Quantum Chemistry

Dr. Ron Rusay

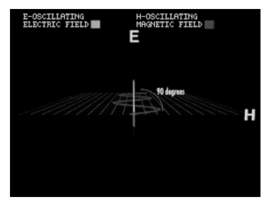
• 7. Atomic Structure and Periodicity

- 7.1 Electromagnetic Radiation
- 7.2 The Nature of Matter
- 7.3 The Atomic Spectrum of Hydrogen
- 7.4 The Bohr Model
- 7.5 The Quantum Mechanical Model of the Atom
- **7.6 Quantum Numbers**
- **7.7 Orbital Shapes and Energies**
- **7.8 Electron Spin and the Pauli Principle**
- **7.9 Polyelectronic Atoms**
- **7.10 The History of the Periodic Table**
- **7.11 The Aufbau Principles and the Periodic Table**
- **7.12 Periodic Trends in Atomic Properties**
- 7.13 The Properties of a Group: The Alkali Metals

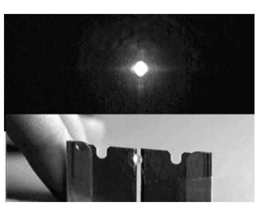
Electromagnetic Radiation

- *Energy that exhibits wave-like behavior.*
- *In a vacuum, electromagnetic energy travels through space at the speed of light.*
- *It is described by the Electromagnetic Spectrum.*

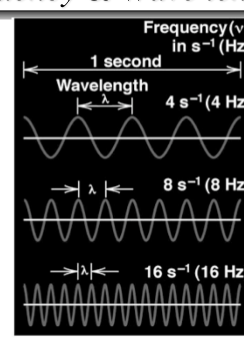
Nature of EM Energy



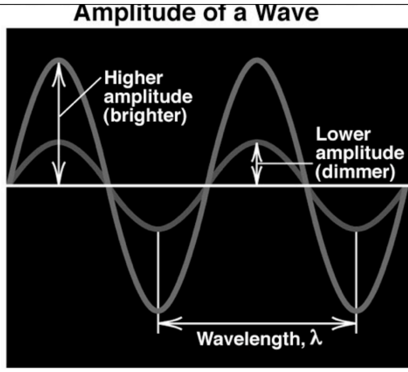
Demonstrating Light's Wave Nature



Frequency & Wave length



Amplitude of a Wave



Waves

http://chemistry.beloit.edu/BlueLight/waves/index.html

- *Waves have 4 primary characteristics:*
- *1. Wavelength: distance between two peaks in a wave.*
- *2. Frequency: number of waves per second that pass a given point in space.*
- *3. Amplitude: the height of the wave.*
- *4. Speed: speed of light is 2.9979×10^8 m/s.*

Waves

http://chemistry.beloit.edu/BlueLight/waves/index.html

- *Focus on 2 of the primary characteristics:*
- *1. **Wavelength:** distance between two peaks in a wave.*
- *2. **Frequency:** number of waves per second that pass a given point in space.*
- *3. Amplitude: the height of the wave.*
- *4. Speed: speed of light is 2.9979×10^8 m/s.*

Wavelength and frequency

$$\nu = c / \lambda$$

- *ν = frequency (s^{-1})*
- *λ = wavelength (m)*
- *c = speed of light (m s^{-1})*

QUESTION

Which of the following frequencies corresponds to light with the longest wavelength?

