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# **Phosphorus, Sulfur and Silicon** Compounds

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**ABSTRACT:** Phosphorus, Sulfur, and Silicon and the Related Elements invites original research submissions, communications, and reviews involving chemistry in which select heteroatoms play a pivotal, central role to the presentation. We therefore consider papers on: -(Bio)organic, (bio)inorganic, heterocyclic, polymer, theoretical, structural, computational, catalytic, interdisciplinary, and spectroscopic chemistry of second row (and beyond) heteroatoms -The chemistry of phosphorus (including heavier Group 15 elements), sulfur (including heavier Group 16 elements), and silicon (including heavier Group 14 elements). Pertinent original articles, communications, and reviews that extend into the lighter main group elements may be considered, if sufficiently justified.

KEYWORDS- phosphorus, silicon, sulfur, compounds, chemistry

# **I.INTRODUCTION**

Phosphorus is a chemical element; it has symbol P and atomic number 15. Elemental phosphorus exists in two major forms, white phosphorus and red phosphorus, but because it is highly reactive, phosphorus is never found as a free element on Earth. It has a concentration in the Earth's crust of about one gram per kilogram (compare copper at about 0.06 grams). In minerals, phosphorus generally occurs as phosphate.[1,2,3]

Elemental phosphorus was first isolated as white phosphorus in 1669. In white phosphorus, phosphorus atoms are arranged in groups of 4, written as  $P_4$ . White phosphorus emits a faint glow when exposed to oxygen—hence the name, taken from Greek mythology,  $\Phi\omega\sigma\phi\phi\rho\sigma\varsigma$  meaning 'light-bearer' (Latin Lucifer), referring to the "Morning Star", the planet Venus. The term phosphorescence, meaning glow after illumination, derives from this property of phosphorus, although the word has since been used for a different physical process that produces a glow. The glow of phosphorus is caused by oxidation of the white (but not red) phosphorus—a process now called chemiluminescence. Phosphorus is classified as a pnictogen, together with nitrogen, arsenic, antimony, bismuth, and moscovium.

Phosphorus is an element essential to sustaining life largely through phosphates, compounds containing the phosphate ion,  $PO_4^{3-}$ . Phosphates are a component of DNA, RNA, ATP, and phospholipids, complex compounds fundamental to cells. Elemental phosphorus was first isolated from human urine, and bone ash was an important early phosphate source. Phosphate mines contain fossils because phosphate is present in the fossilized deposits of animal remains and excreta. Low phosphate levels are an important limit to growth in a number of plant ecosystems. The vast majority of phosphorus compounds mined are consumed as fertilisers. Phosphate is needed to replace the phosphorus that plants remove from the soil, and its annual demand is rising nearly twice as fast as the growth of the human population. Other applications include organophosphorus compounds in detergents, pesticides, and nerve agents.

Characteristics

Allotropes

Phosphorus has several allotropes that exhibit strikingly diverse properties.<sup>[10]</sup> The two most common allotropes are white phosphorus and red phosphorus.<sup>[11]</sup>

From the perspective of applications and chemical literature, the most important form of elemental phosphorus is white phosphorus, often abbreviated as WP. It is a soft, waxy solid which consists of tetrahedral P  $_4$  molecules, in which each atom is bound to the other three atoms by a formal single bond. This P  $_4$  tetrahedron is also present in liquid and gaseous phosphorus up to the temperature of 800 °C (1,500 °F; 1,100 K) when it decomposing to P

<sub>2</sub> molecules.<sup>[12]</sup> The P

 $_4$  molecule in the gas phase has a P-P bond length of  $r_g = 2.1994(3)$  Å as was determined by gas electron diffraction.<sup>[13]</sup> The nature of bonding in this P  $_4$  tetrahedron can be described by spherical aromaticity or cluster bonding, that is the electrons are highly delocalized.

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This has been illustrated by calculations of the magnetically induced currents, which sum up to 29 nA/T, much more than in the archetypical aromatic molecule benzene (11 nA/T).<sup>[13]</sup> Crystalline structures of some phosphorus allotropes



White



Red





Black

White phosphorus exists in two crystalline forms:  $\alpha$  (alpha) and  $\beta$  (beta). At room temperature, the  $\alpha$ -form is stable. It is more common, has cubic crystal structure and at 195.2 K (-78.0 °C), it transforms into  $\beta$ -form, which has hexagonal crystal structure. These forms differ in terms of the relative orientations of the constituent P<sub>4</sub> tetrahedra.<sup>[14][15]</sup> The  $\beta$  form of white phosphorus contains three slightly different P 4 molecules, i.e. 18 different P-P bond lengths between 2.1768(5) and 2.1920(5) Å. The average P-P bond length is 2.183(5) Å.<sup>[16]</sup>

White phosphorus is the least stable, the most reactive, the most volatile, the least dense and the most toxic of the allotropes. White phosphorus gradually changes to red phosphorus. This transformation is accelerated by light and heat, and samples of white phosphorus almost always contain some red phosphorus and accordingly appear yellow. For this reason, white phosphorus that is aged or otherwise impure (e.g., weapons-grade, not lab-grade WP) is also called yellow phosphorus. When exposed to oxygen, white phosphorus glows in the dark with a very faint tinge of green and blue. It is

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highly flammable and pyrophoric (self-igniting) upon contact with air. Owing to its pyrophoricity, white phosphorus is used as an additive in napalm. The odour of combustion of this form has a characteristic garlic smell, and samples are commonly coated with white phosphorus pentoxide, which consists of  $P_4O_{10}$  tetrahedra with oxygen inserted between the phosphorus atoms and at their vertices. White phosphorus is insoluble in water but soluble in carbon disulfide[4,5,6]

Thermal decomposition of  $P_4$  at 1100 K gives diphosphorus,  $P_2$ . This species is not stable as a solid or liquid. The dimeric unit contains a triple bond and is analogous to  $N_2$ . It can also be generated as a transient intermediate in solution by thermolysis of organophosphorus precursor reagents.<sup>[18]</sup> At still higher temperatures,  $P_2$  dissociates into atomic P.<sup>[17]</sup>

Form	white(a)	white( $\beta$ )	red	Violet	black
Symmetry	Body-centred cubic	Triclinic	Amorphous	Monoclinic	Orthorhombic
Pearson symbol		aP24		mP84	oS8
Space group	I43m	P1 No.2		P2/c No.13	Cmce No.64
Density (g/cm <sup>3</sup> )	1.828	1.88	~2.2	2.36	2.69
Band gap (eV)	2.1		1.8	1.5	0.34
Refractive index	1.8244			2.6	2.4

