

UNIT 08: Periodicity

Periodicity

The chemical and physical properties of the elements and their compounds are very dependent upon their outermost (valence) electron configurations. When the elements are arranged in the periodic table in order of ascending atomic number, a regular change in the outermost electronic configuration is observed. In turn, a regular variation of properties is also observed. This called the *periodic law* or *periodicity*.

Thus, as a period is traversed, certain regular repeatable patterns can be observed which lead to the ability to make predictions about the unknown properties of elements and their compounds.

Additionally, elements that are in the same group have similar outer electronic configurations and often behave in a similar manner to one another.

These facts lead to the observation of gradual changes in the physical and chemical properties of the elements and their compounds when moving about the periodic table. In order to illustrate these changes we will consider a number of trends and patterns observable in the periodic table.

**It should be noted that whilst several very useful generalizations and patterns can be discerned, there are also several exceptions and anomalies which need to be appreciated.*

	GROUP NUMBERS**																	
Modern IUPAC	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Headed by Element	H/Li	Be	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	B	C	N	O	F	He
Old IUPAC (European)	IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIIIA	VIIIA	VIIIA	IB	IIB	IIIB	IVB	VB	VIB	VIIIB	VIIIB
CAS (American)	IA	IIA	IIIB	IVB	VB	VIB	VIIIB	VIIIB	VIIIB	VIIIB	IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA

***A note about group numbers. Some confusion over group numbers has arisen because over time, at least four different systems have been used. The modern IUPAC system will be used here.*

The electronic configurations of metals & non-metals and the ions they form

Noble gases (group 18)

All atoms of the noble gases have their outer s and p orbitals filled. We will see later that these atoms require very large amounts of energy to form ions, so much in fact, that they are difficult to alter chemically and as such are considered relatively inert (unreactive), and do not tend to form ions or many compounds

Alkali metals (group 1) & Alkaline Earth metals (group 2)

Group 1 atoms have an electronic structure [noble gas] s^1 . This means that they tend to lose the s electron when they form an ion, leaving behind an inert noble gas type structure. This explains why Group 1 elements tend to only form 1+ ions.

Group 2 atoms have an electronic structure [noble gas] s^2 . This means that they tend to lose the two s electrons when they form an ion, leaving behind an inert noble gas type structure. This explains why Group 2 elements tend to only form 2+ ions.

A similar argument can be applied to group 13 atoms and their simple ions.

Groups 16 & 17 (Chalcogens & Halogens) non-metals

Group 16 atoms have an electronic structure [noble gas] $s^2 p^4$. This means that they tend to gain two, p electrons when they form an ion, in order to reach an inert noble gas type structure with a charge of 2-. Group 17 atoms have an electronic structure [noble gas] $s^2 p^5$. This means that they tend to gain one, p electron when they form an ion, in order to reach an inert noble gas type structure with a charge of 1-.

Ionization energy

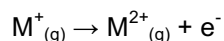
When metals and non-metals undergo chemical reactions they are generally trying to achieve a more stable state. As we have seen above, they do this by either losing electrons (metals) or gaining electrons (non-metals). In order to make some quantitative sense of this we need to consider patterns in ionization energy.

First ionization energy

First ionization energy is formally defined as the energy required to remove one mole of electrons, from one mole of gaseous atoms, to produce one mole of gaseous ions.



The second ionization energy is defined as the energy change accompanying;



Ionization energies are often measured in units of kJ mol^{-1} . They have positive values indicating that energy must be “put in” in order to remove electrons. A positive energy change is described as being *endothermic*.

