4 Different Theories, Different Facts : 'Oxygen' versus 'Phlogiston' in 18th Century Chemistry

This chapter asks, using an historical model whether oxygen is an objective fact of nature - or a social construct, a human construct, a construct moreover which has been altered during a chequered history of struggle, negotiation and modification .

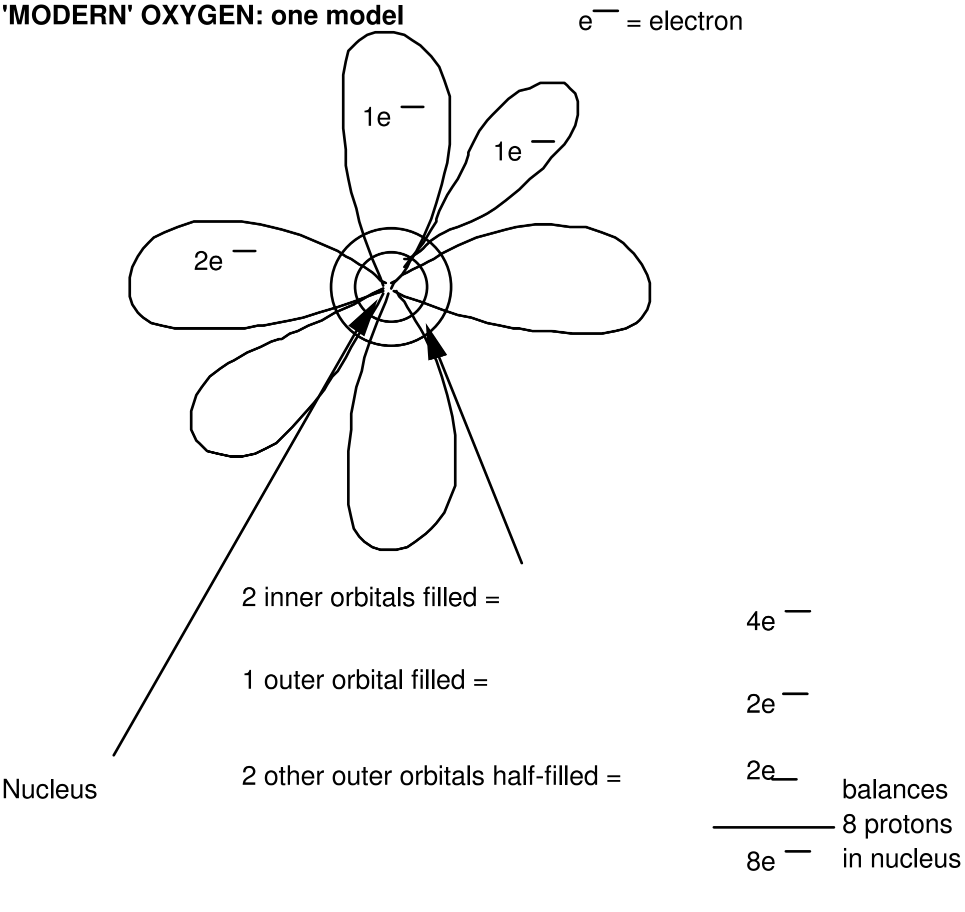
We are going to explore an historical case of the confrontation between two well founded theories (conceptual grids) which in turn conditioned two different sets of facts. These are two chemical theories (and two sets of chemical facts) from the late 18th century, a moment when, as so often happens in the history of science (although the method story does not tell you this) there is a major confrontation/dispute between advocates of two rather different ways of organising and pursuing a science and hence, reporting the supposedly relevant facts.

Over two hundred years ago, in 1789, the French Revolution began, and in that same year a revolutionary textbook of chemistry, *Elementary Treatise of Chemistry* , was printed in French by Antoine-Laurent Lavoisier (1734-94). This book is often considered to have established a revolution in chemical theory that put chemistry 'on the right track'. The book centres around the discovery of oxygen and an oxygen-based chemistry. In this story Lavoisier is a great heroic figure who finally succeeded in applying the scientific method to chemistry, whereas alchemists, mere craftsmen, and charlatans had failed. Applying the method to chemistry, he began to discover the facts; the 'key' fact being that there exists something in the world called "oxygen". This is more or less what a modern chemistry textbook might also say in the preface to the first chapter.