A. 3.00×10^{13} s^{-1}
B. 4.12×10^{5} s^{-1}
C. 8.50×10^{20} s^{-1}
D. 9.12×10^{12} s^{-1}
E. 3.20×10^{9} s^{-1}

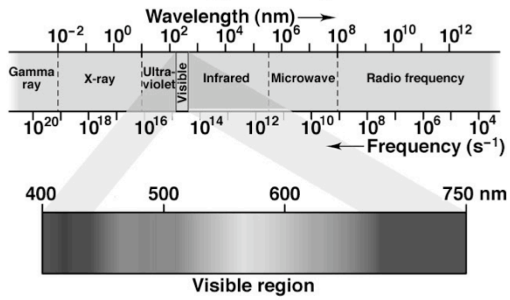
Planck's Constant

Transfer of energy is quantized, and can only occur in discrete units, called quanta.

$$\Delta E = h\nu = \frac{hc}{\lambda}$$

- *ΔE = change in energy, in J*
- *h = Planck's constant, 6.626×10^{-34} J s*
- *ν = frequency, in s^{-1}*
- *λ = wavelength, in m*
- *c = speed of light*

Regions of the Electromagnetic Spectrum



Electromagnetic Energy

ð*EM Spectrum : Chem Connections*

http://chemistry.beloit.edu/Stars/EMSpectrum/index.html

Energy and Mass

ð *Energy has mass*

ð $E = mc^2$

ð *E = energy*

ð *m = mass*

ð *c = speed of light*

Energy and Mass

"Duality"

$$E_{\text{photon}} = \frac{hc}{\lambda}$$

$$m_{\text{photon}} = \frac{h}{\lambda c}$$

(Hence the dual nature of light.)

Wavelength and Mass

de Broglie's Equation

$$\lambda = \frac{h}{mv}$$

ð *λ = wavelength, in m*

ð *h = Planck's constant, 6.626×10^{-34}*

J·s = kg m^2 s^{-1}

ð *m = mass, in kg*

ð *ν = frequency, in s^{-1}*

Atomic Spectrum of Hydrogen

http://chemistry.beloit.edu/BlueLight/pages/color.html

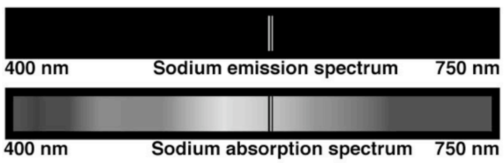
ð *Continuous spectrum: Contains all the wavelengths of light.*

ð *Absorbtion vs.Emission*

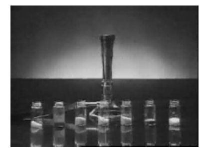
ð *http://chemistry.beloit.edu/BlueLight/pages/elements.html*

ð *Line (discrete) spectrum: Contains only some of the wavelengths of light.*

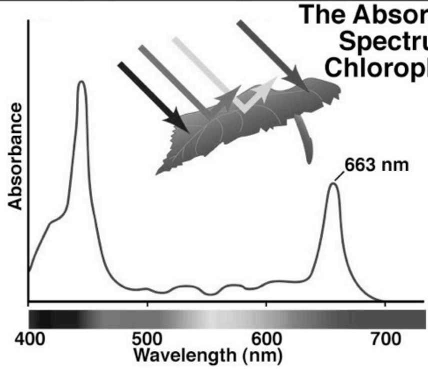
Emission and Absorption Spectra of Sodium Atoms



Emissions: Flame Tests



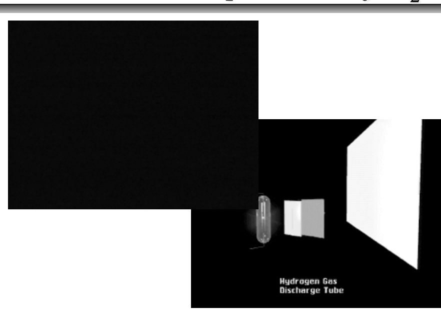
The Absorption Spectrum of Chlorophyll *a*



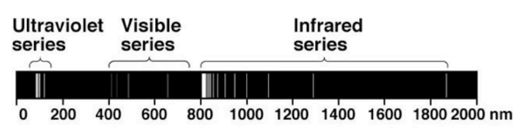
Electromagnetic Energy

- *Visible Light / Color* : ChemConnections
  - *http://chemistry.beloit.edu/Stars/applets/emission/index.html*
- *The Perception of Colors*
  - *http://chemconnections.org/organicchem227/227assign-06.html#vision*

