

Periodic Trends in the Elements

In this section we shall consider the trends in the properties of the elements and their compounds in the second and the third period of the periodic table.

Table I: Some properties of the elements of the second period

Element /property	Li	Be	B	C	N	O	F	Ne
mp (°C)	181	1278	2300	3527	-210	-248	-220	-246
bp (°C)	1347	2970	3658	4827	-196	-183	-188	-246
electrical conductivity	good	good	fair	fair	none	none	none	none
atomic radius (nm)	0.152	0.113	0.088	0.077	0.070	0.066	0.058	0.160
first ionisation energy (kJmol ⁻¹)	513	899	801	1086	1402	1314	1681	2081
electronegativity	0.98	1.57	2.04	2.55	3.04	3.44	3.98	—
bonding	metallic	metallic	covalent macro-molecular	covalent macro-molecular	covalent molecular	covalent molecular	covalent molecular	no bonding atomic

Table II: Some properties of the elements of the third period

Use the Data Book to fill in the table below for the elements of the third period.

Element /property	Na	Mg	Al	Si	P	S	Cl	Ar
mp (°C)								
bp (°C)								
electrical conductivity								
atomic radius (nm)								
first ionisation energy (kJmol ⁻¹)								
electronegativity								

Appearance

The elements on the left of the periodic table have low values of ionisation energy and electronegativity, and so they show the properties associated with metallic bonding: they are shiny and conduct electricity.

In the middle of the periodic table, elements that are semiconductors, show a dull shine and are poor conductors of electricity.

The elements at the right of the periodic table are dull and are such poor conductors of electricity that they are used as insulators.

Melting and boiling points

Metals form giant lattices and their melting and boiling points are a function of the metallic bond. The strength of the metallic bond depends on:

1. If the bonds are short, resulting in greater attraction between the delocalised electrons and the nuclei of the atoms.
2. If there are several electrons that are available for the 'sea of delocalised electrons'.

Hence, Group I have low melting points, because they only have one electron available for the 'sea', whereas, the melting points of Group II and Group III metals are higher since they have more electrons for bonding and their atomic radii are smaller.

(Note: the highest melting points are found in the d-block, because these atoms have small metallic radii and can use both s and d electrons for bonding.)

The semiconductors in the middle of the periodic table have high melting and boiling points, because they form giant covalent structures.

At the right of the periodic table, the non-metallic elements form small discrete molecules and have very low melting and boiling points. This is because these molecules are held by intermolecular forces of attraction.

There is, therefore, a periodic trend in melting and boiling points. They increase from a low value at the left of the periodic table, reach a maximum in the middle, followed by a rapid fall to very low values on the right.

Atomic radius

In general, atomic radius decreases on crossing the period. There are two effects that act in opposition:

1. The increasing nuclear charge makes the inner electron clouds contract
2. The addition of electrons to the outer shell leads to increased repulsion and a slight expansion.

The first effect is larger than the second, so overall there is a contraction in atomic radius on crossing a period.

Ionisation energy

As we go across a period, the ionisation energy increases because each electron experiences a greater effective nuclear charge due to the increased number of protons in the nucleus. (The increase is not the same for electrons in s, p and d orbitals, because they experience different degrees of shielding by the inner electrons).

Periodic patterns across the periods:

soft, low m.p. metals

solids, liquids, or gases

physical

conduct

insulate

ductile / malleable

brittle

chemical

form cations

form anions

basic oxides

acidic oxides

reducing agents

oxidising agents

Periodic trends in the oxides

Properties of the principal oxides of the second period.

Formula	Li ₂ O	BeO	B ₂ O ₃	CO CO ₂	N ₂ O NO NO ₂	O ₂ , O ₃	OF ₂
Type of oxide	alkaline	amphoteric	acidic	neutral acidic	neutral neutral acidic		acidic
Type of bonding	ionic	ionic	giant covalent	simple covalent	simple covalent	simple covalent	simple covalent

Properties of the principal oxides of the third period.

Formula	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₃ P ₂ O ₅	SO ₂ SO ₃	Cl ₂ O Cl ₂ O ₇
Type of oxide	alkaline	basic	amphoteric	acidic	acidic acidic	acidic acidic	acidic acidic
Type of bonding	ionic	ionic	ionic	giant covalent	simple covalent	simple covalent	simple covalent

The oxides that are ionic lattices or giant molecular solids have strong forces between particles; thus they have high melting points. Those that are simple molecular compounds have weak attractive forces between molecules, hence they have low melting points

The reaction of these oxides with water changes across the period.

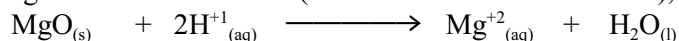
Alkaline and basic oxides

The chemistry of the oxides can be categorized according to its type — alkaline, basic, amphoteric or acidic.

Lithium and sodium oxides are alkaline, these dissolve in water to give solutions with a pH greater than 7:

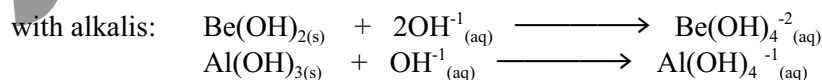
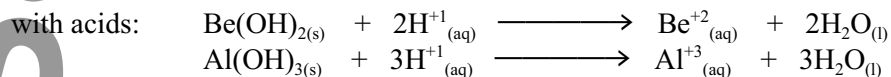
$$M_2O_{(s)} + H_2O_{(l)} \longrightarrow 2 MOH_{(aq)} \quad (M = \text{Li or Na})$$

while magnesium oxide is basic (it is almost insoluble in water), but reacts with acids:



Amphoteric oxides

Aluminium oxide is insoluble in water. But the amphoteric oxides of beryllium and aluminium react extremely slowly with aqueous acids or alkalis, however, their hydroxides react readily:



[Amphoteric hydroxides:

an element M attached to an O—H group can ionise in two different ways:

as an acid: $M-O-H \longrightarrow M-O^{-1} + H^{+1}$

or as a base: $M-O-H \longrightarrow M^{+1} + OH^{-1}$

The way in which the ionisation takes place depends on the electronegativity of M.

