CM1102
Chemistry – The Central Science

AY2022/23 Semester 1

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Contents

Part I

Environment

1 Light

Light is a form of energy that consists of oscillating *electric* and *magnetic* fields, perpendicular to each other.

$c = \lambda \nu$		
	value	**unit**
c	speed of light $= 2.9979 \times 10^8$	m/s
λ	wavelength	m
ν	frequency	s^{-1} or Hz

1.1 Wave-particle Duality of Light

Due to the wave nature of light, light waves that are *in phase* undergo **constructive interference**.

Light waves that are *out of phase* undergo **destructive interference** — cancelling out each other.

Due to the particle nature of light, when an object is heated, it emits electromagnetic radiation known as **blackbody radiation**.

The wavelength of light emitted changes as the temperature of the object increases.

$E = h\nu$		
	value	**unit**
E	energy	J
h	Planck's constant $= 6.626 \times 10^{-34}$	J/s
ν	frequency	s^{-1} or Hz

Putting the two equations above together, we can interconvert between *energy*, *frequency*, and *wavelength*.

$E = \frac{hc}{\lambda}$		
	value	**unit**
E	energy	J
h	Planck's constant $= 6.626 \times 10^{-34}$	J/s
c	speed of light $= 2.9979 \times 10^8$	m/s
λ	wavelength	m

1.2 Photoelectric Effect

Electrons can only be ejected from a surface if incoming **photons** transfer sufficient energy to the atoms on the metal surface.

Electron-volt (eV) is the amount of *kinetic energy* gained by a single electron accelerating from rest though an electric potential difference of 1 volt in vacuum.

$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$

$h\nu = \Phi + KE_{max}$		
	value	**unit**
h	Planck's constant $= 6.626 \times 10^{-34}$	J/s
ν	frequency	s^{-1} or Hz
Φ	work function of the metal	eV
KE_{max}	maximum kinetic energy of the ejected electron	eV

Note that KE_{max} *cannot be negative*, so its minimum value is 0.

1.3 Solar Spectrum

The **electromagnetic spectrum** comprises of, in increasing energy:

1. radio waves,
2. microwaves,
3. infrared,
4. visible,
5. ultraviolet,
6. X-rays,
7. gamma (γ) rays,

White light disperses into a continuous spectrum in the visible spectrum.

However, sunlight is *not continuous* — there are *dark lines* in the **solar spectrum** due to the composition of the sun and the Earth's atmosphere.

1.3.1 Aside: Spectroscopy

The study of the interaction of electromagnetic radiation *with* matter *to obtain information about the identity and structure of substances*.

Absorption spectroscopy reveals that a colored object reflects light of that color and absorbs light of the *opposite color*.

1.3.2 Emission Spectrums

Energy can excite electrons of atoms from their **ground state** to an **excited state**.

In the excited state, electrons have higher energy, and when electrons are relaxed to their ground state, their energy is released as light.

Therefore, the dark lines in the solar spectrum occur due to the absorption of energy by the atoms in the sun's atmosphere.

1.3.3 Rydberg Formula

Used to calculate the wavelengths of a spectral line in hydrogenic species, i.e. H, He$^+$, Li^{2+}, etc.

It generalizes the Balmer series ($n = 2$) for the visible region, the Lyman series ($n = 1$) for the UV region, and the Paschen series ($n = 3$) for the IR region.

$\frac{1}{\lambda} = R_H \left(\frac{1}{n_1{}^2} - \frac{1}{n_2{}^2} \right)$		
	value	unit
λ	wavelength of light emitted	m
R_H	Rydberg constant $= 1.096776 \times 10^7$	m^{-1}
n_1	final electron state (lower energy) $< n_2$	int
n_2	initial electron state (higher energy)	int

2 Energy Levels

In the Bohr model, electrons are allowed only in certain circular orbits around the nucleus, which give rise to the **principal quantum numbers** of n.

