Inorganic chemistry II
Second stage / Second semester
The Fifth lecture 2022/2023 Pro. Dr. Mohammed Hamid

Elements of Group IVA or 14

(Elements of Carbon Family, ns^2 np^2)

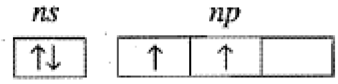
POSITION IN PERIODIC TABLE

Group IVA or 14 of long form of periodic table consists of six elements-carbon (C), silicon (Si), germanium (Ge), tin (Sn), lead (Pb) and ununquadium. These six elements constitute a family known as carbon family. These are *p*-block elements as the last differentiating electron is accommodated in *np* shell. These elements have four electrons in their valency shell and thus placed in the IVth group. The elements of this group show similarities as well as gradation in properties with rise of atomic number and thus their inclusion in the same group is justified on the basis of electronic configuration and physical and chemical properties which are described below

1- Electronic configuration : The electronic configuration of the members of this group are:

Element	At.NO.	Electronic configuration	Inert gas core
Carbon - **C**	6	$1s^22s^22P^2$	[He]$2s^22P^2$
Silicon - Si	14	$1s^22s^22P^63s^23P^2$	[Ne]$3s^23P^2$
Germanium – Ge	32	$1s^22s^22P^63s^23P^63d^{10}4s^24P^2$	[Ar]$3d^{10}4s^24P^2$
Tin – Sn	50	$1s^22s^22P^63s^23P^63d^{10}4s^24P^64d^{10}5s^25P^2$	[Kr]$4d^{10}5s^25P^2$
Lead – Pb	82	$1s^22s^22P^63s^23P^63d^{10}4s^24P^64d^{10}\ 4f^{14}\ 5s^2\ 5P^6\ 5d^{10}\ 6s^2\ 6P^2$	[Xe]$4f^{14}5d^{10}6s^2\ 6P^2$
Ununquadium – Uuq	114	$1s^22s^22P^63s^23P^63d^{10}4s^24P^64d^{10}\ 4f^{14}\ 5s^2\ 5P^65f^{14}\ 5d^{10}\ 6s^2\ 6P^66d^{10}7s^2\ 7P^2$	[Rn]$5f^{14}6d^{10}7s^2\ 7P^2$

The configurations show that these elements have same number of electrons in the valency shell, i.e., 4 electrons in the valency shell, two of which are in *s*-orbital while remaining two in *p*-orbitals. Thus, they have ns^2 np^2 configuration, i.e., *s*-orbital is paired while two *p*-orbitals are unpaired.



The penultimate shell of carbon contains 2 electrons (saturated), of silicon contains 8 electrons (saturated), of germanium contains 18 electrons (saturated) while Sn and Pb contain 18 electrons (unsaturated) each. This shows why carbon differs from silicon in some respects and these two differ from rest of the members of this group. The close resemblance between the elements is quite striking in the case of elements of the first and second groups, but this becomes less evident in the elements of third group and still less evident in the fourth group.

2. Occurrence of the elements :

Carbon is extremely wide spread in nature. It is an essential constituent of all living matter as proteins, carbohydrates and fats. Carbon is the seventeenth and silicon the second most abundant element by mass in the earth's crust. Carbon is found both in native and combined states. Silicon occurs very widely as silica and a wide variety of silicate minerals and clays. Germanium is only found in traces in some silver and zinc ores, and in some types of coal.

No doubt that the abundance of tin and lead is comparatively low, but they occur as concentrated ores. Tin is mined as cassiterite, SnO_2 and lead is found as galena ore, PbS. In the fusion reactions occurring on stars and sun, carbon acts as catalyst. The energy released in the process is called stellar energy.

The last member, ununquadium (114) is recently discovered element. It is synthetic, radioactive and unstable element. Not much is known about its properties.

3.Non-metallic and metallic character :

The change from non-metallic to metallic character with the increase of atomic number is best illustrated by this group. Carbon, the first element, is a non-metal, silicon, the second element has most of the properties of a non-metal but its electrical properties and some of the physical properties are those of a semi-metal (metalloid). Germanium is a metalloid (properties are mixed, i.e., of a metal and a non-metal) while last two members Sn and Pb are distinctly metals.

$$\underbrace{\text{C} \qquad\qquad \text{Si}}_{\text{Non-metals}} \qquad\qquad \underset{\text{Metalloid}}{\text{Ge}} \qquad\qquad \underbrace{\text{Sn} \qquad\qquad \text{Pb}}_{\text{Metals}}$$

The change from non-metallic to metallic character is due to less effective nuclear charge and increased number of available orbitals with increase in the size of the atom.

