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# First-principles thermochemistry for the production of $TiO_2$ from $TiCl_4$


Richard H. West, Gregory J. O. Beran, Willam H. Green[1],

Markus Kraft[2]



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[1] Department of Chemical Engineering
Massachusetts Institute of Technology
77 Massachusetts Avenue, 66-270A
Cambridge, MA 02139
USA
E-mail: whgreen@mit.edu

[2] Department of Chemical Engineering
University of Cambridge
Pembroke Street
Cambridge CB2 3RA
UK
E-mail: mk306@cam.ac.uk



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**Edited by**
Cambridge Centre for Computational Chemical Engineering
Department of Chemical Engineering
University of Cambridge
Cambridge CB2 3RA
United Kingdom.

**Fax:** + 44 (0)1223 334796
**E-Mail:** c4e@cheng.cam.ac.uk
**World Wide Web:** http://www.cheng.cam.ac.uk/c4e/

**Abstract**

Despite the industrial importance of the process, detailed chemistry of the high temperature oxidation of titanium tetrachloride ($TiCl_4$) to produce titania ($TiO_2$) nanoparticles remains unknown, partly due to a lack of thermochemical data. This work presents the thermochemistry of many of the intermediates in the early stages of the mechanism, computed using quantum chemistry. The enthalpies of formation and thermochemical data for TiOCl, $TiOCl_2$, $TiOCl_3$, $TiO_2Cl_2$, $TiO_2Cl_3$, $Ti_2O_2Cl_3$, $Ti_2O_2Cl_4$, $Ti_2O_3Cl_2$, $Ti_2O_3Cl_3$, $Ti_3O_4Cl_4$, and $Ti_5O_6Cl_8$ were calculated using density functional theory (DFT). Use of isodesmic and isogyric reactions was shown to be important for determining standard enthlapy of formation ($\Delta_f H^\circ_{298\,K}$) values for these transition metal oxychloride species. $TiOCl_2$, of particluar importance in this mechanism, was also studied with CCSD(T) and found to have $\Delta_f H^\circ_{298\,K} = -598 \pm 20$ kJ/mol. Finally, equilibrium calculations are performed to try to identify which intermediates are likely to be most prevalent in the high temperature industrial process, and as a first attempt to identify the size of the critical nucleus.

# Contents

# 1 Introduction

Titanium dioxide is currently produced at a rate over 4 million tons per year; half is used in paint, a quarter in plastics such as carrier bags and refrigerator doors, and most of the rest in paper, synthetic fibres and ceramics. It is also used as a catalyst support and photocatalyst. The preferred production method is the chloride process, during which purified titanium tetrachloride is oxidized at high temperatures (1500–2000 K) in a pure oxygen plasma or flame to produce $TiO_2$ nanoparticles. The overall stoichiometry of this oxidation process is:

$$TiCl_4 + O_2 \rightarrow TiO_{2\,\text{(rutile nanoparticles)}} + 2\,Cl_2. \tag{1}$$

Although the chloride process is a mature technology, which has been used in industry since 1958, understanding of the gas-phase reactions of $TiCl_4$ oxidation remains incomplete [21].

Over the years, various mechanisms have been proposed to describe $TiCl_4$ oxidation. Pratsinis *et al.*[32] proposed a mechanism in which $TiCl_4$ decomposes to $TiCl_z$ radicals ($z < 4$) via thermal decomposition and abstraction reactions. These radicals are then oxidized to various $TiO_yCl_z$ oxychlorides ($y \leqslant 2$, $z < 4$) . The oxychlorides then dimerize to form $Ti_xO_yCl_z$ ($x = 2$, $y \leqslant 4$) before reacting to yield species with $x > 2$, with subsequent reactions resulting in $(TiO_2)_n$ nanoparticles ($n \gg 100$). Like Pratsinis, Karlemo *et al.*[21] proposed a mechanism via oxychloride intermediates, specifically $TiOCl_2$, which they found in detectable quantities. Despite these proposed mechanisms, no detailed simulations have been attempted due to a lack of thermochemical data for the intermediate species.

Experimentally, the only oxychloride intermediate to have been observed directly is $TiOCl_2$ [19, 21]; its presence at detectable levels suggests that it is likely to play an important role in the mechanism. Yet, the only thermochemical data currently available for $TiOCl_2$ and TiOCl, which are from the NIST JANAF Thermochemical Tables[7], were estimated in 1963. Other reactive intermediates in the chloride process are even more poorly characterized. Given that current experimental techniques cannot easily provide detailed thermochemical information for such short-lived reactive intermediates, quantum calculations provide a useful complementary tool.

Quantum calculations have previously been applied to titanium oxide species, particularly in the context of nanoclusters. Albaret *et al.*[2] have studied $Ti_nO_{2n+m}$ clusters ($n = 1..3$, $m = 0, 1$) using pseudopotential plane-wave density functional theory (DFT), and Woodley *et al.*[37] recently used DFT to study the minimum energy structures of small $(TiO_2)_n$ clusters ($n = 1..8$). While these studies shed light on the electronic and structural properties of titania nanoclusters, chlorine-free molecules are not part of the mechanisms proposed by Pratsinis or Karlemo, and are unlikely to play an important role as intermediates in the chloride process[21, 32].

The aim of this work is to provide thermochemical data for some of the titanium oxychloride species ($Ti_xO_yCl_z$), which will enable the development of more detailed kinetic

models of the combustion of titanium tetrachloride. The results from three DFT functionals are compared, giving some indication of the reliability of DFT for these transition metal oxychloride species.

As well as probably playing an important role in the $TiCl_4$ oxidation mechanism, $TiOCl_2$ is a useful reference species for calculating the enthalpies of many other species; it is therefore subjected to a more detailed analysis using coupled cluster CCSD(T), often called "the gold standard of quantum chemistry".

Since the optical and catalytic properties of $TiO_2$ depend strongly on particle size, a major technological issue in this large-scale industrial process is precisely controlling the particle size distribution. The size distribution is expected to depend strongly on the particle nucleation rate, which is strongly related to the size of the critical nucleus. Here we perform equilibrium calculations to try to identify which intermediates are likely to be most prevalent in the high temperature industrial process, and as a first attempt to identify the size of the critical nucleus.

# 2 Methods

## 2.1 Quantum Calculations

Molecular geometries have been optimized and analytical harmonic frequencies calculated using three different DFT functionals: mPWPW91[1, 28, 29], B3LYP[4], and B97-1[14] as recommended by Boese *et al.* [6]. All functionals were as implemented in the Gaussian 03 program package[8].

Jeong et al. [20] chose to use the B3P86 functional for determining energies of atomization in a study of $Ti_xO_y$ molecules, observing that gradient-corrected hybrid exchange correlation functionals were useful for this system, and the P86 functional seemed to work better than for example PW91. The most widely used DFT functional is currently the gradient-corrected hybrid functional B3LYP. Boese et al. [6] suggest the continued popularity of this and other first-generation functionals rather than the more accurate second-generation functionals may be due to sheer user inertia. They recommend the second generation hybrid functional B97-1 as probably the best choice when it comes to using density functional hybrid calculations. Woodley et al. [37] used the reparameterisation of this, B97-2, when optimising small $(TiO_2)_n$ clusters.

The basis set for all reported DFT calculations was 6-311+G(d,p)[8]. This consists of the 6-311G basis set[22] for oxygen; the McLean-Chandler (12s,9p) (621111,52111) "negative ion" basis set [25] for chlorine; the Wachters-Hay all-electron basis set[15, 35] for titanium, using the scaling factors of Raghavachari and Trucks[33]; and supplementary polarization functions (one $d$ function each for O and Cl, and one $f$ function for Ti, since $d$ functions are already present in the latter) and diffuse functions (one $s$ and one $p$ on all three atoms, plus an additional $d$ diffuse function on Ti) . Such a supplemented, triple-zeta basis set should be large enough to ensure that the basis set truncation error is comparable with, or smaller than, the inherent errors in the DFT[6].

Some species, such as $TiOCl_3$, could not be adequately described by the default settings in Gaussian, so the B3LYP and B97-1 calculations were repeated with less restrictive settings: spin restrictions were removed to detect possible spin contamination in singlet species, symmetry constraints were lifted allowing symmetry-breaking Jahn-Teller type distortions, the integral grid was increased to a pruned (99,590) grid[1] and the geometry optimisation convergence criteria were tightened.[2]

To establish the spin multiplicity of the ground state, the lowest-energy state of different spin multiplicity was also calculated in many cases. Although not demonstrated in the case of $TiCl_4$ oxidation, the kinetic role of electronically excited species is important in some other combustion systems[26]. This may be the case in $TiCl_4$ oxidation since the temperature in the process is high (about 1800 K). Therefore we report here the the lowest-energy state of different spin multiplicity in addition to the ground state. Excited states with the same spin multiplicity as the ground state were not considered.

Species required to evaluate the enthalpy of formation of $TiOCl_2$ were investigated in more detail. Geometry optimisation and frequency analyses were performed with BPW91[3, 28, 29] and PW91PW91[28, 29] in addition to the three DFT functionals described above. Using B3LYP optimized geometries, single point coupled cluster CCSD(T) calculations were performed using the software GAMESS-UK version 7[13, 23]. This software can only perform spin restricted CCSD(T) calculations; however, this is not a problem in this case as none of the species studied with CCSD(T) preferred a spin unrestricted solution at the UB3LYP or UHF levels of theory.

Three different basis sets were used for the CCSD(T) calculations. For titanium the two smallest basis sets both used the LANL2 Hay and Wadt Effective Core Potentials (ECPs), with the inner-valence forms used for transition metals[16]. Oxygen and chlorine were taken from 3-21G [5, 10] for the smallest basis set and 6-311G[22] for the intermediate case. For the largest basis set calculations, the all-electron 6-311+G(d,p) basis set was used for all three elements, as with the DFT calculations. Only three small molecules ($TiCl_4$, $TiO_2$ and $TiOCl_2$) were calculated with the larger two basis sets due to the $n^7$ scaling of CCSD(T) and the limited computing resources available.

