

AP Chemistry

Atomic Theory Outline

(APatomicoutline.doc)

A wave can be considered a periodic disturbance in space that carries energy.

Some properties of waves are:

Wavelength (λ (lambda)) = The distance between two consecutive identical points on a wave (often measured from crest to crest). Wavelengths are often expressed in nanometers, but should be converted to meters before being used in an equation.

Amplitude (A) = The distance to the maximum displacement from equilibrium

Frequency (v (nu) or sometimes f) = The number of wave cycles that occur each second. Frequency is normally measured in hertz (Hz). It may also be seen as cycles/sec, 1/s or just s^{-1}

Period (T) = The time for one wave cycle ($= 1/v$)

Velocity (v or sometimes u) = The speed of the wave through space. Electromagnetic waves always travel at a constant rate through the vacuum of space so its velocity is given the constant **c**, and is **3.0×10^8 m/s**.

For an electromagnetic wave, the product of the wavelength and the frequency always equals the speed of light.

$$c = \lambda v$$

Unlike a mechanical wave whose energy is carried on the amplitude of the wave, the energy of an electromagnetic wave is carried on its frequency.

The different types of electromagnetic waves from lowest energy (i.e. lowest frequency and longest wavelength) to highest are:

Radio waves, microwaves, infrared, visible, ultraviolet, X-rays, gamma rays

The visible spectrum runs from about 400nm (blue-violet) to 700nm (red).

All of these waves stem from the same source, namely the transition of an electron from a more energetic position around the nucleus of an atom to a lower energy position.

The model of the atom towards the end of the 1800's was that of the electron behaving like a planet going around the sun, represented by the nucleus. The attraction between the positive nucleus and negative electron was counterbalanced by the angular acceleration of the electron around the nucleus.

The energy of the wave is determined by the difference in energy between the positions.

In the latter part of the nineteenth century, scientists were confused by several aspects of light.

1. Since accelerating charged particles emit energy, they didn't know why electrons didn't spiral into the nucleus.
2. Why rarefied, energized gases only gave off certain frequencies of light instead of a continuous spectrum, since all electron "jumps" should be possible.

3. Why equations based on current knowledge of physics at the time was only able to partially describe the energy emitted at different wavelengths by an object. Some equations described the shorter wavelength region, others the longer wavelengths.

Waves and Energy

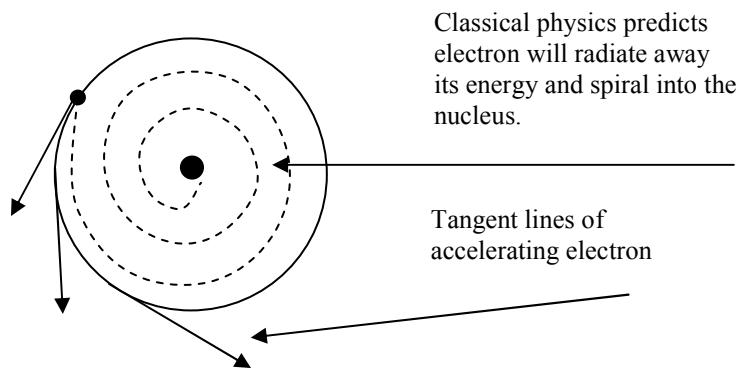
Useful Equations and Constants:

$$c = \lambda\nu, \quad E = h\nu, \quad h = 6.626 \times 10^{-34} \text{Js} \quad c = 3.00 \times 10^8 \text{m/s} \quad 1 \text{nm} = 10^{-9} \text{m}$$

Note: Energy units must be in joules and wavelength in meters to be used in these equations.

Problems with a classical view of the atom.

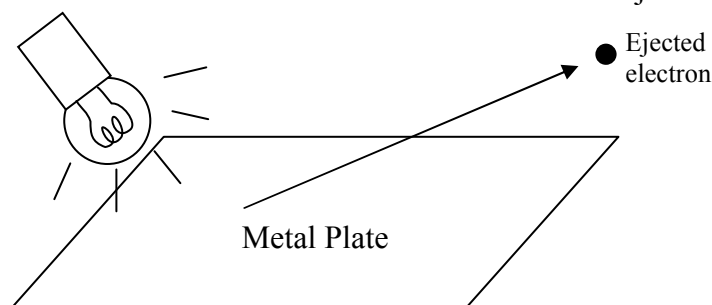
- Why don't electrons radiate their energy away and spiral into the nucleus?
- Why don't all atoms give off energy at all frequencies (i.e. "rainbow" of colors). Spectral lines of light given off by gas discharge showed specific lines instead of a continuous spectrum.



- Why isn't a light that is bright enough (i.e. high enough amplitude), regardless of frequency, able to eject electrons from the atoms of a piece of metal (**photoelectric effect**), but at a certain frequency (**threshold frequency**) at least some electrons are ejected regardless of the intensity of the light? (The energy of physical waves are carried on their amplitude).

