History of Science
Lecture 8 (1,2)

Understanding Discovery

“Anomaly”, “Crisis”, “Revolution”

- The stable growth of normal science is, at times, punctuated by anomalies—moments when conceptual boxes provided by the paradigm fails to resolve certain newly observed anomalies in nature. Anomaly “subverts the existing scientific practice” (p 6). Anomaly leads to the recognition that nature has violated the paradigm-induced expectations that govern normal science.
- Discovery or ‘novelty of fact’ begins with the identification of anomalies.
- A puzzle continues to remain a puzzle until it acquires enough critical mass (i.e., the manifestation of many major puzzles) calling for a certain rethinking of the conceptual matrix itself. This might take decades and might involve bitter fights within the community of scientists. The old-guard of the scientific community resists the changes in their belief-system.
- The deepening of the crisis eventually forces the community to re-evaluate and re-construct prior assumptions and facts. This is not an event but a time-consuming process. This is the moment of scientific revolution. It is only during this moment of transition from one paradigm to another that the scientific community take part in radical debates about the nature of their vocation and tests competing theories: Schools of thought resurface.
- However, when a shift takes place, "a scientist's world is qualitatively transformed [and] quantitatively enriched by fundamental novelties of either fact or theory" (p 7).

Four discoveries of the late 18th century (1765-90) that said to have transformed ‘natural philosophy’ to modern science:

Discovery	Discovery traditionally attributed to	Discipline of science involved
Uranus (to be discussed)	William Herschel (1738-1822)	Astronomy
Oxygen (to be analysed)	Antoine Lavoisier (1743-1794)	Chemistry
Photosynthesis	Joseph Priestley (1733-1804)	Biology
Electrostatic Inverse Law	Coulomb (1736-1806)	Electricity

Two Objectives

1. Are these single and unambiguously authored events, or, are these processes constructed within research communities?>Follow Chapter 6 of the Structure. Here, Kuhn considers the case of the discovery of Oxygen.
2. Through an analysis of the discovery of Oxygen, we will see how in this case a paradigm shift actually happened over a period of more than a century.

Who Discovered Uranus?

Sequence of Events:

1. 10-30 pm, 13 March, 1781: Hershel puts the following entry in his notebook:
   - ‘A curious either nebulous star or perhaps a comet’ in the ‘quartile near Zeta Tauri”

2. Morning, 14 March, 1781:

- ‘I discovered a comet’.
- Is this a moment of discovery? No. 18 such observations were recorded by others including 6 by Le Monnier within a span of 9 nights in January, 1769.
- Note: Le Monnier identified it as a star and Hershel was convinced until 1782 that it was indeed a comet.

Who Discovered Uranus?

Hershel made two subsidiary claims to sustain his characterization of Uranus as a comet:

a) That ‘the comet approaches to us’

b) That ‘the comet has a very visible daily parallax which was sufficient to prove it to be on our side of the Sun’.

- Both these claims became untenable by the Spring of 1782 as the object in question began to recede from the Earth and further away than Saturn.
- So, who owns the discovery of Uranus? By Spring, 1782 a number of Astronomers in Europe described the object as a planet. The discovery cannot be attributed to them as they were not the one to first observe it.

Remember Kuhn’s Conclusions

- ‘There is no single moment or day which the historian, however complete his data, can identify as the point at which the discovery was made’.
- Discovery index for Kuhn: Anomaly: ‘a discoverer must see an anomaly’.
- A discovery begins with the identification of a substantial anomaly which leads to a period of crisis that ends with the establishment of a paradigm.

The Discovery of Oxygen

The Prevailing Phlogiston Paradigm in the 18th century

Johann J Becher (1635-88):

- Combustible objects contain an ‘inflammable principle’ that they release to the air upon burning.
- As metals were observed to turn into powdery substances like ashes (calxes/oxide) upon heating, they must contain the principle of inflammability.
- Since metallic ores upon heating with charcoal give birth to metals, the process of smelting ores adds to the inflammable principle to metals>the combustible material, i.e., charcoal transferred the principle of inflammability to the metal. [In modern parlance of chemistry the expression is: Iron(III) oxide + Carbon → Iron. + Carbon dioxide]

The Prevailing Phlogiston Paradigm

Georg. E. Stahl (1659-1734):

- Identified the principle of inflammability as Phlogiston
- Could the principle of inflammability be transferred to another combustible?
- Experiment: Burning Sulphur, Stahl gets vitriolic acid (what's it known as?) fumes
- Stahl fixed these fumes in potash and heated the derived salt (name it!!) with charcoal to obtain the 'liver of sulphur'.

