Chapter 7 - Atomic Structure and Periodicity

AP Chemistry

Goals

1. Relate wavelength and frequency to energy on the electromagnetic spectrum.
2. Identify three primary components of electromagnetic waves including wavelength, frequency and speed.
3. Use the equation $c=\lambda\nu$ to solve for the frequency or wavelength of an electromagnetic wave.
4. Use the equation $E=h\nu$ to solve for the frequency, wavelength, or energy of a photon.
5. Describe energy as being quantized into "packets" of $h\nu$.
6. Determine the mass of a photon using $m=h/(\lambda c)$.
7. Use de Broglie's equation to determine the wavelength of matter using $\lambda=h/(m\nu)$.
8. Describe why matter exhibits both particulate and wave properties.
9. Differentiate between continuous, emission, and absorption spectra.
10. Use the energy level expression from the Bohr model to determine the change in energy associated with the electron changing energy levels.
11. Describe the modern model of the atom as the quantum mechanical model based upon the Schrödinger equation.
12. Describe the position of an electron as a probability.
13. Use the Heisenberg Uncertainty Principle to conceptually understand uncertainty associated with knowing a particles position and momentum at the same time.
14. Identify the quantum numbers associated with each energy sublevel in an atom.
15. Identify the shapes of s, p, d, and f orbitals.
16. Describe what it means for an orbital to be degenerate.
17. Explain and use the Aufbau Principle when writing electron configurations.
18. Explain and use the Pauli Exclusion Principle when writing electron configurations.
19. Explain and use Hund's Rule when writing electron configurations.
20. Explain trends in ionization energy, and atomic radii with respect to electronic structure.
21. Relate electronic structure to similarities in chemical properties within a group.

Electromagnetic Radiation

- Radiant energy that exhibits wavelike behavior and travels through space at the speed of light in a vacuum
- Wave energies are classified by their wavelength and frequency in the electromagnetic spectrum

Electromagnetic Waves

- Waves have three primary characteristics:
  1. Wavelength (λ) – distance between two consecutive peaks or troughs in a wave
  2. Frequency (υ) – number of waves per second that pass a given point in space
  3. Speed of light (c) – equal to the wavelength multiplied by the frequency

     ($c = \lambda\ \upsilon$) $c = 2.9979 \times 10^8$ m/s

Electromagnetic Wave Example Problem

- An FM radio station broadcasts at 94.7 MHz. Calculate the wavelength of the corresponding radio waves.

The Nature of Matter

- Max Planck determined matter can emit or absorb energy in whole-number multiples of the quantity hʋ, where h is Planck's constant ($h=6.626 \times 10^{-34}$ Js)
- $\Delta E=nh\upsilon$, where n is an integer, h is Planck's constant and ʋ is the frequency
- Energy is quantized into "packets" of energy called quantums

Energy as a Wave Problem

- Calculate the energy associated with the emission of violet light at a wavelength of $4x10^{-7}$ m.

Dual Nature of Light

- Energy can behave as a wave (Planck's description) or as a particle.
- Einstein proposed energy can be viewed as a stream of particles (photoelectric effect)
- $E_{photon}=h\upsilon=h(c/\lambda)$
- Using $E=mc^2$, one can determine the mass of a photon:

  $m=h/(\lambda c)$

Energy of a Photon Problem

- A photon of ultraviolet light possesses enough energy to mutate a strand of human DNA. What is the energy of a single UV photon and a mole of UV photons having a wavelength of 25 nm?

Summary of Planck and Einstein

- Energy is quantized. It can occur only in discrete units called quanta (black body radiation).
- Electromagnetic radiation, which was previously thought to exhibit only wave properties, seems to show certain characteristics of particulate matter as well (photoelectric effect).

Wavelength of a Particle

- de Broglie equation:

  For a particle with velocity v, the corresponding expression is $m=h/(\lambda v)$

Wavelength of a Particle Example

- Compare the wavelength for an electron (mass=9.11×10^{-31} kg) traveling at a speed of 1.0×10^{7} m/s with that for a ball (mass=0.10 kg) traveling at 35 m/s.

Summary

- All matter exhibits both particulate and wave properties.
- Large pieces of matter (baseball) exhibit predominately particle properties.
- Very small pieces of matter (photon) exhibit predominately wave properties.
- Intermediate particles (electron) exhibit particle and wave properties.

