The Phlogiston Theory —A Classic of Science

Chemistry

THE DISCOVERY OF OXYGEN, Part 2. Experiments by Carl Wilhelm Scheele (1777). *Published by the Alembic Club* (*Reprint No.* 8). *Edinburgh*: 1901.

One hundred and fifty years ago, fire was one of the unsolved mysteries of science. Watching its consuming action in their fireplaces, people naturally concluded that it is the escape of some light, gaseous substance. This substance Scheele named "phlogiston." Later, experimenting with simpler substances, the chemists found that metals increase in weight on being burnt. This raised the question as to how the escape of phlogiston increased weight, and many men of science adopted the absurdity, which Scheele rejected, of endowing phlogiston with "negative gravity." The concept is still a boon to authors of pseudo-scientific fiction, but proved a serious handicap to chemistry until Lavoisier's clear thinking swept out the theorizing and solved the problem by experiment. Scheele is here seen to be a true experimentalist, also, but his followers, taking his half-finished work as authority, ran into the pitfall that always awaits arm-chair scientists.

7. General properties of ordinary air.

(1.) Fire must burn for a certain time in a given quantity of air. (2.) If, so far as can be seen, this fire does not produce during combustion any fluid resembling air, then, after the fire has gone out of itself, the quantity of air must be diminished between a third and a fourth part. (3.) It must not unite with common water. (4.) All kinds of animals must live for a certain time in a confined quantity of air. (5.) Seeds, as for example peas, in a given quantity of similarly confined air, must strike roots and attain a certain height with the aid of some water and of a moderate heat.

Consequently, when I have a fluid resembling air in its external appearance, and find that it has not the properties mentioned, even when only one of them is wanting, I feel convinced that it is not ordinary air.

8. Air must be composed of elastic fluids of two kinds.

First Experiment.—I dissolved one ounce of alkaline liver of sulphur in eight ounces of water; I poured 4 ounces of this solution into an empty bottle capable of holding 24 ounces of water, and closed it most securely with a cork; I then inverted the bottle and placed the neck in a small vessel with water; in this position I allowed it to stand for 14 days. During this time the solution had lost a part of its red colour and had also deposited some sulphur: afterwards I took the bottle and held it in the same position in a larger vessel with water, so that the mouth was under and the bottom above the water-level, and withdrew the cork under the water; immediately water rose with violence into the bottle. I closed the bottle again, removed it from the water, and weighed the fluid which it contained. There were 10 ounces. After substracting from this the 4 ounces of solution of sulphur there remain 6 ounces, consequently it is apparent from this experiment that of 20 parts of air 6 parts have been lost in 14 days.

9. Second Experiment.—(a.) I repeated the preceding experiment with the same quantity of liver of sulphur, but with this difference that I only allowed the bottle to stand a week, tightly closed. I then found that of 20 parts of air only 4 had been lost. (*b.*) On another occasion I allowed the very same bottle to stand 4 months; the solution still possessed a somewhat dark yellow colour. But no more air had been lost than in the first experiment, that is to say 6 parts.

10. Third Experiment.—I mixed 2 ounces of caustic ley, which was prepared from alkali of tartar and unslaked lime and did not precipitate lime water, with half an ounce of the preceding solution of sulphur which likewise did not precipitate lime water. This mixture had a yellow colour. I poured it into the same bottle, and after this had stood 14 days, well closed, I found the mixture entirely without colour and also without precipitate. I was enabled to conclude that 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.

11. Fourth Experiment.—(a.) I took 4 ounces of a solution of sulphur in lime water; I poured this solution into a bottle and closed it tightly. After 14 days the yellow colour had disappeared, and of 20 parts of air 4 parts had been lost. The solution contained no sulphur, but had allowed a precipitate to fall which was chiefly gypsum. (*b.*) Volatile liver of sulphur likewise diminishes the bulk of air. (*c.*) Sulphur, however, and volatile spirit of sulphur, undergo no alteration in it.

12. Fifth Experiment.—I hung up over burning sulphur, linen rags which were dipped in a solution of alkali of tartar. After the alkali was saturated with the volatile acid, I placed the rags in a flask, and closed the mouth most carefully with a wet bladder. After 3 weeks had elapsed I found the bladder strongly pressed down; I inverted the flask, held its mouth in water, and made a hole in the bladder; thereupon water rose with violence into the flask and filled the fourth part.

13. Sixth Experiment.—I collected in a bladder the nitrous air which arises in the dissolution of the metals in nitrous acid, and after I had tied the bladder tightly I laid it in a flask and secured the mouth very carefully with a wet bladder. The nitrous air gradually lost its elasticity, the bladder collapsed, and became yellow as if corroded by *aqua fortis*. After 14 days I made a hole in the bladder tied over the flask, having previously held it, inverted, under water; the water rose rapidly into the flask, and it remained only two-thirds empty.

14. Seventh Experiment.—(a.) I immersed the mouth of a flask in a vessel with oil of turpentine. The oil rose in the flask a few lines every day. After the lapse of 14 days the fourth part of the flask was filled with it; I allowed it to stand for 3 weeks longer, but the oil did not rise higher. All those oils which dry in the air, and become converted into resinous substances, possess this property. Oil of turpentine, however, and linseed oil rise up sooner if the flask is previously rinsed out with a concentrated sharp ley. (*b.*) I poured 2 ounces of colourless and transparent animal oil of Dippel into a bottle and closed it very tightly;

after the expiry of two months the oil was thick and black. I then held the bottle, inverted, under water and drew out the cork; the bottle immediately became one-fourth filled with water.