Properties of some allotropes of phosphorus<sup>[10][19]</sup>

Red phosphorus is polymeric in structure. It can be viewed as a derivative of  $P_4$  wherein one P-P bond is broken, and one additional bond is formed with the neighbouring tetrahedron resulting in chains of  $P_{21}$  molecules linked by van der Waals forces.<sup>[20]</sup> Red phosphorus may be formed by heating white phosphorus to 250 °C (482 °F) or by exposing white phosphorus to sunlight.<sup>[21]</sup> Phosphorus after this treatment is amorphous. Upon further heating, this material crystallises. In this sense, red phosphorus is not an allotrope, but rather an intermediate phase between the white and violet phosphorus, and most of its properties have a range of values. For example, freshly prepared, bright red phosphorus is highly reactive and ignites at about 300 °C (572 °F),<sup>[22]</sup> though it is more stable than white phosphorus, which ignites at about 30 °C (86 °F).<sup>[23]</sup> After prolonged heating or storage, the color darkens (see infobox images); the resulting product is more stable and does not spontaneously ignite in air.<sup>[24]</sup>

Violet phosphorus is a form of phosphorus that can be produced by day-long annealing of red phosphorus above 550 °C. In 1865, Hittorf discovered that when phosphorus was recrystallised from molten lead, a red/purple form is obtained. Therefore, this form is sometimes known as "Hittorf's phosphorus" (or violet or  $\alpha$ -metallic phosphorus).<sup>[19]</sup>

Black phosphorus is the least reactive allotrope and the thermodynamically stable form below 550 °C (1,022 °F). It is also known as  $\beta$ -metallic phosphorus and has a structure somewhat resembling that of graphite.<sup>[25][26]</sup> It is obtained by heating white phosphorus under high pressures (about 12,000 standard atmospheres or 1.2 gigapascals). It can also be produced at ambient conditions using metal salts, e.g. mercury, as catalysts.<sup>[27]</sup> In appearance, properties, and structure, it resembles graphite, being black and flaky, a conductor of electricity, and has puckered sheets of linked atoms.<sup>[28]</sup>

Another form, scarlet phosphorus, is obtained by allowing a solution of white phosphorus in carbon disulfide to evaporate in sunlight.<sup>[19]</sup>

Chemiluminescence



White phosphorus exposed to air glows in the dark.

When first isolated, it was observed that the green glow emanating from white phosphorus would persist for a time in a stoppered jar, but then cease. Robert Boyle in the 1680s ascribed it to "debilitation" of the air. Actually, it is oxygen

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being consumed. By the 18th century, it was known that in pure oxygen, phosphorus does not glow at all;<sup>[29]</sup> there is only a range of partial pressures at which it does. Heat can be applied to drive the reaction at higher pressures.<sup>[30]</sup>

In 1974, the glow was explained by R. J. van Zee and A. U. Khan.<sup>[31][32]</sup> A reaction with oxygen takes place at the surface of the solid (or liquid) phosphorus, forming the short-lived molecules HPO and  $P_2O_2$  that both emit visible light. The reaction is slow and only very little of the intermediates are required to produce the luminescence, hence the extended time the glow continues in a stoppered jar.

Since its discovery, phosphors and phosphorescence were used loosely to describe substances that shine in the dark without burning. Although the term phosphorescence is derived from phosphorus, the reaction that gives phosphorus its glow is properly called chemiluminescence (glowing due to a cold chemical reaction), not phosphorescence (re-emitting light that previously fell onto a substance and excited it).<sup>[33]</sup>

Isotopes

There are 22 known isotopes of phosphorus,<sup>[34]</sup> ranging from <sup>26</sup> P to <sup>47</sup>P.<sup>[35]</sup> Only <sup>31</sup>P is stable and is therefore present at 100% abundance. The half-integer nuclear spin and high abundance of <sup>31</sup>P make phosphorus-31 NMR spectroscopy a very useful analytical tool in studies of phosphorus-containing samples.[7,8,9]

Two radioactive isotopes of phosphorus have half-lives suitable for biological scientific experiments. These are:

- <sup>32</sup>P, a beta-emitter (1.71 MeV) with a half-life of 14.3 days, which is used routinely in life-science laboratories, primarily to produce radiolabeled DNA and RNA probes, e.g. for use in Northern blots or Southern blots.
- <sup>33</sup>P, a beta-emitter (0.25 MeV) with a half-life of 25.4 days. It is used in life-science laboratories in applications in which lower energy beta emissions are advantageous such as DNA sequencing.

The high-energy beta particles from <sup>32</sup>P penetrate skin and corneas and any <sup>32</sup>P ingested, inhaled, or absorbed is readily incorporated into bone and nucleic acids. For these reasons, Occupational Safety and Health Administration in the United States, and similar institutions in other developed countries require personnel working with <sup>32</sup>P to wear lab coats, disposable gloves, and safety glasses or goggles to protect the eyes, and avoid working directly over open containers. Monitoring personal, clothing, and surface contamination is also required. Shielding requires special consideration. The high energy of the beta particles gives rise to secondary emission of X-rays via Bremsstrahlung (braking radiation) in dense shielding materials such as lead. Therefore, the radiation must be shielded with low density materials such as acrylic or other plastic, water, or (when transparency is not required), even wood.<sup>[36]</sup>

The most prevalent compounds of phosphorus are derivatives of phosphate ( $PO_4^{3-}$ ), a tetrahedral anion.<sup>[45]</sup> Phosphate is the conjugate base of phosphoric acid, which is produced on a massive scale for use in fertilisers. Being triprotic, phosphoric acid converts stepwise to three conjugate bases:

$$\begin{array}{ll} H_{3}PO_{4} + H_{2}O \rightleftharpoons H_{3}O^{+} + H_{2}PO_{4}^{-} & K_{a1} = 7.25 \times 10^{-3} \\ H_{2}PO_{4}^{-} + H_{2}O \rightleftharpoons H_{3}O^{+} + HPO_{4}^{-2-} & K_{a2} = 6.31 \times 10^{-8} \\ HPO_{4}^{-2-} + H_{2}O \rightleftharpoons H_{3}O^{+} + PO_{4}^{-3-} & K_{a3} = 3.98 \times 10^{-13} \end{array}$$

Phosphate exhibits a tendency to form chains and rings containing P-O-P bonds. Many polyphosphates are known, including ATP. Polyphosphates arise by dehydration of hydrogen phosphates such as  $HPO_4^{2^-}$  and  $H_2PO_4^-$ . For example, the industrially important pentasodium triphosphate (also known as sodium tripolyphosphate, STPP) is produced industrially by the megatonne by this condensation reaction:

$$2 \text{ Na}_2\text{HPO}_4 + \text{Na}\text{H}_2\text{PO}_4 \rightarrow \text{Na}_5\text{P}_3\text{O}_{10} + 2 \text{ H}_2\text{O}$$

Phosphorus pentoxide ( $P_4O_{10}$ ) is the acid anhydride of phosphoric acid, but several intermediates between the two are known. This waxy white solid reacts vigorously with water.[10,11,12]

With metal cations, phosphate forms a variety of salts. These solids are polymeric, featuring P-O-M linkages. When the metal cation has a charge of 2+ or 3+, the salts are generally insoluble, hence they exist as common minerals. Many phosphate salts are derived from hydrogen phosphate (HPO<sub>4</sub><sup>2-</sup>).