Atomic Spectra

- Continuous spectrum – a spectrum that exhibits all wavelengths of visible light
- Emission spectrum – a spectrum showing only certain discrete wavelengths
- Absorption spectrum – a continuous spectrum missing only discrete wavelengths

Hydrogen Line Spectrum

- When hydrogen gas absorbs energy, electrons go to an excited state, excited electrons then release energy corresponding to certain discrete energy levels.
- These energy levels correspond to distinct wavelengths of light.
- Only certain energies are allowed for the electron in the hydrogen atom.

The Bohr Model

- Upon observing experimental results, Niels Bohr developed a quantum model for the hydrogen atom where the electron orbits the nucleus only in certain allowed circular orbits.
- Each orbital distance corresponded to a distinct energy level, n, where n is an integer.

Energy Levels in the Bohr Model

- $E=-2.178\times10^{-18}$ J(Z^2/n^2), where Z is the nuclear charge and n is an integer value describing the energy level of the electron.
- The negative sign means the electron has a lower energy if it is bound to the nucleus as opposed to an infinite distance where there is no interaction and therefore no energy.
- When moving between energy levels:

  $\Delta E=-2.178\times10^{-18}$ J$(1/(n_{final})^2 - 1/(n_{initial})^2)$

Bohr Energy Level Example

- Calculate the energy associated with the electron in a hydrogen atom going from energy level n=2 to n=1. Is this change energetically favorable? What wavelength of light does this emission correspond to?

Summary of Bohr Atom

1. The model correctly fits the quantized energy levels of the hydrogen atom and postulates only certain allowed circular orbits for the electron.
2. As the electron becomes more tightly bound, its energy becomes more negative relative to the zero-energy reference state (corresponding to the electron being at infinite distance from the nucleus). As the electron is brought closer to the nucleus, energy is released for the system.
3. Model falls apart when describing any atom other than hydrogen.

The Quantum Mechanical Model of the Atom

- Werner Heisenberg, Louis de Broglie, and Erwin Schrödinger developed the quantum mechanical model of the atom.
- In this model the location of an electron is described mathematically using a wave function.

Heisenberg’s Uncertainty Principle

- There is a fundamental limitation to just how precisely we can know both the position and the momentum of a particle at a given time.
- The more accurately that we know a particle’s position, the less accurately we know the particle’s momentum and vice versa.
- Therefore, it is not appropriate to describe an electron as moving around the nucleus in well-defined orbitals (like the Bohr Model).

Quantum Mechanical Model

- Gives us a probability of where the electron may be.
- The model gives us no information about the exact position or momentum of the electrons in an atom.
- An orbital provides us with a three dimensional shape encompassing where the electron will be 90% of the time.

Orbital Shapes and Energies

- Each orbital has a unique probability distribution and shape.
- Each orbital represents the surface that surrounds 90% of the total electron probability.
- All orbitals with the same value of n have the same energy and are said to be degenerate.

Orbital Shapes

- s orbital – spherical shape
- p orbital – two lobes, “dumbbell shaped”
- d orbital – four have four lobes, one has two lobes with a “belt”
- f orbital – four have eight lobes, three have two lobes with a “belt”

http://www.orbitals.com/orb/orbtable.htm

http://employees.oneonta.edu/viningwj/modules/CI_shapes_of_atomic_orbitals_7_14.html

Quantum Numbers

- Orbitals, solutions to the Schrödinger equation, can be characterized by quantum numbers.
- Quantum numbers describe various properties of the orbital.

Principal Quantum Number

- The principal quantum number, n, is related to the size and energy of an orbital.
- As n increases, the orbital becomes larger, and the electrons spend more time away from the nucleus.
- An increase in n also means an increase in energy.
- n has integer values: 1, 2, 3, 4, ...

Angular Momentum Quantum Number

- The angular momentum quantum number, ℓ, is related to the shape of the atomic orbital.
- ℓ has integer values from 0 to n - 1.
- $\ell = 0$ is called s, $\ell = 1$ is called p, $\ell = 2$ is called d, $\ell = 3$ is called f.

Examples

- For n = 4, what are the possible values of ℓ?
- Give the numerical values of n and ℓ corresponding to each of the following designations: 3p, 2s, 4f, 5d
- Which of the following represents impossible combinations of n and l: 1p, 4s, 5f, 2d?

Magnetic Quantum Number

- The magnetic quantum number, m_ℓ, is related to each orbital's orientation in space with respect to the other orbitals.
- m_ℓ has integer values between $-\ell$ and ℓ, including 0.

Example

- For $\ell = 2$, what are the possible values of m_ℓ?