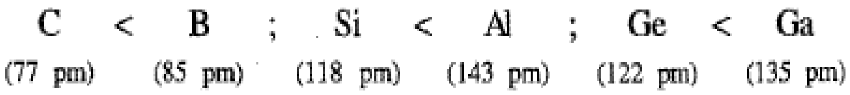
4. Atomic radii atomic volume :

Atomic radii and atomic volume increase gradually on moving down the group. The size increases due to the effect of extra shell being added from member to member.

	C	Si	Ge	Sn	Pb
Atomic radius (pm)	77	118	122	140	146
At.volume(ml)	3.4	11.4	13.6	16.3	18.27

It is observed that there is large increase in atomic radius from carbon to silicon but from silicon onwards, the increase is comparatively small from member to member. This is due to the fact that shielding effect of $S^2 P^6$ electrons of the penultimate shell in silicon is large while the shielding effect of d^{10} electrons in Ge and Sn and $d^{10} f^{14}$ electrons in Pb is less.

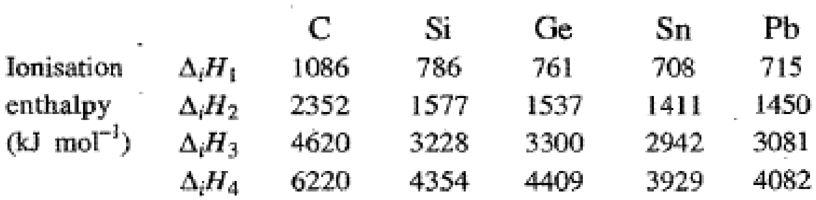
In the same period, the atomic radii of group 14 elements are smaller than the corresponding elements of group 13. This is due to fact that effective nuclear charge increases when we move from group 13 to group 14. This brings contraction in size.



C	<	B	;	Si	<	Al	;	Ge	<	Ga
(77 pm)		(85 pm)		(118 pm)		(143 pm)		(122 pm)		(135 pm)

5. Ionisation potential :

The ionisation potentials decrease gradually from carbon to lead but not systematically as in groups I and II. The value of lead is slightly higher than expected due to lanthanide contraction.



		C	Si	Ge	Sn	Pb
Ionisation	$\Delta_i H_1$	1086	786	761	708	715
enthalpy	$\Delta_i H_2$	2352	1577	1537	1411	1450
(kJ mol^{-1})	$\Delta_i H_3$	4620	3228	3300	2942	3081
	$\Delta_i H_4$	6220	4354	4409	3929	4082

Large decrease in ionisation potential from C to Si is due to increase in size of the atom. Decrease in ionisation potential from silicon onwards is comparatively smaller due to less screening effect of d^{10} electrons in Ge and Sn and due to d^{10} or f^{14} electrons in Pb.

The slight increase in the ionisation energy from Sn to Pb is due to lanthanide contraction and increase of 32 units of nuclear charge in Pb over Sn, i.e. valency electrons are more tightly held in Pb.

The first ionisation energies of group 14 are higher than the corresponding elements of group 13 in the same period

C	>	B	;	Si	>	Al
(1086 kJ mol^{-1})		(800 kJ mol^{-1})		(786 kJ mol^{-1})		(577 kJ mol^{-1})

The increase is due to decrease in size and increase in charge on nucleus of group 14 elements in the same period.

6. Melting and boiling points:

Carbon has an extremely high melting point (4100°C). Silicon melts appreciably lower than carbon but the values of silicon and germanium are still high. (Si = 1420°C; Ge = 945°C). They have the very stable diamond like structure in which smaller atoms are closely packed. Tin and lead are metallic and have much lower melting points (Sn = 232°C; Pb = 327°C) because the M-M bonds are weaker. They do not use all the four outer electrons for metallic bonding

The boiling point of carbon is exceedingly high. It decreases in silicon and then increases in germanium. However, the boiling point decreases from germanium to lead.

7. Electronegativity:

The electronegativity values do not decrease in a regular manner. Carbon is the most electronegative element while Si, Ge, Sn and Pb possess nearly the same values. This is due to filling of *d*-orbitals in Sn and Ge and also *f*-orbitals in lead.

