06. Lavoisier and the Caloric Theory of Heat

1. Air as a vapor.

- *Recall*: 4 elements: earth, air, fire, water.
  - *Can exist in free or fixed forms.*
  - *What is the nature of air?*

Lavoisier's manuscripts of 1766, 1772, 1773

Antoine Lavoisier
(1743-1794)

"Water has a certain degree of heat in expanding. It is reduced to vapor. Is this a dissolution of water in air, or is it in the igneous fluid? Air itself might be an expansible fluid." (1766)

- *Suppose*: Water vapor is composed of water and "igneous fluid".
- *Then*: Perhaps air is also an expansible fluid composed of some substance and igneous fluid.
  - *Air as a vapor*: "...a major and persistent feature in Lavoisier's theory of heat." (Morris, pg. 3.)
  - "igneous fluid" = "matter of fire" = "caloric" (Guyton 1785)

Louis-Bernard Guyton
(1743-1794)

- 1766: Vaporization as *dissolution* in the igneous fluid.
- 1772: Vaporization as chemical *combination* with igneous fluid.
- 1773: Three states of matter: solid, liquid, vapor, depending on how much igneous fluid is combined with it.
  - *Air as an igneous compound: absorbs heat when it is converted to its fluid elastic state; releases heat when it condenses.*

"[Lavoisier's] major concern was with vaporization and he employed his theory of heat primarily for a single purpose: to explain the fixation and release of air and the other phenomena associated with these processes." (Morris, pg. 5.)

1777 1st paper presented to the Academy of Sciences.

"De la combinaison de la matière du feu avec les fluides évaporables, et de la formation des fluides élastiques aëriformes" ("The combination of matter of fire with evaporable fluids and the formation of elastic aeriform fluids").

Jean-Baptiste Colbert and Louis XIV in 1667

"I will assume in this memoir, and in those that follow, that the planet we inhabit is surrounded on all sides by a subtle fluid, which penetrates, as it seems without exception, all the bodies that compose it and that this fluid, I would call *igneous fluid*, *matter of fire*, *heat & light*, tends to get in balance in every body, but it does not penetrate all with equal ease, and finally that this fluid exists sometimes in a free state, sometimes in a fixed form, and combines with bodies."

"As water may act as water of solution or may be combined in substances as the water of composition, so too with the igneous fluid. Fire may be free or fixed and the latter does not register on a thermometer." (Morris, pg. 6.)

- All vapors are the result of the combination of fire matter with some fluid.

"Vapors and aeriform substances in general are composed of fluids dissolved and combined with the matter of fire."

"There is no fundamental difference between vapors and the permanently elastic fluids. Airs are simply the vapors of substances having a boiling point below the temperatures naturally encountered or perhaps artificially produced." (Morris, pg. 6.)

2. Against Phlogiston.

1777 2nd paper presented to Academy of Sciences.

"Mémoire sur la combustion en général" ("Memoir on combustion in general").

The phlogiston theory of combustion (Stahl 1703).

Georg Ernst Stahl
(1659-1734)

- *Phlogiston* = substance contained in flammable bodies and released when they're burned.
  - *Ex. Burning wood produces ash, lighter than wood.*
  - *"Dephlogisticated" air = air low in phlogiston and thus capable of supporting combustion.*

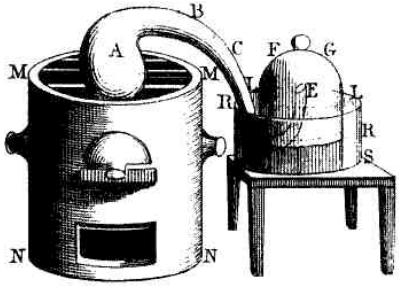
- *But*: ~1770's. Some metals gain weight when burned.
  - *Ex: magnesium.*
  - *Does phlogiston have negative weight?*

- *And*: In enclosed vessels, weight gained is equal to weight loss of surrounding air, and volume of air decreases.
  - *Does combustion involve absorption, rather than emission?*

- Priestley (1774-75):
  - *Experiments burning mercury oxide.*
  - *Identifies product as dephlogisticated air.*

Joseph Priestley
(1733-1804)

- Lavoisier (1775-79):
  - *Determines that Priestley's dephlogisticated air has weight.*
  - *Identifies it as a new type of gas, "oxygen".*
  - *Combustion is based on the absorption of oxygen.*
  - *<u>Assumption:</u> Oxygen is a vapor consisting of a base combined with caloric.*



"The heat and flame of combustion come not from a solid, compact combustible, as Stahl believed. The source of fire is a fluid, elastic air... [Lavoisier's] attention was riveted to the process of vaporization almost to the complete exclusion of everything else... His single-minded purpose was to demonstrate his theory that fluid elasticity is a state, that aeriform liquids are vapors, and that vaporization is a chemical process caused by the combination of the matter of fire influenced by external pressure of the atmosphere." (Morris, pg. 8.)

