

Table 9.2 Coordination geometries of silicon

Coordination number	Examples
2 (bent)	SiF ₂ (g), SiMe ₂ (matrix, 77 K), [$\overline{\text{SiNBu}^+\text{CH}=\text{CHNBu}^+}$] (1) ⁽¹⁴⁾
3 (planar)	Silabenzene, SiC ₅ H ₆ , ⁽¹⁵⁾ silatoluene, C ₅ H ₅ SiMe ⁽¹⁶⁾
3 (pyramidal)	Si ₄ ⁴⁻ , (?)SiH ₃ ⁻ in KSiH ₃ (NaCl structure)
4 (tetrahedral)	SiH ₄ , SiX ₄ , SiX _n Y _{4-n} , SiO ₂ , silicates, etc.
4 (planar)	(see text) ⁽¹⁸⁾ (2)
4 (see-saw, C _{2v})	SiLi ₄ (3) ⁽¹⁹⁾
5 (trigonal bipyramidal)	SiX ₅ ⁻ , <i>cyclo</i> -[Me ₂ NSiH ₃] ₅ , [Si(O ₂ C ₆ H ₄) ₂ (OPPh ₃)] (4) ⁽²⁰⁾
5 (square pyramidal)	[Si(O ₂ C ₆ H ₄) ₂ {OP(NC ₅ H ₁₀)}] (5), ⁽²⁰⁾ [SiF(O ₂ C ₆ H ₄) ₂] ⁽²¹⁾
6 (octahedral)	SiF ₆ ²⁻ , [Si(acac) ₃] ⁺ , [L ₂ SiX ₄], SiO ₂ (stishovite), SiP ₂ O
7 (capped trig. antiprism)	[(2-(Me ₂ NCH ₂)C ₆ H ₄) ₃ SiH] (6) ⁽²²⁾
8 (cubic)	Mg ₂ Si (antifluorite)
9 (capped square antiprism)	[μ ₈ -SiCo ₉ (CO) ₂₁] ²⁻ (7) ⁽²³⁾
10 (various)	TiSi ₂ , CrSi ₂ , MoSi ₂ , ⁽²⁴⁾ [Si(η ⁵ -C ₅ Me ₅) ₂] (8) ⁽²⁵⁾

still far from being unequivocally established.⁽¹⁸⁾ However, a 'one-sided' C_{2v} geometry for SiLi₄ (3) seems probable.⁽¹⁹⁾ Five-coordinate Si can be either trigonal bipyramidal or square pyramidal, e.g. (4), (5), etc.^(20,21) Numerous examples of octahedral 6-coordination are known. A single example of 7-coordinate Si has been identified, (6)⁽²²⁾ and there are occasional examples of higher coordination numbers. Thus, Si has cubic 8-fold coordination in Mg₂Si which has the antifluorite structure, Si occupying the Ca sites and Mg the F sites of the fluorite lattice (p. 118). The capped square antiprismatic structure of the anion [SiCo₉(CO)₂₁]²⁻ has essentially 9-fold coordination about the encapsulated Si atom (7), with Si-Co_{base} 231 pm, Si-Co_{upper} 228 pm and Si-Co_{cap} 252.7 pm; each of the four basal Co atoms has two terminal CO ligands, each of the

other five Co atoms has one, and there are eight bridging CO groups.⁽²³⁾ The coordination number 10 is found in the structures of several transition metal silicides⁽²⁴⁾ and in decamethylsilicocene (8). The crystal structure of this latter compound reveals two types of molecular geometry; one-third of the molecules have the two rings parallel and staggered as in [Fe(C₅Me₅)₂] with Si-C 242 pm whereas the other two-thirds have non-parallel rings, implying a stereochemically active lone pair of electrons on the Si atom.⁽²⁵⁾ The bent (C_s) structure persists in the gas phase, the angle between the two C₅ planes being 22°.

9.3 Compounds

9.3.1 Silicides^(26,27)

As with borides (p. 145) and carbides (p. 297) the formulae of metal silicides cannot be rationalized by the application of simple valency rules, and

¹⁸ W. HÖNLE, U. DETTLAUF-WEGLIKOWSKA, L. WALZ and H. G. VON SCHNERING, *Angew. Chem. Int. Edn. Engl.* **28**, 623-4 (1989), and references cited therein.

¹⁹ P. VON RAGUÉ SCHLEYER and A. E. REED, *J. Am. Chem. Soc.* **110**, 4453-4 (1988).

²⁰ E. HEY-HAWKINS, U. DETTLAUF-WEGLIKOWSKA, D. THIERY and H. G. VON SCHNERING, *Polyhedron* **11**, 1789-94 (1992). See also T. VAN DEN ANKER, B. S. JOLLY, M. F. LAPPERT, C. L. RASTON, B. W. SKELTON and A. H. WHITE, *J. Chem. Soc., Chem. Commun.*, 1006-8 (1990).

²¹ J. J. HARLAND, R. O. DAY, J. F. VOLLANO, A. C. SAU and R. R. HOLMES, *J. Am. Chem. Soc.* **103**, 5269-70 (1981).

²² C. BRELLIERE, F. CARRÉ, R. J. P. CORRIU and G. ROYO, *Organometallics* **7**, 1006-8 (1988).

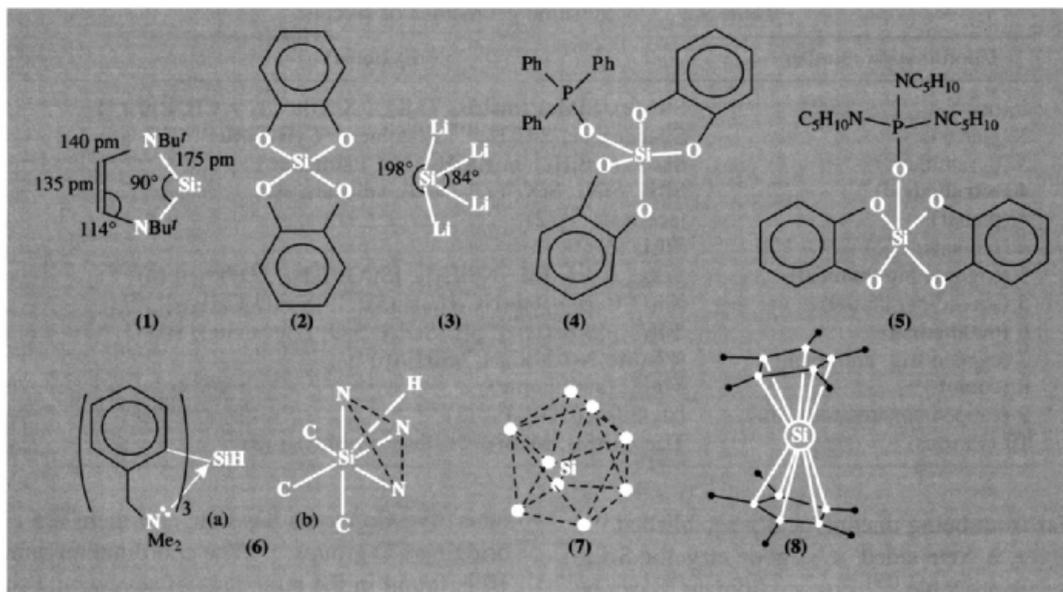
²³ K. M. MACKAY, B. K. NICHOLSON, W. T. ROBINSON and A. W. SIMS, *J. Chem. Soc., Chem. Commun.*, 1276-7 (1984).

