Physics 2028: Great Ideas in Science: The Chemistry Module History of Chemistry Lecture Notes

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Edition 1.0

Abstract

These class notes are designed for use of the instructor and students of the course Physics 2028: Great Ideas in Science. This edition was last modified for the Spring 2008 semester.

I. History of Chemistry

A. Ancient Chemistry.

1. Many ancient philosophies used a set of archetypal **classical "elements"** to explain patterns in nature.

a) To the ancient Greeks, the word *element* in this context refers to a state of matter. They had 4 of these:

i) Earth or dirt (*e.g.*, equivalent to the "solid" <u>state</u> of matter).

ii) Water (*e.g.*, modern "liquid" state of matter).

iii) Air (*e.g.*, modern "gaseous" state of matter).

iv) Fire (*e.g.*, essentially thermal heat or energy).

b) The ancient Greeks often referred to a fifth element as well which describes that which was beyond the material world. Various words were used to describe this 5th element including **idea**, **aether**, and **quintessence**.

c) The ancient Chinese had five elements:

i) Earth.

ii) Water.

iii) Metal.

iv) Wood.

v) Fire.

d) The modern definition of the **chemical elements** did not arise until the 17th century.

2. The science of chemistry begins with the discovery of fire at the dawn of man; then metallurgy which allowed purification of metals and the making of alloys, followed by attempts to explain the nature of matter and its transformations through the protoscience of alchemy.

B. Chemistry and Alchemy.

1. Chemistry and alchemy were essentially the same thing prior to the 1600s.

2. **Alchemy** was the study of the techniques used to turn elements and compound from one type to another.

   a) For instance, alchemy was heavily involved in the attempt to turn various metals into gold.

   b) What the alchemists failed to realize, from lack of knowledge, was that changing the identity of elements requires nuclear physics through the manipulation nuclear particles (*i.e.*, protons) and not chemistry through the manipulation of electrons.

   c) One needs to change the number of protons in an atomic nucleus in order to change an element from one type to another, say lead into gold.

3. Chemistry begins to emerge when the distinction is made between chemistry and alchemy by Robert Boyle in his work The Sceptical Chymist in 1661.

a) In the form of a dialogue, the Sceptical Chymist presented Boyle's hypothesis that matter consisted of atoms and clusters of atoms in motion and that every phenomenon was the result of collisions of particles in motion.

b) He appealed to chemists to experiment and asserted that experiments denied the limiting of chemical elements to only the classic four: earth, fire, air, and water.

c) He also pleaded that chemistry should cease to be subservient to medicine or to alchemy, and rise to the status of a science.

d) Importantly, he advocated a rigorous approach to scientific experiment following what Galileo did for physics.

e) Hence he believed all theories must be proved experimentally before being regarded as true.

f) For these reasons Robert Boyle has been called the founder of modern chemistry.

4. Chemistry then becomes a full-fledged science when Antoine Lavoisier develops his law of **conservation of mass**, which demands careful measurements, and quantitative observations of chemical phenomena.

5. While both alchemy and chemistry are concerned with the nature of matter and its transformations, it is only the chemists who apply the **scientific method**.

6. The history of chemistry is intertwined with the history of thermodynamics (which was described last semester), especially through the work of Willard Gibbs.

C. Phlogiston Theory.

1. In 1667, Johann Joachim Becher, published his *Physica Subterranea*, which was the first mention of what would become the **phlogiston theory**.

a) Becher eliminated fire and air from the classical element model and replaced them with three forms of earth:

i) **Terra lapidea**: This represented the degree of fusibility.

ii) **Terra mercurialis**: Also called **terra fluida**, indicated the degree of fluidity, subtility, volatility, and metallicity.

iii) **Terra pinguis**: This is the element which imparted oily, sulphureous, or combustible properties.

b) Becher believed that terra pinguis was a key feature of combustion and was released when combustible substances were burned.

c) Georg Ernst Stahl, a German chemist, was a student of Becher's who expanded on his theories with several publications in the period between 1703 and 1731.

i) In a 1718 work, Stahl was the first to rename terra pinguis as **phlogiston** from the Ancient Greek phlogios for "fiery."

ii) Stahl's work analyzed the role of phlogiston in combustion and calcination, the 17th century term for oxidation.

2. The theory holds that all flammable materials contain phlogiston, a substance without color, odor, taste, or mass that is liberated in burning. Once burned, the "dephlogisticated" substance was held to be in its "true" form, the **calx**.

a) "Phlogisticated" substances are those that contain phlogiston and are "dephlogisticated" when burned.

b) In general, substances that burned in air were said to be rich in phlogiston; the fact that combustion soon ceased in an enclosed space was taken as clear-cut evidence that air had the capacity to absorb only a definite amount of phlogiston.

c) When air had become completely phlogisticated it would no longer serve to support combustion of any material, nor would a metal heated in it yield a calx; nor could phlogisticated air support life, for the role of air in respiration was to remove the phlogiston from the body.

d) Thus, phlogiston as first conceived was a sort of anti-oxygen.

3. Joseph Black's student Daniel Rutherford discovered nitrogen in 1772 and the pair used the theory to explain his results:

a) The residue of air left after burning, in fact a mixture of nitrogen and carbon dioxide, was sometimes referred to as *phlogisticated air*, having taken up all of the phlogiston.

b) Conversely, when oxygen was first discovered it was thought to be *dephlogisticated air*, capable of combining with more phlogiston and thus supporting combustion for longer than ordinary air.

