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NATIONAL BUREAU OF STANDARDS REPORT

6645

PRELIMINARY REPORT ON THE THERMODYNAMIC PROPERTIES OF SELECTED LIGHT-ELEMENT COMPOUNDS

(SUPPLEMENT TO NBS REPORTS 6297 AND 6484)

1 January 1960

(Amended 1 April 1960)

NBS

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

THE NATIONAL BUREAU OF STANDARDS

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NATIONAL BUREAU OF STANDARDS REPORT

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PRELIMINARY REPORT
ON THE THERMODYNAMIC PROPERTIES OF SELECTED LIGHT-ELEMENT COMPOUNDS
(SUPPLEMENT TO NBS REPORTS 6297 AND 6484)

Third Technical Summary Report
to the Advanced Research Projects Agency
on the Thermodynamic Properties
of Light-Element Compounds

Reference: ARPA Order No. 20-60

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U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

PREFACE

The National Bureau of Standards has undertaken an experimental and theoretical investigation of the thermodynamic properties of light-element compounds, with the goal of securing the basic information needed to determine accurately the energies and equilibrium proportions of these substances in the solid, liquid, and gaseous states up to 6,000°K and 100 atmospheres pressure. The light elements thus far included are Li, Be, Mg, Al, H, F, Cl, O, N, and C, with, in addition, some recent attention to Ti and its nitrides and carbides. (Boron compounds have been intensively studied along similar lines in earlier NBS programs). There are research groups in calorimetry (low-temperature, high-temperature, fluorine-combustion, and other heat-of-reaction), in vaporization equilibria (of refractories, halides, and hydride decomposition), and in gas properties (high-temperature high-pressure transient phenomena, molecular spectra, and statistical thermodynamics).

The present report supplements the two (unpublished) reports issued to the sponsoring agency on 1 January 1959 and 1 July 1959. The various experimental groups at the Bureau are currently in advanced stages of building, testing, and developing new apparatus and techniques, and only two have thus far obtained complete sets of data, which are presented and discussed in succeeding pages. In addition, a comprehensive and up-to-date literature survey was made on the reported thermodynamic properties of the nitrides and carbides of the light-element metals enumerated above. A large part of the present report is devoted to presenting and discussing the data found, but the task of systematically examining these for interconsistency is incomplete. It is well known that there are many gaps and inconsistencies in our knowledge of these nitrides and carbides. Pending future accurate measurements, thermal properties have been estimated and extrapolated where necessary in order to obtain provisional tables of their condensed-state thermodynamic functions. It appears that in many cases such tables can be used to predict their high-temperature decomposition with considerably less uncertainty than by use of the existing direct measurements.

The present report corrects a few inadvertent errors in our earlier reports, and discusses some new data which have recently appeared. We should appreciate our attention being called to other errors and to significant sources of information which we have overlooked.

Chas W Beckett

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ABSTRACT

Two earlier NBS Reports on light-element thermodynamics (1 January 1959 and 1 July 1959) are hereby supplemented.

The results of a comprehensive literature survey on the thermodynamic properties of the known nitrides and carbides of Li, Be, Mg, Al, and Ti are presented. Calorimetric heats of formation are examined critically. In the numerous cases where heat-content data are meager or totally lacking, entropies and high-temperature heat capacities were estimated as a basis for provisional tables of high-temperature thermodynamic functions presented for eleven solid (and liquid) nitrides and carbides. Tables are given also for graphite (revised), solid and liquid titanium, and nitrogen gas. These nitrides and carbides decompose by vaporization predominantly to the free elements under the experimental conditions investigated. The reported decomposition data are summarized, and the initial results of examining them for thermodynamic consistency with the thermal data are presented.

New experimental data from the Bureau on the preparation and thermodynamic properties of five other light-element compounds are given. Beryllium hydride was prepared by a slight modification of a procedure reported in the literature. New precise heats of formation are given for the perchlorates of ammonium, lithium, and potassium. Preliminary data are given for the vapor pressure and degree of dissociation of the compound $AlH_3 \cdot 2N(CH_3)_3$. Some results from other institutions are discussed, on (a) reactions of ammonia with the hydrides of aluminum and beryllium, and (b) very recently determined entropies and heats of formation of a few light elements and their compounds. A few errors in the two earlier NBS Reports are corrected.

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PART A

NITRIDES AND CARBIDES OF LIGHT ELEMENTS

Chapter A1

INTRODUCTION

Many metals combine with nitrogen or carbon at moderately high temperatures to form stable solids. Although these compounds have binding energies comparable to those of the corresponding oxides and fluorides, the heats and free energies of formation of the nitrides and carbides are much less. These large differences may be explained by comparing the binding energies of the elements in their standard states: C, 170; N, 113; O, 59; F, 18 kcal. per gm. atom. Hence, the useful energy released in forming a unit amount of compound is less for the carbide or nitride than for the oxide or fluoride.

The volume and molecular weight of the gaseous products also enter into the evaluation. Optimum conditions occur when a relatively large amount of hydrogen is formed. In a hydrogen-rich environment, nitrides and carbides may occur as constituents in many cases, hence their thermodynamic properties are of practical interest.

This brief discussion may be terminated with a list of the areas in which there are the most serious deficiencies in the existing thermodynamic data of the light-element nitrides and carbides:

(1) Lack of high-purity samples. (Zone melting and other single-crystal purification methods should be considered.)

(2) Lack of heat-content data. (This is equivalent to a lack of entropies, specific heats, and heats of fusion.)

(3) Thermodynamic inconsistency in many cases between directly measured equilibrium constants and calorimetrically determined heats of formation.

(4) Limitations of techniques now available for obtaining thermodynamic data in the region of higher temperatures and pressures.

Chapter A2

THE HEATS OF FORMATION OF CARBIDES AND NITRIDES OF ALUMINUM, BERYLLIUM, MAGNESIUM, LITHIUM AND TITANIUM.

George T. Armstrong and L. A. Krieger

The heats of formation reported in NBS Report 6484 [1] have been repeated here, with minor modifications in the text, based on newly reported data with the exception of $Al_2C_2(g)$ for which an error of interpretation was discovered and corrected. A reconsideration of the inconsistencies between the direct heat measurements and the high temperature vaporization data of Al_4C_3 and AlN appears desirable. The uncertainty in the heat of formation of $BeC_2(g)$ is not given, because the value derivable from the only available experimental data merely provides a lower limit.

The data on heats of formation of titanium nitride and carbide have been examined critically and values have been proposed. The heats of formation as found by combustion experiments on these two compounds are dependent upon the heat of formation of TiO_2 (rutile). The pertinent data on the latter compound have, therefore, also been examined critically and a value selected for its heat of formation.

1. AlN(c) $\Delta Hf^\circ_{298} = -76.5$ kcal/mole.

The heat of formation by nitriding aluminum directly in a bomb calorimeter was determined by Neugebauer and Margrave [2], whose value is -76.5 kcal/mole. Other determinations have been made by Neumann, Kroger, and Haebler [3], who found -57.4 kcal/mole, using the same method; by Fichter and Jenny [4], who found -71.5 kcal/mole from the heat of combustion of AlN; by Schissel and Williams [5] who found -63 kcal/mole in a mass spectrometric study of the vaporization from a Knudson cell. Prescott and Hincke [6] studied the equilibrium between AlN and C. The heat of formation of AlN calculated from their study is dependent upon the heat of formation of Al_4C_3. Apin, Lebedev and Nefedova[7] have reported $\Delta Hf = -57.6$ kcal/mole based on a method of exploding lead azide mixed with aluminum. A reexamination of the above data is required in order to establish possible reasons for the wide variations found by various workers.

2. AlC (g) $\Delta Hf^\circ_0 = 209$ kcal/mole.

Zeeman [8] measured spectroscopically 1.6 ± 0.2 e.v. for the dissociation energy of a molecule which they thought to be AlC. The species has not been otherwise observed.

3. $Al_2C_2(g)$ $\Delta Hf^\circ_{298} = 121 \pm 10$ kcal/mole.

Chupka, Berkowitz, Giese and Inghram [10] determined that Al_2C_2 appears as a vapor over Al_4C_3 to the extent of about 0.001 of the amount of Al(g) at about 2100°K. Using estimated molecular constants, they derived the heat of formation from Al(g) and C(c), and the heat of dissociation to metal and $C_2(g)$.

4. $Al_4C_3(c)$ $\Delta Hf^\circ_{298} = -48.6 \pm 10$ kcal/mole.

The heat of combustion of Al_4C_3 has been determined by Berthelot [11] , by Wohler and Hober [12] , by Meichsner and Roth [13] , and by Kameyama and Yoshida [14] , using not very pure material. The measurements of Meichsner and Roth appear to have been done most carefully, using the purest material, and have been adopted for this work. Their calculations have been redone, using -400.4 kcal/mole for the heat of formation of Al_2O_3, to obtain the value listed above. This assumes that α-Al_2O_3 was the principal aluminum oxide formed. Meichsner and Roth made no examination of the crystalline form of the product Al_2O_3. However, Foster, Long, and Hunter [15] suggest that a delta-like phase of Al_2O_3 is stabilized in the presence of a carbonaceous promoter. The formation of such a phase, if it formed a principal part of the combustion product, could cause a rather large error in the heat of formation of Al_4C_3. A study of the vapor pressure of Al(g) over $Al_4C_3(c)$ by Meschi and Searcy [9] led them to a value of -51 kcal/mole for ΔHf°_{298} [$Al_4C_3(c)$] , in reasonably good agreement with the above value. A number of other values have been reported for the heat of formation of Al_4C_3, based on equilibrium gas pressures in the systems Al_4C_3-N_2 and Al_2O_3-C. Kelley [16] reviewed the work of Prescott and Hincke [17] , and of Brunner [18] , and calculated a value, which when adjusted to more recent values for the heat of formation of Al_2O_3 gives -117.1 kcal/mole for the heat of formation of Al_4C_3. More recent work has been reported informally by Hilmer and colleagues [19] and by Gross [20] . Because of the difficulty of the measurements, the results obtained in the equilibrium studies have not been used here. A reexamination of the various data reported above is justified in order to establish the reasons for the inconsistencies.

