DISCOVERING OXYGEN: EXPERIMENTAL TECHNIQUES AND LOGIC OF A GREAT CHEMIST, CARL WILHELM SCHEELE

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Abstract

The purpose of this paper is to briefly review the outstanding experimental results of Scheele described in the book *Chemical Observations and Experiments on Air and Fire* and leading to the discovery of oxygen. Following the principles of the phlogiston theory he was able, thanks to a judicious guess on the nature of heat and with tenacious perseverance and excellent chemical expertise, to isolate *fire air* (O_2) by strongly heating numerous substances and to identify this *air* with that part of common air responsible for combustion. As a prerequisite of this epochal finding, Scheele also discovered in a long series of experiments the nature of common air as a mixture of two fluids, *fire air* and *vitiated air* (N_2) and distinguished, among combustion processes, those occurring with and without production of *aerial acid* (CO_2).

Introduction

The discovery of oxygen and the interpretation of its role in combustion and calcination processes constitute decisive points in the history of chemistry (1-3). The subject has stimulated critical analyses among science historians, perhaps more than any other chemical issue. There is agreement about Scheele's priority for the discovery in 1771-1772, i.e., at least two years before Priestley (1, 4, 5). It is evident from the laboratory notebooks of those years that he obtained this *air* by heating *black manganese* (or *magnesia nigra*, MnO_2) in *oil of vitriol* (H_2SO_4 concentrated), called it *air of vitriol* and was able to distinguish from common air (5, 6). In present-day terms the reaction is

$$MnO_2 + H_2SO_4 \rightarrow MnSO_4 + \tfrac{1}{2}O_2 + H_2O$$

A series of unfortunate circumstances and delays prevented Scheele from receiving the full recognition of the discovery. First of all, no mention of the new *air* appeared in the original paper reporting on *black manganese* (5). Second, although the discovery was preliminarily summarized by Torbern Bergman, the leading chemist of the University of Uppsala and Scheele patron and teacher, in a memoir on Elective Attractions (7) whose print edition was supposedly (4) not later than 1 August 1774 (the announcement date of the discovery by Priestley (8)), the publication date of Bergman's memoir has been questioned (5, 9) because a possible last-minute insertion in it appears to refer to events dating from spring 1776. In the third place, the Scheele book *Chemische Abhandlung von der Luft und dem Feuer* (*Chemical Observations and Experiments on Air and Fire*) (10) describing the discovery, though written in the autumn of 1775 and sent to the printer in December 1775, was not published until summer 1777 due to Bergman's diligence in repeating many of the reported experiments and in making explicit in the book's Introduction that they were all correct (1). In the meantime, the breakthrough was superseded by the appearance of papers dealing with the same subject and coming from renowned scientific personalities such as Priestley (8) and Lavoisier (11).

In our opinion, a second but by no means less important aspect of the discovery concerns the experimental techniques and logic that brought Scheele to obtain *fire air* (oxygen) following the principles of the phlogiston theory. Scheele had reason to believe that heat was the combination of something in common air and phlogiston (2), as will be illustrated below. He therefore tried to dissociate heat in presence of a receptor showing more affinity for phlogiston than this component of common air. The matter has been discussed at length elsewhere (1, 2). An excellent summary was given in Latin by Bergman when repeating in 1775 some of Scheele's experiments on *calxes*: "demonstrabit experimentis D. Scheele materiam caloris nihil esse aliud, quam phlogiston aëri puro [oxygen] intime unitum" (12).

In this paper we wish to illustrate the experiments described in the book with the purpose of giving evidence for the discovery of a scientific milestone reached with a simple apparatus and great perseverance. After the biographical profile in the following section, key points of book will be revisited and interpreted to emphasize Scheele's experimental skill and chemical expertise. In the Conclusions section some considerations about the human and scientific personality of Scheele, whose contributions to chemistry have been sometimes overshadowed by those of contemporaries Priestley and Lavoisier, will be summarized. It is hoped that our results will not be without interest for scholars in this field.

Biography of Carl Wilhelm Scheele

A number of books and papers have reported on the life and the scientific personality of Scheele (1-3, 13-22). The original documentation and biographical notes may be found in the correspondence and laboratory notes selected and published by A. E. Nordenskiöld (23) and C.W. Oseen (6). The publication of all available material regarding the Scheele research activity and life with English translation and commentary has been undertaken by U. Boklund (24). The collected papers of Scheele have been also translated from the Swedish and German originals by L. Dobbin (25).

Carl Wilhelm Scheele was born in Stralsund, West Pomerania, at the time a German-speaking region under Swedish jurisdiction. The birth date is uncertain, 9 or 19 December 1742 (1). Carl Wilhelm was the seventh of a family of eleven children. His father, Joachim Christian, was a rather unsuccessful merchant while his mother, Margaretha Eleonora Warnekros, was the daughter of the head of a brewery firm. After having received a good elementary education (1) and learned while still a boy from two friends of family about writing chemical symbols and reading prescriptions (15), in 1757 Scheele entered the pharmacy "at the Unicorn" in Göteborg as an apprentice (20). There he replaced his elder brother, Johann Martin, who died of typhoid two years earlier. Martin Anders Bauch, the owner, was a competent pharmacist and had in his library a number of up-to-date chemistry books such as Neumann's *Praelectiones Chemicae*, Lemery's *Cours de Chymie*, Kunckel's *Laboratorium Chymicum* (highly appreciated by the young Carl Wilhelm) which greatly affected the scientific formation of the apprentice. Further, Scheele was allowed to make chemical experiments, a good supply of chemicals and laboratory apparatus being available in the pharmacy. Scheele remained in this pharmacy for apprenticeship until 1765 taking the qualification of journeyman (skilled worker).