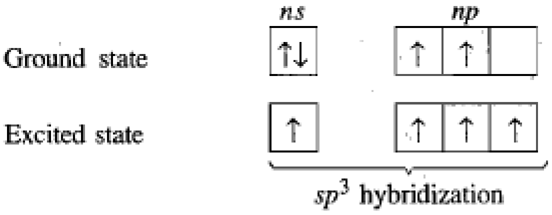
	C	Si	Ge	Sn	Pb
Electronegativity	2.5	1.8	1.8	1.8	1.9

8. Allotropy :

Except lead , all other elements of this group show allotropy. For example, carbon exists as diamond, graphite, coal, charcoal and lampblack; silicon exists in two forms, crystalline and amorphous; germanium exists in two crystalline forms and tin exists in three forms; grey tin, white tin and rhombic tin.

9. Valency :

All these elements show a covalency of 4. The tetravalency is explained on the basis of the shifting of one of the paired *ns* electrons to the vacant *np* orbital in the same shell.



These four half filled orbitals mix together to give four sp^3 hybrid orbitals resulting in a tetrahedral structure and each having one unpaired electron.

When ns^2 electrons of outermost shell do not participate in bonding it is called inert pair and the effect is called inert pair effect. The last three elements have a tendency to form M^{2+} ions as well as M^{4+} ions. Since, the inert pair effect increases from Ge to Pb, the stability of M^{4+} ions decreases and that of M^{2+} ions increases. Thus, the stability of these ions follows the following order:

$$Ge^{2+} < Sn^{2} < Pb^{2+}$$

$$Ge^{4+} > Sn^{4+} > Pb^{4+}$$

The compounds of Ge^{2+} are unstable while compounds of Ge^{4+} are stable. Thus, the compounds of Ge^{2+} get oxidised into Ge^{4+} easily and act as reducing agents.

$$\underset{\text{Less stable}}{Ge^{2+}} \xrightarrow{-2e} \underset{\text{More stable}}{Ge^{4+}}$$

(Reducing agent)

The compounds of Sn^{2+} are less stable than Sn^{4+}. Thus Sn^{2+} compounds also act as reducing agents. In the case of lead, Pb^{2+} compounds are more stable than Pb^{4+} compounds. the Pb^{2+} compounds , thus , act as oxidizing agents.

$$\underset{\text{Less stable}}{Pb^{4+}} + 2e \longrightarrow \underset{\text{More stable}}{Pb^{2+}}$$

(Oxidising agent)

Since M^{4+} ions are smaller than M^{2+} ions, in general, M^{4+} compounds behave as covalent due to high polarisation (small size and high charge) and M^{2+} compounds are ionic.

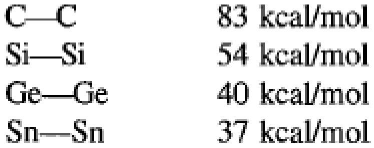
10. Multiple bonding :

Carbon, the first member of group 14, possesses a pronounced ability to form stable p_π- p_π multiple bonds (double and triple bonds) with itself and with other first row elements such as nitrogen and oxygen. The compounds
containing >C=C<,-C≡C-, -C≡ N, >C=O, and >C=S bonds are common. Graphite, an allotropic form of carbon, is also an example of p_π- p_π bonding. Silicon and other elements of this group show their reluctance in forming p_π- p_π multiple bonding due to their large atomic sizes. However, silicon and other elements of this group have vacant *d*-orbitals in their valence shell. These elements can form d_π- p_π double bonds with nitrogen and oxygen. This bond is formed by the donation of an electron pair from filled *2p*-orbitals of N or O to the vacant *3d*-orbitals of silicon or other elements of group 14. The existence of d_π- p_π bonding explains the structures of trimethylamine, $(CH_3)_3N$, and trisilylamine $N(SiH_3)_3$ and their basic nature.

In trimethylamine, the N atom undergoes sp^3-hybridisation giving tetrahedral configuration. The geometry of the molecule is pyramidal as one of the tetrahedral positions is occupied by a lone pair. p_π-d_π bonding cannot occur in this molecule as carbon does not have *d*-orbitals. This lone pair, $:N(CH_3)_3$, can be donated to Lewis acids and thus it shows a basic nature. In trisilylamine, sp^2-hybridisation occurs giving trigonal planar geometry to the molecule. The lone pair of electrons is present in unhybridised *p*-orbital. This overlaps with empty *d*-orbital of any one of the silicon atoms forming *pπ-dπ* back bonding. Due to non-availability of lone pair, this molecule does not show basic nature.