Sthal's conclusions:

- 'Since liver of sulphur resulted from mixing sulphur and potash, the phlogiston from the charcoal had combined with the vitriolic acid fumes to produce sulphur. Hence, phlogiston could be transferred from one combustible to another'. Lavoisier once called this 'Stahl's great discovery'.
- Ability to burn depends on the level of availability of phlogiston in a substance.

Initial Anomalies and Auxiliary Hypotheses

Initial Anomalies/Puzzles:

- Why does combustion soon cease in an enclosed volume of air?
- Why is the volume of air reduced by it?
- Why won't things burn at all in a vacuum?

Stahl comes up with a set of auxiliary hypotheses:

- Air is the medium to carry away phlogiston from a combustible, and that a given volume of air can absorb only a certain amount of it. Air in a confined space becomes saturated with phlogiston and it turns to phlogistigated air. Therefore, a) nothing will burn in a vacuum and b) combustion must cease in a confined space.
- Ash is lighter (less dense) than the metal since it has released phlogiston into air upon burning.

A Third Anomaly in Phlogiston Paradigm and Response

Anomaly:

- Why, if calcination is the release of phlogiston, do ashes weigh (although may be lighter in terms of density) *more* than the original metals?
- Both Becher and Stahl knew of this anomaly.
- This anomaly was already pointed out by Jean Rey in 1630 and later confirmed by Robert Boyle in 1673.

A Third set of Auxiliary Hypotheses:

- These scholars still reconciled this observed anomaly with phlogiston theory by attributing ‘negative weight’ or positive lightness as its flame tends to rise defying gravity.
- In 1673, Robert Boyle opined that the weight of the ashes (calxes) was more because of the addition of ‘fire particles’ in them: ‘It is no wonder that, being wedged into the pores, . . . the accession of so many little bodies, that want not gravity, should, because of their multitudes, be considerable upon a balance’
- Guyton de Morveau in 1772 postulated that Phlogiston was lighter than air and hence, removing it from an object immersed in air would cause a weight gain in the object releasing Phlogiston.

The Phlogiston Paradigm Continues: Cavendish’s Experiment

- Henry Cavendish (1731-1810) in 1766 synced three metals iron, zinc and tin in vitriolic and hydrochloric acids and preserved the gas emerging out of these reactions. Cavendish observed that the gas he captured was indeed 11 times lighter than the air and was highly inflammable. To put it in modern language of chemistry:

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$$

- Cavendish’s conclusion: When metals are immersed in acids ‘their phlogiston flies off, without having its nature changed by the acid, and forms inflammable air’.
- Cavendish sustained this conclusion through a complementary experiment: he found that the metallic calxes when immersed in acids produced the same salt without the inflammable air (but water!!). ($ZnO + H_2SO_4 \rightarrow ZnSO_4 + H_2O$ in modern chemical language).

A New Set of Anomalies

- So, Cavendish’s experiment identified Phlogiston as the ‘inflammable air’. His experiments forged some very elaborate connection between phlogiston and observed phenomena with concrete practical operations.
- This identification advanced certain important anomalies:

1. When things are burnt, they are supposed to release Phlogiston and Cavendish says phlogiston itself burns. So, when Phlogiston burns it must have released it from itself!!
2. Cavendish’s later experiments (presumably done in late 1770s and early 1780s) found that the metals immersed in concentrated vitriolic acid didn’t produce phlogiston, which made him conclude the following: ‘Concentrated vitriolic acid on reaction with metals produce salt, water and the product of reduction of sulphur’.
3. All these findings made him tentative about his 1766 conclusions. However, the 1766 experiment remained iconic in chemistry for a long time.