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 $PCl_5$  and  $PF_5$  are common compounds.  $PF_5$  is a colourless gas and the molecules have trigonal bipyramidal geometry.  $PCl_5$  is a colourless solid which has an ionic formulation of  $PCl_4^+ PCl_6^-$ , but adopts the trigonal bipyramidal geometry when molten or in the vapour phase.<sup>[17]</sup>  $PBr_5$  is an unstable solid formulated as  $PBr_4^+Br^-$  and  $PI_5$  is not known.<sup>[17]</sup> The pentachloride and pentafluoride are Lewis acids. With fluoride,  $PF_5$  forms  $PF_6^-$ , an anion that is isoelectronic with  $SF_6$ . The most important oxyhalide is phosphorus oxychloride, (POCl<sub>3</sub>), which is approximately tetrahedral.

Before extensive computer calculations were feasible, it was thought that bonding in phosphorus(V) compounds involved d orbitals. Computer modeling of molecular orbital theory indicates that this bonding involves only s- and p-orbitals.<sup>[46]</sup>

### Phosphorus(III)

All four symmetrical trihalides are well known: gaseous  $PF_3$ , the yellowish liquids  $PCl_3$  and  $PBr_3$ , and the solid  $PI_3$ . These materials are moisture sensitive, hydrolysing to give phosphorous acid. The trichloride, a common reagent, is produced by chlorination of white phosphorus:

 $P_4 + 6 Cl_2 \rightarrow 4 PCl_3$ 

The trifluoride is produced from the trichloride by halide exchange. PF<sub>3</sub> is toxic because it binds to haemoglobin.

Phosphorus(III) oxide,  $P_4O_6$  (also called tetraphosphorus hexoxide) is the anhydride of  $P(OH)_3$ , the minor tautomer of phosphorous acid. The structure of  $P_4O_6$  is like that of  $P_4O_{10}$  without the terminal oxide groups.

Phosphorus(I) and phosphorus(II)



A stable diphosphene, a derivative of phosphorus(I)

These compounds generally feature P-P bonds.<sup>[17]</sup> Examples include catenated derivatives of phosphine and organophosphines. Compounds containing P=P double bonds have also been observed, although they are rare. Phosphides and phosphines

Phosphides arise by reaction of metals with red phosphorus. The alkali metals (group 1) and alkaline earth metals can form ionic compounds containing the phosphide ion,  $P^{3-}$ . These compounds react with water to form phosphine. Other phosphides, for example Na<sub>3</sub>P<sub>7</sub>, are known for these reactive metals. With the transition metals as well as the monophosphides there are metal-rich phosphides, which are generally hard refractory compounds with a metallic lustre, and phosphorus-rich phosphides which are less stable and include semiconductors.<sup>[17]</sup> Schreibersite is a naturally occurring metal-rich phosphide found in meteorites. The structures of the metal-rich and phosphorus-rich phosphides can be complex.

Phosphine (PH<sub>3</sub>) and its organic derivatives (PR<sub>3</sub>) are structural analogues of ammonia (NH<sub>3</sub>), but the bond angles at phosphorus are closer to 90° for phosphine and its organic derivatives. Phosphine is an ill-smelling, toxic gas. Phosphorus has an oxidation number of -3 in phosphine. Phosphine is produced by hydrolysis of calcium phosphide, Ca<sub>3</sub>P<sub>2</sub>. Unlike ammonia, phosphine is oxidised by air. Phosphine is also far less basic than ammonia. Other phosphines are known which contain chains of up to nine phosphorus atoms and have the formula P<sub>n</sub>H<sub>n+2</sub>.<sup>[17]</sup> The highly flammable gas diphosphine (P<sub>2</sub>H<sub>4</sub>) is an analogue of hydrazine.

Oxoacids[13,14,15]

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Phosphorus oxoacids are extensive, often commercially important, and sometimes structurally complicated. They all have acidic protons bound to oxygen atoms, some have nonacidic protons that are bonded directly to phosphorus and some contain phosphorus–phosphorus bonds.<sup>[17]</sup> Although many oxoacids of phosphorus are formed, only nine are commercially important, and three of them, hypophosphorous acid, phosphorous acid, and phosphoric acid, are particularly important.

Oxidation state	Formula	Name	Acidic protons	Compounds
+1	HH <sub>2</sub> PO <sub>2</sub>	hypophosphorous acid	1	acid, salts
+3	H <sub>3</sub> PO <sub>3</sub>	phosphorous acid (phosphonic acid)	2	acid, salts
+3	HPO <sub>2</sub>	metaphosphorous acid	1	salts
+4	$H_4P_2O_6$	hypophosphoric acid	4	acid, salts
+5	(HPO <sub>3</sub> ) <sub>n</sub>	metaphosphoric acids	n	salts (n = 3,4,6)
+5	H(HPO <sub>3</sub> ) <sub>n</sub> OH	polyphosphoric acids	n+2	acids, salts $(n = 1-6)$
+5	$H_5P_3O_{10}$	tripolyphosphoric acid	3	salts
+5	$H_4P_2O_7$	pyrophosphoric acid	4	acid, salts
+5	$H_3PO_4$	(ortho)phosphoric acid	3	acid, salts

Nitrides

The PN molecule is considered unstable, but is a product of crystalline phosphorus nitride decomposition at 1100 K. Similarly,  $H_2PN$  is considered unstable, and phosphorus nitride halogens like  $F_2PN$ ,  $Cl_2PN$ ,  $Br_2PN$ , and  $I_2PN$  oligomerise into cyclic polyphosphazenes. For example, compounds of the formula  $(PNCl_2)_n$  exist mainly as rings such as the trimer hexachlorophosphazene. The phosphazenes arise by treatment of phosphorus pentachloride with ammonium chloride:

 $PCl_5 + NH_4Cl \rightarrow 1/n (NPCl_2)_n + 4 HCl$ 

When the chloride groups are replaced by alkoxide (RO<sup>-</sup>), a family of polymers is produced with potentially useful properties.<sup>[47]</sup>

Sulfides

Phosphorus forms a wide range of sulfides, where the phosphorus can be in P(V), P(III) or other oxidation states. The three-fold symmetric  $P_4S_3$  is used in strike-anywhere matches.  $P_4S_{10}$  and  $P_4O_{10}$  have analogous structures.<sup>[48]</sup> Mixed oxyhalides and oxyhydrides of phosphorus(III) are almost unknown.

Organophosphorus compounds

Compounds with P-C and P-O-C bonds are often classified as organophosphorus compounds. They are widely used commercially. The PCl<sub>3</sub> serves as a source of  $P^{3+}$  in routes to organophosphorus(III) compounds. For example, it is the precursor to triphenylphosphine:

 $PCl_3 + 6 \text{ Na} + 3 \text{ } C_6\text{H}_5\text{Cl} \rightarrow P(C_6\text{H}_5)_3 + 6 \text{ NaCl}$ 

Treatment of phosphorus trihalides with alcohols and phenols gives phosphites, e.g. triphenylphosphite:  $PCl_3 + 3 C_6H_5OH \rightarrow P(OC_6H_5)_3 + 3 HCl$ 

Similar reactions occur for phosphorus oxychloride, affording triphenylphosphate: OPCl<sub>3</sub> + 3 C<sub>6</sub>H<sub>5</sub>OH  $\rightarrow$  OP(OC<sub>6</sub>H<sub>5</sub>)<sub>3</sub> + 3 HCl

# **II, DISCUSSION**

Sulfur compounds are chemical compounds formed the element sulfur (S). Common oxidation states of sulfur range from -2 to +6. Sulfur forms stable compounds with all elements except the noble gases.