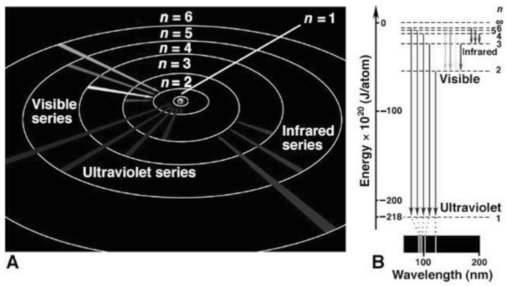
Atomic Emission Spectrum of H_2

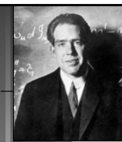


Three Series of Spectral Lines



The Bohr Model Explanation of the Three Series of Spectral Lines





The Bohr Model

"The electron in a hydrogen atom moves around the nucleus only in certain allowed circular orbits."

$$E = -2.178 \times 10^{-18} \text{ J } (z^2 / n^2)$$

- *E = energy of the levels in the H-atom*
- *z = nuclear charge (for H, z = 1)*
- *n = an integer*

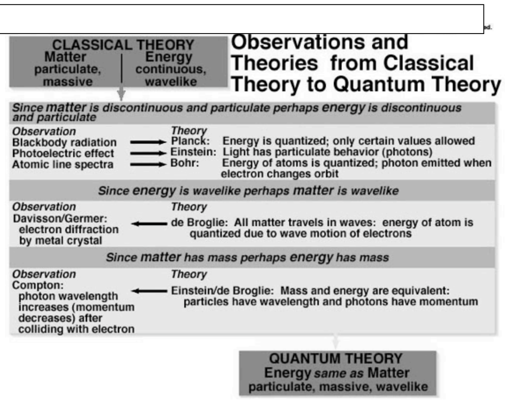
The Bohr Model

- *Ground State: The lowest possible energy state for an atom (n = 1).*

Energy Changes in the Hydrogen Atom

- $\Delta E = E_{final\ state} - E_{initial\ state}$

$$\lambda = \frac{hc}{\Delta E}$$



Heisenberg Uncertainty Principle

- *The more accurately we know a particle's position, the less accurately we can know its momentum or vice versa.*

Quantum Superposition

Schrödinger's Cat: Alive or Dead?

Can something be in two places at the same time?

In quantum microstates, YES.

Science, 272, 1132 (1996)

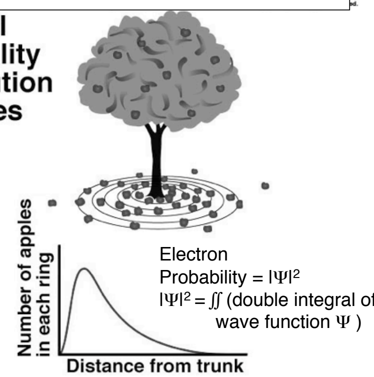
Quantum Numbers (QN) for Electrons

(Solutions for the Schrödinger Equation: $H\Psi = E\Psi$)
Where: Ψ = Wave function

- *1. Principal QN (integer n = 1, 2, 3, . . .) : relates to size and energy of the orbital.*
- *2. Angular Momentum QN (integer l or λ)= 0 to n − 1) : relates to shape of the orbital.*
- *3. Magnetic QN (integer m_l or m_λ = + l to − l) : relates to orientation of the orbital in space relative to other orbitals.*
- *4. Electron Spin QN : ($m_s = +1/2, -1/2$) : relates to the spin state of the electron.*

"ORBITAL":

A Radial Probability Distribution of Apples



Periodic Table Classifications

Electron Configurations & Quantum Numbers

- *Representative Elements (A Groups): s (l=0) and p (l=1) (N, C, Al, Ne, F, O)*
- *Transition Elements: d (l=2) orbitals (Fe, Co, Ni, etc.)*
- *Lanthanide and Actinide Series (inner transition elements): f (l=3) orbitals (Eu, Am, Es)*

Valence Electrons

Valence electrons are the outermost electrons in the highest principal quantum level of an atom. They are found in the s- and p- orbitals and are the bonding electrons.