Vibrational frequencies were not calculated at the HF, MP2, CCSD or CCSD(T) levels so these enthalpies have been corrected with thermal contributions according to B97-1/6-311+G(d,p) frequencies and rotational constants.

## 2.2 Frequency Scaling

As explained by Scott and Radom [34], scaling factors designed to predict frequencies in their own right are not optimal for predicting thermodynamic properties derived from those frequencies. [34] provides suitable scaling factors for a variety of quantum calculation methods and basis sets, derived by minimising the least squares error in the thermal

[1] Gaussian keyword `Integral(Grid=UltraFine)`.

[2] Gaussian keyword `opt=(Tight)`. Criteria: maximum force $< 1.5 \times 10^{-5}$, RMS force $< 1 \times 10^{-5}$, maximum displacement $< 6 \times 10^{-5}$, RMS displacement $< 4 \times 10^{-5}$.

contribution to $H$ and $S$. To estimate the appropriate scaling factors for basis sets not studied by Scott and Radom, a relationship was derived by comparing Scott and Radom's scaling factors to those for the same methods and basis sets in the NIST CCCBDB[27] database (Figure 1). This method was used to calculate a scaling factor of 1.01 for thermodynamic properties derived from B3LYP/6-311G(d,p) calculations (without the diffuse functions). No recommended scaling factors for B97-1 or B3LYP/6-311+G(d,p) (with diffuse functions) could be found, so the frequencies were left unscaled. Because the recommended scaling for B3LYP/6-311G(d,p) is so close to 1.0, it is unlikely that significant errors will be introduced by leaving the frequencies unscaled.

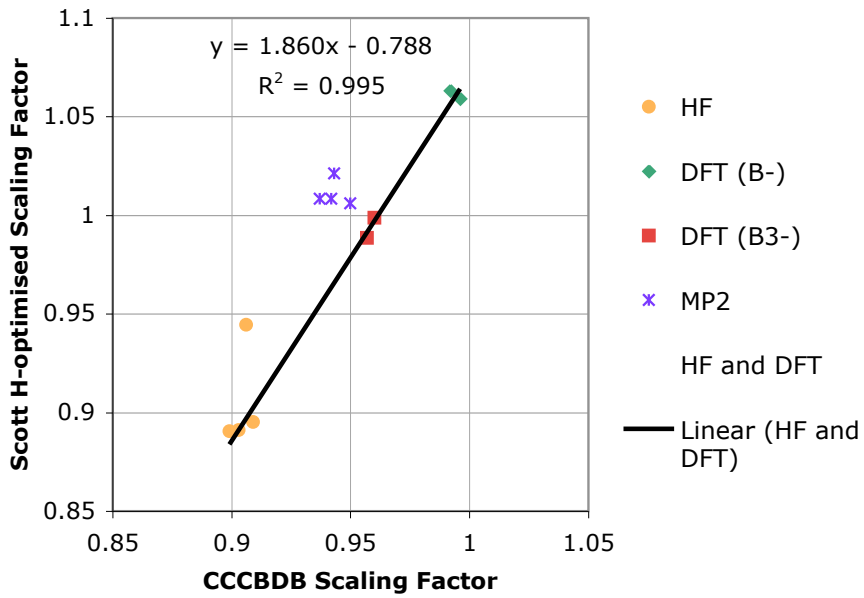


**Figure 1:** *Scaling factors applicable for calculation of thermal contributions to $\Delta_f H^\circ_{298\,K}$ recommended by [34] plotted against scaling factors from the CCCBDB. The linear relationship shown was used to estimate suitable scaling factors based on the CCCBDB.*

## 2.3 Statistical Mechanics and Equilibrium Composition

Heat capacities ($C_\mathrm{p}$), integrated heat capacites ($H(T) - H(0\ \mathrm{K})$) and entropies ($S$) were calculated for temperatures in the range 100–3000 K using the rigid rotator harmonic oscillator (RRHO) approximation, taking unscaled vibrational frequencies and rotational constants from the B97-1 calculations (see Tab. 4).

Polynomials in the NASA form [11] were fitted to $C_\mathrm{p}(T)/R$, $H^\circ$ and $S^\circ$ over the temperature ranges 100-1000 K and 1000-3000 K, constrained to ensure $C_p(T)$ and its first two derivatives matched at 1000 K. Using the fitted polynomials for $C_p(T)$, $H^\circ(T)$ and $S^\circ(T)$, the equilibrium composition as a function of temperature was calculated using the open source software Cantera[9].

## 2.4 Enthalpies of formation: Isodesmic and Isogyric Reactions

The atomization energies reported in Section 3.2 were found by subtracting the DFT-computed absolute energies of the component atoms in isolation, from the absolute energies of the species computed at the same level of theory. Standard enthalpies of formation ($\Delta_f H^\circ_{298\,K}$) are found by relating the computed absolute enthalpies of the unknown species to those of other reference species with previously known standard enthalpies. Although a common choice for these reference species are the isolated atoms, this can lead to systematic errors in the DFT propagating to the final enthalpies; better results can usually be obtained using reference species that are more similar in terms of electronic structure to the unknown species.

Ideally the reference species are chosen such that they are linked to the unknown species via an isodesmic reaction, in which the type of the bonds broken are the same as the type of bonds formed. Because the products and reactants have similar electronic structures, systematic errors in the DFT are largely cancelled out[17]. While less desirable than isodesmic reactions, isogyric reactions, which conserve the number of electron pairs in reactants and products, are still better than using atomization reactions[30, 31].

Reaction choice is particularly important with the titanium oxychloride species, as shown here with the radical $TiO_2Cl_3$. Calculation of standard enthalpy of formation from atomization energies is equivalent to using the reaction

$$\mathrm{TiO_2Cl_3} \rightleftharpoons \mathrm{Ti_{(atoms)}} + 2\mathrm{O_{(atoms)}} + 3\mathrm{Cl_{(atoms)}}. \tag{2}$$

Here a doublet reactant (one unpaired electron) is compared to three triplet and three doublet species (total of nine unpaired electrons). Using this reaction to establish the standard enthalpy of formation, with the 6-311+G(d,p) basis set, the mPWPW91, B3LYP and B97-1 functionals give formation enthalpies for $TiO_2Cl_3$ of $-865$, $-612$ and $-694$ kJ/mol respectively. This is a spread of 253 kJ/mol, far exceeding the expected accuracy of DFT calculations[6].

Reliable enthalpies of formation are available for $TiCl_3$ and $O_2$, therefore an alternative choice of reaction is

$$\mathrm{TiO_2Cl_3} \rightleftharpoons \mathrm{TiCl_3} + \mathrm{O_2}. \tag{3}$$

However, on the left hand side is a doublet with the spin concentrated on the oxygen atoms, which are in the $2-$ oxidation state, and on the right is one doublet with the spin on the titanium and one triplet with the oxygen atoms in the ground oxidation state. Using this scheme to establish enthalpies changes the mPWPW91 value to $-702$ kJ/mol, a change of 163 kJ/mol relative to the atomization scheme. The B3LYP and B97-1 functionals give $-648$ and $-657$ kJ/mol respectively, reducing the overall spread to 54 kJ/mol.

A third alternative reaction is

$$\mathrm{TiO_2Cl_3} + \mathrm{Cl_2} \rightleftharpoons \mathrm{OClO} + \mathrm{TiCl_4}. \tag{4}$$

This reaction is isogyric, as there are 61 electron pairs and one unpaired electron on both the reactant and product sides, with one doublet and one singlet on each side of the reaction. Linking the absolute energies to standard values with this isogyric reaction places

the standard enthalpy of formation of $TiO_2Cl_3$ at $-734$, $-772$ and $-771$ kJ/mol according to the mPWPW91, B3LYP and B97-1 functionals respectively. The overall spread of 38 kJ/mol and the very close agreement of the latter two functionals adds confidence to the numbers achieved this way. The variation of up to 160 kJ/mol between reaction schemes shows both the importance of their choice and the challenge of obtaining a uniformly accurate treatment of these transition metal species with different spin states[12].

Due to the paucity of thermochemical data for transition metal oxychloride species, it was not possible to find isodesmic or isogyric reactions linking the species studied in this work to species with reliable literature values for $\Delta_f H^\circ_{298\,K}$. However, any reaction that leaves some bonds intact is preferable to atomization. The reactions used to evaluate standard enthalpies of formation are shown in Table 1.