He left Göteborg in that year and as a journeyman worked in the next ten years in Malmö (1765-1768), Stockholm (1768-1770) and Uppsala (1770-1775). In Malmö he served as apothecary clerk in the pharmacy "at the Spread Eagle" (Fläkta Örn) (19, 20) under the direction of Peter Magnus Kjellström, who quickly realized the experimental ability of Scheele, and allowed him to do practical research using the pharmacy workbench. In those years Scheele had his first contact with the academic world through Anders Jahan Retzius, then lecturer of chemistry at the nearby University of Lund. Attracted by better facilities and (probably) the proximity of the celebrated University of Uppsala, Scheele moved to Stockholm where he was employed at the "Gilded Raven" (Förgyllda Korpen) pharmacy (19, 20) run by Johan Scharenberg, where he worked on handling prescriptions and had no access to the pharmacy's laboratory. Nevertheless, he managed to prepare tartaric acid from the *cream of tartar* (potassium hydrogen tartrate, $KHC_4H_4O_6$), and a written acknowledgment to him for the preparative method was given by Retzius in his memoir on tartaric acid. Starting from the solution of *cream of tartar*, the brilliant procedure consisted in precipitating the salt by adding *lime water* (a saturated $Ca(OH)_2$ solution), dissolving the salt in diluted *oil of vitriol* and crystallizing the tartaric acid from solution after filtering off the sediment ($CaSO_4$) (17). In a similar way in later years the isolation of other organic acids from vegetable and animal sources was accomplished, among them lactic, citric, malic and oxalic acid (17). While in Stockholm, Scheele had the opportunity of making a second connection with the academic milieu, Johann Gottlieb Gahn, assistant to Bergman's chair of chemistry in Uppsala.

Since the job at the pharmacy did not meet his expectations Scheele moved to Uppsala, accepting a position as laboratory assistant in the Upland's Arms (Uplands Wapen) pharmacy (19) owned by Christian Ludwig Lokk. In that city he was introduced to the famous professor of chemistry by Gahn. It has been reported (1) that according to some Scheele biographers the occasion was the clever answer to an unexplained behaviour of *saltpetre* (potassium nitrate, KNO_3), bought in the Lokk shop by Bergman, giving red vapours with acid. Scheele told Gahn that *saltpetre* on heating is *phlogisticated* and transformed to a salt of another acid (nitrous acid, HNO_2). A different anecdote, quoted in Ref. 19, was told by Gahn himself referring to a meeting in Lokk's pharmacy where the young apothecary explained why *antimonium diaphoreticum* (*calx* of antimony, Sb_2O_3) mixed with *sal acetosellae* (potassium hydrogen oxalate, KHC_2O_4) smelled of *aqua fortis* (concentrated HNO_3). Impressed by the chemical knowledge, Bergman encouraged Scheele to investigate pyrolusite (*magnesia nigra*, MnO_2 (26)). The results established his reputation as a chemist, showing that pyrolusite (a) dissolves in *oil of vitriol* only in presence of a substance rich in phlogiston, (b) dissolves in *marine acid* (hydrochloric acid, HCl) to form a new *air* (namely, chlorine, Cl_2) which, in agreement with the phlogiston theory, was interpreted as *dephlogisticated marine acid*, and (c) contains a small amount of another substance which he named *heavy earth* (barium carbonate or baryta, $BaCO_3$). During the years in Uppsala Scheele made the discovery of *fire air*. The many and varied experiments leading to the discovery, which were already undertaken according to Retzius (1, 15) in the years 1768-1770 in Stockholm, merged into Scheele's book on air and fire. The analysis of the experiments will be deferred to the next section. Here we note only that Scheele, although a phlogistonist, had opinions sensibly different from the conventional view on important aspects of the phlogiston theory. For instance, in the years 1767-1768 he had found (15, 17) that silver could be obtained from *lunar caustic* (silver nitrate, $AgNO_3$) simply by heating, without the necessity of adding charcoal as an reagent rich in phlogiston. In his opinion phlogiston was already in the heat delivered to the reaction.

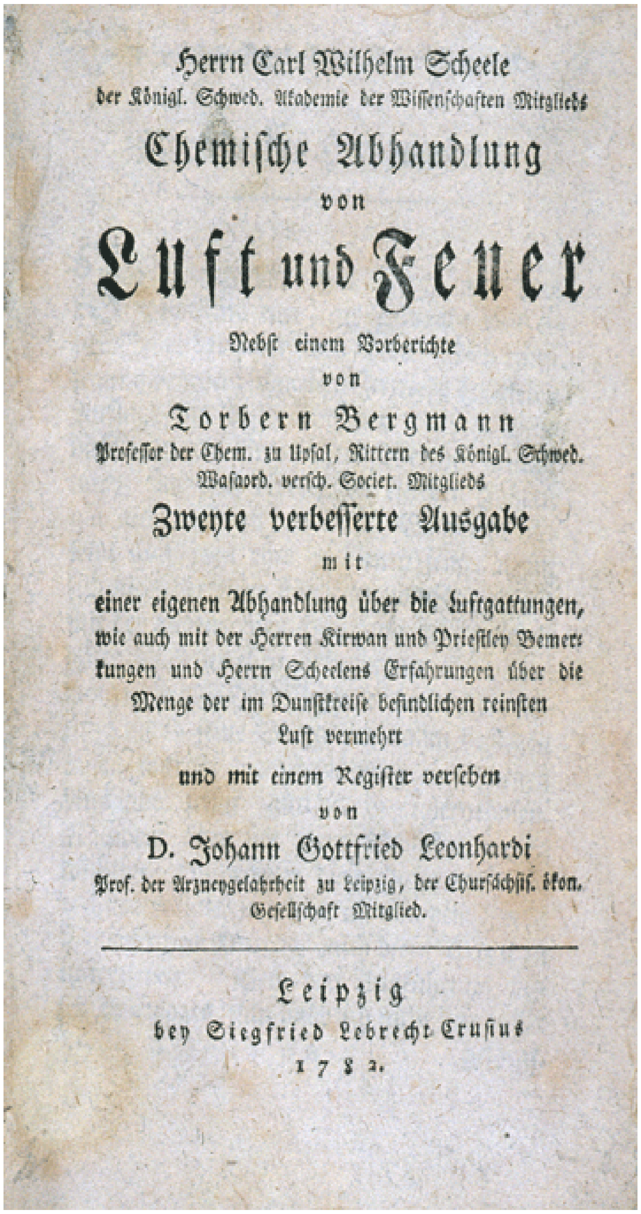
Due to all these achievements, on the proposal of Peter Jonas Bergius, professor of pharmacology at the University of Uppsala, Scheele was elected member of the Swedish Academy of Sciences at the February 4, 1775, meeting in presence of the King, an unprecedented honor for a person still an apothecary assistant or *studiosus pharmaciae*. In that same year Scheele had the occasion to superintend a pharmacy (15, 16, 21). Sara Margaretha Sonneman was the owner of a license due to the fact that her husband, Herman Pohl, pharmacist in the small city of Köping, had died. Scheele moved to Köping and agreed with the widow to become "provisor," i.e., to be the pharmacy supervisor without ownership. His management was so appreciated among citizens that they demanded his permanence as city's pharmacist, notwithstanding a profitable offer from a wealthy pharmacist that widow Pohl had already decided to accept (15). The dispute was settled in favour of Scheele who bought the license and promised to marry the widow (16, 21). He remained in Köping for the rest of his life. He left the city only once to attend his formal admission to the Royal Academy on October 29, 1777, and to undergo the final pharmacy examination and oath on November 11, 1777. At Köping he continued research on organic acids and inorganic minerals, including the *calxes* of molybdenum and tungsten (17). Among additional discoveries, the *stinking sulphurous air* (hydrogen sulphide, H_2S), phosphorus, and silicon fluoride are noteworthy as well as the action of light on silver salts (1). He declined the lucrative invitation from Frederick the Great to be the successor of the chemist Andreas Sigismund Marggraf in Berlin, following an official letter from D'Alembert on December 15, 1777. Scheele died on May 21 or 26, 1786 at 43 (1). Three days before dying he married the widow Pohl so that the pharmacy license returned to her hands. The death was ascribed to a number of complications such as rheumatism caused by uncomfortable working conditions over the years and later gout ("no apothecary escapes the gout" he said (1)). In addition, his habit to taste various chemicals, including arsenic and lead, during preparations, may have contributed to such an early death.