The Birth of the Oxygen Paradigm

- In 1772, Lavoisier burned sulphur with phosphorus in air confined over water and observed the reduction in the volume of the air and the increase in weight of the sulphur and phosphorus (Musgrave 1976).
- Lavoisier's Three-stage conclusion:

1. 10 September, 1772: 'When phosphorus burns, air is absorbed'.

2. 20 October, 1772: 'As phosphorus releases phlogiston, it absorbs air'.

3. 1 November, 1772: 'About eight days ago I discovered that sulphur in burning, far from losing weight, on the contrary gains it; it is the same with phosphorus; this increase of weight arises from a prodigious quantity of air that is fixed during combustion and combines with the vapours. This discovery, which I have established by experiments, that I regard as decisive, has led me to think that what is observed in the case of sulphur and phosphorus may well take place in the case of all substances that gain in weight by combustion and calcination; and I am persuaded that the increase in weight of metallic calxes is due to the same cause' (quoted in Musgrave 1776).

Lavoisier in conversation with Boyle

- Lavoisier now compared his understanding of weight gain of calxes against Boyle’s theory (discussed in the last class).
- Boyle said if metal is calcinated in a sealed container the additional weight came from outside the container. He did not weigh the entire container. Lavoisier had weighed the entire container and didn’t notice any overall weight gain. This made him conclude that the weight increase in the calx must have come from inside the bottle (Musgrave 1976).
- This was an important stepping-stone for the new paradigm.

Priestley’s Experiments (follow the specific portion in Musgrave 1976)

- Priestley’s basic idea about ‘airs’: Different airs are all composed of some earth, nitrous acid and phlogiston in various proportions. He had a graded understanding of airs:

‘Upon the whole, I think, it may safely be concluded, that the purest air is that which contains the least phlogiston: that air is impure... in proportion as it contains more of that principle; and that there is a regular gradation from *dephlogisticated air,* through common air, and *phlogistigated air,* down to nitrous air; the last species of air containing the most, and the first mentioned the least phlogiston possible, the common basis of them all being the nitrous acid; so that all these kinds of air differ chiefly in the quantity of phlogiston they contain’ (Musgrave 1976).

- He found that the weight of calxes increased by an air that ‘would not dissolve in water’. Air from the mercury calx must be a new kind of air that supports combustion better than normal air. He called it dephlogisticated air.
- Priestley’s experiments were completed by 1774. Before the discovery was published he visited Paris and shared his observations with Lavoisier.
- After the meeting, Lavoisier repeats Priestley’s experiments and famously comments in 1774: “Dr. Priestley’s work represented a train of experiments, not much interrupted by any reasoning, an assemblage of facts”. Hence, I am justified in using such an assemblage as a quarry for more developed chemical theorising.

The Discovery of Oxygen (follow Schaffer 1986)

- 15 March, 1775: Priestly dispatches a letter to Royal Society: “the most remarkable of all the kinds of air that I have produced . . . is one that is five or six times better than common air, for the purpose of respiration, inflammation, and, I believe, every other use of common atmospherical air.”
- 26 April, 1775: Lavoisier submits an account to the Royal Academy of Science describing a set of experiments on the air generated from heating the red mercury calx. He calls this air the ‘purest portion of the air in which we live’.
- Late February, 1775: An entry in Lavoisier’s notebook reads as follows: ‘some form of matter of fire was an emanation from metals in calcination and then combined with common air…all of this agrees very much with the system of Priestley…however there is nevertheless a very noticeable difference’.
- For a long time, the difference he senses remains unarticulated in Lavoisier papers.
- Even the entry on 13 February, 1776 gives us a sense that Lavoisier is still using Priestley’s techniques for the assessment of air.
- April, 1776: He begins to refer to ‘a principle of fire much more ancient than the phlogiston of Priestley’.
- 1783: In a paper on the subject, Lavoisier stakes claim on a discovery saying that it took place on 26 April, 1775. He writes: The impartial public had now judged that I myself should be considered as the author of the discovery of the cause of the increase in the weight of the metallic calxes’.
- ‘Combustion and calcination are combinations of substances with the pure part of the air; fixed air is a combination of the pure part of the air with charcoal; any calx reduced without charcoal will yield the pure part of the air’.