**Table 1:** *Reactions used to evaluate standard enthalpies of formation ($\Delta_f H^\circ_{298\,K}$) from computed absolute enthalpies.*

| species | type | reaction |
|---|---|---|
| TiOCl | isodesmic | $TiOCl_2$[a] + $TiCl_3$[b] $\leftrightharpoons$ TiOCl + $TiCl_4$[c] |
| $TiOCl_2$ | isogyric | $\frac{1}{2}$ $TiCl_4$[c] + $\frac{1}{2}$ $TiO_2$[c] $\leftrightharpoons$ $TiOCl_2$ |
| $TiOCl_3$ | anisogyric | $TiCl_4$[c] + $TiOCl_2$[a] $\leftrightharpoons$ $TiOCl_3$ + $TiCl_3$[b] |
| $TiO_2Cl_3$ | isogyric | $TiCl_4$[c] + OClO[c] $\leftrightharpoons$ $TiO_2Cl_3$ + $Cl_2$[c] |
| $TiO_2Cl_2$ | anisogyric | $TiCl_2$[b] + $O_2$[c] $\leftrightharpoons$ $TiO_2Cl_2$ |
| $Ti_2O_2Cl_4$ | isogyric | 2 $TiOCl_2$[a] $\leftrightharpoons$ $Ti_2O_2Cl_4$ |
| $Ti_2O_2Cl_3$ | isogyric | 2 $TiOCl_2$[a] + $TiCl_3$[b] $\leftrightharpoons$ $Ti_2O_2Cl_3$ + $TiCl_4$[c] |
| $Ti_2O_3Cl_3$ | anisogyric | 3 $TiOCl_2$[a] $\leftrightharpoons$ $Ti_2O_3Cl_3$ + $TiCl_3$[b] |
| $Ti_2O_3Cl_2$ | isogyric | 2 $TiOCl_2$[a] + $TiOCl_2$[a] $\leftrightharpoons$ $Ti_2O_3Cl_2$ + $TiCl_4$[c] |
| $Ti_3O_4Cl_4$ | isogyric | 2 $TiOCl_2$[a] + $TiO_2$[b] $\leftrightharpoons$ $Ti_3O_4Cl_4$ |
| $Ti_5O_6Cl_8$ | isogyric | 6 $TiOCl_2$[a] $\leftrightharpoons$ $Ti_5O_6Cl_8$ + $TiCl_4$[c] |

[a] Enthalpy of formation from this work.

[b] Enthalpy of formation from Hildenbrand (1996)[18]

[c] Enthalpy of formation from NIST-JANAF tables [7]

# 3 Results and Discussion

## 3.1 Geometries

Figure 2 shows the molecular geometries of the ground state of each molecule after optimisation with B97-1/6-311+G(d,p).

At this level of theory, $TiOCl_3$ in a $C_{3v}$ conformation has an imaginary frequency. This

is due to a Jahn-Teller distortion, which results from a very low-lying first excited state (0.21 eV for the $C_{3v}$ structure according to TDDFT with the B3LYP functional). The $C_s$ geometry reported here is stable at this level of theory.

Two stable geometries for $TiO_2Cl_2$ were located. At the B97-1/6-311+G(d,p) level the isomer with a trigonal Ti center and a dangling –O–O has an electronic energy 201 kJ/mol higher than the structure with the distorted tetrahedral geometry reported here where the O atoms are both bonded to the Ti.

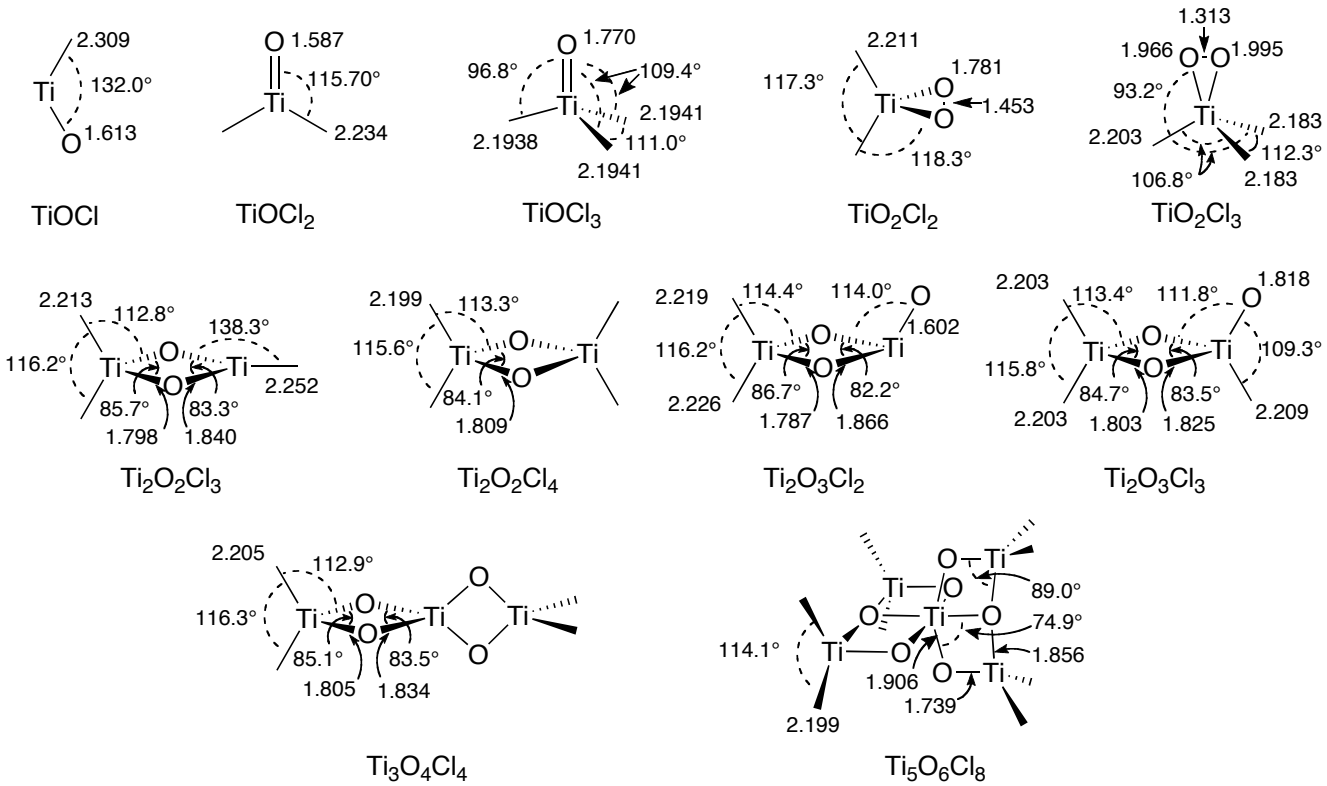


**Figure 2:** *Molecular geometries after optimisation with B97-1/6-311+G(d,p). Bond lengths are in Ångströms, and unlabelled atoms are chlorine.*

## 3.2 Atomization Energies

Although we have not used atomization reactions to calculate enthalpies of formation, we report atomization energies here to facilitate reproduction of our results. Table 2 shows the atomization energies for the ground electronic state calculated with the 6-311+G(d,p) basis set using three DFT functionals: mPWPW91, B3LYP, and B97-1.

The lowest-energy states of different spin multiplicity from the ground states were of considerably higher energies. The smallest gap was for TiCl in which the doublet state is ∼40 kJ/mol higher than the quartet state; all the other gaps were at least 100 kJ/mol.

**Table 2:** *Atomization Energies at 0 K in kJ/mol with 6-311+G(d,p) basis set. DFT calculations include ZPE correction.*

| species | spin state | mPWPW91 | B3LYP | B97-1 | Literature |
|---|---|---|---|---|---|
| $TiO_2$ | Singlet | -1436 | -1226 | -1269 | -1268 [a] |
| | Triplet | | | | - |
| $TiCl_4$ | Singlet | -1828 | -1641 | -1719 | -1687 [a] |
| | Triplet | | | - | - |
| $TiCl_3$ | Doublet | -1424 | -1296 | -1354 | -1335 [b] |
| | Quartet | | | - | - |
| $TiCl_2$ | Triplet | -974 | -840 | -921 | -913 [b] |
| | Singlet | | | | - |
| TiCl | Quartet | -481 | -428 | -438 | -405 [b] |
| | Doublet | | | | - |
| TiOCl | Doublet | -1231 | -1085 | -1127 | -1074 [a] |
| | Quartet | | | | - |
| $TiOCl_2$ | Singlet | -1675 | -1490 | -1552 | -1489 [a] |
| | Triplet | | | | - |
| $TiOCl_3$ | Doublet | -1838 | -1627 | -1694 | - |
| | Quartet | | | | - |
| $TiO_2Cl_2$ | Singlet | -1953 | -1715 | -1785 | - |
| | Triplet | | | - | - |
| $TiO_2Cl_3$ | Doublet | -2188 | -1935 | -2018 | - |
| | Quartet | | | | - |
| $Ti_2O_2Cl_4$ | Singlet | -3705 | -3335 | -3457 | - |
| | Triplet | | | | - |
| $Ti_2O_2Cl_3$ | Doublet | -3281 | -2960 | -3061 | - |
| | Quartet | | | | - |
| $Ti_2O_3Cl_2$ | Singlet | -3515 | -3133 | -3238 | - |
| | Triplet | | | | - |
| $Ti_2O_3Cl_3$ | Doublet | -3697 | -3300 | -3421 | - |
| | Quartet | | | | - |
| $Ti_3O_4Cl_4$ | Singlet | -5558 | -5001 | -5167 | - |
| | Triplet | | | | - |
| $Ti_5O_6Cl_8$ | Singlet | - | -8481 | -8771 | - |
| | Triplet | - | - | - | - |

[a] NIST-JANAF tables [7]

[b] Atomization enthalpy at 298 K based on Hildenbrand[19] and the NIST-JANAF tables [7]

### 3.3 $TiOCl_2$

As explained in the introduction, $TiOCl_2$ and the species required to find its enthalpy of formation ($TiCl_4$ and $TiO_2$), were subjected to a more detailed analysis using two additional DFT functionals as well as HF, MP2 and coupled cluster calculations. The enthalpies of formation derived from these calculations are reported in Table 3.