Atom	Valence Electrons
Ca	2
N	5
Br	7

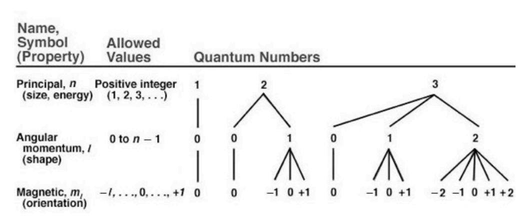
Inner electrons are called core electrons.

QUESTION

If *n* = 2, how many orbitals are possible?

A) 3
B) 4
C) 2
D) 8
E) 6

The Hierarchy of Quantum Numbers for Atomic Orbitals

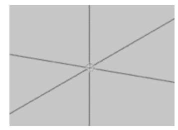


QUESTION

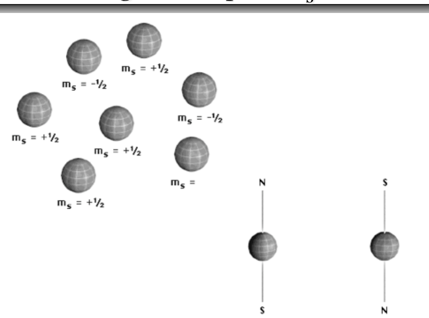
How many *f* orbitals have the value *n* = 3?

A) 0
B) 3
C) 5
D) 7
E) 1

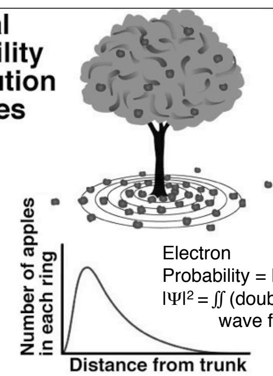
Quantum Numbers : l, m_l
Orbital Shape & Orientation



Magnetic Spin m_s

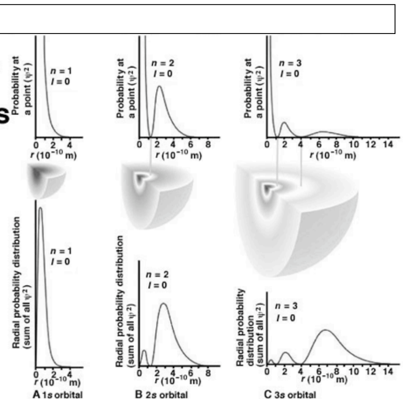


A Radial Probability Distribution of Apples

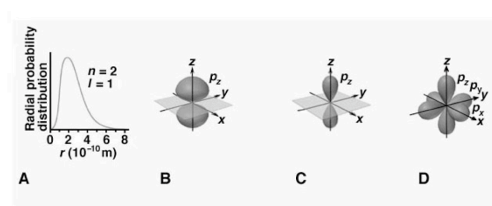


Electron
Probability = |Ψ|²
|Ψ|² = ∬ (double integral of wave function Ψ)