Electron transfer reactions

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Lapis lazuli owes its blue color to a trisulfur radical anion  $(S_3)$ 

Sulfur polycations,  $S_8^{2+}$ ,  $S_4^{2+}$  and  $S_{16}^{2+}$  are produced when sulfur is reacted with oxidising agents in a strongly acidic solution.<sup>[1]</sup> The colored solutions produced by dissolving sulfur in oleum were first reported as early as 1804 by C.F. Bucholz, but the cause of the color and the structure of the polycations involved was only determined in the late 1960s.  $S_8^{2+}$  is deep blue,  $S_4^{2+}$  is yellow and  $S_{16}^{2+}$  is red.<sup>[2]</sup>

Reduction of sulfur gives various polysulfides with the formula  $S_x^{2-}$ , many of which have been obtained crystalline form. Illustrative is the production of sodium tetrasulfide:

 $4 \text{ Na} + S_8 \rightarrow 2 \text{ Na}_2S_4$ 

Some of these dianions dissociate to give radical anions, such as  $S_3$  gives the blue color of the rock lapis lazuli.



Two parallel sulfur chains grown inside a single-wall carbon nanotube (CNT, a). Zig-zag (b) and straight (c) S chains inside double-wall CNTs<sup>[3]</sup>

This reaction highlights a distinctive property of sulfur: its ability to catenate (bind to itself by formation of chains). Protonation of these polysulfide anions produces the polysulfanes,  $H_2S_x$  where x= 2, 3, and 4.<sup>[4]</sup> Ultimately, reduction of sulfur produces sulfide salts:

 $16 \text{ Na} + \text{S}_8 \rightarrow 8 \text{ Na}_2\text{S}$ 

The interconversion of these species is exploited in the sodium-sulfur battery.

#### Hydrogen sulfide

Treatment of sulfur with hydrogen gives hydrogen sulfide. When dissolved in water, hydrogen sulfide is mildly acidic:<sup>[5]</sup>

 $H_2S \rightleftharpoons HS^- + H^+$ 

Hydrogen sulfide gas and the hydrosulfide anion are extremely toxic to mammals, due to their inhibition of the oxygen-carrying capacity of hemoglobin and certain cytochromes in a manner analogous to cyanide and azide. Oxides

The two principal sulfur oxides are obtained by burning sulfur:

 $S + O_2 \rightarrow SO_2$  (sulfur dioxide)

 $2 \text{ SO}_2 + \text{O}_2 \rightarrow 2 \text{ SO}_3$  (sulfur trioxide)

Many other sulfur oxides are observed including the sulfur-rich oxides include sulfur monoxide, disulfur monoxide, disulfur dioxides, and higher oxides containing peroxo groups.



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# Halides

Sulfur reacts with fluorine to give the highly reactive sulfur tetrafluoride and the highly inert Sulfur hexafluoride.<sup>[6]</sup> Whereas fluorine gives S(IV) and S(VI) compounds, chlorine gives S(II) and S(I) derivatives. Thus, sulfur dichloride, disulfur dichloride, and higher chlorosulfanes arise from the chlorination of sulfur. Sulfuryl chloride and chlorosulfuric acid are derivatives of sulfuric acid; thionyl chloride (SOCl<sub>2</sub>) is a common reagent in organic synthesis.<sup>[7]</sup>

Pseudohalides

Sulfur oxidizes cyanide and sulfite to give thiocyanate and thiosulfate, respectively.

Metal sulfides

Sulfur reacts with many metals. Electropositive metals give polysulfide salts. Copper, zinc and silver are tarnished by sulfur. Although many metal sulfides are known, most are prepared by high temperature reactions of the elements.<sup>[8]</sup> Sulfide minerals contain the sulfide ( $S^{2-}$ ) or disulfide ( $S_{2-}^{2-}$ ) anions.

Organic compounds

Illustrative organosulfur compounds

Allicin, a chemical compound in garlic



(R)-cysteine, an amino acid containing a thiol group



Methionine, an amino acid containing a thioether



Diphenyl disulfide, a representative disulfide

Perfluorooctanesulfonic acid, a surfactant

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Dibenzothiophene, a component of crude oil



Penicillin, an antibiotic where "R" is the variable group

Some of the main classes of sulfur-containing organic compounds include the following:<sup>[9]</sup>

- Thiols or mercaptans (so called because they capture mercury as chelators) are the sulfur analogs of alcohols; treatment of thiols with base gives thiolate ions.
- Thioethers are the sulfur analogs of ethers.
- Sulfonium ions have three groups attached to a cationic sulfur center. Dimethylsulfoniopropionate (DMSP) is one such compound, important in the marine organic sulfur cycle.
- Sulfoxides and sulfones are thioethers with one and two oxygen atoms attached to the sulfur atom, respectively. The simplest sulfoxide, dimethyl sulfoxide, is a common solvent; a common sulfone is sulfolane.
- Sulfonic acids are used in many detergents.

Compounds with carbon–sulfur multiple bonds are uncommon, an exception being carbon disulfide, a volatile colorless liquid that is structurally similar to carbon dioxide. It is used as a reagent to make the polymer rayon and many organosulfur compounds. Unlike carbon monoxide, carbon monosulfide is stable only as an extremely dilute gas, found between solar systems[16,17]

Organosulfur compounds are responsible for some of the unpleasant odors of decaying organic matter. They are widely known as the odorant in domestic natural gas, garlic odor, and skunk spray. Not all organic sulfur compounds smell unpleasant at all concentrations: the sulfur-containing monoterpenoid (grapefruit mercaptan) in small concentrations is the characteristic scent of grapefruit, but has a generic thiol odor at larger concentrations. Sulfur mustard, a potent vesicant, was used in World War I as a disabling agent.<sup>[11]</sup>

Sulfur–sulfur bonds are a structural component used to stiffen rubber, similar to the disulfide bridges that rigidify proteins (see biological below). In the most common type of industrial "curing" or hardening and strengthening of natural rubber, elemental sulfur is heated with the rubber to the point that chemical reactions form disulfide bridges between isoprene units of the polymer. This process, patented in 1843, made rubber a major industrial product, especially in automobile tires. Because of the heat and sulfur, the process was named vulcanization, after the Roman god of the forge and volcanism.

# **III.RESULTS**

Silicon compounds are compounds containing the element silicon (Si). As a carbon group element, silicon often forms compounds in the +4 oxidation state, though many unusual compounds have been discovered that differ from expectations based on its valence electrons, including the silicides and some silanes. Metal silicides, silicon halides, and similar inorganic compounds can be prepared by directly reacting elemental silicon or silicon dioxide with stable metals or with halogens. Silanes, compounds of silicon and hydrogen, are often used as strong reducing agents, and can be prepared from aluminum–silicon alloys and hydrochloric acid.