5. $Be_3N_2(c)$ $\Delta Hf^\circ_{298} = -132. \pm 3$ kcal/mole.

Neumann, Kroger, and Haebler [3] measured the heat of formation of Be_3N_2 to be -133.4 ± 0.6 kcal/mole by nitriding Be (99.5 percent pure) directly in a high temperature bomb calorimeter. Neumann, Kroger, and Kunz [21] measured the heat of combustion of Be_3N_2 (91.2 percent pure). Their value, corrected for impurities and using -143.1 kcal/mole for the heat of formation of BeO gives -129.0 kcal/mole for the heat of formation of Be_3N_2. Because of the strong dependence of the combustion experiment upon the value accepted for the heat of formation of BeO, greater weight is given to the nitriding experiment. See also Apin, Lebedev and Nefedova [7] who report -135 kcal/mole.

6. $BeC_2(g)$ $\Delta Hf^\circ_0 > 134.3$ kcal/mole.

Chupka, Berkowitz, Giese, and Inghram [10] studied the vaporization of BeC_2. No vapor species was observed at temperatures up to 1900°K. The entropy and free energy function of $BeC_2(g)$ were estimated by analogy to BeO in order to estimate the minimum heat of formation. The actual heat of formation may be considerably greater.

7. $Be_2C(c)$ $\Delta Hf^\circ_{298} = -22.2 \pm 5$ kcal/mole.

Pollock [22] measured the vapor pressure of beryllium over beryllium carbide by an effusion process. From his equilibrium vapor pressure and an estimated correction for ΔCp we calculate -22.2 ± 5 for the heat of formation of $Be_2C(c)$.

8. $Mg_3N_2(c)$ $\Delta Hf^\circ_{298} = -110.2 \pm 1$ kcal/mole.

Mitchell [23] in 1949 dissolved Mg_3N_2 in a 1N HCl solution and found -287.9 kcal/mole for the heat of solution which leads to -110.2 kcal/mole for the heat of formation of Mg_3N_2. Other determinations have been -113.9 kcal/mole by Neumann, Kroger, and Kunz [21] , from the heat of solution in HCl, -114.9 kcal/mole by Brunner [18] from the heat of solution of Mg_3N_2 in water, with the evolution of ammonia, and a less reliable value, -134.3 kcal/mole found by Matignon [24] from the solution of Mg_3N_2 in aqueous sulfuric acid . Neumann, Kroger, and Haebler [3] by nitriding Mg directly in a high temperature bomb calorimeter found the heat of formation to be -116 ± 2 kcal/mole. Apin, Lebedev and Nefedova [7] report -110.7 kcal/mole.

9. $MgC_2(c)$ $\Delta Hf^\circ_{298} = 21. \pm 5$ kcal/mole.

Irmann [25] determined the heat of solution of MgC_2 (56.8 - 66.8% pure) and Mg_2C_3 (67 - 82% pure) in aqueous HCl. See also Chapter A5 for a relevant discussion of decomposition temperatures. The decomposition data reported are not inconsistent with the heats of formation reported.

10. $Mg_2C_3(c)$ $\Delta Hf^\circ_{298} = 19. \pm 8$ kcal/mole.

See $MgC_2(c)$.

11. $Li_3N(c)$ $\Delta Hf^\circ_{298} = -47.5 \pm 2$ kcal/mole.

Guntz [26] measured the heat of solution of Li_3N in water, giving a solution of lithium hydroxide and aqueous ammonia. The heat of solution, -131.1 kcal/mole, leads to a heat of formation for Li_3N of -47.8 kcal/mole. Neumann, Kroger, and Haebler [3] determined the heat of formation of Li_3N by direct nitridation of lithium in a high temperature bomb calorimeter. The result of this measurement is -47.166 kcal/mole.

12. $Li_2C_2(c)$ $\Delta Hf^\circ_{298} = -14.2 \pm 2$ kcal/mole.

This value, reported in NBS Circular 500, is based on a single study of the heat of reaction of lithium carbide with water, by Guntz [27], but is probably not in serious error, because the carbide, an acetylide, is well defined.

13. TiO_2 (rutile) $\Delta Hf^\circ_{298} = -225.5 \pm 1.0$ kcal/mole.

Studies of the heat of formation of TiO_2 (rutile) have been reported in kilocalories per mole, as follows: Mixter (-215.6) [28]; Weiss and Kaiser (-97.772) [29]; Mixter (-218.4) [30, 31]; Sieverts and Gotta (-220.7 ± 0.3, corrected to constant pressure) [32]; Roth and Becker (-218.7 ± 0.3) [33, 34]; Neumann, Kroger and Kunz (-225.3 ± 0.3) [21]; Roth and Wolf (-219 ± 1.5) [35], Humphrey (-225.5 ± 0.23) [36].

All except the first value by Mixter were determined by combustion of the metal in an oxygen bomb. The attempted direct combustion by Weiss and Kaiser seems to have been subject to serious error. The remaining data cluster in two groups, around -218 and -225 kcal/mole. All researchers except Humphrey were troubled by incomplete combustion. The only other workers achieving nearly complete combustion were Neumann, Kroger and Kunz, who had completeness ranging from 94 to 98.9%. Roth and Wolf observed a heat of reaction of (-224.3 ± 2.3 kcal/mole) based upon the absorbed amount of oxygen; however, they made a correction for hypothesized amounts of lower oxides. In view of the agreement in the two values resulting from experiments with most nearly complete combustion the best value for the heat of formation of TiO_2 is ΔHf°_{298} $[TiO_2(c)] = -225.5 \pm 1.0$ kcal/mole. This value is supported by vaporization studies on TiC and TiN, which see.

14. **TiC(c)** **$\Delta Hf^\circ_{298} = -43.8 \pm 2.0$ kcal/mole.**

Humphrey [36] determined the heat of combustion of TiC to CO_2 and TiO_2 (rutile) to be $\Delta H^\circ_{298} = -275.7_2 \pm 0.3$ kcal/mole. Combining this with the selected value for the heat of formation of TiO_2 and that from [42] for CO_2, we obtain ΔHf°_{298} $[TiC] = -43.8$ kcal/mole. A relatively higher uncertainty is assigned in spite of the good internal consistency of Humphrey's work because of the lack of other direct heat measurements. Chupka, Berkowitz, Giese and Inghram [10] determined an approximate vapor pressure of Ti(g) over TiC(c) at about 2500°K. Using their observed pressure as the equilibrium constant for the reaction, $TiC(c) \longrightarrow Ti(g) + C(c)$, at 2500°K we calculate ΔHf°_{298} $[TiC] = -45.9$ kcal/mole. For this calculation we use thermal functions for C and TiC found in Appendix II of this report. The free-energy function for Ti(g) is obtained from Rossini, Cowie, Ellison, and Browne [37]. The heat of sublimation of titanium is taken from Edwards, Johnston, and Ditmars [38]. The value derived for the heat of formation of TiC from the work of Chupka et al, lends support to the value selected for the heat of formation of TiO_2. A lower value, in the range -218 kcal/mole, supported by several early investigations would require unreasonably large errors in the work of Chupka et al.

15. **TiN(c)** **$\Delta Hf^\circ_{298} = -80.5 \pm 1.5$ kcal/mole.**

Humphrey [34] determined the heat of combustion, ΔH°_{298}, of TiN(c) to be -145.05 ± 0.14 kcal/mole as the average of six measurements. Neumann, Kroger and Kung [21] found $\Delta H^\circ_{298} = -144.98 \pm 0.11$ kcal/mole as the result of two measurements of the heat of combustion. Taking the average and using the selected value, ΔHf°_{298} [TiO_2] (c)] = -225.5 ± 1.0 kcal/mole, we obtain ΔHf°_{298} [TiN] = -80.5 kcal/mole.

The vaporization process of TiN was studied in the range 1987-2241°K by Hoch, Dingledy and Johnston [39], who derived for the reaction, $TiN(c) \rightarrow Ti(g) + 1/2\ N_2(g)$, ΔH°_0 = 191.20 ± 0.96 kcal/mole. For the calculation from the vapor pressure data they used free-energy functions of nitrogen from Johnston and Davis [40], and for Ti and TiN values were obtained from Skinner, Johnston and Beckett [41]. These values do not differ appreciably from the values listed in this report. Use of ΔHf°_0 [Ti(g)] = 112.763 [38] for the heat of sublimation of titanium leads to ΔHf°_0[TiN(c)] = -78.5 kcal/mole and to ΔHf°_{298} [TiN(c)] = -79.4, to which we assign an uncertainty of ± 1.4 kcal/mole. The value thus found is within the experimental uncertainties of the value selected above on the basis of heats of combustion. The good agreement here is an additional indication of the probable correctness of the value selected for the heat of formation of TiO_2.

