Group IV

The elements of Group IV are:

	symbol	electron configuration
carbon	C	$[He]2s^2 2p^2$
silicon	Si	$[Ne]3s^2 3p^2$
germanium	Ge	$[Ar]3d^{10} 4s^2 4p^2$
tin	Sn	$[Kr]4d^{10} 5s^2 5p^2$
lead	Pb	$[Xe]4f^{14} 5d^{10} 6s^2 6p^2$

Appearance

The expected similarity in appearance between elements in the same Group is much less apparent in Group IV, where there is a considerable change in character on descending the Group. Carbon is a dull black colour in the form of graphite, or hard and transparent in the form of diamond; silicon and germanium are dull grey or black; tin and lead are a shiny grey colour.

General Reactivity

In Group IV the elements change from non-metallic in character at the top of the Group to metallic at the bottom. Carbon is a non-metal, silicon and germanium are metalloids, and tin and lead are typical metals. The general reactivity of the Group as a whole is therefore difficult to ascertain, and the reactivity of each element must be considered individually.

Carbon exists in two important allotropic forms, diamond and graphite. Diamond has an extended covalently-bonded structure in which each carbon atom is bonded to 4 others. This compact, rigid arrangement explains why diamond is both extremely hard and chemically inert. Graphite has a layer structure. Planes of covalently-bonded carbon atoms are held together by weak van der Waals forces, and slide over each other easily. Chemically, graphite is more reactive than diamond but still does not react easily. However, it does oxidise at high temperatures and this is the reason why carbon is used in various forms as fuel.

Silicon is chemically unreactive.

Germanium is also unreactive and not widely used, so will not be considered further. It does, however, have excellent semi-conducting properties so may become more widely used in a few years' time.

Both tin and lead are generally unreactive metals. Tin has two common allotropes. At room temperature the stable form is white tin; below 286.2K the stable form is grey tin. Tin has a tendency to displace lead, and not vice versa as may be expected.

Occurrence and Extraction

Carbon, tin and lead can all be found in the elemental form in the earth's crust, and are readily mined.

Silicon is found in mineral deposits and purified from them. Very pure silicon is required for semi-conductors, and is obtained from silicon (IV) chloride. This is first purified by fractional distillation, then reduced to give the element. The silicon is then further purified by zone refining, in which a molten zone is moved along a silicon rod several times, carrying impurities to one end where they are removed.

Physical Properties

The physical properties of Group IV elements vary quite widely from one element to another, consistent with the increasing metallic character on descending the Group. The structures change from giant molecular lattices in carbon and silicon to giant metallic lattices in tin and lead, and this is the reason for the changes in physical properties. The change in bonding from covalent to metallic down the Group causes a decrease in melting point, boiling point, heat of atomisation and first ionisation energy. At the same time, the increasing metallic character causes a general increase in density and conductivity. Carbon and silicon do not conduct electricity.

Diamond has a very high refractive index (the reason for its sparkle) and this, along with its rarity, has made it valuable as a jewel. However, it is also the hardest natural substance known and so is important industrially.

The most important physical property of silicon is that it is a semi-conductor. Small silicon chips, just a few millimetres square, have revolutionised the computer and microprocessor industries.

Tin and lead, as typical metals, are good conductors of electricity.

Chemical Properties

In general, chemical reactivity increases on descending the Group.

The first member of the Group, carbon, is strikingly different from the others as it has the unique ability to form stable compounds containing long chains and rings of carbon atoms. This property, called catenation, results in carbon forming an enormous range of organic compounds. The ability to catenate results from the C-C bond having almost the same bond energy as the C-O bond, so that oxidation of carbon compounds is energetically favourable. Also, the small size of the carbon atom allows 2 carbon atoms to approach close together and allow overlap of p-orbitals, so that multiple bonds can be formed. The organic compounds formed from carbon have a chemistry entirely different to any inorganic counterpart.

The C-C and C-Si bond energies are very similar, so many organo-silicon compounds are known. Silicon does not, however, form multiple bonds.

