Unit 1
The Atom

"Chemistry The Central Science", Brown, LeMay, Bursten, and Murphy , 11th Edition.

Suggested Reading

Chapter 2

Sections 2.1-2.4

Chapter 6

Sections 6.1-6.9

Suggested Problems (Blackboard)

Unit 1 The Atom Problems

previous exam questions and great practice

Suggested Problems (Text)

Chapter 2; 2.1, 4, 13, 15, 17, 19, 21, 23, 25

Chapter 6; 6.2, 5, 15, 17, 25, 27, 31, 41, 47, 63, 71

The Atom

History

The History of the Structure of the Atom.

- Fundamental Particles
- The Discovery of the Electron
- The Discovery of the Proton
- The Discovery of the Nucleus
- The Discovery of the Atomic Number
- The Discovery of the Neutron

The Electronic Structures of the Atom

- Electromagnetic Radiation
- Atomic Spectra
- Wave Properties of the Electron
- Quantum Mechanics of Electrons
- Quantum Numbers
- Atomic Orbitals
- Electronic Configurations
- The Periodic Table

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The Atom; History

The structure of atoms

It is important to understand the history of the atom, so we can understand how we study atoms.

The history of the atom

Some of the beginning understanding of atomic structure came from the English chemist Humphrey Davy (1778 – 1829). He found that passing an electric current through some substances, those substances decomposed.

He concluded chemical compounds were held together with electric forces.

His student, Michael Faraday (1791-1867), quantified this relationship. He determined the relationship between the amount of electricity used and the amount of chemical reaction that occurred.

Studies of this work done by George Stoney (1826-1911), led to the hypothesis that atoms contain units with an electrical charge, and he suggested they be called electrons.

Convincing evidence for the electron came at the turn of the century, but studies done with a cathode-ray tube.

The Atom; History

1897, J.J.Thomson, studied the degree of deflections of the cathode rays at different strengths of electric and magnetic fields. He deteremined the ratio of an electrons charge to its mass. Even more important, this was the same ratio, regardless of gas in the tube, composition of electrodes, or nature of the power source!!

$e/m = 1.75882 \times 10^{8}$ coulomb (C)/g

This finding implied the electrons were a fundamental particle in every atom!!

With this charge to mass ratio determined a way to measure either charge or mass was needed in order to calculate the other.

In 1909, Robert Millikan performed his famous "oil-drop" experiment to determine the charge of an electron.

All of the values measured by Millikan turned out to be integral multiples of the same number.

This number was assumed to be the charge of one electron, 1.60218×10^{-19} coulomb.

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The History of the Proton

Also around the turn of the century, **Eugene Goldstein** observed the cathode-ray tube also generated a stream of positively charged particles. These were called canal rays. These positive ions are created when the gas in the tube loses electrons. The charge to mass ratio was studied for these positive ions as well,

but the e/m ratio was different for each element!!

This lead to the hypothesis that there is a unit of positive charge and that it resides in the particle the proton.

The proton was 1836 times larger than the electron!!

At this point, scientists knew there were positively charged protons and negatively charged electrons in every element, but how were they distributed??

The Atom; History

In 1897 Becquerel discovered natural radioactivity in uranium, which led to the next series of discoveries on the atom.

In 1909 Ernest Rutherford, established α-particles were positively charged particles that were spontaneously emited by some radioactive elements.

In 1910, Rutherford's research group bombarded a very thin piece of gold foil with α-particles. These particles were assumed to be extremely dense, much more dense than gold atoms, and it was assumed the positive particles would have been deflected at very small angles. This was not the case!!

Most of the particles did not deflect!! And those that did, deflected at very high angles, some even at 180°!!

This prompted Rutherford to scrap the old theory of "plum pudding" for the structure of the atom and propose the

idea of a positively charged nucleus, surrounded by the very light electrons and a lot of space!!

The Atom; History

Only a few years later, H.G.J. Mosley, studied the X-rays given off by various elements. Mosley aimed a beam of high energy electrons at a solid target made up of a single element. Each experiment was "photographed" and a series of lines appeared for each element…..but the series of lines was unique to each element!!

Mathematically, these spectra differed in a linear fashion and the hypothesis of atomic number was born… Moseley came up with the idea of atomic number and that the elements could be arranged in order of increasing atomic numbers.

Each element differs from the proceeding element by having one more positive charge in its nucleus.

This discovery lead to the realization that atomic number was more relevant to determining the properties of the elements than atomic weight.

