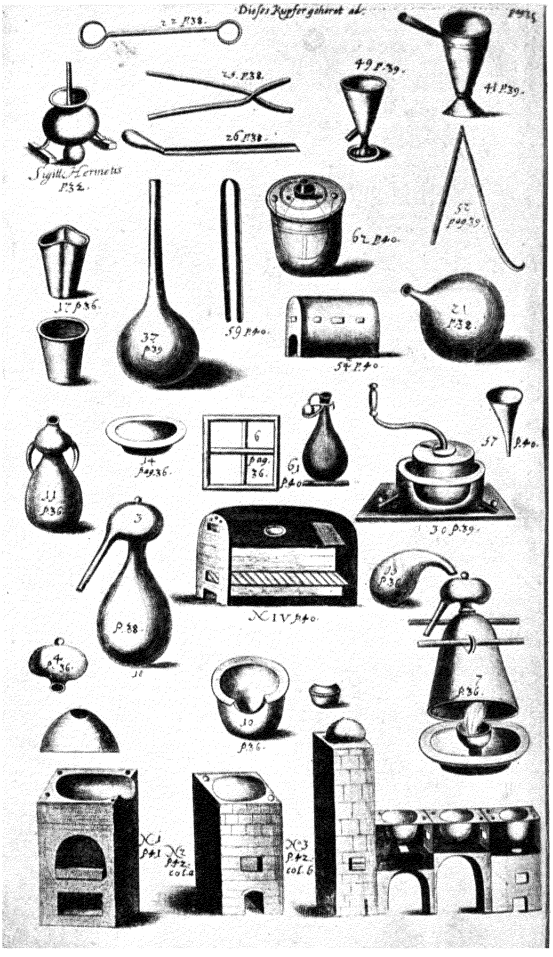


PLATE 95

Usual appliances for a pharmacist's laboratory in the seventeenth century.

From "Vollständige und Nutzreiche Apotheke," by J. Schroeder, published by Daniel Koschwitz, Nürnberg, 1693.

15. Cornuta (Retorta). Retorts of glass or good earthenware, for distilling.
10. Catinus. Cupel (suitable for either sand-bath or water-bath).
7. Campana vitrea. Glass bell-jars for preparing spiritus sulphuris (sulphuric acid).
1, 2, 3. Various kinds of furnace (assay furnaces, one with athanor).
22. Ferrum dicatum discindendis Vitris. Iron instrument for cutting glass. (The glass to be cut is surrounded by the red-hot metal ring: cold water is then applied and the glass breaks where the ring has touched it.)

B. *Vessels*

(*a*) For heating

1. Of specified material

(α) *glass*

Phials, *circulating vessels*, *pelicans*, *dyota* (double pelicans or " brothers "). *philosopher's egg*

(β) mineral, *metallic*

for refining (e.g. by dry distillation),

flasks (vesica)

boilers (ahenum)

for fusion

moulds (infundibulum)

casting-cone (pyramis)

earthenware

containing the material itself

for fusion

ash cupels

crucibles (crucibulum)

not for fusion

cementation box

containing another vessel

sand-bath

muffle (tegula)

2. Of any material,

alembic with delivery tube

closed alembic

flasks (cucurbita)

retorts

(*b*) Not for heating

1. Storage vessels

receivers (receptaculum)

dishes (concha)

2. vessels for transferring

funnels (tritorium)

separating funnels (separatorium).

II. *Accessories*

A. Instruments

(*a*) for use in the fire

1. necessary

poker, *coal shovel*

2. optional

spatula, *tongs*, *ladle*, *glass-cutter*

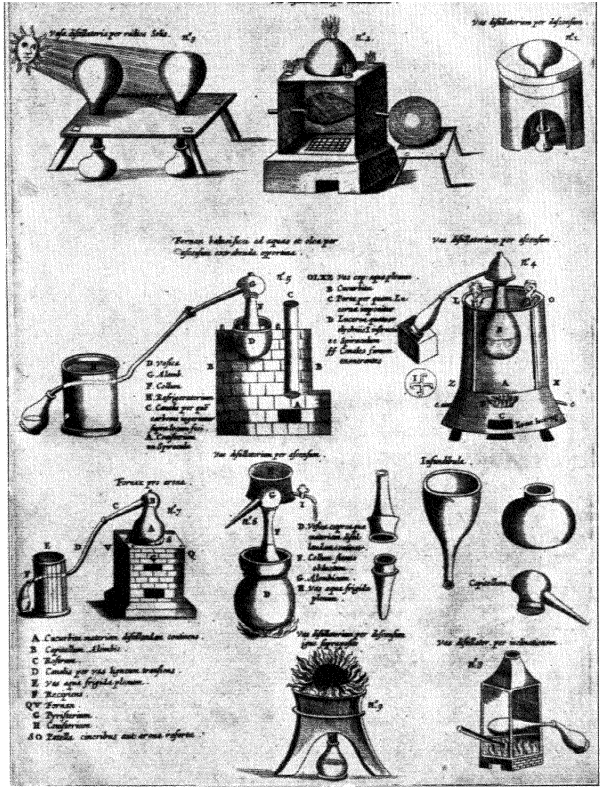


PLATE 96

Distilling vessels with various sources of heat, water-baths and sand-baths.
Upward, downward and lateral distillation.
Athanasius Kircher, 1665.

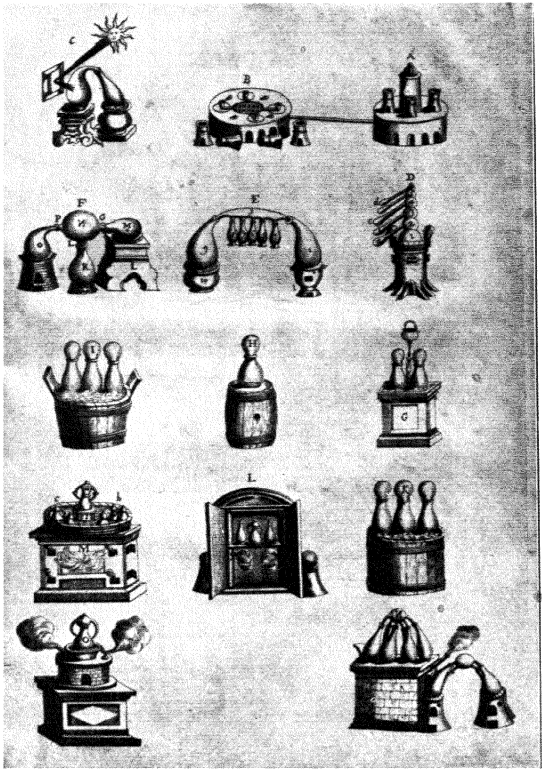


PLATE 97

Chemical apparatus *Athanasius Kircher* (1662).

A, B Athanors. C Distillation by means of a concave mirror. D, E, F Stills with fractionation. G, H, I, K, M, N, O Digestion and circulation vessels. L Steam oven.

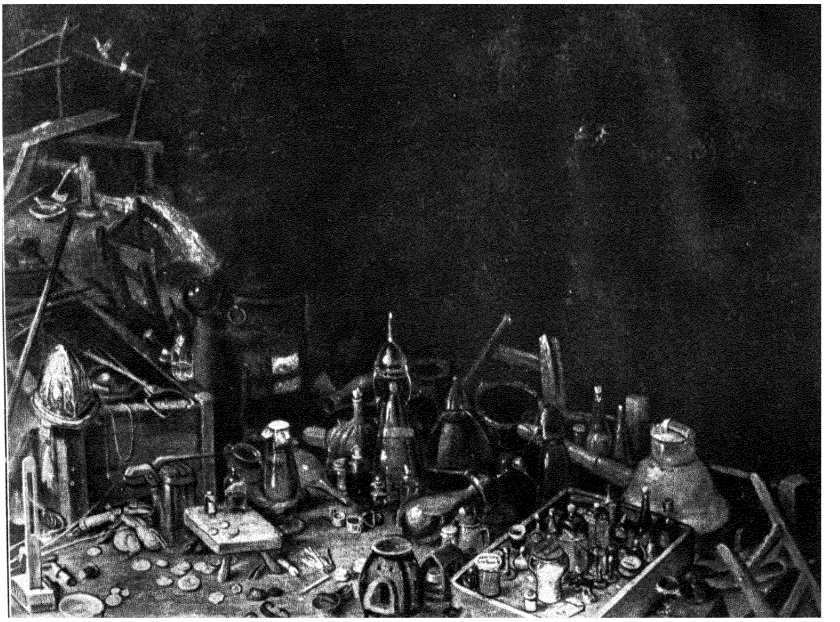


PLATE 98

Equipment of an unknown seventeenth-century chemist.

The value of this picture lies in the fact that even small and unimportant details are faithfully reproduced. In this way facts emerge which are not thought worthy of mention in treatises on the subject. Among the more important objects illustrated are stills, smelting furnaces, muffle, circulating vessel, "Moor's head," alembic, scales, vessels for preparations, with characteristic stoppers, spills and tinder box.

(*b*) not for use in the fire
wooden,
Dyoptra (for protecting the eyes from bright objects)
metallic,
testing foil, mortar.

B. *Sources of heat*
(*a*) natural
rays of the sun
(*b*) artificial
for digesting (moderate)
athanor, dung-bath
for separating (stronger)
distillation, ash-bath
strong, indirect
sand-bath, bath of iron filings
strong, direct
coal fire, flames.

The Operations of Chemists in the Sixteenth and Seventeenth Centuries

A. *Chemical liberation (solution)*

I. *Calcination* (involving decomposition, later sometimes termed oxidation)
- (*a*) *Corrosion*
  1. *by vapours*, of acids
  2. *by immersion*, pouring, filling up
     - in the wet way
       - *amalgamation*, *precipitation*
     - in the dry way
       - *cementation*
- (*b*) *Ignition*
  1. *combustion* and *vitrification*
  2. *reverberation* and *incineration*

II. *Dissolution*
- (*a*) *Sublimation*
  1. by operations of short duration
  - (α) *elevation*
    - in the dry way
      - *sublimation*
    - in the wet way
      - *distillation* upwards with alembic or flask
        sideways with retorts
  - (β) *descension*
    - hot
      - *downward distillation*
    - cold
      - *draining*
  2. by operations of long duration
  - (α) *exaltation* (improvement)
    - *circulation* (in a pelican or closed alembic)
    - *ablution*, by *deliquescence* (deliquium) or *filtration*
  - (β) *digestion*
    - *putrefaction* (fermentation), *extraction*
- (*b*) *Liquefaction*
  1. *single*
  2. analytical
     - *cupel test*, *antimony test*

B. *Chemical coagulation*

I. by *heat*

II. in the cold
- (*a*) *crystallisation*
- (*b*) *separation from melts*.

For comparison we shall now give a third table, in which the operations of a chemist of this period are represented somewhat differently, an attempt being made to classify them, especially as regards the changes of state involved. It is almost to be wished that a modern chemist would attempt a similar classification.

The chemist of 1700 *prepared :—*

I. *Liquids from solids :*

(*a*) by solution

1. with liquid solvents, in the wet way



PLATE 99

Silver loving-cup.

Beginning of the eighteenth century. From the Castle Museum, Berlin. Showing a view of a laboratory.

2. by fusion with salt-like or sulphurous substances, in the dry way

(*b*) by extraction (partial solution)

(*c*) by amalgamation (solution and liquefaction of metals by means of mercury)

(*d*) by deliquium (deliquescence by atmospheric moisture).

II. *Solids from liquids :*
- (*a*) by coagulation
- (*b*) by evaporating solutions (inspissation, abstraction)
- (*c*) by crystallisation
- (*d*) by precipitation (by the addition of chemical substances and solutions)

III. *He split up substances* (especially into their earthy, viscid and aqueous components)
- (*a*) by digestion (maceration, warm)
- (*b*) by fermentation (which gives rise to alcoholic spirits)
- (*c*) by putrefaction (which gives rise to urinary ammoniacal spirits)
- (*d*) by distillation
  1. downwards, *per descensum*
  2. upwards, from flasks
  3. sideways, by means of retorts
- (*e*) by rectification (redistillation, cohobation)
- (*f*) by dephlegmation (separation of vapours by condensing the higher boiling fraction)

IV. *He transformed substances* in virtue of their instability to fire, and he changed their stability to fire :—
- (*a*) by sublimation, giving
  1. fine powders (flowers)
  2. solid masses (sublimates)
- (*b*) by volatilisation
- (*c*) by fixation (partial or total removal of volatility)

V. *He changed the continuity* (*homogeneity*), and in the case of metals the metallic character (e.g. ductility) :—

(α) *Continuity was removed*
- (*a*) by calcination (later termed oxidation)
  1. by heating in a flame (reverberation)
  2. by detonation with saltpetre
  3. by heating with salts and sulphurous substances (cementation ; also corrosion of metals by sulphur, arsenic, salts, etc.)
- (*b*) by vitrefaction and by cupellation (melting a noble metal alloy with lead in a cupel)

(β) *Continuity was restored*
- (*a*) by reduction (recovery of metals from their calxes, also the reconversion to their original state of other burnt substances)

(*b*) by revivifaction (in the case of mercury this word was used in place of reduction).

The attentive reader will find much valuable knowledge in the above table.[1]

[1] The system of weights used was still that of the ancients. A pound contained 12 ounces, 24 lots, 96 drachms, 288 scruples, 576 obolus, 5,560 grains.

The Nurnberg pound in 1555 was 357·66 grams, and the ounce was 29·8 grams, while the Venetian pound was 301·25 grams.

The Roman measures of volume were also used.



PLATE 100

From "Dispensatorium Pharmaceuticum Austriaco-Viennense," Vienna, 1770.

THE FOUNDERS OF SCIENTIFIC CHEMISTRY

From the Middle of the Seventeenth to the End of the Eighteenth Century

THE chief characteristic of this period is that the scientific chemist acquired and retained a greater importance than the purely practical worker. It is therefore necessary in the first instance to consider theoretical chemistry.

We must first consider new ideas about elements, which are largely associated with the name of *Robert Boyle* (1627–1691). Boyle's views on the element concept are dealt with thoroughly in his work, *The Sceptical Chymist*, 1661. It should however be noted that Boyle's ideas never reached the clarity later attained by Lavoisier. According to E. and M. Fürber, Boyle's most important contribution lies not in his ideas on elements, but in the methods he employed in seeking for the "unchangeable constituents" of substances. Since in the opinion of many, Boyle's work prepared the way for Lavoisier's conception of elements, the subject is one of great importance. Boyle attacked the alchemist's elements: sulphur, salt, mercury; and also the Aristotelian elements water and earth. Boyle states:[1] "When a chemist analyses a substance by means of fire, the great analyst, then if he obtains a substance which will burn and absorbs no water, it is called 'sulphur.' If it tastes and is soluble in water, it is 'salt.' Anything solid and insoluble in water is 'earth.' Any volatile substance is described as 'mercury.' These volatile substances, often also termed 'spirits,' must thus be classed as mercury, while distilled oils which are greasy and insoluble in water are termed sulphur. Spirits of wine are however also classed as sulphur, though they do not

[1] Boyle did not consider fire (i.e. heat) to be a universal analysing agent, although in actual fact it is if we include temperatures much greater than those which Boyle was able to reach.

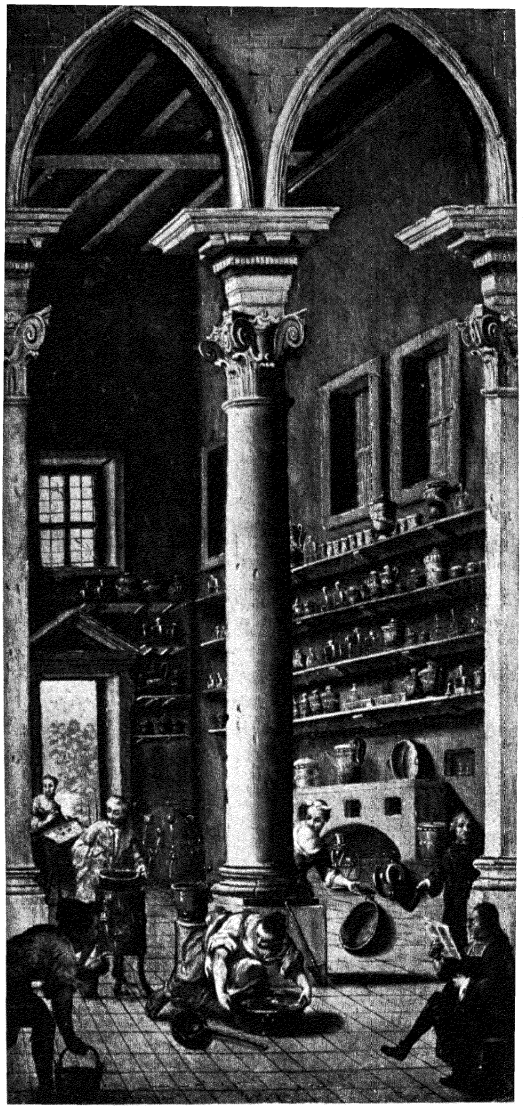


PLATE 101

Interior of an Italian pharmacy (eighteenth century).

Oil painting by Giuseppe Zais, Dörr Collection, Stuttgart.

In the background an interesting distilling furnace (circular furnace with a large number of alembics).

possess the latter properties and might therefore be better described as mercury."

It will be seen that Boyle is well versed in old views about elements. However, he does injustice to the scientists of antiquity, at least the more enlightened ones. Although many chemists (in particular most of the alchemists) may have taken the words "mercury, sulphur, salt, water and earth" in a literal and material sense, this was not true of the genuine natural philosophers. Boyle quotes a sentence from Beguin, the excellent French investigator and doctor, which shows clearly that "mercury" is not an element in Boyle's sense of the word. Boyle must also have known the view of the Aristotelians that their elements (water and earth) were actually compound substances, and the same is true of "mercury," "sulphur" and "salt." The ancients did not connect the concept of elements closely with the view that elements were not themselves complex substances. Boyle's misunderstanding can only be attributed to the materialistic views of the alchemists, since (as we have previously shown) the original concept of elements was in no way related to the view that they could not be split up. All books on historical chemistry since the time of Boyle have misrepresented this point, and even present-day chemists are loth to

accept the facts of the matter, in spite of the fact that the disintegration of elements is now well recognised!

According to Boyle a substance is an element only if it is completely homogeneous. Since the time of Lavoisier the world of chemistry has been under this spell, and not until the twentieth century was it shown that such homogeneous substances do not exist at all. Natural philosophers of all periods have been doubtful about such a possibility, holding that the concept of an element as something homogeneous and indivisible was a fantastic idealisation.



PLATE 102

Johann Joachim Becher, born at Speyer, 1635; died in England, 1680.

Since Boyle moved in circles of materialistic thinkers, it is clear that he will have regarded gold (for example) as an element, since he was unable to destroy it. He did not, however, always express himself as clearly as this, and later again rejected these materialistic principles; thus he gives as the true elements of the world the trinity: matter, motion and rest. According to Boyle all properties such as colour, smell, taste, state of aggregation could be ultimately referred to these three principles. In this Boyle shows himself as a true scientist. If we improve his three principles by omitting "rest" and allowing that matter is one of the manifestations of energy, and can therefore also be omitted, then we come very near to the most modern views on the subject. However, these words of Boyle's were uttered at too early a date to have an appreciable effect on later developments.

In general the succeeding period (especially after Lavoisier) deals with purely materialistic ideas, at first chiefly expressed in terms of the phlogiston theory. This theory was not far removed from Boyle's views. Thus he states that sulphur is composed of "spiritus vitrioli" and a combustible essence; this is in the exact spirit of the phlogiston theory.

After these theoretical considerations we must deal briefly with the actual practical contributions of chemists of Boyle's period. J. J. Becher (1615–1682) has attempted to give a summary of the substances known, but owing to his deficient knowledge the result is unsatisfactory. He classifies the substances as follows :—

Mineral (mostly ores). *Metals*, in which he counts only the seven earliest known, and not antimony, bismuth and zinc. These last three are described

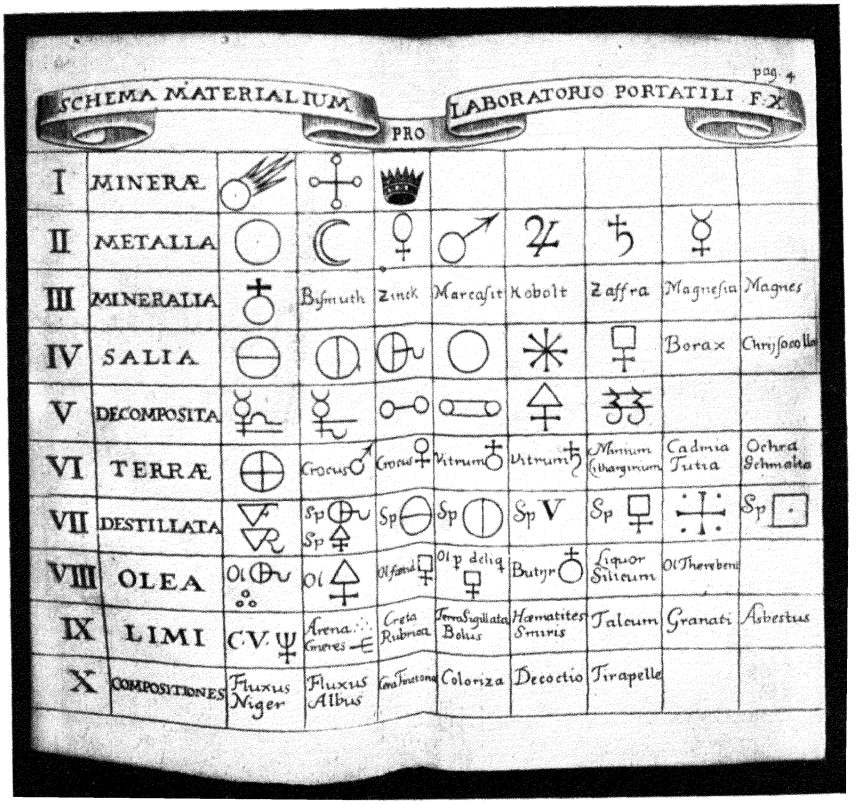


PLATE 103

Table from J. J. Becher's "Opuscula chymica."

as *mineralia*, most of which are ores. The other classes are *salia* (salts), *decomposita* (a collection of all possible inorganic materials), *terræ* (mostly oxides), *destillata* (mineral acids, also ammonia and spirits of wine), *olea* (various substances, including oil of vitriol, water-glass and turpentine), *limi* (various minerals), *compositiones* (secret preparations). Only the sections *salia* and *terræ* are at all reasonable, the remainder being confused and useless.



PLATE 104

The equipment of J. J. Becher's portable laboratory, from his work "Tripus hermeticus," 1680.

Very much better is Becher's illustrated catalogue to his "*Laboratorium portatile*," where he describes in words and pictures the equipment necessary for the chemist. Since the list and the illustrations are reproduced here, no further description is necessary. Historically it is of interest to note the mention of a laboratory overall, tobacco, tobacco pipes and theriak (as a poison antidote). It may also be noted that he prescribes three balances (one of them a sensitive analytical balance in a glass case), thus again disproving the view that balances were not used before the time of Lavoisier.

Schema instrumentorum laboratorio portatili inserventium

(see Plate 104)

From *Tripus hermeticus* (1680) by Johann Joachim Becher (1635–1682)

1. Muffle (Fornix probatorius).
2. Cupels (Capella, Testa, Cineritium).
3. Porcelain or glass dish (Patella figulina vitrificatoria).
4. Catinus (Pro candefacienda calce auri vel argenti).
5. Catinus probatorius (Cum fluxu nigro præsertim pro cupro).
6. Crucible with lid and stand (Crucibulum cum operculo et predestallo).
7. Cementation crucible (Pyxis cæmentatoria).
8. Conical mould (Cornus pro fundendo Regulo Antimonii).
9. Mould (Infundibulum pro lingonibus).
10. Mould (Infundibulum pro plumbo vitrificato eiusque regulo imbuta).
11. Metal mould for forming cupels.
12. Mortar (Mortarium cum pistillo) and amalgamation mill.
13. Coal tongs (Forceps pro carbonibus).
14. Crucible tongs (Forceps pro tigillis).
15. Assaying tongs (Forceps pro granis argenti et auri).
16. Ordinary tongs (Forceps pro communi usu).
17. Iron rods for stirring (Virga ferrea pro movenda massa in crucibulis) and iron instrument for cutting glass (Ferramentum pro præscindendis vitris).
18. Iron ladle (Cochlear ferr. pro injiciendis speciebus in crucibula).
19. Iron pan (Sartago ferrea pro calcinatione Saturni et faciendis cineribus Jovis).
20. Chisel (Scalprum).
21. File (Lima).
22. Assaying brush (Scopæ ex filis orichalceis pro mundandis granis argenti remantibus in capella).
23. Hammer (Malleus).
24. Anvil (Incus).
25. Vice (Helix).
26. Tripod (Tripus pro vitris separatoriis et crucibulis).
27. Sieve (Cribrum).
28. Hare's paw (Pes leporinus pro verrendis pulveribus).
29. Eye shade (Umbraculum adversus ignem).
30. Trough (Situla lavatoria pro mineris).
31. Shears (Forfex communis).
32. Metal shears (Forfex pro laminis metallicis).
33. Bellows (Fellis).
34. Wooden box for granulation (Pyxis lignea pro granulatione).
35. Catinus (Cupreus pro calce argenti in separatione per aquam fortam).
36. Earthenware dish (Patina figulina).

37. Bucket (Catinus ligneus).
38. Cauldron (Ahenum).
39. Filtering bag (Manica Hippocratis sive Emporeticum laneum).
40. Jug (Urceus).
41. Analytical balance (Statera docimastica).
42. Gold balance (Bilanx pro ponicrando auro).
43. Ordinary balance (Bilanx civilis).
44. Parting flasks (Crucibula separatoria pro aqua forti).
45. Distilling flasks (Cucurbita pro destillatione).
46. Still-head (Alembicus).
47. Distillation receiver (Excipulum destillatorium).
48. Glass receiver.
49. Retorts (Retorta).
50. Phials (Phiola).
51. Philosopher's egg (Sublimatorium fixatorium vulgo ovum philosophorum).
52. Funnel (Filtratorium).
53. Separating funnel (Separatorium pro oleis).
54. Florence flask (Urcolus vitreus pro infusione).
55. Filtering glass (Vitrum pro filtratione).
56. Preparation glass (Vitrum pro receptione et conservatione liquorum).
57. Flat glass dishes (Patrina vitrea pro resolutione per deliquium).
58. Testing needles (Acus probatoria pro auro et argento).
59. Assaying stone (Lapis Lydius).
60. Pig's bladder (Vesica Suilla cum volumine chordæ sive filamenti).
61. Cork and wax (Suber et cera).
62. Towel and apron (Mantile et præciutorium).
63. Overall (Suparus sive Perizoma lineum).
64. Theriak, tobacco, tobacco pipes, candles, hour-glass (Theriaca Tabacus, Pipæ, Candella, Clepsydra).

This is clearly an excellent collection of the most important chemical equipment.

As regards lists of substances, that compiled by *G. Roth* (1721) is more noteworthy. Roth divides substances into *saline* (salina), including both salts themselves and salt-forming substances, *sulphureous* (sulphurea), i.e. all combustible substances, including phlogiston, and *earthy* (terræ). The last class includes not only substances unaffected by heat, but also substances which are partly volatile when heated: this constitutes the weakest point of the test. Roth subdivides these classes further, as follows:—

I. Saline Substances

A. *Alkaline:* (1) fixed (potash, soda). (2) Volatile (ammonia and ammonium salts, such as sal-ammoniac and ammonium carbonate. *Acid:*

(1) Unchanged (sulphuric acid, dilute and fuming, nitric acid, aqua regia, hydrochloric acid, also butter of antimony). (2) Sweetened by the action of spirits of wine (ether, ethyl nitrate, ethyl chloride).

B. *Salt-like:* (1) Salts in the literal sense: (*a*) fixed (common salt, sodium and potassium sulphate, saltpetre), (*b*) volatile, either partly (potassium acetate and tartrate) or completely (ammonium sulphate, ammonium succinate).

(2) Salts of the heavy metals: iron and copper vitriol, verdigris, lunar caustic, sugar of lead, gold salts, mercury salts (sublimate, precipitate, turpethum).

II. Sulphureous Substances

A. *Liquid, volatile:* (1) Distilled oils (ethereal oils, combustible oils). (2) Combustible spirits, (*a*) by simple fermentation (spirits of wine and other spirits), (*b*) by fermentation with added drugs containing ethereal oils, (*c*) extracts made with spirits of wine (perfumes and liqueurs).

B. *Less volatile, sulphureous:* (1) Essences and extracts from vegetable sources. (2) Oils obtained by pressing. (3) Solid substances (resins, solid organic substances, unfortunately also sulphur and phosphorus).

III. Earthy Substances

A. *Completely fixed* (heavy metal oxides, burnt lime, bone ash). B. *Partly volatilised by heat*, i.e. antimony and its compounds, silver chloride, lead chloride and most "precipitates" (i.e. precipitated substances insoluble in water). This is the weakest part of Roth's classification.

The Phlogiston Theory

The phlogiston theory, which flourished through the greater part of the eighteenth century, was largely founded by Georg Ernst *Stahl* (1660–1734). This theory is also fundamentally a materialistic one. It states that all combustible matter contains an invisible and imponderable substance termed phlogiston. When combustion takes place the phlogiston is given off, e.g. when copper burns to give copper oxide, phlogiston is lost from the copper. Applying Boyle's concept of elements, we should thus regard copper oxide as the element and copper as the compound. Conversely, phlogiston can be given back to the copper oxide by heating it with a substance which is readily combustible and hence contains a large supply of phlogiston, e.g. carbon. We may note how the phlogiston theory lends support to the views of the alchemists.

It should, however, also be realised that by means of the phlogiston theory it is possible to classify a large body of oxidation and reduction phenomena from a single point of view, and in this way to "explain" them. There is thus

not the slightest reason for ridiculing this theory, especially when we consider that it was supported by great men like Cavendish and Scheele. The phlogiston theory shed the first ray of light upon a mass of phenomena in a way



PLATE 105

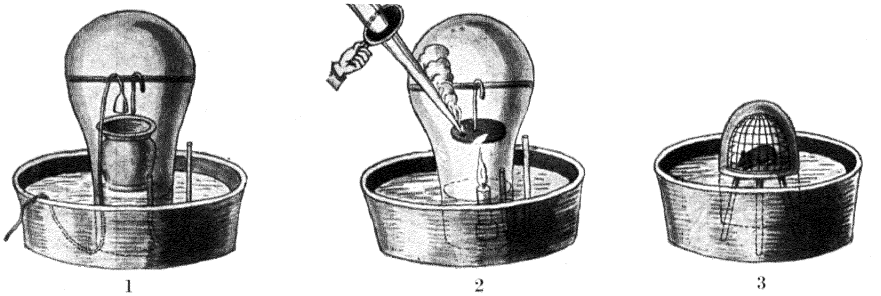
Georg Ernst Stahl, born 1660, at Anspach, became professor of medicine and chemistry at Halle, 1693, royal physician in Berlin, 1719; died in Berlin, 1734.

which Boyle was quite unable to do, and it does not therefore represent a retrograde step, but a very considerable advance on Boyle's views.

At this date it must have been known to all chemists of any importance that substances became heavier on burning. In order to explain this fact the

adherents of the phlogiston theory had resort to all kinds of wild theories and false deductions. Thus, according to Morveau (1762) phlogiston is lighter than the air in which weighing takes place, so that when phlogiston is lost the substance will become heavier (!) Gren states that phlogiston has no weight at all, but a positive " lightness " which is able to deprive the metals of a part of their weight.

The nature of oxidation and combustion and the *increase in weight* which is observed were first completely explained by Lavoisier, but he had forerunners in this respect. We have already heard of Jean Rey, van Helmont, etc. Walden also mentions (among others) Le Febure (le Fèbre), who, in 1660, observed the correct increase of weight in the combustion of antimony. Tachenius (1660–1666) did the same in the case of lead, and also J. J. Becher (1669).



1 2 3

PLATE 106

The fundamental experiments of John Mayow, 1669.

1. By dissolving iron in nitric acid in a confined quantity of air, the volume of air decreases by ¼.
2. A candle burning in a confined quantity of air is extinguished after a certain time. A piece of camphor cannot be ignited with a burning-glass in the remaining air.
3. A mouse suffocates in a confined quantity of air : the air remaining behaves as in the preceding experiment.

The most interesting of such experiments are those of *John Mayow* (1669). He explained the increase of weight by the absorption of the " nitrous constituent " of air by the metal. This is exactly right if we understand by " nitrous " any substance which gives saltpetre its oxidising power. Mayow investigated the matter by experiments with air in which a candle, a mouse, or nitric oxide produced from iron and nitric acid were confined over water in a bell-jar.

The increase in weight on combustion was also observed by Boyle. Unfortunately he gave a wrong explanation for this, which Walden has rightly described as a backward step relative to Mayow. The same is true of Lémery, Kunckel, Marggraf. It was not until Priestley discovered oxygen (1774) that the antiphlogistic system really began in April, 1774.

Lavoisier was the first to carry out a thorough and successful study of oxidation and reduction phenomena (though we may note that in 1774 the French pharmacist, Pierre Bayen, taught that the increase in weight during calcination came from the air).