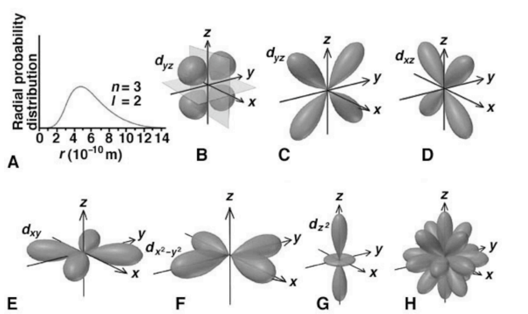
The 1*s*, 2*s*, 3*s* Orbitals



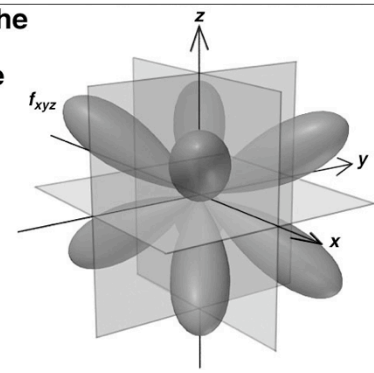
The 2*p* Orbitals



The 3*d* Orbitals



One of the Seven Possible 4*f* Orbitals

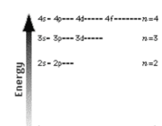


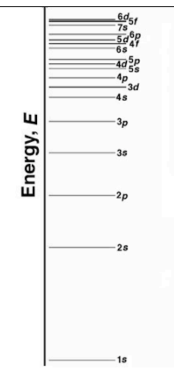
Orbitals

- See:
  http://chemconnections.org/organic/chem226/Labs/atomic-orbitals/1orb-H-jmol.html

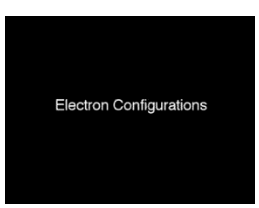
  Identify the unknown orbitals by comparing their shapes to the known orbitals and assign quantum numbers to each orbital.

Order for Filling Energy Sublevels with Electrons

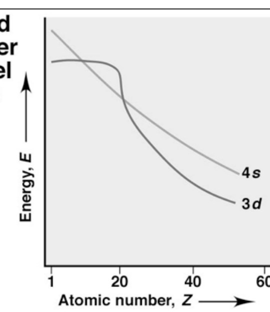




Multi-electron Atoms
Electron Configuration



The Period 4 Crossover in Sublevel Energies



Aufbau Principle

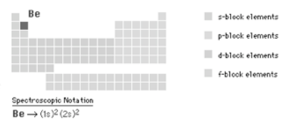
- *As protons are added one by one to the nucleus to build up the elements, electrons are similarly added to these hydrogen-like orbitals.*

Aufbau Principle

Condensed Ground-State Electron Configurations

Period	1A (1)	2A (2)	3A (13)	4A (14)	5A (15)	6A (16)	7A (17)	8A (18)
1	1 **H** $1s^1$							2 **He** $1s^2$
2	3 **Li** [He] $2s^1$	4 **Be** [He] $2s^2$	5 **B** [He] $2s^22p^1$	6 **C** [He] $2s^22p^2$	7 **N** [He] $2s^22p^3$	8 **O** [He] $2s^22^4$	9 **F** [He] $2s^22p^5$	10 **Ne** [He] $2s^22p^6$
3	11 **Na** [Ne] $3s^1$	12 **Mg** [Ne] $3s^2$	13 **Al** [Ne] $3s^23p^1$	14 **Si** [Ne] $3s^23p^2$	15 **P** [Ne] $3s^23p^3$	16 **S** [Ne] $3s^23p^4$	17 **Cl** [Ne] $3s^23p^5$	18 **Ar** [Ne] $3s^23p^6$

Full electron configuration (Spectroscopic notation) --->



QUESTION

The electron configuration for the barium atom is:

A) $1s^22s^22p^63s^23p^63d^{10}4s^2$
B) [Xe] $6s^2$
C) $1s^22s^22p^63s^23p^64s^1$
D) $1s^22s^22p^63s^23p^64s^2$
E) none of these

Pauli Exclusion Principle

- *In a given atom, no two electrons can have the same set of four quantum numbers (**n, l, m_l, m_s**).*
- *Therefore, an orbital can hold only two electrons, and they must have opposite spins.*

QUESTION

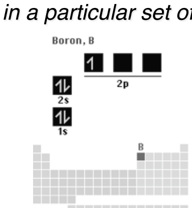
If *l* = 3, how many electrons can be contained in all the possible orbitals?