This is the basis for what we know today, that each element has an equal number of protons and electrons and the elements are identified by their number of protons!!

The Atom; History

The history of the neutron

The neutron wasn't discovered until 1932, while James Chadwick was bombarding beryllium with high energy α-particles. This experiment showed that a neutral particle with a mass slightly greater than a proton was produced.

At this point the atomic model now included, protons and neutrons in the nucleus, and electrons outside of the nucleus with an enormous amount of space between them!!

For example, the diameter of the nucleus is about 10^{-5} nm where the atomic diameter is 10^{-1} nm.

Remember, an isotope is the variation of numbers of neutrons of an element!!

The Atom; Structure

The Electronic Structures of Atoms

The atomic model is good so far, but it doesn't answer our questions of, why do molecules form? Why do the elements have such different properties?

Electromagnetic radiation

To understand electromagnetic radiation, we must review waves.

Waves are a repetitive in nature and measured in wavelength.

Waves are characterized by the measure of wavelength, which is the distance between two adjacent points on the wave. The second characterization is frequency, that is the number waves passing a given point over a given period of time.

Electromagnetic radiation is an electric and magnetic field which also vary repetitively in a wave.

Light is a form of elecrtromagnetic radiation!!

The wavelength determines the color!!

The range of electromagnetic radiation:

The Atom; Structure

Isaac Newton first recorded the separation of sunlight into the color spectrum we know today by passing light through a glass prism.

We know the spectrum is much larger than the visible colors we see!!

Electromagnetic radiation travels at the same speed, in a vacuum, for all wavelengths.

Now, light is a wave, but it also has particles!!

These particles are called photons.

Each photon has **a specific amount** of energy (a quantum). This energy is dependant on the frequency of the light.

The Atom; Structure

The photoelectric effect

In 1905 Einstein extended Planck's idea of the photon to atoms. He theorized that a ***single photon of light can transfer its energy to a single electron during a collision.***

If that energy is equal to or greater than the energy need to liberate the electron, the electron will "escape" to join the photoelectric current.

He won the Noble Prize in Physics in 1921 for this explanation.

Where do we see this today?

The Atom; Structure

Atomic Spectra

When an electric current is passed through a gas in a vacuum at low pressures, the light can be dispersed through a prism into distinct lines.

This spectrum of lines produced can be photographed and wavelengths calculated!!

This is called **emission spectrum**.

We can also shine white light through a gas and analyze the beam that emerges. Certain wavelengths will be absorbed and thus give an **absorption spectrum.**

Each element absorbs and emits the same wavelengths, but the wavelengths are different for each element!!

These “lines” serve as fingerprints for each element!!

In the late 19th century these lines were observed for hydrogen, and a mathematical relationship was observed.

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In 1913, Niels Bohr, a Danish Physicist, provided the explanation for these observations. He concluded the electrons in hydrogen were revolving around the nucleus in circular orbitals. He further explained that since the electronic energy is quantized, that is only certain energy levels are possible, electrons are in discrete orbitals and that they emit or absorb specific amounts of energy as they move form orbital to orbital!!

This is incredibly important!!

Let's restate it.

Electrons exist in orbitals that correspond to definite energy levels!!

They require a specific amount of energy to "jump" into another orbital, that energy is *absorbed*.

When electrons "jump" into a lower orbital the *emit* a specific amount of energy.

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We now accept that electrons occupy certain orbitals with specific energy levels, and that they can absorb or emit definite amounts of energy to move between these orbitals, often within the range of visible light.

But, how many electrons are in which orbitals? How do they behave? How are they arranged?

Electrons are particles and waves.

In 1927, this property of electrons was observed.

Through this early work on electrons and their wave properties, we now know that electrons are better treated as standing waves, than particles. Large objects follow Newton's Laws of mechanics, but very small particles, such as electrons, protons, and atoms behave more as standing waves and follow the principles of quantum mechanics.

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One of the fundamental principles of quantum mechanics is that we cannot precisely determine the paths electrons follow around the atomic nuclei!!

This is called the **Heisenberg Uncertainty Principle**. Werner Heisenberg stated in 1927,

that it is impossible to determine accurately both momentum and the position of an electron simultaneously.

Consider this……we have just learned that we use electromagnetic radiation to study electrons. This is an absorption or emission of energy by an electron, that act alone greatly distorts the path an electron takes.

So, we revert to statistical approaches to calculating the probability of finding an electron within a certain region of space.

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Some basic principles of quantum mechanics.

