# Low-lying Electronic States and Revised Thermochemistry of TiCl, $TiCl_2$, and $TiCl_3$

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Thermochemical analyses of gaseous equilibrium data involving the species TiCl, $TiCl_2$, and $TiCl_3$ were revised with the aid of more recent information on the low-lying electronic states, yielding more reliable values for the enthalpies of formation, $\Delta_f H^\circ_{298}$, of 40.9, −49.0, and −121.5 kcal mol$^{-1}$, all ±2 kcal mol$^{-1}$, for gaseous TiCl, $TiCl_2$, and $TiCl_3$, respectively. The new thermochemical data are in good agreement with the results of recent theoretical calculations, but they differ from earlier experimental results involving the reactions of Ti (s), $TiCl_2$(s, g), $TiCl_3$(s, g) and $TiCl_4$(g).

## Introduction

Earlier[1] we reported high-temperature equilibrium data and derived thermochemical values for the gaseous species TiCl, $TiCl_2$, and $TiCl_3$. The gaseous reaction equilibria

$$TiCl + Ag = Ti + AgCl \quad (1)$$

$$TiCl_2 + Ag = TiCl + AgCl \quad (2)$$

$$TiCl_3 + Ag + TiCl_2 + AgCl \quad (3)$$

were monitored by effusion beam mass spectrometry at seven temperatures over the range 1494 to 1612 K, and reaction enthalpies were evaluated from third-law analysis of the derived equilibrium data. Standard enthalpies of formation, $\Delta_f H^\circ_{298}$, of the Ti−Cl species were then evaluated by reference to the accurately known[2] dissociation energy of AgCl, $D^\circ_{298} = 75.1 \pm 0.4$ kcal mol$^{-1}$. At the time, however, little was known about the energy levels and configurations of the low-lying electronic states of the Ti−Cl species, a critical item in the thermochemical analysis of these transition species, with their unfilled 3d shells.

As substitutes for these unknown electronic levels, the energy levels of the metal ions[3] $Ti^+$, $Ti^{+2}$, and $Ti^{+3}$ were used, an approach suggested earlier by Brewer and colleagues[4,5] when the desired data are missing. Recently, however, molecular theory has been providing a valuable source of reliable information on electronic energy levels. With the advent of such information for some of the Ti−Cl species of interest here, we have revised the earlier thermochemical analysis and now report more reliable $\Delta_f H^\circ_{298}$ values and dissociation energies for TiCl, $TiCl_2$, and $TiCl_3$. Recent experience indicates that, as expected, the positive ion levels tend to overestimate the actual molecular energy levels. In this paper we present revised thermochemical data for TiCl, $TiCl_2$, and $TiCl_3$, generated with the aid of more realistic data on the electronic levels. From a practical standpoint, only those levels below about 5000 cm$^{-1}$ have a significant effect on calculated properties for temperatures ranging up to about 2000 K.

**Treatment of Equilibrium Data.** In the original work[1] reported earlier, which fully describes the experimental details, the Ti−Cl and Ag−Cl species were generated by reaction of AgCl(g) with Ti(s) in the effusion beam source at the elevated temperatures noted above, and reaction equilibrium constants, $K$, were derived from the measured parent ion signals. The desired reaction enthalpies were evaluated from the relation $\Delta H^\circ_{298} = T(\Delta \mathrm{gef}_{298} - R \ln K)$, where $\mathrm{gef}_{298}$ is the Gibbs energy function, the thermodynamic quantity $-(G^\circ_T - H^\circ_{298})/T$, which can be evaluated for each gaseous species from spectroscopic and molecular constant data, including the properties of the relevant electronic states; this is the so-called third-law method of deriving reaction enthalpies from equilibrium data.