In modern chemical theory Oxygen is an element, one of the 92 naturally occurring chemical elements. Oxygen is involved in combustion which is, put simply, the combining of some other substance with oxygen -- another name for combustion is oxidation. Oxygen is also central to the phenomena of organic chemistry. Plants, which absorb some of the carbon dioxide that nature and our technology emits, use solar energy to convert the carbon dioxide into sugars and other more complicated molecules. During the process a fair amount of water and oxygen is put back into the atmosphere for humans and animals to breathe.

What does oxygen look like? There are many ways of representing chemical structure. Fig 1 demonstrates a simplistic way of representing what is now known: Oxygen consists of atoms; its atomic number is 8 therefore it contains 8 protons (as well as neutrons) in its nucleus, which is in turn surrounded by 8 electrons. The electrons fill 'orbitals' around the nucleus--one pair in the lowest oribital, another further out, and a pair entirely filling one of the three orthogonal orbitals beyond that. The other two orbitals are only half filled, having only one electron each, hence oxygen's considerable 'hunger' for bonding with other atoms to fill those orbitals.

FIGURE 1
'MODERN' OXYGEN: one model



Now that we know a little of what the modern chemical theory of oxygen is let's return to Lavoisier, our hero of science, the originator of modern chemistry through the 'discovery' of oxygen. Perhaps you know he is also a hero to the second-order of magnitude, for many people believe Lavoisier was a martyr of science. Antoine Lavoisier was guillotined to death in 1794. At that time the French Revolution was in the hands of a group of radical democrats of lower middle class origin, who were extremely anti-artistocratic, anti-clerical and who created a reign of terror through judicial murder.

There is a wonderful myth that the French Revolution was anti-scientific and that Lavoisier was sentenced to death because of his experiments and discovery of oxygen. I must stress that Lavoisier was not guillotined for any of his scientific pursuits, but because he gained his living from being a 'Tax Farmer'. In the pre-Revolutionary government of France the collection of taxes was privatized. If you had sufficient influence with the King or enough money, you could form a company and gain a licence to collect taxes for the government. The whole tax system in France was very interesting, for if you could claim noble ancestry then there were many taxes from which you were exempt. Needless to say there were many noblemen in France. This left all the poor peasants of France to pay the taxes which were collected by the tax agents of Tax Farmers. Obviously, only a very small proportion of the money collected by the Tax Farmers eventually came to the King, which led to chronic bankruptcy and the impoverishment of the State. This was especially difficult for the State because several virtual 'world wars' were being fought between the French and the English in the 18th century--from Europe to India to North America. Lavoisier is not a martyr of science, but it is important to remember that he was a very powerful and influential man.

Let's turn to Lavoisier's conception of oxygen, which of course he would have considered not just a 'conception' but a 'discovery' that he made, a discovery of a fact and not just a set of ideas. My point in doing this is to show you that Lavoisier's oxygen bears only a very slim ancestral relationship to our modern conception of oxygen.

For example, Lavoisier believed, as did most chemists of his time, that ultimately all chemicals and substances consist of some kind of particles. But there was no systematic atomic theory involved in Lavoisier's chemistry nor was there any interest in any systematic atomic theory. Lavoisier did not tell you the story of oxygen atoms because atoms were not important in 18th century chemistry. Lavoisier was a typical 18th century chemist in that he believed chemistry consisted in the manipulation, analysis and synthesis of chemical species that could be handled in the laboratory. Atomic theory began to develop 15 or 20 years after his death but not in the form that we now know it. Our atoms, with their electrons, protons, neutrons are a product of work done 100 years after Lavoisier starting in the late 19th century.

Lavoisier's oxygen is termed 'oxygen', which is a Greek term meaning 'acid maker'. His whole course of research was motivated by the search for the `principle' or `essence' of acidity: What makes things acid or not acid? Lavoisier claimed that oxygen was that principle as it was present in all acids and all acids contained oxygen. Around 1810 a British chemist named Humphry Davy, using the newly devised electro-chemical pile tried to decompose a certain kind of acid which we call hydrochloric acid, finding no oxygen in it. To make a long story short, oxygen is <u>not</u> the criterion of acidity in modern chemistry and in fact, over the last two hundred years there have been a number of disputes in chemistry about the proper criteria for classifying 'acids' and their opposites, 'bases'. The boundary line between what is an 'acid' and what is a 'base' is a matter of on-going theoretical dispute, flaming up in chemistry from time to time. Lavoisier's view is not accepted and is not to be found in modern textbooks. So here again, strangely, Lavoisier's 'oxygen' is not our 'oxygen'.

