Journal of Physical and Chemical Reference Data

Computer Methods Applied to the Assessment of Thermochemical Data. Part 1. The Establishment of a Computerized Thermochemical Data Base Illustrated by Data for $TiCl_4$(g), $TiCl_4$(l), $TiCl_3$(cr), and $TiCl_2$(cr)

Cite as: Journal of Physical and Chemical Reference Data **15**, 943 (1986); https://doi.org/10.1063/1.555760
Submitted: 24 August 1984 . Published Online: 15 October 2009

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Computer Methods Applied to the Assessment of Thermochemical Data. Part I. The Establishment of a Computerized Thermochemical Data Base Illustrated by Data for $TiCl_4(g)$, $TiCl_4(l)$, $TiCl_3(cr)$, and $TiCl_2(cr)$

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Received August 24, 1984; revised manuscript received January 10, 1986

Computer methods are described for the storage, retrieval, and processing of large amounts of thermochemical data and related textual material. The procedures are illustrated by a critical evaluation of data for $TiCl_4(g)$, $TiCl_4(l)$, $TiCl_3(cr)$, and $TiCl_2(cr)$; values for standard enthalpies of formation and entropies at 298.15 K are selected for these species.

Key words: computer methods; critically evaluated data; data processing; data retrieval; data storage; enthalpy of formation; entropy; thermochemical data base; $TiCl_2(cr)$; $TiCl_3(cr)$; $TiCl_4(g)$; $TiCl_4(l)$.

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1. Introduction

This paper describes the development of computer techniques for storing and manipulating thermochemical data and corresponding textual material. The methods are illustrated by their application to the assessment of data on $TiCl_4(g)$, $TiCl_4(l)$, $TiCl_3(cr)$, and $TiCl_2(cr)$ for which recommended values for standard enthalpies of formation and entropies are given. Future papers will deal with the application of these methods to the full range of transition metal halides.

1.1. Data Compilations

Without implying any order of importance, the essential attributes of a compilation of inorganic thermochemical data are reliability, consistency, updating facilities, ease of access, and comprehensive coverage, but to date no single compilation satisfies all of these criteria. There is a wide variation in the range of information contained in currently available compilations (Refs. 1–5); some present the numerical data with little or no documentation whereas others, for example, JANAF[3] and the most recent Russian tables,[5] give full references and include brief accounts justifying the recommended values. Many users of thermochemical data would welcome more detailed documentation but publishing costs and restrictions on space have, in the past, limited the amount of material presented. A computerized data base, however, allows the inclusion of much fuller details and many of the desirable attributes enumerated above could be provided by a central computerized system to which individual groups of assessors could contribute.

An important deficiency in all current compilations is that most of the detailed work carried out by the assessors of data is lost to future assessors. When thermochemical properties of species need to be reevaluated in the light of new information, the assessor must study all the original papers on the species and identify relevant experimental measurements; subsidiary data (thermal functions, activity coefficients, etc.) must be reconsidered and, almost invariably, extensive calculations must be carried out. Much of this labor may be a repetition of the unrecorded work done by earlier assessors.

1.2. Computer Methods Applied to Data Assessment

Modern computers have the facility to store vast quantities of both textual and numerical information and to process them very rapidly. If the essential features of a piece of experimental work, including later workers' comments upon it, can be extracted from the literature and stored in a computer together with the related calculations, future assessors of thermochemical data will be able to benefit directly from their predecessors' work. The material can readily be retrieved, and the new assessor's task will be simplified since he or she will be able to add to the stored information and, using simple computer programs, recalculate selected "best" values for thermochemical properties of substances. There are other advantages in the use of computers in the field of thermochemical data compilations: information is always accurately reproduced, obviating the need for proofreading, a particularly tedious task in the case of tabulated numerical data; data can readily be generated in any required system of units, and material put into the system in one format can easily be translated into another format; information may be presented on a computer terminal or generated as line-printer output at any site having access to the computer via local, national, or international networks.

The methods described here are an extension of earlier work on automated thermochemical data assessment developed at the University of Sussex and the National Bureau of Standards (U. S.) in Gaithersburg, MD, and in association with the CODATA Task Group on Chemical Thermodynamic Tables (see Refs. 6–9).

1.3. The Sussex Computerized Thermochemical Data Base

This paper describes the contents of the Sussex Computerized Thermochemical Data Base and the computer methods devised at the University of Sussex for the retrieval and processing of data in the base. A set of programs has been written to store and maintain information in computer files; the programs have been designed specifically to allow for modifications to treat information in any format. Second and third law enthalpies of reaction can be calculated from experimental measurements, and stored and processed information on a species or range of species can be retrieved and displayed on a visual display unit or produced as printed copy. Computer generated graphs of gibbs energies as a function of temperature can be produced as an aid to assessment. These techniques are illustrated by a detailed assessment of the thermochemical properties of $TiCl_4(g)$, $TiCl_4(l)$, $TiCl_3(cr)$, and $TiCl_2(cr)$. It must, however, be remembered that although computer techniques provide valuable assistance, assessment is an intellectual activity relying on the judgment of the assessor and it cannot therefore be completely automated.

At present the data base contains data on only the halides of first-row transition elements, but flexible structuring permits the inclusion of thermochemical data on any chemical species. Users of the base have access to information at several levels of detail. At the simplest level, recommended values for thermochemical properties of a set of species may be retrieved; at another level, a list is available of references and equations upon which the recommended values have been based; if fuller information is required, details of individual papers, including processing of the experimental data, may be accessed. Other search and retrieval facilities, described in Sec. 2.1, allow access to detailed assessment work which, in the past, has not been preserved and systematically recorded.

An earlier paper[6] described the methodology of the critical assessment and computer processing of thermochemical data for gaseous monoxides, and presented assessed values for standard enthalpies of formation and dissociation energies for these species. Values for their gibbs energy functions and enthalpy functions were calculated from molecular parameters and tabulated over the temperature range 0–4000 K.

The present work is intended as a model for a central computerized system for the storage and handling of thermochemical data on inorganic compounds. It is a development from the monoxide project[6] with emphasis on more general techniques for treating thermochemical data for any chemical species. It must be emphasized that although the examples shown here are restricted to a small set of titanium chlorides and associated species, the methods used are applicable to a wide variety of species, although they are not yet transferable to other computer systems.

The methodology in the present work is in many ways similar to that used for the monoxides.[6] Where two or more species are interrelated, a hierarchical system of assessment is used. For instance, in the monoxide data there are many exchange processes such as $AlO(g) + Sm(g) = SmO(g) + Al(g)$; data for $AlO(g)$ are well defined from other processes and values for $SmO(g)$ may therefore be derived from this and other similar relationships. In the same way a value for one titanium halide may depend on another better established value, for example, values for $TiCl_2(cr)$ and $TiCl_3(cr)$ may depend on those for $TiCl_4(l)$ and $TiCl_4(g)$ via a set of calorimetric and vapor pressure measurements. For monoxides, a study of trends in dissociation energies within the context of the periodic table was used to estimate values for some species, whereas for halides a number of correlations may be examined; for instance, data for different oxidation states of one transition element may be compared with those of another transition element, and data for combinations of a given transition element with different halogens or of a given halogen with different transition elements may be studied.

Other features of the present work are a major advance on the system for assessment of the monoxides. We have now devised a graphical technique, described in Sec. 4.1 and illustrated in Figs. 2(a)–3(b), which has proved to be a powerful tool in assessment work. Another new development relates to the thermal functions used to reduce experimental data at other temperatures to standard enthalpies of reaction at 298.15 K. In the work on monoxides[6] thermal functions were derived from a fixed set of molecular parameters for each monoxide. The present system includes different sets of raw thermal function data for some species, allowing trials of different values to maximize agreement between second and third law enthalpies of reaction and between values derived from independent measurements.

Since none of the data extracted from the literature for the titanium chlorides are in SI units, the data in the files and their processing have involved non-SI units; the discussion is therefore in terms of calories to maintain continuity with the original data, but final results are given in joules.

Although the unsophisticated method of sequential searching of computer files was adequate for the relatively small amount of information stored for gaseous monoxides, techniques designed for the treatment of thermochemical data in general must allow for the handling of much larger quantities of material. Rapid access to records in computer files, described in the following section, is therefore an important feature of the present work.

2. Computer Storage of Data

Conceptually the data base comprises a number of data files, each containing a particular type of data, although in practice all the data may be contained in one file. The structure and contents of the files used for the titanium chloride data are described in Secs. 2.1–2.3.

2.1. Experimental Data File

A primary aim of the present work is to define the essential features present in a given paper containing thermochemical data, and to codify and store that information in a computerized data base in such a way that it can be extracted and manipulated at will. The Experimental Data File contains textual and numerical data extracted from the literature and inserted in chronological and alphabetic order of authors; Table 1 shows a specimen entry from the file. The reference codes used in Table 1, and throughout this work, consist of the date of publication and three-letter contractions of the first two authors named. For instance, in Table 1, 55SKI/RUE identifies a paper by Skinner and Ruehrwein published in 1955. If the same authors have published more than one paper in a given year, the codes are distinguished by an added number, e.g., 55FAR/DAR1 and 55FAR/DAR2.

The numbering down the left-hand side of Table 1 is for explanatory purposes only and is not part of the computer file. Each line is stored as an 80-character record in the file. The program reads the file sequentially and expects to find at least one record for each of the 13 items of information listed in the key to Table 1.

For items other than those labeled "8," the character "@" appears in the first column of each continuation line if more than one record is needed to store an item of information; in the section labeled "8," which can contain a number of separate records, one for each reference cited in the given paper, the character ";" must appear after the code for each such reference.

The end of the section labeled "12" is indicated by the presence of the characters " + / − " in the last line, and the program continues to read sets of lines 10, 11, and 12 until a blank line, labeled 13, is reached, denoting the end of the information on that paper. The whole process is then repeated for subsequent papers.

As the file is read, items of information from every paper are stored in a series of separate files corresponding to Secs. 2–12, indexed under the code specified in record 1, allowing rapid access and retrieval of any type of information. For example, a list of all papers published by a particular author can be retrieved from the stored information in line 2; those put into the system by individual assessors can be collected (line 5), or key words can be used to identify papers involving specific experimental techniques (line 6). The lines labeled "8" in Table 1 contain reference codes for earlier papers cited; the code may be followed by the formulas of one or more compounds and/or comments. These items are doubly indexed under the code of the paper in which they are cited and under each cited reference, so that all comments on a specific paper can be collected.

