Reese Ch. 26, Part A2

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- Chemistry and Atomic Theory (1789-1869)
- Spectroscopy (1859-1890)
- The Electron and the Plum Pudding Atom (1897-1904)
- Rutherford Scattering and the Nuclear Atom (1908-1911)
- Bohr's Model for the Hydrogen Atom (1913)

Chemistry and Atomic Theory: I

- Before Lavoisier:
  Atoms, Alchemy, and All That
- Antoine Lavoisier (1743-1794)
  - Conservation of mass verified with a balance.
  - Elements of Chemistry (1789)
- John Dalton (1766-1844)
  - "Elementary particles" (atoms) combine in specific proportions to form "compound particles" (molecules).
  - New System of Chemical Philosophy (1808)

Chemistry and Atomic Theory: II

- Humphry Davy (1778-1829) and
  Michael Faraday (1791-1867)
  - Both used the voltaic pile (battery) to electrolyze water and other compounds; this led to the discovery of many new elements.
  - Faraday determined the proportionality between charge transfer and mass liberated in electrolysis.
- Dmitri Mendeleev (1834-1907)
  - Periodic Law (1869): "If all the elements be arranged in order of their atomic weight, a periodic repetition of properties is observed."

Spectroscopy: I

- Robert Bunsen (1811-1899) devised many new devices for chemical analysis, including the spectroscope (1859), which he co-invented with …
- Gustav Kirchoff (1824-1887). In 1859, Kirchoff published three experimental laws of spectroscopy:
  - (1) An incandescent solid gives off a continuous spectrum.
  - (2) When a vapor is excited by a flame or a spark, it gives off a bright-line spectrum and the wavelengths of the lines are characteristic of the atomic species in the vapor.
  - (3) White light passed through a vapor has dark lines at the same wavelengths where that vapor can emit light.

Spectroscopy: II

- In 1868, Janssen and Lockyer discovered a spectral line in the Sun's spectrum and propose that it is produced by a previously unknown element. The new element was named "helium" after the Greek for Sun. Helium was later found in trace quantities in various minerals.
- In 1885, J. J. Balmer (1825-1898) published a paper showing that four of the prominent lines in the spectrum of atomic hydrogen have wavelengths given by the formula

$$\lambda_n = 364.56 \text{ nm} \times \left(\frac{n^2}{n^2 - 4} \right)$$

for n = 3,4,5,6

Spectroscopy: III

- In 1890, J. R. Rydberg rewrote and generalized the Balmer formula in terms of inverse wavelength (wavenumber). Eventually it came to be written as:

$$\boxed{\frac{1}{\lambda_n} = R \times \left(\frac{1}{2^2} - \frac{1}{n^2} \right)}$$

The constant R (the "Rydberg constant") has the experimental value R = 1.097 x 10^7 meters^{-1}.

The Electron and the Plum Pudding Atom: I

- In 1897, Thomson discovered the electron and showed that it is a constituent of a variety of cathode materials.
- The electron's very high ratio of charge to mass implied that most of the **mass** of atoms is due to positively charged material. It was an open question whether the **volume** of an atom is due mainly to electrons or to the positive material.

The Electron and the Plum Pudding Atom: II

- It seemed clear that the atom could not be like a miniature solar system with electrons orbiting a tiny central positive object. Why not? -- because Maxwell's electromagnetic theory implies that accelerating electric charges radiate. The atom would self-destruct: electrons in a planetary atom would rapidly spiral into the central object, giving off a burst of light.

The Electron and the Plum Pudding Atom: III

- In 1904, J. J. Thomson (based on a suggestion by Lord Kelvin) proposed that the size of the atom was just the size of a ball of positive jelly, that the electrons were not only much lighter than the positive object but also much smaller, and that the electrons resided within the positive jelly, like plums in a plum pudding.
- In this model, the natural (or unexcited) state of hydrogen (the lightest and therefore presumably the simplest atom) would have one electron at rest at the center of a ball of positive charge. The spectrum of hydrogen would be determined by the various oscillations exhibited by the electron when the atom is excited.

Rutherford Scattering and the Nuclear Atom: I

- Physicists did not have much success in their attempts to understand the spectrum of hydrogen using this model, but what really "killed" the plum-pudding atom were the results obtained by Ernest Rutherford's group on the scattering of alpha rays from thin foils of heavy metals (such as gold).
- Alpha rays were emitted by radioactive materials; by 1908, Rutherford and Hans Geiger had proved that α's are high-speed and doubly-charged helium ions.

Rutherford Scattering and the Nuclear Atom: II

- In 1909, Geiger and Ernest Marsden carefully studied what happened when alpha rays were incident on a thin metal foil.
- On the basis of a plum-pudding model, it was expected that almost all of the alphas would go through undeflected and that those which were deflected would only be turned through very small angles. What did they observe?

Rutherford Scattering and the Nuclear Atom: III

- Geiger and Marsden found that "too many" alphas were being scattered through substantial angles. In fact, roughly 1 in 10^4 of the incident alphas were deflected by more than 90^o – they were bouncing back from the very thin foil!
- These results prompted Rutherford to conclude that the atom has a nucleus (a tiny, very dense positive center) and that overall size of the atom is defined by orbiting electrons!

Bohr's Model for Hydrogen: I

- The "Rutherford scattering" results presented a big conceptual problem, because Maxwell's theory implies that a nuclear atom is unstable.
- In 1913, the young Danish physicist Niels Bohr (1885-1962) published a remarkable paper which explained the spectrum of hydrogen in terms of a strange combination of Newtonian mechanics with Einstein's idea of light energy being carried in bundles (photons) and Rutherford's idea of an atomic nucleus.
- What were Bohr's main assumptions?

Bohr's Model for Hydrogen: II

Bohr's First Assumption

An atom has a number of possible "stationary states." In any one of these states the electron performs uniform circular motion around the nucleus according to the laws of Newtonian mechanics, but the electron **DOES NOT RADIATE** as long as it remains in one of these special circular orbits.

Bohr's Model for Hydrogen: III

Bohr's Second Assumption

For the nth allowed orbit, the electron has orbital angular momentum equal to n times Planck's constant, divided by 2π:

$$L_{\substack{nth \\ orbit}} = m_e v_n r_n = \frac{nh}{2\pi} \equiv n\hbar$$

Bohr's Model for Hydrogen: III

Bohr's Third Assumption

When an atom passes from one stationary state to one or lower energy (corresponding to a change of orbit, or "quantum jump"), a photon is emitted. The energy of the photon is just the energy difference between the initial and final states of the atom. The frequency of the radiation is given by:

$$\nu = \frac{E_{photon}}{h} = \frac{E_{atom}(initial) - E_{atom}(final)}{h}$$

Bohr's Correspondence Principle

Niels Bohr was able to show that for large values of the "quantum number" n, the frequency emitted in a transition from orbit **n** to orbit **n-1** matches the orbital frequency of the nth orbit. That means it agrees with or "corresponds to" the classical prediction. The convergence of quantum and classical predictions in the limit of large quantum numbers is called the correspondence principle. Bohr often utilized this principle in his analyses of various atomic systems.

Bohr's Atomic Model

- Bohr's model accounted for the Balmer formula (including the value of the Rydberg constant) in terms of previously known physical constants.
- However ….
  - Bohr's model only works for single-electron atoms.
  - It assigns the wrong angular momentum value to the ground state of hydrogen.
- Extensions of Bohr's ideas in the form of the Bohr-Sommerfeld theory were only partially successful. In the mid-1920's, Schroedinger and Heisenberg created (nonrelativistic) quantum mechanics, which has worked well (and given people headaches!) ever since.