**Table 3:** *Enthalpies of formation of $TiOCl_2$ derived from the isogyric reaction described in Table 1. HF, MP2, CCSD and CCSD(T) calculations were based on B3LYP/6-311+G(d,p) geometries and have been corrected for thermal contributions to enthalpy using B97-1/6-311+G(d,p) frequencies.*

| basis set | method | $\Delta_f H^\circ_{298\,K}$ [a] |
|---|---|---|
| | Literature [b] | -546 |
| LANL2 & 3-21G | HF | -652 |
| | MP2 | -635 |
| | CCSD | -636 |
| | CCSD(T) | -620 |
| LANL2 & 6-311G(d,p) | HF | -636 |
| | MP2 | -623 |
| | CCSD | -623 |
| | CCSD(T) | -609 |
| 6-311+G(d,p) | PW91PW91 | -578 |
| | BPW91 | -579 |
| | mPWPW91 | -579 |
| | B3LYP | -590 |
| | B97-1 | -591 |
| | HF | -638 |
| | MP2 | -607 |
| | CCSD | -610 |
| | CCSD(T) | -598 |

[a] kJ/mol [b] NIST/JANAF tables[7]

The MP2/CCSD/CCSD(T) results converge nicely with respect to basis set and increasing level of correlation treatment. CCSD and MP2, which both include up to double excitations from the HF reference, agree very closely, lowering the enthalpy by 28-31 kJ/mol relative to HF/6-311+G(d,p). The additional perturbative inclusion of triple excitations in CCSD(T), though important, introduces a smaller correction, changing the energy by 9–12 kJ/mol from MP2 and CCSD in the 6-311+G(d,p) basis set. These results suggest that

the correlation treatment is well-behaved with respect to systematic improvement, and it seems reasonable to expect that higher order excitations would not alter the enthalpy of formation by more than $\sim$10 kJ/mol. The good agreements with B3LYP and B97-1 (8 and 7 kJ/mol lower, respectively) further inspire confidence in the predictions within this basis set.

Although a supplemented triple-zeta basis set is sufficient for DFT calculations[6], it is possible that the CCSD(T) calculations are limited by basis set truncation error and would benefit from a larger basis set. Moving O and Cl from 3-21G, a poor double-zeta basis set, to 6-311G(d,p), a better triple-zeta basis set with polarization functions, lowers the enthalpy of $TiOCl_2$ by 11 kJ/mol for CCSD(T). A further 11 kJ/mol change occurs when the all-electron triple-zeta basis is used instead of the ECP for Ti and diffuse functions are added to all atoms. These relatively small changes in enthalpy suggest that basis set errors are not too large.

Based on these calculations we recommend a value of $\Delta_f H^\circ_{298\,K} = -598 \pm 20$ kJ/mol for $TiOCl_2$. The NIST/JANAF value of $-546$ kJ/mol, which apparently is an old estimate not based on any direct measurement, lies outside our estimated uncertainty, and so should be considered for revision. We have used the value calculated here ($-598$ kJ/mol) in deriving $\Delta_f H^\circ_{298\,K}$ values for other species in this paper.

## 3.4 Thermochemistry

The recommended standard entropies and enthalpies of formation at 298 K are given in table 4 along with B97-1 frequencies. With the exception of $TiOCl_2$ the recommended enthalpies are based on the B97-1 functional, which is probably the most accurate[6]. For $TiOCl_2$ the electronic energy is from the CCSD(T)/6-311+G(d,p) calculation based on the B3LYP geometry, with the thermal energy based on B97-1 frequencies reported here.

For most species the enthalpies derived from B3LYP calculations differed from the B97-1 enthalpies by less than 2 kJ/mol. The exceptions were the three species that were evaluated through anisodesmic reactions: $TiOCl_3$, $TiO_2Cl_2$, and $Ti_2O_3Cl_3$, for which the B3LYP enthalpies were respectively 15 kJ/mol lower, 22 kJ/mol higher, and 7 kJ/mol lower than the B97-1 enthalpies. While this close agreement increases confidence in the calculations, it is worth remembering that the actual error will be larger than this; B3LYP and B97-1 are both hybrid DFT functionals with some exact (HF) exchange so behave similarly. MPWPW91, a pure DFT functional, gives enthalpies that differ from B97-1 by $\sim$ 20 kJ/mol on average and as much as 59 kJ/mol for the anisodesmic reaction to find $TiO_2Cl_2$. In addition to errors in the DFT calculations, errors in the reference species enthalpies will propagate to the enthalpies that are derived from them.

**Table 4:** *Calculated thermochemistry at 298 K.*

| species | $\Delta_f H^\circ_{298\,K}$ kJ/mol | $S^\circ_{298\,K}$ J/mol K | rot. const. GHz | vibrational frequencies $cm^{-1}$ |
|---|---|---|---|---|
| TiOCl | -274[a] | 292 | 39.120 2.9782 2.7676 | 113 398 1036 |
| $TiOCl_2$ | -598[b] | 335 | 5.4126 1.7850 1.3423 | 23.0 113 212 378 506 1091 |
| $TiOCl_3$ | -639 | 379 | 1.6461 1.5723 1.0712 | 77.1 94.0 116 144 155 378 469 483 669 |
| $TiO_2Cl_2$ | -558 | 342 | 2.6652 1.8968 1.1982 | 110 125 149 174 384 493 658 683 966 |
| $TiO_2Cl_3$ | -774 | 404 | 1.2747 1.2687 1.1039 | 33.0 108 127 140 147 160 389 405 470 493 549 1229 |
| $Ti_2O_2Cl_3$ | -1257 | 438 | 1.7164 0.4549 0.3859 | 14.1 72.4 82.7 100 140 161 273 278 393 422 495 539 695 708 760 |
| $Ti_2O_2Cl_4$ | -1552 | 449 | 0.9517 0.4544 0.3262 | 40.4 65.8 91.6 97.1 102 116 152 214 294 302 398 410 489 527 539 710 731 767 |
| $Ti_2O_3Cl_2$ | -1331 | 402 | 1.6100 0.7549 0.5699 | 59.6 101 122 142 164 256 303 335 462 488 494 707 722 776 1065 |
| $Ti_2O_3Cl_3$ | -1418 | 461 | 1.2145 0.5034 0.3813 | 44.0 61.3 89.0 105 108 135 159 187 293 315 330 420 504 533 690 703 732 765 |
| $Ti_3O_4Cl_4$ | -2301 | 538 | 0.8631 0.1581 0.1581 | 30.3 31.9 50.6 85.3 85.9 87.8 108 138 140 163 235 239 290 291 354 439 439 444 507 508 534 709 714 717 739 765 778 |
| $Ti_5O_6Cl_8$ | -4011 | 823 | 0.1297 0.0875 0.0875 | 19.4 20.8 20.8 28.5 28.5 39.0 58.0 61.9 67.8 77.8 80.7 83.8 83.8 99.3 109 109 110 129 140 141 141 220 223 223 246 246 283 321 327 327 331 371 383 429 429 484 486 486 494 499 510 510 521 555 626 754 754 823 876 881 881 |

[a] JANAF value: $-244$ kJ/mol (estimated in 1963).

[b] Electronic energy from CCSD(T)/6-311+G(d,p) at B3LYP/6-311+G(d,p) geometry. Thermal contribution to enthalpy from B97-1/6-3111+G(d,p) frequencies. JANAF value: $-546$ kJ/mol (estimated in 1963).

## 3.5 Equilibrium Composition

Figure 3 shows the computed equilibrium composition of a gas initially comprising a stoichiometric mixture of $TiCl_4$ and $O_2$, at a pressure of 3 bar, similar to that of the industrial process, and temperatures between 100 and 3000 K. The thermochemical data for TiOCl, $TiOCl_2$, $TiOCl_3$, $TiO_2Cl_2$, $TiO_2Cl_3$, $Ti_2O_2Cl_3$, $Ti_2O_2Cl_4$, $Ti_2O_3Cl_2$, $Ti_2O_3Cl_3$, $Ti_3O_4Cl_4$, and $Ti_5O_6Cl_8$, were taken from this work. Those for $TiCl_4$, $TiCl_3$, $TiCl_2$, TiCl, Ti, TiO, $TiO_2$, O, $O_2$, $O_3$, Cl, ClO, $ClO_2$, $Cl_2$, and $Cl_2O$ were taken from the NASA database[11, 24] supplied with Cantera. All other species, including solid $TiO_2$, were excluded from the simulation.