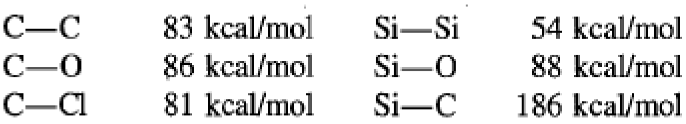
11. Catenation :

The linking of identical atoms with each other to form long chains is called catenation. All the elements of this group have the property of catenation. However, this property decreases from carbon to lead. Thus, carbon has the maximum property of catenation, silicon has much lesser tendency, germanium has still lesser tendency whereas tin and lead hardly show this property. The decrease of this property is associated with *M-M* bond energy which decreases from carbon to lead.



C—C	83 kcal/mol
Si—Si	54 kcal/mol
Ge—Ge	40 kcal/mol
Sn—Sn	37 kcal/mol

The reason for greater tendency of carbon for catenation than other elements may further be explained by the fact that C-C bond energy is approximately of the same value as the energies of bonds between carbon and other elements. On the other hand Si-Si bond is weaker than the bonds between silicon and other elements.



C—C	83 kcal/mol	Si—Si	54 kcal/mol
C—O	86 kcal/mol	Si—O	88 kcal/mol
C—Cl	81 kcal/mol	Si—C	186 kcal/mol

Thus, carbon forms a number of compounds in which a large number of carbon atoms are linked together in the form of straight chains, branched chains or closed rings. The property of catenation is responsible for a very large number of compounds of carbon.

12. Maximum covalency :

Carbon has only two energy shells, K and L. L shell (outermost shell) has four orbitals 2s, $2P_x$, $2p_y$, and $2p_z$. These four orbitals can accommodate a maximum of 8 electrons forming four covalent bonds. Thus, maximum covalency of carbon is four because it has no *d*-orbitals or vacant orbitals which can be used to accommodate more electrons.

The remaining elements, however, have vacant *d*-orbitals. These permit the formation of coordinate bonds with other atoms or ions having lone pairs of electrons. For example, SiF_4 can combine with $2F^{1-}$ ions.

$$SiF_4 + 2F^{1-} \longrightarrow [SiF_6]^{2-}$$

Thus, the maximum covalency of silicon can be 6. Similarly, other members can show maximum covalency of six involving sp^3d^2 hybridization.

Since all these elements except carbon satisfy the following three conditions for the formation of complexes, they have the tendency to form complexes using *d*-orbitals.

(i) small size of the atom or ion
(ii) high charge
(iii) availability of vacant orbitals of appropriate energy.

13. Reactivity:

The elements of this group are relatively less reactive but reactivity increases down the group. Lead often appears more unreactive than expected. This is partly due to surface coating of the oxide and partly due to the high overpotential for the reduction of H^+ to H_2 at a lead surface.

(i) Reactivity towards air : These elements react with the oxygen of the air on strong heating when their exides are formed.

$$C + O_2 \longrightarrow CO_2 ; \qquad Si + O_2 \longrightarrow SiO_2$$

$$Ge + O_2 \longrightarrow GeO_2 ; \qquad 2Pb + O_2 \longrightarrow 2PbO$$

Mono-oxides CO, SiO, GeO are also known. SiO is unstable.

(ii) Reactivity towards water : C, Si and Ge are unaffected by water. However, on red heating, these elements except lead decompose steam.

$$C + H_2O \longrightarrow CO + H_2$$

$$Si + 2H_2O \longrightarrow SiO_2 + 2H_2$$

$$Sn + 2H_2O \longrightarrow SnO_2 + 2H_2$$

Lead is unaffected by water, probably, because of a protective oxide film.

(iii) Reactivity towards acids : Non-oxidising acids do not attack carbon and silicon, Germanium is not attacked by dilute HCl. However, when metal is heated in a stream of HCl gas, germanium chloroform is formed.

$$Ge + 3HCl \rightarrow GeHCl_3 + H_2$$

Tin dissolves slowly in dilute HCl but readily in concentration HCl

$$Sn + 2HCl \longrightarrow SnCl_2 + H_2$$

Lead also dissolves in dilute HCl

Lead also dissolves in dilute HCl

Lead dissolves in concentrated HCl forming chloroplumbous acid, but the reaction stops after sometime due to deposition of $PbCl_2$.