Several inorganic compounds have been formed with silicon and other nonmetals such as sulfur and nitrogen; most of these compounds are highly incompatible with water. One of the most useful and successfully marketed inorganic silicon compounds is silicon carbide.

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Naturally occurring silicon is found in silicate and aluminosilicate minerals. One of the most common silicon compounds found in the Earth's crust is silicon dioxide or silica, which often occurs as quartz.

Organosilicon compounds are fairly stable due to the similarity in strength of the Si–C bond to the C–C bond. Organosilicates include silicone polymers.

Silicides





Many metal silicides are known, most of which have formulae that cannot be explained through simple appeals to valence: their bonding ranges from metallic to ionic and covalent.

 $_{6}$ . They are structurally more similar to the borides than the carbides, in keeping with the diagonal relationship between boron and silicon, although the larger size of silicon than boron means that exact structural analogies are few and far between. The heats of formation of the silicides are usually similar to those of the borides and carbides of the same elements, but they usually melt at lower temperatures.<sup>[1]</sup> Silicides are known for all stable elements in groups 1–10, with the exception of beryllium: in particular, uranium and the transition metals of groups 4–10 show the widest range of stoichiometries. Except for copper, the metals in groups 11–15 do not form silicides. Instead, most form eutectic mixtures, although the heaviest stable ones – mercury, thallium, lead, and bismuth – are completely immiscible with liquid silicon.<sup>[2]</sup>

Usually, silicides are prepared by direct reaction of the elements. For example, the alkali metals and alkaline earth metals react with silicon or silicon oxide to give silicides. Nevertheless, even with these highly electropositive elements true silicon anions are not obtainable, and most of these compounds are semiconductors. For example, the alkali metal silicides .

The silicides of the group 1 and 2 metals usually are more reactive than the transition metal silicides. The latter usually do not react with aqueous reagents, except for hydrofluoric acid; however, they do react with much more aggressive reagents such as liquid potassium hydroxide, or gaseous fluorine or chlorine when red-hot. The pre-transition metal silicides instead readily react with water and aqueous acids, usually producing hydrogen or silanes[18,19]

Products often vary with the stoichiometry of the silicide reactant. For example,  $Ca_2Si$  is polar and non-conducting and has the anti-PbCl<sub>2</sub> structure with single isolated silicon atoms, and reacts with water to produce calcium hydroxide, hydrated silicon dioxide, and hydrogen gas. CaSi with its zigzag chains of silicon atoms instead reacts to give silanes and polymeric SiH<sub>2</sub>, while CaSi<sub>2</sub> with its puckered layers of silicon atoms does not react with water, but will react with dilute hydrochloric acid: the product is a yellow polymeric solid with stoichiometry  $Si_2H_2O$ .<sup>[2]</sup>

Speculation on silicon hydride chemistry started in the 1830s, contemporary with the development of synthetic organic chemistry. Silane itself, as well as trichlorosilane, were first synthesised by Friedrich Wöhler and Heinrich Buff in 1857

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by reacting aluminium–silicon alloys with hydrochloric acid, and characterised followed in 1902, when it was first made by Henri Moissan and Samuel Smiles by the protonolysis of magnesium silicides. Further investigation had to wait until 1916 because of the great reactivity and thermal instability of the silanes; it was then that Alfred Stock began to study silicon hydrides in earnest with new greaseless vacuum techniques, as they were found as contaminants of his focus, the boron hydrides. The names silanes and boranes are his, based on analogy with the alkanes.<sup>[4][5][6]</sup> The Moissan and Smiles method of preparation of silanes and silane derivatives via protonolysis of metal silicides is still used, although the yield is lowered by the hydrolysis of the products that occurs simultaneously, so that the preferred route today is to treat substituted silanes with hydride reducing agents such as lithium aluminium hydride in etheric solutions at low temperatures. Direct reaction of HX or RX with silicon, possibly with a catalyst such as copper, is also a viable method of producing substituted silanes.<sup>[4]</sup>

The silanes comprise a homologous series of silicon hydrides with a general formula of Si are also known. The first two, silane and disilane, are colourless gases; the heavier members of the series are volatile liquids. All silanes are very reactive and catch fire or explode spontaneously in air. They become less thermally stable with room temperature, so that only silane is indefinitely stable at room temperature, although disilane does not decompose very quickly (only 2.5% of a sample decomposes after the passage of eight months).<sup>[4]</sup> They decompose to form polymeric polysilicon hydride and hydrogen gas.<sup>[7][8]</sup> As expected from the difference in atomic weight, the silanes are less volatile than the corresponding alkanes and boranes, but more so than the corresponding germanes. They are much more reactive than the corresponding alkanes, because of the larger radius of silicon compared to carbon facilitating nucleophilic attack at the silicon, the greater polarity of the Si-H bond compared to the C-H bond, and the ability of silicon to expand its octet and hence form adducts and lower the reaction's activation energy.<sup>[4]</sup>

Silane pyrolysis gives polymeric species and finally elemental silicon and hydrogen; indeed ultrapure silicon is commercially produced by the pyrolysis of silane. While the thermal decomposition of alkanes starts by the breaking of a C–H or C–C bond and the formation of radical intermediates, polysilanes decompose by eliminating silylenes :SiH  $_2$  or :SiHR, as the activation energy of this process (~210 kJ/mol) is much less than the Si–Si and Si–H bond energies. While pure silanes do not react with pure water or dilute acids, traces of alkali catalyse immediate hydrolysis to hydrated silicon dioxide. If the reaction is carried out in methanol, controlled solvolysis results in the products SiH The Si–H bond also adds to alkenes, a reaction which proceeds slowly and speeds up with increasing substitution of the silane involved. At 450 °C, silane participates in an addition reaction with acetone, as well as a ring-opening reaction with ethylene oxide. Direct reaction of the silanes with chlorine or bromine results in explosions at room temperature, but the reaction of silane with bromine at -80 °C is controlled and yields bromosilane and dibromosilane.