In order to clear up the question finally, Lavoisier burnt numerous substances in confined volumes of air, and observed the change in weight when combustion was complete. For example, he burnt tin, mercury, sulphur,

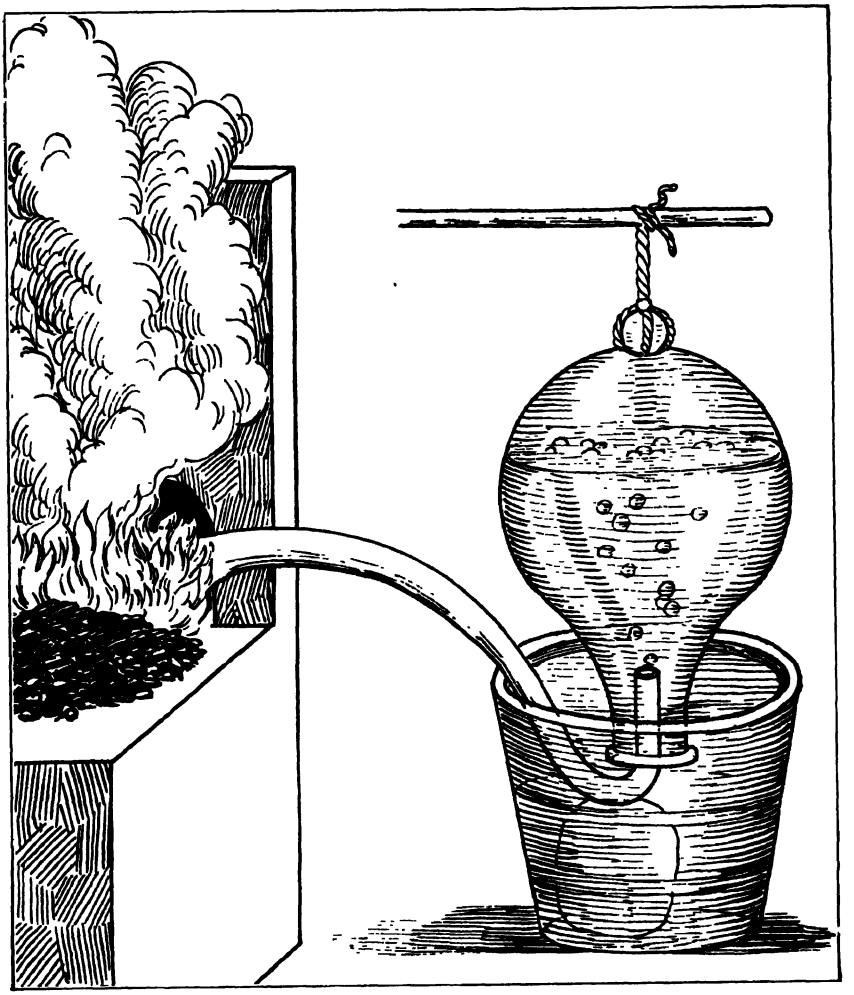


PLATE 107

Apparatus for the evolution and collection of gases: Hales.
(Displacement of water.)

phosphorus, hydrogen and carbon, including diamond. In many cases he supplemented his experiments by de-oxidation (reduction), during which he discovered the famous reduction of water by means of hot iron, and the reduction of metallic oxides by hydrogen. He established the fact that breathing

consists of the uptake of oxygen, and was the first to interpret the well-known experiments with air (Mayow, Hales, Scheele) in terms of the antiphlogistic theory. Combustions are not decompositions, but combinations, and it is the oxygen of the air which combines with the burning substance. In these experiments Lavoisier used not only the balance, but also vessels for measuring gases, and he was able to show that the increase in the weight of the substance burnt was exactly equal to the amount of oxygen absorbed.

It was also Lavoisier who cleared up Boyle's rather vague concept of elements. With the exception of " heat " and " light," his table of elements is still valid to-day. At that date it was not possible to decompose potash, soda and baryta : nevertheless, Lavoisier predicted that they could be split up,

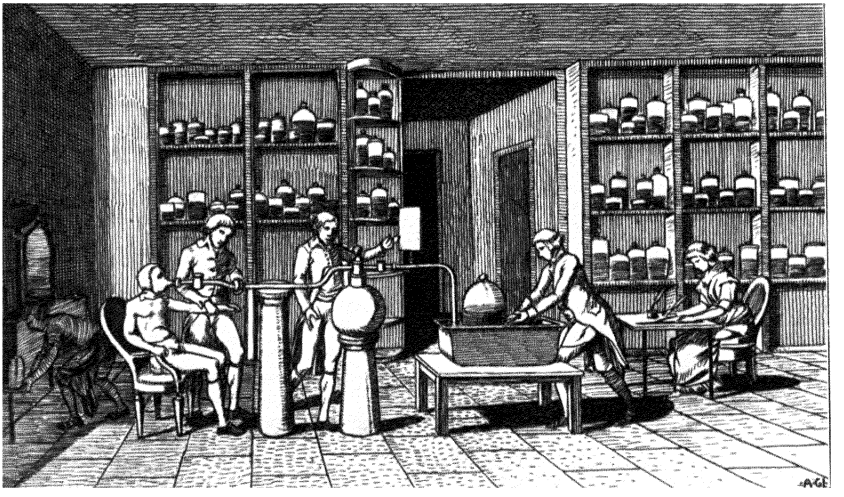


PLATE 108

Physiological experiments in Lavoisier's laboratory.

although he did not make the same prediction for lime, magnesia, alumina and silica. Otherwise the table still stands, i.e. acid-producing element (oxygen), azotic element (nitrogen), hydrogen, sulphur, phosphorus, carbon, marine acid element (chlorine was then considered to be an oxide, a mistake first rectified by Davy), fluorine, boron, antimony, arsenic, silver, bismuth, cobalt, copper, tin, iron, manganese, mercury, molybdenum, nickel, gold, platinum, lead, tungsten and zinc.

The elements are the primary substances. After them come secondary substances especially their compounds with oxygen (oxides) and the acids and bases derived from these. Then follow tertiary substances, i.e. those formed by the combination of acids and bases, mainly salts.

Lavoisier's systematic tables represent a masterpiece of the highest rank,

and in virtue of these alone he must be reckoned as one of the brightest stars in the chemical firmament. He may well be regarded as one of the founders of modern chemistry. However, there is some truth in the view that his activities may in some respects have retarded the development of chemistry. Thus Walden has rightly stated: "The antiphlogistic school of chemistry claimed only to deal exclusively with ponderable substances and the splitting up of these substances." This represents a one-sided view of the subject, although there were (and are still) many to maintain that Lavoisier's chemistry represents the final goal of the science. It must not be forgotten that it only represents chemistry regarded from a materialistic point of view, in the light

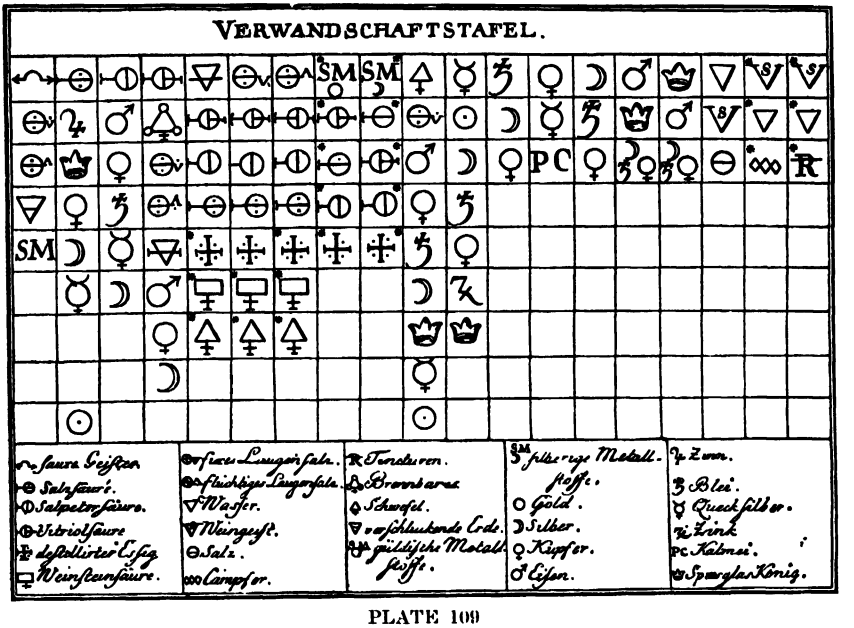


PLATE 109

Table of affinity (Geoffroy—improved by Bergmann).

Geoffroy's table of affinity was published in 1718 in the memoirs of the Paris academy. The table was arranged so that the affinity between two substances in the same vertical column decreases with increasing distance between them. This table represents one of the first attempts to throw light on chemical affinity.

of a materialistic conception of the world. In fact to-day we only regard Lavoisier's elements as specially stable configurations of a few kinds of energy centres, and the concept of elements in the sense of Boyle and Lavoisier is really completely overthrown, since it has proved quite inadequate as a strict philosophical concept. The old element concept has lasted so long merely because the relative weak energy sources available in the past were not sufficient to produce any noticeable disintegration of the elements, and because the balance is not a sufficiently delicate instrument to detect the interconversion of matter

and energy. It is probable that in the future it will be recognised that the use of the balance retarded the development of theoretical chemistry more than it promoted it.

The law of conservation of mass (which Lavoisier brought into prominence, though he did not first propose it) was really a mistake. The energetic aspect of the subject was neglected in favour of the materialistic aspect for several centuries. It is the duty of chemical historians to call attention to this unfavourable aspect of Lavoisier's work.

Chemical affinity had, of course, been recognised at a much earlier date. Glauber carried out experiments for comparing the "affinity" of acids for metals. Stahl gives a kind of displacement list. However, Geoffroy was the first to publish an affinity table (1718, in the *Proceedings of the French Academy*), embracing a large number of substances, including non-metals. The table (see Plate 109) is constructed in such a way that the affinity between two substances decreases with increasing vertical distance between them. The table can only be regarded as an attempt, but prepared the way for the more accurate affinity tables of Gellert (1750) and Bergmann (1775).

Examples of "double elective affinity" were also known from an early date, of which we may quote the following examples :—

Glauber, 1650 : common salt + lead acetate = lead chloride + sodium acetate.

Tachenius, 1660 : ferrous sulphate + potassium carbonate = potassium sulphate + ferrous carbonate.

Mayow, 1697 : potassium sulphate + calcium salts (chloride, nitrate, acetate) = calcium sulphate + potassium salts.

Black, 1754 : magnesium sulphate + potassium carbonate = magnesium carbonate + potassium sulphate : magnesium carbonate + sal-ammoniac = ammonium carbonate + magnesium chloride.

Hagen, 1768 : sodium sulphate + potassium carbonate = potassium sulphate + sodium carbonate.

The law that the reaction of two neutral salts leads to neutral substances is often said to be due to Jer. Benj. Richter, but it cannot be attributed either to him or to Wenzel, since it was a well-known fact at that time.

Knowledge of *stoichiometric relations* also advanced during this period. Boyle and Lémery used the correct quantities in their chemical experiments. Lémery gives figures for the amount of silver chloride precipitated by sodium chloride, the amount of mercury obtained from cinnabar and the amount of potassium carbonate obtained from saltpetre. According to Walden his values are so accurate that it is absurd to maintain that chemists of this period had no ability for or understanding of quantitative work.

The pharmacist Sigismund Marggraf (1709–1782) was a master of quantitative analysis, as is shown by his silver analyses. It is, however, a mistake to assume that he was the only worker of the period possessing such knowledge.

The law of constant proportions was, however, first worked out correctly by C. F. Wenzel (1740–1793). The fact that Wenzel was an adherent of the

phlogiston theory does not detract in the least from his achievements. His chief aim was the determination of combining weights (i.e. equivalent weights). According to Walden the values he obtained for some metals (expressed in terms of our modern system) are Cu 61, Fe 55·25, Zn 65·5 (instead of Cu 63·57, Fe 55·84, Zn 65·37), which values are astonishingly accurate.

The equivalent (or atomic) weight of sulphur was found with great accuracy by analysing its compounds with copper, iron, lead and silver. Instead of 32, Wenzel obtained the values 32·6, 31·3, 31·5, 31·9. The equivalent weights of lead and silver were also determined with considerable accuracy. His analyses of metallic oxides reached a high degree of precision. He also established the correct proportions in the *formation of neutral salts from acids and bases*.

Attempts to determine these last equivalents had been made previously by Homberg (1699) and Plumer (1729). Thus Plumer neutralised potash with hydrochloric, nitric, sulphuric and acetic acids.

It was, however, Wenzel's thorough experiments which anticipated Richter's neutralisation law, i.e. if one and the same quantity of an acid is neutralised by different amounts of several bases, then these amounts of the bases concerned are equivalent, and will require equal amounts of another acid for their neutralisation.

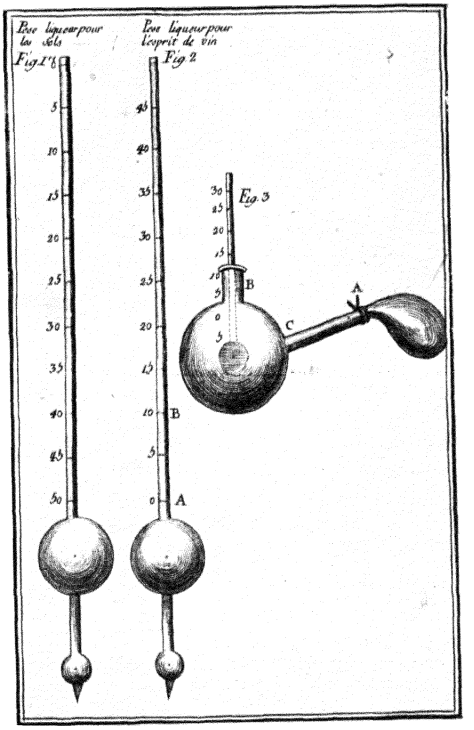


PLATE 110

Ant. Baumé's hydrometer. (Eléments de Pharmacie, 1768.)
For salt solutions and alcoholic mixtures.

The general content of the law of constant proportions was first stated clearly in words by Joseph Louis *Proust* (1754–1826), though he would probably not have been able to do so without the analytical work of Wenzel.

The law states that when substances unite to form compounds they do so in definite and fixed proportions, and that in chemical decompositions definite and fixed weights of the decomposition products are formed. At first this law was regarded with much suspicion, since there are many borderline cases in which it is difficult to distinguish between mixtures and compounds.

Thus Proust had for several years (1799–1805) a verbal duel with no less

a man than Berthollet. Proust won. Berthollet's point was that the quantitative course of a reaction is often affected by other factors, such as the time



PLATE 111

Apparatus for evolving and collecting gases (*Stephen Hales*, 1727).

The beginnings of chemical apparatus for working with gases are to be found in the apparatus for preparing and collecting gases devised by Stephen Heles (1677–1761). Hales was the first to collect gases in a vessel filled with water and inverted over water. The apparatus for collecting the gas could be separated from the evolution apparatus.

Apparatus for finding the quantity of gas given off on heating a substance.
r Small retort. *a*, *b* Glass vessels with a large hole at the bottom. At *a* they are luted together with a cement of clay, some meal and hair. The bulb is supported by small pieces of wood. *y*, *z* Siphon-like tube. (The receiver was immersed in water and the gas emerged through the siphon. The siphon was then removed so that the water maintained the level *a*.) *x*, *x* Trough.

Apparatus for gas evolution.
b Glass flask with the substance for evolving the gas. *a*, *y* Glass cylinder. *z x* Trough.

Measurement of the air consumed by the combustion of candles, or of sulphur and saltpetre : or by the breathing of animals.
x x Trough containing a candlestick. *z z*, *a a* Glass bell-jar. The air is removed from the bell-jar as far as *z z* by a siphon, using either bellows or suction by the mouth. Phosphorus or paper impregnated with saltpetre can be ignited under the bell-jar by a burning glass.

Apparatus for evolving and collecting gases.
r r Retort made out of a musket barrel, with a siphon-shaped leaden tube fixed into it. *x x* Water trough. *a b* Receiver.

and the state and amount of the substances. Like many other chemists, he could not at first understand that the law of constant proportions is not affected by these considerations, since the amounts of the substances which finally combine are always in a fixed proportion, independent of whether the amounts are large or small.

Our general considerations can now be extended to include *physical chemistry*.

The following *physico-chemical observations* are worthy of note in the eighteenth century :—

Réamur knew of the *volume change* accompanying the mixing of two liquids, and Geoffroy observed the *heat evolution* in the same process. The dependence of solubility on temperature was recognised by Eiler, Spielmann and Lomonossow.

Gases were weighed and measured by Joseph Black, 1755. The first expert in gas chemistry was H. Cavendish. Black worked chiefly with carbon dioxide, and Cavendish with carbon dioxide and hydrogen.

After Thölde (1603), *hydrometers* were specially used in chemistry by Giles Persone (1663), Fahrenheit (1724) and Baumé (1768). The pycnometer was used by Homberg (1699). Hydrostatic weighing was employed by J. Fr. Brander (1771).

It appears that the first to use the *thermometer* in chemical work was the Frenchman, Le Febure (le Fèbre), 1660. Boyle used it extensively. His boiling-point values for spirit, water, nitric acid, sulphuric acid and caustic soda are in some cases excellent. The thermometer was very frequently used by Boerhaave, Joseph Black and Lavoisier. Dutrône (1786) measured the sugar content of solutions by determining their boiling point.

Electrochemistry also had its beginnings in the eighteenth century. Cavendish used an electric spark in 1783 to explode a mixture of hydrogen and oxygen in a eudiometer. In 1787 he prepared nitric acid from air by means of an electric spark. In 1784 Berthollet decomposed ammonia gas in the same way and thus analysed it.

In 1789 Deimann and Paets van Troostwyk decomposed water by means of frictional electricity. Somewhat later, in 1799, the great Alessandro Volta discovered galvanic electricity and made the voltaic cell. This could be used for numerous electrochemical experiments, which were, however, mostly later than 1800.[1]

Catalytic phenomena were involved in the preparation of chamber sulphuric acid and of ether (after 1540), and also in the preparation of ethylene from alcohol (Priestley, 1783 ; Deimann, 1795).

One of the chief features of chemistry in this period was the foundation and development of the *chemistry of gases*, although some steps in this direction had already been taken by van Helmont. The most important experiments are those of *J. Mayow* in 1669, which we have already mentioned. A candle

[1] The electric gas discharge lamp (mercury in a vacuum) was discovered by Christian Winkler in 1742 (though Hauksbee in 1705 had observed the luminescence of an evacuated glass globe).

burning in a bell-jar sealed by water causes the water to rise and is eventually extinguished. When this has taken place, a piece of camphor in the bell-jar can no longer be ignited by means of a burning glass. This experiment really serves to *characterise nitrogen*, and precedes the clumsier experiments of Rutherford in 1772, which showed that a flame was no longer able to burn in air in which a mouse had suffocated. (This experiment was in any case also made by Mayow.) Finally Mayow prepared nitric oxide under a bell-jar by

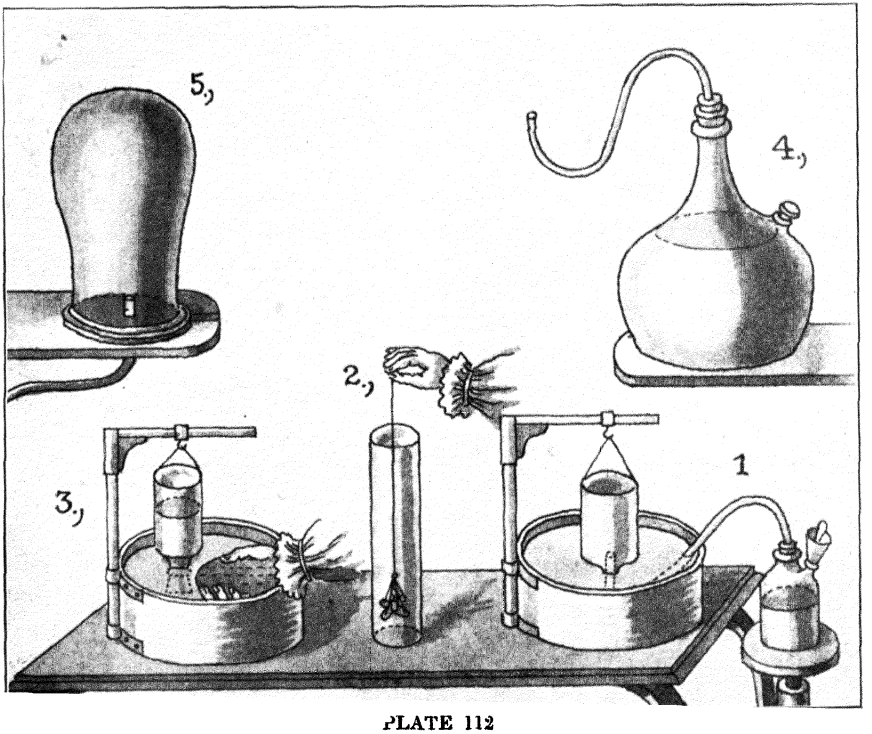


PLATE 112

Apparatus from T. Bergmann, 1752.

1. Preparation of carbon dioxide from calc-spar and sulphuric acid.
2. A candle extinguished in carbon dioxide.
3. A flask being filled with carbon dioxide.
4. Flask for evolving carbon dioxide from yeast and sugar.
5. Vessel for observing the effect of carbon dioxide on living things.

the action of iron on nitric acid, and found that the water rose in the bell-jar owing to the combination of the nitric oxide with the oxygen present. At this time *a convenient apparatus for the evolution and collection of gases* was not known, and it was the Englishman, *Stephen Hales* (1677–1761) who first discovered the well-known method of the displacement of water in 1727. In the simplest form of apparatus the evolution flask stands in the water trough, and is surmounted by an inverted gas-jar filled with water. In a more convenient form

the gas evolution vessel is separated from the collecting vessel, and only the end of the delivery tube passes under the receiver filled with water. Hales repeated Mayow's experiments, and also burnt sulphur and phosphorus under bell-jars.

Hales' apparatus was modified in many ways, e.g. by *T. Bergmann* (1735–1784), to whom are probably due the experiments with carbon dioxide which are now carried out in every schoolroom. He prepared carbon dioxide by the action of sulphuric acid on calcite,[1] and also by fermentation with yeast. The further manipulation of the gas was done with pigs' bladders. An apparatus for expelling and collecting dissolved gases from mineral waters is specially noteworthy. Hales also prepared artificial aerated water. He used measuring cylinders for gases. Similar arrangements were used by *H. Cavendish* (preparation of carbon dioxide, manipulation by bladders, preparation of bicarbonates). Among his most important contributions is the eudiometer, consisting of a graduated tube with two wires fused in for allowing an electric discharge to act on the confined gases. (This method was probably first used by Watson and by Nollet.) He also knew arrangements for weighing gases.

Hales' apparatus could not be used for collecting and observing gases which are appreciably soluble in water. This defect was first remedied by *Joseph Priestley* (1733–1804), who used mercury in place of water for collecting the gas. This alteration made it possible to extend investigations to gases soluble in water, and the technique introduced by Priestley has not been improved upon to the present day.

Many of the permanently valid principles of *analytical chemistry* were also discovered in this period.

Analysis in the dry way was already well established, and was still further improved. This is illustrated by the book, *Elementa Artis Docimasticæ* (1744), by the skilled analyst Johann Andreas Cramer, which contains detailed illustrations of all the apparatus used. We again find assay furnaces, crucibles, muffles, cupels, moulds, parting flasks, cementation boxes, etc., but in addition to these use was made of the blow-pipe; this had been used in metallurgy and was probably introduced into chemistry by Andreas von Swab (and later by Cronstedt, Henckel, etc.). The illustration of Engeström's pocket laboratory (1774: Plate 113) gives a good idea of this field. It contains blow-pipes with wind reservoir, hammer, anvil with ring, wax candle with holder, forceps, hardness tester, magnet, file, washing trough, testing flasks, silver and golden spoons, carbon, and small bottles for holding the dry reagents then used (soda, borax and microcosmic salt; later also cobalt solutions). Bergmann's set of apparatus is simpler, comprising only blow-pipe, hammer and anvil, candle, forceps and silver spoon.

There can be no doubt that the blow-pipe was a great convenience to the chemist, especially since it made possible the use of very small quantities of substance. Instead of heating the sample in a crucible with a coal fire and bellows it could now be heated on a small piece of charcoal and subjected to

[1] This method was also used by Joh. Bernouilli in 1690 (chalk + sulphuric acid), though it is impossible to say whether he discovered it.

the oxidising or reducing action of the mouth blow-pipe. The bellows blow-pipe used in glass-blowing was also used in analysis.

Bergmann and Gahn characterised the following elements by their

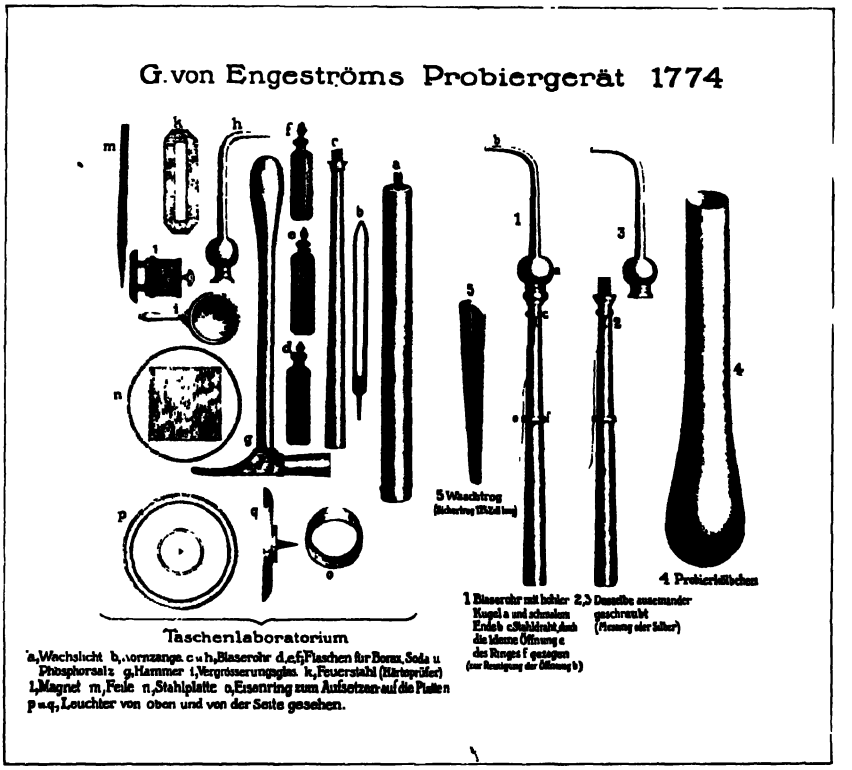


PLATE 113

Qualitative analysis of substances in the dry way was much facilitated at the beginning of the eighteenth century by the introduction of blow-pipes and accessories. Practical instruction for the use of these was given by the Swede G. v. Engestrom in his "Mineralogischen Taschen Laboratorium" published at Greifswald (1765–1782).

G. von Engestrom's analytical equipment (1774).

Pocket laboratory. *a* Wax candle. *b* Forceps. *c* and *h* Blow-pipes. *f* Small bottles for borax, soda and microcosmic salt. *g* Hammer. *i* Magnifying glass. *k* Steel for testing hardness. *l* Magnet. *m* File. *n* Steel plate. *o* Iron ring for putting on the plate. *p* and *q* Candlestick, plan and elevation.

1 Blow-pipe with hollow sphere *a* and narrow orifice *b*. *c* is a steel wire passing through the small opening *e* of the ring *f*, and used to clean the aperture *b*.

2, 3 The blow-pipe dismantled (brass or silver).

4 Testing flask.

5 Washing trough (12½ inches long).

behaviour on charcoal under the blow-pipe: gold, silver, lead, copper, iron, bismuth, nickel, cobalt, arsenic, antimony and tin. The reagents used were those mentioned above. The use of a bead of microcosmic salt was introduced by Marggraf.

Apart from the older examples already mentioned, *analysis in the wet way* was largely begun by Robert Boyle. It was also he who introduced the terms analysis, reaction and reagent in the chemical sense. He used *litmus* (and also the tinctures of violets and cornflowers) for detecting acids and alkalies. He also used test papers. He practised the following tests: sulphuric acid by means of calcium salts, hydrochloric acid and common salt by means of silver solutions (cf. Tachenius), ammonia by the formation of fumes with acids and by means of mercuric chloride, copper by means of ammonia, gold and silver by means of mercury, iron by means of tannin (cf. Pliny) and with a magnet. He separated silver from copper in solution by precipitation with copper, and differentiated between fixed, volatile and carbonate alkalies, the latter by their effervescence with acids.

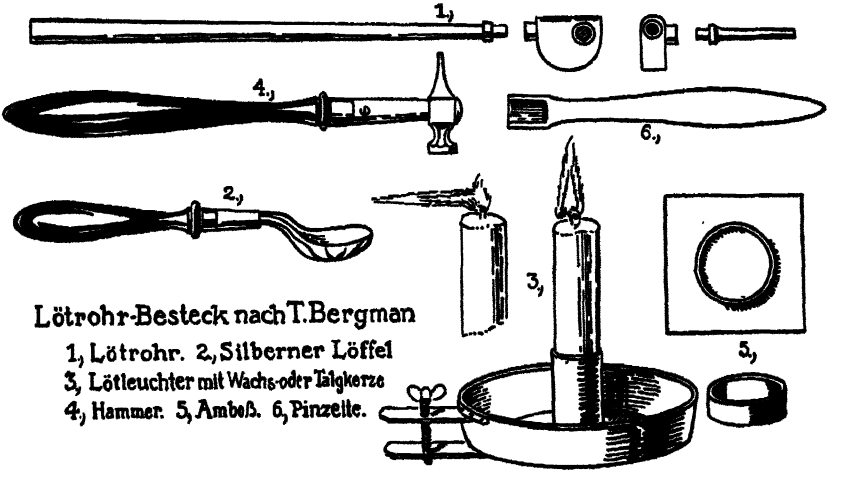


PLATE 114

Blow-pipe outfit of T. Bergmann.

1. Blow-pipe. 2. Silver spoon. 3. Candlestick with wax or tallow candle. 4. Hammer. 5. Anvil. 6. Tweezers.

Bergmann added the following reagents to Boyle's list: extract of Brazil wood for alkalies, ferrocyanide for iron and copper (cf. Marggraf), sulphuric acid for barium, nitric acid for sulphuretted hydrogen, oxalic acid for calcium, potash and caustic alkalies for metals and ores, lime-water for carbonic acid, barium chloride for sulphuric acid, spirits of wine for separating salts, mercuric nitrate, corrosive sublimate, ferrous sulphate, lead acetate, liver of sulphur, and alcoholic soap solutions for testing drinking water. Marggraf distinguished between the flame colours of sodium and potassium, and also introduced the microscope into analysis. The reagents used in *gas analysis* (by Scheele and Priestley) were lime-water and caustic alkali for carbon dioxide; liver of sulphur, ferrous sulphide, ferrous hydroxide, phosphorus and nitric oxide for oxygen.

In 1648 Boyle carried out analyses of drinking water and mineral waters, and also determinations of specific gravities. Friedrich Hoffmann tested mineral water for carbon dioxide, common salt, iron, sulphur and copper. Marggraf detected iron by means of potassium ferrocyanide, and Bergmann determined the hardness of water with alcoholic soap solution.



PLATE 115

Johann Christoph Sommerhoff, pharmacist in Neu-Hanau, born January 3rd, 1644. His "Lexicon pharmaceutico-chymicum" (published 1701 at Nürnberg, second edition, 1713) is the most fruitful source of contemporary chemical and pharmaceutical nomenclature.

Mineralogical analysis was the work of Bergmann and his collaborators. Both qualitative and quantitative analysis had reached such a high level at the end of the eighteenth century (e.g. Klaproth, 1743–1817) that inorganic analysis had probably advanced as far as was possible with the methods then available.

Chemical Symbols

We have already mentioned the large collection of chemical symbols given by Sommerhoff in his lexicon. Similar symbols were also used by Becher and by Kunckel, but the more important chemists of this period made little or no use of them. Thus Lémery (in his text-book of 1675) and Boerhaave (*Elementa chemiæ*, 1732) employ only the signs of the seven metals. Geoffroy, on the other hand, uses symbols in his table of affinity (1718), including some for acids, bases and salts, although he

does not appear to have devised them himself. Bergmann, however, published in 1775 a list of fifty-nine different symbols, partly of his own devising. He also used them in his affinity table and to express chemical transformations.

Although the phlogistic theory demanded that the metals should be regarded as complex substances, the symbols used for them are those of single substances: in fact, Bergmann represented the metal calxes by attaching a special sign devised by him to the symbols for the metals.

The symbols used by Scheele are shown in Plate 117. Lavoisier made



PLATE 116

Table of symbols from N. Lémery's "Cours de Chymie."

experiments with a system of signs to include the quantities taking part in chemical reactions, but they were very clumsy to use. *Hassenfratz* and *Adet* (1787) introduced an entirely new system of symbols which are the direct predecessors of the Berzelius symbols still used to-day. They used the initial letters of the elements, adding a second letter when necessary. Like Berzelius, they used symbols to represent not only elements, but also parts of compounds (radicals). This wise procedure might well be adopted to-day in place of the laborious method generally in use. (It was Liebig who first brought such simplifications out of fashion.)

