

Rocket-Propellant Characteristics of Silanes/O₂

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We present a theoretical analysis of the applicability of various silicon hydrides (silanes) as rocket propellants. Thermodynamic data sets for 12 different silanes ranging from monosilane SiH₄ to pentasilane Si₅H₁₂ were generated based on existing data. They were derived from empirically corrected thermochemical *ab initio* calculations and used in conjunction with the well-known computer packages NASA CEA2 and CHEMKIN to calculate equilibrium compositions and rocket performance indices. The thermodynamic datasets are now publicly available online for future calculations. Chemical equilibrium combustion compositions and adiabatic flame temperatures in rocket combustion chambers and the specific impulses at the nozzle exit assuming shifting equilibrium were calculated for several silane fuels using oxygen as oxidizer. The computational results created by CEA2 and CHEMKIN are in very good agreement to each other and are compared to conventional fuels such as liquid hydrogen (LH), hydrocarbons and hydrazines. Compared to alkane fuels, the combustion of silanes with oxygen—despite the much higher average molecular mass of the combustion products—results in similar maximum specific impulses and adiabatic flame temperatures due to the high positive values of the heats of formation of the silanes, indicating that silanes may be interesting candidates as rocket propulsion fuels.

I. Introduction

LOWER silicon hydrides (silanes)—especially monosilane SiH₄—play an important role in various chemical vapor deposition techniques in the production of microelectronics. Monosilane has already been considered and successfully tested as an ignition promoter and piloting gas in hydrogen-fueled supersonic jet engines.^{1–4} However, little attention has been spent on full-scale combustion of silanes, especially higher silanes, being silicon hydrides, which contain five or more silicon atoms.

Because of their position within the periodic system and the chemical affinity of silicon and carbon, it is reasonable to compare silicon hydrides with hydrocarbons. However, the different electronic structure of silicon compared to carbon also leads to important differences between the two hydrides.

Under standard conditions of temperature and pressure (STP), lower silanes are gaseous and extremely pyrophoric. With increasing chain length, however, silanes are liquid at STP. Although alkanes are liquid only from pentane on, the silanes with their much higher molecular masses are in the liquid state and therefore pumpable already from trisilane Si₃H₈ on. Figure 1 shows melting and boiling points of straight-chained alkanes and silanes, with data from *n*-octasilane onward being graphically extrapolated because experimental data were not available for these species. The temperature region where the silanes are liquid is shifted towards considerably higher temperatures and is also a bit broader if compared to the corresponding alkanes.

Amazingly, from Si₇H₁₆ on, silanes are no longer self-ignitable at air^{5,6} because the vapor pressure decreases with increasing chain length. It was experimentally observed that *n*-hexasilane does not self-ignite spontaneously anymore at temperatures below 0°C and

estimated theoretically that *n*-pentasilane loses this ability at temperatures below –27°C (Ref. 7). Therefore, handling of silanes gets easier with increasing chain length. The loss of autoignition capability of higher silanes was discovered already in the 1970s (Ref. 5), but the result was never properly published until the year 1998 (Ref. 6). Some present-day textbooks still do not report on this property of higher silanes adequately.

Reliable thermochemical data for silanes, especially higher silanes, were scarce for a long time. Experimentally observed negative heats of formation of silanes^{8–14} must be discarded because all were measured by means of calorimetric combustion with oxygen at room temperature. Under these circumstances, varying amounts of the silicon might not react to SiO₂ because the elementary silicon can get partially enclosed by a thin protective coating of SiO₂ and afterwards cannot participate in the oxidation process¹⁵—an effect known from many metals like aluminum or magnesium. Thus, the measured heats of formation that were calculated under the assumption that all silicon would react completely to SiO₂ ($\Delta H_{f,298}^\circ = -910.5$ kJ/mol) were shifted towards negative values.