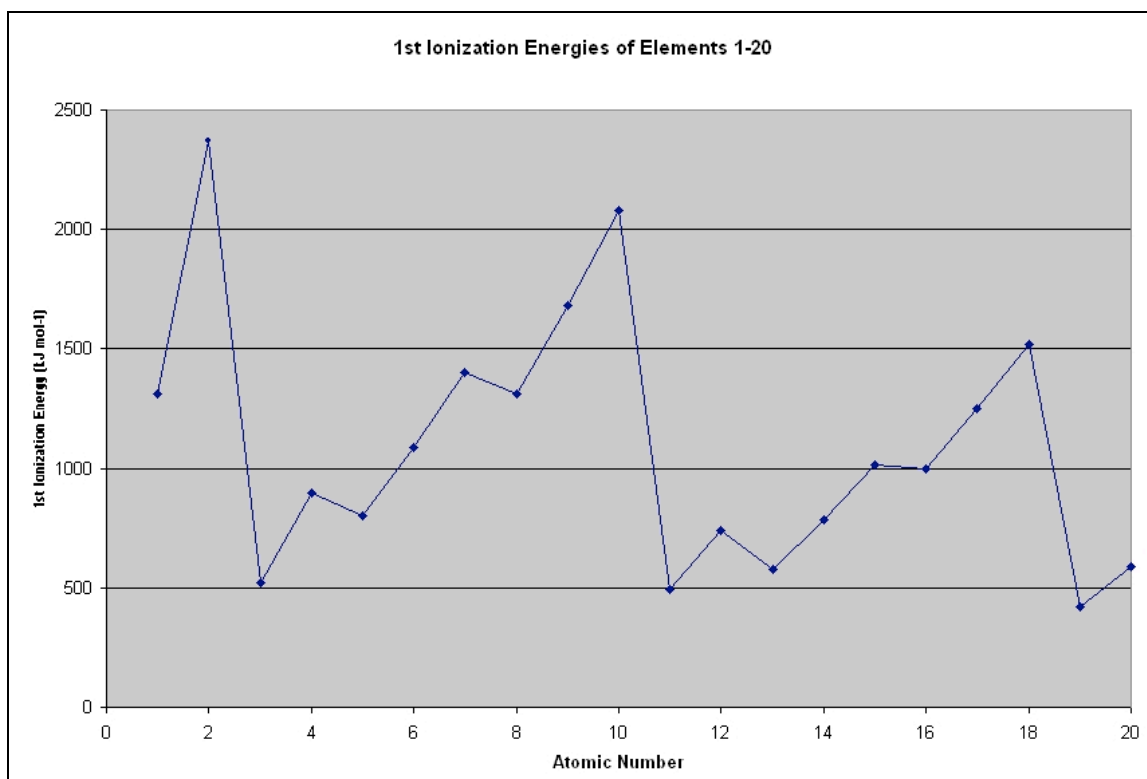
The magnitude of the ionization energy is determined by the attraction of the positive nucleus for the negative electrons that are being removed (essentially Coulomb's law) and the force of attraction is dependent upon two factors;

1. The nuclear charge (how many protons are present).
2. The shielding effect of the inner electrons (the extent to which inner electrons protect the outer electrons from the nuclear charge). Shielding is related to the distance of the electrons from the nucleus; the greater the distance the shell is from the nuclear charge, the smaller the attraction.

As a period is traversed from left to right, the first ionization energy of the elements will steadily *increase*. This is because the nuclear charge increases (greater positive charge, extra protons) but the electrons are being removed from the same quantum shell, experiencing no extra distance from the nucleus, and are therefore held more strongly.

As a group is descended the first ionization energy of the elements will *decrease*. This is because although there is again an increase in nuclear charge, the valence electrons are in new shells, further away from the nucleus, experience more shielding due to the core electrons, and are therefore held less strongly. Increased distance, rather than the increasing number of protons, is found to be the more important factor.

Consider the plot of first ionization energy versus atomic number, below.



The slightly odd behavior of boron & aluminum and oxygen & sulfur can be explained thus;

Boron & aluminum: Elements in group 13 have the valence (outer) electronic configuration $s^2 p^1$. The outer p^1 electron is in a p orbital that has a slightly higher energy than the corresponding s orbital (from which the previous elements first electron is removed) and experiences slightly more shielding from the full s^2 sub-shell in addition to the inner complete shells. As a result, these elements exhibit slightly lower first ionization energies than would otherwise be expected.

Oxygen & sulfur: Elements in group 16 have the valence (outer) electronic configuration $s^2 p^4$. The electron that is being removed in an ionization process is paired with another in one of the p orbitals and as a result experiences repulsion. This repulsion means it is more easily lost, and as a result these elements exhibit slightly lower first ionization energies than would otherwise be expected.

Successive ionization energies in a single element

It is possible to remove more than one electron from a single atom and it is found that removing a subsequent electron is progressively more difficult. This is because once an electron has been removed, the remaining electrons experience a reduced mutual repulsion. They move slightly closer to the nucleus and as a result become slightly more attracted to the nucleus. This makes them more difficult to remove and each subsequent ionization energy increases. In addition, once one electron has been lost from the atom, subsequent electrons are being removed from a now, positive species.

As we saw with magnesium above, this effect is even more pronounced when moving to an inner shell closer to the nucleus, and can be used to make predictions about the group a particular element is found. Consider the following data for sodium.