$$Pb+2HCl \longrightarrow PbCl_2 + H_2$$
$$PbCl+2HCl \longrightarrow H_2PbCl_4$$

Tin dissolves in dilute H_2SO_4, conc. H_2SO_4, dil. HNO_3 and conc. HNO_3.

$$Sn + H_2SO_4\,(\text{dil.}) \longrightarrow SnSO_4 + H_2$$
$$Sn + 4H_2SO_4\,(\text{conc.}) \longrightarrow Sn(SO_4)_2 + 2SO_2 + 4H_2O$$
$$4Sn + 10HNO_3\,(\text{dil.}) \longrightarrow 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O$$
$$Sn + 4HNO_3\,(\text{conc.}) \longrightarrow \underset{\substack{\text{Metastannic}\\ \text{acid}}}{H_2SnO_3} + 4NO_2 + H_2O$$

Lead is not affected by dil. H_2SO_4. Hot conc. H_2SO_4 dissolves lead but the reaction becomes slower due to formation of insoluble $PbSO_4$.

$$Pb + 2H_2SO_4 \longrightarrow PbSO_4 + SO_2 + 2H_2O$$

HNO_3 is the best solvent for lead.

$$3Pb + 8HNO_3\,(\text{dil.}) \longrightarrow 3Pb(NO_3)_2 + 2NO + 4H_2O$$
$$Pb + 4HNO_3\,(\text{conc.}) \longrightarrow Pb(NO_3)_2 + 2NO_2 + 2H_2O$$

Organic acids dissolve lead in presence of oxygen.

$$Pb + 2CH_3COOH + 1/2\,O_2 \longrightarrow Pb(CH_3COO)_2 + H_2O$$

(iv) Reactivity towards alkalies: Carbon is unaffected by alkalies. Silicon reacts slowly with cold aqueous NaOH and readily with hot solution giving solution of silicate.

$$Si + 2NaOH + H_2O \longrightarrow Na_2SiO_3 + 2H_2$$

Sn and Pb are slowly attacked by cold alkali but readily by hot alkali giving stannates and plumbates. Thus, Sn and Pb are somewhat amphoteric.

$$Sn + 2NaOH + H_2O \longrightarrow Na_2SnO_3 + 2H_2$$
$$Pb + 2NaOH + H_2O \longrightarrow Na_2PbO_3 + 2H_2$$

14. Compounds :

(i) Hydrides : All the members of this group form covalent hydrides directly or indirectly. The number of hydrides, their stability and the case of formation decreases as we move down from carbon to lead. However, all the members form hydrides of the type MH_4. Besides MH_4, carbon forms a large number of hydrides, saturated as well as unsaturated. Silicon forms only limited number of saturated hydrides. Germanium gives a still smaller number of hydrides while Sn and Pb give only one hydride each.

The hydrides of MH_4 type are gaseous and their thermal stability decreases and consequently the reducing nature increases from top to bottom. However, among the hydrides, silicon hydrides are least stable to hydrolysis.

Hydrides	CH_4	SiH_4	GeH_4	SnH_4	PbH_4
Decomposition temp (^0C)	800	450	285	150	0

The hydrides of silicon (silanes) are much more reactive than the alkanes. The difference in behavior is attributed to a various factors:

(a) Electronegativity values are: C 2.5, Si = 1,8 and H = 2.1. Thus, the bonding electrons between C and H or Si and H are not equally shared and silicon is vulnerable to attack by nucleophilic reagents.

$$C^{\delta-} - H^{\delta+} \qquad Si^{\delta+} - H^{\delta-}$$

(b) The larger size of Si is easier to be attacked.

(c) Si has low energy *d*-orbitals which may be used to form an intermediate compound and thus lower the activation energy of the process.

$$SiH_4 + 2NaOH + H_2O \longrightarrow Na_2SiO_3 + 4H_2$$
$$SiH_4 + 3H_2O \longrightarrow H_2SiO_3 + 4H_2$$
$$SiH_4 + 4AgNO_3 \longrightarrow Si + 4Ag + 4HNO_3$$
$$SiH_4 + 2Cl_2 \longrightarrow Si + 4HCl\ ]$$

