Trends in the Periodic Table

Reading: Gray: (2-2) to (2-4) and (2-9)
OGN: (3.1), (15.8) and (15.9)
Now We Can Understand

- Arrangement of the Periodic Table of Elements
- Trends in Atomic Size
- Trends in Ionization Energy
- Trends in Electron Affinity
- Trends in Electronegativity
- Various Types of Chemical Bonds
- Combining Ratios of Oxides and Hydrides
- Shapes of Molecules
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Invented the periodic table in 1869. Also in that year, he published his book, "Principles of Chemistry." His book compared the atomic weights and the properties of elements that were not known back then.

1906: One vote away from winning a Nobel Prize
Died in 1907
In 1875, Lothar Meyer deduces a periodic trend
Energy of One Electron in a H atom

* $E(\text{eV})$

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<td>9</td>
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<td>4p</td>
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* $E = \frac{-k}{n^2}$

where $k = 13.6 \text{ eV}$;

$n$ is the principal quantum number
None of the e\textsuperscript{-} eclipsed: $Z_{\text{eff}} = Z$

One e\textsuperscript{-} eclipsed: $Z_{\text{eff}} = Z - 1$

On Average, $Z_{\text{eff}} < Z$
How Much Less $Z_{\text{eff}} < Z$ Determines Atomic Properties
An electron in the 2p orbital penetrates somewhat into the 1s orbital.

\[ r^2R^2 = \text{probability of finding an electron on the sphere of radius } r \]
But a 2s electron penetrates the 1s orbital better than a 2p electron.
A 3s electron penetrates the 1s orbital better than a 3p electron.
A 4s electron penetrates the 1s orbital better than a 4p electron
Another View of 2s vs 2p Shielding

2s Penetrates More into 1s Than Does 2p
2s is Therefore Lower in E Than 2p
due to shielding, orbitals with the same principal quantum number (n) do NOT have the same energies
Mnemonic for Filling Order

hence the filling order is:

1s, 2s, 2p, 3s, 3p, 4s, 3d, etc.
Valence Electrons:
electrons in the outermost shell (in other words, the set of electrons with highest principal quantum number)

1. H (1s)$^1$
2. He (1s)$^2$
3. Li (1s)$^2$(2s)$^1$
4. Be (1s)$^2$(2s)$^2$
5. B (1s)$^2$(2s)$^2$(2p)$^1$
6. C (1s)$^2$(2s)$^2$(2p)$^2$
7. N (1s)$^2$(2s)$^2$(2p)$^3$
8. O (1s)$^2$(2s)$^2$(2p)$^4$
9. F (1s)$^2$(2s)$^2$(2p)$^5$
10. Ne (1s)$^2$(2s)$^2$(2p)$^6$
e t c.
Orbital Filling Energies

Example:

lowest energy for 3 electrons in $p$ orbital

\[
\uparrow \quad \uparrow \quad \uparrow
\]

energy increases when a second electron is put in same orbital

\[
\uparrow \downarrow \quad \uparrow \
\]

energy also increases when spins are mixed in orbitals

\[
\uparrow \quad \uparrow \quad \downarrow
\]
Organization of Periodic Chart

1s
2s
3s
4s
5s
6s
7s

1s
2p
3p
4p
5p
6p

4f
5f
### Exceptions to Filling Order

|    | H    | Li   | Be   | Mg   | Ca   | Sr   | Ba   | Ra   | He   | Ne   | Ar   | Kr   | Xe   | Rn   |\n|----|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| 1s | 2s   | 3s   | 4s   |      |      |      |      |      |      |      |      |      |      |      |
| 2p |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
| 3d |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
| 4p |      |      |      |      |      |      |      |      |      |      |      |      |      |      |

**Exceptions occur because electrons don’t like to pair up in orbitals; so the highlighted atoms have lower energy.**

- **23. V** \((4s)^2(3d)^3\)
- **24. Cr** \((4s)^1(3d)^5\)
- **25. Mn** \((4s)^2(3d)^5\)
- **40. Zr** \((5s)^2(4d)^2\)
- **41. Nb** \((5s)^1(4d)^4\)
- **42. Mo** \((5s)^1(4d)^5\)
Hydrogen: From Greek: Hydro-genes: “Water forming”

- Alkali metals
- Alkali earths
- Transition metals
- Inert or Noble gases
- Halogens
- Lanthanides
- Actinides
Iodine: violet crystals
From Greek “iodes”: “violet”

Alkali metals

Transition metals

Alkali earths

Halogenes

Inert or Noble gases

Lanthanides

Actinides
Carbon
From Latin “carbo”: “charcoal”