Hassenfratz also surrounded the letters by a geometrical figure. Elements were denoted by a circle, acid radicals by a square, basic radicals by an equilateral triangle, the vertex being upward for the alkalies and downward for the alkaline earths. In compounds the two symbols were placed together, the basic radical preceding the acid one as is still done. In the acid salts, however, the base symbol was placed *above* the acid symbol. Caloric substance was indicated by a line, following the idea of Lavoisier, according to which the liquid and gaseous states could be considered as compounds of the solid state

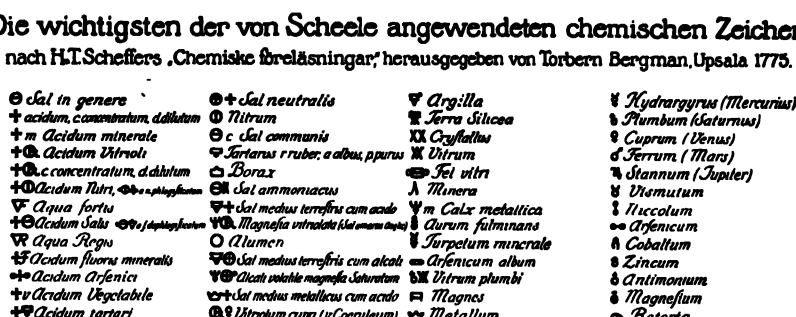


PLATE 117

The most important chemical symbols used by Scheele.

From H. T. Scheffer's "Chemiske föreläsningar," published by Torbern Bergmann, Upsala, 1775.

with heat. A line pointing upwards from the symbol indicated liquid, and a line downwards indicated gas. To-day we have no corresponding symbols for representing the state of aggregation. On the other hand the important heat changes accompanying chemical reactions were not taken into account by Hassenfratz and Adet, or (at a later date) by Berzelius.

The symbols of Hassenfratz were approved by Lavoisier.

What has already been said by no means exhausts the progress of chemical knowledge during this period. We shall therefore give a short list of names with some of the substances which they discovered.

Robert Boyle (1627–1691), an Englishman of noble birth, was (as already

stated) the real founder of analysis in the wet way. He improved the air pump, and used it in carrying out distillations under reduced pressure in an apparatus of his own design. He also carried out reactions under increased air-pressure, in which he was much ahead of his time. Boyle knew wood spirit (1661), acetone (1661), and phosphoric acid (1670), while he prepared phosphorus by the method discovered by Brand (1670), and distinguished between cuprous and cupric chlorides.

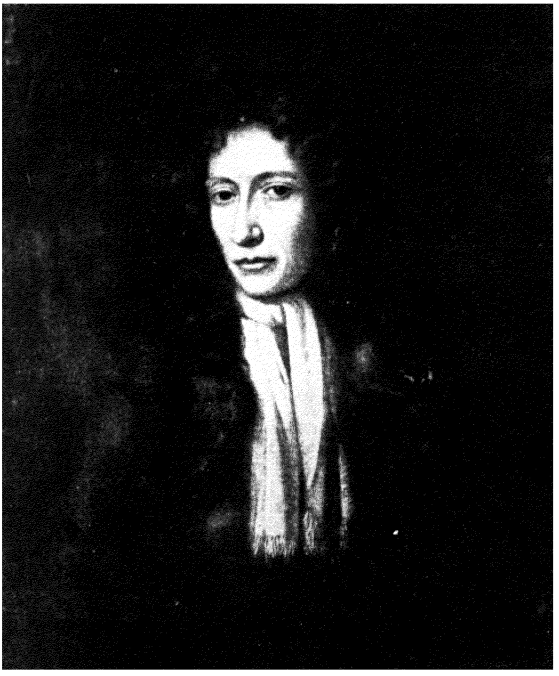


PLATE 118

Robert Boyle (1627–1691).

His contributions to chemical analysis and the concept of elements have been described in the text. Boyle founded analysis in the wet way, was one of the founders of the Royal Society, and is buried in Westminster Abbey. He discovered Boyle's law.

Wilhelm Holmberg (1652–1715), a doctor of German extraction who lived chiefly in Paris, was a versatile chemist. He was one of the first to deal with the saturation behaviour of acids (1699); he discovered the readily fusible alloy later known by the name of Rose's metal, and he fused the heavy metals by means of a concave mirror. Holmberg was the first to give an accurate description of boric acid (1702), and he also worked on the analytical classification of vegetable drugs.

Nicolaus Lémery (1645–1715) was a French pharmacist and physician. His *Cours de Chymie* is by far the best chemical text-book of the period, and his *Dictionnaire des droges simples* the best pharmaceutical manual. This last work was first published in 1698, while its last edition appeared in the nineteenth century. The discovery of flake white (basic bismuth carbonate) and of mercurous oxide is attributed to him.

Georg Ernst Stahl (1660–1734) of Ansbach was a Prussian physician in ordinary, and one of the most famous of the physician-chemists. He was the chief founder of the phlogiston theory (*q.v.*). In spite of this fact, his ideas on living processes were vitalistic rather than materialistic, and he was an opponent

of iatro-chemistry. Stahl defined the scope of chemistry with great clarity, describing it as the science of splitting up complex substances and combining together simple ones. Like Glauber, Stahl supposed that salts were composed of an acid and an alkaline component. He realised the special position of alumina, and distinguished clearly between sodium and potassium salts. He describes the combustible nature of pure acetic acid, and appears to have been the first to prepare mercuric acetate.

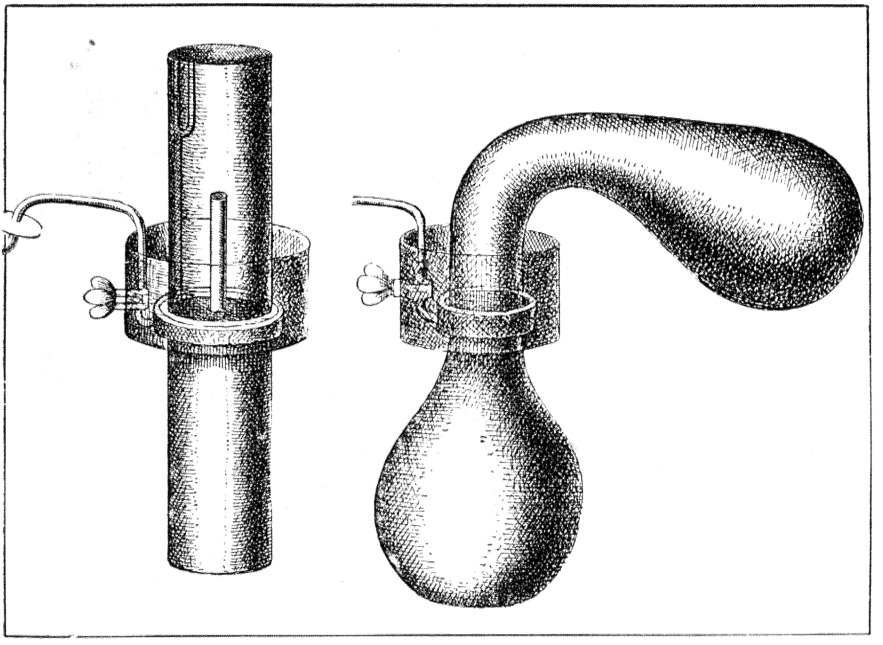


PLATE 119

Vacuum distillation apparatus, R. Boyle (1627–1691).

Boyle was the first to employ vacuum distillation. He carried out experiments both under reduced and increased pressures. This apparatus was not generally used in the laboratory until two hundred years later, when it was recommended by Dr. Romershausen and Buchner. Boyle's collected works have been arranged by Peter Shaw and published as "The philosophical works of the honourable R. Boyle," London, 1725.

Friedrich Hoffmann (1660–1742) is another of the most important physician-chemists, though an opponent of iatro-chemistry. His name is best known in connection with Hoffmann's drops, Hoffmann's balsam, and Hoffmann's elixir. He investigated ethereal oils, determined their specific gravities, and studied magnesium compounds (at that time being introduced into medicine) and alumina. Hoffmann prepared artificial cinnabar in the wet way, and was the first to recognise the acid nature of carbon dioxide. His classification of

mineral waters resembles that still in use, i.e. acid (carbonated) water, alkaline, ferruginous, bitter, sulphurous. He was the first to prepare artificial mineral water, thus anticipating Priestley (1772).

Hermann Boerhaave (1668–1738) was a famous Belgian physician-chemist. Characteristically, he was not an adherent of the phlogiston theory. His text-book *Elementa Chemiæ* was second only to Lémery's in this period. In 1732 he observed (like Geoffroy in 1718) that water is formed in the combustion of spirits of wine. He produces the following good explanation for this phenomenon: the alcohol contains a combustible substance (Pabulum ignis, i.e. hydrogen) which is destroyed by the fire, forming water. Boerhaave also knew that the products of combustion of alcohol weigh more than the alcohol itself before combustion. He believed in the presence of a " vital substance " in the air. He characterised acetone precisely, and knew the mustard oil obtained from black mustard seed.

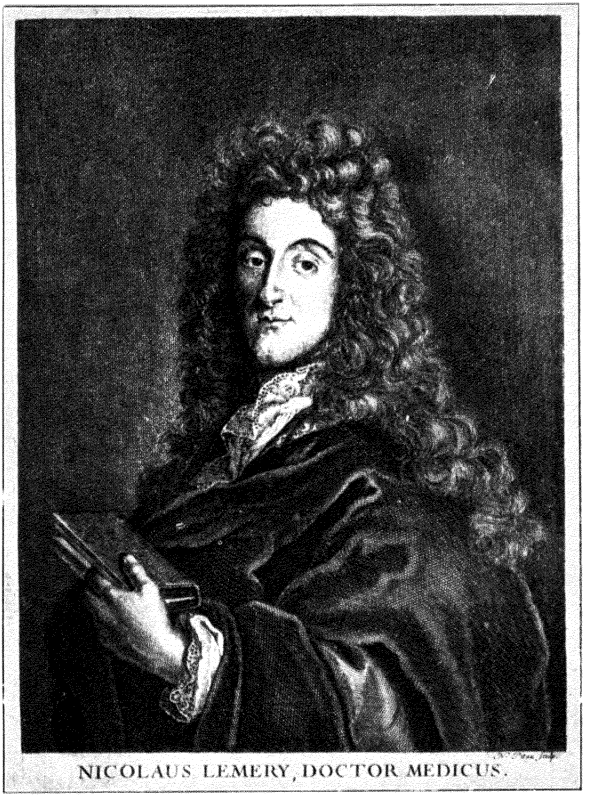


PLATE 120

Nicolaus Lémery (1645–1715) at first devoted himself to the study of pharmacy, but later turned to medicine and natural science. He was pharmacist and professor in Paris and a member of the Académie des Sciences. He reformed pharmaceutical chemistry in France and wrote a number of text-books having a wide circulation.

Etienne François Geoffroy (1672–1731) was a French pharmacist and doctor. He has already been mentioned as the first to set up tables of chemical affinity. His work, *De materia medica* (1741), represents the first scientific pharmacopœia in the modern sense of the word. He discovered cinnamic acid.

Caspar Neumann (1683–1737) was the court pharmacist in Berlin and the teacher of Marggraf. He was the first German pharmacist to write in the



PLATE 121

Friedrich Hoffmann, born 1660 at Halle, died 1742 at Berlin. He was royal physician in Berlin and a pharmaceutical chemist.

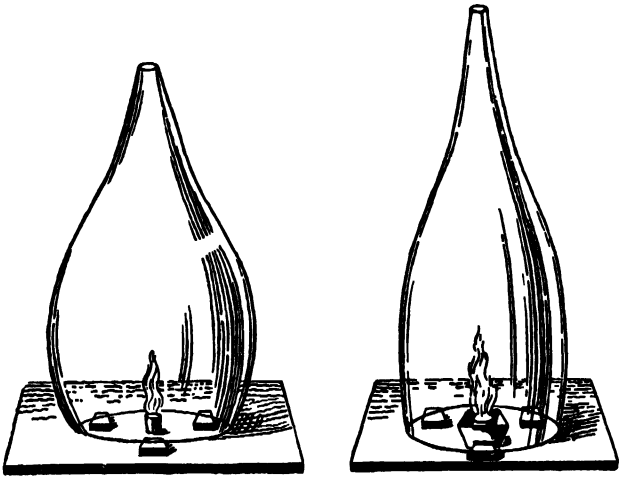
German language, and carried out scientific pharmacological investigations (with formic acid and thymol). His chief work, *Chymia medica*, first appeared, 1749–1755.

Johann Heinrich Schulze (1687–1744), a physician, discovered in 1727 the photo-sensitivity of silver salts.

Guillaume François Rouelle (1703–1770), pharmacist, was the teacher of Lavoisier. It is to him that we owe the general definition of " salts," a point which was much confused before his time.

Andreas Sigismund Marggraf (1709–1783) was one of the most important of a long series of famous pharmaceutical chemists. He was State pharmacist in Berlin, and an adherent of the phlogiston theory.

He prepared phosphorus from urine, carbon and sand, and studied phosphorus pentoxide and phosphoric acid. He observed the increase in



Boerhave bemerkt bei Verbrennen von Alkohol unter einer Glasglocke die Entstehung des Verbrennungsproduktes Wasser.

PLATE 122

Boerhaave's experiments on combustion.

" Pabulum ignis igne consumtum, aqua relinquit."

Boerhaave noticed that when alcohol was burnt under a glass bell-jar, water was formed as one of the products of combustion.

weight when phosphorus is burnt. He obtained various phosphates, and also metallic phosphides (copper phosphide and zinc phosphide, 1747), also phosphorus sulphide. He detected phosphorus in plant ash, and prepared alum synthetically. (His analytical work has been mentioned in a previous section.) He recognised gypsum as calcium sulphate, obtained phosphorescent calcium sulphide from it, and did work on sulphur trioxide, nitrogen peroxide and hydrogen chloride. He demonstrated by analysis the presence of magnesium in serpentine, talc, and other minerals, and found magnesium chloride in the mother liquors from brine. Marggraf showed the presence of aluminium in clay, and knew that it was combined with silicic acid. He was the first to discover the chloroplatinates of potassium and ammonium.

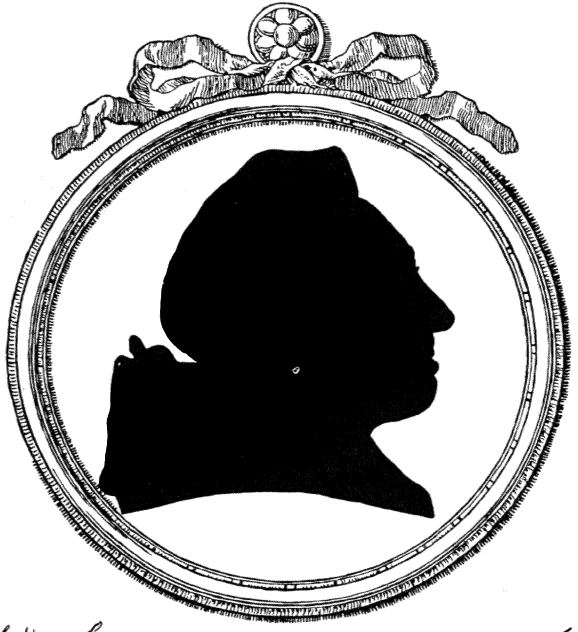


PLATE 123

Andreas Sigesmund Marggraf.

The discoverer of beet-sugar.
Born in Berlin, 1709, the son of the State pharmacist, H. C. Marggraf.
Died as director of the chemical laboratory of the State pharmacy.



PLATE 124

Guillaume François Rouelle, 1703–1770.

He recognised the existence of two acetates of mercury (mercurous and mercuric, 1745), prepared the silver and mercury salts of a number of organic acids (acetic, oxalic, tartaric, citric, 1746 and 1761), knew formic acid (1749), knew that madder lake could be obtained from alizarin and alumina, and used the term indigo for the blue colouring matter of woad. His discovery of cane sugar in the beetroot laid the foundation for the German sugar beet industry. It appears that he prepared potassium cyanide before Scheele.

Pierre Joseph Macquer (1718–1784) was a chemist, and the author of the first chemical dictionary, *Dictionnaire de Chymie*, 1760. He also carried out significant researches on arsenic acid and Prussian blue.

Axel Fredrick Cronstedt (1722–1765) was a Swedish burgomaster and mineralogist. He was the first to use the blow-pipe in chemical work (see section on analysis). He discovered metallic nickel in 1751. This metal had been known much earlier by the Chinese and used to prepare the alloy " packfong " (since about 1500). German silver was not prepared in considerable amounts in Europe until after about 1823. Nickel ores were probably known in Europe even in the Middle Ages, and certainly by the time of Hjärne, 1694. Cronstedt prepared nickel oxide and nickel sulphide, and mentions tungsten ores (1752).

Jacob Reinbold Spielmann (1722–1783) was a Strasbourg pharmacist and taught chemistry to Goethe. He wrote *Institutiones chymicæ* (1763), which was widely read and translated into many languages : also *Pharmacopœia generalis* (1783).

Jean François Demachy (1728–1803) was a well-known French chemical technologist and pharmacist. He wrote the first text-book of chemical technology (1773), which deals particularly with the manufacture of mineral acids.

Antoine Baumé (1728–1804) was a French pharmacist who contributed to chemical technology (manufacture of sal-ammoniac, 1778), distilling, and improvement of the hydrometer. He also wrote a chemical manual, *Eléments de pharmacie théorique et pratique* (1762), specially suited to the practising pharmacist.

Joseph Black (1728–1799) was a Scot who investigated caustic alkalies and carbonates, the chemistry of lime burning and the manufacture of mortar. He also investigated carbon dioxide (which he termed " fixed air ") and recognised its acid nature.

Jan Ingenhousz (1730–1799), a Dutch doctor, is well known as the discoverer of the assimilation of carbon dioxide by plants in sunlight, accompanied by the production of oxygen : this is one of the most important existing chemical processes. Ingenhousz was probably also the first to prepare phosphorus matches consisting of a yellow phosphorus tip on a piece of wood, which ignited on rubbing. He also invented the experiment of burning a piece of steel wire in oxygen.

Henry Cavendish (1731–1810) was the son of Lord Charles Cavendish, brother of the third Duke of Devonshire, and is one of the greatest names in the history of chemistry. One of his most famous investigations is the

burning of nitrogen. His very simple apparatus consisted of two wine glasses filled with mercury, into each of which dipped one limb of a V-shaped



PLATE 125
Antoine Baumé (1728 1804).
Pharmacist and chemist.

tube. The bend of the tube contained some air and was fitted with two electrodes for a spark from an electrostatic machine. The mercury in the limbs of

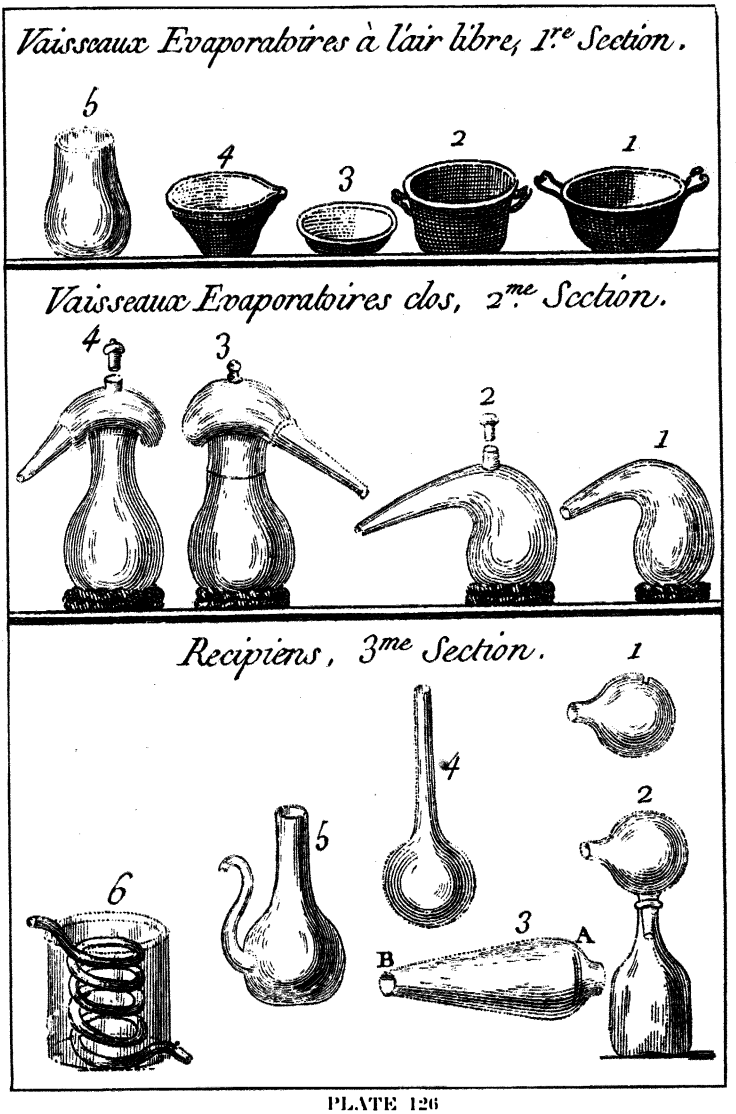


PLATE 126

Chemical apparatus from Baumé (1728–1804).

From "Chymie expérimentale et raisonée," by M. Baumé, 1773.
Note the glass cooling spiral No. 6 and the tubulation on alembic No. 4 and retort No. 2.

the tube was covered with some alkali to absorb the nitrogen oxides formed by the electric discharge. In this way he established the composition of nitric acid. In investigating air he found that after allowing for the content of water vapour, carbon dioxide, oxygen and nitrogen, a residue was left unaccounted

for: thus he was (without knowing it) the discoverer of the rare gas argon (1785). He determined the composition of water by synthesising it from hydrogen and oxygen (1780). In this experiment he used the explosion eudiometer of Priestley, consisting of a measuring cylinder with electrodes fused into it. C. also investigated hydrogen and carbon dioxide, including the solubility of the latter in water.

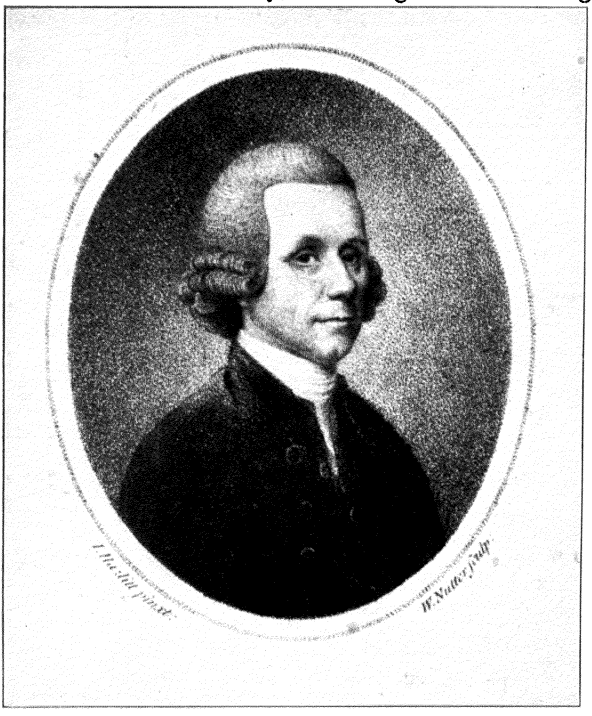


PLATE 127

Joseph Priestley, born 1733 at Telhand (England); died 1804 at Northumberland (Pennsylvania).

Priestley was by profession a teacher of languages and a theologian, and as such he taught Latin, Greek, French, Italian and Hebrew, and wrote comprehensive philosophical and theological treatises. Although he did not turn to scientific studies until late in life, his exceptional gifts as an experimenter enabled him to accomplish a great deal. He investigated the field of pneumatic chemistry, discovered that plants breathe out oxygen in sunlight, was the first to collect gases over mercury, and obtained oxygen by heating red mercuric oxide.

Joseph Priestley (1733–1804) was an English amateur scientist of varied interests. He showed in 1771 that human beings and animals breathe out carbon dioxide, while plants absorb it. He investigated nitric oxide and a number of other gases, e.g. hydrogen chloride, ammonia, sulphur dioxide and silicon tetrafluoride. (The pneumatic trough which he used in these experiments has been already described.) Priestley appears to have been the first to isolate laughing gas from iron and nitrous acid (its physiological action being first discovered by Davy in 1799). He also investigated carbon monoxide (1776). He discovered the preparation of oxygen by heating red mercuric oxide with a burning glass. (However, the French pharmacist Pierre Bayen described in 1774 the production of "une fluide élastique" by heating red mercuric oxide.) Priestley prepared artificial aerated water and showed that water and carbon dioxide were products of the combustion of oils.

Torbern Bergmann (1735–1784) was a Swedish adherent of the phlogiston

theory, and the chief expert on analysis of his period. He contributed largely to the foundation of mineral chemistry.

We have already given an account of his analytical work and his investigations of gases. He reduced inorganic analysis to a system which is essentially that still in use to-day. In 1774 Bergmann recognised " fixed air " (i.e. carbon dioxide) as an acid. He discovered nickel sulphate in 1775, analysed tartar emetic in 1773, discovered prussic acid in 1775, cyanuric acid in 1776, uric acid in 1776 and oxalic acid in 1776 (the last substance having been previously discovered by Wiegleb in 1769). Bergmann was the first to classify substances as organic and inorganic, and the term " elective affinity " is due to him.



PLATE 128

Torbern Bergmann (1735–1784).

Professor of physics, mineralogy and chemistry at Upsala. Torbern Bergmann is one of the most important representatives of the end of the phlogiston period. He was one of the chief founders of analytical and mineralogical chemistry.

Carl Friedrich Wenzel (1740–1793), chemist at the Meissen porcelain works, is one of the greatest figures in chemistry, though his name is often passed over in favour of others. It was Wenzel who really established the law of constant proportions (see above), and he made a number of other important discoveries. He describes the hydrolysis of the chlorides of tin, bismuth, antimony and arsenic, and of the nitrates of iron, lead and bismuth, and he observed the " lead tree." He knew of the light-sensitivity of silver salts, prepared colloidal copper and silver, and described the alkali salts of the hydroxides of zinc, lead, tin, aluminium and copper. He investigated the solubility of substances in water and in spirits of wine, made experiments on water of crystallisation, and described the flame colorations of copper, boric acid,

bismuth and arsenic. He prepared ethyl chloride by the action of spirits of wine on antimony trichloride. In 1782 he made measurements on the neutralisation of acetic, tartaric, oxalic and succinic acids with different bases.



PLATE 129
C. W. Scheele (1742–1786).

Karl Wilhelm Scheele (1742–1786) was at first a pharmacist in Stralsund, and later in Köping in Sweden.

Scheele obtained phosphorus from bones (1770), characterised hydrofluoric acid (which had been used for etching glass at least since 1670), and discovered hydrofluosilicic acid. In 1774 he prepared chlorine from pyrolusite and hydrochloric acid, a process which was by no means new, but which

apparently had never before been closely studied. He recognised baryta as a special substance, and prepared barium chloride. He was probably the first to prepare various manganese compounds, e.g. manganous sulphate (1774).

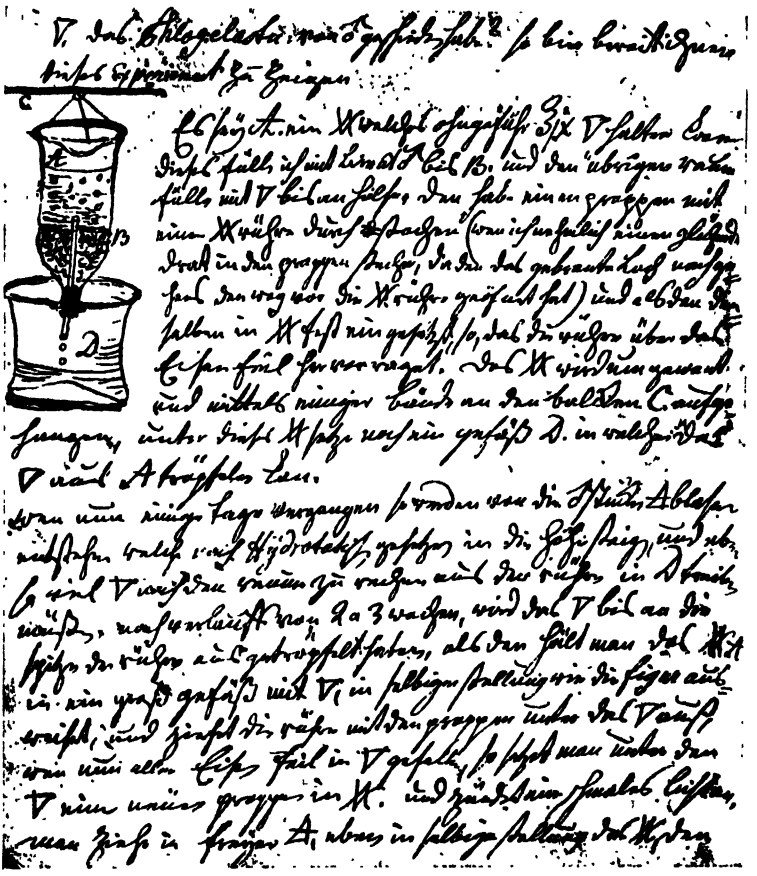


PLATE 130

Manuscript by C. W. Scheele.

Translation of the M.S: "A is a glass vessel which can hold about 9 ounces of water. I fill this with iron filings as far as B, and fill the remaining space with water up to the neck. I then take a cork pierced by a glass tube (this is done by sticking a red hot wire into the cork, thus making a hole to receive the tube) and make it fast in the glass vessel so that the tube protrudes above the top of the iron filings. The vessel is inverted and hung from the beam C by means of strings. Under it is placed a second vessel D in which the water from A can drip."

He is particularly famous for preparing oxygen earlier than Priestley (1771), though he did not publish it until later. He used various methods, e.g. from pyrolusite and arsenic acid, from mercuric oxide, etc. Scheele distinguished between nitrites and nitrates and prepared sodium nitrite. In 1778 he recog-

nised molybdenum and tungsten compounds as definite classes, though these ores had been known earlier (Agricola; Cronstedt, 1758). Scheele prepared tungstic acid and sodium tungstate (1781) and recognised graphite as a modification of carbon (1779).

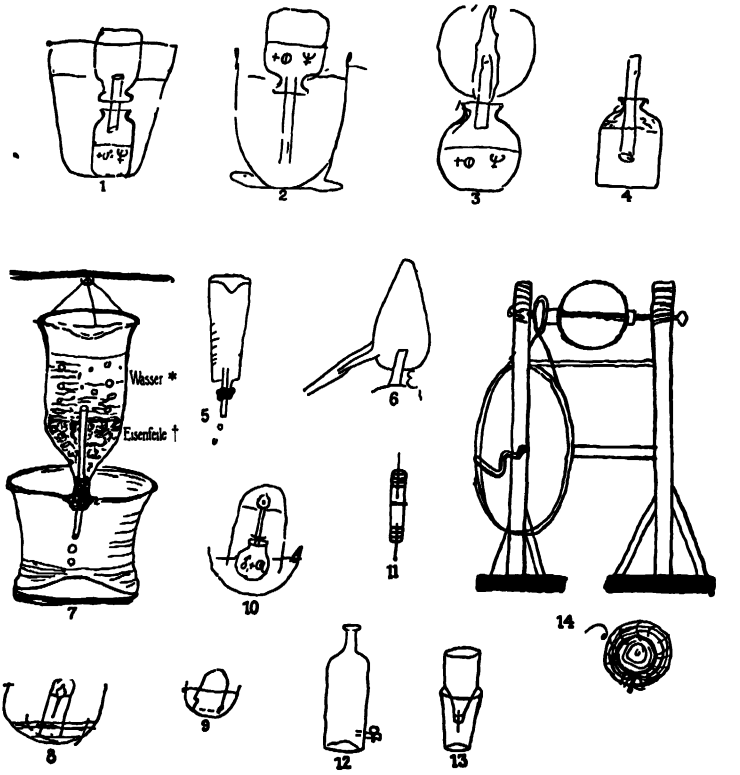


PLATE 131

Chemical apparatus from original drawings by C. W. Scheele.

1, 2, 3. Apparatus for collecting carbon dioxide in bottles and bladders.
4. Introduction of a moist piece of paper into a bottle containing hydrogen chloride.
5. Arrangement for acting on pyrolusite with sulphuric acid.
6. Blow-pipe flame.
7. Apparatus for obtaining hydrogen from water and iron filings.
8, 9, 10. Apparatus for investigating the composition of air.
11. Arrangement for experiments with electric sparks.
12. Vessel for storing acid fruit juices.
13. Investigation of the process of solution of caustic alkalies.
14. Scheele's electrostatic machine and friction pad.
Note the simplicity of the experimental arrangements.
* Water. † Iron filings.

He was the author of the well-known method for obtaining hydrogen sulphide from ferrous sulphide and acid (a reaction which had been observed before). He probably also discovered arsine (1775) and the copper arsenite

known as Scheele's green (1778). His most famous experiments on combustion under bell-jars (with hydrogen, candles, animals) are repetitions of those of Mayow and Hales. The use of lime-water as a confining liquid in combustions giving off carbon dioxide had been introduced by Black.