Now we come to the most bizarre and peculiar aspect of Lavoisier's theory of oxygen. This has to do with the behaviour of oxygen as a gas and the behaviour of oxygen during combustion. In order to explain both of these phenomena, Lavoisier had to invent or discover something else in addition to oxygen. This he called 'caloric'. Physicists and chemists in Europe believed in caloric for 50 or 60 years, up until to the mid-19th century when the theory of energy and energy conservation was invented. According to Lavoiser and his contemporaries, caloric is a "weightless fluid"; there is only a certain amount of caloric in the universe, and it can be moved around but cannot be made or destroyed; its presence causes heat. Another property of this caloric is that its particles repel each other at a distance. so if you have two spatially separated blobs of caloric, the two blobs will exert a net repulsive force upon each other.

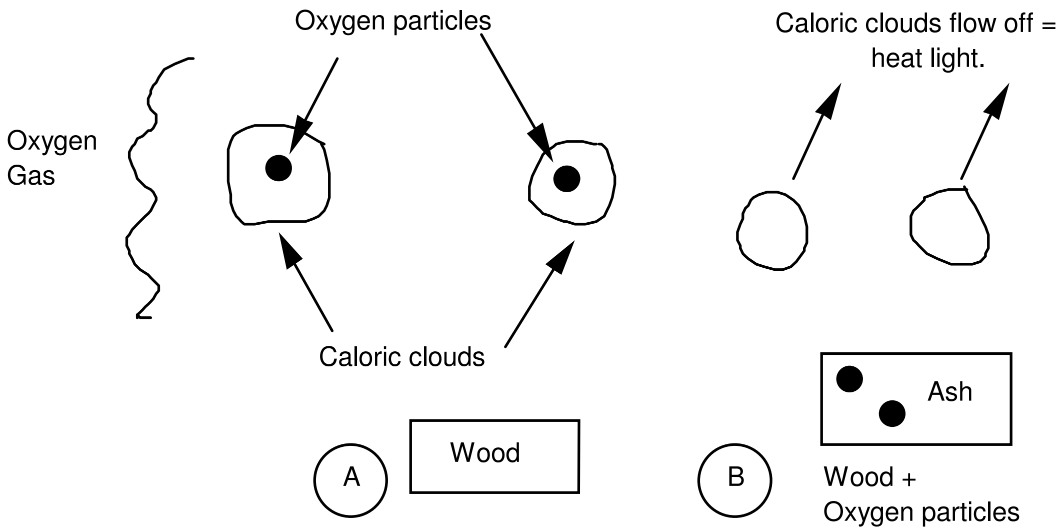
It is not surprising that Lavoisier 'discovered' 'caloric' because 18th century physicists and chemists had 'discovered' many such weightless fluids! For example, there was a weightless, conserved self-repellent fluid of magnetism, and another for electricity, as well as a weightless conserved self-repellent fluid of nervous action which was found inside the nerves.

18th century physics and chemistry were built around these weightless conserved fluids. The most wonderful thing about Caloric is that it was mathematicized. The mathematical equations written about caloric for the behaviour of gases by some French physicists around 1810 are virtually the same gas laws that we learn without the benefit of caloric! You see from this how you can perform good science and solve many problems and gain control over nature with ideas and concepts, and, if you like, 'facts', that 20, 100 or 500 years later may seem ludicrous. This is what we are driving toward -- there is no reason to assume that we ever grasp the facts 'raw', for they are always theory-loaded, and shaped by human social interaction. But, just because they are theory-laden and socially shaped does not mean that they cannot do things for us or that we cannot do things with them.

According to the theory of Lavoisier, Caloric turns things into gases, it explains the gaseous state of matter. For instance, if I have some water and I boil it, the caloric is oozing up from the stove into the water. The caloric is gathering around the water particles so that small clouds of caloric form around clumps of water particles. Now, if I have clumps of water particles surrounded by caloric -- hydrogen and oxygen particles -- what do you think they are going to do? Remember that caloric clouds repel each other at a distance: they will spread apart and from the surface of the boiling water they will float up into the air. Hence, according to Lavoisier you gain water vapour, which is the gas of water. In general, then, a substance is turned into its gaseous state when its particles are surrounded by clouds of caloric. This applies to oxygen gas, for there are oxygen particles in the clouds surrounded by caloric.