²⁴ A. F. WELLS, *Structural Inorganic Chemistry*, 5th edn., Oxford University Press, Oxford, pp. 987-91 (1984).

²⁵ P. JUTZI, U. HOLTSMANN, D. KANNE, C. KRÜGER, R. BLOM, R. GLEITER and I. HYLAKRYSPIKIN *Chem. Ber.* **122**, 1629-39 (1989).

²⁶ A. S. BEREZHAI, *Silicon and its Binary Systems*, Consultants Bureau, New York, 1960, 275 pp.

²⁷ B. ARONSSON, T. LUNDSTRÖM and S. RUNDQVIST, *Borides, Silicides, and Phosphides*, Methuen, London, 1965, 120 pp.

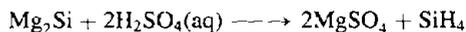
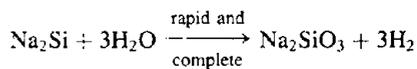


the bonding varies from essentially metallic to ionic and covalent. Observed stoichiometries include M_6Si , M_5Si , M_4Si , $M_{15}Si_4$, M_3Si , M_5Si_2 , M_2Si , M_5Si_3 , M_3Si_2 , MSi , M_2Si_3 , MSi_2 , MSi_3 and MSi_6 . Silicon, like boron, is more electropositive than carbon, and structurally the silicides are more closely related to the borides than the carbides (cf. diagonal relation, p. 27). However, the covalent radius of Si (118 pm) is appreciably larger than for B (88 pm) and few silicides are actually isostructural with the corresponding borides. Silicides have been reported for virtually all elements in Groups 1–10 except Be, the greatest range of stoichiometries being shown by the transition metals in Groups 4–10 and uranium. No silicides are known for the metals in Groups 11–15 except Cu; most form simple eutectic mixtures, but the heaviest post-transition metals Hg, Tl, Pb and Bi are completely immiscible with molten Si.

Some metal-rich silicides have isolated Si atoms and these occur either in typical metal-like structures or in more polar structures. With increasing Si content, there is an increasing tendency to catenate into isolated Si_2 or Si_4 , or into chains, layers or 3D networks of Si atoms. Examples are in Table 9.3 and further structural details are in refs. 24, 26 and 27.

Silicides are usually prepared by direct fusion of the elements but coreduction of SiO_2 and a metal oxide with C or Al is sometimes used. Heats of formation are similar to those of borides and carbides but mps are substantially lower; e.g. TiC 3140°, TiB_2 2980°, $TiSi_2$ 1540°; and TaC 3800°, TaB_2 3100°, $TaSi_2$ 1560°C. Few silicides melt as high as 2000–2500°, and above this temperature only SiC is solid (decomp \sim 2700°C).

Silicides of groups 1 and 2 are generally much more reactive than those of the transition elements (cf. borides and carbides). Hydrogen and/or silanes are typical products; e.g.:



Products also depend on stoichiometry (i.e. structural type). For example, the polar, non-conducting Ca_2Si (anti- $PbCl_2$ structure with isolated Si atoms) reacts with water to give $Ca(OH)_2$, SiO_2 (hydrated), and H_2 , whereas $CaSi$ (which features zigzag Si chains) gives silanes and the polymeric SiH_2 . By contrast $CaSi_2$, which has puckered layers of Si atoms, does not react with pure water, but with dilute hydrochloric acid it yields a yellow polymeric solid of overall composition Si_2H_2O . Transition metal silicides

Table 9.3 Structural units in metal silicides

Unit	Examples	
Isolated Si	Cu ₅ Si (β -Mn structure)	} Metal structures (good electrical conductors)
	M ₃ Si (β -W structure) M = V, Cr, Mo	
	Fe ₃ Si (Fe ₃ Al superstructure)	} Non-metal structures (non-conductors)
	Mn ₃ Si (random bcc)	
	M ₂ Si (anti-CaF ₂); M = Mg, Ge, Sn, Pb	}
	M ₂ Si (anti-PbCl ₂); M = Ca, Ru, Ce, Rh, Ir, Ni	
Si ₂ pairs	U ₃ Si ₂ (Si-Si 230 pm), also for Hf and Th	
Si ₄ tetrahedra	KS ₂ Si (Si-Si 243 pm), i.e. [M ⁺] ₄ [Si ₄] ⁴⁻ cf. isoelectronic P ₄ (M = Li, K, Rb, Cs; also for M ₄ Ge ₄)	
Si chains	USi (FeB structure) (Si-Si 236 pm); also for Ti, Zr, Hf, Th, Ce, Pu CaSi (CrB structure) (Si-Si 247 pm); also for Sr, Y	
Plane hexagonal Si nets	β -USi ₂ (AlB ₂ structure) (Si-Si 222-236 pm); also for other actinoids and lanthanoids	
Puckered hexagonal Si nets	CaSi ₂ (Si-Si 248 pm) — as in "puckered graphite" layer	
Open 3D Si frameworks	SrSi ₂ , α -ThSi ₂ (Si-Si 239 pm; closely related to AlB ₂), α -USi ₂	

are usually inert to aqueous reagents except HF, but yield to more aggressive reagents such as molten KOH, or F₂ (Cl₂) at red heat.

9.3.2 Silicon hydrides (silanes)

The great development which occurred in synthetic organic chemistry from the 1830s onward encouraged early speculations that a similar extensive chemistry might be generated based on Si. The first silanes were made in 1857 by F. Wöhler and H. Buff who reacted Al/Si alloys with aqueous HCl; the compounds prepared were shown to be SiH₄ and SiHCl₃ by C. Friedel and A. Ladenburg in 1867 but it was not until 1902 that the first homologue, Si₂H₆, was prepared by H. Moissan and S. Smiles from the protonolysis of magnesium silicide. The thermal instability and great chemical reactivity of the compounds precluded further advances until A. Stock developed his greaseless vacuum techniques and first began to study them as contaminants of his boron hydrides in 1916. He proposed the names silanes and boranes (p. 151) by analogy with the alkanes.

Silanes Si_nH_{2n+2} are now known as unbranched and branched chains (up to n = 8) and as cyclic compounds Si_nH_{2n} (n = 5, 6). Silanes are colourless gases or volatile liquids; they

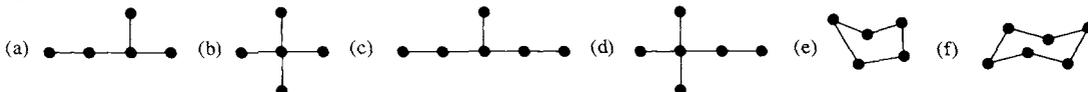
are extremely reactive and spontaneously ignite or explode in air. Thermal stability decreases with increasing chain length and only SiH₄ is stable indefinitely at room temperature; Si₂H₆ decomposes very slowly (2.5% in 8 months), Si₃H₈ slowly and the tetrasilanes more rapidly, at room temperature. Some physical properties are in Table 9.4 from which it can be seen that silanes are less volatile than both the alkanes and boranes (p. 163) of similar formula, but more volatile than the corresponding germanes (p. 375).