A) 7
B) 6
C) 14
D) 10
E) 5

Hund's Rule
orbital diagrams

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

Orbital Diagram ->

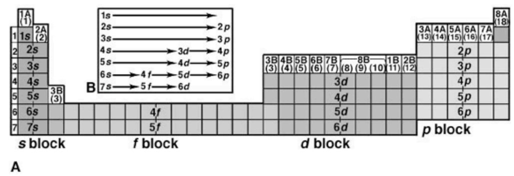


Partial Orbital Diagrams and Electron Configurations*

Atomic Number	Element	Partial Orbital Diagram (4s, 3d, and 4p Sublevels Only) 4s	3d	4p	Full Electron Configuration	Condensed Electron Configuration
19	K	↑			$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^1$	$[Ar]\ 4s^1$
20	Ca	↑↓			$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2$	$[Ar]\ 4s^2$
21	Sc	↑↓	↑		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2 3d^1$	$[Ar]\ 4s^2 3d^1$
22	Ti	↑↓	↑ ↑		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2 3d^2$	$[Ar]\ 4s^2 3d^2$
23	V	↑↓	↑ ↑ ↑		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2 3d^3$	$[Ar]\ 4s^2 3d^3$
24	Cr	↑	↑ ↑ ↑ ↑ ↑		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^1 3d^5$	$[Ar]\ 4s^1 3d^5$
25	Mn	↑↓	↑ ↑ ↑ ↑ ↑		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2 3d^5$	$[Ar]\ 4s^2 3d^5$
26	Fe	↑↓	↑↓ ↑ ↑ ↑ ↑		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2 3d^6$	$[Ar]\ 4s^2 3d^6$
27	Co	↑↓	↑↓ ↑↓ ↑ ↑ ↑		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2 3d^7$	$[Ar]\ 4s^2 3d^7$
28	Ni	↑↓	↑↓ ↑↓ ↑↓ ↑ ↑		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2 3d^8$	$[Ar]\ 4s^2 3d^8$
29	Cu	↑	↑↓ ↑↓ ↑↓ ↑↓ ↑↓		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^1 3d^{10}$	$[Ar]\ 4s^1 3d^{10}$
30	Zn	↑↓	↑↓ ↑↓ ↑↓ ↑↓ ↑↓		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2 3d^{10}$	$[Ar]\ 4s^2 3d^{10}$
31	Ga	↑↓	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑	$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2 3d^{10} 4p^1$	$[Ar]4s^2 3d^{10} 4p^1$
32	Ge	↑↓	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑ ↑	$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2 3d^{10} 4p^2$	$[Ar]4s^2 3d^{10} 4p^2$
33	As	↑↓	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑ ↑ ↑	$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2 3d^{10} 4p^3$	$[Ar]4s^2 3d^{10} 4p^3$
34	Se	↑↓	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓ ↑ ↑	$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2 3d^{10} 4p^4$	$[Ar]4s^2 3d^{10} 4p^4$
35	Br	↑↓	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓ ↑↓ ↑	$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2 3d^{10} 4p^5$	$[Ar]4s^2 3d^{10} 4p^5$
36	Kr	↑↓	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓ ↑↓ ↑↓	$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2 3d^{10} 4p^6$	$[Ar]4s^2 3d^{10} 4p^6$

*Colored type indicates sublevel(s) whose occupancy changes when last electron is added.

Relation Between Orbital Filling and the Periodic Table



Periodic Table Classifications

Electron Configurations

- *Representative Elements (A Groups): fill s and p orbitals (Na, Al, Ne, O)*
- *Transition Elements: fill d orbitals (Fe, Co, Ni)*
- *Lanthanide and Actinide Series (inner transition elements): fill 4f and 5f orbitals (Eu, Am, Es)*

Valence Electrons

Valence electrons are the outermost electrons in the highest principal quantum level of an atom. They are found in the s- and p- orbitals and are the bonding electrons.