Silicon is unreactive chemically because an oxide layer seals the surface from attack, and high temperatures are required for oxidation to occur. Silicon does, however, react with fluorine at room temperature. It is not attacked by aqueous acids, but does react with concentrated alkalis.

Tin and lead are quite easily oxidised, tin usually to tin (IV) and lead to lead (II). Both tin and lead reduce the halogens.

Oxides

There are many oxides of Group IV elements. The major oxides are:

CO (gas), CO_2 (gas), SiO_2 (solid), SnO (solid), SnO_2 (solid), PbO (solid), Pb_3O_4 (solid), PbO_2 (solid).

Oxides with a lower oxidation number become more stable going down the Group. Carbon dioxide is essential to life as it is the source of carbon for plants. During photosynthesis carbon is combined with water to form carbohydrates. Solid carbon dioxide sublimes directly to a gas, so is widely used as a cheap refrigerant.

Silicon forms a strong bond with oxygen in silica, SiO_2, one form of which is quartz. Sand is impure quartz. Oxoanions derived from silica are called silicates. They are very common in nature and have structures based on SiO_4 tetrahedra. One of these is asbestos.

Tin (IV) oxide, tin (II) oxide and lead (II) oxide are amphoteric.

Halides

All the elements of Group IV form tetrahalides, but only tin and lead form dihalides. The tetrahalides are covalent tetrahedral molecules whereas the dihalides are best regarded as ionic.

Hydrides

The hydrides of carbon are the hydrocarbons - organic compounds.

Silicon forms a series of hydrides called the silanes, with the general formula Si_nH_{2n+2}.

Oxidation States and Ionisation Energies

Group IV elements exist in 2 oxidation states, +2 and +4. There is a steady increase in the stability of the +2 oxidation state on descending the Group.

The elements in this Group have 4 electrons in their outermost shell, 2 s electrons and 2 p electrons. The first 4 ionisation energies rise in a fairly even manner, and the 5th ionisation energy is very large, reflecting the removal of an electron from a filled level nearer to the nucleus. Compounds of tin and lead in which the Group IV element has an oxidation number +2 are regarded as ionic. In these compounds, the Sn^{2+} and Pb^{2+} ions are formed by loss of the outermost 2 electrons, whilst the 2 s electrons remain relatively stable in their filled sub-shell. This is called the “inert pair effect”.

Industrial Information

The industrial importance of carbon in petrochemicals is immense. These hydrocarbons are used extensively in almost all areas of modern civilisation; clothing, dyes, fertilisers, agrochemicals, fuels and new materials.

Silicon also contributes to new technology in the silicon chip, which has revolutionised the computer and high-tech industries. Germanium is, like silicon, a semi-conductor used in similar devices, but it is less widely used.

Tin and lead have more traditional industrial uses. Tin is used as a coating for other metals to prevent corrosion, such as in tin cans, but it is in alloys that tin is used most extensively. These alloys include bronze, soft solder, type metal, phosphor bronze and pewter. Lead is used in great quantities in storage batteries. It is also used in cable covering, ammunition and in the manufacture of tetraethyl lead, an anti-knocking compound added to petrol.

Further Information

For further information look up the individual elements.

Data

	Atomic Number	Relative Atomic Mass	Melting Point/K	Density/kg m^{-3}
C	6	12.011	3820 (diamond)	3513
Si	14	28.086	1683	2329
Ge	32	72.61	1210.6	5323
Sn	50	118.71	505.1	7130
Pb	82	207.2	600.65	11350

Ionisation Energies/kJ mol-1

	1st	2nd	3rd	4th	5th
C	1086.2	2352	4620	6222	37827
Si	786.5	1577.1	3231.4	4355.5	16091
Ge	762.1	1537	3302	4410	9020
Sn	708.6	1411.8	2943	3930.2	6974
Pb	715.5	1450.4	3081.5	4083	6640

	Atomic Radius/nm	Ionic Radii/nm
C	0.077	
Si	0.117	
Ge	0.122	
Sn	0.140	0.093 (Sn^{2+}) 0.074 (Sn^{4+})
Pb	0.154	0.132 (Pb^{2+}) 0.084 (Pb^{4+})