Alkali metals

Be Li Na K Rb Cs Fr

Alkali earths

Be Mg Ca Sr Ba Ra

Transition metals

Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr

Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe

La Hf Ta W Re Os Ir Pt Au Hg Ti Pb Bi Po At Rn

Halogens

B C N O F Ne Br Kr

Al S i P S Cl Ar

Ga Ge As Se Br Kr

In Sn Sb Te I Xe

TL Pb Bi Po At Rn

Inert or Noble gases

He Ne Ar Kr Xe Rn

Lanthanides

Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr

Actinides
Iron: Fe
From Latin “iron”: “ferrum”

- Alkali metals
  - H
  - Li
  - Na
  - K
  - Rb
  - Cs
  - Fr
- Alkali earths
  - Be
  - Mg
  - Ca
  - Sr
  - Ba
- Transition metals
  - Sc
  - Ti
  - V
  - Cr
  - Mn
  - Fe
  - Co
  - Ni
  - Cu
  - Zn
  - Ga
  - Ge
  - As
  - Se
  - Br
  - Kr
  - Y
  - Zr
  - Nb
  - Mo
  - Tc
  - Ru
  - Rh
  - Pd
  - Ag
  - Cd
  - In
  - Sn
  - Sb
  - Te
  - I
  - Xe
- Halogens
  - B
  - C
  - N
  - O
  - F
  - Ne
  - Al
  - Si
  - P
  - S
  - Cl
  - Ar
- Inert or Noble gases
  - He
  - Ne
  - Ar
  - Kr
  - Xe
  - Rn
- Lanthanides
  - Ce
  - Pr
  - Nd
  - Pm
  - Sm
  - Eu
  - Gd
  - Tb
  - Dy
  - Ho
  - Er
  - Tm
  - Yb
  - Lu
  - Th
  - Pa
  - U
  - Np
  - Pu
  - Am
  - Cm
  - Bk
  - Cf
  - Es
  - Fm
  - Md
  - No
  - Lr
Gold: Au
From Latin “aurum”: “shining dawn”
Lead: Pb
From Latin “plumbum”: “heavy”
Cobalt: Co

From German “kobold”: “goblin or evil spirits”

Unwanted metal in what were thought to be copper ores

- Alkali metals
- Alkali earths
- Transition metals
- Halogens
- Inert or Noble gases
- Lanthanides
- Actinides
Effective Nuclear Charge

\( (Z_{\text{eff}} = 1.0) \)

\( (Z_{\text{eff}} \approx 0.7) \)

\( (Z_{\text{eff}} = 1.0) \)

\( (Z_{\text{eff}} \approx 1.8) \)
Atomic Size and Ionization Energy

- **H (Neutrons)**
  - Electron: $e^-$
  - Protons: $p$
  - Effective Nuclear Charge: $Z_{\text{eff}} = 1.0$

- **H$^-$ (Neutrons)**
  - Electron: $e^-$
  - Protons: $p$
  - Effective Nuclear Charge: $Z_{\text{eff}} \approx 0.7$

- **H (Neutrons)**
  - Electron: $e^-$
  - Protons: $p$
  - Effective Nuclear Charge: $Z_{\text{eff}} = 1.0$

- **He (Neutrons)**
  - Electron: $e^-$
  - Protons: $p$
  - Effective Nuclear Charge: $Z_{\text{eff}} \approx 1.8$

- **Smaller**
- **Bigger**
Trends in $Z_{\text{eff}}$

- **$\text{H}$** ($Z_{\text{eff}} = 1.0$)
- **$\text{He}$** ($Z_{\text{eff}} \approx 1.8$)
- **$\text{Li}$** ($Z_{\text{eff}} \approx 1.2$ in $n=2$)
- **$\text{Be}$** ($Z_{\text{eff}} \approx 2.0$ in $n=2$)
Solid-State Molar Volumes (3D)
Atomic Radius: A Closer Look

Closed 2s shell; r **Smaller** than expected

2p more fully screened than 2s r **Bigger** than Expected

(relative atomic sizes)

(expected size)

2p:

2s:

1s:
Exceptions to Atomic Radius Trend

Half-filled p Shell
r Smaller Than Expected

Extra Repulsion in 2p set
r Bigger Than Expected

(relative atomic sizes)

(expected sizes)
Ionization Energies

Larger Smaller Atoms

Smaller $r$ → Higher I.E.

$H$ ($Z_{eff} = 1.0$)  $He$ ($Z_{eff} \approx 1.8$)

Smaller Atoms $\rightarrow$ Harder to Remove Electrons
First Ionization Energy (3D)

1st IE (kJ/mol)
Smaller $r$ = Higher I.E.

Ionization Energy (kJ/mol)

Atomic Number

Smaller $r$ = Higher I.E.