If M is more electronegative than hydrogen, the M—O, the substance behaves principally as an acid, example when M is N, P, S or Cl.

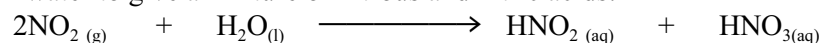
If the electronegativity of M is lower than 1.5, the substance behaves as a base, such as when M is in Group I or II.

If the electronegativity of M is slightly lower than that of hydrogen, the substance could behave as an acid or a base that is, be amphoteric, when M is Be or Al. In summary: if the electronegativity of M is < 1.5, then the oxide is basic, if the electronegativity of M is between 1.5 — 2.5, then the oxide is amphoteric, if the electronegativity of M is > 1.5, then the oxide is acidic.]

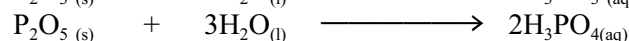
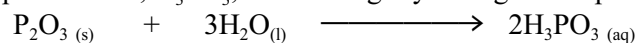
Acidic Oxides

CO₂ dissolves in water to give a weakly acidic solution, less than 0.1% H₂CO_{3(aq)}.

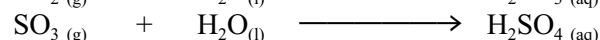
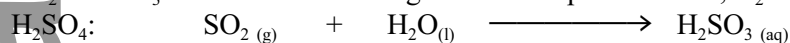
NO₂ dissolves in water to give a mixture of nitrous and nitric acids:



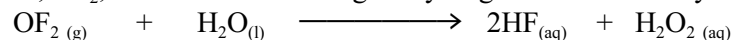
Phosphorus (III) oxide, empirical formula P₂O₃, has the empirical formula P₂O₆ and phosphorus (V) oxide, empirical formula P₂O₅, has the molecular formula P₄O₁₀. These dissolve in water to give the weak acid phosphonic acid, H₃PO₃, and the slightly stronger acid phosphoric (V) acid, H₃PO₄:



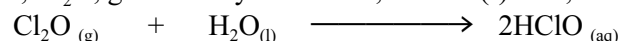
SO₂ and SO₃ dissolve in water to give weak sulphurous acid, H₂SO₃, and the very strong sulphuric acid,



Oxygen difluoride, OF₂, reacts with water to give hydrogen fluoride and hydrogen peroxide:



Dichlorine oxide, Cl₂O, gives a very weak acid, chloric (I) acid, HOCl:



Thus, across the period, ionic oxides react with water to form alkaline solutions while soluble covalent oxides react to form acidic solutions.

Periodic Trends in the Chlorides

On crossing the second and third periods, the chlorides of the elements change in structure from ionic to covalent, similar trend to the oxides. See the tables below:

Properties of the principal chlorides of the second period.

	LiCl	BeCl ₂	BCl ₃	CCl ₄	NCl ₃	Cl ₂ O	ClF
Type of bonding	ionic	covalent	covalent	covalent	covalent	covalent	covalent
Action of water	dissolves	hydrolyses	hydrolyses	—	hydrolyses	hydrolyses	hydrolyses

Properties of the principal chlorides of the third period.

	NaCl	MgCl ₂	AlCl ₃	SiCl ₄	PCl ₃ PCl ₅	S ₂ Cl ₂ SCl ₂	Cl ₂
Type of bonding	ionic	ionic	borderline ionic, covalent	covalent	covalent	covalent	covalent
Action of water	dissolves	dissolves	hydrolyses	hydrolyses	hydrolyses	hydrolyses	hydrolyses

At room temperature both aluminium chloride and phosphorus (V) chloride have unusual properties:

—aluminium chloride exists as a dimer. This is a structure in which two molecules of AlCl₃ link together to form a single molecule, Al₂Cl₆.

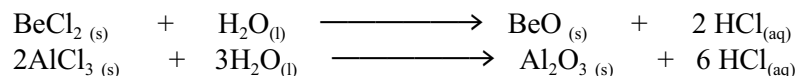
[AlCl₃ is an 'electron- deficient' molecule, it has only 6 electrons in the 'outer shell', but needs 8 electrons to form a stable structure. A lone pair on chlorine forms a dative / coordinate bond to the second aluminium atom of AlCl₃.]

—phosphorus (V) chloride exists as an ionic solid containing the ions PCl₄⁺¹ and PCl₆⁻¹. However, at 162°C it sublimes to form a simple molecular gas, PCl₅.

The reaction of these chlorides changes across the period:

The chlorides of lithium, sodium, and magnesium are ionic and dissolve in water, without chemical reaction taking place, and as a result their solutions are neutral. The ions of these hydrate but undergo no chemical reaction.

Both beryllium and aluminium chloride react rapidly when moistened with water:



This reaction with water is called hydrolysis.

NCl₃ forms ammonia and chloric (I) acid, HClO.

PCl₃ gives H₃PO₃ and HCl, whilst PCl₅ forms H₃PO₄ and HCl.

The fluorides of chlorine, ClF and ClF₃ are even more reactive than fluorine itself, forming HF, HCl, O₂ and O₃.

Across the period, ionic chlorides dissolve in water to form neutral solutions while covalent chlorides are hydrolysed by water to form acidic solutions.