The Discovery of Oxygen

As already outlined in the introduction, there is a gap of almost two years between the writing of *Chemische Abhandlung von der Luft und dem Feuer* (10) and its publication by the printer, Swederus in Uppsala. (See Figure 1.) Misunderstandings with the publisher and the wait for the long Introduction by Bergman caused blame from Scheele and anxiety (1). It has been observed that in absence of Bergman's involvement, the book could have been published one year earlier (1); delays in publications were, however, common in the 18th century (17).

The book, divided in 97 numbered paragraphs to which reference is made below, had English and French translations soon after the German edition. Under Priestley's encouragement the English book, due to J. R. Foster, a German pastor interested in science, was published in London in 1780, and it is now available on the internet (27). The French translation was the work of Baron de Dietrich in 1781 in Paris under support of R. J. Turgot, economist and French minister (28).

In the remainder of the section, we interpret several of Scheele's experiments in terms of present-day chemical equations and explain some of them in terms of the phlogiston theory as he understood it.



Herrn Carl Wilhelm Scheele
der Königl. Schwed. Akademie der Wiſſenſchaften Mitglieds
Chemiſche Abhandlung
von
Luft und Feuer
Nebſt einem Vorberichte
von
Torbern Bergmann
Profeſſor der Chem. zu Upſal, Rittern des Königl. Schwed.
Waſaord. verſch. Societ. Mitglieds
Zweyte verbeſſerte Ausgabe
mit
einer eigenen Abhandlung über die Luftgattungen,
wie auch mit der Herren Kirwan und Prieſtley Bemer-
kungen und Herrn Scheelens Erfahrungen über die
Menge der im Dunſtkreiſe befindlichen reinſten
Luft vermehrt
und mit einem Regiſter verſehen
von
D. Johann Gottfried Leonhardi
Prof. der Arzneygelahrheit zu Leipzig, der Churſächſiſ. ökon.
Geſellſchaft Mitglied.

Leipzig
bey Siegfried Lebrecht Cruſius
1782.

Figure 1*. Title page of the German edition of* Chemische Abhandlung von der Luft und dem Feuer.

The Nature of Ordinary Air

In a first series of experiments (§ 8-16) the nature of ordinary air is investigated. The experiment on *liver of sulphur* (*hepar sulphuris*, a red-coloured mixture of potassium sulfide and, to a smaller extent, potassium polysulfide) is reported in detail (§ 8). Four ounces (1 Swedish ounce = 29.69 g (1) ≈ 29.69 mL of water) of the *liver* solution in water was poured into a bottle whose capacity, about 712.6 mL, had been previously determined by filling it with 24 ounces of water. The volume of the bottle occupied by the air was therefore (24 – 4)·29.69 = 593.8 mL. The bottle was corked and held upside down for 14 days. During this time the red colour faded and some sulfur precipitated. With the neck immersed in a large water vessel the bottle was uncorked. Immediately the water rose with violence along the neck and it was possible to weigh the liquid in the bottle, 10 ounces. Considering the starting solution, 4 ounces, the weight increase amounted to 6 ounces. Correspondingly, the loss of air was 6·29.69 ≈ 178.1 mL, going from the initial volume, 593.8 mL, to 415.7 mL.

Looking at this experiment from our present-day point of view, it should be first noted that the reaction occurred in partial absence of oxygen. Assuming for simplicity pure K_2S as solute and knowing that the sulfide ion S^{2-} is completely hydrolyzed to HS^- in water solution (29) the reaction is

$$HS^- + \frac{1}{2}O_2 \rightarrow S + OH^-$$

The moles of HS^- may be calculated from the reported data relative to the sample preparation (1 ounce of *liver of sulfur* dissolved in 8 ounces of water and then half of the quantity, 4 ounces, taken) and found to be n_{HS-} = 0.135 mol. The reaction would go to completion with n_{O2} = 0.0675 mol, i.e., with 1.512 L of oxygen at STP conditions assuming ideal gas behavior. The volume of oxygen in 20 ounces of common air, using the current accepted value of 20% for the oxygen fraction, is found to be 20 oz·29.69 (g/oz)·10^{-3} (L/g)·0.2 = 0.119 L. It is concluded that the reaction is O_2-limited under the reported experimental conditions.