Atom	Valence Electrons
Ca	2
N	5
Br	7

Inner electrons are called core electrons.

QUESTION

In which groups do all the elements have the same number of valence electrons?

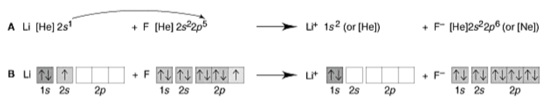
A) P, S, Cl
B) Ag, Cd, Ar
C) Na, Ca, Ba
D) P, As, Se
E) none

QUESTION

Which of these is an isoelectronic series?

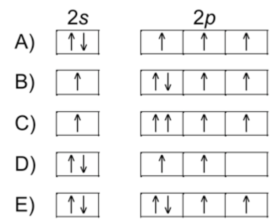
A) Na^+, K^+, Rb^+, Cs^+
B) K^+, Ca^{2+}, Ar, S^{2-}
C) Na^+, Mg^{2+}, S^{2-}, Cl^-
D) Li, Be, B, C
E) None of these

Two ways of showing the formation of lithium fluoride: LiF; [Li^+ and F^-] using electron configurations & diagrams



QUESTION

Nitrogen has 5 valence electrons. Consider the following electron arrangements.



Which represents the ground state for the N– ion?

Paramagnetism & Diamagnetism

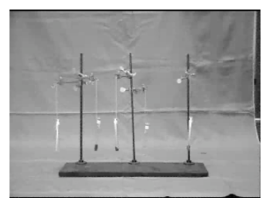
Electron Configuration & Magnetic Properties

- *Diamagnetic materials have all electrons paired and are not attracted to a magnetic field.*
- *Paramagnetic materials have unpaired electrons and the magnetic attraction (magnetism) is generally proportional to the number of unpaired electrons. (Note: not all metals follow this rule.)*

Electron Diagrams

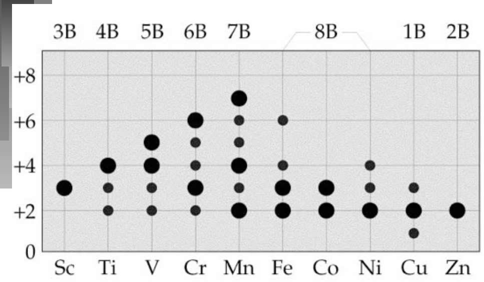
Magnetic Properties

#1 = $H_2O(l)$ # 2 = $Fe_2O_3(s)$ # 3 = FeO(s) #4= Fe(s)

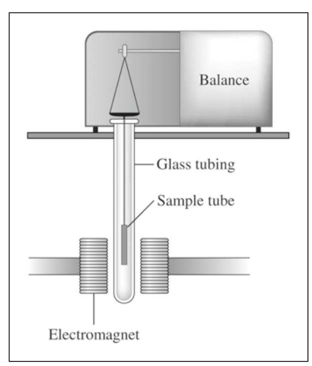


Transition Metal Ions (B Groups)

Oxidation Numbers (States)

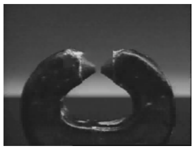


Apparatus Used to Measure Paramagnetism NOTE: O_2 is paramagnetic, N_2 is not!



Electron Diagrams

Magnetic Properties



- *Ground state configurations of nitrogen (N) and oxygen (O) have 3 and 2 unpaired electrons in their electron diagrams respectively, what can be going on in the video?*
- *Ground state diagrams do work very well for the Transition metals but not many others because of bonding, which forms pairs of electrons. (molecular orbitals vs. atomic orbitals).Eg. water, nitrogen and oxygen.*

Summary: Information from the Periodic Table

- *1. Can obtain Group A valence electron configurations*
- *2. Can determine individual electron configurations.*

This information can be used to:

- *a. Predict the physical properties and general chemical behavior of the elements.*
- *b. Identify metals and nonmetals.*