Solution to "c" above:

Albert Einstein stated that light has particle as well as wave properties. The light particle is referred to as a **photon**. The photon contains a specific "bundle" of energy that either has or doesn't have enough energy to eject an electron. The energy doesn't "build up" like a wave. The *energy of the light is dependant upon its frequency*. The amplitude or intensity of the light correlates to how many photons are emitted per unit time, therefore determines the rate at which electrons are ejected from the metal, if any.

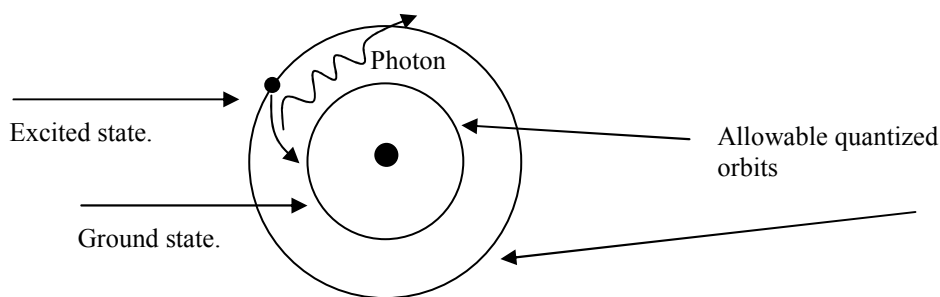


Photoelectric Effect

Solutions to a and b above:

Based on the work of **Max Planck** who stated that the energy of an electron must be quantized (i.e. have only specific allowable values), **Niels Bohr** proposed a model for the atom in which the electron orbits the nucleus of the atom in only specific allowable orbits that corresponded to those specific energy values. When an electron absorbs energy, it transitions from its **ground state** orbit to an **excited state** orbit that is higher in energy by an amount equal to the energy absorbed. The electron is unstable in this excited state and quickly jumps back down to its ground state in one or more quantized steps. Each time the electron jumps from a higher to lower orbit, a photon of electromagnetic radiation is given off with an energy equal to the difference in energy between the orbits. This is where the discrete spectral lines come from instead of the continuous rainbow.

The energy of the photon is given by the equation $E = h\nu$, where E is the energy in joules, h is Planck's constant = 6.626×10^{-34} Js and ν is the frequency of the light in hertz (Hz).

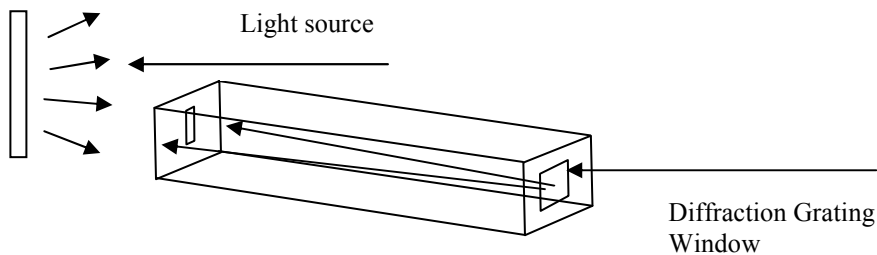


Note that the difference in energy between the two electron orbits corresponds to the frequency of the radiation that will be emitted by the electron.

$$\Delta E = h\nu$$

Seeing spectral lines:

The spectral lines of different atoms in the gaseous state can be seen by viewing the light through a diffraction grating which is basically a small piece of plastic with many closely spaced lines etched into them (usually over 10,000 per inch). These lines break up the light into its component colors much the same way that a prism does. By looking at the light through a spectroscope one can see the distinct lines given off by the electrons as they transition from higher to lower energy states. The spectral lines of the elements are so unique that they are known as the "fingerprints of the elements".



Max Planck proposed a solution to the problem by stating that atoms and molecules could only emit (or absorb) energy in discrete, "quantized" packets called a **quanta** of energy.

The energy of the quantum is given by:

$$E = h\nu, \text{ where } h \text{ is called Planck's constant} = 6.626 \times 10^{-34} \text{ Js}$$

In 1905, Albert Einstein used this idea to explain the *photoelectric effect*.

The photoelectric effect is a phenomenon in which radiant energy is shined on the surface of a metal to provide the energy required to remove an electron from around the nucleus of an atom of the metal. Scientists assumed that the intensity (brightness, which is a function of the amplitude) would provide the energy needed to remove the electron. What they found was that whether or not an electron was removed was dependant upon the frequency of the light (blue vs. red, etc.) instead of on the amplitude (brightness). This could not be explained by the wave nature of light. Einstein proposed that light is actually a particle which he called a **photon**. A photon's energy is determined by the Planck equation. The intensity of the light correlated with the number of photons per unit time, but the energy was dependant only upon the frequency. A minimum frequency (called the **threshold frequency**) is needed to overcome the force of attraction between an electron and the nucleus. Any excess energy is turned into the kinetic energy of the ejected electron.