Further, Scheele noted that the reaction does not proceed indefinitely; starting with the same amount of reagent and waiting 4 months instead of 14 days the same air is lost, again 6 ounces out of 20. This observation, straightforward on the basis of the stoichiometric considerations mentioned above (but not yet known at that time), is interpreted by the following words intended to confirm the combination of air with the phlogiston contained in *liver of sulfur* (30, § 16):

> It may also be seen from the above experiments that a given quantity of air can only unite with, and at the same time saturate, a certain quantity of the inflammable substance [phlogiston].

Following the same experimental procedure, the contraction of a confined volume of air in contact with various other materials, including sulfur, *nitrous air* (NO), oil of turpentine, and *green calx of iron* ($Fe(OH)_2$), was reported. The yellow solution of sulfur in solution of *caustic lye* (in modern terms, a solution of potassium hydroxide), discoloured completely in 14 days (§ 10), proceeding by

$$S + 3/2\ O_2 + 2OH^- \rightarrow SO_4^{2-} + H_2O$$

The reaction allowed Scheele to say (30, § 10)

> The air in this bottle had likewise diminished, from the fact that air rushed into the bottle with a hissing sound after I had made a small hole in the cork.

Dissolving *green vitriol* ($FeSO_4$) in water and then adding *caustic lye,* the dark *green calx of iron* sedimented (§ 15). Inserting the *calx* with some water into a bottle, the colour changed in 14 days from green to yellow, the colour of the *crocus of iron*, due to the reaction

$$2\ Fe(OH)_2 + ½\ O_2 \rightarrow Fe_2O_3{\bullet}H_2O + H_2O$$

The loss of air in the bottle was 12 parts out of 40.

It was a main point of the phlogiston theory, shared also by Scheele, that the inflammable principle (phlogiston, Φ) was a fluid present in all substances in varying quantities and that the above reactions could be simply explained as due to the attraction of air toward phlogiston. Since the reactions were carried out in a limited volume of air, the transfer of phlogiston from the substance to the air was accompanied by a second effect, i.e., an appreciable part of the air was lost (§ 16). So, the crucial question Scheele tried to answer is the following: is the phlogiston present in the residual air, compressing it, or has the lost air been fixed by the reacting materials? In his own words (30, § 16)

> But whether the phlogiston which was lost by the substances was still present in the air left behind in the bottle, or whether the air which was lost had united and fixed itself with the materials such as liver of sulphur, oils, etc., are questions of importance.

We may describe the two hypotheses by the following schemes

(a) $(calx + \Phi) + \text{air} \rightarrow calx + (\text{air} + \Phi)$

(b) $(calx + \Phi) + \text{air} \rightarrow (calx + \text{air} + \Phi)$

In the first hypothesis phlogiston is part of the compressed air. Thus, due to compression this air must be "specifically heavier than ordinary air," for instance by a factor (20/14) in the experiment with *liver of sulphur*. Scheele carefully tested this hypothesis and realized, on the contrary, that the weight of this air did not even counterpoise that of an equal volume of ordinary air: it actually was lighter. The possible objection that phlogiston in the residual air makes it lighter implies a negative weight for phlogiston (30, § 24)

> But since phlogiston is a substance, which always presupposes some weight, I much doubt whether such hypothesis has any foundation.

Ordinary air is composed of two fluids, in proportions of two or three to one by volume, with different behavior with respect to phlogiston (30, § 16)

> the one of which [nitrogen] does not manifest in the least the property of attracting phlogiston, while the other [which he would later call *fire air*, and which we know as oxygen], which composes between the third and the fourth part of the whole mass of the air, is peculiarly disposed to such attraction.

This conclusion is strongly at variance with the tenet that air is one of the four elements together with fire, water and earth (17). In the previous century John Mayow had put forward a similar view saying that air contains two types of particles, of which only the nitro-aerial particles are active in combustion and respiration processes (1, 3).

If, on the other hand, the second hypothesis is correct, Scheele argues that the lost air could be separated as *fixed air* from the reaction products. He searched for *fixed air* adding *lime water* to the final solution and looking for *chalk* (calcium carbonate, $CaCO_3$) precipitation. No such reaction was observed. All other numerous attempts in the same direction were equally unsuccessful. So, it was left as an open issue to study with further experiments the fate of this *air* after union with phlogiston (30, § 16)

> But where this latter kind of air has gone to after it has united with the inflammable substance, is a question which must be decided by further experiments, and not by conjectures.

Air and Fire

The next question is about the role of air "towards inflammable substances when they get into fiery motion" (30, § 16, referring to §§ 17-23). Scheele distinguished two types of combustion reactions, according to the absence or presence of any fluid resembling air among reaction products. Examples of the first group are the combinations of phosphorus and *inflammable air* (H_2) with air

$P_4 + 5\ O_2 \rightarrow 2\ P_2O_5$

$2\ H_2 + O_2 \rightarrow 2\ H_2O$

In the first experiment Scheele inserted a small quantity of phosphorus in a thin flask of 30 ounces capacity (≈ 0.89 L) and then corked tightly (§ 17). Warming the sample with a candle, phosphorus quickly melted and burned giving *"white flowers"* on the inside walls of the flask. These are *"the dry acid of phosphorus"* (phosphorus pentoxide, P_2O_5). Back to room temperature, the flask was turned upside down over water and the cork removed. The water pushed into the flask occupied 9/30 of the total volume. Repeating the experiment without the action of fire but waiting for six weeks *"until* (phosphorus) *no longer glowed"* a similar reduction factor, (1/3), was determined.

In a second and most famous experiment, *inflammable air* was produced by adding dilute *oil of vitriol* to iron filings in the small bottle A (§ 19, see Figure 2, upper part, center). When "violent heating and fermentation" decreased, the bottle was placed at the centre of the large vessel BB of hot water and connected through a cork to a long and small-sized pipe. *Inflammable air* quickly evolved and approaching a candlelight to the upper orifice C the *air* burned with a yellowish-green flame. With the usual apparatus, i.e., pipe + flame under the cap of a 20-ounce flask and neck immersed into the water, the liquid began to rise inside the flask until the maximum D, corresponding to the flame extinction. At this moment the water lowered to the initial level, due to the uninterrupted production of *inflammable air* inside the bottle. Having measured the volume occupied by the rising water, four ounces, Scheele concluded that "the fifth part of the air had been lost" (30, § 19). *Aerial acid* (carbon dioxide, CO_2) was not formed during the combustion since upon adding *lime water* no *chalk* precipitated.