The sources of most of the molecular constant data, other than the newly selected values for the electronic states of TiCl, $TiCl_2$, and $TiCl_3$, are given in ref 1. Table 1 lists the adopted values of the molecular constants for the Ti−Cl and AgCl species treated here, in terms of the internuclear distance, $r_e$, the moment of inertia, $I$, the vibrational frequency, $\omega$, the ground state, $X$, and the energy, $T_e$, and degeneracy, $g$, of the electronic state. For TiCl, $I$ and $\omega$ were taken from the spectroscopic data reported by Ram and Bernath.[6] For completeness, the molecular constants and calculated thermal functions of $TiCl_4$ are also included in the paper.

**Low-lying Electronic Levels.** From studies of the emission spectrum of TiCl, Ram and Bernath[6] identified the C $^4\Delta$ state, lying about 3300 cm$^{-1}$ above ground, and also tentatively assigned the ground-state as $^4\Phi$. Shortly thereafter, Focsa et al.[7] reported the results of DFT calculations, also predicting a $^4\Phi$ ground-state for TiCl, plus a series of states lying at the indicated energies: $^4\Sigma$ (1575 cm$^{-1}$); $^4\Delta$ (3801 cm$^{-1}$); $^4\Sigma$ (5294 cm$^{-1}$); and $^4\Delta$ (6182 cm$^{-1}$). The lower $^4\Delta$ calculated state and predicted ground-state are in good accord with the results of Ram and Bernath,[6] and we adopt these values. The CCSD calculations of Boldyrev and Simons[8] support the TiCl $^4\Phi$ ground-state assignment, and their calculated energy of 1904 cm$^{-1}$ is compatible with the energy of the lowest $^4\Sigma$ state of Focsa et al.[7] However, the MRCPA calculations of Sakai et al.[9] also support the TiCl ground-state assignment but predict the lowest $^4\Sigma$ state at 823 cm$^{-1}$ (which was not adopted), noting that "This difference in the term energies may be mainly due to the difference in the methods used."

For $TiCl_2$, the MRCI calculations of Vogel and Wenzel[10] predict a $^3\Delta$ ground-state and low-lying states with adiabatic excitation energies as follows: $^3\Phi$ (968 cm$^{-1}$); $^3\Sigma$ (1370 cm$^{-1}$); and $^3\Pi$ (2660 cm$^{-1}$). The MRCI calculations[10] also support the adopted[1] linear structure of $TiCl_2$. The DFT calculations of Wang and Schwartz[11] agree on the $^3\Delta$ ground-state but predict only the lowest $^3\Sigma$ state at 3065 cm$^{-1}$, which we do not adopt.

After reviewing the available information in 1968, and in the absence of published data, the JANAF Table[12] compilers estimated a group of electronic states for $TiCl_3$ as follows: all

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**TABLE 1: Molecular Constants of Ti−Cl and AgCl Species Used In Calculating Thermal Functions**

| species | $I$ or $I_xI_yI_z$ | $\sigma$ | $\omega$, $cm^{-1}$ |
|---|---|---|---|
| TiCl | $17.2 \times 10^{-39}$ g $cm^2$ | 1 | 404 |
| $TiCl_2$ | $57.1 \times 10^{-39}$ g $cm^2$ | 2 | 320, 122(2), 486 |
| $TiCl_3$ | $1.57 \times 10^{-112}$ $g^3$ $cm^6$ | 6 | 350, 110, 505(2), 135(2) |
| $TiCl_4$ | $4.21 \times 10^{-112}$ $g^3$ $cm^6$ | 12 | 368,111(2), 498(3), 131(3) |
| AgCl | $22.8 \times 10^{-39}$ g $cm^2$ | 1 | 342 |

| species | | $\varepsilon$, $cm^{-1}$ |
|---|---|---|
| TiCl | (g, $\varepsilon$) | (8, 0); (4, 1575); (8, 3801); (4, 5294); (8, 6182) |
| $TiCl_2$ | (g, $\varepsilon$) | (6, 0); (6, 968); (3, 1370); (6, 2660) |
| $TiCl_3$ | (g, $\varepsilon$) | (2, 0); (2, 600); (2, 1500); (2, 4000) |
| $TiCl_4$ | (g, $\varepsilon$) | (1, 0) |
| AgCl | (g, $\varepsilon$) | (1, 0) |