Scheele is one of the chief founders of organic chemistry. It is, however, only partly correct to attribute to him the discovery of a number of organic acids. 'Among these are tartaric acid (Scheele, 1769), lactic acid (1780), oxalic acid (1776 : cf. Bergmann, 1776 and Wiegleb, 1769), malic acid (1785 : Monro

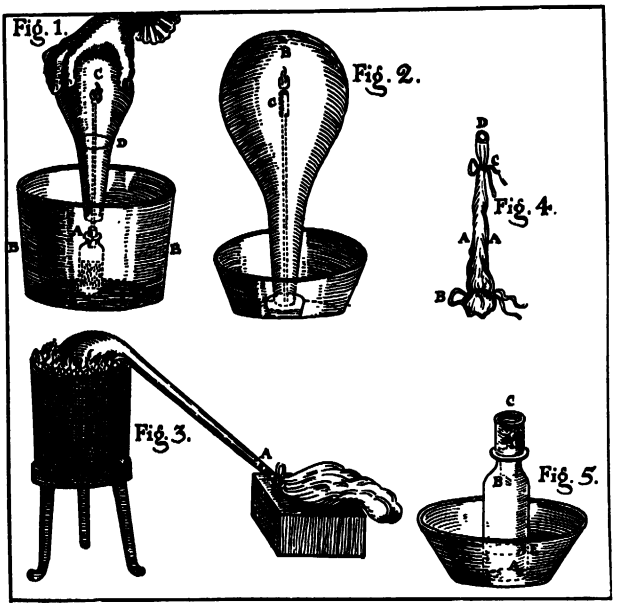


PLATE 132

Apparatus of C. W. Scheele for investigating the composition of air and the processes of combustion and respiration.

1. Hydrogen flame in a volume of air confined by water.
2. Candle flame confined by lime water.
5. Breathing insect confined by lime water.
3. Apparatus for evolving gases and collecting them in bladders.

mentions sodium malate in 1782). These substances must all have been known at a much earlier date, though they had not been properly characterised. The same is true of uric acid (Scheele, 1776). Prussic acid (Scheele, 1783) had already been discovered by Bergmann in 1775, but sodium and potassium cyanides (1783) and mercuric cyanide (1782) were probably first discovered by Scheele, though potassium cyanide may have been prepared by Marggraf. Scheele analysed mucic acid (1780), pyrogallol (1786), ethyl benzoate (1780) and fusel oil. Glycerine (1783) was carefully characterised by Scheele, though it obviously must have been known earlier to soap-boilers. In 1782 Scheele

demonstrated the saponification of esters by means of alkalies. It should be specially noted that in spite of thousands of statements to the contrary, *the first synthesis of an organic compound from its elements* was not carried out by Wöhler, but by Scheele, who in 1783 obtained prussic acid from carbon, sal-ammoniac and potash. Scheele was the first to show that proteins occur in vegetable as well as in animal matter. The apparatus which Scheele employed in his researches was the simplest imaginable, and might well be termed meagre. His work proves that the greatest possible chemical discoveries can be made without using complicated apparatus. Although our ignorance of history has caused Scheele to be credited with many discoveries which others had made before him, enough remains to place him among the greatest chemists of the past.

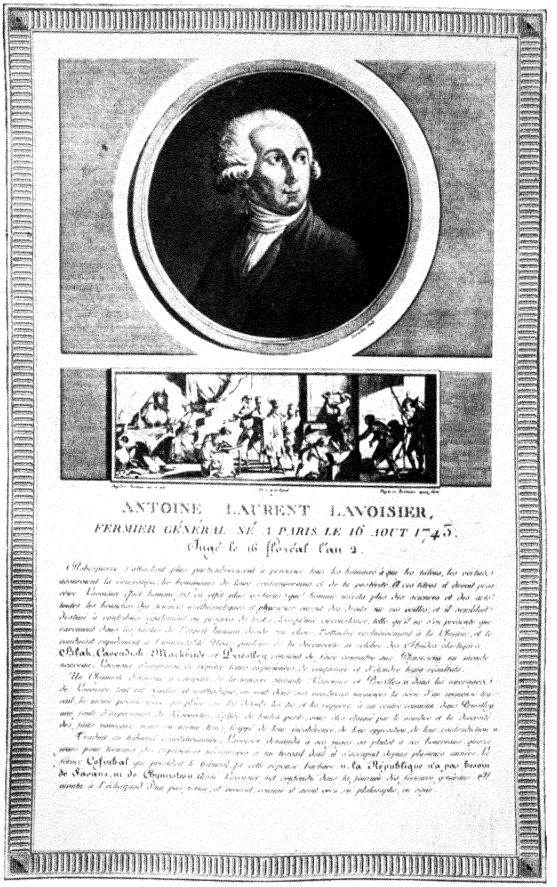


PLATE 133

Counter-revolutionary broad-sheet on the occasion of the execution of Lavoisier, May 8th, 1794.

Antoine Lavoisier, the most important French chemist and a member of the Academie des Sciences, was born in Paris, 1743. He was condemned to death by the revolutionary tribunal on futile charges, and was executed on May 8th, 1794.

Martin Heinrich Klaproth (1743–1817) was another of the great Berlin pharmacists. He was a very fortunate investigator, in that he possessed an unusual mastery of both qualitative and quantitative analysis. It may be noted that he and Hermbstädt were two of the first German supporters of Lavoisier. He realised the chemical individuality of compounds of uranium (1789: uranium oxide and hydrated oxide: uranium ores had been known much earlier), titanium (1795: but cf. Gregor, 1789), compounds of zirconium (1789), strontium (1793: strontium ores appear to have been

known to Crawford, 1790) and cerium (1803). He prepared tellurium compounds (tellurous acid, 1798) and discovered mellitic acid.

Antoine Laurent Lavoisier (1743–1794), a French chemist, was executed in the Revolution on demonstrably false accusations. His chief work has already been described, and is summarised in his *Traité élémentaire de chimie*.

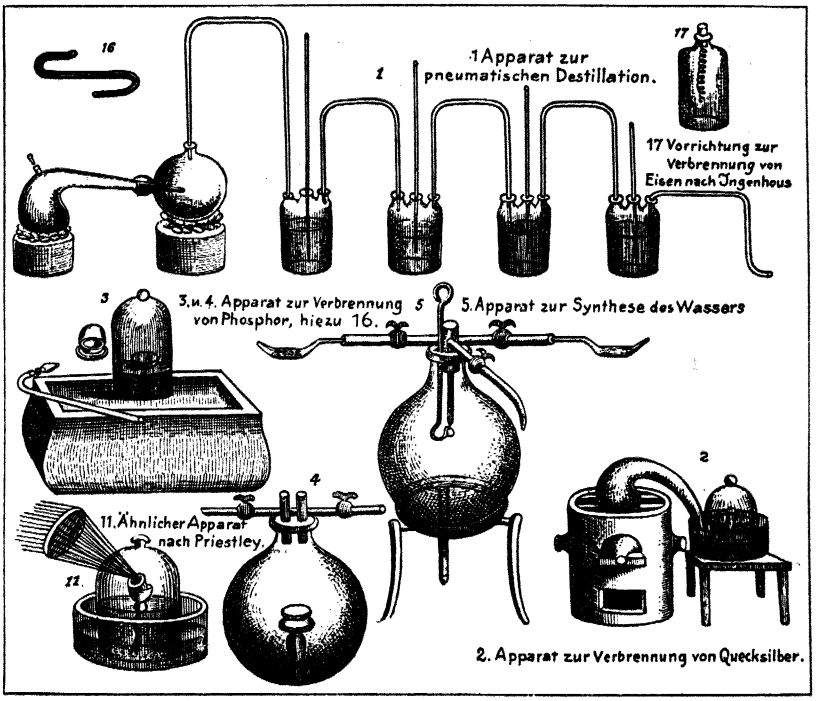


PLATE 134

Apparatus by Lavoisier.

Lavoisier's mastery also extended to the design of apparatus.

1. Apparatus for evolving gas with Woulfe's bottles for washing it.
2. The famous oxidation of mercury.
4 and 11. Apparatus for the combustion of phosphorus.
3. The same with pneumatic trough of marble.
5. Apparatus for the synthesis of water, using electric sparks.

In most of his famous combustion experiments the substance used was burnt in a confined volume of air in a bell-jar, retort or glass globe. In the oxidation of mercury he used a retort attached to a pneumatic trough (Priestley), the retort being heated by a small furnace. Phosphorus was

ignited inside the globe by means of a burning glass, and hydrogen by an electric spark (cf. Cavendish).

The apparatus for the reduction of water consisted of a steam generator, a red-hot tube filled with iron turnings, a vessel for condensing undecomposed water, and a pneumatic trough for collecting the hydrogen. Lavoisier often used Woulfe's bottles in his apparatus for preparing gases, and the first practical apparatus for weighing gases is apparently due to him. Lavoisier knew that all organic compounds consisted of carbon, hydrogen and oxygen, with the addition (especially in animal products) of nitrogen, sulphur and phosphorus. Lavoisier also contributed greatly to the foundations of organic chemistry by

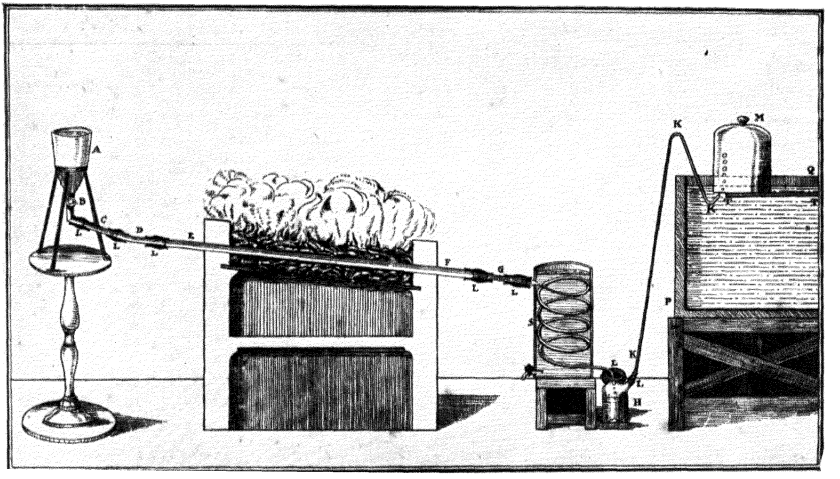


PLATE 135

Decomposition of water, A. L. Lavoisier.

The water vapour is decomposed by passing through an iron tube filled with iron filings which is heated to redness. The oxygen combines with the iron, undecomposed water vapour is condensed in the cooled spiral, and the hydrogen formed is collected in the bell-jar in the pneumatic trough.

laying down the principles of analysing organic compounds for the elements. His method consisted of burning the organic substance and collecting the gaseous combustion products, water vapour and carbon dioxide. Lavoisier also measured the amount of oxygen necessary for combustion, using very complicated gasometers. He also attempted to carry out the combustion by means of mercuric oxide and potassium chlorate (1788). Although Lavoisier did not obtain very satisfactory results in his organic analyses, he established methods of absorbing the combustion products (carbon dioxide with caustic potash, water with calcium chloride) which are still in use to-day and which have not been improved upon. Lavoisier also investigated the phenomena of fermentation. He and his collaborators founded *organic nomenclature* (1787), introducing the terms alcohol, ether, organic acid, etc.

Johann Gottlieb Gahn (1745–1818) was a Swedish chemist of Bergmann's school. He taught that bone ash was composed chiefly of calcium phosphate (which had, however, been obtained from bones even in the seventeenth century). He was aware of the presence of barium in heavy spar, was the first to prepare manganese metal (by reducing pyrolusite with carbon, 1774), and was a master of blow-pipe analysis.

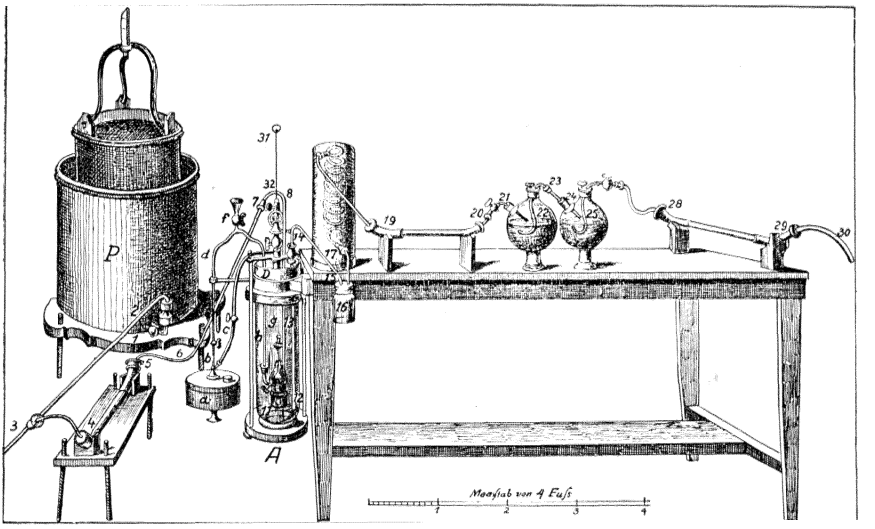


PLATE 136

Apparatus for analysing oils by combustion, A. L. Lavoisier.

P Gasometer filled with air. 1. Gasometer tap. 2, 3. Tubes leading to a second (reserve) gasometer. 4, 5. Vessels filled with hygroscopic salt for drying the air in the gasometer. 5, 6, 7, 8, 9, 10. Tubes leading to the lamp 11. A Large jar.
12, 13, 14, 15. Tubes for leading off the combustion gases. 16, 17. Flask and spiral for condensing water vapour. 19, 20. Tubes (like 4 and 5) for retaining the rest of the water vapour. 22 and 25. Vessels half filled with potash for absorbing carbon dioxide. 20, 21, 23, 24. Tubes leading to the potash vessels. 28, 29. Drying tubes. 29, 30. Tubes to the gasometer for determining the amount of unused gas. The proportions of oxygen and nitrogen in this gas also had to be determined.
a Oil container. *b, c, d, e, f, g* Siphon for supplying oil to the lamp. *h, i* Tubes carrying oil. 31, 32. Rod for raising and lowering the wick. D Cover with an iron cap fitting into a groove in the glass vessel. This groove is filled with mercury, thus making the vessel gas-tight.
This is the first apparatus for organic analysis. Owing to its undue complexity it did not give accurate results. It is, however, important, since it introduces the principles of absorbing water in calcium chloride and carbon dioxide in caustic potash.
Scale in feet.

Claude Louis Berthollet (1748–1822), a French chemist, was the first to clear up the composition of ammonia (1784), of hydrogen sulphide (1785), of methane (1783) and of prussic acid and its salts (1783). In 1786 he showed that prussic acid contains no oxygen, thus disproving Lavoisier's view that acids must contain oxygen. He discovered cyanogen chloride (1787) and fulminating silver (1788): the latter was, however, known earlier to Kunckel. He showed that

potassium ferrocyanide contained iron, discovered the bleaching action of chlorine and hypochlorites (potassium hypochlorite, 1787) and discovered potassium chlorate (cf. however, Higgins, 1777).

In contrast to Proust's hypothesis of constant proportions, he emphasised the effect of the quantities used on the course of a reaction. He could not at

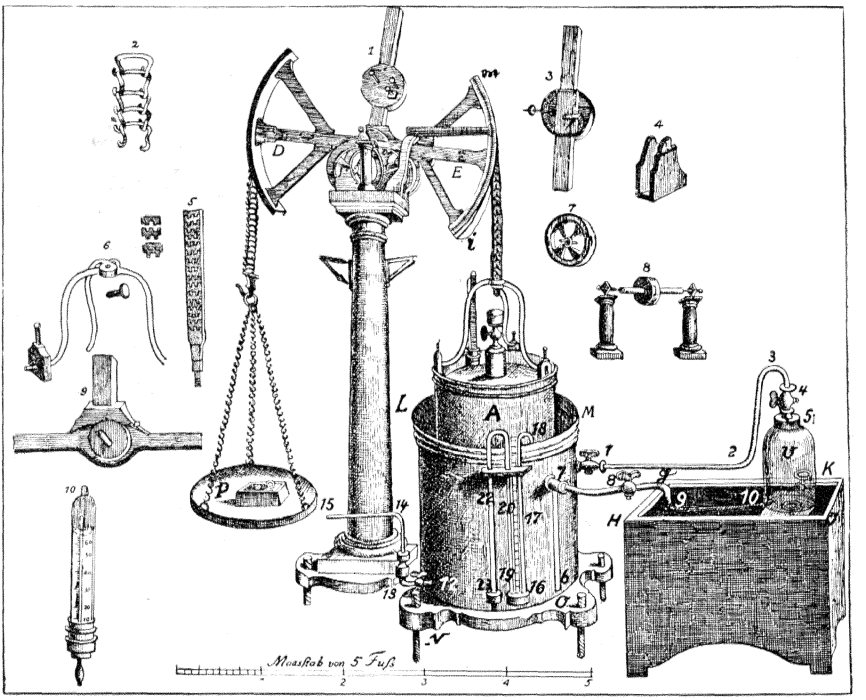


PLATE 137

Gasometer, A. L. Lavoisier.

D E Iron beam with an iron arc at each end; the beam rests on movable rollers. P Wooden scale-pan. *m n* Chain carrying the copper bell-jar A: this bell-jar is open at the bottom and dips into the copper container L, M, N, O. G, H, I, K Pneumatic trough. V Glass bell-jar.

1, 2, 3, 4, 5. Tubes for leading the gas into the gasometer.

6, 7, 8, 9, 10. Tubes for filling the glass bell-jar with gas.

12, 13, 14, 15. Tubes for leading the gas to any required spot.

16 23. Tubes for equalising and measuring the pressure inside and outside the glass bell-jar A. Lavoisier's gasometer appears to have been a true measuring instrument, and not merely a vessel for storage.

first understand that this point was consistent with the law of constant proportions. Finally, Berthollet demonstrated the *presence of nitrogen in proteins*.

Sigismund Friedrich Hermbstädt (1758–1833), pharmacist and professor, was the first representative of Lavoisier's school of chemistry in Germany, and translated Lavoisier's chief writings. He promoted chemical technology

(e.g. the extraction of beet sugar) and pharmacology, especially the classification of vegetable drugs and the use of chemical analysis in pharmacy.

Johann Bartholomäus Trommsdorff (1770–1837), pharmacist, founded in Erfurt in 1795 the first German university pharmaceutical institute. Göttingen was the first university to include pharmacy among its subjects for study.

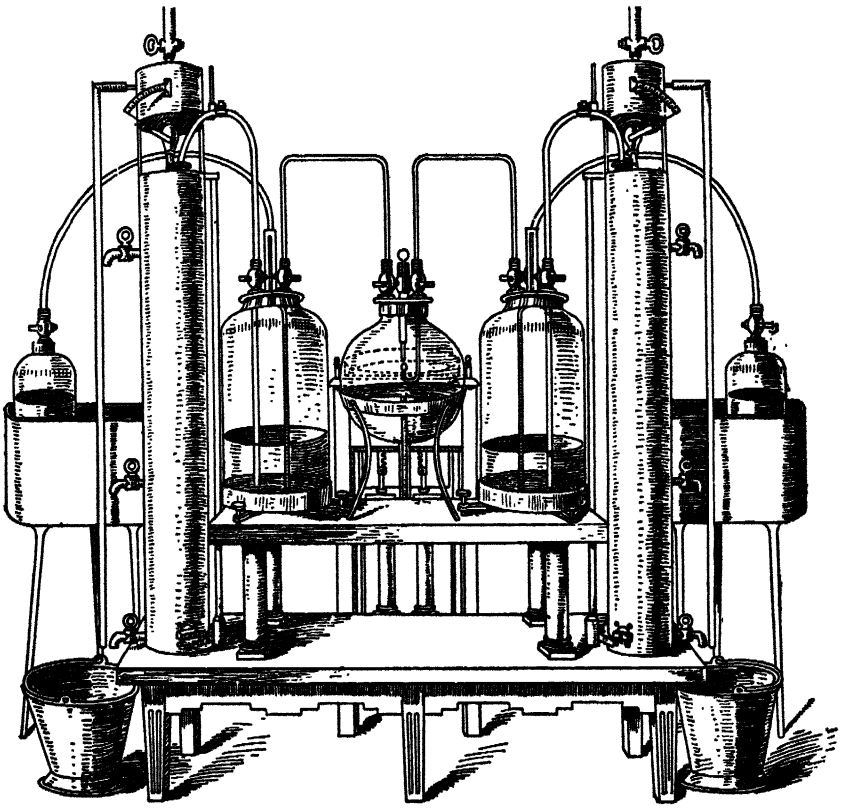


PLATE 138

Apparatus for the synthesis of water, van Marum, about 1800.

This apparatus makes it possible to take measured quantities of hydrogen and oxygen, which are combined by an electric spark to give water in the Lavoisier globe in the centre. It may be noted that van Marum observed the smell of ozone in 1785.

Before Trommsdorff, Wiegleb had an institute for pharmacy in Langensalza, and Hermbstädt for a time in Berlin. Trommsdorff also founded one of the first independent factories for chemical pharmaceutical products. His systematic text-book had several editions, and his *Handbuch der pharmazeutischen Warenkunde* (1799) was the first of its kind in the German language.

In addition to the substances already mentioned in the preceding sections,

the following were discovered or described fully for the first time in the period up to 1800 :—

I. Inorganic Substances

Elementary phosphorus, first obtained by Brand in 1669.[1]

Magnesium compounds, Nehemiah Grew (1695); metallic cobalt and some cobalt salts, Brandt (1735); manganese compounds, S. J. v. Waitz (1704), potassium permanganate, Pott (1740); platinum (known much earlier to the Indians), Wood (1741), de Ulloa (1748); tellurium, Müller von Reichenstein (1782) (tellurium ores were known earlier); metallic molybdenum, Hjelm (1782); metallic tungsten, J. and F. d'Elhujar (1783); titanium, Gregor (1789); yttrium ores, Gadolin (1794); chromium metal, chromic acid, potassium bichromate, chromium oxide, chrome yellow, chrome green, Vauquelin (1797) (though chromium ores were known to J. G. Lehmann, 1766); beryllium ores, Vauquelin (1798); Vauquelin also found chromium in spinelle and emerald in 1798; hydrofluoric acid, Schwanhardt (1670), Pauli (1725); sodium nitrate (known earlier but not well characterised), Bohn (1683); aluminium sulphate, Ettmüller (1684); cuprammonium chloride, Stibber (1693); fusible metal (Rose's metal), Valentine Rose (1771) (but cf. Holmberg, 1699); sodium phosphate, Hellot (1735); sodium arsenate (Macquer (1748); potassium bicarbonate, J. Bohn (1685), Cartheuser (1757); marsh gas (analysed), Volta (1775); carbon monoxide, Lassone (1776); potassium chlorate, Higgins (1777); sulphur chloride, Hagemann (1782); phosphine (spontaneously inflammable), Gengembre (1783) (stable), Pelletier (1790); potassium arsenite, J. Schultz (1786); artificial cinnabar made in the wet way, J. Schultz (1787); magnesium ammonium double salts, Fourcroy (1790); tin oxide and dioxide, Pelletier (1792); barium and strontium nitrates, Pelletier (1791); calcium phosphate, Smithson Tennant (1791); ammonium chlorate, van Mons (1796); carbon disulphide, Lampadius (1796); chloride of lime, Smithson Tennant (1798); nickel (found in meteoric iron), Proust (1799); sodium thiosulphate, Chaussier (1799).

II. Organic Substances

Potassium oxalate, Duclos (1661); ethylene from alcohol and sulphuric acid, Becher (1669); formic acid, Wray (1670), Fischer (1670); Rochelle salt, Seignette (1672); potassium ammonium tartrate, Lémery (1675); bergamot oil, Barbe (1693); prussian blue, Diesbach (1704); thymol (known earlier, but not described), Neumann (1719), Kleber Beccari (1731); safrol, Maud (1738); potassium ferrocyanide, Dippel (1710), Marggraf (1750), Macquer (1752); cinnamic acid, Geoffroy (1757); ethyl acetate, Comte de Lauragais (1759); cacodyl, Cadet (1760); mercuric tartrate, Monnet (1766); sodium malate, Monro (1767); oxalic acid, Wiegleb (1769), Fr. P. Savary

[1] Phosphorus was probably known to Alchid Bechid (MS. in the Paris library) and to other alchemists.

(1773); menthol (carefully described), Gaubins (1771); picric acid, Woulfe (1771) (cf. Glauber); urea, H. V. Rouelle (1773), Fourcroy and Vauquelin (1797); citric acid, Retzius (1776); ethyl formate, Afzelius (1777), Bucholz (1782), Fontana (1777) noticed that gases were absorbed by charcoal; camphoric acid, Kosegarten (1785); calcium quinate, Hermbstädt (1785); diastase, Irvine (1785); suberic acid, Brugnatelli (1786); cholesterin, Gren (1788), Conradi (1775); picric acid, Haasmann (1788); glacial acetic acid, Lavitz (1789); quinic acid, F. Ch. Hoffmann (1790); grape sugar (found in diabetic urine), Frank (1791); casein as a protein containing phosphorus, Leidenfrost (1791); grape sugar and fructose found in honey, Lavitz (1793); gallic acid from gall-nuts, Deyeux (1793); monochloracetic and trichloracetic acids, Lavitz (1793); ethylene and ethylene chloride, Troostwyck and Deimann (1795); narcotine, Baumé (1797); ethyl sulphuric acid, Dabit (1799); Daniel Ludovici (1671) appears to have obtained morphine.[1]

As regards *pharmaceutical chemistry*, there are a large number of important chemists, many of whom (as already mentioned) began as pharmacists. Among the most important we may mention (omitting many other names), Lémery, Geoffroy, Neumann, Rouelle, Marggraf, Spielmann, Demachy, Baumé, Scheele, Klaproth, Hermbstädt, Trommsdorff. As always we may note that the true practical chemists can only be trained in the laboratories of pharmacies and metallurgical works (Cronstedt, Cramer, Gahn).

The eighteenth century saw the beginning of investigations to discover the active principles of drugs, and hence also the development of scientific pharmacology. There can hardly be any period in which more special work on herbs and drugs was carried out than in the eighteenth century.

The analysis of drugs in the eighteenth century depended on the following processes :—

Firstly, *distillation* with water or steam (as in the preparation of ethereal oils, previously described).

Secondly, by *heating :* dry distillation, sublimation, incineration.

Thirdly, by *extraction* with solvents (water, acetic acid, alcohol, ether).

Thus, for example, Lémery prepared extracts from rhubarb, aloes, opium, etc., tinctures from gum benzoin, myrrh, etc., and distillation products from guaiacum and tobacco. From julep extract he obtained a " magisterium," i.e. a solid obtained by precipitation.

Geoffroy used such analytical experiments to discover cinnamic acid, and Neumann to characterise thymol, while the plant acids mentioned earlier

[1] At the end of the eighteenth century chemical periodicals began to appear, e.g. Crell's *Chemisches Journal* and *Chemische Annalen* and the French *Annales de Chimie et de Physique*. The flood of chemical periodicals set in the nineteenth century, e.g. in Germany, *Schweiger's Journal*, 1821, *Poggendorff's Annalen*, 1824, *Journal für technische und ökonomische Chemie*, 1878, *Journal für praktische Chemie*, 1834, *Liebig's Annalen* 1837 (founded as *Annalen der Pharmazie* and not called *Annalen der Chemie* until 1874 : from vol. 33 onwards the title is *Annalen der Chemie und Pharmazie*).

Among pharmaceutical periodicals we may mention the following : 1780, Göttling's *Almanach für Scheidekünstler und Apotheker*; 1794, *Trommsdorff's Journal*, 1794, *Berlinisches Jahrbuch der Pharmazie ;* 1815, *Gehlen's Repertorium der Pharmazie ;* 1823, *Magazin für Pharmazie*.

came into the same category. Kunckel and Homberg showed that the incineration of vegetable drugs leads always to essentially the same kind of ash, and not (as had been previously supposed) to a different ash for each drug. (It is of course true that the salts in the ash vary in respect of their content of traces of iodine, fluorine, boron, manganese, magnesium and bromine, which may be of great medicinal importance.)

These analytical processes did not of course reach perfection in the eighteenth century.

Among local pharmacopœias we may mention the following:— Brandenburg (1698), Sweden (1705), Prussia-Brandenburg (1713), London

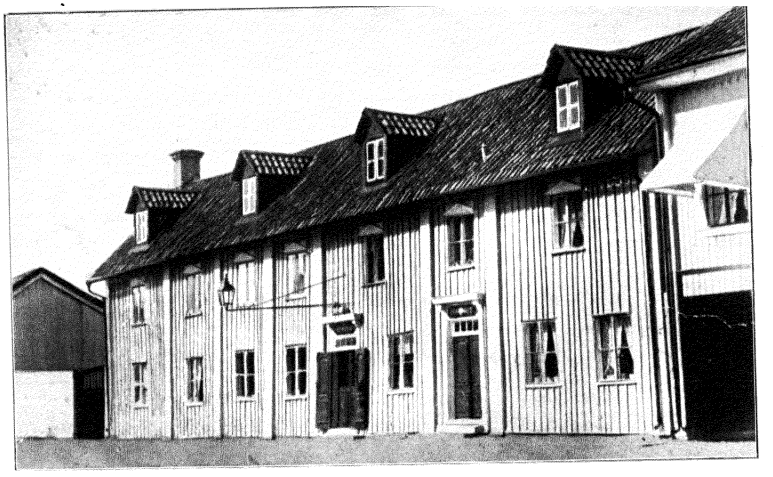


PLATE 139

The pharmacy at Köping (Sweden).

Wilhelm Scheele (1742-1786) lived and worked. In his modest laboratory he made a large number of brilliant discoveries, including that of oxygen.

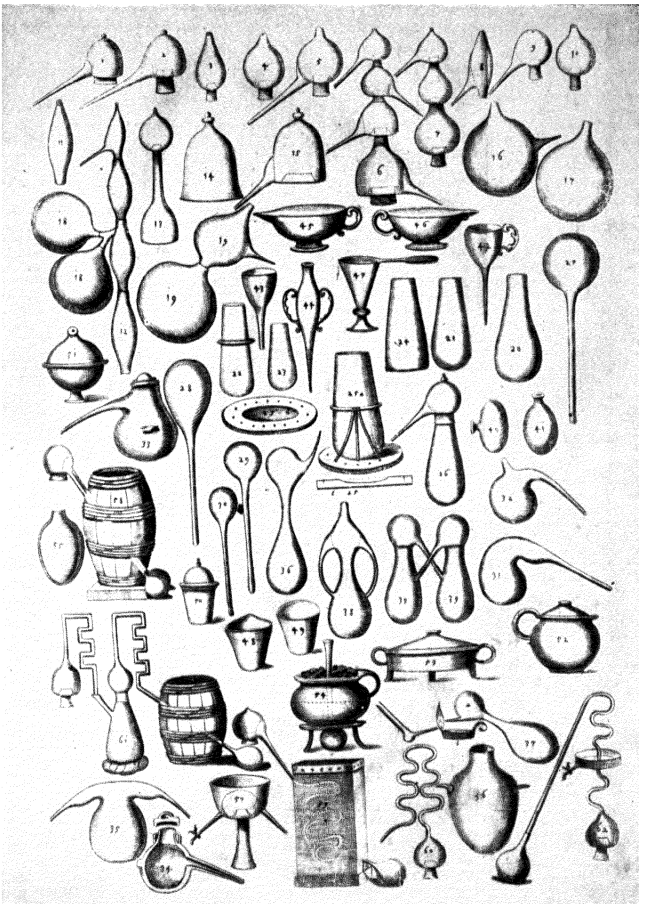
(1713), Vienna (1729), Württemberg (considered to be specially valuable, 1754). They do not differ in any essential respect from present-day pharmacopœias.

Pharmacy naturally made use of the new chemical discoveries of the period. The following are the most important substances in question:—

Magnesium compounds (oxide, carbonate, sulphate), phosphorus, phosphoric acid, calcium and sodium phosphates, calcium chloride, ammonium acetate, sodium thiosulphate, potassium chlorate, chloride of lime, barium chloride, potassium permanganate, chromic acid, potassium bichromate, sodium nitrite, sodium acetate, mercuric cyanide, formic acid, ethyl acetate, trichloracetic acid, acetone, glycerine, lactic acid, tartaric acid, Rochelle salt, citric acid and sodium citrate, cinnamic acid, sodium benzoate, menthol, thymol (probably known in England before the time of Neumann), gallic acid, pyrogallol, tannic acid.

PLATE 140

Chemical apparatus, Antonio de Sgobbis, Theatro Farmaceutico, 1682.