There are three general types of preparative route to the silanes and their derivatives. Early methods (pre-1945) treated materials such as metal silicides which contained negatively charged Si^{δ-} with a protonic reagent such as an aqueous acid. Concurrent hydrolysis of the products limited the yield but considerable improvement resulted from the use of nonaqueous systems such as NH₄Br/liq NH₃ (1934). The second general preparative route involves treatment of compounds such as SiX₄ (Si^{δ+}) with hydridic reagents such as LiH, NaH, LiAlH₄, etc., in ether solvents at low temperatures. This is now the preferred route: e.g. reaction of Si_nCl_{2n+2} (n = 1, 2, 3) with LiAlH₄ gives essentially quantitative

²⁸ Ref. 13, Suppl. B1, 1982, 259 pp. (Si-H) and references cited therein.

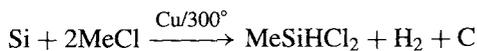
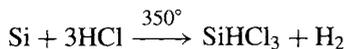
Table 9.4 Some properties of silanes⁽²⁸⁾

Property	MP/°C	BP(extrap)/°C	$d(20^\circ)/\text{g cm}^{-3}$	Property	MP/°C	BP(extrap)/°C	$d(20^\circ)/\text{g cm}^{-3}$
SiH ₄	-184.7°	-111.8°	0.68 (-185°)	<i>neo</i> -Si ₅ H ₁₂ ^(b)	-57.8°	130°	—
Si ₂ H ₆	-132.5°	-14.3°	0.686 (-25°)	<i>n</i> -Si ₆ H ₁₄	-44.7°	193.6°	0.847
Si ₃ H ₈	-117.4°	+53.1°	0.739	Si ₆ H ₁₄ ^(c)	-78.4°	185.2°	0.840
<i>n</i> -Si ₄ H ₁₀	-89.9°	108.1°	0.792	Si ₆ H ₁₄ ^(d)	-57.8°	134.3°	0.815
<i>i</i> -Si ₄ H ₁₀	-99.4°	101.7°	0.793	<i>n</i> -Si ₇ H ₁₄	-30.1°	226.8°	0.859
<i>n</i> -Si ₅ H ₁₂	-72.8°	153.2°	0.827	<i>cyclo</i> -Si ₅ H ₁₀ ^(e)	-10.5°	194.3°	0.963
<i>i</i> -Si ₅ H ₁₂ ^(a)	-109.8°	146.2°	0.820	<i>cyclo</i> -Si ₆ H ₁₂ ^(f)	+16.5°	226°	—

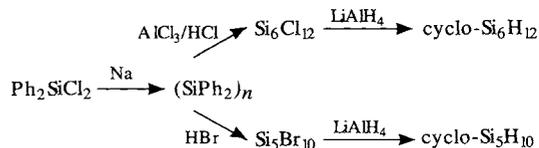
Table 9.5 Some typical bond energies/kJ mol⁻¹

X	=	C	Si	H	F	Cl	Br	I	O-	N<
C-X		368	360	435	453	351	293	216	~360	~305
Si-X		360	340	393	565	381	310	234	452	322

yields of SiH₄, Si₂H₆, and Si₃H₈. Organosilanes can be prepared similarly, e.g. Me₂SiCl₂ gives Me₂SiH₂. The third general method for preparing Si-H compounds involves direct reaction of HX or RX with Si or a ferrosilicon alloy in the presence of a catalyst such as Cu when necessary (p. 364), e.g.:



Combination of these various methods has led to a vast number of derivatives in which H is progressively replaced by one or more monofunctional group such as F, Cl, Br, I, CN, R, Ar, OR, SH, SR, NH₂, NR₂, etc.⁽¹⁾ The cyclic silanes Si₅H₁₀ and Si₆H₁₂ were prepared in the late 1970s⁽²⁹⁾ via (SiPh)_n which were themselves the first known homocyclic silane derivatives (F. S. Kipping, 1921):



Silanes are much more reactive than the corresponding C compounds.^(1,2,30) This has been ascribed to several factors including: (a) the larger radius of Si which would facilitate attack by nucleophiles, (b) the great polarity of Si-X bonds, and (c) the presence of low-lying d orbitals which permit the formation of 1:1 and 1:2 adducts, thereby lowering the activation energy of the reaction. The relative magnitude of the various bond energies is also an important factor in deciding which bonds will survive and which will be formed. Thus, it can be seen in Table 9.5, Si-Si < Si-C < C-C and Si-H < C-H, whereas for bonds for the other elements the energy C-X < Si-X. These data should

²⁹ E. HENGGE and G. BAUER, *Monatshefte für Chemie* **106**, 503-12 (1975). E. HENGGE and D. KOVAR, *Z. anorg. allg. Chem.* **459**, 123-30 (1979).

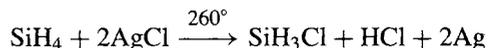
³⁰ E. WIBERG and E. AMBERGER, *Hydrides of the Elements of Main Groups I-IV*, Chap. 7, pp. 462-638, Elsevier, Amsterdam, 1971. A comprehensive review of compounds containing Si-H bonds; over 700 references.

be used only for broad comparisons since the estimated bond energies depend markedly on the particular compounds being studied and also on the experimental technique employed and the method of computation.

The pyrolysis of silanes leads to polymeric species and ultimately to Si and H₂; indeed, pyrolysis of SiH₄ is a commercial route to ultrapure Si. The reactions occurring have been less studied than those of alkanes (and boranes, p. 164), but it is clear that there are significant differences. Thus the initial step in the thermal decomposition of alkanes is the cleavage of a C–H or C–C bond with formation of radical intermediates R₃C•. However, studies using deuterium-substituted compounds suggest that the initial step in the decomposition of polysilanes is the elimination of silenes :SiH₂ or :SiHR.⁽³¹⁾ Activation energies for this process (~210 kJ mol⁻¹) are substantially less than Si–Si and Si–H bond energies and the reaction appears to involve a 1,2-H shift with a 5-coordinate transition state.

³¹ I. M. T. DAVIDSON and A. V. HOWARD, *J. Chem. Soc., Faraday I*, **71**, 69–77 (1975) and references therein. C. H. HAAS and M. A. RING, *Inorg. Chem.* **14**, 2253–6 (1975). A. J. VANDERWIELEN, M. A. RING and H. E. O'NEAL, *J. Am. Chem. Soc.* **97**, 993–8 (1975).