**TABLE 2: Derived Reaction Enthalpies and $\Delta_fH^\circ_{298}$ Values, kcal $mol^{-1}$**

| | third-law $\Delta H^\circ_{298}$ | |
|---|---|---|
| gaseous reaction | this work | previous[1] |
| TiCl + Ag = Ti + AgCl | 26.2 | 21.8 |
| Second law | 26.4 ± 3.5 | |
| $TiCl_2$ + Ag = TiCl + AgCl | 43.8 | 46.2 |
| Second law | 47.0 ± 3.4 | |
| $TiCl_3$ + Ag = $TiCl_2$ + AgCl | 26.4 | 25.8 |
| Second law | 30.6 ± 3.6 | |

| | $\Delta_fH^\circ_{298}$ | |
|---|---|---|
| gaseous species | this work | previous[1] |
| TiCl | 40.9 | 45.3 |
| $TiCl_2$ | −49.0 | −47.0 |
| $TiCl_3$ | −121.5 | −118.9 |

**TABLE 3: Comparison of $\Delta_fH^\circ_{298}$ Values with Literature Values**

| | | $\Delta_fH^\circ_{298}$, kcal $mol^{-1}$ | | |
|---|---|---|---|---|
| method | year | TiCl(g) | $TiCl_2$(g) | $TiCl_3$(g) |
| review/compil.[12] | 1968 | 36.9 ± 10 | −56.7 ± 3 | −128.9 ± 1.5 |
| equil. meas.[16] | 1992 | 36.4 ± 3.6 | −62.6 ± 0.5 | −126.7 ± 0.5 |
| review/compil.[13] | 1993 | 36.0 ± 10 | −53.7 ± 10 | −124.5 ± 10 |
| theory | 1998[17] | 45.2 | −47.6 | −121.7 |
| MS equil. − this work | | 40.9 ± 2 | −49.0 ± 2 | −121.5 ± 2 |

**TABLE 4: Ideal Gas Thermodynamic Functions of TiCl**

$\Delta_fH^\circ_{298}$= +40.9 kcal $mol^{-1}$

| $T$, K | $-(G^\circ - H^\circ_{298})/T$, cal $deg^{-1}$ $mol^{-1}$ | $S^\circ_{298}$, cal $deg^{-1}$ $mol^{-1}$ | $H^\circ_T - H^\circ_{298}$, kcal $mol^{-1}$ | $C_p$, cal $deg^{-1}$ $mol^{-1}$ |
|---|---|---|---|---|
| 298 | 60.45 | 60.45 | −0.00 | 8.45 |
| 300 | 60.45 | 60.51 | 0.02 | 8.45 |
| 400 | 60.79 | 62.98 | 0.88 | 8.74 |
| 500 | 61.43 | 64.95 | 1.76 | 8.95 |
| 600 | 62.16 | 66.60 | 2.67 | 9.13 |
| 700 | 62.90 | 68.02 | 3.59 | 9.28 |
| 800 | 63.62 | 69.27 | 4.52 | 9.40 |
| 900 | 64.31 | 70.38 | 5.47 | 9.52 |
| 1000 | 64.97 | 71.39 | 6.42 | 9.64 |
| 1100 | 65.59 | 72.31 | 7.39 | 9.75 |
| 1200 | 66.19 | 73.17 | 8.37 | 9.85 |
| 1300 | 66.76 | 73.96 | 9.36 | 9.95 |
| 1400 | 67.30 | 74.70 | 10.36 | 10.05 |
| 1500 | 67.81 | 75.40 | 11.37 | 10.13 |
| 1600 | 68.31 | 76.05 | 12.39 | 10.20 |
| 1700 | 68.78 | 76.67 | 13.41 | 10.27 |
| 1800 | 69.24 | 77.26 | 14.44 | 10.32 |
| 1900 | 69.67 | 77.82 | 15.48 | 10.36 |
| 2000 | 70.10 | 78.35 | 16.51 | 10.39 |