Table 1. Specimen Paper from Experimental Data File

```
 1   55SKI/RUE
 2   Skinner, G.B.; Ruehrwein, R.A.
 3   "Thermodynamic Properties of the Titanium Chlorides"
 4   J.Phys.Chem.; 59, 113-117 (1955)
 5   68JANAF 83PED/MAR
 6   Calorimetry, vapour pressures from transfer method and by
     @manometry.
 7   DfH298 TiCl4(l)=-191+/-3 kcal mol-1, TiCl3(cr)=-170+/-0.8 kcal
     @mol-1. Thermal functions estimated
 8   22LAT;TiCl4(cr),TiCl4(l). Cp at low temperature
     49KEL;TiCl4(g). Thermal functions from molecular parameters
     50KEL;TiCl4(g). Thermal functions from molecular parameters
     54JOH/NEL; TiCl4(l). (Unpublished) Consider 54JOH/NEL's value
     @of 192.9+/-0.6 for DfH298 of TiCl4(l) to be more accurate
 9   DrH from Table I, and from combination of equations 1,2,3
     @and 5, vapour pressures from Tables II, III and V
10   Ti(cr)+2Cl2(g)=TiCl4(l)
11   DH
12   298 -190+/-3
10   Ti(cr)+3HCl(10H2O)=TiCl3(cr)+3/2H2(g)
11   DH
12   298 -54.15+/-0.8
10   TiCl3(cr)=TiCl3(g)
11   PP mm
12   802 4.0
     849 15.2
     863 21.9
     900 58
     928 105
     DH298+/-2.3
10   2TiCl3(cr)=TiCl2(cr)+TiCl4(g)
11   PP mm
12   849 38.7
     863 53.2
     900 123
     928 232
     DH298+/-3.0
13
```

```
KEY TO TABLE 1

Line     Item of Information
Number

 1       Reference code
 2       Authors
 3       Title
 4       Reference
 5       Codes for source of reference, date and names of assessors
 6       Experimental techniques
 7       Authors' results
 8       Reference codes for papers cited
 9       Location of data in paper
10       Equation for process
11       Codes for type of measurement and units which may be any
         of the following:

         Allowed Codes
         -------------
         PP    Partial Pressure
         K     Equilibrium Constant
         LK    Log of Equilibrium Constant
         LKC   Log of Equilibrium Constant in Functional Form
         DH    Enthalpy Change for the Reaction
         DG    Gibbs Energy Change for the Reaction
         EMF   Electromotive Force

         Allowed Units
         -------------
         By default these are:
         Temperatures in Kelvin
         Partial Pressures in Atmospheres
         Enthalpies and Gibbs Energies in kcal mol^-1

         Other systems of units may be used and are indicated
         as follows;

         mm  mm Hg
          C  Centigrade
          J  Joules
         kJ  kilojoules
         mV  millivolts
         eV  electron volts
          V  Volts

12       For codes K, LK, DG, EMF (see 11 above):
         Temperature, followed by value of measurement. May be
         repeated for up to 100 temperatures. Terminated by line
         "DH298+/-" followed by uncertainty on enthalpy of
         reaction.  The uncertainty is either that derived by the
         authors specified in line 2, or estimated by us, in which
         case this fact is noted in line 9.

         For code DH:
         Temperature, value for DH immediately followed by uncertainty
         assigned as above.

         For code PP:
         Temperature, partial pressure for each gaseous species in
         same order as in equation.  Terminated by line containing
         "DH298+/-" as above.

         For code LKC:
         Temperature range to which the subsequent expression for
         log K applies.  Uncertainty either incorporated in expression
         or in terminating line "DH298+/-" as above.

13       Blank line indicating end of information extracted from
         paper.

@     indicates a continuation line
```

Nearly 400 articles similar to the example shown in Table 1 are stored in the Experimental Data File for papers on transition element halides and a further 200 articles are stored in a similar file for gaseous monoxides.

Appendix I contains full references, listed under the reference codes, for all the papers used in the assessment of $TiCl_4(g)$, $TiCl_4(l)$, $TiCl_2(cr)$, and $TiCl_3(cr)$. The date of the most recent reference is 1974; in spite of extensive searches in the literature, we have been unable to find evidence of any later work on the titanium chlorides under review here.

The most frequent type of search is for equations (line 10) containing specific compounds, and the associated data (lines 11 and 12). Each equation in the file is indexed under all the species present in the equation; data for a compound or set of compounds can therefore be retrieved and processed to give second and third law values, at 298.15 K, for standard enthalpy, gibbs energy, and entropy changes for the reactions, calculated as described in Sec. 3.3. Lines 10, 11, and 12 are repeated for each process considered in the paper. Details of the codes and formats used for lines 11 and 12 for the titanium chloride data are given in the key to Table 1. The programs have been designed in a modular form so that other types of data can readily be accommodated.

The experimental data are stored in a form which is as close as possible to the actual measurements, the most fundamental information being partial pressures of the gaseous species at specified temperatures. Authors do not always give this basic information, in which case their calculated value for the equilibrium constant, gibbs energy change for the reaction or even enthalpy change for the reaction has to be accepted, although the less basic the data, the greater the danger of introducing inconsistencies, since choice of subsidiary data can vary considerably from one study to another. The errors presented with the data are either those given by the authors of the paper, or our provisional estimates in which case a note to that effect appears in line 9.

2.2. Selected Reference Temperature Data File

This file contains the current selected values for standard enthalpies of formation and entropies at 298.15 K for all the species present in the Experimental Data File. Initially these data are taken from standard compilations but during assessment, values may be adjusted, and, in its final form, the file contains recommended values for the species under consideration. A section of the file showing initial values for $TiCl_2(cr)$, $TiCl_3(cr)$, $TiCl_4(l)$, $TiCl_4(g)$, and associated subsidiary compounds is shown in Appendix II. It should be noted that the formulas are listed in strict alphabetic order of elements and are in uppercase characters, e.g., $TiCl_2$ becomes CL2TI1, and the number 1 is included where a single atom of the element occurs. This format allows for the inclusion of chemical equations using only uppercase characters. The next four columns contain values for the standard enthalpy of formation and entropy, each property being followed by its uncertainty. The last three columns give, respectively, the source of the data (see key to Appendix II), the location of the currently accepted values for thermal functions in the Tabulated Thermal Function Data File (see Sec. 3.2), and the location of the most recent entry for the species in the Experimental Data File. Previous entries are indicated by pointers in that file and it is therefore possible to retrieve rapidly and efficiently all data on a given compound or set of compounds; lists of definitive equations for individual compounds, similar to those shown in Tables 3–6, may be generated in this way.

2.3. Thermal Function Data File

For assessment purposes it is necessary to reduce the numerical data in the Experimental Data File to standard conditions at 298.15 K, and thermal function data are therefore required. The Thermal Function Data File contains the basic data from which thermal functions can be calculated for all the species occurring in the equations in the Experimental Data File. An extract from the Thermal Function Data File is shown in Appendix III. For other types of measurement the file could contain properties such as activity coefficients for conversion of data on aqueous species to standard conditions.

The thermal function data can be stored in the form of molecular parameters, as tabulated values, or in functional form. At present the programs can treat data for four different types of molecular parameters but other formats could be accommodated. Parameters for atoms, diatomic molecules, linear polyatomic molecules and non-linear polyatomic molecules can be processed to generate thermal functions using methods similar to those described in the 1971 edition of the JANAF Tables,[11] except in the case of diatomic species where partition functions are calculated by discrete summation over electronic and vibrational states and integration over rotational levels. Full details of the latter calculations are given in the paper on gaseous monoxides.[6] The results of processing these data, to generate tabulated thermal functions for all the compounds relevant to this paper, are given in Appendix IV (see Sec. 3.2).

Tabulated values stored in the Thermal Function Data File (see Appendix III) comprise heat capacities, entropies, and enthalpy functions. The latter are always relative to 298.15 K, whereas entropies may either be relative to 0 K (labeled CS0H) or to 298.15 K (labeled CSH). For $TiCl_4$(l), $TiCl_3$(cr), $TiCl_2$(cr), and some subsidiary species, tabulated values are copied directly from the JANAF Thermochemical Tables[3] and for economy of space they are not listed in Appendix III since they are transferred unchanged (apart from scaling relative to 298.15 K) into the functions given in Appendix IV (see Sec. 3).

Although not illustrated in the titanium chloride data, values for heat capacities may be stored in the functional form $a + bT + cT^2 + dT^{-2}$ over a specified temperature range, and other functional forms can be accommodated, for example, the seven-term gibbs energy function (see Ref. 5).

The Thermal Function Data File contains multiple entries for some species so that the effect of choosing different thermal functions in the data processing can be assessed. The extract shown in Appendix III contains two entries for each of the species $TiCl_2$(cr) and $TiCl_3$(cr). In each case the first entry corresponds to data taken directly from the JANAF Tables,[3] and the second entry is a combination of JANAF[3] data at low temperatures and data based on the measurements of 69VAS/POD at higher temperatures (for details see Sec. 5.1). The difference between the two sets of data at higher temperatures can be seen in Appendix IV.

3. Data Processing

3.1. Introduction

For assessment purposes it is necessary to convert the experimental data, which may be in the form of partial pressures, equilibrium constants, etc., to standard state and reference temperature. In the case of titanium chlorides this entails the use of thermal functions to reduce the data to standard enthalpies of reaction at 298.15 K.

Values for relative atomic masses were taken from Ref. 12 and fundamental constants from Ref. 2. Corrections arising from differences in temperature scales (Ref. 13) have not been made as they are invariably negligible compared with experimental uncertainty.

3.2. Tabulation of Thermal Function Data

The thermal function data file is processed to produce a file containing tabulated values for C_p°, $S^\circ - S_{298}^\circ$, $-(G_T^\circ - H_{298}^\circ)/T - S_{298}^\circ$, and $H_T^\circ - H_{298}^\circ$, indexed under the formula for each species (see Appendix IV). As described in Sec. 4.1, it is essential to be able to adjust the entropy at 298.15 K and to scale up or down the corresponding values for entropies and gibbs energy functions at all temperatures above 298.15 K. For this reason, these properties are tabulated relative to 298.15 K and absolute values are derived by adding the entropy at 298.15 K, taken from the file of selected reference temperature data (see Appendix II).

The tabulated format allows simple quadratic interpolation and extrapolation at required temperatures during processing of the experimental data rather than the calculation of each value from basic thermal function data. The values are calculated and tabulated at intervals of 100 K and in the temperature range 0 to 6000 K if they are derived from molecular parameters, otherwise the intervals and temperature range are as specified in the Thermal Function Data File. If the file contains multiple entries, the most recent entry corresponds to the currently selected data and is used in the processing. Thermal functions used for the titanium chlorides and associated compounds are given in Appendix IV where, for economy of space, values are listed only at the temperatures required for processing the data in the Experimental Data File.

3.3. Reduction to Standard State and Reference Temperature

An example of a calculation is shown in Table 2. If measurements are given at more than one temperature, second law calculations are carried out using least-squares fitting to values of $\Delta G^\circ/T$ (labeled DG/T) and 1000/T to

Table 2. Results of Processing some of the Data from Table 1

```
55SKI/RUE
Skinner, G.B.; Ruehrwein, R.A.
"Thermodynamic Properties of the Titanium Chlorides"
J.Phys.Chem.; 59, 113-117 (1955)
---
(Other textual information as in table 1)
---

2TiCl3(cr)=TiCl2(cr)+TiCl4(g)
PP mm
849 38.7
863 53.2
900 123
928 232
DH298+/-3.0

 Calculations
 ------------
  T/K       DG     Residual   1000/T    DG/T    Residual
           /kcal mol-1        /K-1            /cal mol-1 K-1

 849.00    5.023   -5.757    1.178    5.916    -6.781
 863.00    4.560   -5.809    1.159    5.284    -6.731
 900.00    3.257   -6.032    1.111    3.619    -6.703
 928.00    2.188   -6.296    1.078    2.358    -6.784

                   DH3          DH2           DS2
                     /kcal mol-1          /cal mol-1 K-1

 Values at 298   33.026       38.876        42.335
  Residual       -5.974       -0.124         6.605

                Average T*      DH            DS
                    /K      /kcal mol-1   /cal mol-1 K-1
 2nd Law Values
 at Average T*      883       35.461        35.824

* Average T is the temperature corresponding to the average
  reciprocal temperature of the experimental data.
```

give values for the standard enthalpy and entropy changes (DH and DS, respectively) for the reaction at the average reciprocal temperature as shown. Hence second law values at 298.15 K (DH2 and DS2) are derived using enthalpy functions and entropies, interpolated quadratically from the tables set up as described in Sec. 3.2. Similarly, third law values for enthalpies of reaction at 298.15 K (DH3) are calculated using gibbs energy functions from Appendix IV and enthalpies of formation about Appendix II.

Values labeled "Residual" in Table 2 show the discrepancies between the values derived from the experimental data and those calculated from currently selected data. These values can indicate possible errors in the selected data.

For assessment purposes it is useful to present all the relevant information on a given paper; although it is not shown in its entirety in Table 2, in practice all the textual material is generated with the processed data. The full information derived from all the papers on the titanium chlorides is generated automatically by executing the data processing program for compounds containing only "Ti" and "Cl", or, if data for a particular compound are required, the program may be executed for all equations containing, for example, "TiCl3(cr)". This full information is essential for a complete understanding of the detailed assessment which follows, but space does not permit the inclusion here of all such material as about 50 pp. of computer printout are involved. It is, however, available from the authors on request.