1. Still-head with wide opening. 2. Still-head with narrow opening. 3. Still-head without delivery tube: open beneath for fitting on a condenser. 4. Still-head without delivery tube, with a narrow opening at the top which can be closed. 5. Still-head with delivery tube and an opening at the top for fitting a second condenser. 6. Set of four still-heads, the uppermost closed. 7. Set of three still-heads, only the last of which has a delivery tube, and is closed. 8. Long helm with delivery tube, can be used for sublimation. 9. Round still-head with delivery tube and small opening at the top. 10. Sublimation vessel, open at the top. 11. Sublimation vessel with opening at the top. 12. Four sublimation vessels superimposed, the top one closed and with delivery tube. 13. Wide fitting with a long neck surmounted by a sublimation vessel open at the top. 14. Bell-jar without rim or delivery tube. 15. Bell-shaped still-head with rim and delivery tube. 16. Round receiver with side tube to which a second receiver can be attached. 17. Round receiver. 18. Two round receivers, connected by a tube. 19. Two round receivers, the upper one with a side tube. 20. Large bulbous flask. 21. Elongated flask. 22. Flask with ring and strings or supports for hanging in a water-bath. 23. Small flask. 24. Flat-bottomed flasks. 25 *a*, *b*, *c*. Flasks on lead stands, the stand being shown in plan and elevation. 26. Flask with still-head and delivery tube. 27. Large round phial with long neck. 28. Phial with oval bulb. 29, 30. Small phials. 31. Retort. 32. Tubulated retort. 33. Glauber's stoppered retort with lateral supports. 34. Section of 33. 35. Retort with two delivery tubes. 36. Circulating vessel with delivery tube. 37. Circulating vessel with fused-in delivery tube. 38. Pelican, open at the top. 39. Double circulating vessel. 40. Philosopher's egg with lateral opening. 41. Philosopher's egg, opening at the top. 42. Funnel with handle. 43. Funnel without handle. 44. Separating funnel for separating oil and water. 45, 46. Jugs of glass or other material. 47. Bronze mould for separating metallic reguli. 48. Triangular crucible. 49. Round crucible. 50. Pottery vase with lid. 51. Round pottery vase with opening at the top. 52. Pot with lid. 53. Flat earthenware pot with lid, for putting in the open fire. 54. Pot with glowing coals, for putting round the neck of a flask to be sealed up. 55. Small distilling flask. 56. Large distilling flask with lateral supports. 57. Still-head with "Moor's head," having a tube for running off the cooling water. 58. Still-head with two delivery tubes passing through a cooling vessel and two receivers. 59. Square cooling vessel with spiral condenser, still-head and receiver. 60. Distilling arrangement consisting of a still-head with an air-cooled spiral attached. 61. Still-head with a spiral condenser leading to a second flask, from which a second spiral is connected to the cooling vessel. 62. Still-head with air-cooled spiral: in the centre a cooling vessel with a tap for running off the warm cooling water.

Several vegetable drugs are also of interest, although it is very difficult to say whether they were new at this time. Thus (to mention only a few examples), arnica was recommended by Joël in the second half of the seven-

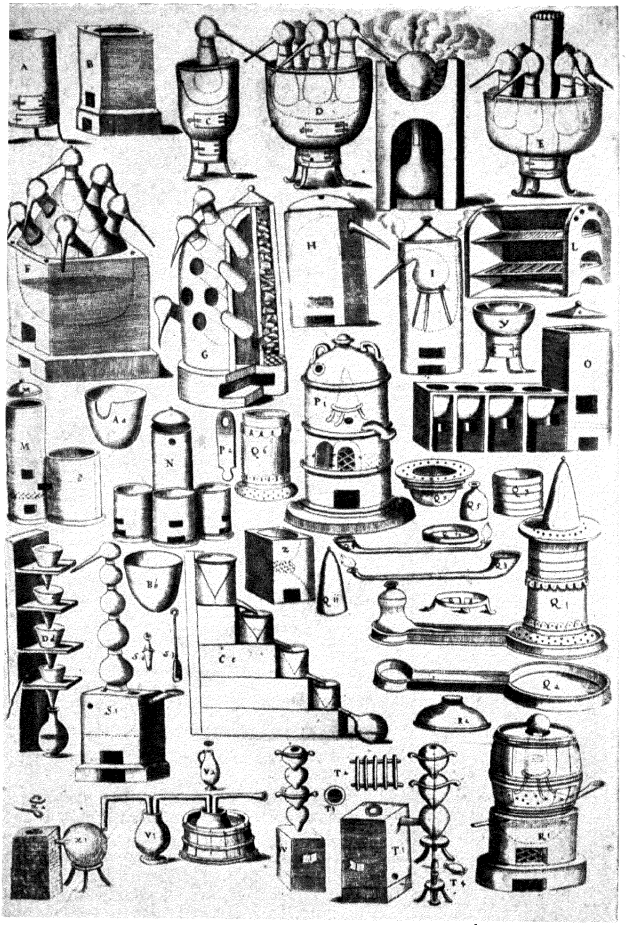


PLATE 141

Chemical apparatus · *Antonio de Sgobbis, Theatro Farmaceutico*, 1682.

Round still furnace A, square still furnace B, copper water-bath furnace with still C, water-bath with a number of flasks D, the same with heating tube through the middle E, steam-bath furnace with a number of flasks F, air furnace for heating the latter, with fuel storage tower G, retort furnace H, the same with retort on a tripod J, desecnsorium K, drying oven L, furnaces for distilling nitric acid with subsidiary furnaces L, M, N, athanor with flue P, philosopher's oven heated by spirits of wine, with accessories Q, dung bath and accessories R, sublimation furnace and accessories S, Glauber's retort furnace and accessories T, Glauber's still V, sublimation apparatus (Glauber) W, Glauber's retort furnace X, ordinary copper furnace with bellows Y, brick bellows furnace Z, cupel for containing retorts Aa, the same for phials and flasks Bb, filtration stand with vessels Cc, Dd. The two last pieces of apparatus are specially noteworthy, also the furnace with spirit lamp.



PLATE 142

Universal furnace, J. J. Becher.

The furnace could be separated into several parts, and these could be put together so as to form a still furnace, a sublimation furnace, a descensorium, a water-bath furnace, etc.

teenth century, but had been used as a domestic remedy much earlier : similarly digitalis (Withering, 1775) was probably used in England and Wales even in the Middle Ages. It may be noted that the use of vegetables against scurvy was

first practised by the Austrian military doctor Kamer in the war against the Turks (eighteenth century), while oranges and lemons were similarly used by Backstrom (1734) and Lind (1757).

Much of the interesting apparatus of the period has already been mentioned. Mention may be made of Becher's portable universal furnace from his *Laboratorium portatile*, 1680. The furnace was fitted with bellows and could be used for all purposes : fusion, assaying, water-bath, distillation (including *destillatio per campanam* and *per descensum*). It would not appear, however, that this furnace found many adherents.

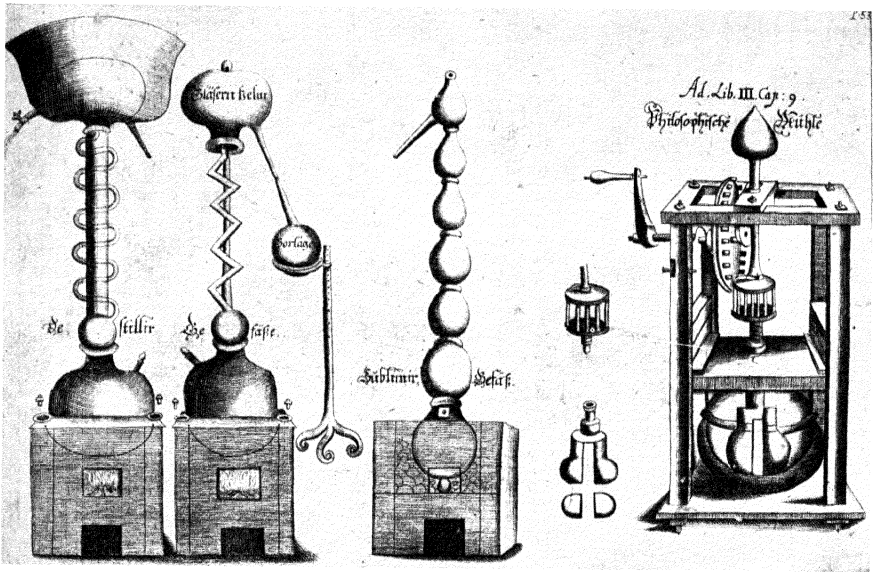


PLATE 143

Apparatus illustrated in Joh. Schröder's Pharmakopœa medicochymica.

German edition by Koschwitz, Frankfurt and Leipzig, 1709.

Large "Moor's head" still on furnace ; still with air-cooling by a zig-zag tube, the receiver being on an adjustable stand ; large aludel with five bulbs and still-head ; the "philosopher's mill," a mechanically driven mill based on the pestle and mortar. (This type of mill was known to Theophilis, 950.)

The use of oil and spirit lamps for heating gradually gained ground : cf. the lamp furnaces of A. de Sgobbis (1682), A. de Heide (1690 : with raised oil reservoir at the side) and of Baumé.

Distillation made an essential step forward in this period with the discovery of the *counter-current condenser* by Chr. Ehrenfried Weigel in 1771.[1]

[1] Dariot's "Moor's head" distillation apparatus (1533–1594) has been described as the forerunner of Weigel's : the cooling water ran continuously into the cooling jacket, and left it near the top. This arrangement did not, however, constitute a satisfactory counter-current condenser. In Dariot's second apparatus the stem of the receiver was cooled by a long inclined water vessel, thus resembling externally Weigel's condenser : it did not, however, have a continuous flow of cooling water.

In Weigel's apparatus the stream of water entered at the bottom of the condenser, which surrounded the lower end of the delivery tube, near the receiver. The water thus flowed round the delivery tube and left the condenser at the upper end, merely overflowing into a waste funnel. Göttling improved this very simple arrangement by introducing an exit tube for the condenser water. The advantage of Weigel's apparatus lies in the fact that the freshest cooling water meets the coolest vapour, thus providing efficient

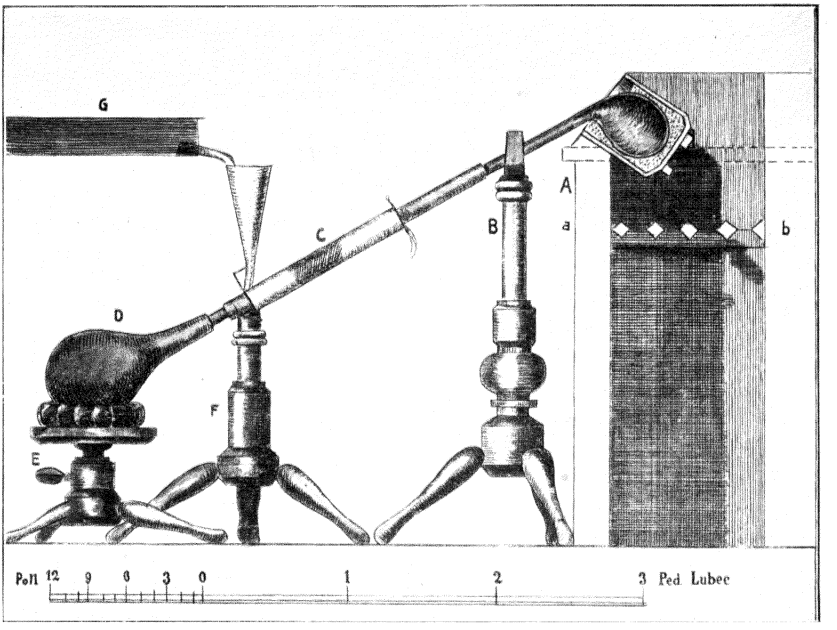


PLATE 144

Weigel's counter current condenser, end of the eighteenth century.

Stove with retort. The condenser consists of a tube through which water flows in the opposite direction to that in which the vapour issues from the retort. In this way the coolest vapour meets the coolest water. A Retort. *a, b* Grate. B Support for the neck of the retort. C Cooling tube surrounding the glass delivery tube. D Receiver. E, F Supports. G Wooden water trough.

condensation. The condenser stand is also due to Weigel, but was considerably improved by Gay-Lussac. The apparatus was later known as a Liebig condenser, since its extended use was largely due to Liebig.[1]

The *two-necked flask* is generally attributed to Woulfe (1767), who used it in his apparatus for preparing ethyl nitrate. The original Woulfe flasks are not, however, like the later ones, since they really only have one neck,

[1] Another improvement in distillation lay in improved fractionation. It was actually Caspar Neumann (1683–1738) who first had the idea of adding the distillate to fresh raw material (instead of to the residue), thus utilising the extraction liquid more fully.

the second opening being a lateral tubus. It is probably more correct to attribute the introduction of flasks with two or more necks to Angelo Saluzzi (1759). He used flasks with two and three necks earlier than Woulfe, and it

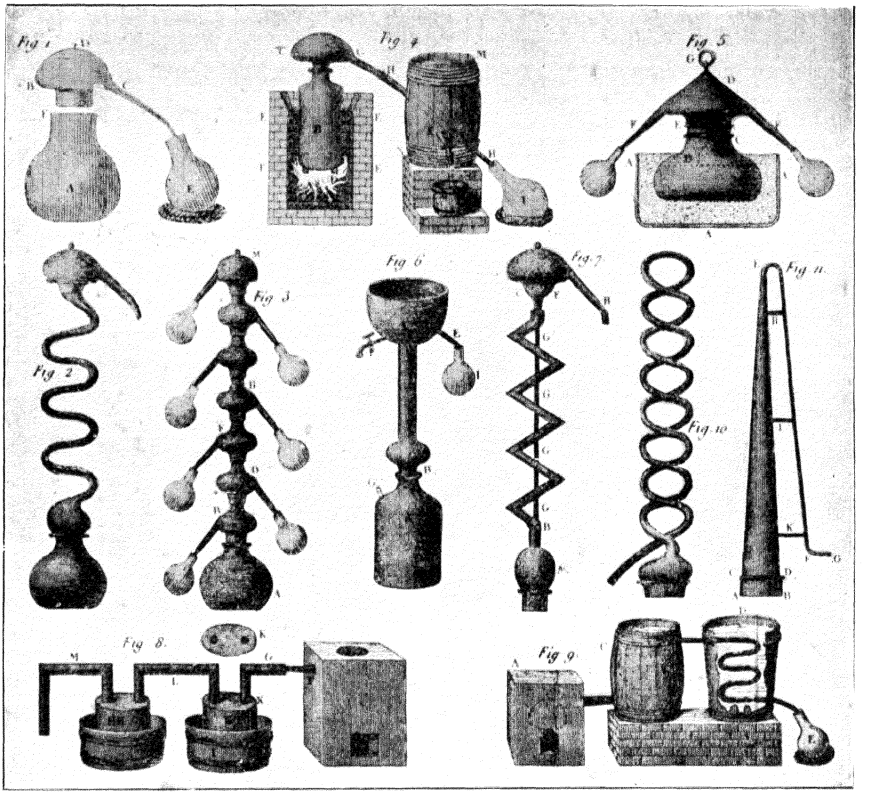


PLATE 145

Important types of distilling apparatus in the seventeenth and eighteenth centuries.

From Normand, L'art du destillateur.

Fig. 1. Antique form of alembic.
" 2, 3. Apparatus from Porta.
" 4. Apparatus for obtaining essences and ethereal oils, Lémery.
" 5. Apparatus for distilling vegetable substances.
" 6. Cooling apparatus, Le Févre.
" 7. Old apparatus for the first stage distillation of spirits of wine.
" 8. Alembic, Glauber.
" 9. Alembic with spiral condenser.
" 10. Spiral condenser, Barchusen.
" 11. Cooling tube, Boerhaave.

is probably from him that Lavoisier and Bergmann learnt their use. The first *oxygen blow-pipe* appears to be due to F. L. Ehrmann in Strasbourg (1786).

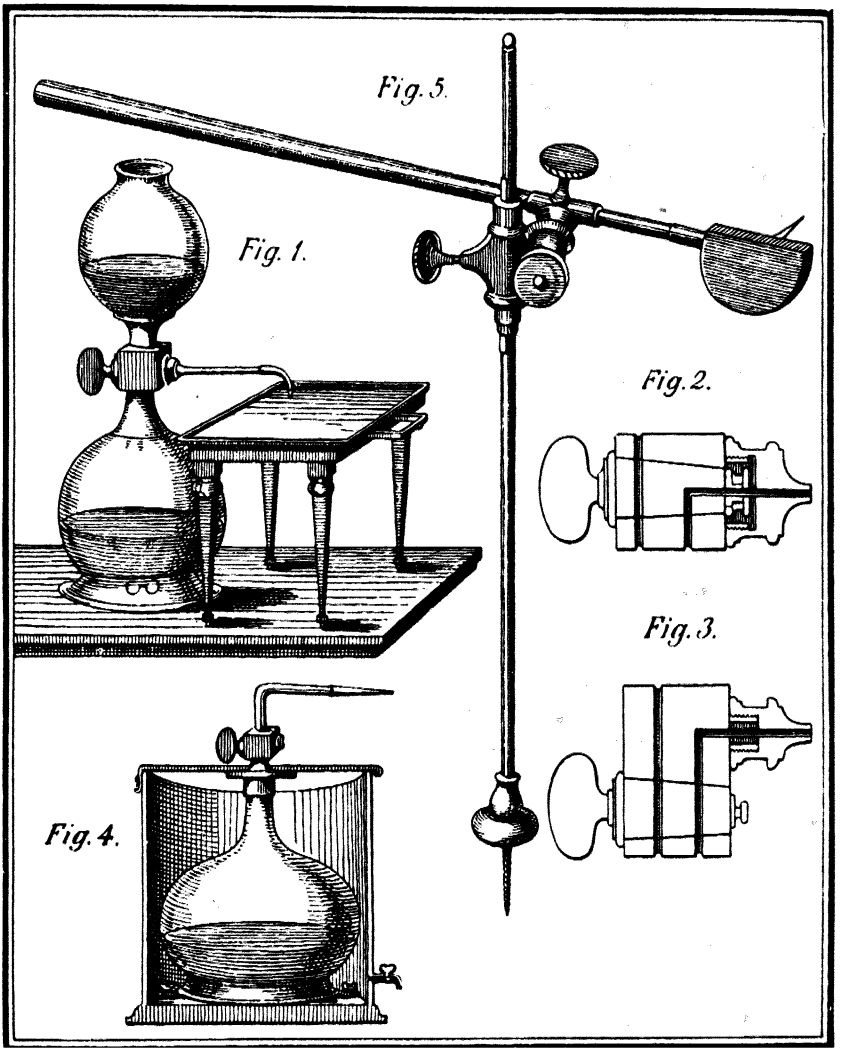


PLATE 146

Earliest illustration of oxygen blow-pipe.

F. L. Ehrmann, 1786. (Figs. 1–4.) Also blow-pipe on stand, Saussure (Fig. 5).

Porous filter-papers are mentioned in Schröder's *Pharmacopeia Universalis* (seventeenth century), but are certainly older than this. The same applies to separating funnels.

Considerable interest attaches to the electrical ignition apparatus of Fürstenberger (1770), who prepared hydrogen from zinc and sulphuric acid and ignited the issuing gas by an electrophorus built into the apparatus.

We may also note a number of pieces of apparatus for making artificial aerated water. The first practicable device was that of J. M. North (1775) consisting of three globes. The lowest globe contained the generating sub-

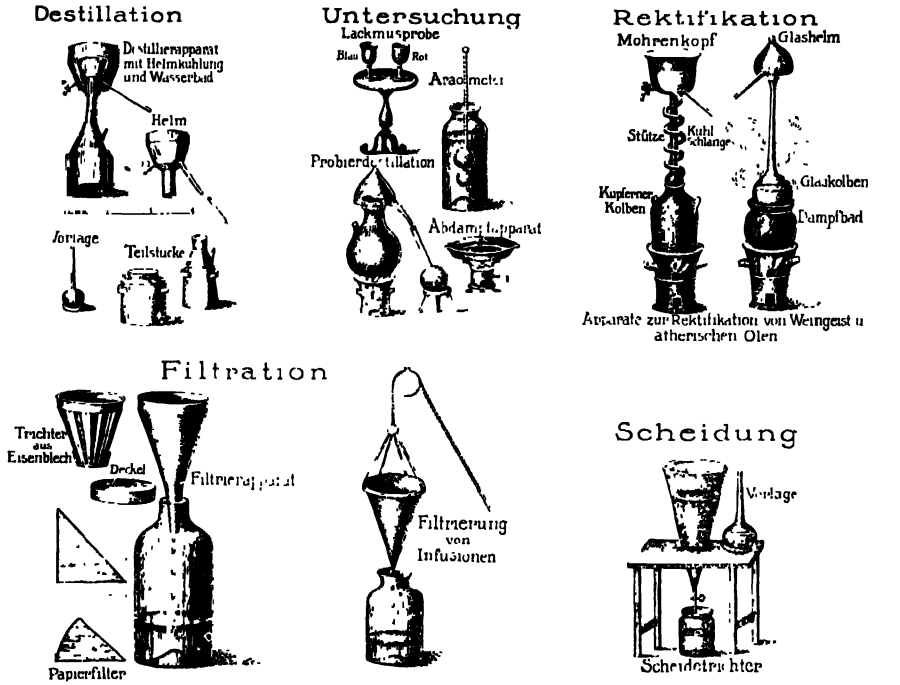


PLATE 147

Apparatus for obtaining ethereal oils, eighteenth century.

Rectification was done by redistillation. Note the illustration of filter paper and of a separating funnel with tap.

Distillation.
Distilling apparatus with cooled still-head and water-bath.
Still-head.
Investigation.
Litmus test.
Blue.
Red.
Hydrometer.
Test distillation.
Evaporating apparatus.
Rectification.
Moor's head.
Glass still-head.
Supports.
Spiral condenser.
Copper flask.
Glass flask.
Steam-bath.
Apparatus for rectifying spirits of wine and ethereal oils.
Filtration.
Funnel of sheet iron.
Lid.
Filtering apparatus.
Filter paper.
Filtration of infusions.
Separation.
Receiver.
Separating funnel.

stances, chalk and sulphuric acid. The two upper globes could be removed and shaken, thus causing the carbon dioxide to dissolve. This arrangement was improved by Parker, and later by Magellan. The saturation of water

with carbon dioxide under pressure was practised by Warltire (1776). Soda water was manufactured on a large scale by J. A. Weber (1781), Joseph Baader (1784), and Paul (in Geneva) (1789).

With the exception of pharmaceutical laboratories, there are not many illustrations of laboratories of this period (i.e. the end of the seventeenth and the beginning of the eighteenth century). This is partly due to the fact that few university laboratories existed at this date. The most famous example of a contemporary university laboratory is that of the Altdorf University at Nürnberg (1682), illustrated by Johann Moritz Hoffmann. It is a large and

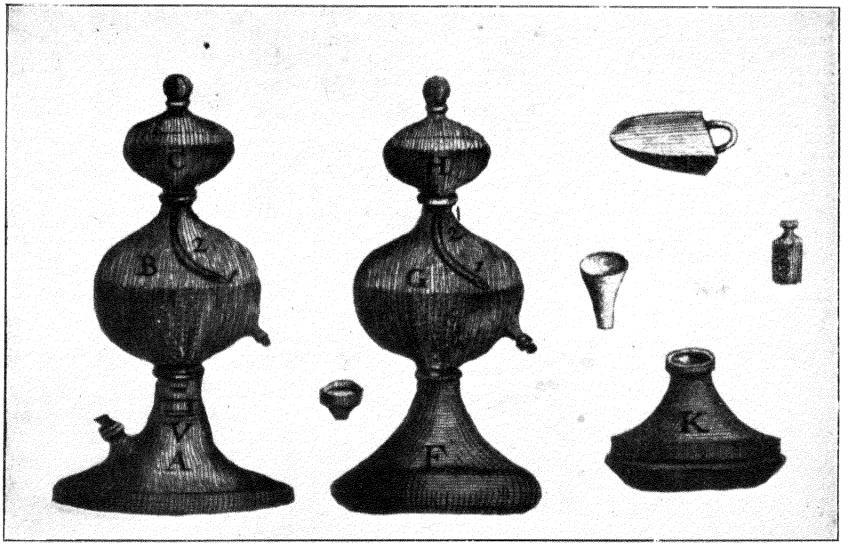


PLATE 148

Mineral water flasks : Parker and Magellan.

(Preparation of carbon dioxide from chalk and oil of vitriol.)

A Evolution vessel
B Absorption vessel
C Pressure vessel
} Parker

F Evolution vessel
G Absorption vessel
H Pressure vessel
} Magellan.

K Stand, funnel, measure, shovel.

magnificent laboratory, with furnaces for fusion, assaying, distillation (all under draught hoods), an iron laboratory furnace, fine glass vessels, alembics, sublimation apparatus, and many other things. The same building served as a lecture theatre and has a lecture desk and seats for the students. It does, however, give the impression of being designed more for appearance and show than for actually carrying out chemical work. J. K. Barchusen's laboratory at Utrecht is less grand, but probably much better adapted to real work.

The little vignette of one of Scheele's works shows a chemical laboratory

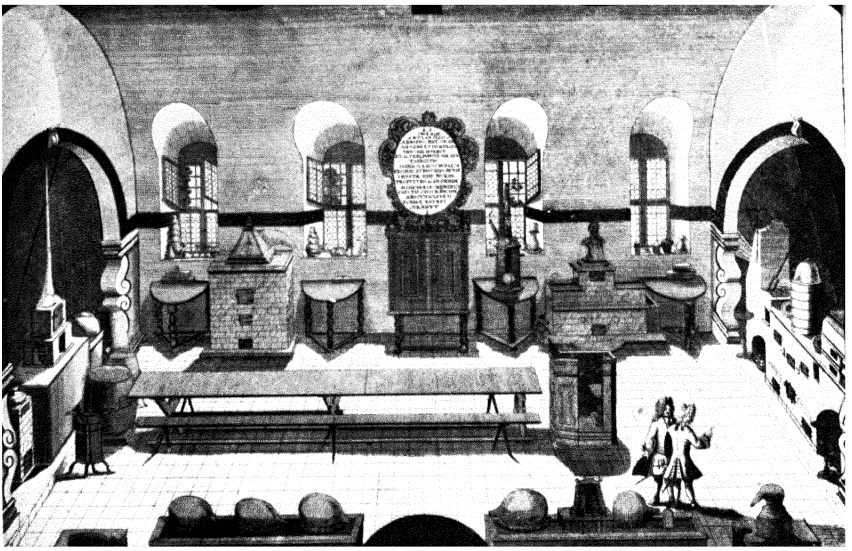


PLATE 149

The chemical laboratory of the Altdorf University.

The Altdorf university laboratory (1682), in late baroque style, is the earliest German university laboratory of which we possess a picture. It was thirty-six feet long, fifteen wide and fourteen high. It also served as an auditorium. Two large draught hoods with continuously burning furnace, bellows furnace, fusion furnace, assay furnace, lamp furnace, sand-, ash- and water-baths, steam distillation apparatus, "Moor's head" still, small iron furnace, interesting glass vessels in the windows. The excellent equipment gives the impression that it was used for display rather than for working with.

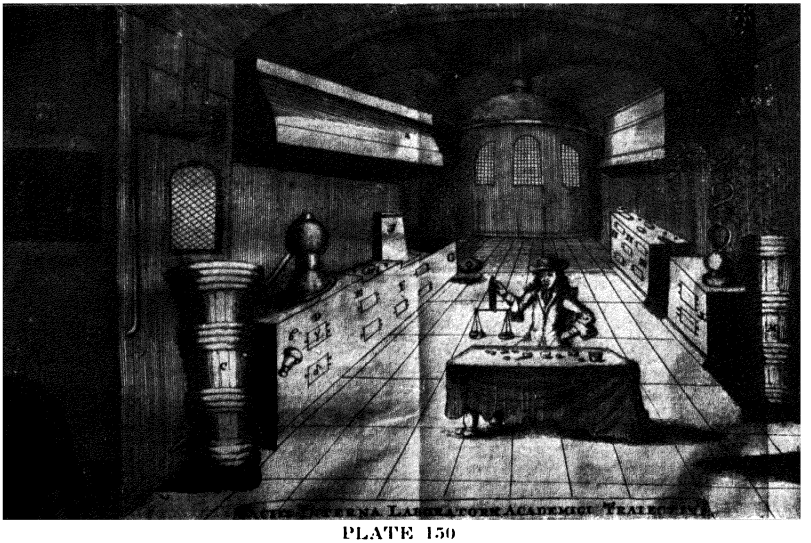


PLATE 150

Barchusen's laboratory at Utrecht, 1698.

Joh. Konr. Barchusen's laboratory shows a smelting furnace with bellows, stills with cooling vessels, digestion bath with fuel container, reverberatory furnace for retorts, cupel furnace for sand-bath distillation, etc.

which must have been old-fashioned even at that time. The apparatus depicted relates chiefly to the testing and separation of gold and silver. It must be regarded as an artistic composition rather than as a picture of Scheele's laboratory.

The picture of Priestley's laboratory, with the ordinary fireplace adapted to chemical use, illustrates chiefly the simple nature of Priestley's equipment.

The next good example of a chemical laboratory of this period is provided by the pictures in the *Dictionnaire raisonné des sciences, des arts et des métiers*, 1780.

The laboratory illustrated here is well designed. The furnaces and stoves stand under a large draught hood, though this, of course, was no innovation. Bellows fitted high up can be used to supply different furnaces at will. Besides old-fashioned vessels such as alembics, campana, aludels, there is also apparatus for preparing sulphuric acid by burning sulphur, vessels for measuring gases, and filtration stands. The whole equipment is, however, somewhat inferior to Lavoisier's.



PLATE 151

Analytical laboratory, about 1715.

From a chemical work published in 1715 under a pseudonym.

Illustrations of analysis of metals with draught hood and assay furnace, muffle, crucible, cupels, parting flasks, large scales for ore, small analytical balance in case, anvil and equipment for working metals.

There is much more material available in views of pharmaceutical laboratories. Of these we may mention the well-executed pictures of Balthasar Schnurin, 1676; the Capucins pharmacy in Paris; pictures of English laboratories in the "Universal Magazine," 1747; Caspar Neumann's pictures in Berlin, 1738; Hagen's picture of the Königsberg pharmacy, 1778; and

illustrations of the wonderful laboratories of the Berlin state pharmacy at the end of the eighteenth century.

The abundance of material in this field still further emphasises the fact

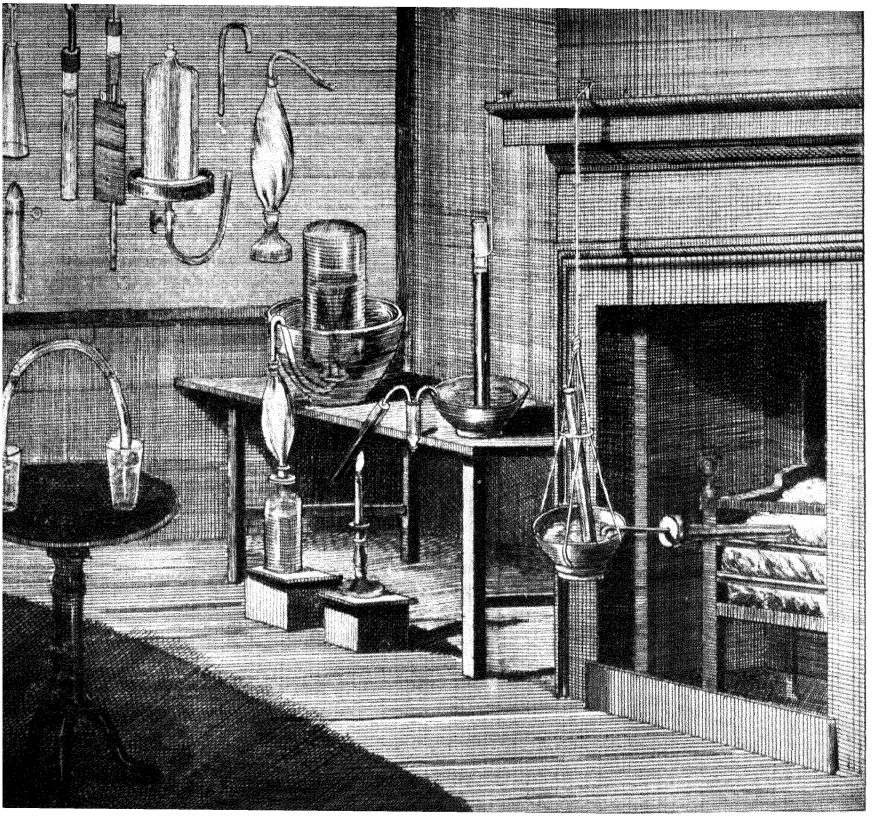


PLATE 152

J. Priestley's laboratory, 1775.

Important discoveries in pneumatic chemistry are due to Priestley, as recalled by this illustration. He introduced mercury as the confining liquid in the pneumatic trough (discovered in 1727 by Hales (1677–1761)). In this way he was able to collect and investigate gases which are absorbed by water (e.g. hydrogen chloride, sulphur dioxide and ammonia), or react with it (e.g. silica tetrafluoride). The picture shows a fire grate in which a gun-barrel is heated. The gases thus evolved are collected in a eudiometer over mercury. On the table is further apparatus for collecting gases, and on the small table on the left is an apparatus for investigating the action of electric sparks upon air.

that in the eighteenth century real practical chemistry was almost confined to the laboratories of pharmacies and metallurgical works. Right up to the end of the eighteenth century it was practically impossible for a student to study chemistry at a German college. Hardly any institutions had lectures

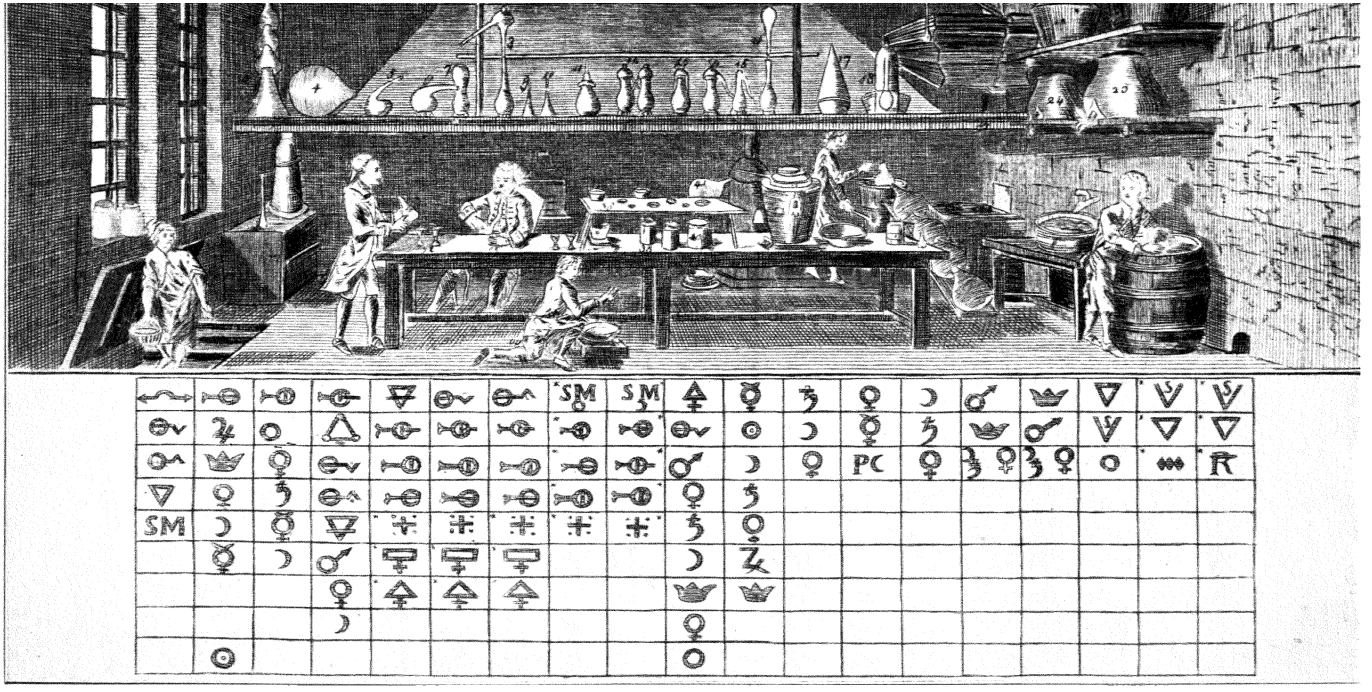


PLATE 153

Chemical laboratory, middle of the eighteenth century, and table of chemical affinity.