Therefore, the energy levels in atomic structures are *quantized*, and the energy levels associated with each electron orbit has a fixed value, hence the term **quantized energy level**.

$E_n = -\frac{2\pi^2 m_e e^4}{n^2 h^2}$		
	value	unit
E_n	energy level	J
m_e	electron mass $= 9.1094 \times 10^{-31}$	kg
e	electron charge $= 1.602 \times 10^{-19}$	C
n	principal quantum number	int
h	Planck's constant $= 6.626 \times 10^{-34}$	$J \cdot sec$

Since the only variable is n, the equation is generalizable:

$E_n \cong -2.18 \times 10^{-18} \left(\frac{1}{n^2} \right)$ J
$E_n \cong -13.6 \left(\frac{1}{n^2} \right)$ eV

The **ground state** of electrons, $n = 1$, has the lowest energy level and the most stable.

The **excited states** have values of $n > 1$.

The energy required to excite an electron from the ground state to an excited state $\Delta E = E_{\text{final}} - E_{\text{initial}}$ can be determined using the E_n formula above.

If $\Delta E > 0$, this is known as an **absorption** (or excitation) process, going from a lower energy state to a higher energy state.

Conversely, if $\Delta E < 0$, this is known as an **emission** (or relaxation) process, going from a higher energy state to a lower energy state, which releases energy.

The **ionization continuum** occurs as $n \to \infty, E_n \to 0$, such that energy levels are no longer quantized.

The **ionization energy** is the minimum energy required to remove one electron from a gaseous atom or molecule.

In the case of hydrogen, $\Delta E = E_\infty - E_1 = +13.6 \text{eV}$.

However, this only applies to 1-electron systems, as we otherwise need to account for electron-electron repulsion, which requires taking into account the nuclear charge, Z^2:

$E_n \cong -2.18 \times 10^{-18} \left(\frac{Z^2}{n^2} \right)$ J
$E_n \cong -13.6 \left(\frac{Z^2}{n^2} \right)$ eV

3 Atomic Structure

Electrons, and all matter, behave like waves, which can undergo constructive and destructive interference.

$\lambda = \frac{h}{mv}$		
	value	unit
λ	De Broglie wavelength	m
h	Planck's constant $= 6.626 \times 10^{-34}$	J/s
m	particle mass	kg
v	particle velocity	m/sec

By **Heisenberg's uncertainty principle**, it is impossible to know the precise position of electrons in an atom.

3.1 Quantum Mechanical Model

A **wave equation** describes the behavior of a specific electron in an atom.

The solution to the wave equation is called a **wave function** (ψ), or an **orbital** — the space boundary where there is a 95% chance of finding the electron.

$|\psi|^2$ is proportional to the *probability density* of an electron being found in 3D space.

The position of an electron could be described using *Cartesian coordinates*, using the wave equation $\psi(x, y, z)$.

Alternatively, using *spherical coordinates*, $\psi(r, \theta, \phi)$:

$\psi(r, \theta, \phi) = \mathbf{R}(r) \times \mathbf{Y}(\theta, \phi)$		
	value	unit
$\mathbf{R}(r)$	**radial wave function**	–
r	distance of the electron from the nucleus	–
$\mathbf{Y}(\theta, \phi)$	**angular wave function**	–
θ	vertical angle perpendicular to the x-y plane	–
ϕ	angle on the x-y plane	–

Radial nodes are 3D *spherical* regions where where no electrons are found. The *radial* component of the wave function passes through 0.

Angular nodes are 2D *planar* or 3D *conical* regions where where no electrons are found. The *angular*

component of the wave function passes through 0.

In orbital diagrams, the regions corresponding to positive values of the wave function are shaded, while the regions corresponding to negative values are not.