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Chapter A 3

ENTROPIES OF SOME CARBIDES AND NITRIDES AND TITANIUM METAL AT 298.15°K

George T. Furukawa, Martin L. Reilly, and Jeanette Henning Piccirelli

The low-temperature heat-capacity phase of literature survey and data analysis described in the preliminary report (National Bureau of Standards Report No. 6484, July 1, 1959) was concerned with available experimental data on lithium, beryllium, magnesium, aluminum, and their compounds of hydrogen, oxygen, fluorine, and chlorine. In the present report the survey of low-temperature heat-capacity data on the carbides and nitrides of lithium, beryllium, boron, sodium, magnesium, aluminum, silicon, and titanium and titanium metal is described. The survey has revealed that experimental low-temperature data are available on very few of these compounds. Above room temperature a little more data are available in the form of relative enthalpy measurements. Although there is a lack of low-temperature heat-capacity data on these substances, there are available a number of estimates of the entropy at 298.15°K. These estimates of the entropy are summarized in this report and, wherever available, experimental data are described. The data on titanium metal, titanium carbide, and titanium nitride have been re-analyzed and a table of thermodynamic properties calculated.

Almost all of the estimates of the entropy at 298.15°K described in this report were taken from the compilations given in the Bureau of Mines Bulletin 407 (K. K. Kelley, contributions to the Data on Theoretical Metallurgy. VIII. The Thermodynamic Properties of Metal Carbides and Nitrides), in The Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics (L. Brewer, L. A. Bromley, P. W. Gilles, and N. L. Lofgren, Paper No. 4, National Nuclear Energy Series, Division IV, Volume 19B, edited by L. L. Quill, McGraw-Hill Book Company, Inc., New York, 1950), in the National Bureau of Standards Circular 500 (F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe; Selected Values of Chemical Thermodynamic Properties, February, 1952), in Thermodynamic Properties of the Carbides (O. H. Krikorian, High Temperature Studies, University of California, Radiation Laboratory, Berkeley, California, UCRL-2888, April, 1955), or in Metallurgical Thermochemistry (O. Kubaschewski and E. Ll. Evans, Pergamon Press, Ltd., London, 1958, Third edition).

The values of S°_{298}[a] are given in Bureau of Mines Bulletin 407, in NBS Circular 500, and in Metallurgical Thermodynamics by Kubaschewski and Evans, while values of ΔS°_{298} are given in the compilations by Brewer, et al. and by Krikorian. The values of ΔS°_{298} were converted to S°_{298} for comparison. Each substance is discussed separately, first the carbides and then the nitrides in the ascending order of the atomic number of the more electro-positive elemental constituent. Wherever experimental data are available, the reference and the range of the measurements are given. The numbers in the brackets indicate literature references and those in parentheses the range of measurements. A table of entropy values considered best has been assembled.

1. Carbides

Lithium Carbide (Acetylide), Li_2C_2, 37.902

No low-temperature heat-capacity data have been found. Krikorian [18] lists $\Delta S^\circ_{298} = -1.3 \pm 1.0$ e.u. per equivalent carbon. This leads to $S^\circ_{298} = 14 \pm 1$ e.u. for Li_2C_2. This value was accepted.

Beryllium Carbide, Be_2C, 30.037

No low-temperature heat-capacity data have been found. Krikorian [18] lists $\Delta S^\circ_{298} = -2.0 \pm 1.0$ per equivalent carbon which leads to $S^\circ_{298} = 4 \pm 1$ e.u. for Be_2C. This value was accepted.

Boron Carbide, B_4C, 55.291

Kelley [14] determined the heat capacity of a sample containing 96 per cent B_4C and 4 per cent included graphite from about 50° to 300°K. King [16] measured the enthalpy of the same sample relative to 298°K up to 1726°K. Furukawa and Reilly [7] recently determined the heat capacity in the range 15° to 380°K of a sample that analyzed 99.2 per cent B and C and 4.12 B/C ratio. X-ray analysis showed, however, strong graphite lines. No estimate of the free graphite content has been obtainable. Assuming 100 per cent pure, Furukawa and Reilly [7] obtained 6.49 cal/deg mole for the entropy of B_4C. Kelley [14] reported 6.47 ±0.03 cal/deg mole after correcting for the graphite in his sample. NBS Circular 500 [23] lists 6.47 e.u. The value 6.47 ±0.03 e.u. is recommended.

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[a] The entropy at 298.15°K will be designated hereinafter as S°_{298} for simplicity. The uncertainty in the values of entropy given is much larger than the contribution from the temperature difference of 0.15°K. The entropy of formation at 298.15°K will be designated similarly as ΔS°_{298}. The unit cal/deg mole will be given as e.u.

Sodium Carbide (Acetylide), Na_2C_2, 70.016

No low-temperature heat-capacity data have been found. Krikorian [18] gives $\Delta S^\circ_{298} = -2.3 \pm 1.5$ e.u. per equivalent carbon. This gives $S^\circ_{298} = 23 \pm 3$ e.u. for Na_2C_2. Brewer et al. [2] list $\Delta S^\circ_{298} = -5.2$ e.u. per equivalent carbon, which yields $S_{298} = 17$ e.u. The value 23 ±3 e.u. was accepted.

Magnesium Carbide (Methyl Acetylide), Mg_2C_3, 84.673

Krikorian [18] lists $\Delta S^\circ_{298} = 1.5 \pm 1.0$ per equivalent of carbon. This yields $S^\circ_{298} = 24 \pm 3$ e.u. for Mg_2C_3. This value was accepted.

Magnesium Carbide (Acetylide), MgC_2, 48.342

Krikorian [18] lists $\Delta S^\circ_{298} = 1.0 \pm 1.0$ e.u. per equivalent carbon. This gives $S^\circ_{298} = 13 \pm 2$ e.u. for MgC_2. Kubaschewski and Evans [19] list $S^\circ_{298} = 14.0 \pm 2.5$ e.u. for MgC_2. The value 13 ±2 e.u. was accepted.

Aluminum Carbide, Al_4C_3, 143.953

No low-temperature heat-capacity data have been found. Kelley [12] has calculated $S^\circ_{298} = 26.3$ e.u. for Al_4C_3 from equilibrium data for the reaction:

$$2Al_2O_3\,(c) + 9C_{(c)} = Al_4C_3\,(c) + 6CO_{(g)},$$

obtained by Brunner [3]. Kelley [12] also estimated $S^\circ_{298} = 25$ e.u. Brewer et al. [2] give $\Delta S^\circ_{298} = -2.0$ e.u. for $1/3\ Al_4C_3$. This yields $S^\circ_{298} = 25.4$ e.u. NBS Circular 500 [23] lists 25 e.u. Krikorian [18] gives $\Delta S^\circ_{298} = -2.0 \pm 1.0$ e.u. for an equivalent carbon, which yields $S^\circ_{298} = 25 \pm 3$ e.u. Kubaschewski and Evans [19] list $S^\circ_{298} = 31.3 \pm 3.0$ e.u. The value 25 ±3 e.u. was accepted.

Silicon Carbide, SiC, 40.101

Measurements of the heat capacity have been reported by Russell [24] (83° to 318°K), Nernst and Schwers [22] (22° to 97°K), Günther [22] (27° to 74°K), Kelley [14] (53° to 298°K), and Humphrey, Todd, Coughlin, and King [10] (53° to 296°K). Kelley [14] investigated a light-green and semi-transparent sample of the hexagonal crystal modification reported to contain 99 per cent SiC and 0.6 per cent SiO_2. The value of $S^\circ_{298} = 3.95$ e.u. was obtained. Humphrey et al. [10] investigated both hexagonal (type II) and cubic samples of SiC and obtained $S^\circ_{298} = 3.94 \pm 0.02$ and 3.97 ± 0.02 e.u., respectively. The hexagonal (type II) sample contained 69.84 per cent silicon, 29.89 per cent carbon, 0.18 per cent iron, 0.06 per cent aluminum, and less than 0.01 per cent calcium. It was estimated to be 99.73 per cent hexagonal (type II) silicon carbide. The information the investigators had on the cubic SiC gave 0.34 per cent free carbon, 0.17 per cent SiO_2, 0.06 per cent aluminum, 0.013 per cent free silicon, 0.004 per cent iron, and less than 1 per cent hexagonal (type II) SiC.

The values of ΔS°_{298} given by Brewer et al. [2] and by Krikorian [18] are compatible with $S^\circ_{298} = 3.95$ e.u. Kubaschewski and Evans [19] list $S^\circ_{298} = 3.95$ e.u. with reference to Kelley [14]. NBS Circular 500 [23] lists 3.935 e.u. The value $S^\circ_{298} = 3.95 \pm 0.03$ e.u. is recommended since it is the value that has been generally used and is about mid-way between practically the same S°_{298} values obtained by Humphrey, et al. [10] for the hexagonal (type II) and cubic varieties.

Titanium Carbide, TiC, 59.911

Kelley [15] (55° to 295°K) determined the heat capacity of TiC of 96.08 per cent purity prepared from rutile of 99 per cent purity and petroleum coke by heating to temperatures as high as 3000°C. The value $S^\circ_{298} = 5.80 \pm 0.10$ e.u. was obtained on re-analysis of the data.