Pure silanes do not react with pure water or dilute acids in silica vessels, but even traces of alkali dissolved out of glass apparatus catalyse the hydrolysis which is then rapid and complete (SiO₂.nH₂O + 4H₂). Solvolysis with MeOH can be controlled to give several products SiH_{4-n}-(OMe)_n (n = 2, 3, 4). Si–H adds (with difficulty) to alkenes though the reaction occurs more readily with substituted silanes. Similarly, SiH₄ adds to Me₂CO at 450° to give C₃H₇OSiH₃, and it ring-opens ethylene oxide at the same temperature to give EtOSiH₃ and other products. Silanes explode in the presence of Cl₂ or Br₂ but the reaction with Br₂ can be moderated at –80° to give good yields of SiH₃Br and SiH₂Br₂. More conveniently, halogenosilanes SiH₃X can be made by the catalysed reaction of SiH₄ and HX in the presence of Al₂X₆, or by the reaction with solid AgX in a heated flow reactor, e.g.:



SiH₃I in particular is a valuable synthetic intermediate and some of its reactions are summarized in Table 9.6. SiH₃I is a dense, colourless, mobile liquid, mp –57.0°, bp +45.4°, *d*(15°) 2.035 g cm⁻³.

Another valuable reagent is KSiH₃, a colourless crystalline compound with NaCl-type

Table 9.6 Some reactions of SiH₃I^(a)

Reagent	Major Si product	Reagent	Major Si product
Na/Hg	Si ₂ H ₆	N ₂ H ₄	(SiH ₃) ₂ NN(SiH ₃) ₂
H ₂ O	O(SiH ₃) ₂	LiN(SiCl ₃) ₂	SiH ₃ N(SiCl ₃) ₂
HgS	S(SiH ₃) ₂	P ₄	(SiH ₃) _n PI _{3-n} (n = 1, 2, 3)
Ag ₂ Se	Se(SiH ₃) ₂	AgXCN (N ₂ atm)	SiH ₃ NCX (X = O, Se)
Li ₂ Te	Te(SiH ₃) ₂	AgSCN	SiH ₃ NCS
Si ₂ H ₅ Br + H ₂ O	SiH ₃ OSi ₂ H ₅	AgCN	SiH ₃ CN
Hg(SCF ₃) ₂	SiH ₃ SCF ₃	Ag ₂ NCN	(SiH ₃) ₂ NCN
Hg(SeCF ₃) ₂	SiH ₃ SeCF ₃	HC≡CMgBr	SiH ₃ C≡CH
NH ₃	N(SiH ₃) ₃	NaMn(CO) ₅	[Mn(CO) ₅ (SiH ₃)]
R ₂ NH	SiH ₃ NR ₂	Na ₂ Fe(CO) ₄	[Fe(CO) ₄ (SiH ₃) ₂]
NMe ₃ ^(b)	SiH ₃ I.NMe ₃ and SiH ₃ I.2NMe ₃	[Co(CO) ₄] ⁻	[Co(CO) ₄ (SiH ₃)]

^(a)Detailed references to conditions, yields and other minor products are given in ref. 1 [2nd edn. Vol. 18, pp. 172–215 (1969)] which also summarizes the extensive reaction chemistry of O(SiH₃)₂, S(SiH₃)₂, and N(SiH₃)₃.

^(b)Many other ligands (L) also give 1:1 and 1:2 adducts.

structure; it is stable up to $\sim 200^\circ$ and is prepared by direct reaction of potassium on silane in monoglyme or diglyme:

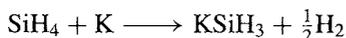
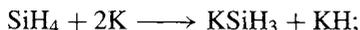


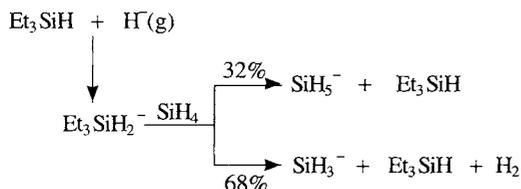
Table 9.7 Some reactions of KSiH_3 ^(a)

Reagent	Major Si product	Reagent	Major Si product
H_2O	$\text{SiO}_2 \cdot n\text{H}_2\text{O}$	Me_3SiCl	$[\text{SiMe}_3(\text{SiH}_3)]$
MeOH	$\text{Si}(\text{OMe})_4$	Me_3GeBr	$[\text{GeMe}_3(\text{SiH}_3)]$
HCl	SiH_4	Me_3SnBr	$[\text{SnMe}_3(\text{SiH}_3)]$
MeI	SiH_3Me	GeH_3Cl	GeH_3SiH_3
SiH_3Br	$\text{Si}_2\text{H}_6, \text{SiH}_4$	MeOCH_2Cl	$\text{SiH}_3(\text{CH}_2\text{OMe})$
$\text{Si}_2\text{H}_5\text{Br}$	$\text{Si}_3\text{H}_8, \text{Si}_2\text{H}_6$		

^(a)See footnote (a) to Table 9.6.

When hexamethylphosphoramide, $(\text{NMe}_2)_3\text{PO}$, is used as solvent only the second reaction occurs. The synthetic utility of KSiH_3 can be gauged from Table 9.7 which summarizes some of its reactions. In addition, PCl_3 gives polymeric $(\text{PH})_x$, CO_2 gives CO plus HCO_2K (formate), and N_2O gives $\text{N}_2 + \text{H}_2$ (plus) some SiH_4 in each case.⁽³²⁾

The hypervalent silicon hydride anion, SiH_5^- (cf. SiF_5^- below), has been synthesized as a reactive species in a low-pressure flow reactor:⁽³³⁾



9.3.3 Silicon halides and related complexes

Silicon and silicon carbide both react readily with all the halogens to form colourless

volatile reactive products SiX_4 . SiCl_4 is particularly important and is manufactured on the multikilotonne scale for producing boron-free transistor grade Si, fumed silica (p. 345), and various silicon esters. When two different tetrahalides are heated together they equilibrate to form an approximately random distribution of silicon halides which, on cooling, can be separated and characterized:



Mixed halides can also be made by halogen exchange reaction, e.g. by use of SbF_3 to successively fluorinate SiCl_4 or SiBr_4 . The mps and bps of these numerous species are compared with those of the parent hydride and halides in Fig. 9.1. While there is a clear trend to higher mps and bps with increase in molecular weight, this is by no means always regular. More notable is the enormous drop in mp (bp) which occurs for the halides of Si when compared with Al and earlier elements in the same row of the periodic table, e.g.:

Compound	NaF	MgF ₂	AlF ₃	SiF ₄	PF ₅	SF ₆
MP/°C	988	1266	1291	-90	-94	-50
				(subl)		

This is sometimes erroneously ascribed to a discontinuous change from "ionic" to "covalent" bonding, but the electronegativity and other bonding parameters of Al are fairly similar to those of Si and the difference is more convincingly seen merely as a consequence of the change from an infinite lattice structure (in which each Al is surrounded by 6 F) to a lattice of discrete SiF_4 molecules as dictated by stoichiometry and size. Several other examples of this effect will be noticed amongst compounds of the Group 14 elements. Another instructive trend is in the Si-F interatomic distance in binary Si/F species: in tetrahedral $\text{SiF}_4(\text{c})$ it is 154.0 pm; in trigonal bipyramidal SiF_5^- it is 159.4 and 164.6 pm, respectively, for equatorial and axial bonds, and in SiF_6^{2-} it is 168.5 pm. The trend is to longer distances with increase in coordination number, presumably reflecting a gradual decrease in bond order. The 3.3% increase in going from

³² V. A. WILLIAMS and D. M. RITTER, *Inorg. Chem.* **24**, 3278-80 (1985).