3.1.1 Radial Distribution Function (RDF)

$RDF : 4\pi r^2 \cdot \mathbf{R}(r)^2$		
	value	**unit**
$4\pi r^2$	surface area of a sphere	–
$\mathbf{R}(r)$	radial wave function	–
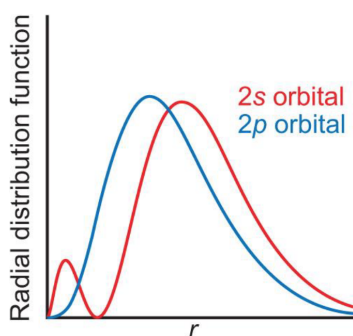
The maximum value of the RDF (i.e. the peak) is the most probable distance of the electron from the nucleus.

Even though the larger peak of the $2p$ orbital is closer than that of the $2s$ orbital, the $2s$ orbital has a higher energy level than the $2p$ orbital due to the **penetration** from the smaller peak.

Therefore, within shells of the same quantum number, orbital energy increases as follows: $s < p < d < f$.

Radial nodes can be counted from the x-intercepts, so from the diagram above, the $2s$ orbital has 1 radial node, while the $2p$ orbital has none.

3.1.2 Quantum Numbers

nl_{m_l}, e.g. $2p_z$		
	value	**range**
n	principal QN	$1, 2, 3, \ldots$
l	magnetic QN	$0, 1, \ldots, n-1$
m_l	orbital angular momentum QN	$-l, \ldots, 0, \ldots, +l$
m_s	electron spin QN	$-\frac{1}{2}, +\frac{1}{2}$

The principal QN relates to the *size* and *energy* of the orbital — higher principal QNs have larger orbitals with higher energy levels.

The magnetic QN relates to the *shape* of the orbital.

The orbital angular momentum QN relates to the *orientation* of the orbital.

number of angular nodes	l
number of radial nodes	$n - l - 1$
number of orbitals	$2l + 1$

3.2 Electronic Configuration

Pauli's exclusion principle: No two electrons in a given atom can have the exact same set of quantum numbers (n, l, m_l, m_s).

$\implies$ An atomic orbital has a maximum of 2 electrons of *opposite* spins.

Aufbau principle: Electrons are always placed in the lowest energy sublevel available.

$\implies$ Fill orbitals starting with the *lowest* energy to get the *ground state*.

Hund's rule: *Degenerate* orbitals are always filled with single electrons before any of them are doubly occupied, and electrons fill separate orbitals with their *spins aligned*.

$\implies$ Spin-aligned electrons have lower interelectronic repulsion, so the system has less energy.

3.2.1 Exceptions: Cr, Cu

These elements have a lower energy level in these configurations than would typically be expected:
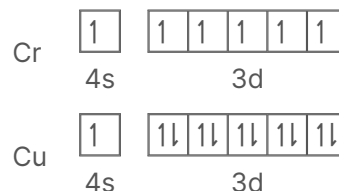
3.3 Trends in Atomic Properties

trend	$\rightarrow$ period	$\downarrow$ group
atomic radius	decreases	increases
ionization energy	increases	decreases
electron affinity	increases	decreases
electronegativity	increases	decreases

Atomic radius is affected by the **effective nuclear charge** (Z_{eff}) of the atom.

Interelectronic repulsion decreases effective nuclear charge through the **shielding effect** and **penetration**.

Electrons in the inner energy levels have a greater shielding effect than electrons of the same energy level — 2s are more effective at shielding than 2p electrons.

$Z_{\text{eff}} = Z - S$		
	value	**unit**
Z	nuclear charge (atomic number)	int
S	shielding constant	real

Ionization energy is the energy required to remove an electron from a gaseous atom or ion.

Electron affinity is the energy released when an electron is added to a gaseous atom to form an anion.

4 Molecular Structure

Any object that is heated to high temperatures *emits electromagnetic radiation*.

The wavelength emitted depends on the temperature, by **Wien's displacement law**:

$\lambda_{\max} = \frac{b}{T}$		
	value	**unit**
$\lambda_{\max}$	peak wavelength	m
b	Wien's displacement constant $\approx 2.898 \times 10^{-3}$	m K
T	absolute temperature	K

Ideal blackbody radiators are objects which are *perfect absorbers and emitters* of radiation.