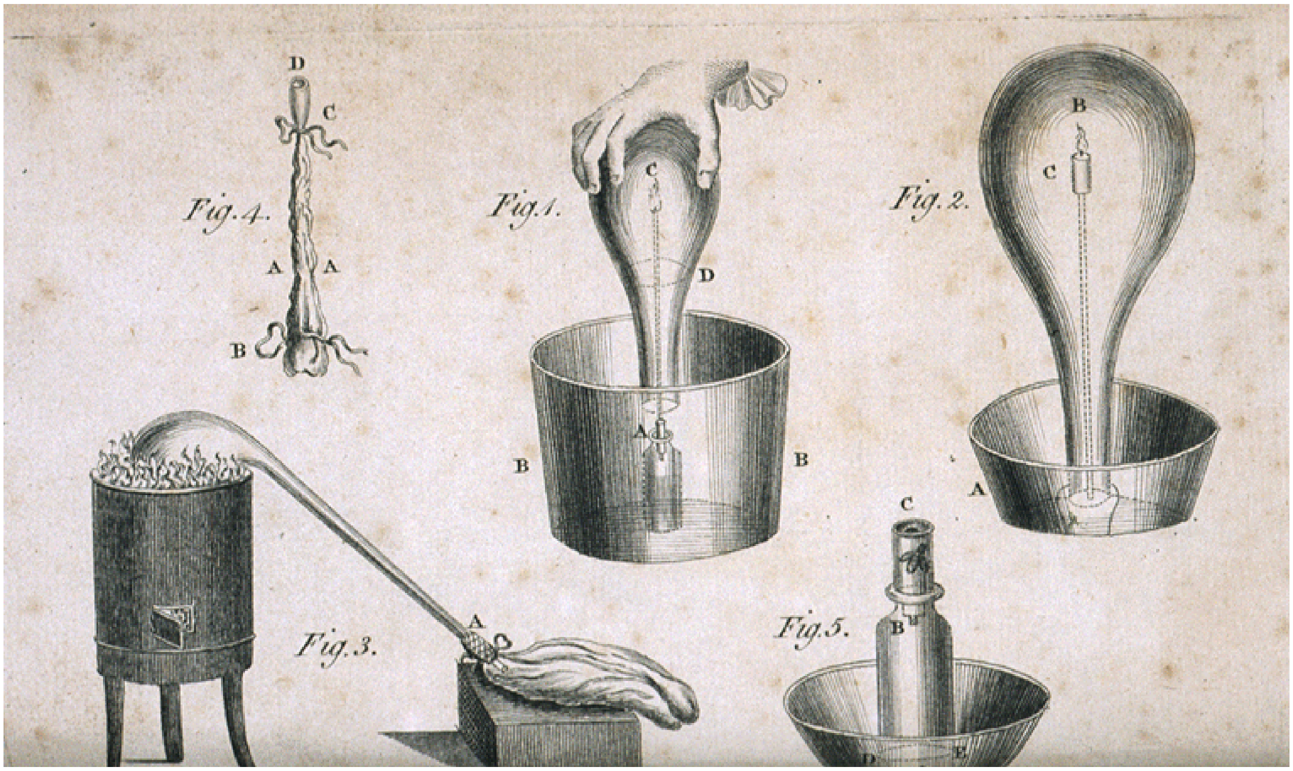


***Figure 2**. Original drawings of the experiments described in the* Chemical Observations*, English edition (27).*

Scheele's great chemical skill and critical analysis of data may be appreciated going to the second group of combustion reactions, those giving "fluid resembling air" (30, § 16, referring to §§ 20-22). Initially Scheele tried to measure the air loss when a candle burns under a flask inverted over water. Although the air volume in the flask was reduced by the fourth part he was dissatisfied with this experiment. He noted that large air bubbles were generated by heat due to air expansion, leading to the hypothesis that the air was "driven out by the heat of the flame." The experiment was improved fixing the candle to a thick iron wire, affixed onto a waxy mass and placed on a dish (Figure 2, upper right). The candle was lighted, enshrouded within a 160-ounce flask whose neck was pressed into the waxy mass. Only after completing this preparation the dish was filled with water. At the end of the combustion the flask was opened under water and only two ounces of liquid entered. The small contraction was ascribed to air expansion even before that the neck was sealed, rather than to the air absorption by the inflammable substance. This was even more true, according to Scheele, since repeating the experiment with a 20 ounces flask the same contraction of two ounces was found; on the contrary "had the former two ounces measure of air been absorbed then there should have been two drachms measure absorbed in this experiment." He concluded (30, § 21)

> These experiments seem to prove that the transference of phlogiston to the air does not always diminish its bulk which, however, the experiments mentioned in §§ 8-16 shew distinctly.

But he continued with this decisive statement (30, § 21)

> But the following will show that that portion of air which unites with the inflammable substance, and is at the same time absorbed by it, is replaced by the newly formed aerial acid [CO_2].

The point was proven by pouring *milk of lime* (a suspension of calcium hydroxide, $Ca(OH)_2$) in the flask and shaking thoroughly. Scheele was able to repeat this operation four times; a small orifice was carefully opened after each time and water rose into the flask. The final reduction factor was 1/19, due to the absorption of *aerial acid* by *milk of lime*. The small contraction, 1/19, with respect to that of phosphorus, 1/3, was explained by the fact that "it is known that one part of aerial acid mixed with ten parts of ordinary air extinguishes fire" (30, § 22). Therefore, the combustion stopped before all air was absorbed. On the contrary, after adding *milk of lime* the candle could burn once again for a short time.