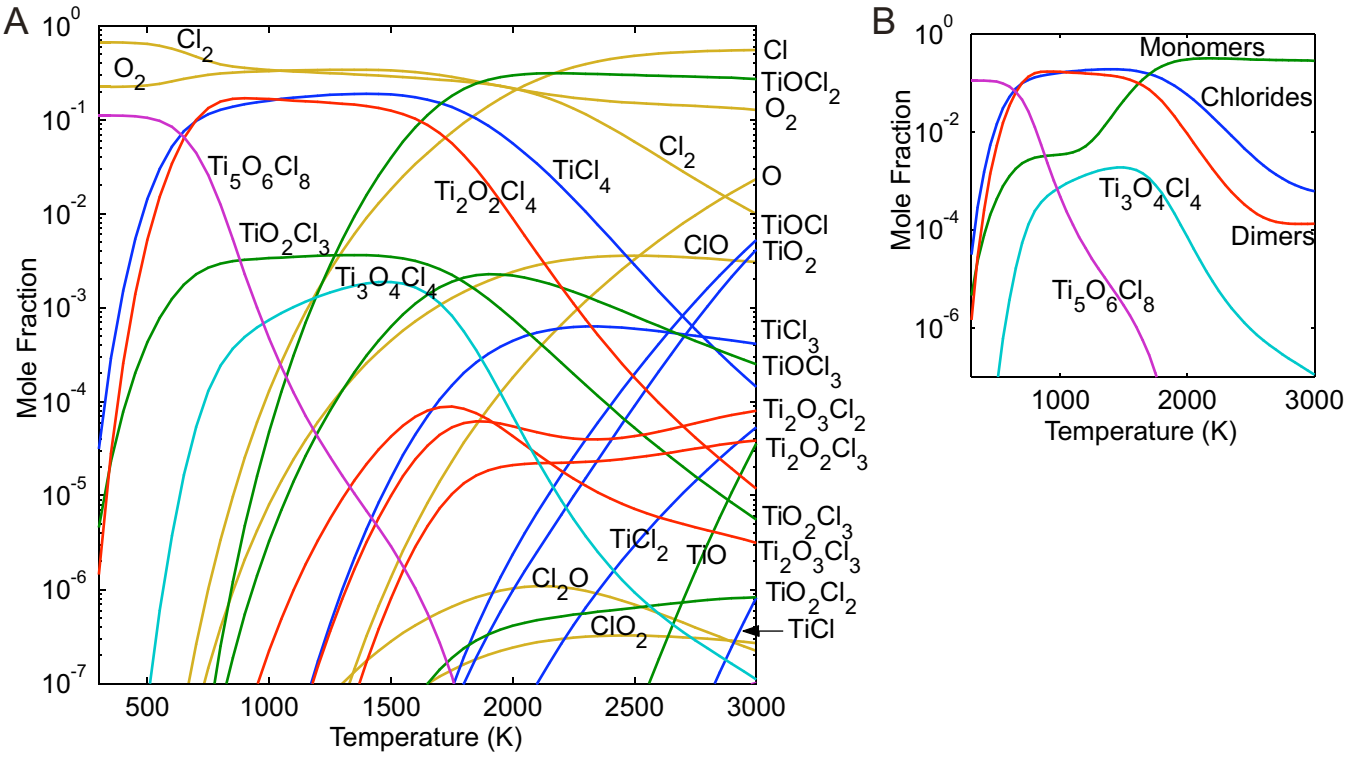


**Figure 3:** *Computed equilibrium composition of a mixture initially containing 50 mol% $TiCl_4$ in $O_2$, at 3 bar and 300–3000 K. (A) Detailed composition. (B) Summary with chlorides ($TiCl_z$), monomers ($TiO_yCl_z$), and dimers ($Ti_2O_yCl_z$) grouped.*

As anticipated, $TiOCl_2$ has the highest equilibrium concentration of all $Ti_1$ species except, below 2400 K, for the reactant $TiCl_4$. Although less stable than $TiOCl_2$, the other $TiO_yCl_z$ species are no less important for the kinetic mechanism, because $TiOCl_2$ is unlikely to be formed directly from $TiCl_z$ radicals, instead proceeding via $TiO_2Cl_2$ or $TiO_2Cl_3$ from reaction with $O_2$, or via $TiOCl_3$ from reaction with ClO. Due to the stability of $TiOCl_2$ relative to other reactive $Ti_1$ species, the most likely collision that leads to a $Ti_2$ species is between two $TiOCl_2$ molecules. The product of $TiOCl_2$ dimerisation, $Ti_2O_2Cl_4$, is stable relative to the monomer at all temperatures below 2400 K, and is therefore likely to play an important role in the mechanism. $Ti_2O_2Cl_4$ can undergo chlorine abstraction and oxidation reactions to form other $Ti_2$ intermediates such as $Ti_2O_2Cl_3$, $Ti_2O_3Cl_2$, and

$Ti_2O_3Cl_3$, so although these are less stable than $Ti_2O_2Cl_4$ at most temperatures, they may still feature in a detailed kinetic mechanism, much like the lesser $TiO_yCl_z$ species.

Of the many possible $Ti_3$ species, we expect $Ti_3O_4Cl_4$ to be one of the more stable due to the double-oxygen bridge between each of the Ti atoms. However, the equilibrium concentration of this species is predicted to be lower than that of the dimer by at least an order of magnitude. This implies that the critical nucleus size, above which molecules grow irreversibly and can be safely treated as particles[36], is larger than $Ti_2$.

Below $\sim$600 K the largest species in our simulation, $Ti_5O_6Cl_8$, is predicted to have the highest concentration of the species containing titanium. This suggests that at low temperatures the critical nucleus size has five or fewer Ti atoms. However, at the high temperatures employed to speed the kinetics in the industrial process, the $Ti_5$ species is unstable relative to the reactants $TiCl_4$ + $O_2$, suggesting that the critical nucleus size is even larger under those conditions.

# 4 Conclusion

Quantum calculations were used to obtain thermochemical data, including standard entropies and enthalpies of formation, for some titanium oxychloride species, $Ti_xO_yCl_z$, many of which were not previously reported in the literature and are impossible to obtain with the available experimental techniques. These thermochemical data will enable the development of more detailed kinetic models of the combustion of titanium tetrachloride to produce titanium dioxide. A comparison of the results from these calculations with the NIST and JANAF tables suggests that the literature values for $TiOCl_2$ should be revised.

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# 6 Appendices

Thermochemical tables and polynomial coefficients in NASA form, formatted for Cantera software[9], for $C_p(T)$, $H^\circ(T)$ and $S^\circ(T)$ are available for the species TiOCl, $TiOCl_2$, $TiOCl_3$, $TiO_2Cl_2$, $TiO_2Cl_3$, $Ti_2O_3Cl_3$, $Ti_2O_3Cl_2$, $Ti_2O_2Cl_3$, $Ti_3O_4Cl_4$, $Ti_2O_2Cl_4$, and $Ti_5O_6Cl_8$.

If viewing this document in Adobe Acrobat Reader, the full mechanism in Cantera format can be extracted by clicking on this paperclip:

**Table 5:** *TiOCl thermochemistry*

| T (K) | $C_p$ (J/mol/K) | H (kJ/mol) | S (J/mol/K) |
|---|---|---|---|
| 100 | 40.86 | -283.51 | 242.76 |
| 150 | 43.63 | -281.39 | 259.88 |
| 200 | 45.77 | -279.16 | 272.73 |
| 250 | 47.52 | -276.82 | 283.14 |
| 298.15 | 48.96 | -274.50 | 291.64 |
| 300 | 49.01 | -274.41 | 291.94 |
| 350 | 50.30 | -271.93 | 299.60 |
| 400 | 51.41 | -269.38 | 306.39 |
| 450 | 52.34 | -266.79 | 312.50 |
| 500 | 53.12 | -264.15 | 318.05 |
| 600 | 54.33 | -258.77 | 327.85 |
| 700 | 55.18 | -253.30 | 336.29 |
| 800 | 55.79 | -247.75 | 343.70 |
| 900 | 56.24 | -242.14 | 350.30 |
| 1000 | 56.58 | -236.50 | 356.25 |
| 1100 | 56.84 | -230.83 | 361.65 |
| 1200 | 57.04 | -225.14 | 366.61 |
| 1300 | 57.20 | -219.42 | 371.18 |
| 1400 | 57.34 | -213.70 | 375.42 |
| 1500 | 57.44 | -207.96 | 379.38 |
| 1600 | 57.53 | -202.21 | 383.09 |
| 1700 | 57.60 | -196.45 | 386.58 |
| 1800 | 57.67 | -190.69 | 389.88 |
| 1900 | 57.72 | -184.92 | 393.00 |
| 2000 | 57.77 | -179.14 | 395.96 |
| 2100 | 57.81 | -173.37 | 398.78 |
| 2200 | 57.84 | -167.58 | 401.47 |
| 2300 | 57.87 | -161.80 | 404.04 |
| 2400 | 57.90 | -156.01 | 406.50 |
| 2500 | 57.92 | -150.22 | 408.87 |
| 2600 | 57.94 | -144.43 | 411.14 |
| 2700 | 57.96 | -138.63 | 413.33 |
| 2800 | 57.98 | -132.83 | 415.43 |
| 2900 | 57.99 | -127.03 | 417.47 |
| 3000 | 58.01 | -121.24 | 419.44 |

**Table 6:** *$TiOCl_2$ thermochemistry*

| T (K) | $C_p$ (J/mol/K) | H (kJ/mol) | S (J/mol/K) |
|---|---|---|---|
| 100 | 53.63 | -610.53 | 267.83 |
| 150 | 59.70 | -607.69 | 290.78 |
| 200 | 64.20 | -604.58 | 308.60 |
| 250 | 67.54 | -601.28 | 323.30 |
| 298.15 | 70.03 | -597.97 | 335.42 |
| 300 | 70.12 | -597.84 | 335.86 |
| 350 | 72.17 | -594.28 | 346.82 |
| 400 | 73.83 | -590.63 | 356.57 |
| 450 | 75.18 | -586.90 | 365.35 |
| 500 | 76.28 | -583.12 | 373.33 |
| 600 | 77.95 | -575.40 | 387.39 |
| 700 | 79.10 | -567.54 | 399.50 |
| 800 | 79.93 | -559.59 | 410.12 |
| 900 | 80.53 | -551.57 | 419.57 |
| 1000 | 80.99 | -543.49 | 428.08 |
| 1100 | 81.33 | -535.37 | 435.82 |
| 1200 | 81.61 | -527.22 | 442.91 |
| 1300 | 81.82 | -519.05 | 449.45 |
| 1400 | 82.00 | -510.86 | 455.52 |
| 1500 | 82.14 | -502.65 | 461.18 |
| 1600 | 82.26 | -494.43 | 466.49 |
| 1700 | 82.35 | -486.20 | 471.47 |
| 1800 | 82.44 | -477.96 | 476.18 |
| 1900 | 82.51 | -469.72 | 480.64 |
| 2000 | 82.57 | -461.46 | 484.88 |
| 2100 | 82.62 | -453.20 | 488.91 |
| 2200 | 82.67 | -444.94 | 492.75 |
| 2300 | 82.71 | -436.67 | 496.43 |
| 2400 | 82.74 | -428.40 | 499.95 |
| 2500 | 82.77 | -420.12 | 503.33 |
| 2600 | 82.80 | -411.84 | 506.57 |
| 2700 | 82.83 | -403.56 | 509.70 |
| 2800 | 82.85 | -395.28 | 512.71 |
| 2900 | 82.87 | -386.99 | 515.62 |
| 3000 | 82.89 | -378.70 | 518.43 |