2p vs 2s shielding

2p pairing penalty
Radius decreases for isoelectronic atoms as Positive charge increases ( ).

Discontinuity at K\(^+\) due to d-orbitals (increased Z\(_{\text{eff}}\))
Lanthanide Contraction

All are 5s²5p⁶4fⁿ⁻¹

Responsible for many features of TM’s that follow
Lanthanides in periodic table
Electron Affinity

Energy Released By Addition of an Electron to the Element

\[
\text{H} + e^- \rightarrow \text{H}^- \\
E = -77 \text{ kJ/mol} \\
\text{E.A.} = 77 \text{ kJ/mol}
\]

By Definition, E.A is **Positive** when Energy is **Released** (Opposite the thermodynamic definition!)
Electron Affinity vs. Ionization Energy

\[ (+) \text{ Electron Affinity of Element X} \]
\[ (+) \text{ Ionization Energy of Anion X}^{-} \]
Electron Affinity (3D)

Note: Black elements have negative EA’s
Electron Affinity vs. Ionization Energy

Electron Affinity
• Can be either + or - in sign
• No atom has a positive 2\textsuperscript{nd} E.A.

Ionization Energy
• Always Positive
• 2\textsuperscript{nd} I.E.s are always > 1\textsuperscript{st} I.E.’s
Electronegativity

\[ \text{EN} = \frac{\text{I.E.} + \text{E.A.}}{2} \]

Electronegativity Generally Follows I.E. Trend

Larger
• In a bond, the distribution of electrons is determined by how much each atom pulls on its own as well as the other atom’s electrons. So electronegativity = I.E. + E.A.

Example:

• Na has low E.A. and I.E.
• Cl has high E.A. and I.E.
• Electronegativity = (I.E. + E.A.)/2
  
  Cl is more electronegative than Na.
Some Representative Electronegativities

Electronegativities:

Be = 1.6  
Na = 0.9  
Fr = 0.7  
C = 2.6  
As = 2.2  
F = 4.0

• Fluorine has the highest electronegativity, Francium has the lowest E.N.
Types of Chemical Bonds

Ionic Bonding

\[ \text{Na}^- + \text{Cl}^- \rightarrow [\text{Na}]^+ [\text{Cl}]^- \]

Na has Low I.E., low E.A. \(\Rightarrow\) Lower EN; loses e⁻
Cl has High I.E., high E.A. \(\Rightarrow\) Higher EN; gains e⁻

\[ \text{Li}^- + \text{H}^- \rightarrow [\text{Li}]^+ [\text{H}]^- \]

Li has Low I.E., low E.A. \(\Rightarrow\) Lower EN; loses e⁻
H has High I.E., high E.A. \(\Rightarrow\) Higher EN; gains e⁻
Types of Chemical Bonds

**Covalent Bonding**

\[
\begin{align*}
\text{Cl}^- + \text{Cl}^- & \rightarrow \text{Cl}^:\text{Cl} = \text{Cl—Cl} \\
\text{H}^- + \text{Br}^- & \rightarrow \text{H}^:\text{Br} = \text{H—Br}
\end{align*}
\]

Electrons Shared $\approx$ Equally

**Hydrogen Bonding:** Cl—H···OH$_2$

**Van der Waals Bonding:** Ar···HCl
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- Trends in Electron Affinity
- Trends in Electronegativity
- Various Types of Chemical Bonds
- Combining Ratios of Oxides and Hydrides
- Shapes of Molecules
Periodic Trends in Bonding

Stoichiometry of Binary Hydrides

LiH, BeH₂, NaH, MgH₂

BH₃, CH₄, NH₃, H₂O, HF, AlH₃, SiH₄, PH₃, H₂S, HCl

H⁻ ⟷ H⁺
Periodic Trends in Bonding

Stoichiometry of Binary Oxides

Li₂O  BeO  MgO
Na₂O  H₂O  O₂

B₂O₃  CO₂  N₂O₅  O₂  OF₂
Al₂O₃  SiO₂  P₂O₅  SO₃  OCl₂

HₐXₐ for Hydrides; Oₐ/2Xₐ (Usually) for Oxides
Al normally inert due to formation of tough surface coating of $\text{Al}_2\text{O}_3$
Al metal burns in air and if hot enough, will form $\text{Al}_2\text{O}_3$ continuously from $\text{H}_2\text{O}$
Basic oxides have pushed too much electron density onto O, and it loses it by reacting with H₂O (liberating OH⁻).

Acidic oxides have less electron density than they can accommodate, and so grab more O from H₂O (liberating H⁺).
Acid/Base Properties of Oxides

Acidity increases going up and to right
Trends in the Periodic Table

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OGN: (3.1), (15.8) and (15.9)