Successive IONIZATION ENERGIES of Na in kJ mol^{-1}

1 st	2 nd	3 rd	4 th	5 th	6 th	7 th	8 th	9 th	10 th	11 th
496	4562	6912	9543	13353	16610	20114	25490	28933	141360	159074

The large "jump" in the data between the 1st and 2nd ionization energies shows that it is relatively easy to remove the 1st electron but extremely difficult to remove the 2nd (the ionization energy increases approximately times 10). It can be reasonably assumed that the 2nd electron is in a new shell, is closer to the nucleus, is more difficult to remove (higher ionization energy) and therefore the 1st electron was in the valence shell, on its' own, hence group 1. There is another large "jump" between the 9th and 10th ionization energies. This indicates the start of the inner (1st) shell.

Task 8a

1. Give a brief but complete explanation of the changes in ionization energy as the following transitions in the periodic table are made.

- Passing from magnesium to strontium
- Passing from sodium to argon

2. Consider the following successive ionization energies (kJ mol^{-1}) of elements X & Y.

	1 st	2 nd	3 rd	4 th	5 th	6 th
X	513	7298	11814	-	-	-
Y	737	1450	7732	10540	13360	17995

- (a) In which group is X likely to be found?
 (b) In which group is Y likely to be found?
 (c) There are only three ionization energies listed for X. Suggest a reason.
3. Define the term 'first ionization energy' and state the two factors which influence its magnitude.
4. Consider the following successive ionization energies (kJ mol^{-1}) of element R.

1 st	2 nd	3 rd	4 th	5 th	6 th
737	1450	7732	10540	13360	17995

- (a) What is the most likely formula of R's oxide?
 (b) Why is the value for the 2nd ionization energy greater than the 1st?
5. Why is there a general increase in ionization energy on passing from Li to Ne?
6. Explain why helium has the largest ionization energy of all the noble gases.

Atomic and ionic size

Variation of atomic size across a period

As a period is traversed from left to right, the atomic size *decreases*. This is because the nuclear charge increases (greater positive charge, extra protons) and the subsequent electrons enter the same shell, experiencing no extra shielding from inner electrons and are therefore attracted (pulled in) more tightly.

Variation of atomic size down a group

As a group is descended the atomic size *increases*. This is because that although there is again an increase in nuclear charge (greater positive charge, extra protons), the valence electrons enter new

shells, further away from the nucleus. As a result, the atomic size increases since the greater the number of shells occupied in an atom, the larger the atom.

Cation (positive ion) size

When an atom loses electrons to form a cation, the remaining electrons will experience less mutual repulsion and as a result they are drawn closer than they were in the atom, and the cation is smaller than the parent atom. It is also true to say that when a cation is formed, an atom often loses a complete valence shell of electrons which has the effect of decreasing the size of the cationic species compared to the parent atom.

Anion (negative ion) size

When an atom gains electrons to form an anion the extra electrons that have been added to form the anion tend to repel one another. This has the effect of slightly enlarging the new anionic species making the anion larger than the corresponding atom.

Task 8b

Arrange the following species in order of increasing size.

Ar , K^+ , Ca^{2+} , S^{2-} , Cl

Electronegativity

Electronegativity is defined as the ability of an atom within a covalent bond, to attract electrons to itself. Non-metal elements in the top right of the periodic table tend to want to attract electrons more than metal atoms, since in order to achieve full, valence s and p sub-shells, the non-metals need to acquire electrons. Smaller non-metals tend to have greater attractions for electrons, since the negative electrons can get closer to the positive nuclei and feel a stronger Coulombic attraction. Given that the noble gases already have filled s and p sub-shells and are as such have no need to attract electrons, the most electronegative elements are the halogens, and the most electronegative of the halogens is fluorine. Metal elements that want to lose electrons in order to achieve filled s and p valence sub-shells have very low electronegativity's.

In summary, excluding the noble gases, electronegativity increases across a period, and decreases down a group.

Periodic properties of the elements and their compounds

Physical properties within a group

The value of a property tends to change uniformly from top to bottom in a group. For example, consider some of the physical properties of the elements of group 17, the halogens

	Melting point in Kelvin	Boiling point in Kelvin	State at RT	Color
Fluorine	53	85	Gas	Pale green
Chlorine	172	239	Gas	Yellow/green
Bromine	266	332	Liquid	Brown/orange
Iodine	387	458	Solid	Purple/black

These properties illustrate that there are gradual changes within the group.