2. Nitrides

Lithium Nitride, Li_3N, 34.828

No low-temperature heat-capacity data have been found. Kelley [12] estimated $\Delta S^\circ_{298} = -34.0$ e.u. for the reaction:

$$3\ Li + 1/2\ N_2 = Li_3N\ ,$$

which leads to $S^\circ_{298} = 9$ e.u. Brewer et al. [2] give $\Delta S^\circ_{298} = -34.2$ e.u., obtained from Kelley's value for S°_{298}. The value 9 ±2 e.u. was accepted.

Beryllium Nitride, Be_3N_2, 55.055

No low-temperature heat-capacity data have been found. Kelley [12] estimated $S^\circ_{298} = 12$ e.u. Brewer et al. [2] give $\Delta S^\circ_{298} = -20.3$ e.u. per equivalent nitrogen, obtained from Kelley's value for S°_{298}. The value 12 ±2 e.u. was accepted.

Boron Nitride, BN, 24.828

Measurements of the heat capacity of BN have been made by Magnus and Danz [20] (22° to 900°C), Dworkin, Sasmor, and Van Artsdalen [5], (18° to 300°K), and Westrum [26] (5° to 300°K). The sample investigated by Dworkin et al. [5] contained 1.5 per cent iron as Fe_3O_4. After correcting for iron they reported $S^\circ_{298} = 3.67$ e.u. Westrum [26] recently investigated a purer sample of BN and obtained $S^\circ_{298} = 3.54$ e.u. Brewer et al. [2] lists $\Delta S^\circ_{298} = -12.9$ which leads to $S^\circ_{298} = 11$ e.u. Kubaschewski and Evans [19] list $S^\circ_{298} = 3.67$ e.u., probably obtained from Dworkin et al. The value 3.54 ±0.02 e.u. was accepted.

Sodium Nitride, Na_3N, 82.999

No low-temperature heat-capacity data have been found. The value $S^\circ_{298} = 24 \pm 3$ e.u. was estimated by analogy.

Magnesium Nitride, Mg_3N_2, 100.976

No low-temperature heat-capacity data have been found. Mitchell [21] reported measurements of the heat content, relative to 25°C, up to 1000°C. Mitchell estimated $S^\circ_{298} = 22.4$ e.u. Kelley [12] estimated $S^\circ_{298} = 20.9$ e.u. Kubaschewski and Evans [19] list $S^\circ_{298} = 21.0 \pm 2.0$ e.u. with reference to Kelley [12]. Brewer et al. [2] list $\Delta S^\circ_{298} = -47.2$ e.u. per equivalent nitrogen, which leads to $S^\circ_{298} = 22.0$ e.u. The value 21 ±2 e.u. was accepted.

Aluminum Nitride, AlN, 40.988

No low-temperature heat-capacity data have been found. Kelley [12] estimated $S^\circ_{298} = 5$ e.u. From the value of $\Delta S^\circ_{298} = -25.8$ e.u. given by Brewer et al. [2], $S^\circ_{298} = 4$ e.u. was calculated. NBS Circular 500 [23] lists 5 e.u. Kubaschewski and Evans [19] list $S^\circ_{298} = 5.0 \pm 1.0$ e.u. with reference to Kelley [12]. The value 5 ±1 e.u. was accepted.

Silicon Nitride, Si_3N_4, 140.302

No low-temperature heat-capacity data have been found. Kelley [12] using equilibrium data for the reaction:

$$Si_3N_{4\,(c)} = 3\,Si_{(l)} + 2\,N_{2\,(g)}\ ,$$

obtained by Hincke and Brantley [9], calculated $S^\circ_{298} = 22.8$ e.u. as compared to his estimated value of 23.8 e.u. Brewer et al. [2] give $\Delta S^\circ_{298} = -20.4$ e.u. per nitrogen which leads to $S^\circ_{298} = 23.5$ e.u. NBS Circular 500 [23] lists 22.4 e.u. Kubaschewski and Evans [19] list $S^\circ_{298} = 23.0 \pm 2.5$ e.u. with reference to Kelley [12]. A recent work by Kaiser and Thurmond [11] shows that the pressure of nitrogen over Si_3N_4 is lower than that observed by Hincke and Brantley [9]. At 1415°C, Hincke and Brantley [9] observed $p = 1$ mm Hg, while Kaiser and Thurmond [11] found $p < 5 \times 10^{-2}$ mm Hg. The value 23 ±2 e.u. was accepted.

Titanium Nitride, TiN, 61.908

Shomate [25] (52° to 296°K) measured the heat capacity of TiN prepared by passing a stream of purified nitrogen and hydrogen over titanium metal at 1400°C. Analysis indicated the sample to be at least 99.5 per cent pure, the principal impurity being Si_3N_4. Shomate's [25] data were re-analyzed[b] and a table of thermodynamic properties was obtained. The value of $S^\circ_{298} = 7.19 \pm 0.04$ e.u. obtained was accepted. This is essentially the same value as that obtained by Shomate [25].

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[b] See NBS Report 6484 for the description of the method of analysis.

3. Titanium Metal

Titanium, Ti, 47.90

Heat-capacity measurements have been reported by Kelley [15] (53° to 295°K); Estermann, Friedberg, and Goldman [6] (1.8 to 4.2°K); Kothen and Johnston [17] (15° to 305°K); Aven, Craig, Waite, and Wallace [1] (4° to 15°K); Wolcott [27] (1.2° to 20°K); and Burk, Estermann, and Friedberg [4] (20° to 200°K). Kelley's [15] titanium sample was 98.75 per cent pure, principal impurities being Si - 0.50%, Fe - 0.27%, and V - 0.15%. The sample investigated by Kothen and Johnston [17] was prepared by the iodide process (van Arkel) and was better than 99.9 per cent pure, the principal impurities being 0.0082% Mn, 0.007% Si, 0.0066% Al, and a total of 0.02% of N, Te, Pb and Cu. The sample investigated by Aven <u>et</u> <u>al</u>. [1] was also prepared by the van Arkel process and was 99.5 to 99.9 per cent pure. The purity of the sample investigated by Wolcott [27] is not given explicitly. Since the sample was prepared by the van Arkel process the purity is expected to be high. The samples used by Estermann <u>et</u> <u>al</u>. [6] and by Burk <u>et</u> <u>al</u>. [4] are essentially the same and were better than 99 per cent pure. The value $S^{\circ}_{298} = 7.32 \pm 0.02$ e.u. obtained through analysis of the available data was accepted. This is essentially the same value obtained by Kothen and Johnston [17].

ENTROPIES OF SOME CARBIDES AND NITRIDES AND TITANIUM METAL

Chemical Formula	Gram Formula Mass	S° 298.15°K cal/deg mole	References
Li_2C_2	37.902	14 ±1	18
Be_2C	30.037	4 ±1	18
B_4C	55.291	6.47 ±0.03	7, 14. 23
Na_2C_2	70.016	23 ±3	2, 18
Mg_2C_3	84.673	24 ±3	18
MgC_2	48.342	13 ±2	18, 19
$A\ell_4C_3$	143.953	25 ±3	2, 12, 18, 19, 23
SiC	40.101	3.95 ±0.03	2, 10, 14, 18, 19, 23
TiC	59.911	5.80 ±0.10	15
Li_3N	34.828	9 ±2	2, 12
Be_3N_2	55.055	12 ±2	2, 12
BN	24.828	3.54 ±0.02	2, 5, 26
Na_3N	82.999	24 ±3	(By analogy)
Mg_3N_2	100.976	21 ±2	2, 12, 19, 21
$A\ell N$	40.988	5 ±1	2, 12, 19, 23
Si_3N_4	140.302	23 ±2	2, 12, 19, 23
TiN	61.908	7.19 ±0.04	25
Ti	47.90	7.32 ±0.02	15, 17

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Chapter A4

HIGH-TEMPERATURE HEAT CONTENTS

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As shown in the following chapter, such rather limited data as exist on the high-temperature behavior of the condensed-phase nitrides and carbides of lithium, beryllium, magnesium, aluminum, and titanium, show that they volatilize very predominantly by decomposition to their constituent chemical elements in the ranges of temperature and pressure investigated. Insofar as the thermal data on these compounds and their (free) elements (heats of formation, heat contents, and entropies) are accurate,* the equilibrium constants of these decomposition reactions can be calculated without recourse to direct decomposition data, which are often subject to large experimental uncertainties. This forms also a good starting point for using such experimental data on gaseous nitride and carbide species as may have been obtained by some future time: if their dissociation energies are known, their relative abundances at equilibrium can be estimated, or if upper limits can be set to their abundances in given systems, upper limits for their dissociation energies can readily be estimated.

The standard heats of formation of the solid nitrides and carbides in question were discussed and tabulated in previous NBS reports [1, 2]; this material is repeated (with a few corrections and changes) in Chapter A2 of the present report. Their standard entropies (at 298.15°K) were estimated (except in the few cases where low-temperature heat-capacity measurements are available) as described in Chapter A3. The present chapter describes how high-temperature heat-content functions were arrived at. The resulting tables of condensed-state thermodynamic functions are given in Appendix 2. Tables are included in the appendices for N_2 (gas), C (graphite), and Ti (solid and liquid), the thermodynamic functions for the other pertinent free-element species having been given in the earlier reports [1, 2].