Now let's consider the second key phenomenon in question for Lavoisier--combustion. If we burn a piece of wood ie: "oxidise" it, according to Lavoisier what happens is that we create the physical conditions whereby the particles of oxygen gas combine with the wood and produce a chemical change. (Fig 2). If the oxygen particles are now in the wood what has happened to the caloric clouds that surrounded the oxygen particles in oxygen gas? Well, clearly, the caloric clouds dissipated into the atmosphere as heat and flame! So, oxygen combines with things when they burn, with the heat and flame coming with the release of the caloric.

FIGURE 2



If Lavoisier had discovered oxygen the way the textbooks tell us, then they should also tell us that he discovered 'caloric' as well. The problem is that oxygen has a **close but not identical** descendant among our concepts, while caloric has a kind of descendant in energy but it is really quite different, and when energy was discovered (I mean constructed), caloric was consciously discarded by the scientists of the day.

Lavoisier's 'discovery' is one of both oxygen and caloric. His whole chemical theory does not work unless oxygen and caloric exist in the way that he states they do. If you turn in the <u>Elements of Chemistry</u> to his table of chemical elements you will see at the top of the table along with hydrogen, nitrogen, sulphur, phosphorous, silver, copper, cobalt there is also caloric. If Lavoisier 'discovered' something that is not quite what we believe in--modern books think he discovered our oxygen--he discovered his oxygen <u>and</u> caloric--or better he invented both of them.

Whilst it would be interesting to compare Lavoisier's oxygen with a modern chemist's version of oxygen, we will for the moment just compare it with what Lavoisier was trying to overthrow. Lavoisier did not face a void, because there was an existing discipline of chemistry well before he came along. The concepts (and facts) associated with pre-Lavoisier chemistry were used by intelligent people doing serious work. Lavoisier's oxygen is an alternative to what they thought existed, which was something called 'Phlogiston', indeed 18th century chemistry was organised around the theory of 'Phlogiston'.
Following the Scientific Revolution of the 17th century, chemistry had been presented with a great opportunity. Previously chemistry had been pursued in

many different places and traditions: for example, there was alchemy, the chemical crafts--mining, metallurgy, there was pharmacy. After the defeat of alchemy as a world view, in the 17th century, an opportunity was created by the followers of Newton in the early 18th century to reorganise chemistry on a more unified basis. The Phlogiston theory was the main linchpin of this early creation of chemistry and was originally created by Georg Ernst Stahl (1660-1734) a German chemist, mining expert and physician.

It is important that we take Phlogiston theory seriously. In the history of science we do not make fun of what people thought previously in science. That is, we avoid `Whig History of science'. We assume they had well worked out grids of theory and perception, and that their theories eventually were overthown not because of some stupidity, bias or 'lack of method' on their part, but through complex historical processes of conflict and argument, during which scientists' grids were changed or modified in some way, to produce new theories, perceptions and facts. If it was all just a question of overcoming bias, stupidity or poor use of 'method', the story would be easy and pretty--but it would not accord with what our historical inquires show about the nature of scientific change.

Phlogiston is in most interpretations a weightless substance. It is the cause of heat, fire and combustion when it is released from those substances within which it is naturally contained. All combustible substances contain Phlogiston, argued Stahl, and when they burn, they give up their Phlogiston to the atmosphere, leaving the other substances they were combined with as ash (Fig 3).

FIGURE 3

WOOD ---------------> ASH + PHLOGISTON

(ASH + PHLOGISTON) -------------> ASH + PHLOGISTON

When you strike a match and it burns, the match head and wood are releasing the phlogiston they contain, and through the process they decompose to ash. Here's a nice experiment that supports Phlogiston theory: Have you ever tried to burn a candle in a closed jar? After a time the candle goes out. Did you wonder why? Lavoisier says lack of oxygen but Stahl says that when Phlogiston is released into the air by a burning body, the air acts like a sponge and it absorbs the Phlogiston. You know how a sponge works -- it has a saturation point -- therefore, air at any time has a certain saturation point for

Phlogiston. Now obviously if I take a small amount of air and put it in a jar, and light a candle in the jar, after a while the Phlogiston pouring out of the candle saturates the limited supply of air in the jar: It has reached its chemical limit of Phlogiston absorption and therefore it cannot receive any more, and the outpouring of Phlogiston from the burning candle chokes the flame. **Different descriptions for different theories--that is different facts for different theories!!**