 $(KSiH_3)$  are very useful synthetic intermediates in the production of more complicated silicon-containing compounds: the latter is a colourless crystalline ionic solid containing K<sup>+</sup> cations and SiH<sup>-</sup><sub>3</sub> anions in the NaCl structure, and is made by the reduction of silane by potassium metal.<sup>[9]</sup> Additionally, the reactive hypervalent species With suitable organic substituents it is possible to produce stable polysilanes: they have surprisingly high electric conductivities, arising from sigma delocalisation of the electrons in the chain.<sup>[10]</sup>

Halides

Silicon and silicon carbide readily react with all four stable halogens, forming the colourless, reactive, and volatile silicon tetrahalides.<sup>[11]</sup> Silicon tetrafluoride also may be made by fluorinating the other silicon halides, and is produced by the attack of hydrofluoric acid on glass.<sup>[12]</sup> Heating two different tetrahalides together also produces a random mixture of mixed halides, which may also be produced by halogen exchange reactions. The melting and boiling points of these species usually rise with increasing atomic weight, though there are many exceptions: for example, the melting and boiling points drop The shift from the hypoelectronic elements in Group 13 and earlier to the Group 14 elements is illustrated by the change from an infinite ionic structure in aluminium fluoride to a lattice of simple covalent silicon tetrafluoride molecules, as dictated by the lower electronegativity of aluminium than silicon, the stoichiometry (the +4 oxidation state being too high for true ionicity), and the smaller size of the silicon atom compared to the aluminium atom.<sup>[11]</sup>

Silicon tetrachloride is manufactured on a huge scale as a precursor to the production of pure silicon, silicon dioxide, and some silicon esters.<sup>[11]</sup> The silicon tetrahalides hydrolyse readily in water, unlike the carbon tetrahalides, again because of the larger size of the silicon atom rendering it more open to nucleophilic attack and the ability of the silicon atom to expand its octet which carbon lacks.<sup>[12]</sup> The reaction of silicon tetrafluoride with excess hydrofluoric acid produces the octahedral hexafluorosilicate anion SiF<sup>2–</sup>

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also are known. While catenation in carbon compounds is maximised in the hydrogen compounds rather than the halides, the opposite is true for silicon A suggested explanation for this phenomenon is the compensation for the electron loss of silicon to the more electronegative halogen atoms by pi backbonding from the filled  $p_{\pi}$  orbitals on the halogen atoms to the empty  $d_{\pi}$  orbitals on silicon: this is similar to the situation of carbon monoxide in metal carbonyl complexes and explains their stability. These halopolysilanes may be produced by comproportionation of silicon tetrahalides with elemental silicon, or by condensation of lighter halopolysilanes (trimethylammonium being a useful catalyst for this reaction).<sup>[11]</sup>

Silica

Silicon dioxide known as silica, is one of the best-studied compounds, second only to water. Twelve different crystal modifications of silica are known, the most common being  $\alpha$ -quartz, a major constituent of many rocks such as granite and sandstone. It also is known to occur in a pure form as rock crystal; impure forms are known as rose quartz, smoky quartz, morion, amethyst, and citrine. Some poorly crystalline forms of quartz are also known, such as chalcedony, chrysoprase, carnelian, agate, onyx, jasper, heliotrope, and flint. Other modifications of silicon dioxide are known in some other minerals such as tridymite and cristobalite, as well as the much less common coesite and stishovite. Biologically generated forms are also known as kieselguhr and diatomaceous earth. Vitreous silicon dioxide is known as tektites, and obsidian, and rarely as lechatelierite. Some synthetic forms are known as keatite. Opals are composed of complicated crystalline aggregates of partially hydrated silicon dioxide.<sup>[13]</sup>



Quartz



Agate



Tridymite



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## Cristobalite



Coesite

Most crystalline forms of silica are made of infinite arrangements of SiO tetrahedra (with Si at the center) connected at their corners, with each oxygen atom linked to two silicon atoms. In the thermodynamically stable room-temperature form,  $\alpha$ -quartz, these tetrahedra are linked in intertwined helical chains with two different Si–O distances (159.7 and 161.7 pm) with a Si–O–Si angle of 144°. These helices can be either leftor right-handed, so that individual  $\alpha$ -quartz crystals are optically active. At 537 °C, this transforms quickly and reversibly into the similar  $\beta$ -quartz, with a change of the Si–O–Si angle to 155° but a retention of handedness. Further heating to 867 °C results in another reversible phase transition to β-tridymite, in which some Si-O bonds are broken to allow for the arrangement of the SiO tetrahedra into a more open and less dense hexagonal structure. This transition is slow and hence tridymite occurs as a metastable mineral even below this transition temperature; when cooled to about 120 °C it quickly and reversibly transforms by slight displacements of individual silicon and oxygen atoms to  $\alpha$ -tridymite, similarly to the transition from  $\alpha$ -quartz to  $\beta$ -quartz.  $\beta$ -tridymite slowly transforms to cubic  $\beta$ -cristobalite at about 1470 °C, which once again exists metastably below this transition temperature and transforms at 200–280  $^{\circ}$ C to  $\alpha$ -cristobalite via small atomic displacements.  $\beta$ -cristobalite melts at 1713 °C; the freezing of silica from the melt is quite slow and vitrification, or the formation of a glass, is likely to occur instead. In vitreous silica, the SiO tetrahedra remain corner-connected, but the symmetry and periodicity of the crystalline forms are lost. Because of the slow conversions between these three forms, it is possible upon rapid heating to melt  $\beta$ -quartz (1550 °C) or  $\beta$ tridymite (1703 °C). Silica boils at approximately 2800 °C. Other high-pressure forms of silica are known, such as coesite and stishovite: these are known in nature, formed under the shock pressure of a meteorite impact and then rapidly quenched to preserve the crystal structure. Similar melting and cooling of silica occurs following lightning strikes, forming glassy lechatelierite. W-silica is an unstable low-density form involving SiO tetrahedra sharing opposite edges instead of corners, forming parallel chains similarly to silicon disulfide

Silica is rather inert chemically. It is not attacked by any acids other than hydrofluoric acid. However, it slowly dissolves in hot concentrated alkalis, and does so rather quickly in fused metal hydroxides or carbonates, to give metal silicates. Among the elements, it is attacked only by fluorine at room temperature to form silicon tetrafluoride: hydrogen and carbon also react, but require temperatures over 1000 °C to do so. Silica nevertheless reacts with many metal and metalloid oxides to form a wide variety of compounds important in the glass and ceramic industries above all, but also have many other uses: for example, sodium silicate is often used in detergents due to its buffering, saponifying, and emulsifying properties.<sup>[14]</sup>

Silicic acid - adding water to silica drops its melting point by around 800 °C due to the breaking of the structure by replacing Si-O-Si linkages with terminating Si-OH groups. Increasing water concentration results in the formation of hydrated silica gels and colloidal silica dispersions. Many hydrates and silicic acids exist in the most dilute of aqueous solutions, but these are rather insoluble and quickly precipitate and variable condense and cross-link to form various polysilicic acids of combinations n, similar to the behaviour of boron, aluminium, and iron, among other elements. Hence, although some simple silicic acids have been identified in dilute solutions, such as orthosilicic acid Si(OH) 4 and metasilicic acid SiO(OH)

<sub>2</sub>, none of these are likely to exist in the solid state.<sup>[14]</sup>

#### Silicate minerals

Typical coordination of metal cations in silicates (ionic radii in pm)<sup>[15]</sup>

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CN 4	Li <sup>1</sup> (59)	Be <sup>II</sup> (27)	Al <sup>III</sup> (39)	Si <sup>IV</sup> (26)	
CN 6	Na <sup>I</sup> (102)	Mg <sup>II</sup> (72)	$\mathrm{Al}^{\mathrm{III}}(54)$	Ti <sup>IV</sup> (61)	Fe <sup>II</sup> (78)
CN 8	K <sup>I</sup> (151)	Ca <sup>II</sup> (112)			
CN 12	K <sup>I</sup> (164)				