We comment with the help of the reaction stoichiometry. The candle combustion occurs in a 4.75 L (≈ 160 ounces) flask, and the reaction takes place in excess of paraffin wax. If we assume for simplicity that the paraffin wax is composed only by the single high-numbered saturated hydrocarbon $C_{30}H_{62}$ the combustion may be written as

$$2\ C_{30}H_{62} + 91\ O_2 \rightarrow 60\ CO_2 + 62\ H_2O$$

On the basis of the O_2 volume, 1/5 of the atmospheric volume, and consuming $(1/5)\cdot 4.75$ L = 0.95 L of O_2, $(60/91)\cdot 0.95$ L = 0.62 L of CO_2 are produced with a net loss of 0.33 L. The reduction factor, 0.33/4.75 = 0.069, appears to be appreciably close to the factor 1/19 = 0.052 and consistent with Scheele's observation that the candle could still burn a bit more if the *fixed air* was removed.

Searching and Obtaining *Fire Air*

Scheele analyzed under a close scrutiny the *inflammable air* experiment searching for the lost air. It could be neither in the residual air, being this latter lighter than ordinary air, nor in the aqueous solution since no *aerial acid* was detected. Since he worked over hot water, the true product, in the form of dew droplets inside the flask, was missed. He hypothesized that from the union of air and phlogiston (27, §24)

> a compound [heat] is formed, so subtle as to pass through the fine pores of the glass and disperse all over the air.

Scheele thus considered heat as a fluid arising from the reaction of *fire air* with phlogiston (1)

fire air + phlogiston → heat.

The purpose of the ensuing experiments (§ 25-29) was the dissociation of heat, having as a necessary consequence the setting free of *fire air*. The affinity for phlogiston of the *acid of nitre* (nitric acid, HNO_3) was first evaluated (30, § 27)

> The acid of nitre can attract phlogiston in varying quantity, when it likewise receives other properties with each proportion".

Scheele established the phlogiston content of *nitrous air* (NO), dinitrogen trioxide (N_2O_3), *red fumes* (NO_2) and *acid of nitre* (HNO_3) on the basis of the following experiments (§ 25-27). Dissolving a metal, rich in phlogiston, in *acid of nitre* this latter is converted into a more *phlogisticated* substance, *nitrous air*, an *air* not soluble in water and not reacting with alkali and *"alkaline earths"* (oxides such as MgO and CaO)

$$\begin{array}{lcl} (\textit{calx} + \Phi) + \textit{acid of nitre} & \rightarrow & \textit{calx} + (\textit{acid of nitre} + \Phi) \\ \text{metal} & & \text{nitrous air} \\ 3\ Cu + 2\ NO_3^- + 8H^+ & \rightarrow & 3\ Cu^{2+} + 2\ NO + 4\ H_2O \end{array}$$

Phlogiston in *nitrous air* attracts common air and the reaction gives less *phlogisticated* vapors, the *red fumes*,

(*acid of nitre* + Φ) + air	→	(*acid of nitre* + air + Φ)
nitrous air		*red fumes*
$NO + ½ O_2$	→	NO_2

Red fumes are soluble in alkali,

$2 NO_2 + 2 OH^– \rightarrow NO_3^– + NO_2^– + H_2O$.

Further, Scheele observed (30, § 27)

> When the acid of nitre receives still somewhat less phlogiston it is likewise converted into a kind of air, which, like the air, is also invisible [N_2O_3] but unites with the alkalies and earths …

(*calx* + Φ) + *acid of nitre* → *calx* + (*acid of nitre* + Φ)

$2 Cu + 2 NO_3^– + 6 H^+ \rightarrow 2 Cu^{2+} + N_2O_3 + 3 H_2O$

Common air is similarly transferred to this *invisible air* (30, § 27)

> When this acid of nitre [N_2O_3] meets the air it also loses its elasticity and is converted into red vapours [$N_2O_3 + ½ O_2 \rightarrow 2NO_2$].

The phlogiston content is in the order *nitrous air* > *invisible air* > *red fumes* > *acid of nitre*. In conclusion (30, § 27) ,

> This acid [HNO_3] holds this small quantity of phlogiston so firmly that even the air, which so strongly attracts the inflammable substance, is not able to separate this from it.

With these premises Scheele explained the behavior of the *fuming acid of nitre* upon distillation. He observed that upon adding *oil of vitriol* to *nitre* (potassium nitrate, KNO_3) the vapors are red colored (*red fumes*) at the beginning of distillation, colorless in the middle and again red at the end of distillation. Further heating with great determination (30, § 25)

> … the whole mixture enters into such frothing that everything goes over into the receiver; and, what is of the great importance, a kind of air goes over during this frothing which deserves no small attention.

The vapors of the *acid of nitre* are not intrinsically red since in the distillation by gentle heating only the first fraction is colored and then a liquid is collected "white and colourless like water," which Scheele called pure *acid of nitre*. (The *fuming acid of nitre* is a mixture whose composition (by weight) is actually 82.5-85.5% (HNO_3), 14% (NO_2) and 1-2% (H_2O) (31, 32).) Scheele now asked the critical question about the appearance of the red color at the end of the distillation (30, § 25)

> Why has not this redness already been driven over at the beginning? Where does it now obtain its phlogiston?

His answer was that pure *acid of nitre* acts with such a strong affinity for phlogiston that displaces it from heat, by analogy to the case of metals, and sets free *fire air*

(*calx* + Φ) + *acid of nitre*	→	*calx* + (*acid of nitre* + Φ)
metal		*nitrous air*
(*fire air* + Φ) + *acid of nitre*	→	*fire air* + (*acid of nitre* + Φ)
heat		red fumes

The description of the experiment (30, § 29) is a fascinating piece of science (underlines and bolds are our additions; the experimental apparatus is shown in Figure 2**,** lower left)

> In the beginning [of the distillation] the acid went over red, then it became colourless and finally all became red again; as soon as I perceived the latter I took away the receiver and tied on a bladder, emptied of air, into which I poured some thick milk of lime in order to prevent the corrosion of the bladder. I then proceeded with the distillation. The bladder began to expand gradually. After this I permitted everything to cool and tied up the bladder. Lastly, I removed it from the neck of the retort. I filled a bottle, which contained 10 ounces of water with the gas, I then placed a small lighted candle in it; scarcely had this been done when the candle began to burn with a large flame, whereby it gave out such a bright light that it was sufficient to dazzle the eyes. I mixed one part of this air with three parts of that kind of air in which fire would not burn; I had here an air which was like the ordinary air in every respect. Since this air is necessarily required for the origination of fire, and makes up about the third part of our common air, I shall call it after this, for the sake of shortness, **Fire-air** [Feuer Luft]; but the other which is not in the least serviceable for the fiery phenomenon, and makes up about two-thirds of our air, I shall designate after this with name already known, of **Vitiated Air** [verdorbene Luft].