**TABLE 5: Ideal Gas Thermodynamic Functions of $TiCl_2$**

$\Delta_fH^\circ_{298}$= −49.0 kcal $mol^{-1}$

| $T$, K | $-(G^\circ - H^\circ_{298})/T$, cal $deg^{-1}$ $mol^{-1}$ | $S^\circ_T$, cal $deg^{-1}$ $mol^{-1}$ | $H^\circ_T - H^\circ_{298}$, kcal $mol^{-1}$ | $C_p$, cal $deg^{-1}$ $mol^{-1}$ |
|---|---|---|---|---|
| 298 | 69.25 | 69.25 | −0.00 | 14.19 |
| 300 | 69.25 | 69.34 | 0.03 | 14.21 |
| 400 | 69.82 | 73.55 | 1.49 | 15.07 |
| 500 | 70.92 | 76.97 | 3.03 | 15.57 |
| 600 | 72.17 | 79.84 | 4.60 | 15.85 |
| 700 | 73.45 | 82.29 | 6.19 | 15.98 |
| 800 | 74.69 | 84.43 | 7.79 | 16.03 |
| 900 | 75.88 | 86.32 | 9.40 | 16.04 |
| 1000 | 77.01 | 88.01 | 11.00 | 16.01 |
| 1100 | 78.08 | 89.53 | 12.60 | 15.97 |
| 1200 | 79.09 | 90.92 | 14.20 | 15.92 |
| 1300 | 80.05 | 92.19 | 15.78 | 15.87 |
| 1400 | 80.96 | 93.37 | 17.37 | 15.81 |
| 1500 | 81.83 | 94.46 | 18.95 | 15.76 |
| 1600 | 82.65 | 95.47 | 20.52 | 15.71 |
| 1700 | 83.43 | 96.42 | 22.09 | 15.66 |
| 1800 | 84.18 | 97.32 | 23.65 | 15.61 |
| 1900 | 84.89 | 98.16 | 25.21 | 15.57 |
| 2000 | 85.57 | 98.96 | 26.77 | 15.53 |

states have a degeneracy, *g*, of 2, and excited states with energies of 600, 1500, and 4000 $cm^{-1}$. It was stated[12] that "... the electronic levels are estimated from the levels of $Ti^{+3}$ (g)", but it was not specified as to just how this was done. However, this estimate seems eminently reasonable for $TiCl_3$ and is adopted, knowing from experience that the $Ti^{3+}$ levels with $\varepsilon(g)$ values of 0(4), and 384 $cm^{-1}$(6) will overestimate the electronic contribution to the thermal functions of the neutral trichloride.

The selected electronic levels of TiCl, $TiCl_2$, and $TiCl_3$ are included in Table 1, along with the other adopted molecular constants. Thermal functions calculated from these data and used in the thermochemical analysis are given in Tables 4−7. These functions are based on the ideal gas state at one bar pressure.