**Table 7:** *$TiOCl_3$ thermochemistry*

| T (K) | $C_p$ (J/mol/K) | H (kJ/mol) | S (J/mol/K) |
|---|---|---|---|
| 100 | 67.99 | -655.79 | 290.45 |
| 150 | 77.85 | -652.13 | 319.98 |
| 200 | 85.35 | -648.04 | 343.45 |
| 250 | 90.84 | -643.63 | 363.12 |
| 298.15 | 94.65 | -639.16 | 379.46 |
| 300 | 94.77 | -638.98 | 380.05 |
| 350 | 97.60 | -634.17 | 394.88 |
| 400 | 99.67 | -629.24 | 408.06 |
| 450 | 101.20 | -624.21 | 419.89 |
| 500 | 102.37 | -619.12 | 430.62 |
| 600 | 103.98 | -608.80 | 449.43 |
| 700 | 105.01 | -598.35 | 465.55 |
| 800 | 105.70 | -587.81 | 479.62 |
| 900 | 106.18 | -577.21 | 492.10 |
| 1000 | 106.53 | -566.58 | 503.30 |
| 1100 | 106.80 | -555.91 | 513.47 |
| 1200 | 107.00 | -545.22 | 522.77 |
| 1300 | 107.16 | -534.51 | 531.34 |
| 1400 | 107.28 | -523.79 | 539.29 |
| 1500 | 107.39 | -513.06 | 546.69 |
| 1600 | 107.47 | -502.31 | 553.63 |
| 1700 | 107.54 | -491.56 | 560.14 |
| 1800 | 107.60 | -480.80 | 566.29 |
| 1900 | 107.65 | -470.04 | 572.11 |
| 2000 | 107.69 | -459.27 | 577.63 |
| 2100 | 107.73 | -448.50 | 582.89 |
| 2200 | 107.76 | -437.73 | 587.90 |
| 2300 | 107.79 | -426.95 | 592.69 |
| 2400 | 107.81 | -416.17 | 597.28 |
| 2500 | 107.83 | -405.39 | 601.68 |
| 2600 | 107.85 | -394.61 | 605.91 |
| 2700 | 107.87 | -383.82 | 609.98 |
| 2800 | 107.89 | -373.03 | 613.90 |
| 2900 | 107.90 | -362.24 | 617.69 |
| 3000 | 107.91 | -351.45 | 621.35 |

**Table 8:** *$TiO_2Cl_2$ thermochemistry*

| T (K) | $C_p$ (J/mol/K) | H (kJ/mol) | S (J/mol/K) |
|---|---|---|---|
| 100 | 58.68 | -572.69 | 263.76 |
| 150 | 67.72 | -569.52 | 289.34 |
| 200 | 75.11 | -565.94 | 309.87 |
| 250 | 81.24 | -562.03 | 327.31 |
| 298.15 | 86.01 | -558.00 | 342.04 |
| 300 | 86.18 | -557.84 | 342.58 |
| 350 | 90.07 | -553.43 | 356.16 |
| 400 | 93.14 | -548.85 | 368.40 |
| 450 | 95.55 | -544.13 | 379.52 |
| 500 | 97.47 | -539.30 | 389.69 |
| 600 | 100.25 | -529.40 | 407.72 |
| 700 | 102.10 | -519.28 | 423.32 |
| 800 | 103.38 | -509.00 | 437.04 |
| 900 | 104.30 | -498.62 | 449.28 |
| 1000 | 104.98 | -488.15 | 460.30 |
| 1100 | 105.49 | -477.63 | 470.33 |
| 1200 | 105.89 | -467.06 | 479.53 |
| 1300 | 106.20 | -456.45 | 488.02 |
| 1400 | 106.46 | -445.82 | 495.90 |
| 1500 | 106.66 | -435.16 | 503.25 |
| 1600 | 106.83 | -424.49 | 510.14 |
| 1700 | 106.97 | -413.80 | 516.62 |
| 1800 | 107.09 | -403.10 | 522.74 |
| 1900 | 107.19 | -392.38 | 528.53 |
| 2000 | 107.28 | -381.66 | 534.03 |
| 2100 | 107.35 | -370.93 | 539.27 |
| 2200 | 107.41 | -360.19 | 544.26 |
| 2300 | 107.47 | -349.44 | 549.04 |
| 2400 | 107.52 | -338.69 | 553.61 |
| 2500 | 107.57 | -327.94 | 558.00 |
| 2600 | 107.60 | -317.18 | 562.22 |
| 2700 | 107.64 | -306.42 | 566.28 |
| 2800 | 107.67 | -295.65 | 570.20 |
| 2900 | 107.70 | -284.88 | 573.98 |
| 3000 | 107.72 | -274.11 | 577.63 |

**Table 9:** *$TiO_2Cl_3$ thermochemistry*

| T (K) | $C_p$ (J/mol/K) | H (kJ/mol) | S (J/mol/K) |
|---|---|---|---|
| 100 | 74.60 | -792.77 | 302.17 |
| 150 | 87.94 | -788.69 | 335.05 |
| 200 | 98.01 | -784.03 | 361.81 |
| 250 | 105.26 | -778.94 | 384.50 |
| 298.15 | 110.35 | -773.74 | 403.50 |
| 300 | 110.52 | -773.54 | 404.18 |
| 350 | 114.45 | -767.91 | 421.53 |
| 400 | 117.46 | -762.11 | 437.02 |
| 450 | 119.84 | -756.17 | 450.99 |
| 500 | 121.73 | -750.13 | 463.72 |
| 600 | 124.52 | -737.81 | 486.18 |
| 700 | 126.43 | -725.25 | 505.53 |
| 800 | 127.79 | -712.54 | 522.50 |
| 900 | 128.78 | -699.71 | 537.62 |
| 1000 | 129.52 | -686.79 | 551.22 |
| 1100 | 130.08 | -673.81 | 563.60 |
| 1200 | 130.52 | -660.78 | 574.93 |
| 1300 | 130.87 | -647.71 | 585.40 |
| 1400 | 131.16 | -634.61 | 595.11 |
| 1500 | 131.39 | -621.48 | 604.16 |
| 1600 | 131.58 | -608.33 | 612.65 |
| 1700 | 131.74 | -595.17 | 620.63 |
| 1800 | 131.88 | -581.98 | 628.16 |
| 1900 | 131.99 | -568.79 | 635.30 |
| 2000 | 132.09 | -555.59 | 642.07 |
| 2100 | 132.18 | -542.37 | 648.52 |
| 2200 | 132.25 | -529.15 | 654.67 |
| 2300 | 132.32 | -515.92 | 660.55 |
| 2400 | 132.37 | -502.69 | 666.18 |
| 2500 | 132.42 | -489.45 | 671.59 |
| 2600 | 132.47 | -476.20 | 676.78 |
| 2700 | 132.51 | -462.95 | 681.78 |
| 2800 | 132.55 | -449.70 | 686.60 |
| 2900 | 132.58 | -436.45 | 691.25 |
| 3000 | 132.61 | -423.19 | 695.75 |

**Table 10:** *$Ti_2O_2Cl_3$ thermochemistry*

| T (K) | $C_p$ (J/mol/K) | H (kJ/mol) | S (J/mol/K) |
|---|---|---|---|
| 100 | 82.43 | -1278.72 | 323.50 |
| 150 | 98.20 | -1274.19 | 360.01 |
| 200 | 111.14 | -1268.95 | 390.10 |
| 250 | 121.26 | -1263.13 | 416.03 |
| 298.15 | 128.70 | -1257.10 | 438.06 |
| 300 | 128.94 | -1256.86 | 438.85 |
| 350 | 134.70 | -1250.26 | 459.18 |
| 400 | 139.04 | -1243.42 | 477.47 |
| 450 | 142.35 | -1236.38 | 494.04 |
| 500 | 144.90 | -1229.19 | 509.18 |
| 600 | 148.49 | -1214.51 | 535.94 |
| 700 | 150.81 | -1199.54 | 559.02 |
| 800 | 152.39 | -1184.37 | 579.26 |
| 900 | 153.51 | -1169.07 | 597.28 |
| 1000 | 154.32 | -1153.68 | 613.50 |
| 1100 | 154.94 | -1138.22 | 628.24 |
| 1200 | 155.41 | -1122.70 | 641.74 |
| 1300 | 155.78 | -1107.14 | 654.20 |
| 1400 | 156.08 | -1091.54 | 665.75 |
| 1500 | 156.32 | -1075.92 | 676.53 |
| 1600 | 156.51 | -1060.28 | 686.62 |
| 1700 | 156.68 | -1044.62 | 696.12 |
| 1800 | 156.82 | -1028.95 | 705.08 |
| 1900 | 156.93 | -1013.26 | 713.56 |
| 2000 | 157.04 | -997.56 | 721.61 |
| 2100 | 157.12 | -981.85 | 729.27 |
| 2200 | 157.20 | -966.14 | 736.59 |
| 2300 | 157.26 | -950.41 | 743.57 |
| 2400 | 157.32 | -934.68 | 750.27 |
| 2500 | 157.37 | -918.95 | 756.69 |
| 2600 | 157.42 | -903.21 | 762.87 |
| 2700 | 157.46 | -887.47 | 768.81 |
| 2800 | 157.49 | -871.72 | 774.53 |
| 2900 | 157.53 | -855.97 | 780.06 |
| 3000 | 157.56 | -840.21 | 785.40 |