With the advance of powerful computer systems, *ab initio* calculations showed that the heats of formation $\Delta H_{f,298}^\circ$ of silanes are instead positive.^{16–22} This is a fundamental difference to hydrocarbons. Whereas alkanes have negative heats of formation (approximately –20 kJ/mol per CH₂ group), the corresponding silanes have positive heats of formation (approximately +40 kJ/mol per SiH₂ group). Table 1 displays thermodynamical data of straight-chained silanes from mono- to pentasilane in comparison to the well-known data of the corresponding hydrocarbons.

Data for the silanes were created using the THERMO computer program,¹⁸ which is based on the extensive *ab initio* calculations of Katzer and coworkers.^{19–21} More recent calculations²² confirm these data. NASA code PAC99^{23–25} was used to create thermodynamic datasets compatible to CHEMKIN²⁶ and the NASA rocket performance program CEA2²⁷ and have been made available online by the authors.[‡]

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‡Data available online at <http://www.unibw.de/lrt10/forschung/projekte/silane> [cited 16 Jan. 2006].

Table 1 Thermochemical properties of acyclic straight-chained silanes up to pentasilane in comparison to the corresponding hydrocarbons (values for silanes created with THERMO)

Species	C_p° , $\text{J mol}^{-1} \text{K}^{-1}$	S_{298}° , $\text{J mol}^{-1} \text{K}^{-1}$	$\Delta H_{f,298}^\circ$, kJ mol^{-1}	Species	$\Delta H_{f,298}^\circ$, kJ mol^{-1}
SiH_4	42.99	204.63	34.05	CH_4	-74.85
Si_2H_6	78.23	275.73	79.76	C_2H_6	-84.67
Si_3H_8	113.74	349.98	120.95	C_3H_8	-103.9
$n\text{-Si}_4\text{H}_{10}$	150.05	425.94	160.64	$n\text{-C}_4\text{H}_{10}$	-124.7
$n\text{-Si}_5\text{H}_{12}$	183.24	496.70	200.60	$n\text{-C}_5\text{H}_{12}$	-146.4

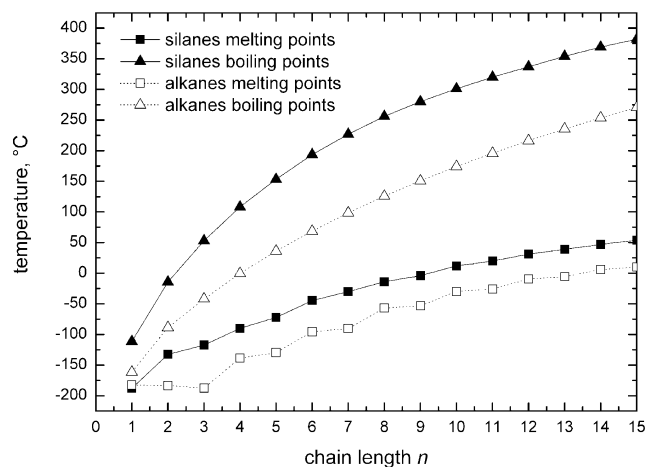


Fig. 1 Melting and boiling points of n -silanes and n -alkanes.

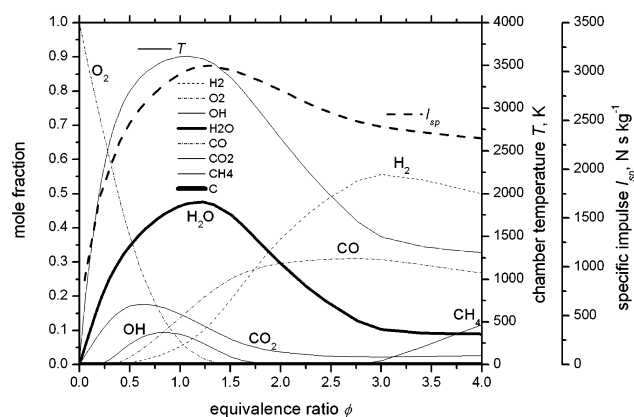


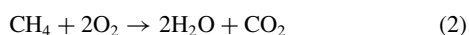
Fig. 2 Chemical equilibrium composition, adiabatic flame temperature, and I_{sp} of the system CH_4/LOX .