From "Dictionnaire raisonné des sciences, des arts et des métiers," 1780.

1. Powder glass. 2. Flask with glass beads. 3. Aludel for preparing flowers of sulphur (Stahl). 4. Large receiver. 5, 6. Retorts. 7. Testing flasks. 8. Glass flask with "Moor's head." 9, 10. Funnels. 11. Boyle's vessel for the oxidation of mercury. 12. Twin flasks. 13. Pelican. 14. Alembic with flasks. 15. Vessel for obtaining heavy ethereal oils (Wenel). 16. Reflux condenser. 17. Sublimation vessel for benzoic acid. 18. Apparatus for measuring the amount of gas formed by fermentation. 19, 20. Draught-hood. 21. Bellows. 22. Water-bath for a glass flask. 23. Vessel with double cooling coil. 24. Copper distilling flask. 25. Still-head for 24. 26. Laboratory assistant carrying coal. 27. Athanor (furnace with coal storage). 28. Digestion flasks. 29. Coal store. 30. Physicist and chemist discussing a solution. 31. Laboratory bench. 32. Glass vessels containing solutions of metals. 33. Chemist. 34. Assay furnace. 35. Funnel for filtering liquids. 36. Filter stand. 37. Vessel for collecting the filtrate. 38. Flask standing under the funnel. 39. Stoppered flask. 40. Flask closed with paper. 41, 42. Receivers for a retort which is in the furnace. 43. Furnace for evaporating dishes. 44. Chemist. 45 Apparatus for investigating the gases formed by igniting saltpetre mixtures. 46. Forge. 47. Water trough beneath the water supply. 48. Laboratory assistant cleaning vessels. 49. Water container. 50. Laboratory assistant.

with experiments, and still less practical classes. There was a laboratory at Jena where the able pharmacist J. F. A. Göttling (1753–1809) taught, but no practical work. There were also laboratories run by Pickel (1751–1838) at Würzburg, and by Franz Ignatz Menzinger (1776–1826) at Freiburg, but again no practical classes. Weigel at Greifswald and Joh. Tob. Mayer at Erlangen had no laboratories, and the same is true of most of the other universities in north and south Germany. At Tübingen, however, there were

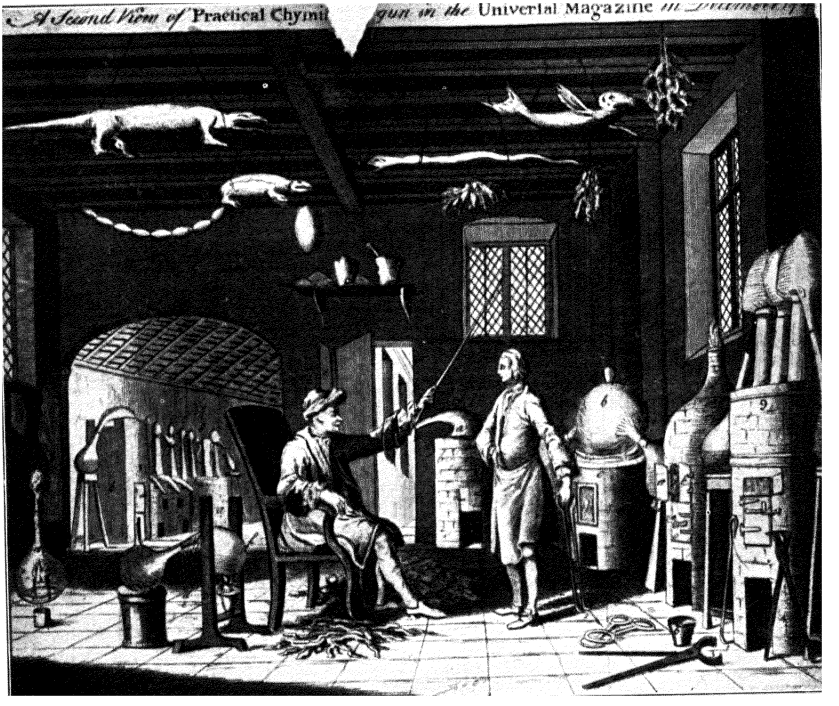


PLATE 154

English pharmacist's laboratory.
From the "Universal Magazine," 1747.

This picture gives the impression that up to the end of the eighteenth century distillation apparatus in all its varied forms was the most important equipment of a pharmacist's laboratory.

practical classes under Joh. Gg. Gmelin (1753–1755), Phil. Friedr. Gmelin (1755–1768), and later K. F. Nielmayer (1796–1817). Similarly, at Freiberg (Saxony) Wilh. Aug. Lampadius gave practical instruction in the laboratory of the mining school from 1794 onwards.

At the university of Ingolstadt the pharmacist G. L. Rousseau taught pharmacy and chemistry, using the German language and carrying out experiments (1760–1794). R. G. Hagen, pharmacist and professor at Königsberg, had a laboratory from 1779 to 1829.

INDUSTRIAL CHEMISTRY

THE technique of preparing mineral acids, founded by Glauber, was considerably improved in France. Thus Demachy describes improvements in the manufacture of nitric acid, and Kasnau (nineteenth century) gives illustrations of improved methods of obtaining oil of vitriol. H. C. Duhamel du Monceau (1700–1782) introduced many technological improvements, e.g. in connection with sal-ammoniac, soap and starch. He was one of the first to

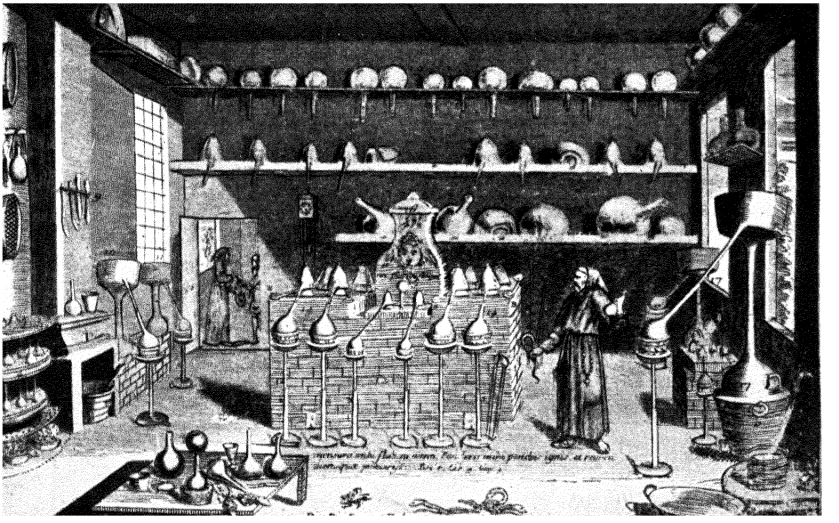


PLATE 155

The laboratory of the Capucins pharmacy, Paris.

Laboratory with numerous arrangements for distillation : alembics and " Moor's heads " of glass and copper, stove with arrangement for continuous burning, water-baths and sand-baths.
The vipers (Coluber Vipera) visible in the picture were of considerable medicinal importance from the middle ages right up to recent times. They were used not only for preparing theriak, but also for a number of other purposes. Vipers' hearts were used as a remedy for love potions and bewitchments, and their livers for Dysenterica epidemica or maligna. Essentia viperarum was prepared from hearts and livers by drying, powdering and extracting with spirits of wine. Viper fat (Pinguedo viperarum) was much used as a remedy for goitre and as a cosmetic for the skin and hair. Whole vipers were much used for preparing Theriaka Andromachi, and old pharmacopœias provide numerous recipes for preparing viper broths, viper tablets, viper oil and many specifics against plagues containing vipers.

make soda from common salt. The sulphate was converted to the sulphide by heating with carbon, the sulphide to acetate, and the acetate to carbonate by calcination. It may be noted that his method includes parts of the Leblanc process. The next step was the work of the unhappy Nicolas Leblanc (1742–1806), who cheated the French Revolution out of his discovery, and then committed suicide. He heated the sulphate with a mixture of coke and lime-

stone, so that on extracting the mass a solution of soda was obtained directly, leaving a residue of calcium sulphide.

The Leblanc soda industry was a necessity, since the supply of soda from mineral and vegetable sources could not possibly meet the demand. The soda industry presupposes the manufacture of sulphuric acid, which also led on to that of chlorine, hydrochloric acid and caustic alkali.

The beginning of the eighteenth century saw the start of the chamber process of sulphuric acid manufacture. This process is derived from the preparation of sulphuric acid *per campanam*, a method mentioned by Biringuccio, known to Libau, and first described clearly by Le Fèbre (Le

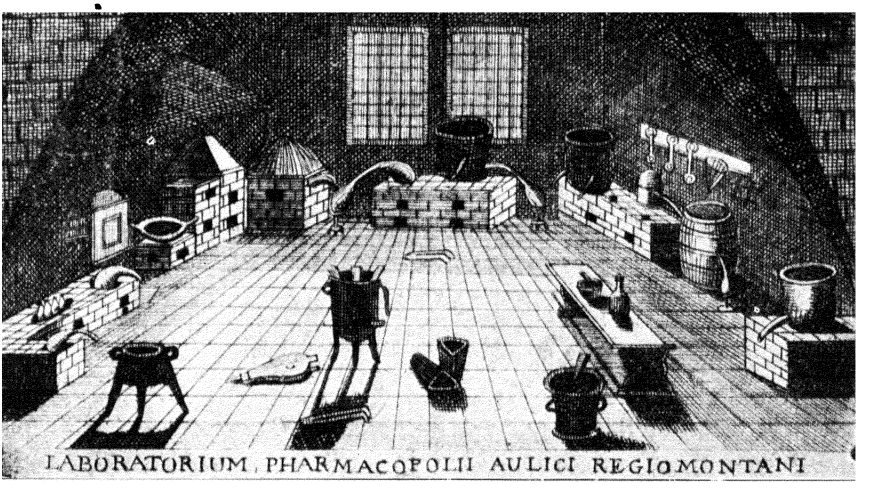


PLATE 156

The laboratory of the royal state pharmacy at Königsberg.

Engraving taken from "Lehrbuch der Apothekerkunst," by Karl Gottfried Hagen, Königsberg, 1778.

Note the simple arrangements: furnace constructed of bricks, small iron stove, arrangements for digestion, etc. The impression is received that work was really done in this laboratory.

Febure). M. Charas (1618–1698) and Lémery give good illustrations of the preparation of chamber acid in the laboratory. Quantities of saltpetre and sulphur were burnt under a bell-jar and the product absorbed in small quantities of water. An earthenware pot was generally used containing a crucible for the combustion and surmounted by a glass bell-jar.

The first large plant was that of Ward at Richmond in 1736, which used large glass vessels, saltpetre, sulphur and a little water. Early plant was also set up in Holland and in Rouen. Demachy also describes large glass globes. These were not, however, sufficiently large or durable, and were therefore replaced by rectangular lead chambers, the first lead chamber plant being that of

Roebuck at Prestonpans, 1744 or 1749. The first German lead chamber process was erected by Baron von Waitz at Ringkuhl near Grossalmerode.

In 1793 it was shown by Clément and Desormes that the oxidation of the sulphur dioxide was not actually carried out by the saltpetre, but by the air, which had to be renewed. The enormous sulphuric acid industry is thus the work of the eighteenth century. Hydrochloric acid is a by-product of the Leblanc process, and can be used for making chlorine (with pyrolusite, cf. Scheele), thus leading to bleaching with chlorine or chloride of lime (1798).[1]

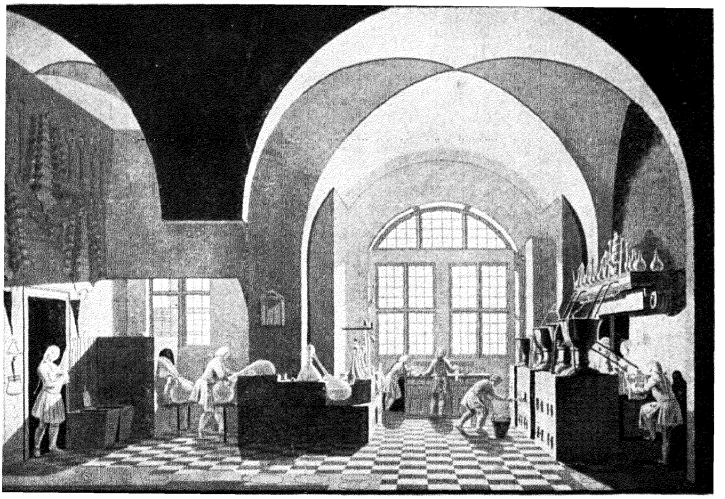


PLATE 157

Laboratory of the former royal state pharmacy in Berlin, second half of the eighteenth century.

From a contemporary glazed pen-and-ink drawing.

Many famous men worked in the laboratory of the state pharmacy, notably Caspar Neumann and his most famous pupil Andreas Sigismund Marggraf, who in the years 1725–1730 received pharmaceutical and chemical instruction there.

The illustration shows a still-room with a large stock of glass ware (alembics and retorts), also large copper stills, probably for preparing products containing spirits of wine.

The Manufacture of Gas

The formation of combustible gas on heating coal was known as early as 1530. The manufacture of coke began in England in 1640, followed by Clayton (1664), Shirley (1667), J. J. Becher (1682), Hales (1726), Watson (1769), Lord Dundonald (1796). The name " coke " has existed since 1669. In 1781 the Belgian professor P. Minkelaers lit his laboratory at Löwen with coal gas.

[1] The manufacture of phosphorescent material was founded by Casciarolus with his phosphorescent barium sulphide, and continued by Chr. Ad. Baldewein with the discovery of phosphorescent calcium sulphide. Franz Hofmann prepared phosphorescent material in 1700 by reducing gypsum, and Lémery from barium sulphate in 1730. He was able to modify the light by the addition of copper, iron or zinc. Marggraf knew that the substances concerned were sulphides of calcium and barium, but the necessity of additions was not realised until later.

The knowledge of wood gas goes right back to antiquity. Various people in the eighteenth century produced wood gas for illumination, e.g. Philipp Lebon (1785) and the pharmacist W. A. Lampadius (1799) in Freiburg-Halsbrugge.



PLATE 158

View in the laboratory of the former royal state pharmacy in Berlin.

Second half of the eighteenth century, contemporary glazed pen-and-ink drawing. The picture shows a second room with an ornamental draught-hood, assay furnace, fine athanor, fountain and large stock of glass apparatus.

The pharmacist Erxleben manufactured illuminating gas from animal remains. All these used iron retorts.

The true founder of gas lighting was, however, the Scottish engineer William Murdoch (1754–1839), who experimented with arrangements for gas lighting from 1792 onwards in his house at Redruth. The first permanent gas lighting was the installation in Soho in 1802. These early workers removed hydrogen sulphide from the gas by means of lime, as discovered by Minkelaers. The first gas-holders were modelled on the pneumatic laboratory vessels.[1]

[1] Laboratory gas-holders were constructed by Beddoes, 1796, and Pepys, 1802.

Metallurgy

The flourishing metallurgical industry of Germany was brought practically to a standstill by the Thirty Years War. Thus in Mansfeld about 1668 the annual output of copper was about 300–400 hundredweights instead of the previous 20,000–30,000. In the seventeenth century Freiberg produced about 10,000 gulden instead of the previous 50,000. It was not until the second half of the eighteenth century that these industries began once more to flourish.

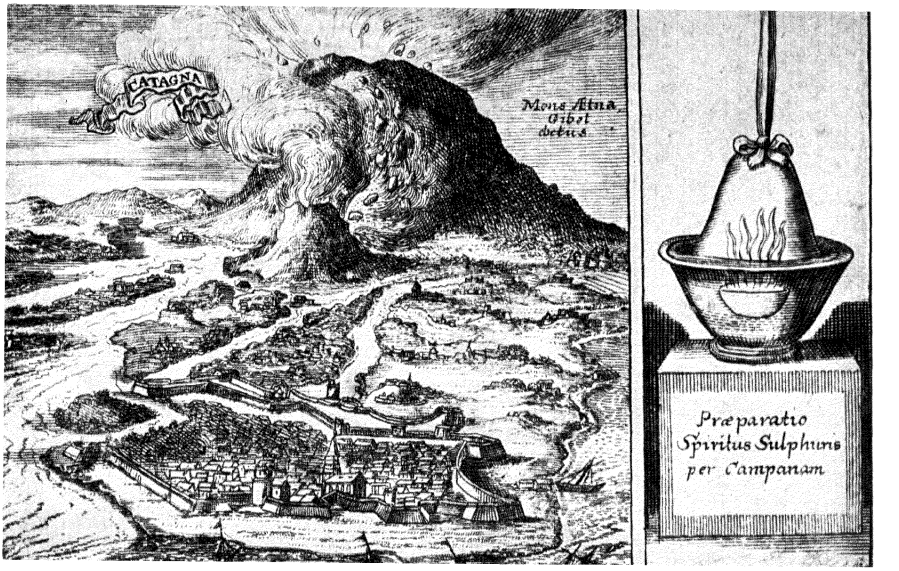


PLATE 159

"*Von dem lebendigen Schwefel*," *M. B. Valentini*, 1704.

The illustration of the volcano Etna in a Sicilian landscape serves to remind us of the volcanic origin of sulphur, and that its chief source is Sicily.
The drawing on the right is apparatus for "Præparatio Spiritus Sulphuris per Campanam," i.e. chamber sulphuric acid. A mixture of sulphur and saltpetre is ignited in a refractory crucible standing in an earthenware basin containing water and covered by a glass bell-jar. Sulphuric acid is formed.

This is true of the Amberg iron industry, the Harz mines, Schlesien, Lothringen and Saar. The Siegen iron industry appears to have suffered least by the Thirty Years War, and must have provided arms and ammunition towards the end of the war.

The production of coke for the purpose of iron smelting, introduced by Abraham Darby, dates from about 1735. The first blast furnace using coke was erected at Coalbrookdale in Shropshire. The first coke blast furnace in Germany was that of Freiherr von Reden at Gleiwitz, 1796.

Among other improvements in the iron industry we may quote the following :—

René Antoine de Réaumur (1673–1757) improved the methods of steel production, especially by cementation.[1]

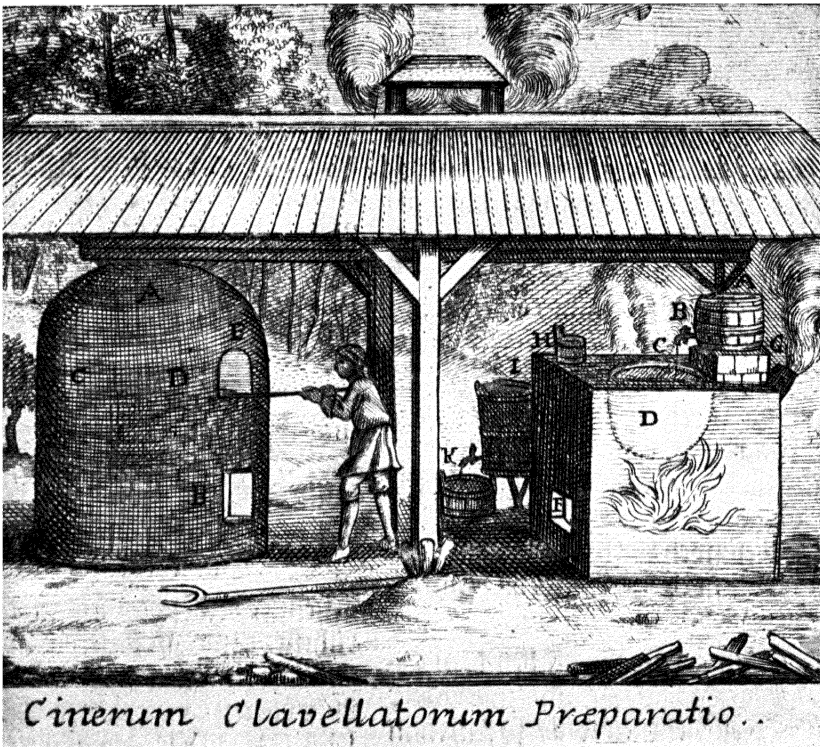


PLATE 160

Manufacture of potash, M. B. Valentini, 1704.

Valentini differentiates between wood ash, prepared for use as a colouring matter from incinerated wine lees, and ordinary potash, originally prepared from the ash of old wine barrels, later from the ash of oak or other wood.
The ash is mixed with water in the butt L and the solution tapped off into the vessel K, the process being repeated if necessary. The lye was then evaporated down in the boiler D, being replaced from B as fast as it boils away. The potash is then removed from the boiler with a chisel. In order to make it white it is heated strongly in the furnace AC.

An extremely important advance in the metallurgy of iron was made in England in 1784, when the puddling process was discovered by Henry Cort (1740–1800). This process contributed considerably to the pre-eminence of England in the iron industry for the next hundred years. Coal could be used

[1] Réaumur was the founder of the famous work in many volumes, *Description des arts et métiers*, the greatest technological work which has ever existed. Even up to the present time no work has appeared which even approximately corresponds to Réaumur's, in spite of the urgent need for such a book.

in the puddling furnaces, since the iron does not come into direct contact with the fuel.

About 1740 the Englishman Benjamin Huntsman discovered the crucible process for making steel.

Glass Manufacture

was advanced considerably by Johann Kunckel (1630–1703). Although Kunckel owed a great deal to P. Antonio Neri (whose work on the manufacture of glass he translated, with additions in 1679), the new empirical discoveries which he made himself are worthy of mention. He knew how to decolorise glass with pyrolusite and arsenic, and made many types of coloured glass. His colouring matters were copper oxide, verdigris, pyrolusite, ferric oxide, magnetic iron oxide, sulphides of potassium, sodium, iron, antimony and arsenic; carbon, cobalt oxide. He also knew how to make white cloudy glass with zinc oxide or bone ash.

He is best known for his ruby glass, i.e. glass coloured red by means of gold. He was in fact an adept at this technique, but he did not discover it, as gold ruby glass was known even to the ancients. In the second half of the seventeenth century both Libau and Glauber knew how to prepare colloidal gold in a form useful in practice, founded on "purple of Cassius." This work was of great assistance to Kunckel. Further, as Kunckel himself admits, Neri also gives a recipe for ruby glass which leads to the desired result. The statement that Kunckel used borosilicate glass for imitating precious stones

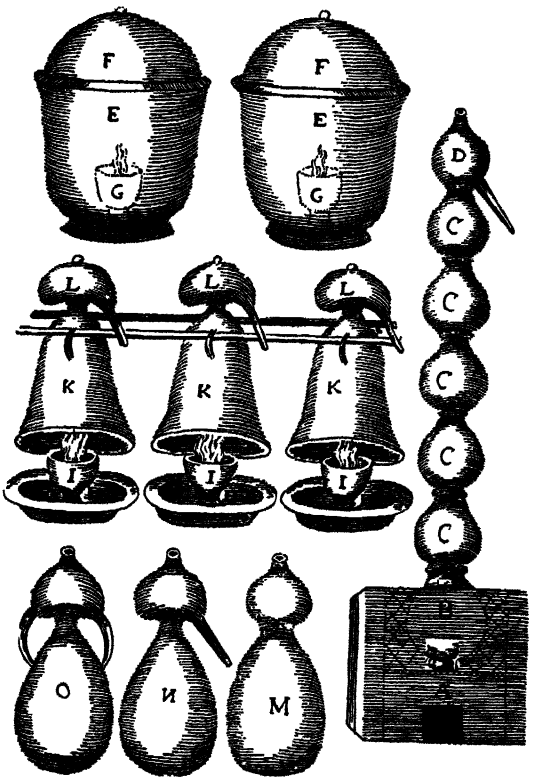


PLATE 161

Apparatus of M. Charas, 1676.

From Charas "Pharmacopée Royale Galénique et Chimique," Paris, 1681.

A–D Aludel on furnace. E Earthenware pots for making sulphuric acid. F Glass bell-jar for the same purpose. G Crucibles for sulphuric acid combustion. H Large glass plates. I Crucibles for sulphuric acid combustion. K. Glass bell-jar. L Still-head. M. Circulating vessel. N. Glass alembic in one piece. O Pelican.

is badly in need of confirmation by analysis of some of the many examples of his work still extant.[1]

The greatest advance in European *ceramic industry* was the rediscovery of genuine Chinese porcelain, made in 1709 by the pharmacist's assistant, Johann Friedrich Böttger.



PLATE 162

Glass blower, from Abraham a Santa Clara, second half of the seventeenth century.

Oil or spirit lamp with foot bellows: fine draught-hood.

In recent times attempts have been made in some quarters to attribute the chief share in this discovery to Ehrenfried Walter von Tschirnhaus (1651–1708) who has come to be regarded as the scientific superintendent of the alchemist Böttger. There is no sufficient documentary or traditional evidence for this assertion; moreover, Tschirnhaus was no longer alive in the year

[1] Kunckel had no higher education, but it is easy to see that he was a skilful practical worker. He worked on phosphorus shortly after Brand, and prepared both ethyl nitrate and ethyl nitrite in 1681.

1709 when the discovery was made. The historian therefore cannot deprive Böttger of this discovery, even though he may have been an outsider and not entirely unobjectionable as a person.

The immediate predecessor of white porcelain was the discovery of the red Chinese stoneware (which was known as Böttger stoneware, never as Tschirnhaus stoneware). White porcelain was not discovered until after Tschirnhaus' death, and reached its full height at the Meissen porcelain works, 1715.

The eighteenth century also saw the first production of white ware, which was unsintered opaque pottery, either white or coloured. Its production depends on the admixture of flint with clay, discovered by Astbury in 1720.

Mention may also be made of Réaumur's frit porcelain (about 1700) and the English bone china (Chaffers, 1752).

Nicolas Jacques Conté (Paris, 1794) discovered the use of graphite mixed with clay for making *lead pencils*, and knew how to produce different degrees of hardness by heat.

Great importance attaches to the discovery of artificially prepared *cement* by Smeaton in England in 1756: cf. also Parker (1796).



PLATE 163

Franz Karl Achard (1753–1821).

A pupil of A. S. Marggraf, he founded the sugar-beet industry, the first sugar factory being started in 1801. His labours first bore fruit during the Napoleonic blockade When the blockade was lifted, most of the factories closed down, and did not begin to flourish again until about 1825, after Achard's death.

The German *sugar industry* derives from S. Marggraf's discovery of cane-sugar in beetroot (1747). A pupil of Marggraf, Franz Karl Achard (1753–1821), developed the discovery and evolved a method of extraction essentially the same as that used to-day. In the year 1799 he was able to present a sample





1 2

PLATE 164

Medal commemorating Andreas Sigismund Marggraf.
Struck by the Swedish designer Adamson.
1. Front. 2. Back.

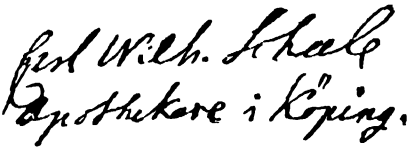


PLATE 165

Scheele's signature (1786).



PLATE 166

The laboratory of the royal state pharmacy at Konigsberg.
Title vignette from "Lehrbuch der Apothekerkunst," by Karl Gottfried Hagen, 1778.

of beet sugar to King Friedrich Wilhelm III of Prussia. (Chicory root was first used in 1771 as a coffee substitute.)

Improvements in the production of *alcoholic liquors* were made by Antoine

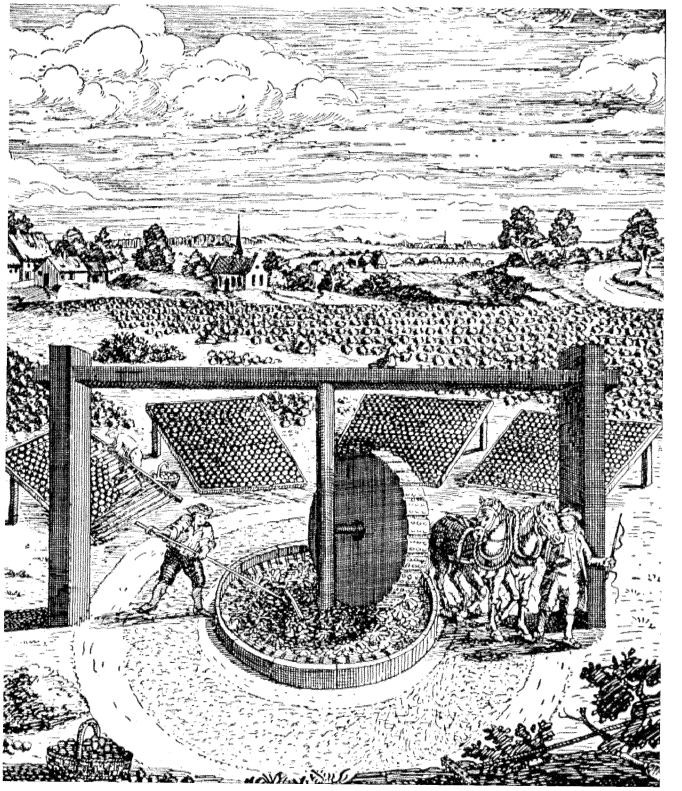


PLATE 167

Woad mill (Schreber, 1752).

The picture shows the treatment of woad (Isatis tinctoria), which was previously used as a blue dye for textiles. The manufacture of woad was at one time of considerable importance in Germany, but after the discovery of the sea route to the East Indies by the Portuguese it was gradually displaced more and more by Indigofera tinctoria, which contains more indigo and is therefore preferred. In many old pharmacies it is still possible to find "Herba Isatidis tinct." in the form of balls, consisting of the crushed woad plants formed together into balls the size of small apples. The picture shows the crushing mill surrounded by drying places for the ball woad. In the left foreground is a basket containing the finished product. The large mill-stones with which the woad was crushed can still be found in Thuringia used as garden tables in country inns. The last woad mill in Thuringia was in Pferdingsleben, and ceased working in 1907.

Baumé by technical work on distillation apparatus and the introduction of hydrometers for measuring alcoholic content (1768).

The manufacture of spirits from potatoes is mentioned by Becher (1685),

but does not appear to have been practised until later. The first potato distillery in Germany started production at Monsheim (1750). In 1709 Giovanni Maria Farina at Cologne started the sale of eau de Cologne, which he had invented.

Rubber manufacture also began (very modestly) in the eighteenth century. Rubber was first brought to Europe by Ch. M. de la Condamine (1736). It was of course discovered by the Indians (first mentioned by Oviedo y Valdez, 1535). Rubber tubes were first made by Grossart in 1768 (at the suggestion of Herissant and Macquer) and in 1770 by Priestley, who also first used rubber erasers.