However, a doubt lingered in Scheele's mind: who could exclude that the air produced is not simply the *dry acid of nitre* (HNO_3 vapor, or perhaps N_2O_5) converted to *red fumes* (§ 31)? To solve the dilemma one argument is presented and a long series of experimental results are reported (§ 31-41). First, in this case the air which has been isolated should be corrosive and soluble in alkali, regenerating nitre, but this does not occur. As we now understand this reaction, "the well-known thermal instability of nitric acid at temperature above its melting point" (33) is the origin of O_2 formation

$2 HNO_3 \rightarrow 2 NO_2 + ½ O_2 + H_2O$

Second and more important, Scheele was able to show that *fire air* is obtained also upon heating several other substances, not only *acid of nitre*. Here we summarize some results.

Given the strong affinity of the *acid of nitre* for phlogiston, this behavior might be replicated by its salts (nitrates). In fact, upon heating in a retort (a) $Mg(NO_3)_2$, i.e., *magnesia alba* (magnesium carbonate, $MgCO_3$) in *aqua fortis* (HNO_3 aqueous solution), and (b) *mercurial nitre* (mercuric nitrate, $Hg(NO_3)_2$), i.e., *red precipitate* (mercuric oxide, HgO) similarly dissolved in *aqua fortis*, Scheele obtained *fire air*. Having in mind that heat is (*fire air* + Φ), the reactions from the phlogiston and actual point of view are

(*calx* + *acid of nitre*) + (*fire air* + Φ) → *calx* + (*acid of nitre* + Φ) + *fire air*

$$Hg(NO_3)_2 \rightarrow HgO + 2NO_2 + ½O_2$$

Dealing with *nitre* (also known as *saltpetre*) Scheele describesd the “cheapest and best method of obtaining fire air” (30, § 35). The formation of *fire air* is carried out without *milk of lime* being necessary in the bladder

nitre + (*fire air* + Φ) → (*nitre* + Φ) + *fire air*

$$KNO_3 \rightarrow KNO_2 + ½ O_2$$

A second source of *fire air* are *calxes* of silver and mercury *“united with a quantity of aerial acid”* (silver and mercury carbonates, Ag_2CO_3 and $HgCO_3$). The *calxes* attract phlogiston and provided that *aerial acid* is absorbed in the bladder by *milk of lime*, pure *fire air* is formed

(*calx* + *aerial acid*) + (*fire air* + Φ) → (*calx* + Φ) + *aerial acid* + *fire air*

$$HgCO_3 \rightarrow Hg + CO_2 + ½ O_2$$

Fire air was equally obtained by heating the *calxes* of mercury (HgO) and gold (Au_2O_3) and arsenic acid (H_3AsO_4).

The *fire air* obtained on heating acid of nitre and all other substances coincides with the air “which composes between the third and the fourth part of the whole mass of the air” (30, § 16). In order to establish the identity, Scheele substituted common air with *fire air* in the combustion experiments with or without fire (§ 42-49). *Fire air* enclosed in a bottle containing a solution of *liver of sulphur*, then immersed upside down over a vessel, is absorbed by the solution, and external water completely fills the volume after bottle opening. If, however, *fire air* and *vitiated air* are mixed in the ratio 4:14 and the same procedure is followed, only four parts of the mixture are absorbed. In another experiment with phosphorus enclosed in a thin bottle containing *fire air*, the substance burns with a brilliant flame but at the end of the combustion the bottle breaks in many fragments. In a thicker bottle the cork could be opened under water and with *fire* and *vitiated air* in the 1:2 ratio only 1/3 of the mixture was lost. The identity is stated in § 49, “these experiments show that this fire air is just that air by means of which fire burns in common air” (30, § 50).

Scheele knew that *vitiated air* was lighter than common air. It follows that *fire air* should be heavier. He was able to weigh as accurately as possible the *fire air* that filled a flask capable of holding 20 ounces of water, and the same volume of common air, and he found the former two grains heavier than the latter (§ 49). Since 1 Swedish ounce = 480 grains = 29.69 grams (1), this means that the *fire air* density is greater than the density of common air by 0.208 g/L. The reported difference between oxygen and air densities amounts to 0.136 g/L at STP conditions (34).

The Experimental Apparatus

Scheele mastered with great expertise all chemical reactions though relying on simple laboratory apparatus made of flasks, retorts, bottles and glasses. The importance of ox bladders, by means of which he could transfer *airs* from one vessel to another, is stressed in § 30 (see Figure 2, upper left) and some examples offer an idea of his experimental talent. The *phlogisticated acid of nitre* or *nitrous air* (NO) was prepared by putting a few metal filings into the bladder which was then well pressed to expel as much common air as possible from inside, and connecting it to a small bottle containing *aqua fortis*. The reaction was activated by the fall of the metal pieces into the bottle and the evolved *nitrous air* was collected in the bladder. The reverse operation, bladder → bottle, is a little more complicated since the bottle has to be filled completely with water, corked and connected to the bladder (containing the *air*). With the bottle up and the bladder down, the cork was withdrawn and the water flowed into the bladder. Thus, *air* displaces water from the bottle and the volume of *air* transferred is equal to the volume of water flowing into the bladder. Modifying slightly the procedure, two kinds of *air*, each dispensed from a different bladder, may be mixed in a bottle. Having again a bottle filled with water, as much water flows into the first bladder as the volume of *air* desired in the bottle, and then all the remaining water into the second bladder, determining the second volume of the mixture.

The bottle now contains two *airs* in a known ratio. This protocol may be reversed, bottle → bladder, and the volume of *air* is equal to the volume of water displaced from the bladder. If *milk of lime* absorbs one of the two *airs*, it is possible to establish the composition (by volume) of the mixture using a bladder filled with a volume of *milk of lime* equal to that of the bottle. Washing the *airs*, bladder up and bottle down, and allowing the *milk of lime* to go back again into the bladder, this operation may be repeated several times. At the end a volume of *milk of lime* will remain in the bottle equal to the absorbed *air*.