$h\nu = KE + IE$, where KE is the kinetic energy $\frac{1}{2} mu^2$ and IE is the ionization energy (different for different metals).

The Bohr Model of the Atom

Niels Bohr synthesized these ideas into a model of the atom which was still similar to a solar system, but in which the "orbits" of the electrons could only take on certain quantized values given by

$E_n = -R_H (1/n^2)$, where R_H is the Rydberg constant = $2.179 \times 10^{-18} J$ and n is an integer corresponding to the ring level (energy level) of the electron around the nucleus.

The difference between two energy levels is $\Delta E = -R_H (1/n_{hi}^2 - 1/n_{lo}^2)$, n_{hi} is the higher energy level and n_{lo} is the lower energy level. Note that ΔE is **negative for energy released**.

The downside of this equation is that it only accurately describes the energy of a single electron atom such as that of hydrogen (or with a correction a singly ionized helium atom, etc.).

The emission lines of a gas are produced by the downward transition of an electron from a higher to lower energy level. The **Balmer** series of spectral lines is a famous set of 5 lines in the visible (mostly) spectrum of hydrogen gas.

Louis De Broglie

In 1924 De Broglie came up with the idea that since an electromagnetic wave can have particle (photon) properties, perhaps a particle can have wave properties. He explained the quantized nature of electrons around the nucleus by stating that the radii of the orbits could only be integer multiples of the wavelength of the particle. The equation is given by

$2\pi r = n\lambda$, r is the radius of the orbit, λ is the "De Broglie" wavelength of the electron and $n = 1, 2, 3, \dots$

The De Broglie wavelength is given by $\lambda = h/mv$ m is the mass of the object (in kg) and v is the velocity in m/s (i.e. the momentum of the object).

Wave Mechanics

Because of inconsistencies in describing the behavior of many-electron atoms (those with greater than one electron), and because of the "wave-like" nature of the electron (i.e. viewing the electron as an extended

object) Werner Heisenberg formulated a theory that described a fundamental law of nature that limits the precision to which one can simultaneously know certain properties about an electron.

Heisenberg Uncertainty Principle: There is a fundamental limit to the precision to which one can simultaneously measure the momentum (velocity) and position of an electron.

$$(\Delta x)(\Delta mv) \geq h/4\pi$$

where Δx is the uncertainty in the position of the electron, Δmv is the uncertainty of its momentum and h is Planck's constant.

From this, **Erwin Schrödinger** developed a complex mathematical formula (known as the wave function, designated by the Greek letter psi, ψ) which allows scientists to determine statistically, the energy and approximate region around the nucleus of an atom that an electron is likely to be found.

Schrödinger's model uses the concept of an **atomic orbital** rather than an orbit. Squaring the psi equation (ψ^2) and plotting the results in 3-dimensional space describes the probability density (likelihood) of finding an electron with a certain energy in a particular region of space. This region is known as an orbital. To describe with 100% certainty the location of an electron you would have to be able to draw the whole universe (which is difficult to do on a piece of paper), the orbital usually drawn describes the **90% probability region** (i.e. where the electron is likely to be found 90% of the time). The greater the cloud density, the greater the probability an electron will be found there.

Quantum Numbers

In order to fully describe the energy associated with a given electron, four unique numbers (known as quantum numbers) are assigned to each electron in an atom. By the **Pauli Exclusion Principle**, each electron must possess a unique set of quantum numbers for that atom, since no two electrons in the same atom can have the exact same energy state.

The four numbers that describe the orbital energy of an electron are as follows:

The principal quantum number (n): This number is related to the overall energy of an orbital. The number n , can take on integer values $n = 1, 2, 3, 4, \dots$

The angular momentum (azimuthal) quantum number (l): This number is related to the shape of the sub-orbitals (i.e. shape of the 90% probability region) that an orbital may possess. The value of l can take on numbers from $l = 0$ to $n-1$

The magnetic quantum number (m_l): This number is related to the orientation of the sub-orbital in 3-dimensional space. Its numbers range from $m_l = -l \dots 0 \dots +l$

The spin quantum number (m_s): This number relates to the spin orientation of an electron in a given orbital. The electron does not have a true "spin" in the classical sense, but is used to account for spectral lines that are produced in the presence of an external magnetic field. The spin quantum number can possess values of $m_s = \pm 1/2$. Therefore only 2 values are possible.

With regard to the angular momentum quantum number, l , scientists have assigned letters that correspond to the numerical values that l can have. This comes from the days of spectroscopy (spectral analysis) and are as follows:

For l equal to:

- 0 → s (sharp)
- 1 → p (principal)
- 2 → d (diffuse)
- 3 → f (fine)

For l equal to 4 and beyond the letters g, h, i,... and so on are used, skipping the letters that have already been used.

Orbitals have specific shapes. For instance an s-orbital is spherical shaped, a p-orbital is dumbbell shaped and so on. These "shapes" represent the 90% probability region. Note that these shapes have volume and that the volume of the shape is not uniform in its density. The denser the region, the greater the probability of finding the electron there.