Quantum Numbers for the First Four Energy Levels

n	ℓ	Orbital	m_ℓ	# of Orbitals (n^2)
1	0	1s	0	1
2	0	2s	0	1
	1	2p	-1, 0, +1	3
3	0	3s	0	1
	1	3p	-1, 0, +1	3
	2	3d	-2, -1, 0, +1, +2	5
4	0	4s	0	1
	1	4p	-1, 0, +1	3
	2	4d	-2, -1, 0, +1, +2	5
	3	4f	-3, -2, -1, 0, +1, +2, +3	7

Quantum Number Examples

- Which of the following are permissible sets of quantum number for an electron in a hydrogen atom?
    a. $n = 2, \ell = 1, m_\ell = 1$
    b. $n = 1, \ell = 0, m_\ell = -1$
    c. $n = 4, \ell = 2, m_\ell = -2$
    d. $n = 3, \ell = 3, m_\ell = 0$

Electron Spin and the Pauli Principle

- The fourth quantum number (in addition to n, ℓ, and m_ℓ) is m_s, called the electron spin quantum number.
- Experimental data showed an electron had a magnetic moment with two different orientations, consistent with two spin states.
- m_s = +1/2 or -1/2, one for each of the two possible direction it can spin.
- Pauli Principle – in a given atom no two electrons can have the same four quantum numbers (n, ℓ, m_ℓ, and m_s)
- The consequence of Pauli's Principle is that each orbital can contain at most two electrons of opposite spin.

Energy Levels Considerations

- Electrons enter orbitals starting with the lowest energy orbital first:

$$E_{ns} < E_{np} < E_{nd} < E_{nf}$$

Electron Configurations and the Arrangement of the Periodic Table

- The greatest triumph of the quantum mechanical model is its use to explain the observed periodic properties of the elements as summarized in the periodic table.
- The chemical properties of an atom are determined by the arrangement of the valence electrons.
- Elements in the same group have the same valence electron configurations, which explains the similarities in their chemical properties.

Valence Electrons

- Electrons in the outermost principal quantum level of an atom

The Aufbau Principle and the Periodic Table

- As protons are added one by one to the nucleus to build up the elements, electrons are similarly added to hydrogen like orbitals.
- When adding electrons to atoms in their ground state, electrons are added to the lowest energy orbital first.

Hund's Rule

- The lowest energy electron configuration for an atom is one having the maximum number of unpaired electrons allowed by the Pauli Exclusion Principle in a particular set of degenerate orbitals.

Trends Among Ground State Electron Configurations

- Elements within the same group have the same valence electron configuration.
- Alkali metals and alkaline earth metals have valence electrons in the s orbitals.
- Transition metals have high energy electrons in the d orbitals.
- Lanthanides and actinides have high energy electrons in the f orbitals.
- Groups 3A-7A have valence electrons in the s and p orbitals.

Electron Configurations

- Write out the ground state electron configuration for the following atoms:
  1. He
  2. O
  3. Ar
  4. Co
  5. Cu
  6. In

Periodic Trends in Atomic Properties

- Ionization energy - energy required to remove an electron from a gaseous atom or ion
- Electron Affinity – energy change associated with the addition of an electron to a gaseous atom
- Atomic Radius – ½ distance between atoms in a chemical compound or diatomic element

Ionization Energy

- $X(g) \rightarrow X^+(g) + e^-$
- First Ionization Energy (I_1) – energy required to remove the highest energy electron from an atom
- Second Ionization Energy (I_2) – energy required to remove the second highest energy electron from an atom

Trends in Ionization Energy

- $Al(g) \rightarrow Al^{+}(g) + e^{-}$ $I_1 = 580$ kJ/mol
- $Al^{+}(g) \rightarrow Al^{2+}(g) + e^{-}$ $I_2 = 1815$ kJ/mol
- $Al^{2+}(g) \rightarrow Al^{3+} + e^{-}$ $I_3 = 2740$ kJ/mol
- $Al^{3+}(g) \rightarrow Al^{4+} + e^{-}$ $I_4 = 11600$ kJ/mol

- Ionization energies increase as lower energy electrons are removed from the atom. Core electrons are bound more tightly than valence electrons!

Ionization Energy Continued

- Ionization energies increase across a period due to an increase in effective nuclear charge.
- Ionization energies decrease down a group because valence electrons are higher energy and are shielded from the nucleus.

Electron Affinity

- $X(g) + e^- \rightarrow X^-(g)$
- Electron affinity increases across a period.
- Electron affinity decreases down a group.
- (By increase we mean give off a greater amount of energy when an electron is added to an orbital)

Atomic Radius

- Atomic radii decrease across a period due to an increase in effective nuclear charge.
- Atomic radii increase down a group due to an increase in orbital size.

The Properties of a Group

- Elements in the same group have similar chemical properties due to the same number of valence electrons in their outermost orbital.