4. Data Assessment

The assessment method comprises the following general procedure. A species or group of species is chosen for consideration and, if not already present, relevant experimental data and textual material from the literature are entered in the Experimental Data File (see Sec. 2.1). Current literature values for standard enthalpies of formation and entropies are entered in the file of Selected Reference Temperature Data (see Sec. 2.2), and data are entered in the basic Thermal Function Data File as described in Sec. 2.3. If the group of compounds to be assessed contains species which are interrelated, a preliminary survey of the data suggests the order in which species should be assessed; this decision may be altered during the course of the assessment. The data processing program is then used to extract all equations containing the first species to be assessed, and to produce the following files:

(i) A file containing the full textual and numerical information for all the papers on the chosen species, as illustrated by the example in Table 2.

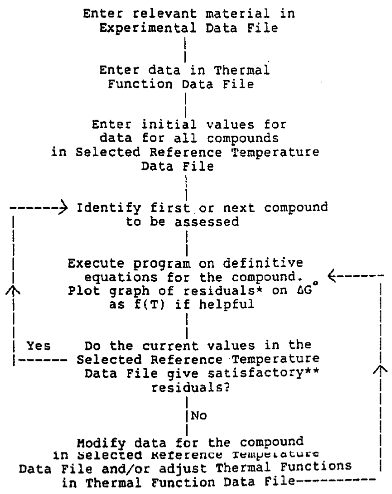
(ii) A file containing data similar to those given in Tables 3–6, showing reference codes, equations, average temperatures, and residuals for second and third law calculations (experimental minus selected values, as shown in Table 2), extracted from file (i). The purpose of this file is to collect together in a convenient form the essential details of all the equations for a compound or set of compounds.

(iii) A file containing temperatures and residuals (column headed "Residual" in Table 2) for input to a graph-plotting program.

The definitive equations for the species, i.e., those equations in which all compounds other than the one under consideration are taken as having fixed well-defined values, are then considered for assessment.

Inspection of the files described in (i) and (ii) above may be sufficient to choose a selected standard enthalpy of formation and entropy for a particular species. It is, however, sometimes difficult to judge from the numerical information by how much the values for the enthalpy of formation and/or the entropy of a compound should be changed to improve the consistency of the experimental data. In these circumstances it is useful to plot graphs of the residuals of either ΔG° vs T or $\Delta G^\circ/T$ vs $1/T$ using the data in file (iii). The graphs provide a visual interpretation of the consistency of the data and have proved valuable in estimating the amounts by which the values for the enthalpy of formation and entropy of the species under assessment should be adjusted. This graphical technique is a new development in assessment work and has produced some interesting results which are described in Secs. 5.2–5.5.

When new values for the standard enthalpy of formation and/or entropy of the compound under assessment have been selected, these are entered on the file of Selected Reference Temperature Data, replacing the former values. If the value for the entropy at 298.15 K is changed, values calculated from the basic Thermal Function Data File at all temperatures are assumed to change by the same amount and are automatically adjusted. (This procedure is justified in detail in the third paragraph of Sec. 5.1). The next compound to be assessed is then identified and the program is executed again, using the new selected values for the previously assessed compounds, and the procedure outlined above is repeated.



*Residuals used in graph plotting are divided by the stoichiometry number for the compound in the reaction under consideration.

**Satisfactory residuals are those which are as low as possible for the equations corresponding to the experimental measurements considered tc be the most reliable; this criterion often results in large residuals on less reliable measurements.

FIG. 1. Assessment procedure.

The method, summarized in Fig. 1, is applied to all the chosen compounds starting with the species identified as being the best defined, and finishing with the species with the least well-defined properties.

There are advantages in treating a set of compounds simultaneously, as described above, rather than treating each compound individually as an independent species. By considering all the equations for a group of related compounds in this way, checks can be made on the consistency of the values for the thermochemical properties of one member of the group with those of another member. In addition, the effect of a change in the value for, say, the entropy of $TiCl_3(cr)$ on the consistency of data for $TiCl_2(cr)$ can readily be judged.

5. Assessment of Data for $TiCl_4(g)$, $TiCl_4(l)$, $TiCl_3(cr)$, and $TiCl_2(cr)$

5.1. Introduction

Since data for the titanium chlorides are closely interrelated, it is necessary to define an order in which the compounds should be assessed. A preliminary survey of the data indicates that $TiCl_4(l)$ and $TiCl_4(g)$ should be assessed first since the other compounds under consideration are strongly dependent upon them. Of all the measurements on these two species, only that on the gas by 59JOH/NEL involves a precisely defined process and $TiCl_4(g)$ is therefore identified as the key compound. Details of the sources of error in measurements on $TiCl_4(l)$ are given below in the assessment for that species in Sec. 5.3.

Values for $TiCl_4(l)$ are assessed from vaporization data and, since the experimental results for $TiCl_3(cr)$ appear to be better defined than those for $TiCl_2(cr)$, $TiCl_3(cr)$ is assessed before $TiCl_2(cr)$.

There is considerable uncertainty concerning values for the entropies of the titanium chlorides. In the gaseous phase, uncertainties arise from a lack of knowledge of electronic states, vibrational frequencies, molecular geometry, anharmonicity, etc. Changing the values of these properties would give entropy changes which are fairly independent of temperature above 298.15 K. Similarly, in the condensed phase there is the possibility of contributions to the entropy at low temperatures arising from the presence of unpaired electrons. High-temperature measurements often reveal discrepancies which may arise from the above causes and which may be resolved by changing the value for the entropy at the reference temperature and assuming that the same change is to be applied to entropies and gibbs energy functions at all temperatures. In the absence of experimental evidence to resolve the uncertainties, this rather arbitrary procedure has been adopted; however, the possibility should also be considered that the "missing" entropy is partially in S°_{298} and partially in $S^\circ_T - S^\circ_{298}$. Further measurements on both high- and low-temperature heat capacities might help to elucidate these problems.

All the major compilations (Refs. 1–3) select almost identical values for the entropies of each of the compounds $TiCl_4(g)$, $TiCl_4(l)$, $TiCl_3(cr)$, and $TiCl_2(cr)$. The heat capacity of $TiCl_3(cr)$ was measured by 61KIN/WEL over the temperature range 53–297 K and the heat content was measured from 298–1000 K; the JANAF[3] value, accepted by the other compilations, is based on these data. The heat capacity of $TiCl_2(cr)$ was measured over the temperature range 6–300 K, and, whilst accepting the value for the entropy at 298.15 K based on these measurements, JANAF[3] suggests that there may be sizable electronic contributions below 6 K.

It is thus evident that the values for the entropies of $TiCl_3(cr)$ and $TiCl_2(cr)$ at 298.15 K, currently available in the compilations, are questionable because of the possibility of significant unidentified contributions to the heat capacity at low temperature.

The work of 69VAS/POD (which postdates the JANAF[3] assessment) supplies information on heat content measurements from 485 to 931 K for $TiCl_2(cr)$ and from 585 to 980 K for $TiCl_3(cr)$. For $TiCl_2(cr)$, entropy values calculated from these data are about 5.2 cal mol^{-1} K^{-1} higher than those given in the JANAF Tables[3] at 900 K and about 1.5 cal mol^{-1} K^{-1} higher at 500 K, tending towards convergence at 400 K. For $TiCl_3(cr)$, the values derived from 69VAS/POD range from 2.9 cal mol^{-1} K^{-1} higher at 900 K to 1.4 cal mol^{-1} K^{-1} higher at 600 K, tending to convergence with JANAF[3] values at 500 K. We therefore use JANAF[3] thermal functions at lower temperatures combined with the data of 69VAS/POD at higher temperatures. These combined data are more consistent with the data for high-temperature measurements than are those given in the JANAF Tables,[3] which are based, for $TiCl_2(cr)$, on extrapolation above 300 K, and for $TiCl_3(cr)$, on the heat content data of 61KIN/WEL.

Table 3. Definitive Equations for $TiCl_4(g)$

		Average Temperature	Residuals		
			3rd Law DH	2nd Law DH	2nd Law DS
(a) Using values from CODATA (10) as follows:					
$\Delta_f H^\circ_{298}$ = -182.4 +/- 0.7 kcal mol^{-1}					
S°_{298} = 84.4 +/- 0.1 cal mol^{-1} K^{-1}					
55FAR/DAR2	TiO2(cr)+4HCl(g)= TiCl4(g)+2H2O(g)	1044	-8.460	-0.851	7.100
59JOH/NEL	Ti(cr)+2Cl2(g)=TiCl4(g)	298	0.000		
(b) Using revised values as follows:					
$\Delta_f H^\circ_{298}$ = -182.4 +/- 0.7 kcal mol^{-1}					
S°_{298} = 85.45 +/- 0.1 cal mol^{-1} K^{-1}					
55FAR/DAR2	TiO2(cr)+4HCl(g)= TiCl4(g)+2H2O(g)	1044	-7.340	-0.851	6.050
59JOH/NEL	Ti(cr)+2Cl2(g)=TiCl4(g)	298	0.000		

The results of the assessment are summarized in Tables 3–6; for each table, section (a) shows the results of processing the experimental data using values for the titanium chlorides taken from the standard compilations specified, and section (b) shows the results for the same experimental data using our revised values for the standard properties. The column headed "Average Temperature" gives the temperatures corresponding to the average reciprocal temperatures of the measurements. The three columns headed "Residuals" give the third law and second law values (first and second columns, respectively) for the enthalpies of reaction at 298.15 K derived from the experimental measurements minus those calculated from the specified set of selected standard enthalpies of formation; the corresponding second law entropy residuals are given in the third column.

5.2. $TiCl_4(g)$

For our initial processing of the definitive equations for $TiCl_4(g)$ we use the values given in CODATA (1978),[10] where the value for $\Delta_f H^\circ_{298}$ is based on the meticulous calorimetric investigation of 59JOH/NEL, whose results are supported by chemical analysis. The CODATA value for the entropy at 298.15 K is based on the molecular constants of 72CLA/HUN, whose data we also use to calculate thermal functions.

The work of Farber and Darnell yields a second law enthalpy of reaction in reasonable agreement with the value derived by 59JOH/NEL but their third law result and entropy change for the reaction are inconsistent with the second law value. The value they derive for the entropy of $TiCl_4(g)$ is 7 cal mol^{-1} K^{-1} higher than that given by JANAF at 1100 K. Such a value cannot, however, be justified by any reasonable changes in the thermal functions of the species involved. Our selected value for the entropy at 298.15 K of $TiCl_4(g)$ is 1.05 cal mol^{-1} K^{-1} higher than the CODATA value as explained in Sec. 5.3 on the assessment of $TiCl_4(l)$.

In Tables 3–6, temperatures are in kelvins, residuals on enthalpies of reaction (columns headed "3rd Law DH" and "2nd Law DH") are in kcal mol^{-1}, and residuals on entropies of reaction (column headed "2nd Law DS") are in cal mol^{-1} K^{-1}. Where no second law values are given, either the temperature range of the measurements is too small (< 100 K) for significant values to be calculated or, more frequently, the "3rd Law DH" corresponds to a direct measurement of the standard enthalpy change for a reaction, usually at 298.15 K.

5.3. $TiCl_4(l)$

The four direct measurements of $\Delta_f H^\circ_{298}$ for $TiCl_4(l)$ (55GRO/HAY, 55SKI/RUE, 56KRI/VAN, and 57GRO/HAY) yield uncertain results since corrections are necessary for the enthalpy of solution of $Cl_2(g)$ in $TiCl_4(l)$. $\Delta_f H^\circ_{298}$ for $TiCl_4(l)$ is therefore derived from $\Delta_f H^\circ_{298}$ for $TiCl_4(g)$ and the measurements of the enthalpy of vaporization of $TiCl_4(l)$. Calculations show that derivations from ideality of the gas and corrections for the volume of the liquid are negligible. Fugacity corrections, assuming Bertholet and Van der Waals type of equations of state, derived from the critical pressure and temperature given in 66LUC amount to < 0.01 kcal mol^{-1} over the temperature range of interest; above 400 K the correction tends to zero.