³³ D. J. HAJDASZ and R. R. SQUIRES, *J. Am. Chem. Soc.* **108**, 3139-40 (1986).

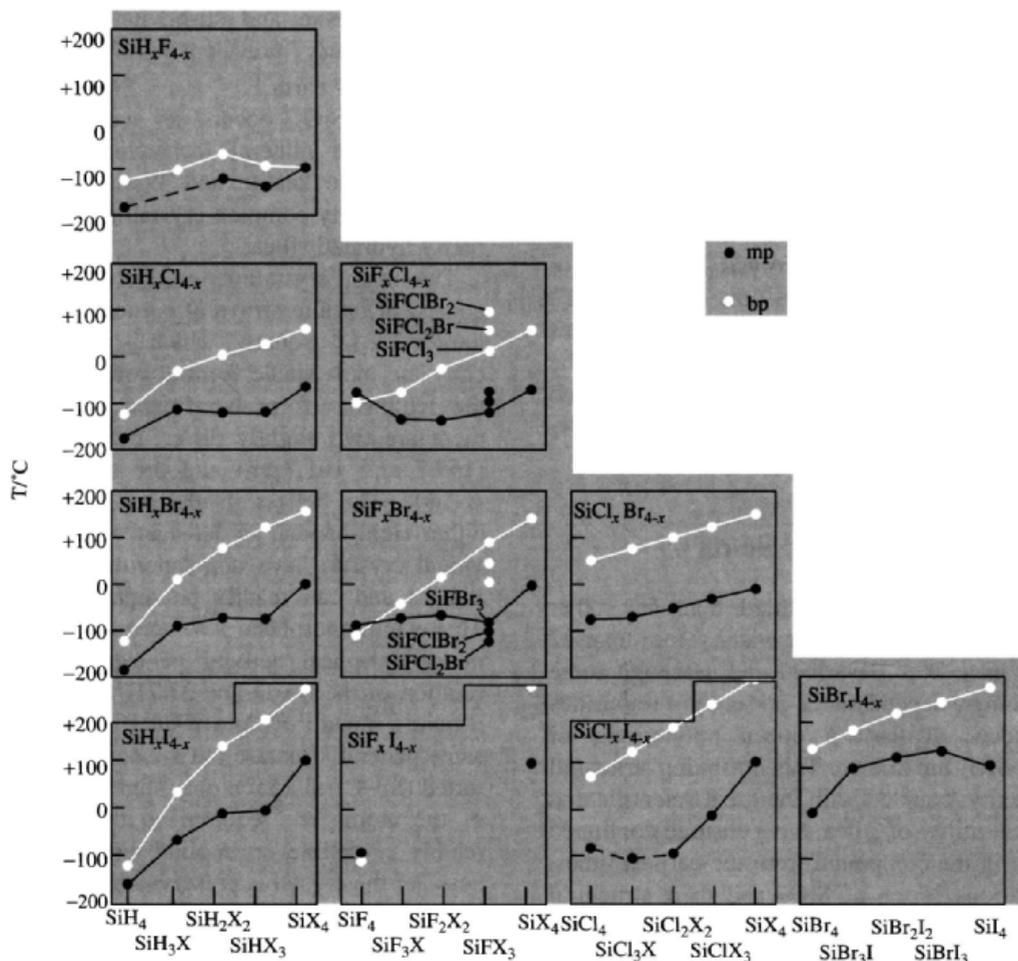


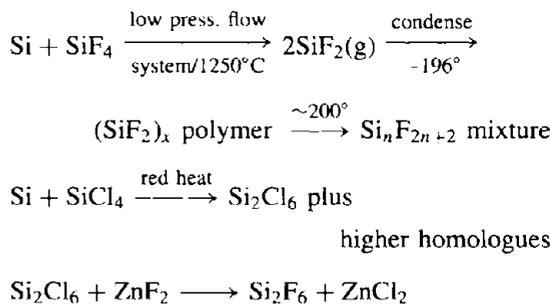
Figure 9.1 Trends in the mp and bp of silicon hydride halides and mixed halides.

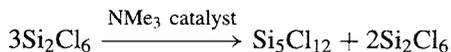
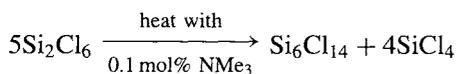
equatorial to axial bonding in SiF_5^- is also in the usual direction.

The reactions of SiX_4 are straightforward and call for little comment.^(1,2)

Higher homologues $\text{Si}_n\text{X}_{2n+2}$ are volatile liquids or solids and, contrary to the situation in carbon chemistry, catenation in Si compounds reaches its maximum in the halides rather than the hydrides. This has been ascribed to additional back-bonding from filled halogen p_π orbitals into the Si d_π orbitals which thus synergically compensates for electron loss from Si via σ bonding to the electronegative halogens (cf. CO, pp. 926–8). Fluoropolysilanes up to $\text{Si}_{14}\text{F}_{30}$ and

other series up to at least $\text{Si}_6\text{Cl}_{14}$ and $\text{Si}_4\text{Br}_{10}$ are known. Preparative routes are exemplified by the following reactions:





These compounds show many unusual reactions and reviews of their chemistry make fascinating reading.^(34,35) Partial hydrolysis of SiCl_4 (or the reaction of $\text{Cl}_2 + \text{O}_2$ on Si at 700°) leads to a series of volatile chlorosiloxanes $\text{Cl}_3\text{Si}(\text{OSiCl}_2)_n\text{OSiCl}_3$ ($n = 0-5$) and to the cyclic $(\text{SiOCl}_2)_4$. The corresponding bromo compounds are prepared similarly, using Br_2 and O_2 .

9.3.4 Silica and silicic acids

Silica has been more studied than any other chemical compound except water. More than 22 phases have been described and, although some of these may depend on the presence of impurities or defects, at least a dozen polymorphs of "pure" SiO_2 are known. This intriguing structural complexity, coupled with the great scientific and technical utility of silica, have ensured continued interest in the compound from the earliest times. The various forms of SiO_2 and their structural inter relations will be described in the following paragraphs. By far the most commonly occurring form of SiO_2 is α -quartz which is a major mineral constituent of many rocks such as granite and sandstone; it also occurs alone as rock crystal and in impure forms as rose quartz, smoky quartz (red brown), morion (dark brown), amethyst (violet) and citrine (yellow). Poorly crystalline forms of quartz include chalcedony (various colours), chrysoprase (leek green), carnelian (deep red), agate (banded), onyx (banded), jasper (various), heliotrope (bloodstone) and flint (often black due to inclusions of carbon). Less-common crystalline modifications of SiO_2 are tridymite, cristobalite and the extremely rare

minerals coesite and stishovite. Earthy forms are particularly prevalent as kieselguhr and diatomaceous earth.[†]

Vitreous SiO_2 occurs as tectites, obsidian and the rare mineral lechatelierite. Synthetic forms include keatite and W-silica. Opals are an exceedingly complex crystalline aggregate of partly hydrated silica.