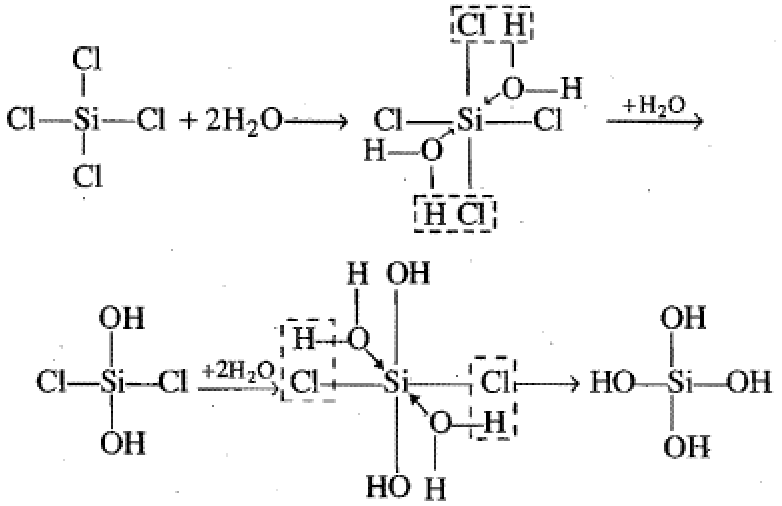
The low stability of GeH_4, SnH_4 and PbH_4 is due to weak M-H bond. It is due to large difference in the size of M and hydrogen atom leading to poor overlapping and weak covalent bond.

[Note: Extremely pure silicon can be obtained by pyrolysis of monosilane, SiH_4, in absence of air. The pure silicon is used as a semiconductor.

$SiCl_4 \xrightarrow{\text{LiAlH}} SiH_4 \xrightarrow{\text{Heat in absence of air}} Si(\text{Pure})]$

(ii) Halides : The members of this group form tetrahalides of the type MX_4 except $PbBr_4$ and Pbl_4.The halides are covalent and formed by sp^3 hybridization. The thermal stability of halides of different elements with a common halogen decreases with increasing atomic number. The thermal stability of tetrahalides of the same element decreases with increase in molecular mass of the tetrahalide.

$$CX_4 > SiX_4 > GeX_4 > SnX_4 > PbX_4$$
$$CF_4 > CCl_4 > CBr_4 > CI_4$$



[Non-existence of $PbBr_4$ and Pbl_4 can be explained on the basis of strong oxidising nature of Pb^{4+}. The ions Br^{1-} and I^{1-} are reducing agents, *i.e.*, in presence of these ions, Pb^{4+} ions are reduced to Pb^{2+} ions.

$$Pb^{4+} + 2Br^{1-} \longrightarrow Pb^{2+} + Br_2$$
$$Pb^{4+} + 2I^{1-} \longrightarrow Pb^{2+} + I_2\ ]$$

Except carbon halides, other halides are readily hydrolysed by water. The trend towards hydrolysis, however, decreases down the group. The hydrolysis is due to utilisation of *d*-orbitals to which water molecules can get attached.

The tetrahalides of Si, Ge, Sn and Pb can form hexahalo complexes like $[SiF_6]^{2-}$, $[GeF_6]^{2-}$ $[GeCl_6]^{2-}$, $[SnCl_6]^{2-}$ and $[PbCl_6]^{2-}$ with the corresponding halide ions. Thus, tetrahalides of Si, Ge, Sn and Pb act as strong Lewis acids.

Carbon does not form dihalides. All the other elements do form dihalides. There is a steady increase in the stability of dihalides.

$$SiX_2 < GeX_2 < Sn\ X_2 < PbX_2$$

(iii) Oxides : All the elements of this group form oxides of the type MO_2.

$$CO_2 \qquad SiO_2 \qquad GeO_2 \qquad SnO_2 \qquad PbO_2$$

The acidic nature decreases with increase of atomic number. CO_2 and SiO_2 are acidic while GeO_2, SnO_2 and PbO_2 are amphoteric. All these dissolve in alkalies giving carbonates, silicates, germanates, stannates and plumbates, respectively.

$$MO_2 + 2NaOH \rightarrow Na_2MO_3 + H_2O$$

The dioxides of Ge, Sn and Pb also dissolve in acids.

$$GeO_2 + 4HCl \longrightarrow GeCl_4 + 2H_2O$$
$$SnO_2 + 4HCl \longrightarrow SnCl_4 + 2H_2O$$
$$PbO_2 + 4HCl \longrightarrow PbCl_2 + Cl_2 + 2H_2O$$

They also form oxides of the type MO. SiO is unstable. CO is neutral while SnO and PbO are amphoteric. Basic character of both mono and dioxide increases down the group.