The thermodynamic properties for nitrogen given in Appendix 1 are values from NBS Circular 564 [10] converted to c.g.s. units. Although based on earlier fundamental constants and spectroscopic data, they are

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*See the discussion in the last section of this chapter.

nevertheless accurate enough for use with the properties of the condensed phases given in Appendix 2. Tables of ideal-gas thermal functions for titanium may be obtained from Stull and Sinke [9].

Summary of Basic Data Assumed. -- Table 1 summarizes the formulas of the nitrides and carbides treated, and lists the values assumed for their standard entropies, melting points, and entropies of fusion. Shown also are the highest temperatures for which direct heat-content measurements were found in the literature. The heat-content equations actually arrived at and used to compute the tables of thermodynamic functions (Appendix 2) are given in analytical form in Table 2. The methods of heat-content data adjustment, extrapolation, and estimation are described subsequently.

Estimation of Solid-State Heat Capacities. -- Only for Ti, TiN, TiC, and Mg_3N_2 have heat-content measurements been made with sufficient precision and over a wide enough temperature range to indicate the general shape of the extrapolated heat-capacity-vs.-temperature curve with any real confidence. For the carbides of Li and Mg no data were found. For the other five substances, linear C_p-vs.-T equations were reported [3, 5], based on measurements having limited precision and extending over a few hundred degrees only.

For these eight compounds whose heat capacities are poorly known or have apparently not been measured at all, provisional heat-capacity curves were estimated up to high temperatures, mostly by often-used methods. In so doing, no attempt was made to use values of parameters such as characteristic temperatures theoretically indicated by other properties of the substance in question. If a short straight-line heat capacity had been reported in the literature, the curve was constructed so as to approximate this line near room temperature and at the same time to correspond approximately to the same over-all heat-content change.

In general, however, it would obviously be erroneous to extrapolate such a straight line linearly, since the atomic heat capacities thus obtained would often reach unreasonably high values at higher temperatures. The first step was naturally to compare the mean atomic heat capacities with well-known cases of other typical "atomic-type" solids. One rough but useful generalization that has been pointed out [see references 3 and 4] is that the heat capacity in the majority of known cases has roughly a constant value, and averages about 7.2 cal/gm. atom-deg K at the first transition temperature (including the melting point). Furthermore, except for a few

Table 1. Chemical Formulas, Standard Entropies, and Fusion Constants
(Values in parentheses were estimated.)

Formula	Melting Point (°K)	Entropy of Fusion (e.u./gm. atom)	$S^\circ_{298.15}$ (e.u./mole)	Mean Uncertainty in Measured $H_T - H_{298}$ (%)	Upper Temperature Limit (°K)	
					of Heat-Content Measurements	of Tables in Appendix 2
Li_3N	*	--	(9)	$(5)^a$	800	1200
Be_3N_2	2470	(2.5)	(12)	$(5)^a$	800	4000
Mg_3N_2	*	--	(21)	$(2)^a$	1300	2500
AlN	*	--	(5)	$(3)^a$	900	2500
TiN	3200	(2.5)	7.2	$(0.5)^a$	1800	4000
Li_2C_2	*	--	(14)	--	--	2000
Be_2C	2400	(2.5)	(4)	$(10\text{-}15)^b$	1400	3500
MgC_2	*	--	(13)	--	--	2500
Mg_2C_3	*	--	(24)	--	--	2500
Al_4C_3	*	--	(25)	$(3)^a$	600	3000
TiC	3410	(2.5)	5.8	$(0.5)^a$	1800	4000
Ti	1950	1.90	7.32	$(1.5)^c$	1350	3500

*No melting point was assumed.

[a] According to [3]. Reference [4] states somewhat greater uncertainties.

[b] According to [5].

Table 2. Heat Content of Condensed Phases Above 298.15°K

$$H_T - H_{298.15} = AT + BT^2 + CT^{-1} + D\log_{10} T + E + FT^3 + GT^4$$

(D = G = 0 in all cases in this table.)

ormula	State	A	B	C	E	F	Temperature range °K	References
l_4C_3	c	43.757	$1.624(10^{-3})$	$10.745(10^5)$	-16794.28	$-4.431(10^{-9})$	298-3000	[3]
lN	c	8.892	$2.086(10^{-3})$	$2.422(10^5)$	-3642.54	$-2.41(10^{-7})$	298-2500	[3]
i_2C_2	c	24.34	$1.22(10^{-3})$	$7.08(10^5)$	-9740.06	0	298-2000	--
i_3N	c	20.856	$7.292(10^{-3})$	$5.816(10^5)$	-8761.15	$-21.12(10^{-7})$	298-1200	[3]
gC_2	c	17.02	$0.77(10^{-3})$	$3.59(10^5)$	-6347.05	0	298-2500	--
g_2C_3	c	28.38	$1.28(10^{-3})$	$5.98(10^5)$	-10580.98	0	298-2500	--
g_3N_2[a]	c(α)	22.81	$3.65(10^{-3})$	0	-7125.26	0	298-823	[6]
g_3N_2[b]	c(β)	29.6	0	0	-10021.18	0	823-1061	[6]
g_3N_2	c(γ)	29.54	0	0	-9697.52	0	1061-2500	[6]
e_2C	c	9.168	$5.382(10^{-3})$	$2.01(10^5)$	-3865.74	$-7.65(10^{-7})$	298-2400	[5]
e_2C	c + ℓ	Heat of fusion = 18,000 cal/mole					2400	[4]
e_2C	ℓ	29.16	$-1.2(10^{-3})$	0	-6425.83	0	2400-3500	--
e_3N_2	c	22.03	$6.85(10^{-3})$	$8.735(10^5)$	-10079.47	$-10.35(10^{-7})$	298-2470	[3]
e_3N_2	c + ℓ	Heat of Fusion = 30,875 cal/mole					2470	[4]
e_3N_2	ℓ	48.90	$-2(10^{-3})$	0	-6823.4	0	2470-4000	--
iC	c	11.83	$4(10^{-4})$	$3.58(10^5)$	-4763.41	0	450-3410	[3]
iC	c + ℓ	Heat of Fusion = 17,050 cal/mole					3410	[4]
iC	ℓ	21.06	$-8(10^{-4})$	0	-5129.0	0	3410-4000	--
iN	c	11.91	$4.7(10^{-4})$	$2.96(10^5)$	-4585.53	0	400-3200	[3]
iN	c + ℓ	Heat of Fusion = 16,000 cal/mole					3200	[4]
iN	ℓ	20.72	$-8(10^{-4})$	0	-3680.23	0	3200-4000	--
i[c]	c(α)	5.485784	$1.13385(10^{-3})$	$1.69132(10^4)$	-1793.10	0	298-1155	--
i	c(β)	7.50	0	0	-1645.2	0	1155-1950	[3]
i	c(β) + ℓ	Heat of Fusion = 3,700 cal/mole					1950	[9]
i	ℓ	9.36	$-4.0(10^{-4})$	0	-51.5	0	1950-3500	--

[a] Mg_3N_2: $\Delta H_{tr}(\alpha \text{ to } \beta)$ = 220 cal/mole [7].

[b] Mg_3N_2: $\Delta H_{tr}(\beta \text{ to } \gamma)$ = 260 cal/mole [7].

[c] Ti: $\Delta H_{tr}(\alpha \text{ to } \beta)$ = 950 cal/mole [3].

Each of the above equations gives the heat content in cal/mole relative to that at 298.15°K of the phase stable at the latter temperature.

cases of upward curvature attributable to electronic heat capacity, lattice vacancies, or anharmonicity, known solid-state heat-capacity curves show a downward curvature (at sufficiently high temperatures) and tend toward linearity at still higher temperatures. Finally, the rather precisely determined curves [3] of about 100 substances were compared with one another (with no effort to convert C_p to C_v). These curves seemed to correlate with each other not so well on the basis of an empirical characteristic temperature for each substance as they did with the simpler but more empirical generalization that many of the curves are nearly parallel when compared on the same temperature scale. When no point on the curve had been determined experimentally, further analogies were needed; for example, the curve for MgC_2 was constructed on the basis of those of MgO, CaC_2, and CaO.