II. Chemical Equilibrium Compositions and Rocket Performance

In Fig. 2 results of CEA2 calculations for the conventional hydrocarbon-based system CH_4/LOX are shown. Species' mole fractions (left y axis) and adiabatic flame temperature (first y axis on the right), as well as the specific impulse (rightmost y axis, thick dashed curve), are plotted as a function of the equivalence ratio

$$\Phi = \frac{f/o}{(f/o)_{\text{stoich}}} \quad (1)$$

where f/o is the fuel-to-oxidizer mass ratio. This corresponds to the stoichiometric global oxidation reaction



and a stoichiometric fuel/oxidizer ratio $(f/o)_{\text{stoich}} \approx 0.251$.

A common expansion ratio of 70 to 1 bar and shifting equilibrium was chosen for all calculations. Note that all figures refer to

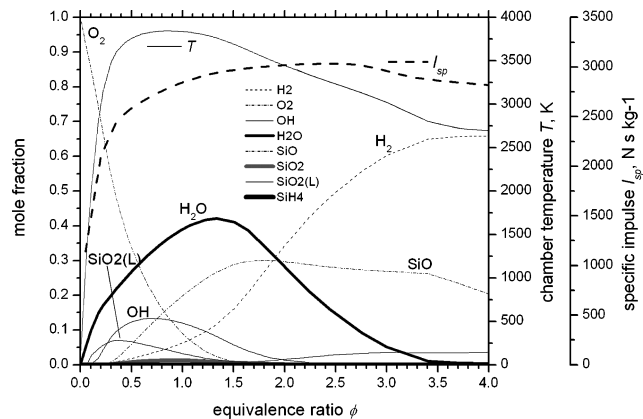


Fig. 3 Chemical equilibrium composition, adiabatic flame temperature, and I_{sp} of the system SiH_4/LOX .

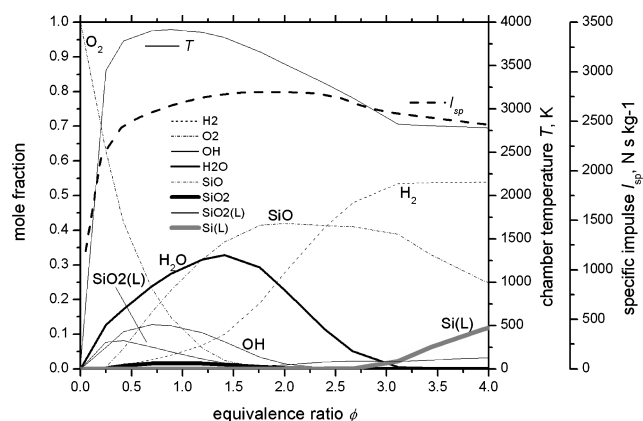
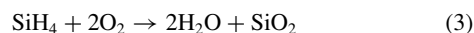


Fig. 4 Chemical equilibrium composition, adiabatic flame temperature, and I_{sp} of the system $\text{Si}_5\text{H}_{12}/\text{LOX}$.

the equilibrium composition in the combustion chamber, not in the nozzle.

For comparison, Fig. 3 shows the corresponding silane-based fuel/oxidizer system SiH_4/LOX with the stoichiometric global reaction



and a stoichiometric fuel/oxidizer ratio $(f/o)_{\text{stoich}} \approx 0.502$.

The maxima of temperature and specific impulse of the methane/LOX system are quite sharp, whereas they have a much broader shape in case of the silane/LOX system. This can be attributed to the positive heat of formation of the silanes, which means that a considerable part of the overall free energy comes from the decomposition of the fuel itself in the fuel-rich region. As a result, the temperature does not decrease very much with increasing Φ . The specific impulse, being proportional to the square root of the ratio of flame temperature T divided by average molecular mass M of the gaseous combustion products

