Lecture 13
Black's Theory of Lime

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Scientific Thought II
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Lime

Lime is a common substance

- The second most widely produced industrial chemical.
- Used in making mortar, plaster, stucco, and glass.
- Used as a fertilizer.
- Small bags of it are sold in grocery stores for pickling.

People have been using it for these purposes for thousands of years.

Method of production and terminology

- Lime is made by strongly heating substances such as limestone, chalk, marble, or shells of oysters or snails.
- In the 18th century the process was called *calcination* and the substances used were called *calcareous earth*.

$$\text{calcareous earth} \xrightarrow[\text{calcination}]{} \text{lime}$$

Dumbarton Castle, Scotland, in 1800
with a lime kiln in the foreground

Chemical activity

- Calcareous earths are innocuous substances.
- Mixing water with freshly made lime causes a violent reaction in which the lime becomes intensely hot.
- Lime that hasn't absorbed any water is called *quicklime*. After it has absorbed as much water as it can it is called *slaked lime*.

$$\text{slaked lime} = \text{quicklime} + \text{water}$$

- Even slaked lime is chemically active. It leaves a burning sensation on the tongue and eats away animal tissues if left on them.

The fire theory

In the ancient world it was believed that lime is calcareous earth with fire added to it.

$$\text{lime} = \text{calcareous earth} + \text{fire}$$

That gives a natural explanation of many facts about lime, for example:

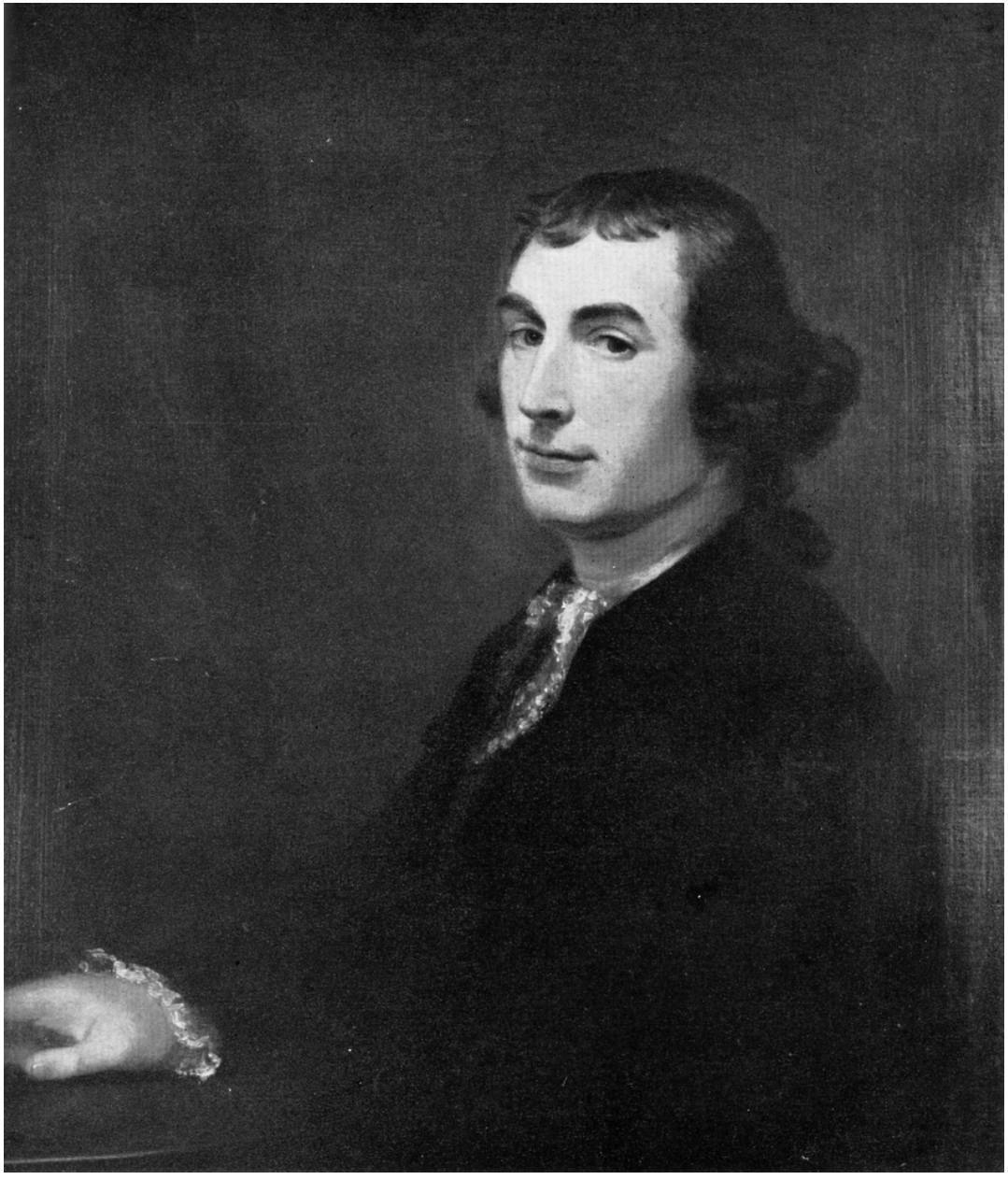
- Why fire is needed to make lime.
- Why lime gives off heat when it is slaked (fire is coming out).
- Why even slaked lime burns the tongue and animal tissues.