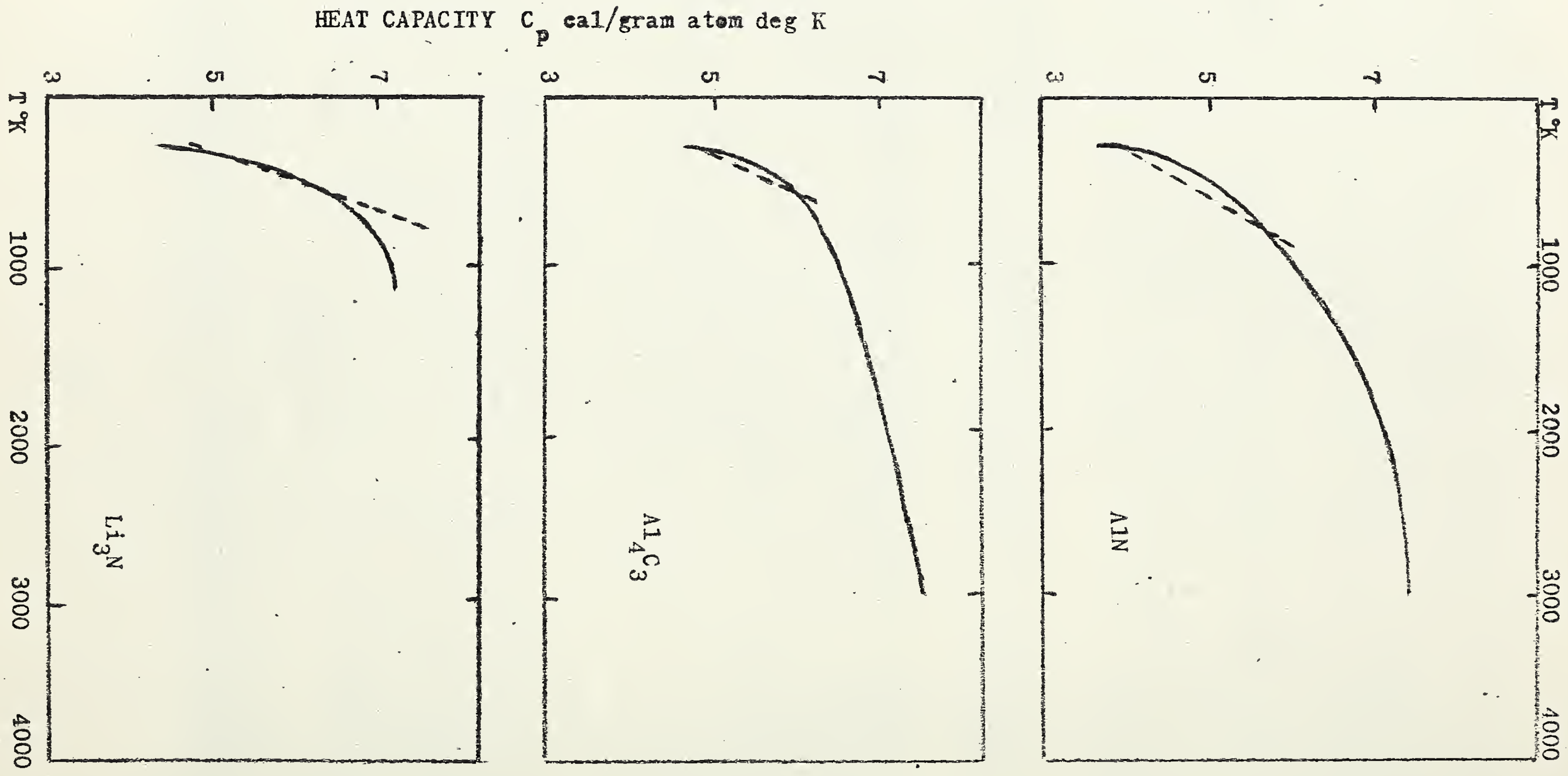
The heat capacity curves estimated by the above methods are shown in Fig. 1 together with the reported experimental curves. The empirical equations derived to fit the selected curves were given above in Table 2.

Choice of Upper-Temperature Limits of Tables of Thermodynamic Properties. -- The terminating temperatures for the tables for nitrides and carbides in Appendix 2 were selected after a cursory examination of the available decomposition data. The tables for the nitrides and carbides of beryllium and titanium were extended into the liquid range because these compounds seem to decompose easily only at temperatures above their reported melting points. Once a melting point, a heat of fusion, and a liquid-state heat capacity had been assumed, there seemed to be little additional uncertainty introduced by extrapolating the liquid properties by as much as 1500° above the melting point.

In the case of each of the other nitrides and carbides, it was believed that the melting point probably lies considerably above the range of reported decomposition temperatures (except of course at high pressures). In these cases intermediate terminating temperatures were selected for the tables, thus obviating the necessity of trying to estimate a melting point which actually might be in error by 1000° or more. A small error in the melting point, however, would have little effect on the calculated decomposition pressures, since the free energies of solid and liquid are not far apart near the true melting point.

Estimation of Heats of Fusion and Liquid-State Heat Capacities. -- The simplest correlation of heats of fusion of atomic-like solids results from a comparison of the corresponding gram-atomic entropies of fusion.

FIGURE 1. HEAT CAPACITY OF NITRIDES AND CARBIDES OF Mg, Be, Al, Li, AND Ti.



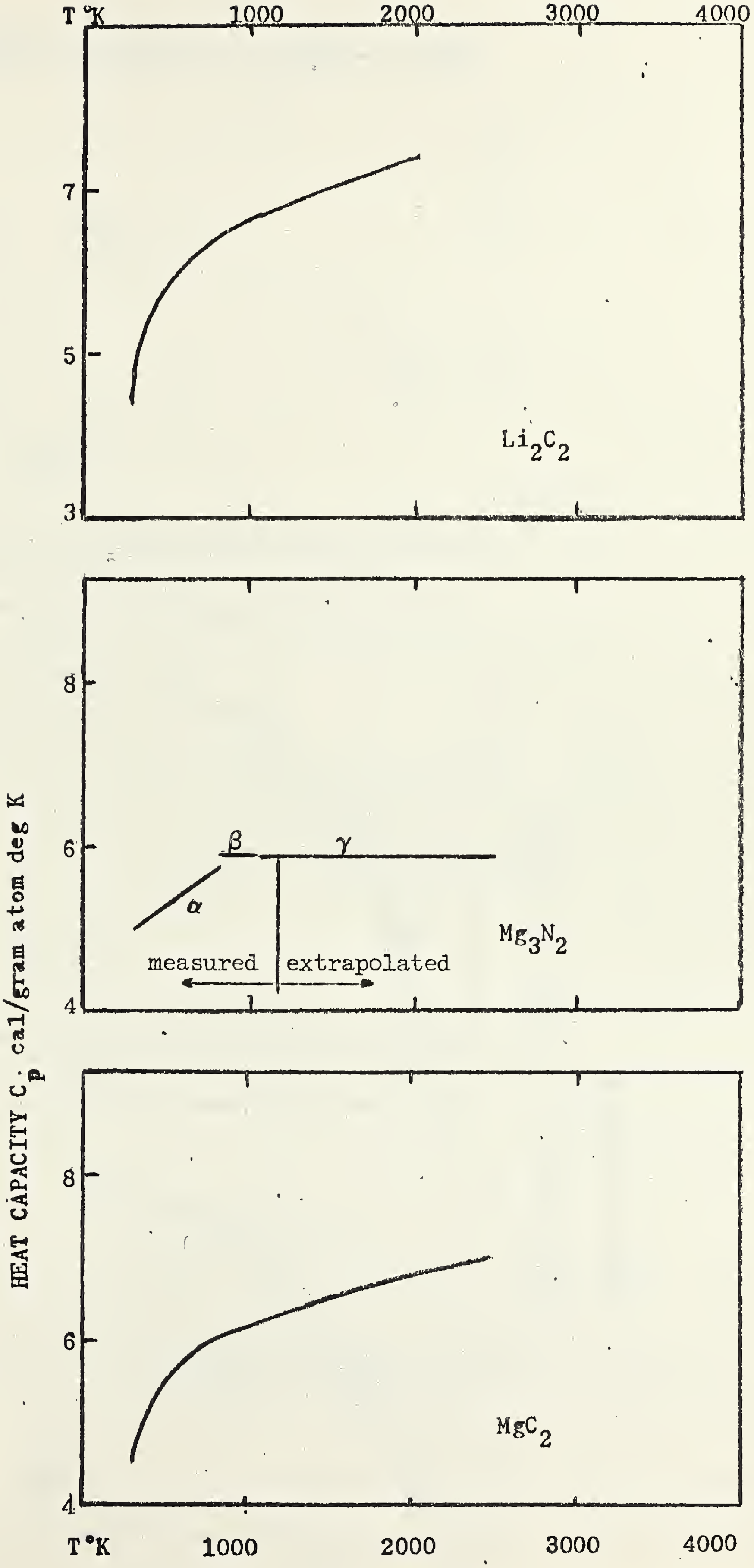


FIGURE 1. (cont.)