Figure 2(a) shows a plot of the residuals for ΔG of vaporization versus temperature for the experimental data relative to those calculated from the chosen current litera-

Table 4. Definitive Equations for $TiCl_4(l)$

		Average Temperature	Residuals 3rd Law DH	2nd Law DH	2nd Law DS
(a) Using values from CODATA (10) as follows: $\Delta_f H^\circ_{298}$ = -192.1 +/ -0.7 kcal mol^{-1} S°_{298} = 60.30 +/- 0.02 cal mol^{-1} K^{-1}					
29ARI	TiCl4(l)=TiCl4(g)	348	-0.046	-0.204	-0.525
53SCH/ZEP	TiCl4(l)=TiCl4(g)	333	0.004	0.218	0.605
55GRO/HAY	Ti(cr)+2Cl2(g)=TiCl4(g)	298	1.800		
55SKI/RUE	Ti(cr)+2Cl2(g)=TiCl4(l)	298	2.102		
56KRI/VAN	Ti(cr)+2Cl2(g)=TiCl4(l)	298	2.102		
56MOR/TOP	TiCl4(l)=TiCl4(g)	360	-0.036	-0.140	-0.332
57GRO/HAY	Ti(cr)+2Cl2(g)=TiCl4(l)	298	0.652		
57SAH/FUN	TiCl4(l)=TiCl4(g)	342	-0.099	-0.393	-1.027
59PIK/FOS	TiCl4(l)=TiCl4(g)	395	-0.030	0.407	1.099
61SER/VAK	TiCl4(l)=TiCl4(g)	383	-0.014	0.236	0.635
62RUB/PON	TiCl4(l)=TiCl4(g)	373	-0.020	0.433	1.188
64SRI/BAR	TiCl4(l)=TiCl4(g)	314	0.036	1.491	4.611
65PEA/MCC	TiCl4(l)=TiCl4(g)	298	-1.992		
66LUC	TiCl4(l)=TiCl4(g)	327	-0.070	-0.360	-1.033
(b) Using revised values as follows: $\Delta_f H^\circ_{298}$ = -192.47 +/- 0.7 kcal mol^{-1} S°_{298} = 60.30 +/- 0.02 cal mol^{-1} K^{-1}					
29ARI	TiCl4(l)=TiCl4(g)	348	-0.045	-0.574	-1.575
53SCH/ZEP	TiCl4(l)=TiCl4(g)	333	-0.014	-0.152	-0.445
55GRO/HAY	Ti(cr)+2Cl2(g)=TiCl4(g)	298	2.170		
55SKI/RUE	Ti(cr)+2Cl2(g)=TiCl4(l)	298	2.472		
56KRI/VAN	Ti(cr)+2Cl2(g)=TiCl4(l)	298	2.472		
56MOR/TOP	TiCl4(l)=TiCl4(g)	360	-0.025	-0.510	-1.382
57GRO/HAY	Ti(cr)+2Cl2(g)=TiCl4(l)	298	1.022		
57SAH/FUN	TiCl4(l)=TiCl4(g)	342	-0.098	-0.763	-2.077
59PIK/FOS	TiCl4(l)=TiCl4(g)	395	0.016	0.037	0.049
61SER/VAK	TiCl4(l)=TiCl4(g)	383	0.020	-0.134	-0.415
62RUB/PON	TiCl4(l)=TiCl4(g)	373	0.003	0.063	0.138
64SRI/BAR	TiCl4(l)=TiCl4(g)	314	-0.004	1.121	3.561
65PEA/MCC	TiCl4(l)=TiCl4(g)	298	-2.362		
66LUC	TiCl4(l)=TiCl4(g)	327	-0.086	-0.730	-2.083

ture data listed in Appendixes II and IV.

From the trends in the values in Fig. 2(a) it can be seen that the consistency of the entropy data could be improved either by increasing S°_{298} for $TiCl_4(g)$ by 1.05 cal mol^{-1} K^{-1} or by decreasing S°_{298} for $TiCl_4(l)$ by the same amount. It is more likely that the previously accepted value for the entropy of the gas is too low since, although there are well established molecular parameters for $TiCl_4(g)$, corrections for anharmonicity, the rotation–vibration interaction constant, and the centrifugal distortion constant are unknown, and contributions from these parameters would increase the value for the entropy. The value for the liquid appears to be well established, therefore the adjustment has been made to the value for the gas. A small decrease of 0.37 kcal mol^{-1} to the CODATA value for $\Delta_f H^\circ_{298}$ of $TiCl_4(l)$ further improves the consistency of the data as shown in Fig. 2(b), in which the measurements of 29ARI and 66LUC below 300 K have been discounted. The residuals on the second and third law $\Delta_r H^\circ_{298}$ and second law $\Delta_r S^\circ_{298}$ for the experimental data for $TiCl_4(l)$, before and after the adjustments, are shown in Table 4, sections (a) and (b). As discussed in the first paragraph of this section, the measurements of 55GRO/HAY, 55SKI/RUE, 56KRI/VAN, and 57GRO/HAY are discounted due to possible errors caused by solution problems. At temperatures above 340 K all measurements are in agreement to within 0.03 kcal mol^{-1}. At lower temperatures the measurements of 29ARI, 66LUC, and 64SRI/BAR diverge from the other data, presumably because of experimental difficulties encountered in the measurement of the lower pressures.

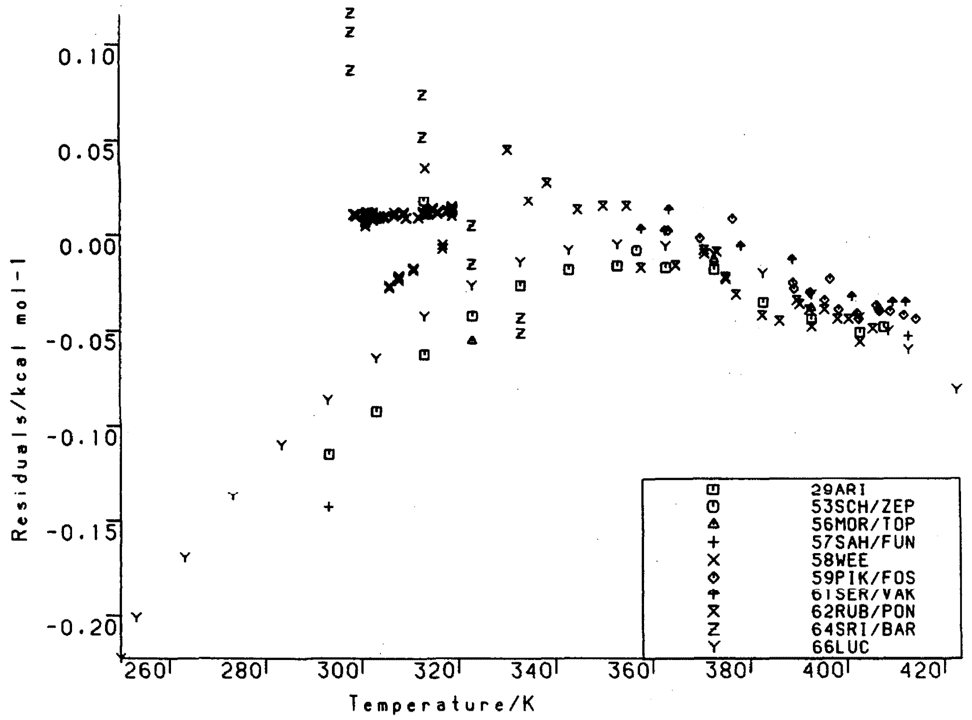


FIG. 2(a). Initial residuals for ΔG° vs temperature for vaporization of $TiCl_4(l)$.

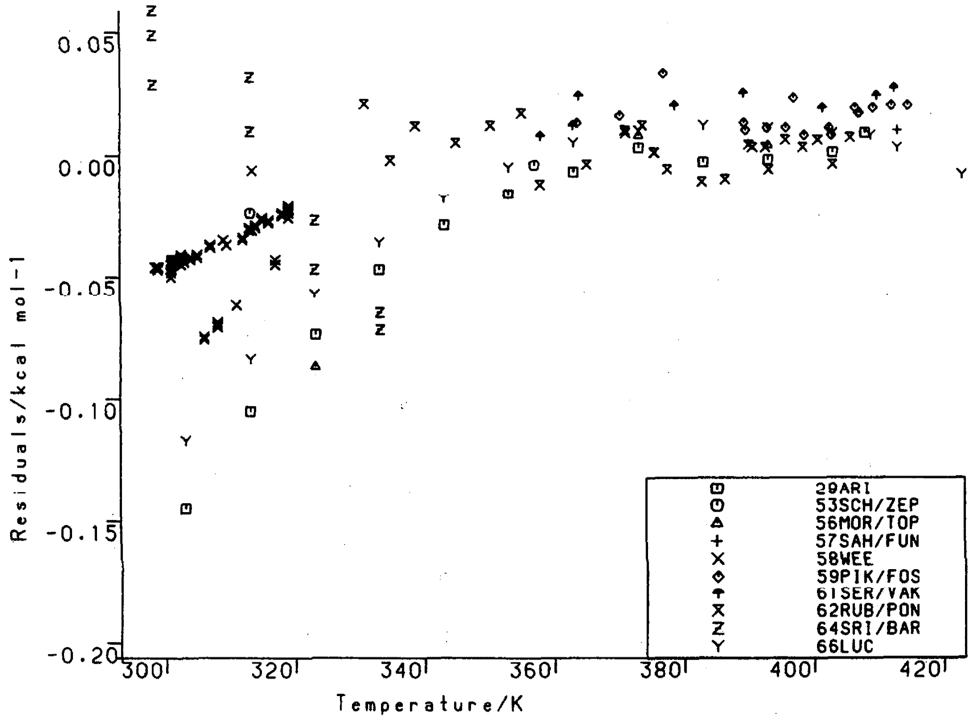


FIG. 2(b). Revised residuals for ΔG° vs temperature for vaporization of $TiCl_4(l)$.

Table 5. Definitive Equations for $TiCl_3$(cr)

(a) Using values from JANAF (3) for $TiCl_3$(cr) as follows:

$\Delta_f H^{\circ}_{298}$ = -172.5 +/- 1.0 kcal mol^{-1}

S°_{298} = 33.4 +/- 0.3 cal mol^{-1} K^{-1}

		Average Temperature	Residuals 3rd Law DH	2nd Law DH	2nd Law DS
54SCH/BRE	TiCl3(cr)+1/2Cl2(g)=TiCl4(g)	330	-0.465		
54SCH/BRE	TiCl4(g)+Hg(l)= TiCl3(cr)+1/2Hg2Cl2(cr)	418	0.669	3.975	7.897
55SKI/RUE	Ti(cr)+3HCl(10H2O)= TiCl3(cr)+3/2H2(g)	298	2.670		
56CLI/MAC1	TiCl3(cr)+1/2Cl2(g)=TiCl4(l)	273	-0.066		
56KRI/MAS	TiCl3(cr)+HCl(g)= TiCl4(g)+1/2H2(g)	688	1.098	0.655	-0.656
56KRI/VAN	TiCl3(cr)+0.5Cl2(g)=TiCl4(l)	298	-0.929		
60HEA	TiCl3(cr)+1/2Cl2(g)=TiCl4(l)	298	-0.629		
60JOH/GIL	TiCl3(cr)+1/2I2(cr)+HCl(g)= TiCl4(l)+HI(g)	298	-0.020		

(b) Using revised values for $TiCl_3$(cr) as follows:

$\Delta_f H^{\circ}_{298}$ = -172.3 +/- 1.0 kcal mol^{-1}.