Physical properties across a period

Periodic physical properties are less easy to predict with certainty, but sometimes the value of a property may reach a peak within a period and then reverse the trend. For example, consider the melting point of the third period elements. Here the melting points rise to a peak at silicon before falling back to similar smaller values as at the beginning of the period.

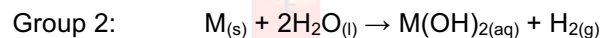
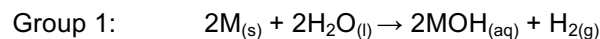
Element	Melting point in Kelvin
Na	371
Mg	922
Al	933
Si	1683
P	863
S	393
Cl	172
Ar	84

Chemical properties within a group

For example, consider the reactivity of group 1 and group 2 metals. We have seen how when a group 1 or a group 2 metal reacts it tends to lose electrons to form a positive ion. We have also seen how ionization energy decreases down a group. Putting these observations together it would be reasonable to assume that on passing down groups 1 and 2, that as the ionization energies decrease, the reactivity would increase. This is found to be true*.

Additionally it would seem reasonable to assume that when comparing group 1 and group 2 metals in the same period that the group 1 metal would be more reactive. This is because ionization energy increases across a period and the fact that the group 2 metal must lose two electrons as opposed to one. Again this is found to be true*.

The group 1 and 2 metals reaction with water can illustrate this reactivity.



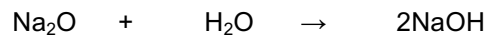
From the assumptions above, we can predict with some certainty that, for example, potassium (group 1) would react more vigorously than calcium (group 2) in the same period. This is also found to be true. We might also predict that beryllium and magnesium (at the top of group 2) would react less vigorously than barium (further down the group). This is found to be true and illustrated by the fact that Be and Mg will not react with cold water at all, but Ba shows a vigorous reaction.

**It should be carefully noted that all of this is complicated by the fact that ionization energy is an isolated process that involves the removal of an electron from a gaseous species, e.g., $Li_{(g)} \rightarrow Li^+_{(g)} + e^-$, and that electrode potentials are a similar, but not identical process where aqueous ions are involved, e.g., $Li_{(s)} \rightarrow Li^+_{(aq)} + e^-$. As such, it is not possible to easily compare ionization energy with reactivity in this context.*

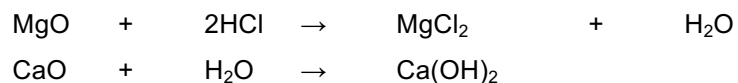
Chemical properties across a period

For example, consider the acid/base behavior of some oxides in periods 2, 3 and 4.

Sodium oxide. (Basic. Oxide ions pick up H^+ from, for example water to produce a base)

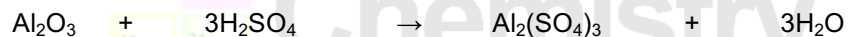


Magnesium oxide & calcium oxide. (Basic. Oxide ions pick up H^+ from, for example from acids to produce a salt and water, or from water to produce a base)



Aluminum oxide. (Shows both acidic and basic properties - AMPHOTERIC)

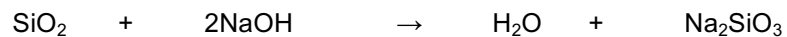
Basic character (react with acid):



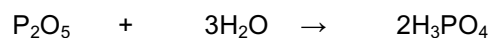
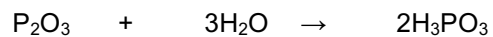
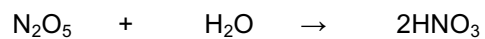
Acidic character (react with base):



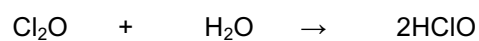
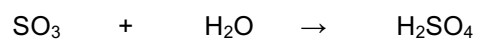
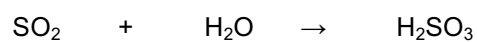
Silicon dioxide. (Insoluble due to its giant macromolecular structure but acts as an acid by reacting with strong solutions of base under forcing conditions)



Other oxides. (Acidic. React with water to produce acids)



(N.B. P_2O_3 and P_2O_5 are sometimes written as P_4O_6 and P_4O_{10} respectively)



In summary, the metal elements on the left of the period (for example sodium and magnesium) form basic oxides. On the right hand side of the period, the oxides of non-metals are acidic. The point of change in the period occurs around group 13 (for example, aluminum), which can act amphotERICALLY.