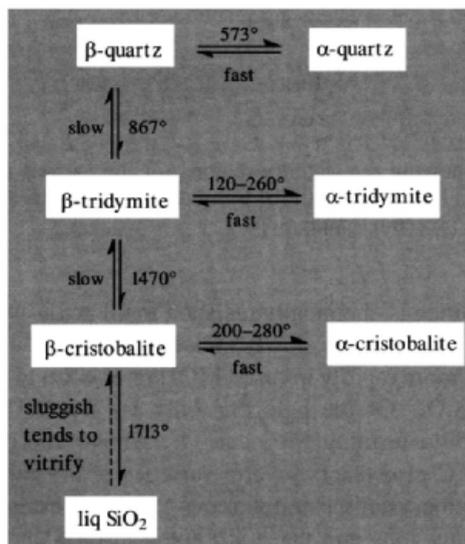
The main crystalline modifications of SiO_2 consist of infinite arrays of corner-shared $\{\text{SiO}_4\}$ tetrahedra. In α -quartz, which is thermodynamically the most stable form at room temperature, the tetrahedra form interlinked helical chains; there are two slightly different Si-O distances (159.7 and 161.7 pm) and the angle Si-O-Si is 144° . The helices in any one crystal can be either right-handed or left-handed so that individual crystals have non-superimposable mirror images and can readily be separated by hand. This enantiomorphism also accounts for the pronounced optical activity of α -quartz (specific rotation of the Na D-line $27.71^\circ/\text{mm}$). At 573°C α -quartz transforms into β -quartz which has the same general structure but is somewhat less distorted (Si-O-Si 155°): only slight displacements of the atoms are required so the transition is readily reversible on cooling and the "handedness" of the crystal is preserved throughout. This is called a non-reconstructive transformation. A more drastic structural change occurs at 867° when β -quartz transforms into β -tridymite. This is a reconstructive transformation which requires the breaking of Si-O bonds to enable the $\{\text{SiO}_4\}$

[†] The names of minerals often give a clue to their properties or discovery. Coesite, stishovite, and keatite are named after their discoverers (p. 343). Quartz derives from *kwardy*, a West Slav dialectal equivalent of the Polish *twardy*, hard. Tridymite was recognized as a new polymorph by von Rath in 1861 because of its typical occurrence as trillings or groups of 3 crystals (Greek *τριδυμος*, *tridyomos*, threefold). Cristobalite was discovered by von Rath in 1884 on the slopes of Mt San Cristobal, Mexico, where tridymite had also first been discovered. Kieselguhr is a combination of the German *Kiesel*, flint, and *Guhr*, earthy deposit. Diatomaceous earth refers to its origin as the remains of minute unicellular algae called diatoms: these marine organisms (0.01–0.1 mm diam) have the astonishing property of accreting silica on their cell walls and this preserves the shape of the organism after death — enormous deposits occur in many places (see p. 345).

³⁴ J. L. MARGRAVE and P. W. WILSON, *Acc. Chem. Res.* **4**, 145–52 (1971).

³⁵ G. URRY, *Acc. Chem. Res.* **3**, 306–12 (1970).

tetrahedra to be rearranged into a simpler, more open hexagonal structure of lower density. For this reason the change is often sluggish and this enables tridymite to occur as a (metastable) mineral phase below the transition temperature. When β -tridymite is cooled to $\sim 120^\circ$ it undergoes a fast, reversible, non-reconstructive transition to (metastable) α -tridymite by slight displacements of the atoms. Conversely, when β -tridymite is heated to 1470° it undergoes a sluggish reconstructive transformation into β -cristobalite and this, in turn, can retain its structure as a metastable phase when cooled below the transition temperature; further slight displacements occur rapidly and reversibly in the temperature range $200\text{--}280^\circ$ to give α -cristobalite (Si-O 161 pm, Si-O-Si 147°). These transitions are summarized below.

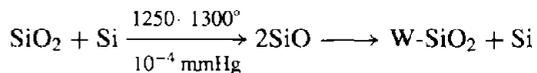


The α -form of each of the three minerals can thus be obtained at room temperature and, because of the sluggishness of the reconstructive interconversions of the β -forms, it is even possible to melt β -quartz (1550°) and β -tridymite (1703°) if they are heated sufficiently rapidly. The bp of SiO_2 is not accurately known but is about 2800°C .

Other forms of SiO_2 can be made at high pressure (Fig. 9.2). Coesite was first made

by L. Coes in 1953 by heating dry Na_2SiO_3 and $(\text{NH}_4)_2\text{HPO}_4$ at 700° and 40 kbar, and was subsequently found in nature at Meteor Crater, Arizona (1960). Its structure consists of 4-connected networks of $\{\text{SiO}_4\}$ in which the smallest rings are 4- and 8-membered, and this compact structure explains its high density (Table 9.8). On being heated it rapidly converts to tridymite or cristobalite. At still higher pressures (40–120 kbar, $380\text{--}585^\circ$) keatite is formed under hydrothermal conditions from amorphous silica and dilute alkali (P. P. Keat, 1959); the $\{\text{SiO}_4\}$ are connected into 5-, 7-, and 8-membered rings as in ice(III) (p. 624). The highest density form of SiO_2 was predicted in 1952 by J. B. Thompson who visualized 6-coordinate Si in a rutile structure (p. 961). It was first synthesized in S. M. Stishov's laboratory (1961) at $1200\text{--}1400^\circ$ and 160–180 kbar, and found to have the predicted structure. It was discovered in association with coesite at Meteor Crater in 1962: presumably both minerals were formed under transient shock pressures following meteorite impact and then preserved by rapid quenching from high temperature. The rapid melting and cooling of pre-existing silica phases also occurs during lightning strikes, and this leads to the formation of lechatelierite, a glassy or vitreous silica mineral.

Finally, a very low-density form of fibrous silica, W- SiO_2 has been made by the disproportionation of (metastable) crystalline SiO :



W- SiO_2 features $\{\text{SiO}_4\}$ tetrahedra linked by sharing opposite edges to form infinite parallel chains analogous to SiS_2 and SiSe_2 ; this edge-sharing of pairs of O atoms between pairs of Si atoms is not observed elsewhere in Si-O chemistry where linking is by corner sharing of single O atoms. The configuration is unstable, and fibrous SiO_2 rapidly reverts to amorphous SiO_2 on heating or in the presence of traces of moisture. It has also recently been shown that reaction of $(\text{SiO})_2$ and O_2 in an argon matrix results in the formation of dimeric molecules