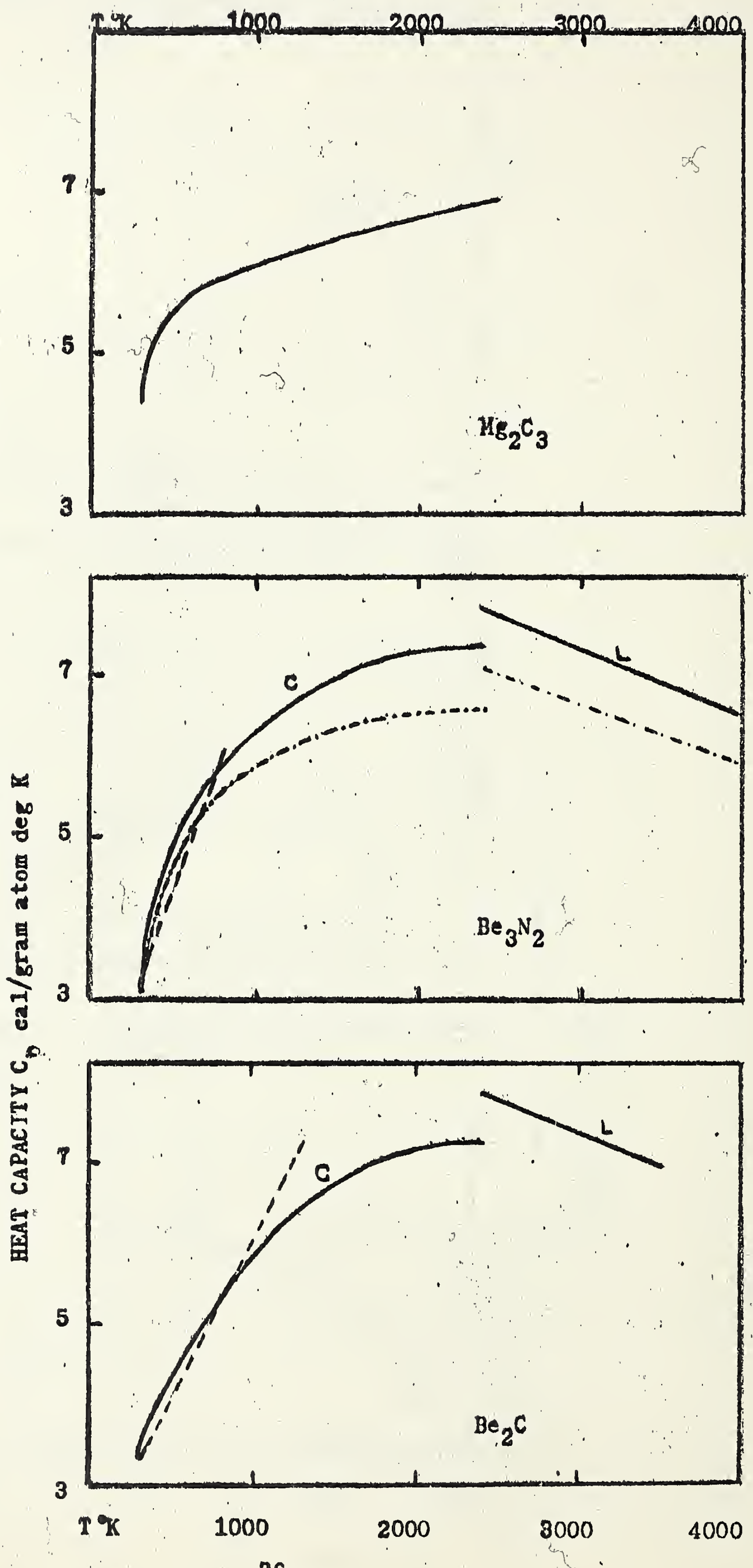
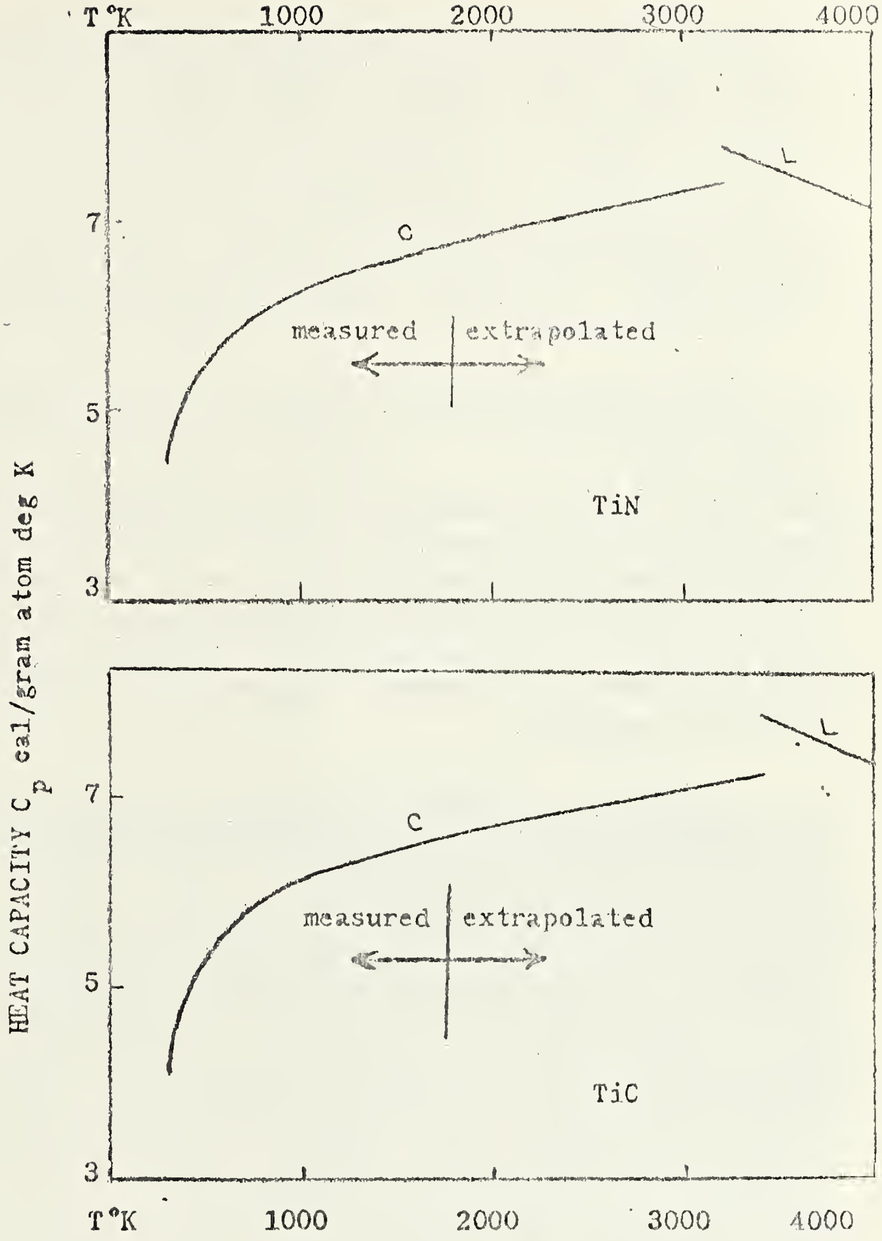


FIGURE 1. (cont.)

FIGURE 1. (cont.)



LEGEND FOR FIGURE 1.

C_p values used in this report ————————

C_p values reported in literature — — — —

C_p hypothetical values ("maximum" negative error) for Be_3N_2. (See text.) —·—·—·—

The latter are far from constant, but average values have often been recommended [3, 4], and 2.5 cal/gm. atom-deg. K was assumed for Be_3N_2, Be_2C, TiN, and TiC. The atomic liquid-state heat capacity and its variation with temperature have been found by several authors [3, 4, 8] to center roughly around certain average values for a large number of metals and salts for which reliable data are available. For the five liquids involved here, the heat capacity was assumed to be 7.8 cal/gm.-atom-deg. K at the melting point and to decrease with increasing temperature by 0.0008 cal./gm.-atom-deg.K per degree.

It is worth pointing out that future experimental work may reveal solid-state transitions not assumed here. In such cases their neglect is thermodynamically equivalent to treating the low-temperature crystalline form as a metastable crystalline phase between its transition temperature and the melting point. Such a procedure does not necessarily increase the thermodynamic errors in the respective temperature regions where the low-temperature crystalline form and the liquid are stable. If a transition occurs whose entropy change is appreciable, it is often true that the actual entropy of fusion is correspondingly lower than that otherwise expected.

Discussion of the Errors in Computed High-Temperature Properties Resulting from Errors in Assumed Heat Contents, Standard Entropy, and Heat of Formation. -- It has long been a common procedure in the literature to calculate dissociation pressures from thermal data (measured or estimated) for comparison with directly "observed" pressures. The labeling of such thermally derived results as "theoretical" tends to obscure the fact that they themselves are often subject to substantial errors, not because of any inexactness in the theory but because of errors in the input thermal data. In view of the wide extrapolations resorted to in arriving at tables of thermodynamic functions for most of the nitrides and carbides treated in this report, it is appropriate to examine the magnitude of error arising from reasonable uncertainties in the assumed heat content and to compare this error with those attributable to uncertainties in the standard entropy and heat of formation of the compound. The thermodynamic properties of the free elements into which the compound dissociates also contribute some uncertainty to the final result, but this source of error is probably much less serious in most cases, and for simplicity will be ignored here.

As a typical example we may take the decomposition of one mole of solid (or liquid) compound to form one or more gaseous elements, such as

$$Be_3N_2(c \text{ or } l) = 3Be(g) + N_2(g),$$

computing for each of several temperatures the factor by which the calculated equilibrium constant is changed as a result of using different underlying thermal data from those used in computing Table 2-29, Appendix 2. Three cases were taken as separate examples.

Case I: The standard entropy (S°_{298}) and heat of formation ($-\Delta Hf^\circ_{298}$) of Be_3N_2(c) were left unchanged. However, the value of heat content ($H^\circ_T - H^\circ_{298}$) was taken to be lower at every temperature T by assuming a heat of fusion 40% lower and by assuming the lower (dot-dash) instead of the higher (full-line) heat-capacity curves for Be_3N_2(c) in Fig. 1. This lowered the assumed heat capacity of the solid by amounts varying from 6% at 298° to 11% at 2500°K (the approximate melting point), and that of the liquid by 10%.

Case II: The only change was the assumption of a new value of S°_{298} lower by 2 e.u./mole. The calculated equilibrium constant of reaction (1) is obviously increased by a factor of $(1.65)^2$, or 2.7, at all temperatures, but the calculated heat of reaction (1) is unaffected.

Case III: The only change was the assumption of a new heat of formation $-\Delta Hf^\circ_{298}$ lower by 5 kcal./mole.

The hypothetical errors so calculated are given in Table 3. It is assumed that the heat of reaction ΔH_T is calculated from thermal data only and not with the use of any observed equilibrium data.