About 95% of the Earth's crustal rocks are made of silica or silicate and aluminosilicate minerals, as reflected in oxygen, silicon, and aluminium being the three most common elements in the crust (in that order).<sup>[15]</sup> Measured by mass, silicon makes up 27.7% of the Earth's crust.<sup>[16]</sup> Pure silicon crystals are very rarely found in nature, but notable exceptions are crystals as large as 0.3 mm across found during sampling gases from the Kudriavy volcano on Iturup, one of the Kuril Islands.<sup>[17][18]</sup>

Silicate and aluminosilicate minerals have many different structures and varying stoichiometry, but they may be classified following some general principles. Tetrahedral SiO units are common to almost all these compounds, either as discrete structures, or combined into larger units by the sharing of corner oxygen atoms. These may be divided into neso-silicates (discrete SiO units) sharing no oxygen atoms, soro-silicates (discrete Si units) sharing one, cyclo-silicates (closed ring structures) and ino-silicates (continuous chain or ribbon structures) both sharing two, phyllo-silicates (continuous sheets) sharing three, and tecto-silicates (continuous three-dimensional frameworks) sharing four. The lattice of oxygen atoms that results is usually close-packed, or close to it, with the charge being balanced by other cations in various different polyhedral sites according to size.<sup>[19]</sup>

The orthosilicates  $_4$  (phenacite) is unusual as both Be<sup>II</sup> and Si<sup>IV</sup> occupy tetrahedral four-coordinated sites; the other divalent cations instead occupy six-coordinated octahedral sites and often isomorphously replace each other as in olivine, (Mg,Fe,Mn)

<sup>4</sup>, demands eight-coordination of the  $Zr^{IV}$  cations due to stoichiometry and because of their larger ionic radius (84 pm). Also significant are the garnets in which the divalent cations (e.g. Ca, Mg, Fe) are eight-coordinated and the trivalent ones are six-coordinated (e.g. Al, Cr, Fe). Regular coordination is not always present: for example, it is not found which mixes six- and eight-coordinate sites for Ca<sup>II</sup>. Soro-silicates, involving discrete double or triple tetrahedral units, are quite rare: metasilicates involving units of corner-abutting tetrahedra forming a polygonal ring are also known.<sup>[15]</sup>

Chain metasilicates, form by corner-sharing of an indefinite chain of linked SiO tetrahedra. Many differences arise due to the differing repeat distances of conformation across the line of tetrahedra. A repeat distance of two is most common, as in most pyroxene minerals, but repeat distances of one, three, four, five, six, seven, nine, and twelve are also known. These chains may then link across each other to form double chains and ribbons, as in the asbestos minerals, involving repeated chains of cyclic tetrahedron rings.<sup>[15]</sup>



A typical zeolite structure

Layer silicates, such as the clay minerals and the micas, are very common, and often are formed by horizontal crosslinking of metasilicate chains or planar condensation of smaller units. An example is kaolinite in many of these minerals cation and anion replacement is common, so that for example tetrahedral Si<sup>IV</sup> may be replaced by Al<sup>III</sup>, octahedral Al<sup>III</sup> by Mg<sup>II</sup>, by  $F^-$ 

. Three-dimensional framework aluminosilicates are structurally very complex; they may be conceived of as starting

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from the structure, but having replaced up to one-half of the Si<sup>IV</sup> atoms with Al<sup>III</sup>, they require more cations to be included in the structure to balance charge. Examples include feldspars (the most abundant minerals on the Earth), zeolites, and ultramarines. Many feldspars can be thought of as forming part of the ternary system Their lattice is destroyed by high pressure prompting Al<sup>III</sup> to undergo six-coordination rather than four-coordination, and this reaction destroying feldspars may be a reason for the Mohorovičić discontinuity, which would imply that the crust and mantle have the same chemical composition, but different lattices, although this is not a universally held view. Zeolites have many polyhedral cavities in their frameworks (truncated cuboctahedra being most common, but other polyhedra also are known as zeolite cavities), allowing them to include loosely bound molecules such as water in their structure. Ultramarines alternate silicon and aluminium atoms and include a variety of other anions such as Cl<sup>-</sup>, SO<sup>2-</sup>

and  $S^{2-}$ 

<sup>4</sup>, <sub>2</sub>, but are otherwise similar to the feldspars.<sup>[15]</sup>

Other inorganic compounds

Silicon disulfide is formed by burning silicon in gaseous sulfur at 100 °C; sublimation of the resulting compound in nitrogen results in white, flexible long fibers reminiscent of asbestos with a structure similar to W-silica. This melts at 1090 °C and sublimes at 1250 °C; at high temperature and pressure this transforms to a crystal structure analogous to cristobalite. 2 lacks the variety of structures of SiO 2, and quickly hydrolyses to silica and hydrogen sulfide. It is also ammonolysed quickly and completely by

<sub>2</sub>, and quickly hydrolyses to silica and hydrogen sulfide. It is also ammonolysed quickly and completely by liquid ammonia as follows to form an imide:<sup>[20]</sup>

It reacts with the sulfides of sodium, magnesium, aluminium, and iron to form metal thiosilicates: reaction with ethanol results in tetraethylsilicate Si(OEt)

<sup>4</sup> and hydrogen sulfide. Ethylsilicate is useful as its controlled hydrolysis produces adhesive or film-like forms of silica. Reacting hydrogen sulfide with silicon tetrahalides yields silicon thiohalides <sup>4</sup>. Despite the double bond rule, stable organosilanethiones RR'Si=S have been made thanks to the stabilising mechanism of intermolecular coordination via an amine group.<sup>[21]</sup>

Silicon nitridemay be formed by directly reacting silicon with nitrogen above 1300 °C, but a more economical means of production is by heating silica and coke in a stream of nitrogen and hydrogen gas at 1500 °C. It would make a promising ceramic if not for the difficulty of working with and sintering it: chemically, it is near-totally inert, and even above 1000 °C it keeps its strength, shape, and continues to be resistant to wear and corrosion. It is very hard (9 on the Mohs hardness scale), dissociates only at 1900 °C at 1 atm, and is quite dense (density 3.185 g/cm<sup>3</sup>), because of formed by heating silicon and silica at 1450 °C in an argon stream containing 5% nitrogen gas, involving 4-coordinate silicon and 3-coordinate nitrogen alternating in puckered hexagonal tilings interlinked by non-linear Si–O–Si linkages to each other.<sup>[21]</sup>

Reacting silyl halides with ammonia or alkylammonia derivatives in the gaseous phase or in ethanolic solution produces various volatile silylamides, which are silicon analogues of the amines:<sup>[21]</sup>