Stahl and his colleagues held other aces up their sleeves, other phenomena explained by phlogiston, and other facts supporting the theory. Here are some other things that his theories could enable him to say: By burning sulphur or phosphorus you gain an acid--sulphuric acid and phosphoric acid respectively. Any 'rational' person, a follower of the 'scientific method', in this grid of ideas is very likely to conclude that sulphur is a chemical compound of sulphuric acid and Phlogiston. (Fig 4)

FIGURE 4

SULPHUR ---------> SULPHURIC ACID + PHLOGISTON

(SULPHURIC ACID + PHLOGISTON) -----------> SULPHURIC ACID + PHLOGISTON

Of course, some of you who have studied chemistry will know that sulphur is now considered to be an element, for it cannot be broken down chemically -- although it can be broken down by atomic physics, you cannot break it down chemically, so it cannot be a compound. However, according to the Phlogiston chemists, it is a compound; moreover, Stahl claimed that he had synthesized sulphur; that is, he took the chemical constituents of sulphur: sulphuric acid and phlogiston and convinced himself that he had produced sulphur. You cannot synthesize sulphur according to Lavoisier because it is an element. Hence again it becomes a matter of different facts for different theories.

The real triumph for Stahl came with his explanation of metallic oxides or what he called CALCES (CALX IN THE SINGULAR). What do you do when you make a metal from ore? In the 18th century you heated charcoal until it is extremely hot then put the calx into it. A lot of flame and fume escape from the ore, but you eventually end up with some 'pure' metal. Now what is charcoal?

Remember we are using Stahl's thought processes. Charcoal is almost pure phlogiston! Hence *calx* + *phlogiston* = metal.
(Fig 5) Conversely, if you burn or roast metal without charcoal ie: "calcinate" the metal as they then said, you are obviously driving off the phlogiston that was in it, hence you have calx.

FIGURE 5

- **Nature of Metals and their production:**

metallic ore = *our* metallic oxide = *their* "calx"

as: copper ore, copper oxides, calx of copper

- **Make a Metal**

calx + charcoal --------> metal

calx + phlogiston -----> metal
(= calx + phlogiston)

- **Reverse process ("calcinate" a metal)**

metal ---------------> calx + phlogiston

(calx + phlogiston) -------> calx + phlogiston

Now we can see how really great Stahl was, for by all this he made the profound 'discovery' that **calcination is the same process as combustion,** for in both processes the substance undergoing combustion or calcination is giving up phlogiston. (They are for Lavoisier later the same process of 'combination with oxygen'). (Fig 6) Not only do we have theory-loaded facts which are very impressive but we are now drawing relationships between theory-laden facts. We are making generalisations--scientific method tells us to do just this, but what it doesn't tell us is that facts are theory-laden to begin with. In the mid 18th century Stahl's theories were considered brilliant.

FIGURE 6

Parallelism of combustion and calcination

(Nobel Prize of 1720 !)

combustible ------------> ash + phlogiston

metal -----------> calx + phlogiston

Here are two more examples for your consideration. If we take an acid and dip metal into it what do we get? Well, in terms of 18th century chemistry you would get what they call a 'salt', an earthy, neutral substance plus an effervescence, a bubbling off of air or a gas. If I take an acid and put a calx into it, I tend to get a 'salt' and no effervescence. These are 'facts', or if you like generalisations of a whole group of smaller facts. Metal is calx + phlogiston which would seem to imply that salt is just acid + calx. The effervescence is phlogiston. (Fig 7)