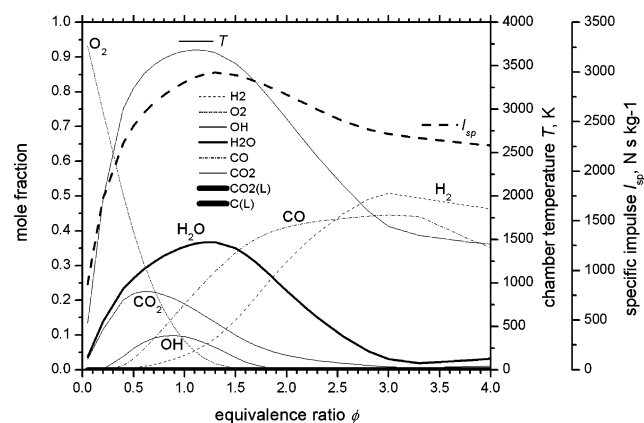
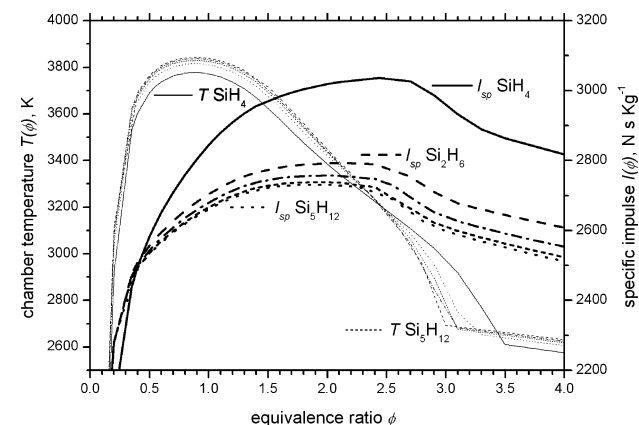
$$I_{sp} \propto \sqrt{T/M} \quad (4)$$

has its maximum shifted to much richer ratios, while the maximum of the specific impulse of the alkane is located very close to the temperature maximum at $\Phi \approx 1$.

The different sign of the heats of formation of alkanes and silanes also is the reason why for very rich alkane/oxygen mixtures part of the alkane fuel remains in the mixture because in this region there is not enough thermal energy available to crack the carbon-hydrogen bonds. In contrast even for very rich silane/oxygen mixtures, all silane fuel is decomposed to form elementary silicon (see n -pentasilane in Fig. 4 for $\Phi > 3$) and hydrogen under energy release

Table 2 Overview of rocket performance characteristics of silanes in comparison to conventional rocket fuels

Fuel (injection temp.)	I_{sp} , Ns kg ⁻¹	T_c , K	ρ at STP, g · cm ⁻³	$(o/f)_{max}$	$\bar{\rho}$, g · cm ⁻³	I_{vol} , Ns · kg ⁻¹
LH (20 K)	3824	2933	0.0709	5.25	0.3346	1280
Monosilane (200 K)	3036	3209	0.68	0.82	0.8328	2528
Disilane (200 K)	2890	3350	0.686	0.84	0.8403	2428
Trisilane (200 K)	2836	3433	0.739	0.87	0.8857	2512
Tetrasilane (200 K)	2807	3493	0.795	0.90	0.9303	2611
Pentasilane (200 K)	2796	3502	0.827	0.88	0.9521	2662
Pentasilane (426 K)	2804	3508	0.827	0.88	0.9521	2670
Cyclo-pentasilane (200 K)	2725	3641	0.973	0.94	1.0509	2863
Methane (L)	3037	3543	0.4211	3.33	0.8064	2449
Pentane (300 K)	2993	3652	0.6213	2.73	0.9358	2801
RP 1 (298 K)	2945	3676	0.773	2.62	1.0128	2983
UDMH (298 K)	3041	3587	0.7914	1.64	0.9809	2983

**Fig. 5** Chemical equilibrium composition, adiabatic flame temperature, and I_{sp} of the system C_5H_{12}/LOX .**Fig. 6** Adiabatic flame temperature and specific impulses of the linear silanes up to n -pentasilane with oxygen at 70 bar.

because of its endothermic character. To complete the picture, Fig. 5 shows results for the C_5H_{12}/LOX system.