## Results

Third-law analysis of reactions 1−3, using the equilibrium data from ref 1 and gef values calculated from the molecular constants listed in Table 1, gave the derived reaction enthalpies, $\Delta H^\circ_{298}$, and $\Delta_fH^\circ_{298}$ values shown in Table 2, where they are compared with the previous values obtained in the earlier work.[1] Note that the second law enthalpies, derived from the temperature dependence of log *K* versus 1/*T*, are consistent with the corresponding third-law values. The differences between the past[1] and present reaction enthalpies are due almost wholly to the newly adopted electronic state assignments described in the text and listed in Table 1. As noted above, the 1996 results[1] were evaluated by assuming that the electronic states of TiCl, $TiCl_2$ and $TiCl_3$ could be reasonably approximated by those of the positive ions $Ti^+$, $Ti^{+2}$, and $Ti^{+3}$, which are accurately known.[3] However, the new values of $gef_{298}$ for TiCl, $TiCl_2$, and $TiCl_3$ at 1500 K are *lower* by 2.8, 1.3, and 1.7 cal $deg^{-1}$ $mol^{-1}$, respectively, than those from the free gaseous ion model previously used.[1] It is now clear that, in the case of the Ti−Cl species, their thermodynamic stabilities are under-estimated by 2−4.4 kcal $mol^{-1}$ using the metal-ion energy level approximation. These new $\Delta_fH^\circ_{298}$ values for TiCl, $TiCl_2$, and $TiCl_3$ are believed to be the most accurate values now available, primarily because the gef evaluations address directly the role of the low-lying electronic states of these species. The new results lead to the following bond dissociation energies at 298 K, all ±2 kcal $mol^{-1}$: $D$(Ti−Cl) = 101.3; $D$(ClTi−Cl) = 118.9; $D$($Cl_2$Ti−Cl) = 101.5; and $D$($Cl_3$Ti−Cl) = 89.9. The first, third, and fourth values are remarkably close together.

In Table 3, the new $\Delta_fH^\circ_{298}$ values of the Ti−Cl species are compared with other values in the literature. The literature values

**TABLE 6: Ideal Gas Thermodynamic Functions of $TiCl_3$**

$\Delta_f H^\circ_{298} = -121.5$ kcal mol$^{-1}$

| $T$, K | $-(G^\circ - H^\circ_{298})/T$, cal deg$^{-1}$ mol$^{-1}$ | $S^\circ_T$, cal deg$^{-1}$ mol$^{-1}$ | $H^\circ_T - H^\circ_{298}$, kcal mol$^{-1}$ | $C_p$, cal deg$^{-1}$ mol$^{-1}$ |
|---|---|---|---|---|
| 298 | 79.55 | 79.55 | −0.00 | 18.67 |
| 300 | 79.55 | 79.67 | 0.03 | 18.70 |
| 400 | 80.30 | 85.20 | 1.96 | 19.66 |
| 500 | 81.74 | 89.64 | 3.95 | 20.13 |
| 600 | 83.37 | 93.33 | 5.98 | 20.36 |
| 700 | 85.03 | 96.48 | 8.02 | 20.47 |
| 800 | 86.63 | 99.22 | 10.07 | 20.52 |
| 900 | 88.17 | 101.64 | 12.12 | 20.54 |
| 1000 | 89.63 | 103.80 | 14.18 | 20.54 |
| 1100 | 91.01 | 105.76 | 16.23 | 20.54 |
| 1200 | 92.31 | 107.55 | 18.28 | 20.54 |
| 1300 | 93.55 | 109.19 | 20.34 | 20.54 |
| 1400 | 94.72 | 110.71 | 22.39 | 20.53 |
| 1500 | 95.83 | 112.13 | 24.44 | 20.52 |
| 1600 | 96.89 | 113.45 | 26.49 | 20.51 |
| 1700 | 97.90 | 114.70 | 28.55 | 20.50 |
| 1800 | 98.87 | 115.87 | 30.59 | 20.49 |
| 1900 | 99.79 | 116.97 | 32.64 | 20.47 |
| 2000 | 100.68 | 118.02 | 34.69 | 20.46 |