Problem: Calcareous earth loses at least 1/3 of its weight when calcined. *Answer (given by Vitruvius, 1st century BCE):* calcareous earth contains water that is evaporated by the fire.

$$\text{lime} = \text{calcareous earth} + \text{fire} - \text{water}$$

This theory was accepted for thousands of years.

Joseph Black



1728: Born in Bordeaux, France.

1754: Medical degree from University of Edinburgh.

1756: "Experiments upon Magnesia Alba, Quicklime, and some other Alkaline Substances" published.

1766: Professor of chemistry and medicine at the University of Edinburgh.

c.1770: This portrait painted.

1799: Died in Edinburgh.

Black's theory of lime

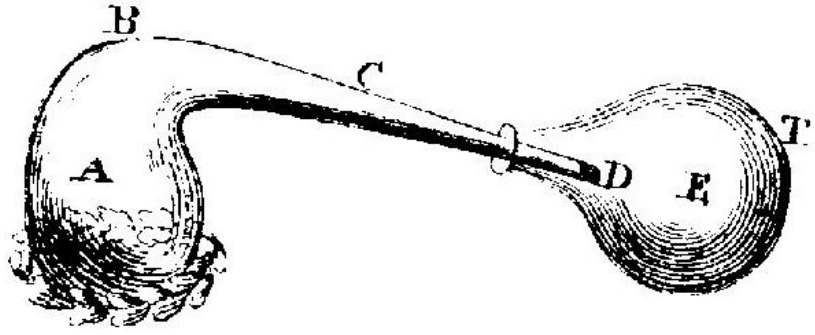
- Calcareous earth consists primarily of lime plus air that is "fixed" in it, together with a small amount of water.

$$\text{calcareous earth} = \text{lime} + \text{fixed air} + \text{water}$$

- When calcareous earth is calcined, the fixed air and the water are driven off, leaving lime. Nothing is added by the fire.
- This is the opposite of the fire theory. The fire theory says we get lime by adding something to calcareous earth; Black says we get lime by taking something away from calcareous earth.

Distillation

- Distillation is a process in which a substance is heated to vaporize part of it and the vapor is collected and condensed.
- A simple apparatus that was often used: The substance to be distilled is placed in a *retort*, which is essentially a bottle with a bent neck. The neck of the retort is inserted into a *receiver*. The retort is heated and vapor passes into the receiver, where it cools and condenses.
- To prevent vapor escaping it is necessary to seal the joint between the retort and receiver. Eighteenth century chemists used clay, possibly mixed with other things; this was called a *lute* (from the Latin word for mud or clay).



Marggraf's distillation (187)

That the calcarious earths really lose a large quantity of air when they are burnt to quick-lime, seems sufficiently proved by an experiment of Mr. Margraaf, an exceedingly accurate and judicious Chemist. He subjected eight ounces of osteocolla to distillation in an earthen retort, finishing the process with the most violent fire of a reverbatory, and caught in the receiver only two drams of water.

- Marggraf was a German chemist whom Black greatly admired but whose name he misspelt.
- Osteocolla is a form of calcareous earth found in Germany; it is petrified tree roots.
- A reverbatory is a furnace that makes intense heat by reflecting the heat back on top of the object.
- There are 8 drams in an ounce, so the water obtained by Marggraf was about 3% of the weight of the calcareous earth.

Marggraf's distillation continued (187–88)

He does not tell us the weight of the osteocolla remaining in the retort, and only says, that it was converted into quick-lime; but as no calcarious earth can be converted into quick-lime, or bear the heat which he applied without losing above a third of its weight, we may safely conclude, that the loss in his experiment was proportional, and proceeded chiefly from the dissipation of fixed air.

- The calcareous earth lost at least 33% of its weight. The water collected accounts for 3%. So at least 30% of the weight has disappeared.
- The experience of chemists was that when weight disappears it is due to air escaping from the apparatus. If the lute doesn't make a perfect seal air can leak out through it.
- Black's conclusion: At least 30% of the weight of calcareous earth is fixed air.

Questions

1. State the meaning of the term "calcareous earth" and give some examples of calcareous earths.
2. What is the fire theory of lime? Describe how this theory explains two facts about lime.
3. Is there a gain or loss of weight when lime is produced? How was this explained by advocates of the fire theory like Vitruvius?
4. What happens when calcareous earth is calcined, according to Black's theory?
5. What was the result when Marggraf distilled calcareous earth? What did Black infer from this? Explain how this conclusion follows.

References

Joseph Black.
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