4. Eventually, quantitative experiments revealed problems, including the fact that some metals, such as magnesium, gained weight when they burned, even though they were supposed to have lost phlogiston.

a) In 1753, Mikhail Lomonosov attempted to repeat experimental work of Robert Boyle that tried to measure the mass of phlogiston. From this work Lomonosov concluded that the **phlogiston theory was false**.

i) He wrote in his diary: "Today I made an experiment in hermetic glass vessels in order to determine whether the mass of metals increases from the action of pure heat."

ii) He concluded: "The experiment demonstrated that the famous Robert Boyle was deluded, for without access of air from outside, the mass of the burnt metal remains the same."

b) Some phlogiston proponents explained Lomonosov's work by concluding that phlogiston had "negative weight."

c) Others, such as Louis-Bernard Guyton de Morveau, gave the more conventional argument that it was lighter than air.

d) However, a more detailed analysis based on the Archimedean principle and the densities of magnesium and its combustion product shows that just being lighter than air cannot account for the increase in mass.

5. Phlogiston remained the dominant theory until Antoine-Laurent Lavoisier in 1778 showed that combustion requires a gas which has weight (oxygen), which could be measured by means of weighing closed vessels.

a) The use of closed vessels negated the buoyancy which had disguised the weight of the gasses of combustion.

b) These observations solved the weight paradox and set the stage for the new **caloric theory of combustion**.

c) As a result of this pioneering work, Lavoisier is considered to be the father of modern chemistry,

6. Phlogiston theory allowed chemists to bring explanation of apparently different phenomena into a coherent structure: combustion, metabolism, and formation of rust.

D. The Periodic Table.

1. Since the mid-1600s, the list of known modern chemical elements steadily increased. A great breakthrough in making sense of this long list (as well as, eventually, in understanding the internal structure of atoms) was (primarily) Dmitri Mendeleev and Lothar Meyer's development of the periodic table in 1869.

a) The table is a visual representation of the periodic law which states that certain properties of elements repeat periodically when arranged by atomic number.

b) The table arranges elements into vertical columns (Groups) and horizontal rows (Periods) to display these commonalities.

2. Mendeleev arranged the elements in a table ordered by atomic mass. It is sometimes said that he played "chemical solitaire" on long train rides using cards with various facts of known elements. Mendeleev used the following rules to construct the periodic table of elements:

a) The elements, if arranged according to their atomic weights, exhibit an apparent periodicity of properties.

b) Elements which are similar as regards to their chemical properties have atomic weights which are either of nearly the same value (*e.g.*, Pt, Ir, Os) or which increase regularly (*e.g.*, K, Rb, Cs).

c) The arrangement of the elements, or of groups of elements in the order of their atomic weights, corresponds to their so-called valencies, as well as, to some extent, to their distinctive chemical properties; as is apparent among other series in that of Li, Be, Ba, C, N, O, and Sn.

d) The elements which are the most widely diffused have small atomic weights.

e) The magnitude of the atomic weight determines the character of the element, just as the magnitude of the molecule determines the character of a compound body.

f) We must expect the discovery of many yet unknown elementsfor example, elements analogous to aluminum and siliconwhose atomic weight would be between 65 and 75.

g) The atomic weight of an element may sometimes be amended by a knowledge of those of its contiguous elements. Thus the atomic weight of tellurium must lie between 123 and 126, and cannot be 128.

h) Certain characteristic properties of elements can be foretold from their atomic weights.

3. Advantages of this periodic table over earlier works include:

a) Mendeleev predicted the discovery of other elements and left space for these new elements, namely eka-silicon (germanium), eka-aluminum (gallium), and eka-boron (scandium). Thus, there was no disturbance in the periodic table.

b) He pointed out that some of the then current atomic weights at that time were incorrect.

c) He provided for variance from atomic weight order.

4. Disadvantages of this periodic table include:

a) There was no place for the isotopes of the various elements.

b) His table did not include any of the noble gases, which hadn't been discovered. But these were added by Sir William Ramsay as Group 0, without any disturbance to the basic concept of the periodic table.

5. Unknown to Mendeleev, Lothar Meyer was also working on a periodic table. In his work published in 1864, Meyer presented only 28 elements, classified not by atomic weight but by valence alone.

a) Meyer never came to the idea of predicting new elements and correcting atomic weights.

b) Only a few months after Mendeleev published his periodic table of all known elements (and predicted several new elements to complete the table, plus some corrected atomic weights), Meyer published a virtually identical table.

c) Some people consider Meyer and Mendeleev the cocreators of the periodic table, although most agree that Mendeleev's accurate prediction of the qualities of the undiscovered elements lands him the larger share of credit.

E. Modern Chemistry.

1. Chemistry of today, like physics, has a variety of sub-branches associated with it. To name a few:

a) Inorganic chemistry: The study of the chemical properties of non-organic matter.

b) Organic chemistry: The study of the chemical properties of organic matter.

c) Biochemistry: The study of the chemical properties of life.

d) Quantum chemistry: Parallel to quantum physics, the use of quantum mechanics to understand the chemical properties of matter.

2. In this course, we will concentrate on organic chemistry and biochemistry to understand the origins and evolution of life.