- Atoms and molecules can only exist in certain energy states.
- In each energy state the atom or molecule has a definite energy,
- When an atom or molecule changes its energy, it must emit or absorb the exact amount of energy needed to bring the next energy state.
- The change in energy of an atom or molecule is related to the wavelength of the light emitted or absorbed.
- The allowed energy states of atoms and molecules can be described by sets of numbers called quantum numbers.

The mathematical approach to an electron is to treat it as a *standing wave*. That is a wave that does not move, so it has at least one point where the amplitude is zero. We call this a node. A standing wave can only vibrate in ways in which there are whole number of half-wavelengths. For electrons this means there are only certain allowed waves, “orbitals” that exist in a certain energy state.

We can calculate these “orbitals” using the Schrodinger equation.

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We can use these calculations to designate the electronic arrangements in all atoms. This is called the **electronic configuration.**

Here are the four quantum numbers and what they mean to us;

The **principal quantum number**, *n*, describes the main energy level. This is the shell that an electron occupies. This number is always a positive integer, n = 1,2,3,4….

The **angular momentum quantum number**, *l*, gives us the shape of the orbital. This number ranges from 0 - (n-1). We give a letter notation for each shape of the orbital. So, l = 0 is *s*, *1* = 1 is *p*, l = 2 is *d*, and l = 3 is *f*.

The **magnetic quantum number**, m, designates the orientation of the electrons and not their energies. The number *m*, may equal –l to +l. So for p, you get p_x, p_y, and p_z.

The **spin quantum number**, m_s, refers to the spin of the electron. The spin number can be +1/2 or -1/2. Each atomic orbital can accommodate no more than 2 electrons, whose spin are +1/2 and -1/2.

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<u>An atomic orbital is a region of space in which the probability of finding an electron is high.</u>

Atomic Orbitals

We are now ready to describe the distribution of electrons in atoms. Remember, for each neutral atom, we assume with number of electrons is equal to the number of protons, thus the atomic number. Each electron occupied an atomic orbital described by a set of four quantum numbers *(n, l, m)*. **In any atom, each orbital can hold a maximum of 2 electrons**.

The main shell of each atomic orbital is described by the principle quantum number, n. The values of n are always integers, i.e. 1, 2, 3, 4, with 1 being closest to the nucleus. These shells are the electrons energy levels and contain all of the subshells *(l, m).* The electron capacity of each shell is $2n^2$, i.e. when $n = 2$, there is the capacity for 8 electrons in that shell.

We distinguish the orbitals by using the principal quantum number with the orbital symbol, i.e. *1s* orbital or the *2p* orbitals.

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Electronic Configuration

We have looked at the solutions to the Schrodinger equation for hydrogen. These quantum numbers are explicit, but the more electrons the more complicated the equation and solutions are no longer explicit. We need to rely on *orbital approximations* for multi-electron elements, these approximations state that the orbitals for each electron superimpose on those calculated for hydrogen.

The orbitals are described the same as for hydrogen, however the order of the energies may be different.

Let us take a look at the ground state electronic configurations for other elements.

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The guiding idea for ground state electronic configuration is that the total energy for the atom is as low as possible. For this we follow the **Aufbau Principle**.

Let's "build up" an atom.

Add the appropriate number of protons and neutrons to the nucleus.

Add the total number of electrons into orbital that give the lowest total energy.

Assign electrons in order of increasing n and l.

For subshells with the same value of $n + l$, assign the lower n number first.

We must also consider the Pauli Exclusion Principle, which states that no two elelctrons in any atom may have the same quantum numbers.

Let's simplify here, when you have two electrons in an orbital, they must have the opposite spin.

One more rule. Hund's Rule. Electrons will occupy all the subshells singly before pairing begins.

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Paramagnetism and Dimagnetism

Substances which contain unpaired electrons and are weakly attracted to a magnetic field are called **paramagnetic**.

Subtances which contain all paired electrons and are weakly repelled by a magnetic field are called **diamagnetic**.

Iron, Cobalt, and Nickel are the only free elements which are **ferromagnetic**, thus they can be permanently magnetized by a strong magnetic field.

Now, once again lets look at the Periodic Table. The elements are arranged by electronic configurations!!

The elements are arranged in blocks according to the highest filled orbitals, i.e. Li and Be are in the s block, C, N, O are in the p block, Cr, Mn, Fe are in the d block…and so on.

Each column has a similar electronic configuration, and therefore similar chemical properties!!