**Table 11:** *$Ti_2O_2Cl_4$ thermochemistry*

| T (K) | $C_p$ (J/mol/K) | H (kJ/mol) | S (J/mol/K) |
|---|---|---|---|
| 100 | 93.52 | -1577.12 | 317.09 |
| 150 | 112.78 | -1571.94 | 358.79 |
| 200 | 128.29 | -1565.90 | 393.45 |
| 250 | 140.27 | -1559.17 | 423.42 |
| 298.15 | 148.98 | -1552.20 | 448.91 |
| 300 | 149.27 | -1551.92 | 449.83 |
| 350 | 155.99 | -1544.28 | 473.37 |
| 400 | 161.03 | -1536.35 | 494.55 |
| 450 | 164.86 | -1528.20 | 513.75 |
| 500 | 167.82 | -1519.88 | 531.27 |
| 600 | 171.97 | -1502.88 | 562.27 |
| 700 | 174.66 | -1485.54 | 588.99 |
| 800 | 176.48 | -1467.97 | 612.44 |
| 900 | 177.77 | -1450.26 | 633.31 |
| 1000 | 178.71 | -1432.43 | 652.09 |
| 1100 | 179.42 | -1414.52 | 669.15 |
| 1200 | 179.96 | -1396.55 | 684.79 |
| 1300 | 180.39 | -1378.54 | 699.21 |
| 1400 | 180.73 | -1360.48 | 712.59 |
| 1500 | 181.01 | -1342.39 | 725.07 |
| 1600 | 181.23 | -1324.28 | 736.76 |
| 1700 | 181.42 | -1306.15 | 747.75 |
| 1800 | 181.58 | -1288.00 | 758.13 |
| 1900 | 181.72 | -1269.83 | 767.95 |
| 2000 | 181.84 | -1251.65 | 777.27 |
| 2100 | 181.94 | -1233.46 | 786.15 |
| 2200 | 182.02 | -1215.27 | 794.61 |
| 2300 | 182.10 | -1197.06 | 802.71 |
| 2400 | 182.16 | -1178.85 | 810.46 |
| 2500 | 182.22 | -1160.63 | 817.90 |
| 2600 | 182.28 | -1142.40 | 825.04 |
| 2700 | 182.32 | -1124.17 | 831.92 |
| 2800 | 182.36 | -1105.94 | 838.55 |
| 2900 | 182.40 | -1087.70 | 844.95 |
| 3000 | 182.43 | -1069.46 | 851.14 |

**Table 12:** *$Ti_2O_3Cl_2$ thermochemistry*

| T (K) | $C_p$ (J/mol/K) | H (kJ/mol) | S (J/mol/K) |
|---|---|---|---|
| 100 | 73.73 | -1350.67 | 296.10 |
| 150 | 90.10 | -1346.56 | 329.21 |
| 200 | 103.28 | -1341.72 | 357.00 |
| 250 | 113.79 | -1336.28 | 381.22 |
| 298.15 | 121.77 | -1330.60 | 401.98 |
| 300 | 122.04 | -1330.37 | 402.73 |
| 350 | 128.48 | -1324.10 | 422.05 |
| 400 | 133.50 | -1317.55 | 439.55 |
| 450 | 137.45 | -1310.77 | 455.51 |
| 500 | 140.57 | -1303.82 | 470.16 |
| 600 | 145.11 | -1289.52 | 496.22 |
| 700 | 148.13 | -1274.85 | 518.83 |
| 800 | 150.23 | -1259.92 | 538.75 |
| 900 | 151.74 | -1244.82 | 556.54 |
| 1000 | 152.85 | -1229.59 | 572.59 |
| 1100 | 153.70 | -1214.26 | 587.20 |
| 1200 | 154.35 | -1198.86 | 600.60 |
| 1300 | 154.87 | -1183.39 | 612.97 |
| 1400 | 155.28 | -1167.88 | 624.47 |
| 1500 | 155.62 | -1152.34 | 635.19 |
| 1600 | 155.90 | -1136.76 | 645.24 |
| 1700 | 156.13 | -1121.16 | 654.70 |
| 1800 | 156.33 | -1105.54 | 663.63 |
| 1900 | 156.49 | -1089.90 | 672.09 |
| 2000 | 156.63 | -1074.24 | 680.12 |
| 2100 | 156.76 | -1058.57 | 687.77 |
| 2200 | 156.86 | -1042.89 | 695.06 |
| 2300 | 156.96 | -1027.20 | 702.04 |
| 2400 | 157.04 | -1011.50 | 708.72 |
| 2500 | 157.11 | -995.79 | 715.13 |
| 2600 | 157.18 | -980.08 | 721.29 |
| 2700 | 157.23 | -964.35 | 727.23 |
| 2800 | 157.29 | -948.63 | 732.95 |
| 2900 | 157.33 | -932.90 | 738.47 |
| 3000 | 157.37 | -917.16 | 743.80 |

**Table 13:** *$Ti_2O_3Cl_3$ thermochemistry*

| T (K) | $C_p$ (J/mol/K) | H (kJ/mol) | S (J/mol/K) |
|---|---|---|---|
| 100 | 93.58 | -1442.59 | 330.06 |
| 150 | 112.52 | -1437.42 | 371.75 |
| 200 | 127.51 | -1431.41 | 406.26 |
| 250 | 139.26 | -1424.72 | 436.03 |
| 298.15 | 147.95 | -1417.80 | 461.33 |
| 300 | 148.24 | -1417.53 | 462.25 |
| 350 | 155.03 | -1409.94 | 485.63 |
| 400 | 160.17 | -1402.05 | 506.69 |
| 450 | 164.11 | -1393.94 | 525.79 |
| 500 | 167.16 | -1385.65 | 543.24 |
| 600 | 171.46 | -1368.71 | 574.13 |
| 700 | 174.26 | -1351.41 | 600.79 |
| 800 | 176.16 | -1333.88 | 624.19 |
| 900 | 177.51 | -1316.20 | 645.02 |
| 1000 | 178.50 | -1298.39 | 663.78 |
| 1100 | 179.24 | -1280.51 | 680.82 |
| 1200 | 179.81 | -1262.55 | 696.45 |
| 1300 | 180.26 | -1244.55 | 710.86 |
| 1400 | 180.62 | -1226.50 | 724.23 |
| 1500 | 180.91 | -1208.43 | 736.70 |
| 1600 | 181.15 | -1190.32 | 748.38 |
| 1700 | 181.35 | -1172.20 | 759.37 |
| 1800 | 181.51 | -1154.06 | 769.74 |
| 1900 | 181.66 | -1135.90 | 779.56 |
| 2000 | 181.78 | -1117.72 | 788.88 |
| 2100 | 181.88 | -1099.54 | 797.75 |
| 2200 | 181.98 | -1081.35 | 806.22 |
| 2300 | 182.05 | -1063.15 | 814.31 |
| 2400 | 182.12 | -1044.94 | 822.06 |
| 2500 | 182.19 | -1026.72 | 829.49 |
| 2600 | 182.24 | -1008.50 | 836.64 |
| 2700 | 182.29 | -990.27 | 843.52 |
| 2800 | 182.33 | -972.04 | 850.15 |
| 2900 | 182.37 | -953.81 | 856.55 |
| 3000 | 182.41 | -935.57 | 862.73 |

**Table 14:** *$Ti_3O_4Cl_4$ thermochemistry*

| T (K) | $C_p$ (J/mol/K) | H (kJ/mol) | S (J/mol/K) |
|---|---|---|---|
| 100 | 119.31 | -2333.52 | 364.74 |
| 150 | 147.02 | -2326.84 | 418.53 |
| 200 | 170.04 | -2318.90 | 464.08 |
| 250 | 188.41 | -2309.92 | 504.09 |
| 298.15 | 202.09 | -2300.50 | 538.49 |
| 300 | 202.55 | -2300.13 | 539.75 |
| 350 | 213.29 | -2289.72 | 571.81 |
| 400 | 221.45 | -2278.84 | 600.85 |
| 450 | 227.71 | -2267.60 | 627.31 |
| 500 | 232.56 | -2256.09 | 651.56 |
| 600 | 239.42 | -2232.47 | 694.62 |
| 700 | 243.89 | -2208.29 | 731.89 |
| 800 | 246.93 | -2183.74 | 764.66 |
| 900 | 249.09 | -2158.93 | 793.88 |
| 1000 | 250.66 | -2133.94 | 820.21 |
| 1100 | 251.85 | -2108.81 | 844.16 |
| 1200 | 252.77 | -2083.58 | 866.11 |
| 1300 | 253.48 | -2058.26 | 886.37 |
| 1400 | 254.06 | -2032.89 | 905.18 |
| 1500 | 254.53 | -2007.46 | 922.72 |
| 1600 | 254.91 | -1981.98 | 939.16 |
| 1700 | 255.23 | -1956.48 | 954.63 |
| 1800 | 255.50 | -1930.94 | 969.22 |
| 1900 | 255.73 | -1905.38 | 983.04 |
| 2000 | 255.92 | -1879.79 | 996.17 |
| 2100 | 256.09 | -1854.19 | 1008.66 |
| 2200 | 256.24 | -1828.58 | 1020.57 |
| 2300 | 256.36 | -1802.95 | 1031.97 |
| 2400 | 256.48 | -1777.31 | 1042.88 |
| 2500 | 256.58 | -1751.65 | 1053.35 |
| 2600 | 256.66 | -1725.99 | 1063.42 |
| 2700 | 256.74 | -1700.32 | 1073.10 |
| 2800 | 256.81 | -1674.64 | 1082.44 |
| 2900 | 256.88 | -1648.96 | 1091.46 |
| 3000 | 256.93 | -1623.27 | 1100.17 |