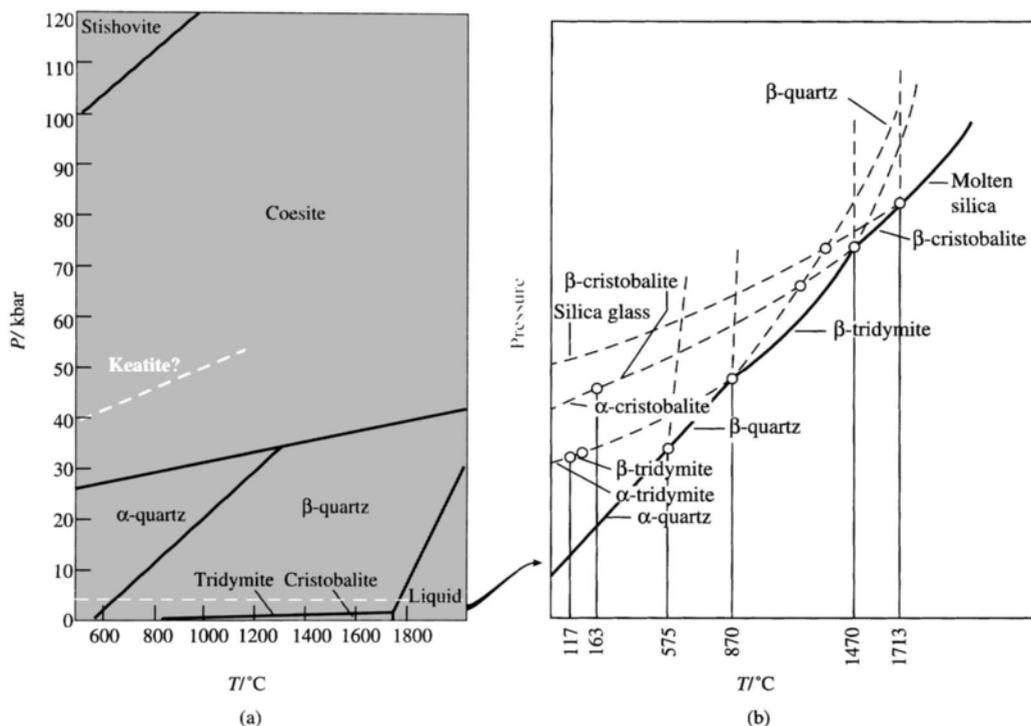


Figure 9.2 (a) Pressure-temperature phase diagram for SiO₂ showing the stability regions for the various polymorphs. The low-pressure segment below the broken line is shown in (b) using an (arbitrary) expanded scale to illustrate the relationships described in the preceding paragraphs.

of silica, $O=Si(\mu-O)_2Si=O$.⁽³⁶⁾ Interaction of molecular SiO with Ag atoms in an argon matrix gives cyclic \overline{AgSiO} with the angle at Si being $\leq 90^\circ$.⁽³⁷⁾

Table 9.8 Density of the main forms of SiO₂ (room temperature)

	$d/g\text{ cm}^{-3}$		$d/g\text{ cm}^{-3}$
W (fibrous)	1.97	β-quartz (600°)	2.533
Lechatelierite	2.19	α-quartz	2.648
Vitreous	2.196	Coesite	2.911
Tridymite	2.265	Keatite	3.010
Cristobalite	2.334	Stishovite	4.287

³⁶ T. MEHNER, H. J. GÖCKE, S. SCHUNCK and H. SCHNOCKEL, *Z. anorg. allg. Chem.* **580**, 121–30 (1990).

³⁷ T. MEHNER, H. SCHNOCKEL, M. J. ALMOND and A. J. DOWNS, *J. Chem. Soc., Chem. Commun.*, 117–9 (1988).

Silica is chemically resistant to all acids except HF but dissolves slowly in hot concentrated alkali and more rapidly in fused MOH or M₂CO₃ to give M₂SiO₃. Of the halogens only F₂ attacks SiO₂ readily, forming SiF₄ and O₂. Above 1000° H₂ and C also react. Several varieties of crystalline, cryptocrystalline and vitreous SiO₂ find extensive applications and these are noted in the Panel. In vitreous silica {SiO₄} tetrahedra are again linked by sharing corners with each O linked to 2Si but the extended three-dimensional network lacks the symmetry and periodicity of the crystalline forms. The Si–O distances are similar to those in other forms of SiO₂ (158–162 pm) but the Si–O–Si angles vary by as much as 15–20° on either side of the mean value of 153°.

The detailed reactions of SiO₂ with the oxides of the metals and semi-metals are of great importance in glass technology and ceramics

but will not be treated here.^(1,2,38) Suffice it to say that, in addition to innumerable crystalline compounds and vitreous phases, many water-soluble compositions are known and many of these find extensive commercial application.

³⁸ S. FRANK, *Glass and Archaeology*, Academic Press, London, 1982, 156 pp. O. V. MAZURIN, M. V. STRELTINA and T. P. SHVAIKO-SHVAIKOVSKAYA, *Handbook of Glass Data*, Elsevier, Amsterdam, Part A, 1983, 670 pp; B, 1985, 806 pp; C, 1987, 1110 pp; D, 1991, 992 pp; E, Supplements, to be published.

Perhaps the best known are the soluble sodium (and potassium) silicates which are made by fusing sand with the appropriate carbonate in a glass-making furnace at $\sim 1400^\circ$. The resulting soluble glass is dissolved in hot water under pressure and any insoluble glass or unreacted sand filtered off. The ternary phase diagram for $\text{Na}_2\text{O}-\text{SiO}_2-\text{H}_2\text{O}$ (Fig. 9.3) indicates that only certain limited regions are of commercial interest, e.g. the stable liquid materials (area 9) in the composition range

Some Uses of Silica¹

The main types of SiO_2 used in industry are high-purity α -quartz, vitreous silica, silica gel, fumed silica and diatomaceous earth. The most important application of quartz is as a piezoelectric material (p. 58); it is used in crystal oscillators and filters for frequency control and modulation, and in electromechanical devices such as transducers and pickups: tens of millions of such devices are made each year. There is insufficient natural quartz of adequate purity so it must be synthesized by hydrothermal growth of a seed crystal using dilute aqueous NaOH and vitreous SiO_2 at 400°C and 1.7 kbar. The technique was first successfully employed by G. R. Spezia in 1905. (Crystal growth from molten SiO_2 cannot be used — why?)

Vitreous silica combines exceptionally low thermal expansion[†] and high thermal shock resistance with high transparency to ultraviolet light, good refractory properties, and general chemical inertness. As a glass it is hard to work because of its very high softening point, high viscosity, short liquid range and high volatility at forming temperatures. It is familiar in high-quality laboratory glassware, particularly for photolysis experiments and as sample cells in ultraviolet/visible spectroscopy; it is also much used as a protective sheath in the form of tubing or as thin films deposited from the vapour.

Silica gel is an amorphous form of SiO_2 with a very porous structure, formed by acidification of aqueous solutions of sodium silicate; the gelatinous precipitate is washed free of electrolytes and then dehydrated either by roasting or spray drying. The properties of the resulting microporous material depend critically on the conditions of preparation, but typical samples have a pore diameter of 2200–2600 pm, a surface area of $750\text{--}800\text{ m}^2\text{ g}^{-1}$, and an apparent bulk density of $0.67\text{--}0.75\text{ g cm}^{-3}$. Such material finds extensive use as a desiccant, selective absorbant, chromatographic support, catalyst substrate and insulator (thermal and sound). It can absorb more than 40% of its own weight of water and, when stained with cobalt salts such as the nitrate or $(\text{NH}_4)_2\text{CoCl}_4$, is familiar as a self-indicating desiccant that can readily be regenerated by heating (anhydrous, blue; hydrated, pink). It is chemically inert, non-toxic and dimensionally stable, and finds a growing application in the food industry as an anticaking agent in cocoa, fruit juice powders, NaHCO_3 and powdered sugar and spices. It is also used as a flattening agent to produce an attractive matte finish on lacquers, varnishes and paints, and on the surface of vinyl plastics and synthetic fabrics.