Many such compounds have been prepared, the only known restriction being that the nitrogen is always tertiary, and species containing the SiH–NH group are unstable at room temperature. The stoichiometry around the nitrogen atom in compounds such as  $N(SiH_3)_3$  is planar. Similarly, trisilylamines are weaker as ligands than their carbon analogues, the tertiary amines, although substitution of some SiH<sub>3</sub> groups by CH<sub>3</sub> groups mitigates this weakness. For example,  $N(SiH_3)_3$  does not form an adduct with BH<sub>3</sub> at all, while MeN(SiH<sub>3</sub>)<sub>2</sub> and Me<sub>2</sub>NSiH<sub>3</sub> form adducts at low temperatures that decompose upon warming. Some silicon analogues of imines, with a Si=N double bond, are known: the first found was Bu<sup>t</sup><sub>2</sub>Si=N–SiBu<sup>t</sup><sub>3</sub>, which was discovered in 1986.<sup>[21]</sup>

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Silicon carbide

Silicon carbide (SiC) was first made by Edward Goodrich Acheson in 1891, who named it carborundum to reference its intermediate hardness and abrasive power between diamond (an allotrope of carbon) and corundum (aluminium oxide). He soon founded a company to manufacture it, and today about one million tonnes are produced each year.<sup>[22]</sup> Silicon carbide exists in about 250 crystalline forms.<sup>[23]</sup> The polymorphism of SiC is characterized by a large family of similar crystalline structures called polytypes. They are variations of the same chemical compound that are identical in two dimensions and differ in the third. Thus they can be viewed as layers stacked in a certain sequence.<sup>[24]</sup> It is made industrially by reduction of quartz sand with excess coke or anthracite at 2000–2500 °C in an electric furnace:<sup>[22]</sup>

$$SiO_2 + 2 C \rightarrow Si + 2 C$$
  
Si + C  $\rightarrow$  SiC

It is the most thermally stable binary silicon compound, only decomposing through loss of silicon starting from around 2700 °C. It is resistant to most aqueous acids, phosphoric acid being an exception. It forms a protective layer of silicon dioxide on the surface and hence only oxidises appreciably in air above 1000 °C; removal of this layer by molten hydroxides or carbonates leads to quick oxidation. Silicon carbide is rapidly attacked by chlorine gas. It is mostly used as an abrasive and a refractory material, as it is chemically stable and very strong, and it fractures to form a very sharp cutting edge. It is also useful as an intrinsic semiconductor, as well as an extrinsic semiconductor upon being doped.<sup>[22]</sup> In its diamond-like behavior it serves as an illustration of the chemical similarity between carbon and silicon.<sup>[25]</sup>

Organosilicon compounds



A hydrosilylation reaction, in which Si-H is added to an unsaturated substrate

Because the Si–C bond is close in strength to the C–C bond, organosilicon compounds tend to be markedly thermally and chemically stable. For example, tetraphenylsilane (SiPh 4) may be distilled in air even at its boiling point of 428 °C, and so may its substituted derivatives which boil at 378 °C and 305 °C respectively. Furthermore, since carbon and silicon are chemical congeners, organosilicon chemistry shows some significant similarities with carbon chemistry, for example in the propensity of such compounds for catenation and forming multiple bonds.<sup>[25]</sup> However, significant differences also arise: since silicon is more electropositive than carbon, bonds to more electronegative elements are generally stronger with silicon than with carbon, and vice versa. Thus the Si–F bond is significantly stronger than even the C–F bond and is one of the strongest single bonds, while the Si–H bond is much weaker than the C–H bond and is readily broken. Furthermore, the ability of silicon to expand its octet is not

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shared by carbon, and hence some organosilicon reactions have no organic analogues. For example, nucleophilic attack on silicon does not proceed by the  $S_N 2$  or  $S_N 1$  processes, but instead goes through a negatively charged true pentacoordinate intermediate and appears like a substitution at a hindered tertiary atom. This works for silicon, unlike for carbon, because the long Si–C bonds reduce the steric hindrance and there are no geometric constraints for nucleophilic attack, unlike for example a C–O  $\sigma^*$  antibonding orbital. Nevertheless, despite these differences, the mechanism is still often called " $S_N 2$  at silicon" for simplicity.<sup>[26]</sup>

One the useful silicon-containing is trimethylsilyl, Me of most groups <sub>3</sub>Si-. The Si-C bond connecting it to the rest of the molecule is reasonably strong, allowing it to remain while the rest of the molecule undergoes reactions, but is not so strong that it cannot be removed specifically when needed, for example by the fluoride ion, which is a very weak nucleophile for carbon compounds but a very strong one for organosilicon compounds. It may be compared to acidic protons; while trimethylsilyl is removed by hard nucleophiles instead of bases, both removals usually promote elimination. As a general rule, while saturated carbon is best attacked by nucleophiles that are neutral compounds, those based on nonmetals far down on the periodic table (e.g. sulfur, selenium, or iodine), or even both, silicon is best attacked by charged nucleophiles, particularly those involving such highly electronegative nonmetals as oxygen, fluorine, or chlorine. For example, enolates react at the carbon in haloalkanes, but at the oxygen in silyl chlorides; and when trimethylsilyl is removed from an organic molecule using hydroxide as a nucleophile, the product of the reaction is not the silanol as one would expect from using carbon chemistry as an analogy, because the siloxide is strongly nucleophilic and attacks the original molecule to yield the silyl ether hexamethyldisiloxane, (Me  $_3Si$ )

 $_{2}$ O. Conversely, while the  $S_{N}2$  reaction is mostly unaffected by the presence of a partial positive charge ( $\delta$ +) at the carbon, the analogous " $S_{N}2$ " reaction at silicon is so affected. Thus, for example, the silyl triflates are so electrophilic that they react  $10^{8}$  to  $10^{9}$  times faster than silyl chlorides with oxygen-containing nucleophiles. Trimethylsilyl triflate is in particular a very good Lewis acid and is used to convert carbonyl compounds to acetals and silyl enol ethers, reacting them together analogously to the aldol reaction.<sup>[26]</sup>

Si–C bonds are commonly formed in three ways. In the laboratory, preparation is often carried out in small quantities by reacting tetrachlorosilane (silicon tetrachloride) with organolithium, Grignard, or organoaluminium reagents, or by catalytic addition of Si–H across C=C double bonds. The second route has the drawback of not being applicable to the most important silanes, the methyl and phenyl silanes. Organosilanes are made industrially by directly reacting alkyl or aryl halides with silicon with 10% by weight metallic copper as a catalyst. Standard organic reactions suffice to produce many derivatives; the resulting organosilanes are often significantly more reactive than their carbon congeners, readily undergoing hydrolysis, and condensation to form cyclic oligomers or linear polymers.<sup>[25]</sup>



Structure of polydimethylsiloxane, the principal component of silicones

# **IV.CONCLUSION**

A period 3 element is an element found on the third period (row) of the periodic table. The row has eight elements sodium, magnesium, aluminium, silicon, phosphorus, sulfur, chlorine, and argon.

Period 3 elements have electrons in the first three electron shells. The first and second electron shells are always full. The third electron shell (valence electrons) fills when atomic number gets bigger. Two electrons join the 3s orbital, and six electrons join the 3p orbitals.[20]

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