Absorption of IR radiation causes **molecular vibrations** — *bending* and *stretching*.

Assymetric stretching has a higher vibrational frequency than symmetric stretching due to preservation of momentum.

4.1 Lewis Structure

Covalent bonds are formed when two neighboring atoms *share a pair of electrons*.

Only **valence electrons** — the electrons in the outermost shell — are involved; valence electrons that are *not involved* are known as **lone-pair electrons**.

Lone-pair electrons determine the shape and chemical properties of a molecule.

Stability of compounds occurs when atoms achieve **noble gas electronic configurations**, but there are exceptions to the **octet rule**:

– the **duet rule**: H_2,
– the **incomplete octet**: BF_3, and,
– the **hypervalent molecules**: SF_6, PCl_5.

Drawing Lewis structures:

1. Find the total number of valence electrons.
2. Place the least electronegative atom in the center.
3. Draw a single bond from each surrounding atom to the central atom.
4. Find the remaining number of electrons.
5. Arrange the remaining electrons as lone pairs or multiple bonds to satisfy the octet rule.
6. Assign charges (if any).

4.1.1 Resonance

Resonance structures are different Lewis structures for the *same molecule* — they have the *same relative positions of atoms*, but *different bonding and lone-pair electrons*.

Resonance hybrids has a *real structure* of its *average resonance structures*. They have lower enegy that any of its contributing structure.

4.1.2 Formal Charge

The extent to which an atom has gained or lost an electron while forming covalent bonds.

$FC = V - L - \frac{1}{2}B$		
	value	**unit**
FC	formal charge	int
V	number of valence electrons	int
L	number of lone-pair electrons	int
B	number of bonding electrons	int

The *sum of formal charges* equals the *actual charge* of the molecule.

The most important resonance structure:

– minimizes *formal charges*,
– minimizes *separation of charges*, and,
– places the negative formal charge on the *more electronegative elements*.

4.2 VSEPR Model

The *valence-shell electron-pair repulsion* (VSEPR) model determines the structure around an atom by *minimizing electron-pair repulsions*.

The strength of electron-pair repulsion depends on the pair (in decreasing order of strength):

– lone-pair – lone-pair
– lone-pair – bonding pair
– bonding pair – bonding pair

Determining molecular structure:

1. Draw the *Lewis structure*.
2. Arrange electron groups to *minimize repulsion*.
3. Identify the molecular structure from the *position of atoms*.

4.2.1 Molecular Polarity

The **molecular shape** and **bond polarity** determine *molecular polarity*, which in turn influences its physical and chemical properties.

Electronegativity is the tendency for an atom to attract shared electrons when forming a chemical bond.

$\implies$ **Electron density** is pulled towards the more electronegative atoms.

$\implies$ **Dipole moments** (μ) are generated, but can cancel each other, e.g. CO_2.

$\implies$ The overall dipole moment affects the **molecular polarity**, cf. **cis-trans isomers**.

Change in dipole moment when the molecule vibrates causes **infrared activity**.

no. of electron groups	molecular shape	formula	no. of bonding groups	bond angle
2 (linear)	linear	AX_2	2	180°
3 (trigonal planar)	trigonal planar	AX_3	3	120°
	V-shaped or bent	AX_2E	2	< 120°
4 (tetrahedral)	tetrahedral	AX_4	4	109.5°
	trigonal pyramidal	AX_3E	3	< 109.5°
	V-shaped or bent	AX_2E_2	2	< 109.5°
5 (trigonal bipyramidal)	trigonal bipyramidal	AX_5	5	90° (ax), 120° (eq)
	seesaw	AX_4E	4	< 90° (ax), < 120° (eq)
	T-shaped	AX_3E_2	3	90° (ax)
	linear	AX_2E_3	2	180°
6 (octahedral)	octahedral	AX_6	6	90°
	square pyramidal	AX_5E	5	< 90°
	square planar	AX_4E_2	4	90°