FIGURE 7

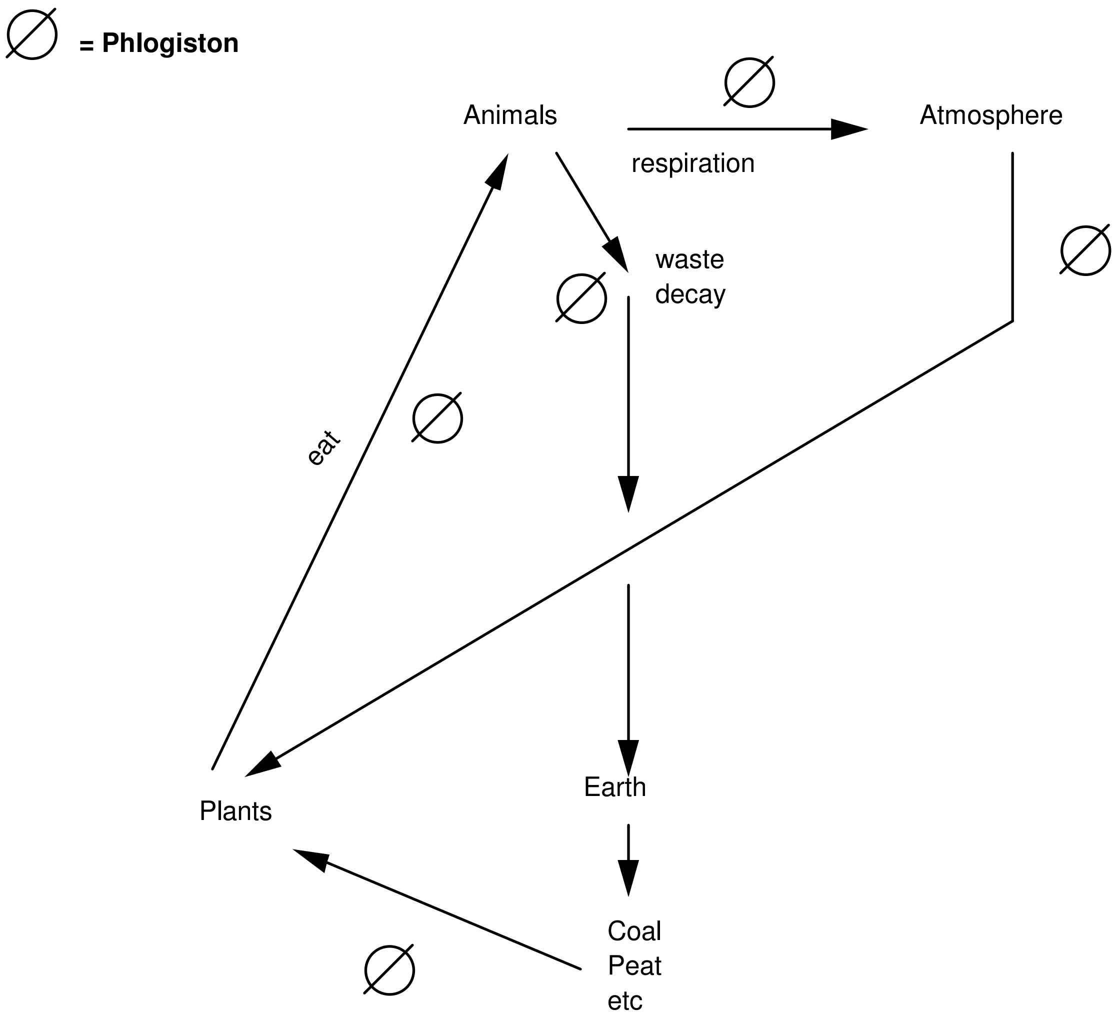
acid + metal ----------> salt + effervescence

acid + calx ---------> salt

Lavoisier and his colleagues had problems with this theory especially before they 'discovered' hydrogen.

Finally, there was even something that we could consider to be a Phlogiston 'ecology'. This involved for the first time a whole theory of the balance of nature. This is how it worked (Fig 8) : humans and other warm-blooded animals give off heat, therefore, we must be burning up fuel in our body in some sense. We must, therefore, be taking in a lot of phlogiston rich food, vegetable matter and such, and burning it up somehow in our body, giving off heat (phlogiston). When we die, or from our waste products and our respiration, we are giving off phlogiston or phlogiston-rich substances. Phlogiston goes into the atmosphere or into the ground, what grows in the ground and absorbs phlogiston from the air but plants, which are made out of phlogiston. (Hence wood, coal etc). So there was a circulation of phlogiston through the great pattern of nature! In fact it was the first great ecological cycle to be recognised based on the theory of Phlogiston.

FIGURE 8 PHLOGISTON ECOLOGY -
SYSTEM OF NATURE AS CYCLE OF PHLOGISTON



Let me leave you with a teaser: Phlogiston Chemists discovered oxygen -- that is they produced what Lavoiser called oxygen, although they did not call it oxygen because they did not believe in oxygen. They discovered what Lavoisier called oxygen before Lavoiser did, and for reasons that we will go into later they called it 'de-phlogisticated air'. Therefore we can also assert that different grids produce different facts!