S°_{298} = 35.3 +/- 1.0 cal mol^{-1} K^{-1}

		Average Temperature	Residuals 3rd Law DH	2nd Law DH	2nd Law DS
54SCH/BRE	TiCl3(cr)+1/2Cl2(g)=TiCl4(g)	330	-0.265		
54SCH/BRE	TiCl4(g)+Hg(l)= TiCl3(cr)+1/2Hg2Cl2(cr)	418	1.264	3.775	5.997
55SKI/RUE	Ti(cr)+3HCl(10H2O) =TiCl3(cr)+3/2H2(g)	298	2.470		
56CLI/MAC1	TiCl3(cr)+1/2Cl2(g)=TiCl4(l)	273	0.134		
56KRI/MAS	TiCl3(cr)+HCl(g)= TiCl4(g)+1/2H2(g)	688	-0.018	0.855	1.244
56KRI/VAN	TiCl3(cr)+0.5Cl2(g)=TiCl4(l)	298	-0.729		
60HEA	TiCl3(cr)+1/2Cl2(g)=TiCl4(l)	298	-0.429		
60JOH/GIL	TiCl3(cr)+1/2I2(cr)+HCl(g)= TiCl4(l)+HI(g)	298	0.180		

5.4. $TiCl_3$(cr)

The data for $TiCl_3$(cr) were assessed using the revised values for $TiCl_4$(g) and $TiCl_4$(l), see Secs. 5.2 and 5.3.

A survey of the data for $TiCl_3$(cr) (see Table 5) shows that all equations other than the first 54SCH/BRE and 56KRI/MAS include species in the liquid phase and therefore require extra care and assessment to take account of possible solution problems; less reliance is therefore placed on the results of 54SCH/BRE (using liquid mercury), 55SKI/RUE (aqueous HCl), 56KRI/VAN, and 60 HEA [both using $TiCl_4$(l)]. The data of 56CLI/MAC1 and 60JOH/GIL are considered to be more reliable since they used solvents capable of converting all the titanium to oxidation state 4.

Taking the average of the residuals from the first equation of 54SCH/BRE and the data of 56CLI/MAC1 and 60JOH/GIL indicates that the value for the standard enthalpy of formation of $TiCl_3$(cr) should be increased by 0.2 kcal mol^{-1} over the value recommended by JANAF.[3]

The work of 56KRI/MAS appears to be reliable and includes careful chemical analysis. Their experimental measurements can be made consistent with the above selected value if the current literature value for the standard entropy at 298.15 K of $TiCl_3$(cr) is increased by 1.9 cal mol^{-1} K^{-1}. A selected value of 35.3 ± 1.0 cal mol^{-1} K^{-1} is therefore adopted.

5.5. $TiCl_2$(cr)

The standard enthalpy of formation of $TiCl_2$(cr) is most reliably defined by available low-temperature measurements since values for thermal functions for this species are not well established. All the equations for $TiCl_2$(cr) shown in Table 6 represent high-temperature processes except the two measurements of 56CLI/MAC2 and that of 56KRI/VAN. The selected value for the standard enthalpy of formation of $TiCl_2$(cr) is therefore based on these three equations. In the solution measurements of 56CLI/MAC2 the processes appear to be clearly defined, and although in 56KRI/

Table 6. Definitive equations for $TiCl_2$(cr)

		Average Temperature	Residuals 3rd Law DH	2nd Law DH	2nd Law DS
(a) Using values from JANAF (3) for $TiCl_2$(cr) as follows:					
$\Delta_f H^\circ_{298}$ = -123.20 +/- 4.0 kcal mol^{-1}					
S°_{298} = 20.88 +/- 1.0 cal mol^{-1} K^{-1}					
55FAR/DAR1	2TiCl3(cr)=TiCl2(cr)+TiCl4(g)	677	-2.309	-2.991	-1.014
55SKI/RUE	2TiCl3(cr)=TiCl2(cr)+TiCl4(g)	883	-5.974	-0.124	6.605
56CLI/MAC2	TiCl2(cr)+Cl2(g)=TiCl4(l)	273	0.422		
56CLI/MAC2	TiCl2(cr)+HCl(9.69H2O) =TiCl3(cr)+0.5H2(g)	298	-0.110		
56FAR/DAR	2TiCl2(cr)=Ti(cr)+TiCl4(g)	844	-2.837	-7.111	-5.075
56KRI/VAN	TiCl2(cr)+Cl2(g)=TiCl4(l)	298	-0.629		
56SAN/MAC	2TiCl3(cr)=TiCl2(cr)+TiCl4(g)	650	-1.635	-5.294	-5.602
56SAN/MAC	2TiCl3(cr)=TiCl2(cr)+TiCl4(g)	749	-5.553	0.597	8.164
57HAR/RIN	2TiCl3(cr)=TiCl2(cr)+TiCl4(g)	890	-6.292	-0.048	6.982
60FUN/UCH	2TiCl2(cr)=Ti(cr)+TiCl4(g)	744	-15.848	-28.643	-16.967
72POL/NOV	2TiCl3(cr)=TiCl2(cr)+TiCl4(g)	847	-9.415	0.413	11.551
72POL/NOV	2TiCl2(cr)=Ti(cr)+TiCl4(g)	1141	-1.765	0.180	1.721
(b) Using revised values as follows:					
$\Delta_f H^\circ_{298}$ = -123.2 +/- 1.5 kcal mol^{-1}					
S°_{298} = 27.9 +/- 3.0 cal mol^{-1} K^{-1}					
55FAR/DAR1	2TiCl3(cr)=TiCl2(cr)+TiCl4(g)	677	2.464	-2.991	-8.034
55SKI/RUE	2TiCl3(cr)=TiCl2(cr)+TiCl4(g)	883	0.239	-0.124	-0.415
56CLI/MAC2	TiCl2(cr)+Cl2(g)=TiCl4(l)	273	0.422		
56CLI/MAC2	TiCl2(cr)+HCl(9.69H2O) =TiCl3(cr)+0.5H2(g)	298	-0.110		
56FAR/DAR	2TiCl2(cr)=Ti(cr)+TiCl4(g)	844	-14.715	-7.111	8.965
56KRI/VAN	TiCl2(cr)+Cl2(g)=TiCl4(l)	298	-0.629		
56SAN/MAC	2TiCl3(cr)=TiCl2(cr)+TiCl4(g)	650	2.974	-5.294	-12.622
56SAN/MAC	2TiCl3(cr)=TiCl2(cr)+TiCl4(g)	749	-0.272	0.597	1.144
57HAR/RIN	2TiCl3(cr)=TiCl2(cr)+TiCl4(g)	890	-0.025	-0.048	-0.038
60FUN/UCH	2TiCl2(cr)=Ti(cr)+TiCl4(g)	744	-26.703	-28.643	-2.927
72POL/NOV	2TiCl3(cr)=TiCl2(cr)+TiCl4(g)	847	-3.448	0.413	4.531
72POL/NOV	2TiCl2(cr)=Ti(cr)+TiCl4(g)	1141	-17.911	0.180	15.761

VAN corrections for solution of chlorine in $TiCl_4$(l) had to be applied, they were less significant than those for $TiCl_3$(cr) (see above). An average of the residuals on these three measurements, weighted by their uncertainties, is approximately zero, indicating that the current JANAF[3] value for the standard enthalpy of formation is acceptable. The uncertainty relative to $TiCl_4$(l) appears to be no greater than 1.0 kcal mol^{-1} and hence the overall uncertainty has been selected as 1.5 kcal mol^{-1} rather than the JANAF[3] value of 4.0 kcal mol^{-1}.

As shown in Fig. 3(a), results for those processes involving Ti(cr) (56FAR/DAR, 60FUN/UCH, and 72POL/NOV) are inconsistent with other high-temperature data, possibly due to failure to identify correctly the processes taking place. The high-temperature data of 55SKI/RUE, 57HAR/RIN, and the second equation of 56SAN/MAC, derived from measurements made by static methods, are very consistent. We have noticed in studying the data for the chlorides of titanium that for high-temperature processes other than congruent vaporization, static methods appear to yield more consistent results than techniques involving effusion and transportation, suggesting that equilibrium may not be established in experiments using the dynamic methods. We therefore recommend a value of 27.9 ± 3 cal mol^{-1} K^{-1} entropy at 298.15 K for $TiCl_2$(cr), which fits the data for the three consistent measurements mentioned above, as shown in Fig. 3(b). This increase of 7 cal mol^{-1} K^{-1} over the JANAF[3] selected value is reasonable considering the large number of low-lying electronic states that could arise from the configuration $3d^2$, which may be assumed for the Ti^{2+} ion; the large error assigned reflects the uncertainty in the thermal function data.

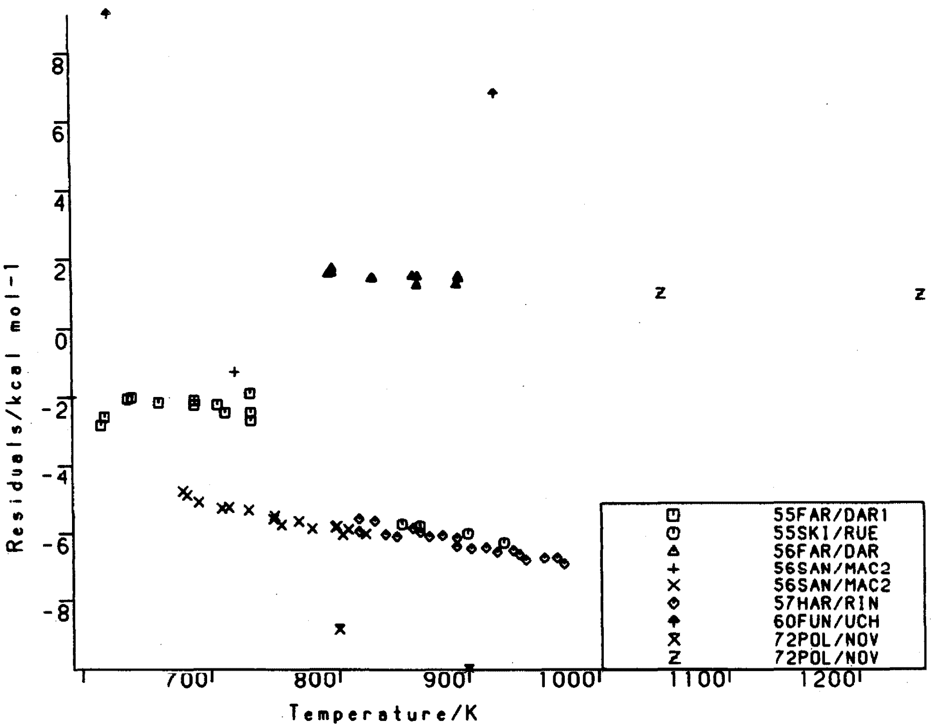


FIG. 3(a). Initial residuals for ΔG° vs temperature for $2TiCl_3(cr) = TiCl_4(g) + TiCl_2(cr)$.

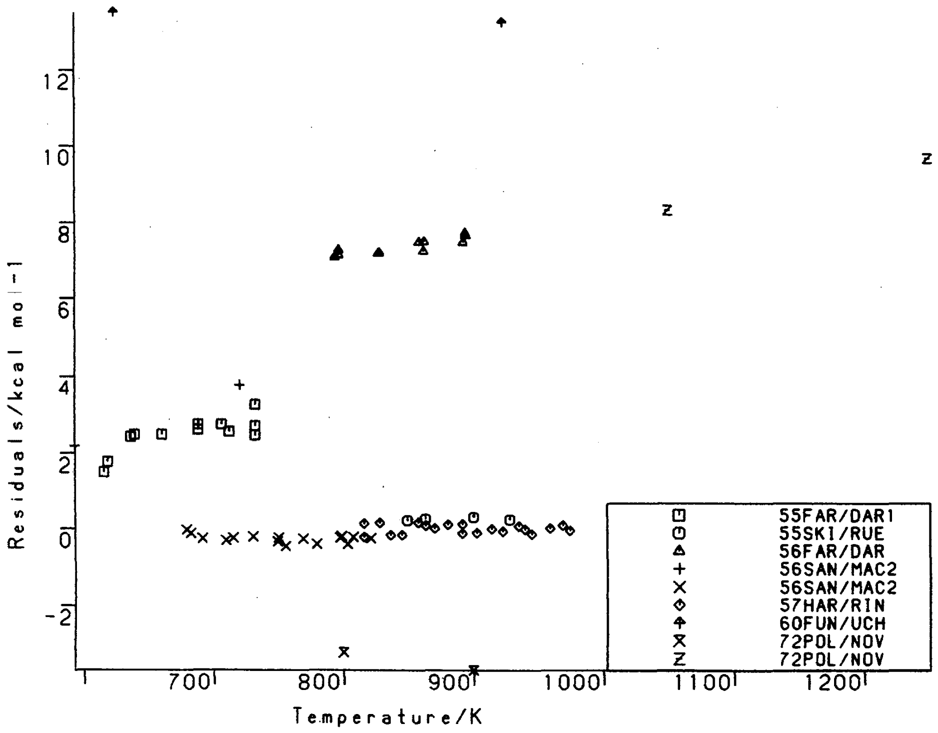


FIG. 3(b). Revised residuals for ΔG° vs temperature for $2TiCl_3(cr) = TiCl_4(g) + TiCl_2(cr)$.