The final comment on the experimental apparatus coming from this great, yet modest and pragmatic chemist, is worth being considered as a wise reminder in our time (30, § 30):

> These are the methods which I employed in my investigations of air. I admit that they will not particularly please some, because they do not decide with great exactness. They afforded me satisfaction, however, in all my investigations; and people will often split a hair where it is not in the least necessary.

Conclusions

In this paper Scheele's outstanding experimental research leading to the discovery of oxygen has been reviewed. It comes from reading the *Chemische Abhandlung* that all the experiments were carefully planned and performed with a systematic approach. There is no doubt about the Scheele's priority of the discovery although in the book he did not claim priority (18). He was also the discoverer of an impressive number of other chemical species. Nevertheless, Scheele maintained a low scientific profile all his life, and discretion was a distinctive attribute of his character (21). He worked hard in a relatively obscure environment, in dramatic contrast with Priestley and Lavoisier, with scarce resources for research and being not fully aware of timing in publication. He did not have links with prestigious institutions like the Royal Society of England and the French Académie des Sciences. He was elected to the Royal Swedish Academy of Science but attended only one meeting. In summary, the emerging picture is that of a man with a tremendous chemical curiosity, totally dedicated to the pursuit of scientific truth by experimenting in laboratory once the work time as apothecary was terminated, and able to reach astonishing results with limited opportunities. The point is well outlined with moving and affectionate words in a long passage of Oliver Sacks's autobiographical memoir *Uncle Tungsten – Memories of a Chemical Boyhood* (35)

> Scheele was one of Uncle Dave's great heroes. Not only had he discovered tungstic acid and molybdic acid (from which the new element molybdenum was made), but hydrofluoric acid, hydrogen sulfide, arsine, and prussic acid, and a dozen organic acids, too. All this, Uncle Dave said, he did by himself, with no assistant, no funds, no university position or salary, but working alone, trying to make ends meet as an apothecary in a small provincial Swedish town. He had discovered oxygen, not by a fluke [referring to Priestley?], but by making it in several different ways; he had discovered chlorine; and he had pointed the way to the discovery of manganese, of barium, of a dozen other things.
>
> Scheele, Uncle Dave would say, was wholly dedicated to his work, caring nothing for fame or money and sharing his knowledge, whatever he had, with anyone and everyone. I was impressed by Scheele's generosity, no less than his resourcefulness, by the way in which (in effect) he gave the actual discovery of elements to his students and friends—the discovery of manganese to Johan Gahn, the discovery of molybdenum to Peter Hjelm, and the discovery of tungsten itself to the d'Elhuyar brothers.
>
> Scheele, it was said, never forgot anything if it had to do with chemistry. He never forgot the look, the feel, the smell of a substance, or the way it was transformed in chemical reactions, never forgot anything he read, or was told, about the phenomena of chemistry. He seemed indifferent, or inattentive, to most things else, being wholly dedicated to his single passion, chemistry. It was this pure and passionate absorption in phenomena—noticing everything, forgetting nothing—that constituted Scheele's special strength.

There is an unfortunate circumstance which sadly exemplifies the scarcely influential role of Scheele in the context of the history of the oxygen discovery in the years 1770-1780. In autumn 1774 Scheele sent a letter to Lavoisier, in French and dated 30 September, answering for the gift of the *Opuscules chimiques et physiques* received few months before (1). A draft copy is conserved in the Centre for History of Science in Stockholm (36) while the letter, which was thought to be lost, amazingly resurfaced in the Archives of the French Académie des Sciences in 1890 thanks to E. Grimaux (37). In this letter Scheele, after words of gratitude for the book, suggests how to prepare *fire air* from *calx* of silver united with *aerial acid* (silver carbonate, Ag_2CO_3), which is nothing less than an announcement of the discovery of oxygen, as follows (quoted from Ref. 21)

> Because I do not have any large burning glass, I beg you to carry out an experiment (a trial) with yours in this way: Dissolve some silver in nitrous acid and

> precipitate it with alkaline tartrate, wash the precipitate [Ag_2CO_3], dry it, and reduce it with the burning glass in your machine, fig. 8 [of the *Opuscules*], but because the air in the bell jar (this receiver) is such that animals die in it and a part of the fixed air separates from the silver in this operation, it is necessary to place a bit of quick lime [CaO] in the water where one has put the bell, so that this fixed air joins more quickly with the lime. This is the way that I hope that you will see how much air is formed during this reduction, and whether a lighted candle can keep burning and animals live in it.

Lavoisier *"malheureusement ne donna pas suite à cette correspondance"* (38), never acknowledging the receipt of the letter. The meaning of this paragraph could hardly have escaped the understanding of Lavoisier but his failure to acknowledge the scientific contributions from other scientists was an unfortunate trait of his personality.

In a successful play written by Roald Hoffman and Carl Djerassi (38), the imaginative plot device is advanced that Madame Lavoisier, laboratory assistant and partner, deliberately hid the letter to legitimate the claim that her husband was the sole discoverer of oxygen. Whether the device is true or false, the play is really about the issue of scientific discovery and interpretation (39). A "retro-Nobel" prize is proposed in 2001, the year marking the centennial of the Nobel prize, to award the chemist credited with the most important discovery predating 1901. Two interlocking stories unfold, in one of which a committee investigates the oxygen discovery without, however, reaching a conclusion about who is the first discoverer. In the other a meeting is imagined in Stockholm in 1777 between Scheele, Priestley, Lavoisier and their wives, where they present their individual claims to priority and the King of Sweden will honor one of them. No agreement is reached between the four members of the committee, three indicating a different chemist and the chair all three. The King decides not to make the award. Who is the real discoverer? Scheele was the first to isolate oxygen without publishing, Priestley obtained oxygen independently and published the results. However, the common belief in the theory of phlogiston was their theoretical limitation. Lavoisier learned from Priestley (and perhaps Scheele) and reached what we now understand to be the best interpretation of the role of oxygen in chemical processes (40).

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