CHEMISTRY IN THE BEGINNING OF THE NINETEENTH CENTURY

We have already seen that the important foundations of the giant structure of modern chemistry were laid by the great chemists of the eighteenth century. However, many of these foundation stones needed reinforcing.

Although the *law of constant proportions* had been demonstrated clearly by Wenzel in practice and by Proust in theory, some extensions were found necessary. Boyle knew that two given substances could sometimes combine together in more than one way, e.g. cuprous and cupric chlorides, mercurous and mercuric chlorides. Cruikshank showed later (1801) that both carbon monoxide and carbon dioxide consisted only of carbon and oxygen, thus constituting a particularly interesting example of this phenomenon.

It was Dalton, himself a bad analyst, who gave a theoretical description of the facts by adding the *law of multiple proportions* to the law of constant proportions. This law of multiple proportions states that if two elements combine together in more than one proportion, then the quantities of the one element combined with a given quantity of the other element in the different compounds bear a simple relation to one another.

It would be very satisfying if Dalton's *atomic theory* had been based on this discovery, since the law of multiple proportions can only be satisfactorily explained by means of the atomic theory. Unfortunately, however, this was not the case, since Dalton's revival of the atomic theory was chiefly a speculative piece of deduction on his part.

John Dalton (1766–1844) advanced the atomic theory in the year 1802. He emphasised clearly the theoretical condition that the ultimate particles of homogeneous substances (elements) should be identical in their weight, form and all other properties, and he regarded it as the most important aim of chemistry to determine the relative weights of these particles. Dalton denoted the elements by means of symbols, which were not, however, adopted by contemporary chemists. It was left to Berzelius to complete what Dalton had aimed at, i.e. the determination of atomic weights and a universal system of symbols.[1]

Dalton was fundamentally correct in his assumptions. His symbols represented atoms, characterised as regards both quality and quantity (weight). According to him compounds also consist of ultimate particles (molecules), formed by the union of atoms.

A well-presented *molecular theory* was first worked out by Avogadro in 1811 and Ampère in 1814. Amadeo Avogadro di Quaregna (1776–1856)

[1] The atomic theory did not of course originate with Dalton, but was proposed by various Greek philosophers, especially Democritus, who denied the unlimited divisibility of matter. It is clear that this denial must have appeared contrary to common sense, since the limited divisibility of matter can only apply within certain limits and under certain conditions. Before the discovery of the law of multiple proportions there was no real necessity for the chemist to adopt the atomic theory.

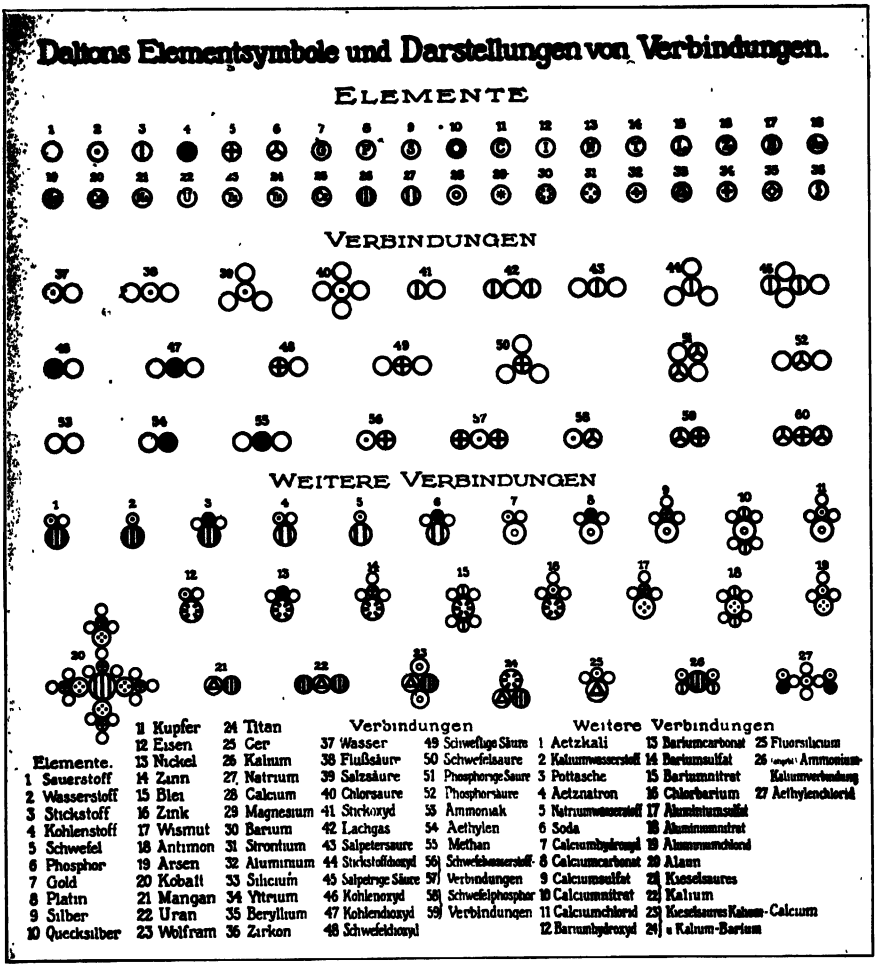


PLATE 168 (A Key will be found on the opposite page).

Dalton's symbols for elements and compounds.

Elements. Compounds. Other compounds.

advanced his famous law, according to which under the same conditions equal volumes of gases contain equal numbers of molecules. A necessary prelude to this law was Gay-Lussac's law, which stated that gases react in definite proportions not only by weight but also by volume (1805).

Avogadro's law made it possible to determine the *molecular weights* of substances from their densities in the gas state.[1]

[1] The clearest definition of molecular weight is that due to Laurent, which states that the molecular weight of an element or compound is that weight of it which in the gaseous state occupies the same volume as two atoms of hydrogen under the same conditions.

KEX TO PLATE 168

Elements.

1. Oxygen.
2. Hydrogen.
3. Nitrogen.
4. Carbon.
5. Sulphur.
6. Phosphorus.
7. Gold.
8. Platinum.
9. Silver.
10. Mercury.
11. Copper.
12. Iron.
13. Nickel.
14. Tin.
15. Lead.
16. Zinc.
17. Bismuth.
18. Antimony.
19. Arsenic.
20. Cobalt.
21. Manganese.
22. Uranium.
23. Tungsten.
24. Titanium.
25. Cerium.
26. Potassium.
27. Sodium.
28. Calcium.
29. Magnesium.
30. Barium.
31. Strontium.
32. Aluminium.
33. Silicon.
34. Yttrium.
35. Beryllium.
36. Zirconium.

Compounds.

37. Water.
38. Hydrofluoric acid.
39. Hydrochloric acid.
40. Chloric acid.
41. Nitric oxide.
42. Nitrous oxide.
43. Nitric acid.
44. Nitrogen peroxide.
45. Nitrous acid.
46. Carbon monoxide.
47. Carbon dioxide.
48. Sulphur dioxide.
49. Sulphurous acid.
50. Sulphuric acid.
51. Phosphorous acid.
52. Phosphoric acid.
53. Ammonia.
54. Ethylene.
55. Methane.
56. } Compounds of sulphur
57. } and hydrogen.
58. } Compounds of sulphur
59. } and phosphorus.

Other compounds.

1. Potassium hydroxide.
2. Potassium hydride.
3. Potassium carbonate.
4. Sodium hydroxide.
5. Sodium hydride.
6. Sodium carbonate.
7. Calcium hydroxide.
8. Calcium carbonate.
9. Calcium sulphate.
10. Calcium nitrate.
11. Calcium chloride.
12. Barium hydroxide.
13. Barium carbonate.
14. Barium sulphate.
15. Barium nitrate.
16. Barium chloride.
17. Aluminium sulphate.
18. Aluminium nitrate.
19. Aluminium chloride.
20. Alum.
21. } Potassium
22. } silicate.
23. Potassium calcium silicate.
24. Potassium barium silicate.
25. Silicon fluoride.
26. Ammonium potassium compound.
27. Ethylene chloride.

The determination of atomic weights was effected by determining their smallest combining weights. This was due partly to Wenzel, and, above all, to Berzelius. By 1818 Berzelius had measured and published over two thousand molecular and atomic weights. The true state of affairs was however first understood completely by Cannizzaro, 1858.[1]

[1] This may be seen from the following statement by Cannizzaro: "It is found from analyses of compounds containing hydrogen that they never contain a smaller amount of hydrogen than half a molecule. This is, therefore, as far as we know, the smallest quantity of hydrogen which can exist, i.e. the atom of hydrogen. The hydrogen molecule thus consists of two atoms, and the molecular weight of hydrogen is equal to twice its atomic weight." The polyatomic nature of the molecules of many elements was not known to Berzelius and his contemporaries.

Berzelius referred atomic weights to oxygen = 100 instead of to hydrogen = 1. In order to give some idea of the reliability of his determinations, we may quote the following figures (converted to the basis of hydrogen = 1): carbon = 12·12, oxygen = 16, sulphur = 32·2. Other values were, however, twice too great, e.g. lead = 416, mercury = 406, iron = 109·1, copper = 129, and some even four times too great, e.g. sodium, 93·5, potassium, 157·6, silver, 433·7. These two- and four-fold errors arose from the fact that Berzelius assumed that only one atom of an element could be present in a compound. In 1826 he gave a new and more correct table, in which only potassium, sodium and silver were given twice the correct values: other values were: chlorine = 35·47, phosphorus = 31·4, arsenic = 75·3, copper = 63·4, etc.

Another problem was the elucidation of the *causes of chemical change*, a question which is still incompletely cleared up. Newton, Bergmann and Buffon attributed chemical processes to gravitation, though Wenzel did not share this view. It was displaced by the electrochemical theory, sponsored by Davy and Berzelius. On the basis of his electrical experiments Davy concluded that the combination of chemical substances was equivalent to the neutralisation of electrical differences. The greater the electrical difference, the greater the corresponding chemical affinity. By supplying electricity to the compounds (electrolysis) they are split up into components having the same polarity as before combination took place. The positive components (metals) migrate to the negative pole, and the negative (non-metallic) components to the positive pole.

Berzelius assumed in 1812 that the atoms themselves were electrical, possessing an excess of either positive or negative electricity. According to the nature of this excess substances were classified as positive or negative. This excess electricity was the cause of chemical affinity. According to Berzelius the chemical combination of elements or compounds (e.g. acids and bases) consists in the attraction of the opposite poles of the atoms, and the consequent electrical neutralisation.

According to this view all chemical compounds must consist of two parts differing in their electrical character: hence the so-called *dualistic system*. The idea that organic compounds (as well as inorganic) were constructed in this way was advanced specially by Liebig. Thus organic radicals such as ethyl, C_2H_5 (or as Liebig then wrote it C_4H_{10}) were supposed to be combined with acids to form esters in the same way that oxides combine with acids to form salts.

These views did not prove tenable. In contrast to Berzelius' electrochemical radical theory Dumas proposed in 1839 his theory of types, which has been termed the *substitution theory*. In place of the dualistic theory he proposed a *unitary theory*, according to which a compound does not consist of two parts, but is a single whole. Thus for example when the three electropositive hydrogen atoms in acetic acid are replaced by three electronegative chlorine atoms (giving trichloracetic acid), the character of the acetic acid remains essentially the same. Dumas concluded that in organic chemistry

there must exist certain types, which retain their character even when atoms are exchanged for atoms of other elements.

Gerhardt combined Dumas' theory of types with the radical theory in his *theory of residues*. Residues are groups of atoms which are bound together by very strong affinities and are therefore not split up in the interaction of different substances. They then combine together, since they cannot exist alone. Gerhardt adopted the substitution theory of Dumas, but introduced the assumption that groups of atoms (i.e. residues) can also act as substituents. Until quite recently little advance has been made on this view.

New methods of atomic weight determination were provided by Dulong and Petit's law and Mitscherlich's rule of isomorphism. F. L. Dulong (1785–1838) and T. A. Petit (1791–1820) found from their experiments that the specific heats of a series of solid elements (mostly metals) were roughly inversely proportional to their atomic weights. For most metals they established the rule that the product of the atomic weight and the specific heat has the constant value 6·4.

E. Mitscherlich (1794–1863) realised in 1819 the relations between crystal form and chemical constitution. He explained the occurrence of isomorphous crystals by assuming that they correspond to analogous chemical composition, e.g. the phosphates and arsenates : the oxides of zinc and magnesium : the oxides of iron, chromium and aluminium : the salts of selenic and sulphuric acids. Berzelius was the first to derive atomic weights from considerations of isomorphism.

Chemical Symbols

Berzelius constructed his system of symbols in the year 1814. Like Hassenfratz he used letters from the Latin names of the elements, either the first letter, or (in the case of metals) the first two, or, if this would cause confusion, the first letter together with the first consonant which does not occur in the name of other elements with the same initial letter. To begin with he wrote plus signs between the symbols for the elements, in keeping with the dualistic theory. In 1819, however, he used a method of writing practically identical with that in use to-day. Double atoms were, however, denoted by a hyphen near the bottom of the symbol. He always wrote salts with a plus sign between the metallic oxide and the acid oxide. Oxygen atoms could also be shown by a raised dot, and sulphur atoms by a raised comma. The electro-positive part of the molecule was written first, as to-day.

Berzelius had the good idea of denoting radicals by symbols. Not all contemporary chemists adopted Berzelius' symbols at once : thus they are not used by Faraday, or in Gmelin's 1821 *Handbuch*. Liebig used them largely, but did not write the figures above the symbols on the right, like Berzelius, but below them on the right, as we do to-day. Döbereiner wrote them directly above the symbols. Liebig discarded the dots and commas, but unfortunately discarded also the symbols for radicals, instead of extending them.

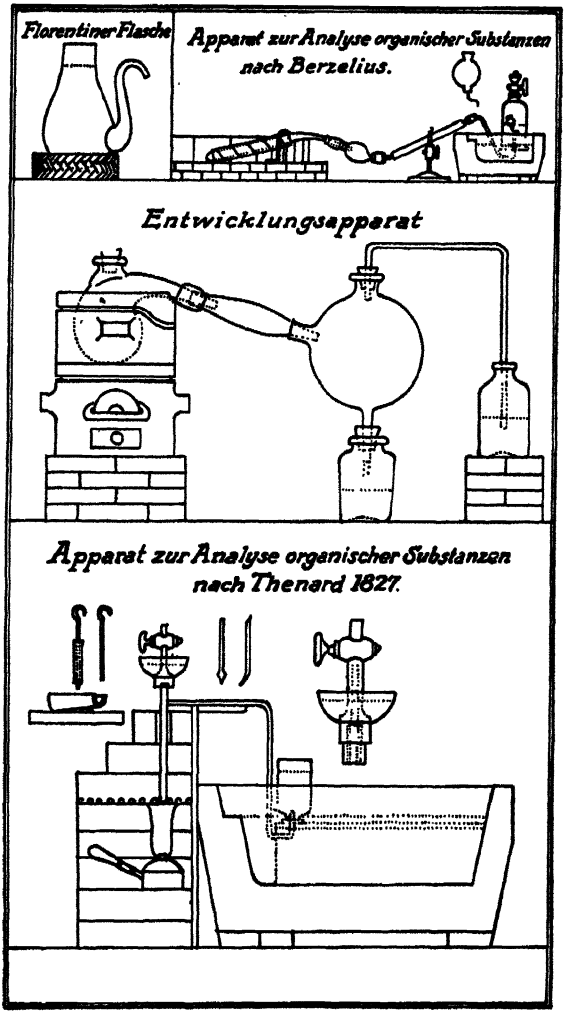


PLATE 169

Apparatus from Thenard's text-book, 1827.

Below is Thenard's apparatus for elementary analysis, combustion by means of potassium chlorate.
Above Berzelius' apparatus for the same purpose. The potash vessel floats on mercury under the bell-jar.
1. Florence flask.
2. Apparatus for analysing organic substances : Berzelius.
3. Apparatus for gas evolution.
4. Apparatus for analysing organic substances : Thenard, 1827.

Walden has quite rightly maintained that Berzelius' symbols are quite inadequate to-day. not being adapted to modern knowledge. They gave no information about state of aggregation or crystallisation, dissociation, valency electrons, or the energy changes associated with chemical processes. Walden has justly pointed out that the substance corresponding (for example) to NaCl does not exist at all.

Organic Chemistry

The complete foundation of organic chemistry belongs to this period. One of the most important requirements was the development of a satisfactory method for analysing organic compounds.

Lavoisier had devised a method, but the results were unsatisfactory. The further development was carried out by Gay-Lussac and Thenard (1810) (combustion with potassium chlorate), Berzelius (1814) (weighing the water and carbon dioxide formed), Gay-Lussac (1815) (use of copper oxide in combustions). In 1821 Avogadro made correct analyses of alcohol, ether, ethyl chloride, ethyl iodide and urea. Prout supplied oxygen in his analyses, at the suggestion of Saussure. In 1828 Saussure analysed dextrose.

In 1830 Dumas introduced a satisfactory method of determining nitrogen, and improved it in 1833. Liebig practised organic analysis with great success from 1831 onwards, and designed an efficient potash bulb. Since that time nothing has been fundamentally altered. The use of lead chromate was introduced by Berzelius in 1838.

The First Syntheses of Organic Compounds from their Elements

As already mentioned, the first synthesis of an organic substance from inorganic materials was Scheele's preparation of prussic acid (1783). We may also mention the preparation of prussic acid from ammonia and carbon (Clouet, 1802) and of thiocyanic acid from potassium cyanide and sulphur (Rink, 1804). Importance attaches to the preparation of xanthogenic acid from carbon disulphide and alcoholic potash (Zeibe, 1821) especially after Faraday and Hennel had shown how alcohol can be synthesised from ethylene through ethyl sulphuric acid.



PLATE 170

Justus Liebig, from an almost unknown daguerreotype of the year 1842.

Other syntheses from the elements were :—

1824, Wöhler. Oxalic acid from aqueous ammonia and cyanogen (giving ammonium oxalate).

1825, L. Gmelin. Croconic acid from carbon monoxide and potassium.

1827, Serulla. Cyanamide from cyanogen and ammonia.

1828, Desfosses. Potassium cyanide from nitrogen, incandescent potash and carbon.

1828, Wöhler. Urea from sal-ammoniac solution and silver cyanate, or from ammonia and lead cyanate.

1831, Pelouze. Formic acid from prussic acid.

The much repeated statement that Wöhler's synthesis of urea disposed of the vitalistic conception of life is, of course, quite absurd. (The same should apply to oxalic acid, which is also a product of metabolism.) The dead substance urea has nothing at all to do with the vitalistic principle, which only appears in living things.

Isomerism

Another principle which was necessary to the progress of chemistry was the theory of isomerism. As a speculation it was by no means new, having

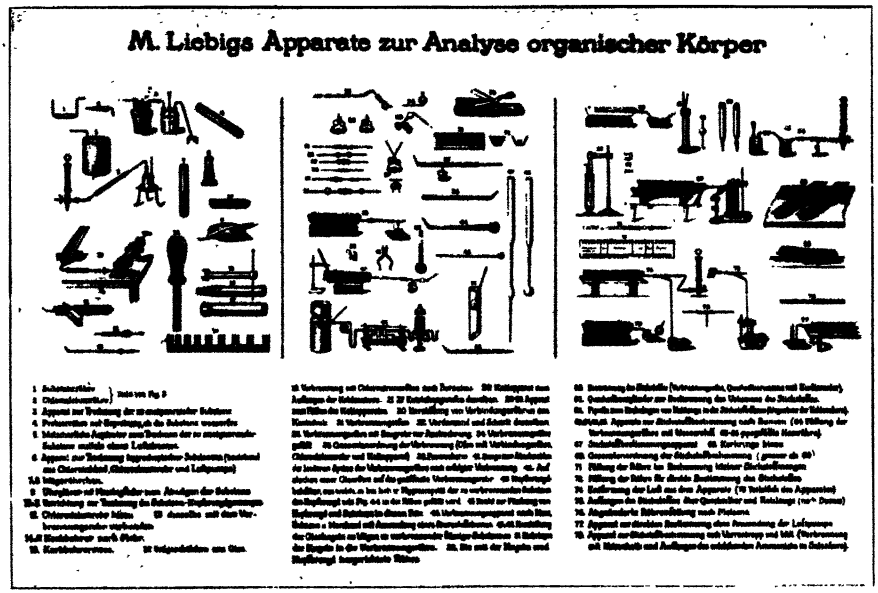


PLATE 171

M. Liebig's apparatus for analysing organic substances.

1. Tube containing substance. 2. Calcium chloride tube. 3. Apparatus for drying the substance to be analysed. 4. Tubes for testing whether the substance is free from water. 5. Mitscherlich's apparatus for drying the substance to be analysed in a current of air. 6. Apparatus for drying hygroscopic substances (consisting of a zinc chloride bath, calcium chloride tube and air pump). 7 and 8. Weighing tubes. 9. Watch glasses and brass spatula for weighing out substance. 10 and 11. Arrangement for drying the mixture of substance and copper oxide. 12. Calcium chloride tube. 13. Calcium chloride tube attached to the combustion tube. 14–17. Cork borers after Mohr. 18. Set of cork screws. 19. Glass weighing vessels. 19. Combustion with calcium chloride tube, after Berzelius. 20. Potash apparatus for absorbing carbon dioxide. 21–27. Stages in making the potash bulb. 28–29. Apparatus for filling the potash bulbs. 30. Preparation of rubber connecting tubes. 31. Combustion furnace. 32. Elevation and section of the combustion furnace. 33. Combustion furnace with suction tube for drying. 34. Combustion furnace filled. 35. Complete equipment for a combustion (furnace with connecting tubes, calcium chloride tubes and potash bulb). 38. Screen. 41. Forceps for cutting off the end of the combustion tube after the completion of a combustion. 42. Attachment of a glass tube to the opened combustion tube. 43. Copper oxide container from which the tube is filled when the substance is very hygroscopic : cf. 44. 45. Wire for mixing the substance with the copper oxide when the former is very hygroscopic. 46. Combustion apparatus after Hoss, Erdmann and Marchand, using a current of oxygen. 47–48. Preparation of glass bulbs for use in the combustion of liquid substances. 51. Transference of bulbs into the combustion tube. 52. Tube charged with bulbs and copper oxide. 60. Determination of nitrogen (combustion furnace, mercury trough and eudiometer). 61. Mercury cylinder for measuring the volume of the nitrogen. 62. Pipette for introducing caustic potash into the nitrogen tube (for absorbing carbon dioxide). 63–66. Apparatus for determining nitrogen after Bunsen. (64. Filling the combustion tube with hydrogen. 65–66. Filled combustion tube.) 67. Apparatus for estimating nitrogen. 68. Cork ring for this apparatus. 69. Complete equipment for estimating nitrogen (more accurate than 60). 71. Filling the tube when estimating small quantities of nitrogen. 72. Filling the tube in the direct estimation of nitrogen. 74. Removing air from the apparatus. (73. Parts of the same apparatus.) 75. Collection of the nitrogen over mercury and caustic potash (Dumas). 76. Alternative method of filling tube (Meisens). 77. Apparatus for direct estimation of nitrogen without using an air pump. 78. Apparatus for determining nitrogen after Varrentrap and Will (combustion with soda-lime and absorption of the ammonia formed in hydrochloric acid).

been put forward by the Greek philosophers. Later the possibility of isomerism was mentioned by Basso, Joachim Jungius (1587–1657), Boyle, and Alexander von Humboldt (end of the eighteenth century).

The first experimental support for the idea was adduced by Gay-Lussac (1824), who showed on the basis of Liebig's analyses that silver cyanate and silver fulminate are isomeric. Gay-Lussac was the first to suggest correctly that their differences were due to the fact that they contain the same atoms differently arranged.

Electrochemistry

was by no means satisfactorily founded in the eighteenth century. This could only be done after Volta's discovery of galvanic electricity.

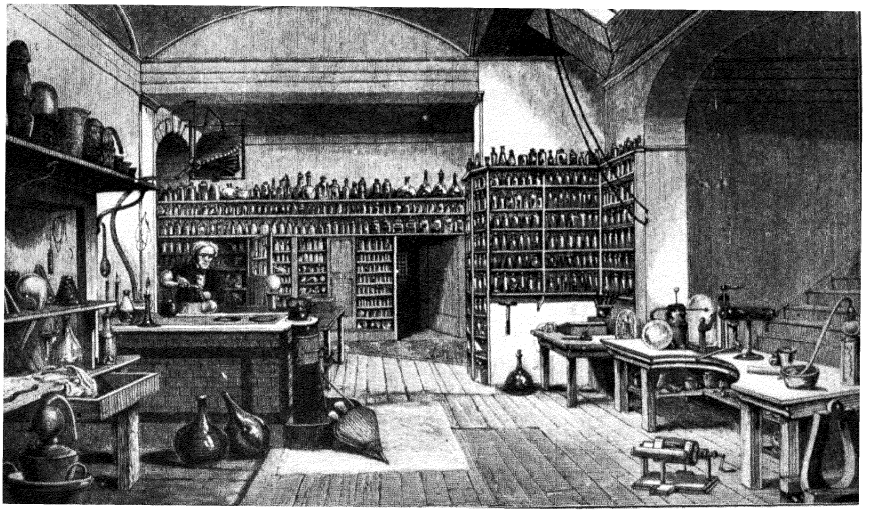


PLATE 172

Faraday's laboratory in 1830.

Faraday's chemical laboratory at the Royal Institution in London was not used for teaching, but only for research. Faraday himself is seen standing behind the stove fitted with bellows. On the right are various pieces of electrical apparatus, e.g. electrostatic machine, Leyden jars, electrolytic apparatus and a very large magnet. No fume cupboard is visible.

The series of historically important experiments began with the *decomposition of water* by Ritter in 1800 and by Nicholson and Carlisle in the same year. In 1801 Cruikshank followed with the electrolytic decomposition of copper and lead salts, and Simon with the electrolytic production of chlorine. In 1802 Brugnatelli, Gahn and Kidd decomposed a number of salts of heavy metals, and Davy electrolysed acids. In 1806 alkali salts were electrolysed by Berzelius and Hisinger, who also obtained potassium chlorate from the chloride

by electrolysis. Ritter obtained lead peroxide electrolytically in 1806. Electrolysis had been applied to organic substances (alcohol) by Davy in 1803.

Special importance attaches to the introduction of the electrolysis of fused salts by Davy, who in 1807 prepared metallic sodium and potassium from fused caustic soda and caustic potash. His apparatus consisted of a platinum spoon as cathode and a platinum wire as anode.

In 1808 Berzelius obtained amalgams of calcium and barium, and Davy amalgams of strontium and magnesium. Davy obtained the pure metals calcium, strontium, barium and magnesium from these amalgams. The famous preparation of ammonium amalgam was carried out by Berzelius and Hisinger in 1808. We have already described the electrochemical theory which was prematurely advanced on the basis of all these experiments

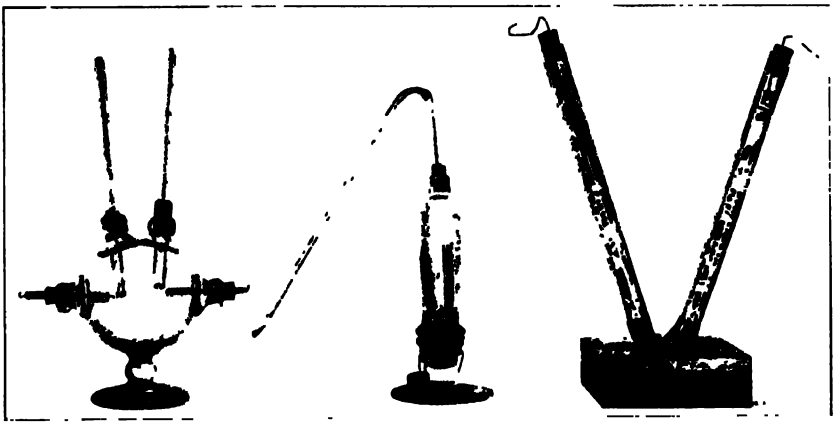


PLATE 173

Faraday's original electrolytic apparatus.

Still preserved in the Royal Institution, London.

More important was the enunciation of the fundamental laws of electrolysis by Faraday in 1833 : i.e. that the amounts of substances liberated by a given current are proportional to the equivalent weights of these substances, and that the amount of substance liberated per unit time is proportional to the strength of the current.

Cruikshank had proposed in 1801 that electrolysis could be used for qualitative analysis. Magnus was, however, the first to propose (in 1856) quantitative electrolytic analysis, which was first carried out by Nickles in 1862.

Carbides were prepared electrically by E. Davy in 1836 (potassium carbide) and by Hare in 1840 (calcium carbide). Ozone was first obtained by Schonbein, 1840.

The first electric furnaces (both arc and resistance furnaces) were made

by Depretz in 1849, cf. also Gaspard Robertson, 1802. Davy had discovered the electric arc at the beginning of the century.

Electrolysis of copper salts was used by M. Jacobi in 1837 for modelling plastic objects. He discovered galvanoplastics, which is of enormous importance for the reproduction of illustrations. Wright (1840) practised gold and silver plating, using potassium cyanide solution. Nickel plating with nickel ammonium sulphate was discovered by R. Böttger in 1842. Brass plating was carried out by Ruolz, 1842. Vacuum discharge tubes were made by Meiniche in 1819, and discharge tubes with platinum electrodes by Geissler in 1856.

Other important physico-chemical discoveries are the following. The determination of *vapour densities*, founded by Lavoisier, was worked on further by Gay-Lussac, and specially by Dumas.

Importance attaches to the discovery of *optical activity*, i.e. the power of substances to rotate the plane of polarised light. Biot and Seebeck observed this phenomenon with cane sugar, dextrose, tartaric acid and turpentine (1815–1819).

Of great importance is the discovery of *spectrum analysis* by Kirchhoff and Bunsen. Exception must be taken to the widespread idea that the colours imparted to flames by various elements were not known before the time of Kirchhoff. This is, of course, quite incorrect, since even the use of flame colorations for recognising substances had been practised much earlier. The great contribution of Kirchhoff and Bunsen was the use of the spectroscope for analytical purposes.

Gases were liquefied by van Marum (1792), Faraday (1823), Nutterer, Andrews (1868) (critical temperature).

Contact Chemistry

made great progress in this period. The word " catalysis " is due to Berzelius, 1835.

Following the experiments of Davy with his platinum lighter (platinum wire over spirits of wine), Johann Wolfgang Döbereiner discovered in 1821–23 the ignition of a mixture of hydrogen and oxygen by means of finely divided platinum. He used this discovery to construct a lighter resembling that of Fürstenberger, but with the electric spark replaced by a platinum catalyst.

Earlier than this (1816) Döbereiner had found that alcohol could be oxidised to acetic acid in presence of a platinum catalyst, and in 1832 he obtained aldehyde in the same way. In 1838 Kuhlmann prepared nitric acid from ammonia using a platinum catalyst, a process which became of the greatest importance in the twentieth century.

New Substances

The following *new elements* or compounds of new elements were discovered :—

Tantalum, Ch. Hatchett (1801); vanadium, A. M. del Rio (1801); cerium, Berzelius and Hisinger (1801); palladium and rhodium, W. H. Wollaston



PLATE 174

Johann Wolfgang Döbereiner.

Born 1780 at Hof; died 1849 at Jena.

Döbereiner studied as a pharmacist at Münchberg, studied chemistry at Strasbourg, and in 1810 succeeded Göttling in the chair of chemistry and pharmacy at Jena. Döbereiner made the first observations on platinum as a catalyst and on the periodic system of the elements. He also contributed to technical questions, and was, for example, a keen protagonist of the erection of gas-works. Döbereiner and Gœthe were in close contact both personally and academically.

(1803–1804); osmium and iridium, Smithson Tennant (1804); metallic potassium and sodium, H. Davy (1807); metallic magnesium, calcium, strontium and barium, H. Davy (1808). (Pure metallic magnesium was first prepared by

Bury in 1830.) Boron, L. J. Gay-Lussac and L. J. Thenard (1808); iodine, Courtois (1821); selenium, Berzelius (1817); lithium carbonate, A. Arfvedson (1817)[1]; cadmium, F. Stromeyer and K. S. L. Hermann (1817); silicon, J. J. Berzelius (1823); yttrium metal, F. Wöhler (1823); metallic zirconium, J. J. Berzelius (1824); bromine and bromides, H. J. Balard (1826); metallic aluminium, F. Wöhler (1827) (from aluminium chloride and potassium: possibly discovered earlier by Örsted in 1825); metallic beryllium, F. Wöhler (1827); thorium, J. J. Berzelius (1828); ores of lanthanum, didymium, terbium and erbium, K. G. Mosander (1839–42); metallic uranium, E. M. Peligot (1841); niobium, H. Rose (1844); ruthenium, K. E. Claus (1845) (cf. Osann (1828)).

The following are a few of the *inorganic substances* discovered during the period; it is impossible to give an exhaustive list.