No calculation yielded sizable amounts ($>0.001\%$) of solid reaction products like Si or SiO_2 .

The I_{sp} of cyclic silanes like cyclo-pentasilane is a bit lower than for the corresponding straight chain isomere. Although the heat of formation of cyclo-pentasilane (215.12 kJ/mol¹⁸) is larger than that of n -pentasilane (200.60 kJ/mol¹⁸), the fact that a cyclic silane has two hydrogen atoms less increases the denominator of Eq. (4) considerably, and this effect dominates here.

Figure 6 compares results of CEA calculations using linear silane fuels up to n -pentasilane. The difference of the specific impulses decreases with increasing chain length because the sum formulas tend from SiH_4 towards SiH_2 , so that differences in hydrogen fraction get less and less significant. At $\Phi \approx 2.5$, the adiabatic flame temperatures of all silanes are nearly the same.

Table 2 shows an overview of rocket performance calculation results for silanes in comparison to conventional fuels (injected at a certain temperature; see brackets). The maximum specific impulses of monosilane and methane are nearly the same, whereas the combustion temperatures at maximum specific impulse with silane fuel is more than 300 K lower than with methane fuel. With increasing chain length, the difference between the specific impulses using silane fuels compared to the corresponding alkane fuels increases, while the temperature difference becomes smaller.

In addition to the specific impulse, a volume specific impulse can be defined by

$$I_{vol} \propto I_{sp} \cdot \bar{\rho} \quad (5)$$

It was calculated additionally in order to emphasize the influence of the density. In rocket engines, a fuel with higher volumetric impulse might be favorable because, in addition to the weight of fuel, the weight of the tanks has to be taken into account. The average density $\bar{\rho}$ is

$$\bar{\rho} = \left[\left(\frac{o}{f} \right)_{max} + 1 \right] / \left[\frac{(o/f)_{max}}{\rho_{oxidizer}} + \frac{1}{\rho_{fuel}} \right] \quad (6)$$

where $(o/f)_{max}$ is the mass ratio of oxidizer o and fuel f , which leads to the maximal I_{sp} . Densities at STP were used in all cases because of lack of temperature-dependent density data of silanes.

The volume specific impulses of the silanes are high because the silane densities are higher than the alkane densities. Although cyclo-pentasilane has a lower specific impulse than n -pentasilane, the volume specific impulse is higher because of the higher density of cyclo-pentasilane. Liquid hydrogen (LH) produces a very low value here because of its very low specific density.²⁸

III. Summary

Empirically corrected ab initio quantum chemistry data were used to create computer-compatible thermodynamic datasets and to perform rocket performance calculations for the system silanes/ LOX for an expansion ratio of 70 to 1 bar with CEA2 as well as with CHEMKIN in order to cross check the results. The striking difference between alkanes and silanes is the sign of the heat of formation: while alkanes are exothermic (-20 kJ/mol per CH_2 group), silanes are quite endothermic substances ($+40$ kJ/mol per SiH_2 group).

The temperature curve in the combustion using silane fuels has a much broader shape than using alkane fuels, although the maximum temperatures are not too different. As a consequence of the positive heats of formation of the silanes, the specific impulses are quite similar for lower alkanes and silanes; whereas the I_{sp} of longer-chained alkanes are higher than those of higher silanes. Regarding the performance index of volume specific impulse, silanes are superior fuels than hydrogen and alkanes, making them interesting candidates as future rocket fuels.

Future investigations should concentrate on the investigation of air as oxidizer for supersonic airbreathing engine applications and other rocket fuels such as silanes/ H_2O_2 . Also, detailed and reduced

kinetic reaction schemes are needed to estimate finite-rate chemistry effects and as a basis for rocket combustion computational-fluid-dynamics calculations. In particular, the possible formation of silicon nitrides through a reaction with the nitrogen in air and the effect of nongaseous combustion products on rocket performance and the flowfield need to be studied in more detail.

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