**TABLE 7: Ideal Gas Thermodynamic Functions of $TiCl_4$**

$\Delta_f H^\circ_{298} = -182.4$ kcal mol$^{-1}$

| $T$, K | $-(G^\circ - H^\circ_{298})/T$, cal deg$^{-1}$ mol$^{-1}$ | $S^\circ_T$, cal deg$^{-1}$ mol$^{-1}$ | $H^\circ_T - H^\circ_{298}$, kcal mol$^{-1}$ | $C_p$, cal deg$^{-1}$ mol$^{-1}$ |
|---|---|---|---|---|
| 298 | 84.88 | 84.88 | 0.00 | 22.90 |
| 300 | 84.88 | 85.02 | 0.04 | 22.93 |
| 400 | 85.79 | 91.78 | 2.40 | 24.04 |
| 500 | 87.55 | 97.22 | 4.83 | 24.63 |
| 600 | 89.55 | 101.74 | 7.31 | 24.98 |
| 700 | 91.58 | 105.61 | 9.82 | 25.19 |
| 800 | 93.55 | 108.98 | 12.35 | 25.34 |
| 900 | 95.43 | 111.97 | 14.89 | 25.44 |
| 1000 | 97.22 | 114.66 | 17.44 | 25.51 |
| 1100 | 98.92 | 117.09 | 19.99 | 25.57 |
| 1200 | 100.53 | 119.32 | 22.55 | 25.61 |
| 1300 | 102.05 | 121.37 | 25.11 | 25.64 |
| 1400 | 103.50 | 123.27 | 27.68 | 25.67 |
| 1500 | 104.88 | 125.04 | 30.25 | 25.69 |
| 1600 | 106.19 | 126.70 | 32.82 | 25.71 |
| 1700 | 107.44 | 128.26 | 35.39 | 25.72 |
| 1800 | 108.64 | 129.73 | 37.96 | 25.73 |
| 1900 | 109.79 | 131.12 | 40.53 | 25.74 |
| 2000 | 110.89 | 132.44 | 43.11 | 25.75 |

are listed in chronological order of their appearance; for the JANAF Table values,[12] the date refers to the last time that data on these species were reviewed. Data for the individual species vary over a range of 5−15 kcal mol$^{-1}$, although the more recent work has a smaller spread. The JANAF Table[12] and presumably the IVTANTHERMO[13] values for $TiCl_2$(g) and $TiCl_3$(g) are based on analysis of the reactions not involving measurement of individual species pressures.

$$2TiCl_3(g) + Ti(s) = 3TiCl_2(g)$$

$$3TiCl_4(g) + Ti(s) = 4TiCl_3(g)$$

$$TiCl_3(s) = TiCl_3(g)$$

Because $TiCl_3$(s) undergoes simultaneous sublimation to $TiCl_3$(g) and disproportionation to $TiCl_4$(g) + $TiCl_2$(s), interpretation of the $TiCl_3$ sublimation thermochemistry[14,15] is not straightforward. Furthermore, the $TiCl_4$ pressure exceeds that of $TiCl_3$ by more than a factor of 10, and species pressures were not monitored separately. Also the inferred $TiCl_3$ sublimation pressures[14,15] differ by a factor of 10. This problem encountered in the earlier work[14,15] was avoided in the present study, where mass spectrometric monitoring was used to study purely gas phase equilibria. The work of Nikitin et al.[16] did involve some mass spectrometric monitoring of reactions involving $TiCl_2$, $TiCl_3$, and $TiCl_4$ only, but they chose to average their results with work reported earlier[12] and obtained similar values. Note that none of the earlier experimental results[12−16] are based on reactions involving TiCl. The JANAF Table[12] estimate of $\Delta_f H^\circ_{298}$(TiCl) is based on similar estimates for the Ti−F system, which were apparently adopted by others.[13,16]

On the other hand, the modified G2 theoretical calculations of Baboul and Schlegel[17] and the results of this work yield thermochemical values that are in good agreement and stand apart from the earlier results. As noted above, these two studies are the first to directly investigate the thermochemistry of TiCl. It is gratifying that theory is rightfully assuming its place as an equal partner with experimentation in providing accurate molecular energy quantities, presently at least for the lighter metal species. This is an important point, now that experimental thermochemical research has declined significantly. The equilibrium modeling of newer, more efficient chemical processes requires reliable thermochemical data with accuracies on the order of ±2 kcal mol$^{-1}$, and molecular theory is likely to be the source of this information in the future, as exemplified by the work of Baboul and Schlegel[17] in support of a CVD process for deposition of TiN(s). In any event, the revised thermochemical results reported here, along with the values obtained from molecular theory,[17] are now sufficiently accurate to permit reliable chemical modeling applications involving the Ti−Cl species.

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