6. Conclusion

This paper has described the contents and structure of the Sussex Computerized Thermochemical Data Base and how it has been used to assist in the assessment of thermochemical data for some titanium chlorides. Future papers will concentrate on assessment and will refer back to the methodology described here.

The reliability of the values recommended for the titanium chloride species under review remains questionable; in particular there are uncertainties concerning thermal functions. Further experimental measurements of heat capacities at both high and low temperature might resolve these problems.

In the past, assessors of thermochemical data have given some information about their assessment procedures, but we claim to be the first to store on computer files permanent records of the detailed documentation (see Table 1) and all aspects of calculation, assessment, and selection. This system should simplify the task of future assessors in updating and reevaluating the thermochemical data presented here if further experimental evidence is produced.

Our selected values for $TiCl_2(cr)$, $TiCl_3(cr)$, $TiCl_4(l)$, and $TiCl_4(g)$ are given in energy units of joules in Tables 7 and 8.

Table 7. Selected Values for Enthalpies of Formation and Entropies at 298.15 K for $TiCl_2(cr)$, $TiCl_3(cr)$, $TiCl_4(l)$ and $TiCl_4(g)$ in Joules

	Enthalpy of Formation $\Delta_f H^\circ_{298}$/kJ mol^{-1}	Entropy S°_{298}/J mol^{-1} K^{-1}
$TiCl_2(cr)$	-515.5 +/- 6.3	116.7 +/- 4.2
$TiCl_3(cr)$	-720.9 +/- 4.2	147.7 +/- 4.2
$TiCl_4(l)$	-805.30 +/- 2.9	252.30 +/- 0.08
$TiCl_4(g)$	-763.2 +/- 2.9	357.52 +/- 0.4

Table 8. Selected Values for Thermal Functions for $TiCl_2$(cr), $TiCl_3$(cr), $TiCl_4$(l) and $TiCl_4$(g) in Joules

T/K	C_p°	$S^\circ-S^\circ_{298}$	$-(G^\circ-H^\circ_{298})/T-S^\circ_{298}$	$H^\circ-H^\circ_{298}$
	(	J mol^{-1} K^{-1}	)	(kJ mol^{-1})
TiCl2(cr)				
0.000	0.000	-87.345	-	-13.301
100.000	37.777	-61.379	55.522	-11.690
200.000	61.505	-26.250	6.155	-6.481
298.150	69.831	0.000	0.000	0.000
300.000	69.898	0.431	-0.001	0.130
400.000	73.392	21.029	2.787	7.297
485.000	92.165	41.396	8.416	15.995
500.000	93.220	44.217	9.447	17.385
600.000	100.240	61.835	16.739	27.058
700.000	107.261	77.814	24.337	37.434
800.000	114.290	92.596	31.959	48.509
900.000	121.303	106.462	39.471	60.291
931.000	123.478	110.604	41.768	64.086
TiCl3(cr)				
0.000	0.000	-139.750	-	-20.920
100.000	54.438	-95.399	88.027	-18.343
200.000	101.926	-44.246	9.351	-10.719
298.150	97.161	0.000	0.000	0.000
300.000	97.194	0.602	0.003	0.180
400.000	98.960	28.807	3.839	9.987
500.000	100.575	51.066	11.134	19.966
585.000	113.445	72.463	19.451	31.012
600.000	114.001	75.341	20.817	32.715
700.000	117.725	93.194	29.908	44.300
800.000	121.445	109.156	38.829	56.262
900.000	125.169	123.679	47.465	68.592
980.000	128.143	134.461	54.133	78.722
TiCl4(l)				
200.000	144.699	-57.856	13.272	-14.226
298.150	145.202	0.000	0.000	0.000
300.000	145.222	0.900	0.007	0.268
400.000	146.172	42.806	5.705	14.841
500.000	147.080	75.521	16.518	29.501
600.000	147.988	102.420	28.663	44.254
700.000	148.892	125.298	40.871	59.099
800.000	149.800	145.239	52.700	74.032
900.000	150.708	162.938	63.986	89.056
1000.000	151.616	178.862	74.689	104.173
TiCl4(g)				
0.000	0.000	-353.497	-	-21.513
100.000	66.879	-89.178	77.789	-16.697
200.000	85.943	-36.332	8.480	-8.962
298.150	95.534	0.000	0.000	0.000
300.000	95.657	0.591	0.002	0.177
400.000	100.408	28.837	3.821	10.007
500.000	102.942	51.542	11.169	20.186
600.000	104.421	70.452	19.518	30.560
700.000	105.351	86.624	27.977	41.052
800.000	105.970	100.734	36.209	51.620
900.000	106.402	113.242	44.086	62.240
1000.000	106.715	124.470	51.573	72.897
1100.000	106.949	134.652	58.670	83.581
1200.000	107.128	143.966	65.396	94.285
1300.000	107.268	152.547	71.774	105.005

Table 8. Selected Values for Thermal Functions for $TiCl_2(cr)$, $TiCl_3(cr)$, $TiCl_4(l)$ and $TiCl_4(g)$ in Joules --Continued

	T/K	C°_p	$S^\circ-S^\circ_{298}$	$-(G^\circ-H^\circ_{298})/T-S^\circ_{298}$	$H^\circ-H^\circ_{298}$
		(	J mol^{-1} K^{-1}	)	(kJ mol^{-1})
$TiCl_4(g)$ (Cont.)	1400.000	107.379	160.500	77.831	115.737
	1500.000	107.469	167.912	83.592	126.480
	1600.000	107.543	174.850	89.081	137.231
	1700.000	107.605	181.372	94.320	147.988
	1800.000	107.656	187.524	99.329	158.751
	1900.000	107.700	193.346	104.125	169.519
	2000.000	107.738	198.871	108.726	180.291
	2100.000	107.770	204.128	113.144	191.067
	2200.000	107.798	209.143	117.395	201.845
	2300.000	107.822	213.935	121.489	212.626
	2400.000	107.844	218.524	125.437	223.409
	2500.000	107.863	222.927	129.249	234.195
	2600.000	107.879	227.158	132.934	244.982
	2700.000	107.894	231.229	136.500	255.770
	2800.000	107.908	235.154	139.953	266.561
	2900.000	107.920	238.940	143.302	277.352
	3000.000	107.931	242.599	146.551	288.145
	3100.000	107.940	246.138	149.707	298.938
	3200.000	107.949	249.566	152.774	309.733
	3300.000	107.958	252.888	155.758	320.528
	3400.000	107.965	256.111	158.662	331.324
	3500.000	107.972	259.240	161.491	342.121
	3600.000	107.978	262.282	164.249	352.918
	3700.000	107.984	265.240	166.939	363.716
	3800.000	107.989	268.120	169.564	374.515
	3900.000	107.994	270.926	172.127	385.314
	4000.000	107.998	273.660	174.631	396.114
	4100.000	108.003	276.326	177.079	406.914
	4200.000	108.007	278.929	179.473	417.714
	4300.000	108.010	281.471	181.816	428.515
	4400.000	108.014	283.954	184.109	439.316
	4500.000	108.017	286.381	186.355	450.118
	4600.000	108.020	288.755	188.555	460.920
	4700.000	108.023	291.078	190.712	471.722
	4800.000	108.025	293.353	192.827	482.524
	4900.000	108.028	295.580	194.901	493.327
	5000.000	108.030	297.763	196.937	504.130
	5100.000	108.032	299.902	198.935	514.933
	5200.000	108.034	302.000	200.897	525.736
	5300.000	108.036	304.058	202.824	536.540
	5400.000	108.038	306.077	204.717	547.344
	5500.000	108.040	308.059	206.578	558.147
	5600.000	108.041	310.006	208.408	568.951
	5700.000	108.043	311.918	210.207	579.755
	5800.000	108.044	313.798	211.977	590.560
	5900.000	108.046	315.644	213.718	601.364
	6000.000	108.047	317.460	215.432	612.169

7. Acknowledgments

The development of this system has taken place over a number of years and has been financially supported by the National Bureau of Standards (U. S.) in Gaithersburg, MD, the United Kingdom Atomic Energy Authority (Atomic Energy Research Establishment, Harwell) and the National Physical Laboratory, Teddington, Middlesex, England. Extensive discussions have taken place with many groups and individuals active in the field, including Dr. T. I. Barry, Dr. M. W. Chase, Dr. D. Garvin, Dr. D. Neumann, Dr. M. H. Rand, and Dr. H. J. White, Jr. Without their active cooperation this work would not have been possible, and their valuable assistance is gratefully acknowledged. The work described in this paper has been funded by the National Physical Laboratory and the authors wish to express their particular gratitude to Dr. T. I. Barry and Dr. M. H. Rand for their help. The authors are also indebted to the referees of the first draft of the paper for their constructive criticism, which prompted clarification of the content and presentation of the work.

8. References

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[9] D. Garvin and H. J. White, Jr., in Proceedings of the First CODATA Symposium on Chemical Thermodynamic and Thermophysical Properties Databases, 9–10 September 1985 (to be published).

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APPENDIX I. KEY TO CODED REFERENCES FOR TITANIUM CHLORIDE DATA

Extracted from Experimental Data File for Transition Element Halides

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29ARI
Arii, K.
"The Vapour Pressure of Titanium Tetrachloride"
Bull.Inst.Phys.Chem.Res.(Tokyo); 2, 86-8 (1929)

53SCH/ZEP
Schafer, H.; Zeppernick, F.
"The Saturation Pressure over Liquid Titanium Tetrachloride"
Z.anorg.und allgem.Chem.; 272, 274-278 (1953)

54SCH/BRE
Schafer, H.; Breil, G.; Pfeffer, G.
"Titanium Chlorides. II. Heat of Formation of Titanium(III)-Chloride"
Z.anorg.und allgem.Chem.; 276, 325-332 (1954)

55FAR/DAR1
Farber, M.; Darnell, A.J.
"The Disproportionation and Vapor Pressure of TiCl3"
J.Phys.Chem.; 59, 156-159 (1955)

55FAR/DAR2
Farber, M.; Darnell, A.J.
"Heat of Formation and Entropy of Titanium Tetrachloride from an
@Investigation of the Equilibrium: TiO2(s)+4HCl(g) = TiCl4(g)+2H2O(g)"
J.Chem.Phys.; 23, 1460-1463 (1955)

55GRO/HAY
Gross, P.; Hayman, C.; Levi, D.L.
"The Heats of Formation of Metallic Halides. Titanium Tetrachloride"
Trans.Faraday Soc.; 51, 626-629 (1955)

55SKI/RUE
Skinner, G.B.; Ruehrwein, R.A.
"Thermodynamic Properties of the Titanium Chlorides"
J.Phys.Chem.; 59, 113-117 (1955)