Chlorine dioxide, Chenevix (1802) potassium peroxide and barium peroxide, Gay-Lussac and Thenard (1809); phosphorus trichloride, Gay-Lussac and Thenard (1809); phosphorus pentachloride and phosphorus oxychloride, Davy (1810); phosgene, Davy (1811); phosphorous acid, Davy (1812); iodic acid, Gay-Lussac (1813); iodine chlorides, Gay-Lussac (1814); hydrogen iodide, Clément and Desormes (1813); mercurous and mercuric iodides, Colin (1813); chloric acid, Gay-Lussac (1814); perchloric acid, Count Stadion (1815); hypophosphorous acid, Dulong (1816); strontium and potassium peroxide, Gay-Lussac and Thenard (1818); metaphosphoric acid, Berzelius and Engelhart (1826); aluminium chloride, Örsted (1826); artificial ultramarine, Guimet, Köttig, Chr. G. Gmelin (1827)[2]; pyrophosphoric acid, Gay-Lussac (1829); potassium perchlorate, Serullas (1831).

The elementary nature of chlorine (previously believed to be an oxide) was demonstrated by Davy. The word allotropy for describing different forms of the same element was introduced by Berzelius.

The following *organic substances* may be mentioned:—

The nature of fats was first recognised by Chevreul in 1811 and the following years. He describes the following fatty acids: stearic, oleic (1823), valeric (1817), capric, caproic. It was Chevreul who first introduced the use of melting and boiling points for characterising organic compounds.

Petroleum was recognised as a hydrocarbon by Saussure in 1817, and turpentine by Houton in 1818.

Dextrose was obtained from starch by G. S. C. Kirchhoff in 1811, and from cellulose by Braconnot in 1819. The celluloses were characterised by Payen in 1839.

The following further organic substances are of interest: Ethyl iodide, Gay-Lussac (1814); cyanogen, Gay-Lussac (1815); fumaric and maleic acids, Braconnot (1817); crotonic acid, Pelletier and Caventou (1818); glycocoll, Braconnot (1819); isovaleric acid, Pentz (1819); ethylene iodide, Faraday

[1] The red flame coloration was noticed by Chr. Gmelin in 1818. Metallic lithium was first prepared by Davy in 1818.

[2] The formation of ultramarine in furnaces had been noticed in the eighteenth century.

(1820); hexachlorethane, Faraday (1820); acetaldehyde, Döbereiner (1821); potassium ferricyanide, L. Gmelin (1822); racemic acid, Kastner (1822); butylene, Faraday (1825); ethyl bromide, Serullas (1827); mercaptan, Zeise (1833); acetylene, E. Davy (1836); camphene, Dumas and Oppermann (1837); quinone, Woskresensky (1838); salicylic acid, Pivia (1838); naphthalene, Garden and Kidd (1819); benzene (from benzoic acid), Faraday (1825);

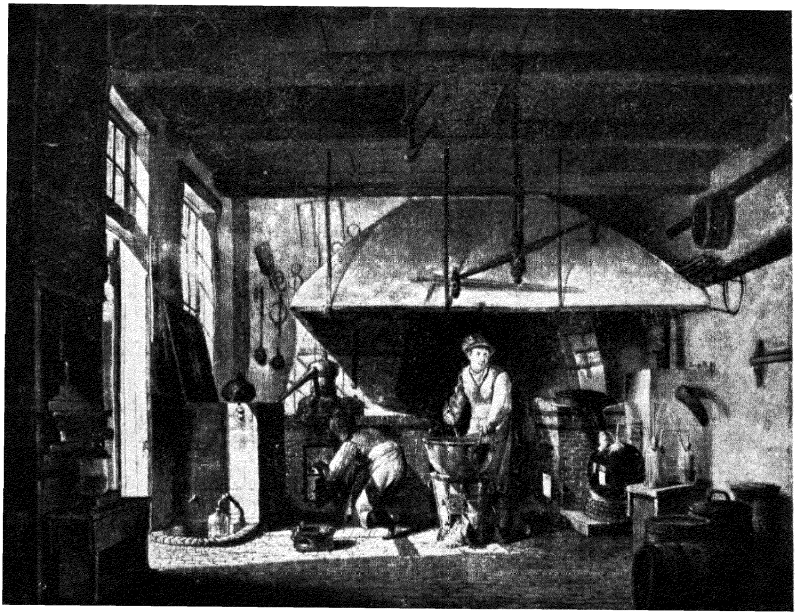


PLATE 175

Laboratory of the pharmacist d'Ailly, first view.

From a painting by Joh. Jelgershuis (1818), National Museum, Amsterdam.

benzene (from coal tar), Leigh (1842); paraffin wax, Reichenbach (1830) (cf. Buchner, 1809); paraffin wax from coal, Young; creosote, Reichenbach (1832); anthracene, Dumas and Laurent (1832–35); aniline, phenol, quinoline, pyrrole, rosalic acid, Runge (1834) (also aniline, Unverdorben, 1826); benzene, nitrobenzene, benzenesulphonic acid, chlorobenzene, bromobenzene, diphenylsulphone, Mitscherlich (1832 onward); phthalic acid, Laurent (1836); toluene, Pelletier and Walter (1836); synthetic aniline, Zinin (1842); methylene chloride, carbon tetrachloride, ethylidene chloride, Regnault (1839–40).

Runge (pharmacist, 1794–1867) and Mitscherlich are the true founders of the industry of coal-tar products.[1]

[1] It may be noted that the ring formula for benzene was proposed before Kekulé by the Viennese physicist Joseph Loschmidt (1821–1895) in the year 1861.

The development of *explosives chemistry* did not begin until later. It was not until 1846 that nitrocellulose was discovered by Schönbein and R. Böttger independently, and in the same year nitroglycerine was discovered by Sobrero. Collodion was first prepared by Meynard in 1846.[1]

Pharmaceutical chemistry continued to develop with great success along the analytical lines described in the last section. One of the greatest achievements was the discovery of *morphine* by the pharmacist Sertürner (Serdignier) in 1805, and the discovery of quinine by the pharmacists Pelletier and Caventou.



PLATE 176

Laboratory of the pharmacist d'Ailly, second view.

From a painting by Johann Jelgershuis (1818), National Museum, Amsterdam. Quinine sulphate (discovered by Pelletier and Caventou in 1817) was prepared commercially in this laboratory in 1823.

Sertürner realised in particular the character of morphine as an organic base capable of forming salts. (Other new discoveries are described below).

Chemical industry was then only in its infancy, and it was therefore necessary for the pharmacist to purify the impure technical products. It was also his task to extract the active principles from drugs and prepare them in as pure a state as possible. This was a matter for each single pharmacy. However, on account of the difficulty of much of the work it was often the custom

[1] Dynamite was not discovered first by A. Nobel, but by Schell, commissioned by Hermann Koch.

for a single concern to specialise in some product and to supply it to others. In this way chemical factories grew out of pharmacies and chemical industries



PLATE 177

Heinrich Emanuel Merck.

Founder of the chemical firm E. Merck, Darmstadt.

out of small scale works. We shall mention a few cases from the first half of the nineteenth century [1] :—

The enormous firm of E. Merck originated in the Engel pharmacy of

[1] Large scale pharmaceutical undertakings had existed before this, e.g. in Venice there was apparently large scale manufacture of Troschisci, Viperarum and Theriak, even in the fourteenth century. From the Middle Ages onwards various monasteries produced specialties which they sent all over the world.

Before the time of Trommsdorff the pharmacist Fikentscher in Marktredwitz set up as a manufacturer of morganic preparations. In addition to the instances mentioned in the text we may mention Wiegleb at Langensalza and Simon in Berlin (beginning of the nineteenth century). The quinine manufacturers, Zimmer & Co. in Frankfurt, are also noteworthy.

Heinrich Emanuel Merck (1794–1855) in Darmstadt. It began chiefly in the production of alkaloids. In 1832 morphine, quinine, emetine and strychnine were produced, in 1833 santonine, 1834 codeine, 1862 cocaine, not to mention many others. In addition there were the well-known pure chemical products, inorganic and organic.

Johann Daniel Riedel (1786–1843), Schweizer pharmacy, Berlin, was the first to prepare quinine in Germany (1827). In 1844 the factory which developed from his pharmacy supplied five hundred and seventy different products.

As already mentioned, the Schwanen-Ring pharmacy of J. B. Trommsdorff in Erfurt developed into a manufacturing concern (pure products, alkaloids).

The following may also be mentioned: Ernst Friedrich Christian Schering (1824–1889), Schmeisser's pharmacy, Berlin. From the first he produced photographic articles as well as pharmaceutical products, including potassium iodide, which was necessary in early photographic technique. Also:—

Friedrich Witte (1829–1893), Hirsch pharmacy, Rostock, caffeine and enzyme preparations; Karl Engelhard, Rosen pharmacy, Frankfurt (1826), galenic preparations; B. Braun, Rosen pharmacy, Melsungen (1835), galenic preparations; Dr. Fresenius, Hirsch pharmacy, Frankfurt, specialities; Adolf August Struve (1820), Solomonis pharmacy, Dresden, artificial mineral waters, tinctures, medicinal wines; W. C. Heräus, Einhorn pharmacy, Hanover, platinum articles; Eduard Beyer, Löwen pharmacy, Chemnitz, copying inks and other products involved in the writing and printing industry. These are only some examples of the older generation, and we cannot begin to mention the numerous important concerns of more recent times.

The following are some examples of new substances introduced into pharmacy in the first half of the nineteenth century:—

Inorganic substances: sodium bicarbonate, Valentin Rose (1801); iodine (and its salts), Courtois (1811); iodides and iodates, Dulong (1816) and Gay-Lussac (1814); hypophosphorous acid, Dulong (1816); lithium compounds, Arfvedson (1817); hydrogen peroxide, Thenard (1818); bromine and its salts, Balard (1826); antimony hydride, L. Thomson (1837).

Organic substances. Investigations on the substances contained in opium were carried out by Derosne (1803), Courtois (1804) and Séguin (1814). Morphine was discovered by Sertürner (1805–1816), nicotine and atropine by Porret (1809) and cinchonine by Gomèz (1811). Other substances are saponin, Schrader (1807) and Bucholz (1811); meconic acid, Sertürner (1816); quinine, cinchonine, brucine, strychnine, emetine, Pelletier, Caventou and Magendie (1817); narcotine, Derosne (1803), Robiquet (1817); hyoscyamine, Brandes (1819); piperine, Örsted (1819); veratrine, Meissner (1819); daphnine, Vauquelin (1817); aconitic acid, Peschier (1820); caffeine, Runge (1820), Robiquet and Pelletier (1821); solanine, Desfosses (1821); iodoform, Serullas (1822); coniine, Giesecke (1827); salicin, Buchner (1828); santonin, Kahler and Alms (1830); ergotin, Wiggers (1831); vanillin, Bley (1831); bromoform and bromal, Löwig (1832); codeine, Robiquet (1832); meconine, Couerbe (1833); narceine, Pelletier (1832); aconitine and colchicin, Pelletier and

Caventou (1820), Geiger and Hesse (1833); thebaine, Pelletier (1833); chloroform, Soubeiran (1831); theobromine, Woskresensky (1841); chloral, chloral hydrate, chloroform, Liebig (1831). The correct formulæ for chloral,



PLATE 178

Louis Jacques Thenard (1774–1857).

chloroform, bromoform and iodoform were given by Dumas in 1834. Decolorisation with animal charcoal is due to Fignier (1810).

Physiological chemistry, which had developed little during the eighteenth century, now began to flourish. The following products were obtained:

From plants: inulin, Heinr. Rose (1804); asparagin, Vauquelin and

Robiquet (1805); legumin, Einhof (1805) and Braconnot (1827); mannite, Proust (1806); amygdalin, Robiquet (1807); brazilin, hæmatoxylin, quercetrin, Chevreul (1808); picrotoxin, Boullay (1812); cumarin, Vogel (1812); emulsin, Vogel (1817); chlorophyll (further investigated), Pelletier and Caventou (1818); pectin, pectic acid, Braconnot (1824); berberine, Hüttenschmidt (1824); sinapin, Henry and Garot (1825); alizarin and purpurin, Colin and Robiquet (1826); orcin, Robiquet (1829); carotin, Wackenroder (1831); dextrin, Vauquelin (1811), Biot and Persoz (1833).[1]

From animals: allantoin, Vauquelin (1800); choleic acid, Thenard (1806); sarco-lactic acid, Berzelius (1808); cystine, Wollaston (1810); lecithin, Vauquelin (1811); casein (characterised), Berzelius (1812); fibrin, Berzelius (1812); xanthine, Marcet (1817); leucine, Proust (1818), Braconnot (1819); murexide, Brugnatelli (1818); cholesterin, Chevreul (1813–1819); albumin (characterised), Brande (1820); chitin, Odier (1823); taurine, L. Gmelin (1824); hæmatin, Tiedemann and Gmelin (1826); "pancreatin," Tiedemann and Gmelin (1826); hippuric acid, Liebig (1829) (cf. H. M. Rouelle, 1776); creatine, Chevreul (1832); pepsin, Schwann (1836).

The classification of human food into proteins, fats and carbohydrates is due to Prout (1827), and is still used to-day.

Apparatus

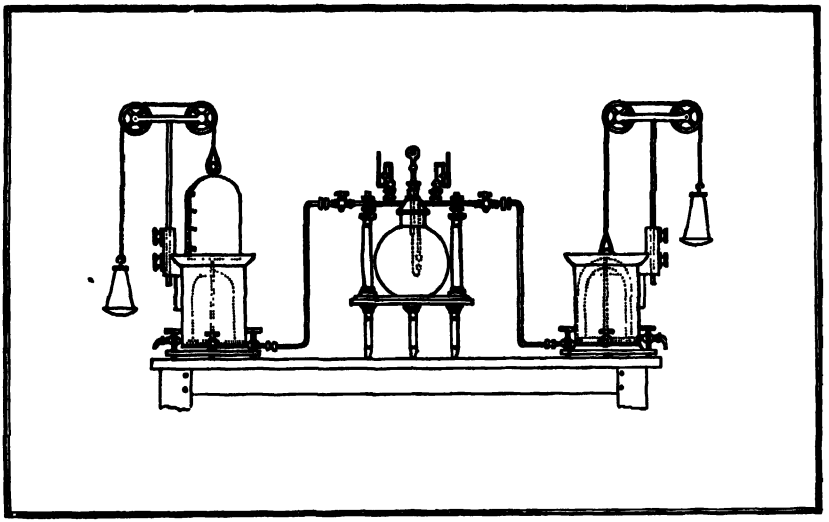
The best sources of information about the apparatus of this period are the text-books of Thenard and Berzelius. Thus among the apparatus mentioned by Thenard are desiccators, apparatus for drying gases, gas-holders, autoclaves, hot-water funnels, and stands and clamps of many kinds.

Interest attaches to Thenard's apparatus for obtaining potassium (by non-electrical means). His fume cupboard (Plate 181) is the forerunner of those used by Liebig at Giessen. (Liebig had worked in the laboratories of Gay-Lussac and Thenard.)

Of particular importance is Gay-Lussac's apparatus for volumetric analysis, based on the test for silver in the wet way. (Since chemical reactions take place according to fixed proportions, it is possible to measure the amount of a substance by determining how much of a reagent of known concentration is necessary to react completely with it.) Gay-Lussac may be regarded as the *founder of volumetric analysis*. It was introduced into Germany by Friedrich Mohr.

Berzelius is best known by his spirit lamp. (Spirit blow-pipes were also known: Neumann, Mitscherlich.) Many other innovations are due to Berzelius: the introduction of special filter-papers (in place of blotting paper), platinum crucibles and other vessels, the wash-bottle, test-tubes and test-tube

[1] The starch-iodine reaction was discovered by Colin and Gaultier in 1814. The action of diastase on starch was observed by Kirchhoff in 1814, while diastase itself was characterised by Payen and Persoz in 1833. Gay-Lussac knew in 1814 that sugar, starch and gum all have the same empirical formula, and in 1815 that the fermentation of dextrose leads to two molecules of alcohol and two of carbon dioxide. The copper test for dextrose was discovered by Vogel in 1815. Phenol was first prepared on a commercial scale by Calvert in 1859.



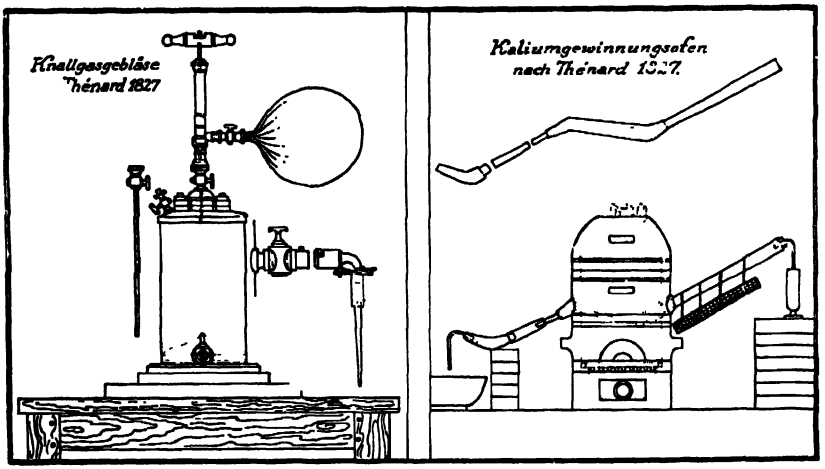


PLATE 179

Apparatus for analytical work with gases. Thenard, 1827.

1. The top apparatus was designed by van Marum.
   The most important apparatus is the furnace for preparing metallic potassium, which Thenard obtained from caustic potash and carbon.
2. Oxy-hydrogen bellows, Thenard, 1827.
3. Furnace for preparing potassium, Thenard, 1827.

stands. In many cases it is difficult to find the discoverer of each single article.[1]

[1] On the other hand it may be noted that Berzelius still used the athanor, alembic, " Moor's head " and aludel.

Davy's safety lamp must not be forgotten.

Dumas knew vacuum drying. E. Mitscherlich's apparatus for testing for phosphorus is of interest. Marsh's apparatus for detecting arsenic is important.

The first laboratory gas-burner is due to Faraday, and it was improved by Sonnenschein, who probably also devised the first arrangement for heating tubes by gas. The first really practical form of burner was devised by Bunsen, who also designed multiple burners and blow-pipe burners.

J. Liebig's laboratory at Giessen (1839) may be regarded as the parent of all laboratories for chemical instruction, and the same applies to his equipment.

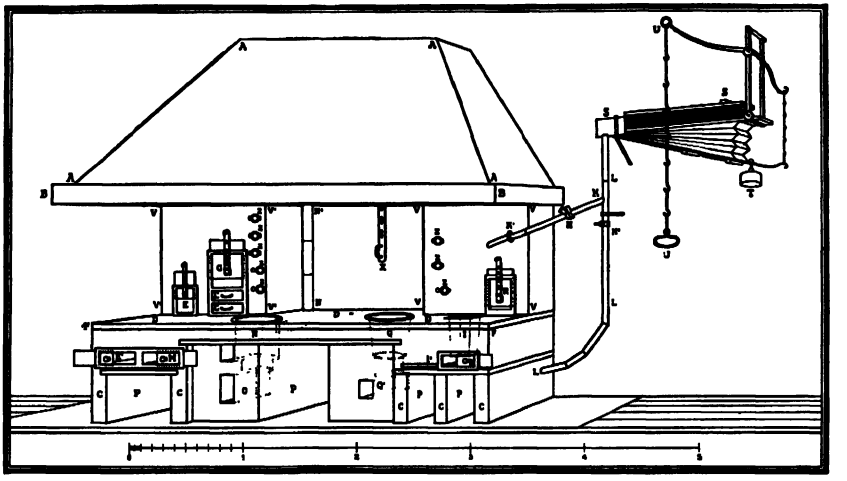


PLATE 180

Digestorium : Thenard, 1827.

A, B Fume hood. C Furnace of bricks and mortar. F Iron top plate. N Evaporating furnace. N′ Exit tube from N. O Firing for N. Q Bellows furnace. Q′ firing for Q. S Bellows. L Wind pipe. W′ Flues. E, G, R Dampers. E′, M, R′ Firing. L′ Tower for storing wood and coal. Z Chimney openings with caps for receiving gas pipes. J Bellows furnace. J′ Firing for J. X Lever for opening and shutting the flap of the fume hood. P Space for coal, etc. K Side tube from bellows. H Tap for K.

His working benches with shelves for reagents and water laid on and his fume cupboards have served as models for all chemical laboratories up to the present day. Liebig's work may still be seen in every student's chemical laboratory.[1]

The Liebig condenser was first used as a reflux condenser by Friedrich Mohr in 1836 (or possibly by Corriel and Berthemot, 1832). The cork-borer and the pinch-cock burette are also due to Mohr.

The extraction apparatus known as the percolator was discovered by the French pharmacist Boullay.

[1] We have already dealt with the so-called Liebig condenser (counter-current condenser). The large so-called Liebig condenser in the Deutsches Museum was not made for Liebig, but for Baeyer, though some of the smaller specimens came from Liebig's Munich Laboratory.

The *education of young chemists* in the first third of the nineteenth century showed a great improvement on the eighteenth century. It is quite wrong to



PLATE 181

Interior view of Liebig's famous laboratory at Giessen

From a drawing by Trautschold, 1842

The picture shows the interior of the main room of Liebig's laboratory at Giessen and also his pupils working there. From right to left they are: 1. 1. *Hofmann*, Liebig's assistant until 1845, later professor in Berlin, died 1892. 2. *Emil Buckmann*, later director of Fries ultramarine factory at Heidelberg. 3. In front of the fume cupboard, turning his back, *Johann Josef Scherer*, later professor of medicine at Wurzburg. 4. Right in the background, 4. *F. C. Streeker*, Liebig's assistant, professor of chemistry in Tubingen, 1860, later university professor in Wurzburg, died 1871. 5. *Franz Varrentrap*, leaning on the bench, later mint warden in Brunschweig. 6. Standing in front of the furnace with both hands in his pockets, *Wyttenbach* from Aarau. 7. *Anbel*, sitting in front of a mortar, Liebig's laboratory servant, later Mayor of Winsack, near Giessen. 8. Demonstrating with a cylinder in his hand, *Heinrich Will*, Liebig's assistant and successor at Giessen, died 1890. 9. Talking to Will, *Wilhelm Keller*, later a practising physician in Philadelphia. 10. In the left foreground, with a black beard, *Ortigosa*, a Mexican. 11. In the fume cupboard between the lecture room and the laboratory, *Anton Louis* from Eschbach, later an architect.

This laboratory became the model for all institutes for chemical teaching. working benches with shelves for reagents and filtering stands, underneath the benches cupboards with drawers and shelves, removable bench tops, water supply and sinks on the benches.

In the centre are ordinary tables, and in the background a metal fume cupboard with movable glass front, under which is a furnace heated by coal. In front of the large heating stove is a pneumatic trough.

Among the equipment we may note beakers, flasks, bell-jars, evaporating basins, mortars, stills, apparatus for evolving oxygen and other gases, the large phosphorus eudiometer stands.

assume that satisfactory teaching was only obtainable at Liebig's laboratory in Giessen. It is true that most German universities had at the most inadequate facilities for chemical teaching, but there were some excellent teaching insti-

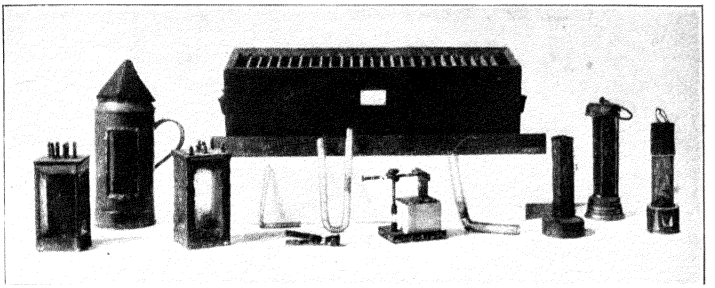


PLATE 182

H. Davy's original apparatus.

Preserved in the Royal Institution, London.
Safety lamps, battery trough.

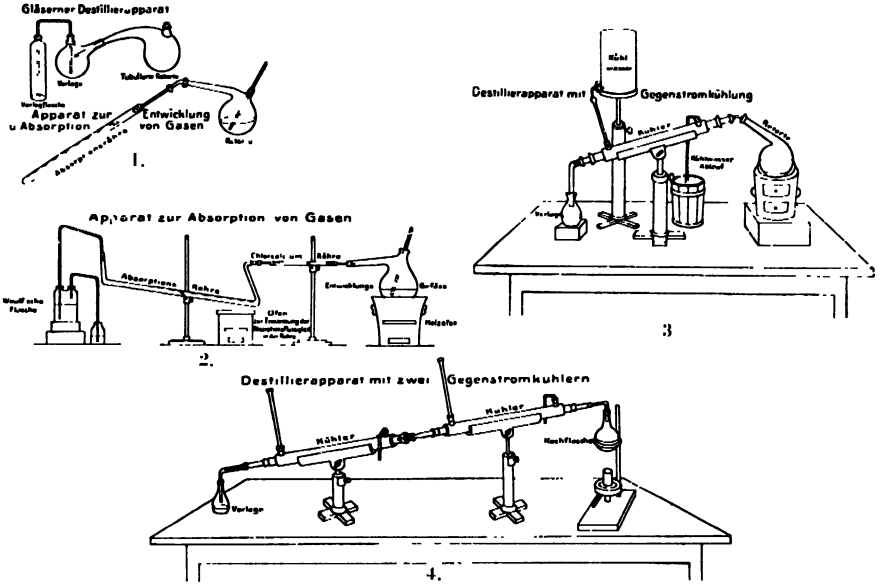


PLATE 183

Distillation apparatus, J. Liebig.

Liebig recommended the use of Weigel's counter-current condenser.

1. Glass distillation apparatus.
   Receiving flask.
   Receiver.
   Tubulated retort.
2. Apparatus for the evolution and absorption of gases.
   Absorption tube.
   Retort.
3. Distillation apparatus with counter-current condenser.
   Cooling water.
   Condenser.
   Exit for cooling water.
   Receiver.
   Retort.
4. Apparatus for the absorption of gases.
   Woulffe's bottle.
   Absorption tube.
   Furnace for heating the absorbing liquid in the tube.
   Calcium chloride tube.
   Vessel for evolving gas.
   Distillation apparatus with two counter-current condensers.
   Receiver.
   Condenser.
   Condenser.
   Boiling flask.

tutes. The earliest of these was the institute of the pharmacist, Johann Bartholomäus Trommsdorff at Erfurt, founded 1795.

Another valuable institute was founded at Göttingen by the physician Stromeyer (1776–1835), who was Bunsen's teacher. Bunsen himself started a teaching laboratory at Marburg in 1839. Thanks to the provision of Goethe, Döbereiner had room for twenty practical workers at Jena. Other chemistry teachers worthy of mention are O. L. Erdmann, who taught in Leipzig from 1827 onwards, Joh. Nep. Fuchs and Joh. And. Buchner at Landhut, and J. J. Scherer at Würzburg. German chemists of this period who wished to reach the greatest heights of scientific learning often studied abroad. This is easily understood when we remember the great contributions to the progress of chemistry made by scientists like Gay-Lussac and Berzelius. Liebig and Schönbein studied with Gay-Lussac and Thenard in Paris, and Mitscherlich and Wöhler with Berzelius in Stockholm.



PLATE 184
Berzelius (1779–1848).

CHEMICAL TECHNOLOGY

THE discovery of beds of sodium nitrate in Chile in 1825 was an event of world-wide importance. On account of the other substances which it contains, Chile saltpetre remains even to-day the best artificial manure.

The vinegar manufacturer, Peregrine Phillips junior, Bristol, discovered in 1831 the contact process for manufacturing sulphuric acid (conversion of sulphur dioxide to the trioxide by means of a platinum catalyst).

Improvements in *distilling apparatus* were made by J. G. Dingler (1815), and Beindorff (1818), whose apparatus for boiling, evaporating, distilling and drying was recommended by Liebig.

The distillation of spirits was improved by Pistorius (1817), whose apparatus included preheating, rectifier, dephlegmators and condensers. It was superseded by the column still with numerous rectification chambers, which was first introduced by Cellier-Blumenthal (1817) and improved by Coffey (1832) and Savalle (1850). These apparatuses form the basis of modern methods of distilling.[1]

An event of great cultural importance was the *introduction of matches*. The first of these were Chancel's dipping matches (1803), consisting of potassium chlorate and an organic substance (later sugar) which were dipped in sulphuric acid. The " Prometheans " of Trevany and Jones (1820) had heads of potassium chlorate and antimony sulphide, which were struck on glass-paper. They are the direct forerunners of modern safety matches. Next, however, came matches with heads of yellow phosphorus and an oxidising agent, at first potassium chlorate. The discoverer of these cannot be specified, and it is hardly possible to speak of an actual discovery. After the discovery (or rather the first accurate description) of red phosphorus by Schrötter in 1847, Böttger in 1848 reintroduced phosphorus-free matches : e.g. he used the " Prometheans " with a striking surface of red phosphorus. These matches were first made on a commercial scale by Bernard Fürth in Schüttenhofen.

A very important discovery was the *vulcanisation of rubber*, started by Hayward and completed by Ch. Goodyear (1840) and T. Hancock (1843). Ebonite was discovered by Goodyear in 1852. Artificial rubber from isoprene was first made by Bouchardat in 1875 and 1879. Gutta-percha was introduced into Europe by José d'Almeida in 1843, and made more widely known by Montgomeric in 1848.

Sintered *Portland cement* was discovered in 1824 by the Englishman John Aspdin. Artificial mixtures of limestone and clay were first used as a starting material for making cement by Johnson in 1844.

The industrial manufacture of artificial lapis lazuli (*ultramarine*) began soon after its discovery by Leverkus in Wernidokuchen in 1834 and by Leykauf in Nürnberg in 1838.

One of the greatest successes of chemistry, and one of universal importance, was the discovery of photography. Joseph Nicéphore Niepce (1765–1833) was the first to obtain images in a camera : these were on bitumen and could be fixed with oil and converted to heliogravures. Louis Jacques Daguerre (1789 1851) was the first to employ a procedure based on the light sensitivity of the silver salts (completed 1839). Daguerre exposed an iodised silver plate in the camera, discovered the method of developing with mercury vapour, and fixed with a hot solution of sodium chloride. Soon afterwards John Herschel (1839) discovered sodium thiosulphate, the best fixing agent, and in 1840 Fizeau discovered the gold toning of pictures.

Almost simultaneously with Daguerre, Fox Talbot (1800–1877) and Steinheil in Munich discovered the use of silver chloride and bromide for

[1] Acting on a suggestion of Lavoisier's (1786), Schützenbach (1823) discovered the rapid method of making vinegar.

photography and printing. At first they used sodium chloride for fixing. Soon afterwards came the use of silver iodide and fixing with gallic acid, sodium bromide and sodium thiosulphate successively. In this way the foundations of photography and photographic printing were laid.

Concluding Remarks

The most important basis of modern chemistry lies in the attempt to find relations between different elements, leading to the *periodic system*.

The English physician *Prout* maintained in 1815–1816 that the atomic weights of all the elements should be integral multiples of the atomic weight of hydrogen : thus if the latter were taken as unity all atomic weights should be whole numbers. Any heavy atom could then be considered as composed of a definite number of hydrogen atoms. In Prout's time there was little exact knowledge of atomic weights, but the interest which his hypothesis aroused was the occasion of a number of atomic weight determinations which finally showed his hypothesis to be false. There were many deviations, and attempts to use one half or one quarter of the hydrogen atom as a fundamental unit were also unsuccessful.[1]

In 1829 Döbereiner pointed out that when three elements are very similar the atomic weight of one is equal to the arithmetic mean of the atomic weights of the other two. Döbereiner termed three such elements a triad (e.g. bromine between chlorine and iodine, sodium between lithium and potassium, selenium between sulphur and tellurium).[2]

Dumas (1861) attempted to extend this idea. He believed that the elements were actually formed from one another, like the organic compounds in an homologous series.

Beguyer de Chancourtois in 1862 arranged the elements in a helix on the surface of a cylinder, drawn so that it cuts the horizontal at an angle of forty-five degrees. The numerical values of the atomic weights were written on this helix, when related elements were found on the same vertical line.

In 1864 Newlands discovered the law of octaves. He arranged the elements in order of increasing atomic weight and numbered them. He then found that (with a few exceptions) two elements differing in number by eight had similar properties. Newlands predicted correctly that the classification of elements according to their atomic weight represented a lasting gain for chemical science. After Newlands' preliminary work it was no longer so difficult for Lothar Meyer and Mendelejeff to construct the periodic table, since the chief law governing the sequence of the elements had been discovered.

[1] The first presentiment of the periodicity of the elements was felt by Joh. Bernh. Hermann in 1786, who compared the series of the elements to octaves in music.

[2] J. H. Gladstone was the first to arrange the elements in order of increasing atomic weight. W. Oelling in 1857 arranged them in vertical columns, so that related elements were opposite one another in a horizontal direction.

Still later work showed that Prout's theory is correct if applied to single isotopes. However, this work belongs to the twentieth century, and will not be treated in this book, which only aims to lead up to the threshold of modern times.

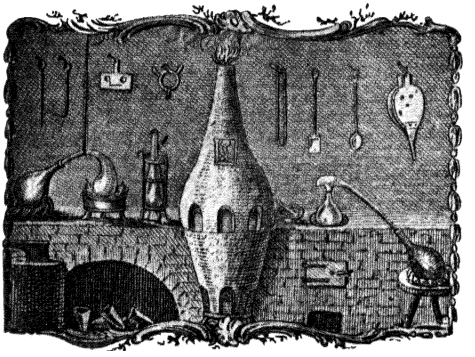


PLATE 185

Title vignette.

From C. W. Scheele's "Chemische Abhandlung," Upsala, 1777.

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