**Table 15:** *$Ti_5O_6Cl_8$ thermochemistry*

| T (K) | $C_p$ (J/mol/K) | H (kJ/mol) | S (J/mol/K) |
|---|---|---|---|
| 100 | 220.67 | -4071.44 | 502.51 |
| 150 | 273.23 | -4059.04 | 602.33 |
| 200 | 314.21 | -4044.31 | 686.81 |
| 250 | 345.17 | -4027.78 | 760.42 |
| 298.15 | 367.57 | -4010.60 | 823.22 |
| 300 | 368.31 | -4009.92 | 825.50 |
| 350 | 385.65 | -3991.05 | 883.64 |
| 400 | 398.75 | -3971.42 | 936.03 |
| 450 | 408.78 | -3951.23 | 983.60 |
| 500 | 416.57 | -3930.58 | 1027.09 |
| 600 | 427.60 | -3888.33 | 1104.09 |
| 700 | 434.80 | -3845.19 | 1170.58 |
| 800 | 439.72 | -3801.45 | 1228.98 |
| 900 | 443.20 | -3757.29 | 1280.99 |
| 1000 | 445.76 | -3712.84 | 1327.82 |
| 1100 | 447.69 | -3668.16 | 1370.40 |
| 1200 | 449.18 | -3623.32 | 1409.42 |
| 1300 | 450.35 | -3578.34 | 1445.42 |
| 1400 | 451.28 | -3533.25 | 1478.83 |
| 1500 | 452.04 | -3488.09 | 1509.99 |
| 1600 | 452.67 | -3442.85 | 1539.19 |
| 1700 | 453.19 | -3397.56 | 1566.65 |
| 1800 | 453.62 | -3352.22 | 1592.56 |
| 1900 | 454.00 | -3306.83 | 1617.10 |
| 2000 | 454.31 | -3261.42 | 1640.40 |
| 2100 | 454.59 | -3215.97 | 1662.57 |
| 2200 | 454.83 | -3170.50 | 1683.72 |
| 2300 | 455.04 | -3125.01 | 1703.94 |
| 2400 | 455.22 | -3079.50 | 1723.31 |
| 2500 | 455.38 | -3033.97 | 1741.90 |
| 2600 | 455.52 | -2988.42 | 1759.76 |
| 2700 | 455.65 | -2942.86 | 1776.96 |
| 2800 | 455.77 | -2897.29 | 1793.53 |
| 2900 | 455.87 | -2851.71 | 1809.53 |
| 3000 | 455.96 | -2806.12 | 1824.98 |

**Table 16:** *Polynomial coefficients formatted for Cantera[9].*

```
species(name = 'TiOCL', # ClOTi(2)
      atoms = 'Ti:1 O:1 Cl:1',
    thermo = (
        NASA( [ 100.00, 1000.00], [ 4.191335334e+000 , 8.594198813e-003 , -1.194247195e-005 ,
                8.231298290e-009 , -2.269569234e-012 , -3.455624647e+004 , 9.094304222e+000 ] ),
        NASA( [ 1000.00, 3000.00], [ 6.022828351e+000 , 1.426477358e-003 , -8.569483759e-007 ,
                2.374434516e-010 , -2.500952595e-014 , -3.494901354e+004 , 1.712366899e-001 ] )
          )
     )
species(name = 'TiOCL2', # Cl2OTi
      atoms = 'Ti:1 O:1 Cl:2',
    thermo = (
        NASA( [ 100.00, 1000.00], [ 4.850999861e+000 , 2.001354777e-002 , -3.465798181e-005 ,
                2.844112110e-008 , -8.907190590e-012 , -7.400245633e+004 , 8.038481407e+000 ] ),
        NASA( [ 1000.00, 3000.00], [ 8.952753228e+000 , 1.304839902e-003 , -6.505917942e-007 ,
                1.454512241e-010 , -1.195622092e-014 , -7.478660155e+004 , -1.138233284e+001 ] )
          )
     )
species(name = 'TiOCL3', # Cl3OTi(2)
      atoms = 'Ti:1 O:1 Cl:3',
    thermo = (
        NASA( [ 100.00, 1000.00], [ 5.303769917e+000 , 3.609899817e-002 , -6.891844111e-005 ,
                5.933749393e-008 , -1.900887435e-011 , -7.956110654e+004 , 7.229069323e+000 ] ),
        NASA( [ 1000.00, 3000.00], [ 1.255201104e+001 , 2.083186728e-004 , 1.458171831e-007 ,
                -1.119486595e-010 , 1.874831780e-014 , -8.082008753e+004 , -2.642188101e+001 ] )
          )
     )
species(name = 'TiO2CL2', # Cl2O2Ti
      atoms = 'Ti:1 O:2 Cl:2',
    thermo = (
        NASA( [ 100.00, 1000.00], [ 4.262345042e+000 , 3.311452396e-002 , -5.408385407e-005 ,
                4.165517914e-008 , -1.232245038e-011 , -6.945311454e+004 , 9.040953840e+000 ] ),
        NASA( [ 1000.00, 3000.00], [ 1.117107315e+001 , 2.614342668e-003 , -1.529401279e-006 ,
                4.119050053e-010 , -4.217585084e-014 , -7.077267466e+004 , -2.378220491e+001 ] )
          )
     )
species(name = 'TiO2CL3', # Cl3O2Ti(2)
      atoms = 'Ti:1 O:2 Cl:3',
    thermo = (
        NASA( [ 100.00, 1000.00], [ 5.269306207e+000 , 4.675346588e-002 , -8.716316859e-005 ,
                7.471267398e-008 , -2.399527772e-011 , -9.607932393e+004 , 7.820210546e+000 ] ),
        NASA( [ 1000.00, 3000.00], [ 1.463673799e+001 , 1.321746381e-003 , -3.974673409e-007 ,
                6.702843464e-012 , 9.279889448e-015 , -9.776532144e+004 , -3.593799597e+001 ] )
          )
     )
species(name = 'Ti2O2CL3', # Cl3O2Ti2(2)
      atoms = 'Ti:2 O:2 Cl:3',
    thermo = (
        NASA( [ 100.00, 1000.00], [ 4.931408223e+000 , 6.023515816e-002 , -1.077364926e-004 ,
                8.860976031e-008 , -2.747908105e-011 , -1.545537194e+005 , 1.068794261e+001 ] ),
        NASA( [ 1000.00, 3000.00], [ 1.722666713e+001 , 2.183796225e-003 , -1.057418655e-006 ,
                2.246625490e-010 , -1.695422095e-014 , -1.567700421e+005 , -4.693670453e+001 ] )
          )
     )
```

```
species(name = 'Ti2O2CL4', # Cl4O2Ti2
      atoms = 'Ti:2 O:2 Cl:4',
    thermo = (
        NASA( [ 100.00, 1000.00], [ 5.287928342e+000 , 7.264555733e-002 , -1.315418425e-004 ,
                1.092099731e-007 , -3.410813206e-011 , -1.905322783e+005 , 7.148863410e+000 ] ),
        NASA( [ 1000.00, 3000.00], [ 2.007576714e+001 , 2.235305708e-003 , -9.861436133e-007 ,
                1.779749240e-010 , -9.419976711e-015 , -1.931830502e+005 , -6.205018457e+001 ] )
          )
     )

species(name = 'Ti2O3CL2', # Cl2O3Ti2
      atoms = 'Ti:2 O:3 Cl:2',
    thermo = (
        NASA( [ 100.00, 1000.00], [ 3.909075052e+000 , 5.965984584e-002 , -1.014950910e-004 ,
                8.092530048e-008 , -2.461517124e-011 , -1.631042851e+005 , 1.212928629e+001 ] ),
        NASA( [ 1000.00, 3000.00], [ 1.623336441e+001 , 3.733781124e-003 , -2.049869971e-006 ,
                5.158950596e-010 , -4.921153511e-014 , -1.654173822e+005 , -4.613878918e+001 ] )
          )
     )
species(name = 'Ti2O3CL3', # Cl3O3Ti2(2)
      atoms = 'Ti:2 O:3 Cl:3',
    thermo = (
        NASA( [ 100.00, 1000.00], [ 5.505996743e+000 , 7.001288499e-002 , -1.246293063e-004 ,
                1.022487306e-007 , -3.167024157e-011 , -1.743635689e+005 , 7.935704258e+000 ] ),
        NASA( [ 1000.00, 3000.00], [ 1.983763106e+001 , 2.680484415e-003 , -1.311081065e-006 ,
                2.829445581e-010 , -2.191453749e-014 , -1.769626336e+005 , -5.931391681e+001 ] )
          )
     )
species(name = 'Ti3O4CL4', # Cl4O4Ti3
      atoms = 'Ti:3 O:4 Cl:4',
    thermo = (
        NASA( [ 100.00, 1000.00], [ 5.479788968e+000 , 1.062529189e-001 , -1.860208915e-004 ,
                1.506020848e-007 , -4.616620602e-011 , -2.816765321e+005 , 8.893090485e+000 ] ),
        NASA( [ 1000.00, 3000.00], [ 2.728670412e+001 , 4.878072197e-003 , -2.581765180e-006 ,
                6.207116407e-010 , -5.602761069e-014 , -2.856556257e+005 , -9.362221280e+001 ] )
          )
     )
species(name = 'Ti5O6CL8', # Cl8O6Ti5
      atoms = 'Ti:5 O:6 Cl:8',
    thermo = (
        NASA( [ 100.00, 1000.00], [ 1.099206826e+001 , 1.918922127e-001 , -3.501070247e-004 ,
                2.929909361e-007 , -9.215555300e-011 , -4.916228702e+005 , -7.694731180e+000 ] ),
        NASA( [ 1000.00, 3000.00], [ 5.001821678e+001 , 5.456972688e-003 , -2.162428702e-006 ,
                3.028700143e-010 , -2.991440285e-015 , -4.986346615e+005 , -1.902903243e+002 ] )
          )
     )
```