Another manufactured form of ultrafine powdered SiO_2 is pyrogenic or fumed silica, formed by the high-temperature hydrolysis of SiCl_4 in an oxyhydrogen flame in specially designed burners; the SiO_2 is formed as a very fine white smoke which is collected on cooled rotating rollers. The bulk density is only $0.03\text{--}0.06\text{ g cm}^{-3}$ and the surface area $150\text{--}500\text{ m}^2\text{ g}^{-1}$. Its main use is as a thixotropic thickening agent in the processing of epoxy and polyester resins and plastics, and as a reinforcing filler in silicone rubbers where, in contrast to carbon black fillers (p. 271), its chemical inertness does not interfere with the peroxide initiated cure (p. 365).

Diatomaceous earth or kieselguhr (p. 342) is mined by open-cast methods on a very substantial scale, particularly in Europe and North America, which respectively account for 59% and 39% of the world production (1.8 million tonnes in 1977). The principal use is in filtration plants, and this accounts for about 60% of the supply; a further 20% is used in abrasives, fillers, light-weight aggregates and insulation material, and the remainder is used as an inert carrier, coating agent or in the manufacture of pozzolan.

[†] The linear coefficient of thermal expansion of vitreous silica is $\sim 0.25 \times 10^{-6}$. This can be compared with a value of $\sim 100 \times 10^{-6}$ for ordinary soda-lime glasses ($\sim 79\% \text{ SiO}_2$, $\sim 12.5\% \text{ Na}_2\text{O}$, $\sim 8.5\% \text{ CaO}$). Addition of B_2O_3 (as in Pyrex) sharply reduces this value to 3×10^{-6} (typical laboratory glassware has a composition 83.9% SiO_2 , 10.6% B_2O_3 , 1.2% Al_2O_3 , 3.9% Na_2O , 0.4% K_2O).

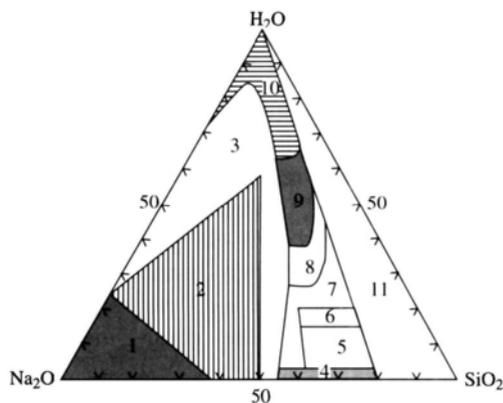


Figure 9.3 Simplified schematic ternary phase diagram for the system $\text{Na}_2\text{O}-\text{SiO}_2-\text{H}_2\text{O}$. Commercially important areas are shaded. (1) anhydrous “ Na_4SiO_4 ” and its granular mixtures with NaOH ; (2) granular crystalline alkaline silicates such as Na_2SiO_3 and its hydrates; (3) uneconomic partially crystallized mixtures; (4) glasses; (5) uneconomic hydrated glasses; (6) dehydrated liquids; (7) uneconomic semi-solids and gels; (8) uneconomic, unstable viscous liquids; (9) ordinary commercial liquids; (10) dilute liquids; (11) unstable liquids and gels. (From J. G. Vail, *Soluble Silicates*, Reinhold, New York, 1952.)

30–40% SiO_2 , 10–20% Na_2O , 60–40% H_2O , i.e. $\sim\text{Na}_2\text{Si}_2\text{O}_5 \cdot 6\text{H}_2\text{O}$. These find extensive use in industrial and domestic liquid detergents because they maintain high pH by means of their buffering ability and can saponify animal and vegetable oils and fats; they also emulsify mineral oils, deflocculate dirt particles, and prevent redeposition of suspended dirt and soil. The more dilute solutions (area 10) are used in production of silica gels by acidification (pp. 345 and below). There are numerous other uses of soluble silicates including adhesives, glues and binders, especially for corrugated cardboard boxes, and as refractory acid-resistant cements and sealants. World production in 1981 was ~ 3.0 million tonnes of which the sodium silicates formed the major part. Price range from \$220–450/tonne depending on composition.

Potassium silicate solutions are equally complex; for example, an aqueous solution prepared from KOH and SiO_2 in which the ratio $\text{K}:\text{Si}$ is 1:1 contains 22 different discrete silicate anions as identified by ^{29}Si COSY nmr studies.⁽³⁹⁾

The system $\text{SiO}_2-\text{H}_2\text{O}$, even in the absence of metal oxides, is particularly complex and of immense geochemical and industrial importance.⁽⁴⁰⁾ The mp of pure SiO_2 decreases dramatically by as much as 800° on addition of 1–2% H_2O (at high pressure), presumably as a result of the structure-breaking effect of replacing $\text{Si}-\text{O}-\text{Si}$ links by “terminal” $\text{Si}-\text{OH}$ groups. With increasing concentrations of H_2O one obtains hydrated silica gels and colloidal dispersions of silica; there are also numerous hydrates and distinct silicic acids in very dilute aqueous solutions, but these tend to be rather insoluble and rapidly precipitate with further condensation when aqueous solutions of soluble silicates are acidified. Structural information is sparse, particularly for the solid state, but in solution evidence has been claimed for at least 5 species (Table 9.9). It is unlikely that any of these species exist in the solid state since precipitation is accompanied by further condensation and cross-linking to form “polysilicic acids” of indefinite and variable composition $[\text{SiO}_x(\text{OH})_{4-2x}]_n$ (cf B, Al, Fe, etc.). However, the crystal structure of $\{(\text{C}-\text{C}_6\text{H}_{11})_7\text{Si}_7\text{O}_9\{\text{O}_3\text{W}(\text{NMe}_2)_3\}_3\}$ has been

Table 9.9 Silicic acids in solution

Formula	$n^{(a)}$	Name	Sol. (H_2O , 20°) mol l^{-1}
$\text{H}_{10}\text{Si}_2\text{O}_9$	2.5	Pentahydrosilicic acid	2.9×10^{-4}
H_4SiO_4	2	Orthosilicic acid	7×10^{-4}
$\text{H}_6\text{Si}_2\text{O}_7$	1.5	Pyrosilicic acid	9.6×10^{-4}
H_2SiO_3	1	Metasilicic acid	10×10^{-4}
$\text{H}_2\text{Si}_2\text{O}_5$	0.5	Disilicic acid	20×10^{-4}

^(a) Number of mols H_2O per mol SiO_2 , i.e. $\text{SiO}_2 \cdot n\text{H}_2\text{O}$.

³⁹ C. T. G. KNIGHT, *J. Chem. Soc., Dalton Trans.*, 1457–60 (1988).

⁴⁰ R. K. ILER, *The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties, and Biochemistry*, Wiley, New York, 1979, 866 pp.