56CLI/MAC1
Clifton, D.G.; MacWood, G.E.
"Thermodynamics of the Titanium Chlorides. I. Heat of Formation of
@Titanium Trichloride"
J.Phys.Chem.; 60, 309-311 (1956)

56CLI/MAC2
Clifton, D.G.; MacWood, G.E.
"Thermodynamics of the Titanium Chlorides. II. Heat of Formation of
@Titanium Dichloride"
J.Phys.Chem.; 60, 311-313 (1956)

56FAR/DAR
Farber, M.; Darnell, A.J.
"Disproportionation and Vapor Pressure of TiCl2"
J.Chem.Phys.; 25, 526-530 (1956)

56KRI/MAS
Krieve, W.F.; Mason, D.M.
"Measurement of Equilibrium of the Reaction: TiCl3(s)+HCl(g)=
@TiCl4(g)+1/2H2(g)"
J.Chem.Phys.; 25, 524-525 (1956)

56KRI/VAN
Krieve, W.F.; Vango, S.P.; Mason, D.M.
"Calorimetric Determination of Heats of Formation of Titanium Chlorides"
J.Chem.Phys.; 25, 519-523 (1956)

56MOR/TOP
Morozov, I.S.; Toptygin, D.Ya.
"The Reaction of Chlorides of Vanadium with Titanium Tetrachloride and
@Carbon Tetrachloride"
Zhur.Neorg.Khim.; 1, 2601-2605, (1956)

56SAN/MAC2
Sanderson, B.S.; MacWood, G.E
"Thermodynamics of the Titanium Chlorides. IV. The Disproportionation
@of the Titanium Chlorides"
J.Phys.Chem.; 60, 316-319 (1956)

57GRO/HAY
Gross, P.; Hayman, C.; Levi, D.L.
"The Heats of Formation of Metal Halides. Titanium Tetrabromide, with
@Revised Data on Titanium Tetrachloride"
Trans.Faraday Soc.; 53, 1601-1605 (1957)

57HAR/RIN
Hartmann, H.; Rinck, G
"Das Disproportionierungsgleichgewicht des Titantrichlorids"
Z.Phys.Chem.; 11, 213-233 (1957)

57SAH/FUN
Saeki, Y.; Funaki, K.
"Chlorination of Titanium Compounds"
Nippon Kagaku Zasshi; 78, 754-759 (1957)

APPENDIX I. KEY TO CODED REFERENCES FOR TITANIUM CHLORIDE DATA--Continued

Extracted from Experimental Data File for Transition Element Halides

---

59JOH/NEL
Johnson, W.H.; Nelson, R.A.; Prosen, E.J.
"Heat of Formation of Titanium Tetrachloride"
J.Res.Nat.Bur.Stand., A; 62, 49-52 (1959)

59PIK/FOS
Pike, F.P.; Foster, C.T.,Jr.;
"Vapor Pressure and Boiling Point of Titanium Tetrachloride"
J.Chem.Eng.Data; 4, 305-306 (1959)

60FUN/UCH
Funaki, K.; Uchimura, K.
"The System Ti-TiCl4"
Bull.Tokyo Inst. Technol.Ser.B; 3, 191-196 (1960)

60HEA
Head, R.B.
"The Thermodynamic Properties of the Lower Chlorides of Titanium"
Aust.J.Chem.; 13, 332-340 (1960)

60JOH/GIL
Johnson,, W.H.; Gilliland, A.A.; Prosen, E.J.
"Heat of Formation of Titanium Trichloride"
J.Res.Nat.Bur.Stand., A; 64, 515-518 (1960)

61KIN/WEL
King, E.G.; Weller, W.W.; Christensen, A.U.; Kelley, K.K.
"Some Thermodynamic Values for Four Titanium Halides"
US Bur.Mines Rept.Invest.; 5799 (1961)

61SER/VAK
Seryakov, G.V.; Vaks, S.A.; Sidorina, L.S.
"Liquid Vapor Phase Equilibrium Studies of TiCl4"
Titan, i ego Splavy, Akad.Nauk SSSR, Inst.Met.; 5, 220-224 (1961)

62RUB/PON
Ruban, N.N.; Ponomarev, V.D.
"Determination of Vapor Pressure of Titanium Tetrachloride"
Tr.Inst.Met.i Obogashch Akad.Nauk Kaz. SSR; 4, 19-27 (1962)

64SRI/BAR
Srinivasan, S.R.; Bhatnagar, P.D.
"Reaction of Titanium with Titanium Tetrachloride"
Trans.Indian Inst.Metals; 17, 127-131 (1964)

65PEA/MCC
Pearce, M.L.; McCabe, N.R.
"The Vapour Pressure of Titanium Tetrachloride"
J.Inorg.Nucl.Chem.; 27, 1876-1878 (1965)

66LUC
Luchinskii, G.P.
"Physical Chemistry of the Titanium Halides. I. Parameters of
@the Phase Transformations of Titanium Tetrachloride"
Russ.J.Phys.Chem.; 40, 318-321 (1966)

67KIM/STO (Cp for TiCl2(cr) 6 - 300 K)
Kim, S.; Stout, J.W.
"Private Communication"
University of Chicago, (1967)

69VAS/POD
Vasil'kova, I.V.; Podzorov, B.jN.; Shapkin, P.S.
"Determination of Heat Capacity of Titanium Chlorides"
Russ.J.Inorg.Chem.; 14, 910-912 (1969)

72CLA/HUN
Clark, R.J.H.; Hunter, B.K.; Rippon, D.M.;
"Vapor-Phase Raman Spectra, Force Constants, and Values for
@Thermodynamic Functions of the Tetrachlorides, Tetrabromides,
@and Tetraiodides of Titanium, Zirconium, and Hafnium"
Inorg.Chem.; 11, 56-61 (1972)

72POL/NOV
Polyachenok, L.D.; Novikov, G.I.; Polyachenok, O.G.
"Thermodynamic Characteristics of Lower Titanium Chlorides and
@Titanium Oxychloride"
Obshch.Prikl.Khim.; 4, 45-48 (1972)

74SIB/SCH
Sibbing, V.E.; Schafer, H.
"Das Dimerisierungsgleichgewicht 2TiCl3(g)=Ti2Cl6(g)"
Z.anorg.und allgem.Chem.; 410 67-74 (1974)

@ indicates a continuation line

APPENDIX II. INITIAL VALUES FOR TITANIUM CHLORIDES AND ASSOCIATED COMPOUNDS

Extracted from Selected Reference Temperature Data File for Transition Element Halides

	Standard Enthalpy of Formation and Uncertainty		Standard Entropy and Uncertainty		Reference Codes:		
	$\Delta_f H^\circ_{298}$/kcal mol^{-1}		S°_{298}/cal mol^{-1} K^{-1}		Source	Th.Fn.	Eqn.
CL1H1(G)	-22.06	0.03	44.64	0.01	2222	88	215
CL1H1(10H20)	-38.56				3000	0	163
CL2(G)	0.00	0.00	53.29	0.01	22	14	314
CL2HG2(CR)	-63.44	0.07	45.80	0.20	2222	95	135
CL2TI1(CR)	-123.20	4.00	20.88	1.00	4444	148	364
CL3TI1(CR)	-172.50	1.00	33.40	0.30	4444	151	364
CL4TI1(L)	-192.10	0.70	60.30	0.02	2222	154	251
CL4TI1(G)	-182.40	0.70	84.40	0.10	2222	155	409
H1I1(G)	6.30	0.19	49.35	0.01	2222	90	215
H2(G)	0.00	0.00	31.21	0.01	22	91	167
H2O1(G)	-57.80	0.01	45.11	0.01	2222	92	150
HG1(L)	0.00	0.00	18.14	0.03	22	93	135
I2(CR)	0.00	0.00	27.76	0.02	22	96	215
O2TI1(CR)	-225.67	0.20	12.03	0.05	2222	145	239
TI1(CR)	0.00	0.00	7.31	0.02	22	144	407

References Codes:

Column headed "Source":

Digits refer respectively to preceding four columns and are as follows:

0 No value assigned
1 Calculated from molecular parameters in Thermal Functions File
2 "CODATA Recommended Key Values for Thermodynamics, 1977." J.Chem. Thermodynamics 10, 903 (1978). "Tentative Set of Key Values for Thermodynamics. Part VII", CODATA Special Report No. 7 (1978)
3 Wagman, D.D., Evans, W.H., et al; "The NBS Tables of Chemical Thermodynamic Properties", J.Phys.Chem.Ref.Data, 11 (1982), Supplement No.2
4 Chase, M.W. (Editor) "JANAF Thermochemical Data"; The Dow Chemical Company, Midland, Michigan, USA (1979).

Column headed "Th.Fn." contains pointers to the locations of thermal functions in the Tabulated Thermal Functions File; column headed "Eqn" contains pointers to the most recent entry for the compound in equations in the Experimental Data File.

APPENDIX III. BASIC THERMAL FUNCTION DATA FOR TITANIUM CHLORIDES AND ASSOCIATED COMPOUNDS

Extracted from Thermal Function Data File for Transition Element Halides

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Key

For each species the first line gives the formula of the compound, and a code for the type of data. Additional data following the type code is described below as line 1.

For all types of data, the reference code and additional information are given in the last line of the entry.
@ at the beginning of a line indicates that it is a continuation of the previous line.
A key to the reference codes is given at the end of the appendix.

Temperatures in Kelvin, tabulated values in calories, spectroscopic energies and vibrational frequencies in cm^{-1}.

Data Type Codes

tab: tabulated values taken from references indicated. (For economy of space tabulated values copied directly from the JANAF Tables have not been listed here).

atp (atomic parameters):
line 1: Number of electronic energy levels
line 2: State, degeneracy, energy

dip (diatomic molecule parameters):
line 1: Symmetry number, number of electronic energy levels, number of energy levels with parameters, number of parameters
line 2 - State, degeneracy, energy, w_e, w_ex_e, B_e, α_e and D_e.

lpp (linear polyatomic parameters):
line 1: Symmetry number
line 2: Degeneracy, electronic energy
line 3: Degeneracy, vibrational frequency
line 4: B_e

plp (non-linear polyatomic parameters):
line 1: Symmetry number
line 2: Degeneracy, electronic energy
line 3: Degeneracy, vibrational frequency
line 4: Moment of inertia

```
Cl2(g) dip 2 4 4 7
1Sig+g 1 0 559.72 2.675 0.24399 0.00149 1.86E-7
3Pi2u  2 [17160] [280] 5.3 0.16256 0.00212 2.365E-7
3Pi1u  2 [17440] [265] 5.3 0.16256 0.00212 2.365E-7
3Pi0u  2  17809  259.5 5.3 0.16256 0.00212 2.365E-7
79HUB/HER. re=1.9879A

HCl(g) dip 1 1 1 7
1Sig+  1 0 2990.9463 52.8186 10.593416 0.30718 5.3194E-4
79HUB/HER. re = 1.274552

H2(g) dip 2 1 1 7
1Sig+g  1 0 4401.213 121.336 60.853 3.062 4.71E-2
79HUB/HER. re=0.74144A

H2O(g) plp 2
1 0
1 3651.1 1 1594.7 1 3755.9
5.7658E-120
79JANAF. I from 71JANAF

Hg(l) tab
61JANAF

Hg2Cl2(cr) tab
61JANAF

I2(cr) tab
61JANAF

Ti(cr) tab     Reference State
79JANAF
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APPENDIX III. BASIC THERMAL FUNCTION DATA FOR TITANIUM CHLORIDES AND ASSOCIATED COMPOUNDS --Continued

Extracted from Thermal Function Data File for Transition Element Halides

```
TiO2(cr) tab    Rutile
73JANAF

TiCl2(cr) tab
68JANAF

TiCl2(cr) tab CSOH
Ts [1581.5]
  0     0.000    0.000    -3.179
 100    9.029    6.206    -2.794
 200   14.700   14.602    -1.549
 298.15   16.690   20.876     0.000
 300   16.706   20.979     0.031
 400   17.541   25.902     1.744
 485   22.028   30.770     3.823
 500   22.280   31.444     4.155
 600   23.958   35.655     6.467
 700   25.636   39.474     8.947
 800   27.316   43.007    11.594
 900   28.992   46.321    14.410
 931   29.512   47.311    15.317
 68JANAF up to 400 K, above 485 K calculated from
 @69VAS/POD Cp=13.89+(16.78E-3)T, 485-931 K