Adair Crawford's (1748-95) Irvinist Influence (*Exp. and Obs. on Animal Heat* 1779)

- Temp changes in chemical transformations due to changes in *heat capacity*.
- Respiration, combustion, calcination involve the transformation of atmospheric air into fixed and phlogisticated air.
  - *Respiration: Atmospheric air transforms into fixed and phlogisticated air; venous blood transforms into arterial blood; excess fire from decrease in heat capacity of air is absorbed by blood.*
  - *Calcination: Transformation of substance into its calx is accompanied by increase in heat capacity and thus an absorption of heat.*

Thus:

- *Phlogiston must be something other than the matter of fire; air is the source of the heat released.*
- *Heat and phlogiston are largely mutually exclusive principles.*
- *Loss of phlogiston causes increase in heat capacity and an absorption of heat.*
- *Gain of phlogiston causes decrease in heat capacity and release of heat.*

1785 Memoir on phlogiston.

"Réflexions sur le phlogistique pour servir de développement à la théorie de la combustion & de la calcination publiée en 1777". ("Reflections on phlogiston toward the development of the theory of combustion & calcination published in 1777.")

"I have deduced a full account of a simple principle, which is that pure air, vital air, is composed of a particular principle of its own, which forms the base, and that I call the *oxygen principle*, combined with the matter of fire and heat. Once this principle is admitted, the main difficulties of chemistry appear to fade and dissipate, and all phenomena are explained with astonishing ease."

Balance of forces:

- Objects expand when heated and contract when cooled.
- *Explanation*: All particles are acted upon by two forces: mutual attractive force, and expansive force of caloric.

Explanation of the relative specific heats of substances.

- Specific heat = capacity of a substance to contain caloric.
- Gases have greater specific heats than solids; solids have greater specific heats than liquids.

> *Why?*
> - More spaces between particles in a liquid.
> - *Thus*: Less attractive force between particules.
> - *Thus*: More caloric required to raise temperature.

Predictions of temperature changes in chemical reactions.

- Influx of caloric can change spacings between particles.
- Change in spacings can affect amount of caloric that can combine with particles.
  - *Thus: A solidifying gas loses capacity to contain caloric, which should be released.*
  - *And: When water is mixed with various substances, heat is observed due to the reduction of particle spacings.*

3. Mature Caloric Theory. (*Mémoires de Chimie* 1805)

- Changes of state are due to the combination of caloric with some other substance.
  - *There is a continuum of states between free caloric and combined caloric.*
- Depending on the type of adhesion, caloric acts chemically or mechanically.
  - *Ex. In vaporization caloric approaches free end of the continuum and acts more as a mechanical agent (with elastic properties), rather than a chemical constituent.*

Is caloric a material substance?

"...this subtle fluid may be hypothetical... [but] it is the only [hypothesis] that I will be forced to adopt. Proponents of the doctrine of phlogiston are not more advanced than I on this topic, and if the existence of igneous fluid is a hypothesis, it is common to their system and to mine." (1785)

- *But*:

[when one considers how easily the concept explains the results of experiments], "...the hypothesis ceases to be an assumption and we can regard it as a truth." (*Mémoires de Chimie*)

Essential Aspects of Lavoisier's Theory

1. Caloric is not a separate species of matter.
   - *Caloric, electric, and magnetic fluids are rarified states of matter.*
   - *Caloric is imponderable (very small weight).*
   - *Self-repulsive property not explained in terms of a unique inherent motion.*

2. The caloric responsible for combustion is to be found not in the combustible, but in oxygen.

3. Caloric reactions involve *changes of state.*

"Lavoisier's innovation is more profound than simply shifting the location of caloric... for associated with this shift was the elevation to a pre-eminent position of a class of phenomena virtually ignored by earlier chemists -- changes of state... the reactions in which caloric becomes combined or released are almost always accompanied by a corresponding change of state." (Morris, pg. 34.)

"For Lavoisier, changes of state were not to be viewed as a separate class of phenomena perhaps associated with but fundamentally independent of chemical transformations *per se*; they assumed a position as part of the chemical process itself and an essential necessary part in every reaction where there is a change of temperature. This was the most striking innovation in Lavoisier's theory of heat." (Morris, pg. 34.)

4. Caloric is necessary to explain combustion.

Phlogiston explained the release of fire during combustion. "Lavoisier might ban phlogiston from chemistry, but to provide a viable alternative, he had to account for this central observation. The caloric theory could do this. That it also enabled him to explain *how* (not merely state the fact *that*) oxygen becomes combined in the process made the concept all the more compelling. *The caloric theory was indeed the foundation stone upon which Lavoisier erected the new chemistry.*" (Morris, pg. 37.)