15. Eighth Experiment.—(a.) I dissolved 2 ounces of vitriol of iron in 32 ounces of water, and precipitated this solution with a caustic ley. After the precipitate had settled, I poured away the clear fluid and put the dark green precipitate of iron so obtained, together with the remaining water, into the before-mentioned bottle (§ 8), and closed it tightly. After 14 days (during which time I shook the bottle frequently), this green calx of iron had acquired the colour of crocus of iron, and of 40 parts of air 12 had been lost. (*b.*) When iron filings are moistened with some water and preserved for a few weeks in a well closed bottle, a portion of the air is likewise lost. (*c.*) The solution of iron in vinegar has the same effect upon air. In this case the vinegar permits the dissolved iron to fall out in the form of a yellow crocus, and becomes completely deprived of this metal. (*d.*) The solution of copper prepared in closed vessels with spirit of salt likewise diminishes air. In none of the foregoing kinds of air can either a candle burn or the smallest spark glow.

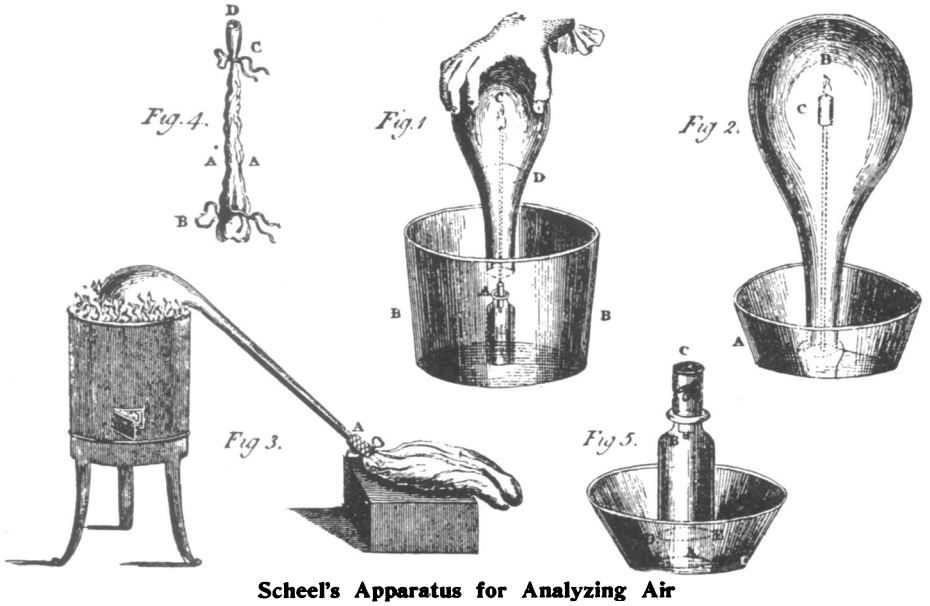
16. It is seen from these experiments that phlogiston, the simple inflammable principle, is present in each of them. It is known that the air strongly attracts to itself the inflammable part of substances and deprives them of it: not only this may be seen from the experiments cited, but it is at the same time evident that on the transference of the inflammable substance to the air a considerable part of the air is lost. But that the inflammable substance alone is the cause of this action, is plain from this, that, according to the 10th paragraph, not the least trace of sulphur remains over, since, according to my experiments this colourless ley contains only some vitriolated tartar. The 11th paragraph likewise shews this. But since sulphur alone, and also the volatile spirit of sulphur, have no effect upon the air (§ 11, *c*), it is clear that the decomposition of liver of sulphur takes place according to the laws of double affinity,—that is to say, that the alkalies and lime attract the vitriolic acid, and the air attracts the phlogiston.

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: this is evident from the 9th paragraph, *letter b.* 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.

From the first view, it would necessarily follow that the inflammable substance possessed the property of depriving the air of part of its elasticity, and that in consequence of this it becomes more closely compressed by the external air. In order now to help myself out of these uncertainties, I formed the opinion that any such air must be specifically heavier than ordinary air, both on account of its containing phlogiston and also of its greater condensation. But how perplexed was I when I saw that a very thin flask which was filled with this air, and most accurately weighed, not only did not counterpoise an equal quantity of ordinary air, but was even somewhat lighter. I then thought that the latter view might be admissible; but in that case it would necessarily follow also that the lost air could be separated again from the materials employed. None of the experiments cited seemed to me capable of showing this more clearly than that according to the 10th paragraph, because this residuum, as already mentioned, consists of vitriolated tartar and alkali. In order therefore to see whether the lost air had been converted into fixed air, I tried whether the latter shewed itself when some of the caustic ley was poured into lime water; but in vain—no precipitation took place. Indeed, I tried in several ways to obtain the lost air from this alkaline mixture, but as the results were similar to the foregoing, in order to avoid prolixity I shall not cite these experiments. Thus much I see from the experiments mentioned, that the air consists of two fluids, differing from each other, the one of which does not manifest in the least the property of attracting phlogiston, while the other, which composes between the third and the fourth part of the whole mass of the air, is peculiarly disposed to such attraction. 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....

24. Experiments which prove that air, consisting of two kinds of elastic fluids, can be compounded again after these have been separated from each other by means of phlogiston.

I have already stated in § 16 that I was not able to find again the lost air. One might indeed object, that the lost air still remains in the residual air which can no more unite with phlogiston; for, since I have found that it is lighter than ordinary air, it might be believed that the phlogiston united with this air makes it lighter, as appears to be known already from other experiments. But since phlogiston is a substance, which always presupposes some weight, I much doubt whether such hypothesis has any foundation.



Scheel's Apparatus for Analyzing Air