TiCl3(cr) tab
68JANAF

TiCl3(cr) tab CSOH
Tt 220.1 Ts [1104.1]
  0     0.000    0.000    -5.000
 100   13.011   10.600    -4.384
 200   24.361   22.826    -2.562
 298.15   23.222   33.401     0.000
 300   23.230   33.545     0.043
 400   23.652   40.286     2.387
 500   24.038   45.606     4.772
 585   27.114   50.720     7.412
 600   27.247   51.408     7.819
 700   28.137   55.675    10.588
 800   29.026   59.490    13.447
 900   29.916   62.961    16.394
 980   30.627   65.538    18.815
 68JANAF up to 500 K, above 585 K calculated from 69VAS/POD
 @Cp=21.91+(8.895E-3)T, 585-980K

TiCl4(l) tab
67JANAF

TiCl4(g) plp 12
1 0
1 388 2 111 3 498.5 3 131
4.2092E-112
67JANAF. re=2.185A, bond angle Cl-Ti-Cl=109 28
@72CLA/HUN fundamental frequencies: 389,114,498,136 at 65C,
@re=2.17A, B=0.03787


Reference Codes
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JANAF       Chase, M.W. (Editor) "JANAF Thermochemical Data"; The Dow
            Chemical Company, Midland, Michigan, USA (1979)
            (Digits preceding the code indicate the year of assessment
            of the data)
69VAS/POD   Vasil'kova, I.V.; Podzorov, B.N.; Shapkin, P.S.
            "Determination of Heat Capacity of Titanium Chlorides"
             Russ.J.Inorg.Chem.; 14, 910-912 (1969)
72CLA/HUN   Clark, R.J.H.; Hunter, B.K.; Rippon, D.M.; "Vapor-Phase
            Raman Spectra, Force Constants, and Values for Thermo-
            dynamic Functions of the Tetrachlorides, Tetrabromides,
            and Tetraiodides of Titanium, Zirconium, and Hafnium"
            Inorg.Chem.; 11, 56 (1972)
79HUB/HER   Huber, K.P., Herzberg, G.; "Molecular Spectra and Molecular
            Structure, IV. Constants of Diatomic Molecules"; Van
            Nostrand Reinhold Company, New York (1979)
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APPENDIX IV. TABULATED THERMAL FUNCTIONS
Calculated from data in Appendix III

T/K	C_p°	$S^\circ-S^\circ_{298}$	$-(G^\circ-H^\circ_{298})/T$ $-S^\circ_{298}$	$H^\circ-H^\circ_{298}$
	(cal mol^{-1} K^{-1}		)	(kcal mol^{-1})
Cl2(g)				
0.000	0.000	-53.243	-	-2.190
100.000	6.999	-8.132	6.818	-1.495
200.000	7.563	-3.129	0.723	-0.770
298.150	8.085	0.000	0.000	0.000
300.000	8.093	0.050	0.000	0.015
400.000	8.397	2.435	0.324	0.844
HCl(g)				
0.000	0.000	-44.634	-	-2.074
100.000	6.956	-7.598	6.184	-1.378
200.000	6.955	-2.777	0.636	-0.683
298.150	6.956	0.000	0.000	0.000
300.000	6.956	0.043	0.000	0.013
400.000	6.962	2.044	0.273	0.708
500.000	6.989	3.596	0.788	1.404
600.000	7.049	4.864	1.365	2.099
700.000	7.142	5.973	1.948	2.817
800.000	7.257	6.935	2.513	3.538
900.000	7.383	7.797	3.053	4.269
1000.000	7.512	8.580	3.567	5.013
1100.000	7.636	9.299	4.056	5.768
1200.000	7.752	9.964	4.521	6.531
H2(g)				
0.000	0.000	-31.175	-	-2.074
100.000	6.987	-7.598	6.184	-1.378
200.000	6.963	-2.777	0.636	-0.683
298.150	6.959	0.000	0.000	0.000
300.000	6.959	0.043	0.000	0.013
400.000	6.957	2.044	0.273	0.708
500.000	6.958	3.596	0.788	1.404
600.000	6.965	4.864	1.365	2.099
700.000	6.984	5.936	1.943	2.795
800.000	7.018	6.865	2.501	3.490
900.000	7.070	7.684	3.033	4.186
1000.000	7.136	8.416	3.535	4.881
H2O(g)				
0.000	0.000	-45.065	-	-2.372
100.000	7.949	-8.691	7.080	-1.577
200.000	7.951	-3.181	0.730	-0.782
298.150	8.002	0.000	0.000	0.000
300.000	8.004	0.050	0.000	0.015
400.000	8.162	2.371	0.316	0.822
500.000	8.393	4.217	0.917	1.650
600.000	8.656	5.770	1.600	2.502
700.000	8.932	7.125	2.294	3.381
800.000	9.219	8.336	2.975	4.289
900.000	9.512	9.439	3.633	5.225
1000.000	9.806	10.456	4.265	6.191
1100.000	10.095	11.405	4.872	7.186
1200.000	10.373	12.295	5.453	8.210
Hg(l)				
298.150	6.687	0.000	0.000	0.000
300.000	6.684	0.041	0.001	0.012
400.000	6.552	1.944	0.261	0.673
500.000	6.495	3.399	0.749	1.325
Hg2Cl2(cr)				
0.000	0.000	-46.017	-	-5.611
100.000	18.940	-23.984	20.466	-4.445
200.000	22.820	-9.431	2.184	-2.323
298.150	24.371	0.000	0.000	0.000
300.000	24.390	0.151	0.001	0.045
400.000	25.340	7.301	0.969	2.533
500.000	26.130	13.043	2.829	5.107
Ti(cr)				
0.000	0.000	-7.352	-	-1.154
100.000	3.426	-5.378	4.822	-1.020
200.000	5.346	-2.278	-2.178	-0.020
298.150	6.032	0.000	0.000	0.000
300.000	6.041	0.037	0.000	0.011
400.000	6.420	1.832	0.242	0.636
500.000	6.663	3.292	0.710	1.291
600.000	6.834	4.523	1.246	1.966
700.000	6.963	5.586	1.792	2.656
800.000	7.144	6.520	2.326	3.355
900.000	7.279	7.362	2.840	4.070
1000.000	7.666	8.147	3.331	4.816
1100.000	8.206	8.902	3.803	5.609
1166.000	8.646	9.392	4.106	6.164
1166.000	6.990	10.247	4.105	7.161
1200.000	7.041	10.449	4.282	7.400
TiO2(cr)				
0.000	0.000	-12.020	-	-2.064
100.000	4.422	-9.596	9.404	-1.900
200.000	10.041	-4.657	1.118	-1.155
298.150	13.170	0.000	0.000	0.000
300.000	13.214	0.082	0.002	0.024
400.000	15.018	4.154	0.544	1.444
500.000	16.062	7.627	1.623	3.002
600.000	16.714	10.617	2.877	4.644
700.000	17.152	13.228	4.174	6.338
800.000	17.466	15.540	5.452	8.070
900.000	17.700	17.611	6.691	9.828
1000.000	17.890	19.486	7.878	11.608

APPENDIX IV. TABULATED THERMAL FUNCTIONS --Continued
Calculated from data in Appendix III

T/K	C_p°	$S^\circ-S^\circ_{298}$	$-(G^\circ-H^\circ_{298})/T$ $-S^\circ_{298}$	$H^\circ-H^\circ_{298}$
	(cal mol^{-1} K^{-1}		)	(kcal mol^{-1})
1100.000	18.040	21.199	9.013	13.405
1200.000	18.170	22.774	10.094	15.216
TiCl2(cr)				
0.000	0.000	-20.876	-	-3.179
100.000	9.029	-14.670	13.270	-2.794
200.000	14.700	-6.274	1.471	-1.549
298.150	16.690	0.000	0.000	0.000
300.000	16.706	0.103	0.000	0.031
400.000	17.541	5.026	0.666	1.744
500.000	18.280	9.021	1.949	3.536
600.000	18.732	12.394	3.416	5.387
700.000	19.184	15.316	4.913	7.282
800.000	19.636	17.907	6.378	9.223
900.000	20.088	20.246	7.790	11.210
1000.000	20.540	22.386	9.145	13.241
1100.000	20.992	24.364	10.439	15.318
1200.000	21.444	26.210	11.677	17.439
TiCl2(cr)				
0.000	0.000	-20.876	-	-3.179
100.000	9.029	-14.670	13.270	-2.794
200.000	14.700	-6.274	1.471	-1.549
298.150	16.690	0.000	0.000	0.000
300.000	16.706	0.103	0.000	0.031
400.000	17.541	5.026	0.666	1.744
485.000	22.028	9.894	2.012	3.823
500.000	22.280	10.568	2.258	4.155
600.000	23.958	14.779	4.001	6.467
700.000	25.636	18.598	5.817	8.947
800.000	27.316	22.131	7.639	11.594
900.000	28.992	25.445	9.434	14.410
931.000	29.512	26.435	9.983	15.317
TiCl3(cr)				
0.000	0.000	-33.401	-	-5.000
100.000	13.011	-22.801	21.039	-4.384
200.000	24.361	-10.575	2.235	-2.562
298.150	23.222	0.000	0.000	0.000
300.000	23.230	0.144	0.001	0.043
400.000	23.652	6.885	0.917	2.387
500.000	24.038	12.205	2.661	4.772
600.000	24.390	16.619	4.629	7.194
700.000	24.677	20.401	6.620	9.647
800.000	24.958	23.714	8.553	12.129
900.000	25.235	26.670	10.404	14.639
1000.000	25.503	29.343	12.167	17.176
TiCl3(cr)				
0.000	0.000	-33.401	-	-5.000
100.000	13.011	-22.801	21.039	-4.384
200.000	24.361	-10.575	2.235	-2.562
298.150	23.222	0.000	0.000	0.000
300.000	23.230	0.144	0.001	0.043
400.000	23.652	6.885	0.917	2.387
500.000	24.038	12.205	2.661	4.772
585.000	27.114	17.319	4.649	7.412
600.000	27.247	18.007	4.975	7.819
700.000	28.137	22.274	7.148	10.588
800.000	29.026	26.089	9.280	13.447
900.000	29.916	29.560	11.344	16.394
980.000	30.627	32.137	12.938	18.815
TiCl4(l)				
200.000	34.584	-13.828	3.172	-3.400
298.150	34.704	0.000	0.000	0.000
300.000	34.709	0.215	0.002	0.064
400.000	34.936	10.231	1.363	3.547
500.000	35.153	18.050	3.948	7.051
600.000	35.370	24.479	6.851	10.577
700.000	35.586	29.947	9.768	14.125
800.000	35.803	34.713	12.596	17.694
900.000	36.020	38.943	15.293	21.285
1000.000	36.237	42.749	17.851	24.898
TiCl4(g)				
0.000	0.000	-84.488	-	-5.142
100.000	15.984	-21.314	10.592	-3.991
200.000	20.541	-8.684	2.027	-2.142
298.150	22.833	0.000	0.000	0.000
300.000	22.862	0.141	0.000	0.042
400.000	23.998	6.892	0.913	2.392
500.000	24.604	12.319	2.670	4.825
600.000	24.957	16.838	4.665	7.304
700.000	25.179	20.704	6.687	9.812
800.000	25.327	24.076	8.654	12.338
900.000	25.431	27.066	10.537	14.876
1000.000	25.506	29.749	12.326	17.423
1100.000	25.561	32.183	14.022	19.976
1200.000	25.604	34.409	15.630	22.535
1300.000	25.638	36.460	17.154	25.097
1400.000	25.664	38.361	18.602	27.662
1500.000	25.686	40.132	19.979	30.229