The errors taken as examples in the above three cases were selected because they were believed to represent typical uncertainties in the heat content, standard entropy, and heat of formation of the majority of the light-metal nitrides and carbides. However, this is a matter of opinion; also, the facts vary from compound to compound. It is interesting to note that the three cases selected do show approximately equal effects in the temperature range 2000°-2500°K. One could easily adjust Table 3 to correspond to different errors in the basic data. Specifically, whatever thermal errors would produce, at a given temperature, the same effect on the equilibrium constant or the heat of formation of reaction (1) would suggest the relative accuracy needed in determining the basic thermal data used to compute the high-temperature properties.

The reported decomposition data for a number of these compounds are examined critically in the next chapter. Table 3 should be helpful in trying to decide whether such thermodynamic inconsistencies as are found are attributable mainly to the experimental difficulties inherent in measuring such equilibria at high temperatures.

Table 3. Errors in Computed Equilibrium Constant and Heat of Reaction (1) Caused by Specific Errors in the Input Data

Temperature (°K)	K_p ("incorrect")/K_p ("correct")			ΔH_T ("incorrect") - ΔH_T ("correct") (kcal./mole)		
	Case I ($H_T - H_{298}$ of $Be_3N_2(c)$ too low by 6 to 18%)	Case II (S°_{298} of $Be_3N_2(c)$ too low by 2 e.u./mole)	Case III ($-\Delta Hf^\circ_{298}$ of $Be_3N_2(c)$ too low by 5 kcal./mole)	Case I ($H_T - H_{298}$ of $Be_3N_2(c)$ too low by 6 to 18%)	Case II (S°_{298} of $Be_3N_2(c)$ too low by 2 e.u./mole)	Case III ($-\Delta Hf^\circ_{298}$ of $Be_3N_2(c)$ too low by 5 kcal./mole)
1000	1.4	2.7	12.	1	0	-5
1500	1.9	2.7	5.4	2	0	-5
2000	2.4	2.7	3.5	4	0	-5
2500(c)	3.1	2.7	2.7	6	0	-5
2500(l)	3.1	2.7	2.7	19	0	-5
3000	6.1	2.7	2.3	20	0	-5
3500	10.	2.7	2.0	22	0	-5
4000	15.	2.7	1.9	24	0	-5

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Chapter A5

CONDENSED AND VAPOR PHASES OF THE CARBIDES, NITRIDES, OXYCARBIDES, and CARBONITRIDES of Al, Be, Mg, Li, and Ti.

J. Efimenko, R.F. Hampson, R.F. Walker and T.B. Douglas

In general, experimental data on the high temperature chemistry of the carbides and nitrides of the light element compounds are more scarce than on the corresponding oxides. The data indicate that, most commonly, the compounds decompose on melting, vaporize predominantly by dissociation to the elements, and are thermodynamically unstable with respect to the oxides. The nitrides are generally less stable than the carbides at high temperatures, but the relative stabilities may be reversed so that the nitrides are more stable at lower temperatures. Complex gaseous molecules may be expected at higher temperatures and pressures than covered by existing data. The occurrence of these molecules will probably increase with the formation of such species as atomic nitrogen in the gas phase. Attempts to set limits to their dissociation energies, and thereby to predict the approximate conditions under which they are important species, will be deferred to a later report.

The following is a brief survey of data on the pertinent systems. Additional analysis of the data will be presented later.

Aluminum Carbide.

There is only one well-established solid phase in the Al-C system, the yellow, rhombohedral compound Al_4C_3. Sheipline and Runck [1] give the melting point as 2800°C. However, the calculated vapor pressures shown in Table 1 indicate that the pressure should exceed one atmosphere by 2700°C. The melting point is, therefore, either below 2700°C or the compound decomposes without melting, except under high pressure. The heat of fusion has not been determined. Neither of the two attempts [2,3] to produce a binary phase diagram of the system Al_2O_3-Al_4C_3 are complete at the carbide-rich end; hence, estimates of the heat of fusion cannot be obtained from their liquidus curves. Using an entropy of fusion of 2.5 cals/gm-atom deg K and 2700°C as the melting point yields a heat of fusion of 52.0 kcals/mole.

The mass-spectrometric measurements of Chupka, *et al.* [4] indicate that at about 2100°K Al_4C_3 vaporizes predominantly by dissociation to the elements. However, a species Al_2C_2 was also found to be present. The relative abundance ratio Al:Al_2C_2 was 1050:1; however, fragmentation of some of the Al_2C_2 molecules may account for the detection also of an Al_2 species. Two other gaseous carbides, Al_2C and AlC_2, were not detected in sufficient quantity to make their appearance certain. The species AlC, which Zeeman [5] reported after analysis of high temperature spectra, was not detected.

Meschi and Searcy [6] used a torsion effusion method to study the dissociation pressure of Al_4C_3. They also collected the vapor by condensation and analyzed for carbon. There was considerable uncertainty in the results, but these indicated that much of the carbon found was attributable to the presence of impurities such as O_2 and H_2O, with which the carbide reacts. On this basis their results were not in conflict with those of Chupka et al [4] in setting a low limit to the occurrence of Al_2C_2 or other gaseous carbides in equilibrium with the condensed phase.

Using the tables of thermal functions given in the Appendix of this report, the heats of formation given in Chapter A2, and the heats of formation* and thermal functions given in NBS Report No. 6484, the data given in Table I has been calculated for the reaction:

$$Al_4C_3(c) = 4Al(g) + 3C(c).$$

As indicated previously, the precise melting point of Al_4C_3 is uncertain. If the compound is liquid at 3000°K, the calculated vapor pressure would be somewhat higher than that shown for this temperature in Table I.

Table I

Dissociation Pressures for Aluminum Carbide.

		Calculated		Measured
T°K	Log K	P_{Al}(mm.)	P_{Al}(atmos.)	P_{Al}(atmos.)
1000	-49.63	2.96×10^{-10}	3.90×10^{-13}	-
1600	-21.04	4.16×10^{-3}	5.48×10^{-6}	4.2×10^{-6} [6]
1700	-18.27	2.06×10^{-2}	2.71×10^{-5}	2.2×10^{-5} [6]
2000	-11.68	0.912	1.20×10^{-3}	-
2100	- 9.93	2.5	3.29×10^{-3}	6×10^{-4} [4]
3000	+ 0.50	1010.	1.33	-

The calculated pressures given in the table are compared with measured values as shown. Meschi and Searcy [6] represent their experimental data on dissociation pressures by the equation:

$$\log P_{atm} = -(1.95 \times 10^4)/T + 6.79.$$

---

* In the analyses of this chapter the heats of formation used in calculations are the "best" calorimetrically-determined values, in order that the thermal and equilibrium data may be compared for thermodynamic interconsistency. In some cases the calorimetric values are so uncertain that the heats of formation indicated by the decomposition data have been given some weight in arriving at the final "best" value adopted in Chapter A2.

Reactions between Aluminum Carbide and Aluminum Nitride.

Prescott and Hinke [7] have studied the reaction between Al_4C_3 and N_2 over the range 1774-1909°K. They synthesized Al_4C_3 by direct combination of the elements, and then approached equilibrium from both directions by introducing nitrogen atmospheres at pressures both above and below the equilibrium value, averaging the two final pressures in each experiment as determined by gas analysis. On the basis of 14 such experiments they gave for the reaction

$$4AlN(c) + 3C(c) = Al_4C_3(c) + 2N_2(g) \tag{1}$$

the equation:

$$\begin{aligned} &\log P(\mathrm{mm}) = 12.772 - 27697/T \\ \text{or} \quad &\log P(\mathrm{atm}) = 9.891 - 27697/T. \end{aligned} \tag{2}$$

A probable error of 11% in pressure or 5.8° in temperature was indicated.

In Table II vapor pressures derived from the above equation are compared with values calculated from the tables of thermal functions in the Appendix of this report and from the sources cited above.

Table II.

Decomposition Pressures for Aluminum Carbide in the Presence of Nitrogen

		Calculated		Measured
T°K	1/2 Log K	P_{N_2}(atmos)	P_{N_2}(mm.)	P_{N_2}(mm.)
1700	-6.058	8.75×10^{-7}	6.65×10^{-4}	3.02×10^{-4}
1800	-5.147	7.13×10^{-6}	5.42×10^{-3}	2.43×10^{-3}
1850	-4.727	1.87×10^{-5}	1.42×10^{-2}	6.32×10^{-3}
1900	-4.330	4.67×10^{-5}	3.55×10^{-2}	1.57×10^{-2}
2000	-3.601	2.51×10^{-4}	1.90×10^{-1}	8.40×10^{-2}

It will be noted that the calculated nitrogen pressures are approximately two times higher than the measured values of Prescott and Hinke. The agreement is, however, fairly good considering all sources of experimental error. The heat of the reaction at 1850°K to produce one mole of nitrogen is 126.7 kcals according to their equation, and 127.5 kcals as calculated from the tabulated thermal functions. Nevertheless, there is some question as to whether Prescott and Hinke's chemical equation correctly expresses the equilibrium in this system.

Von Stackelberg and associates [8,9] reported that an aluminum carbonitride was readily formed from the elements at temperatures comparable to those used by Prescott and Hinke. The composition of the carbonitride was represented as $AlN{\cdot}Al_4C_3$, and its crystal structure was determined by X-ray analysis. As one would expect from its likely close relation to AlN, they found that the carbonitride decomposed with the evolution of nitrogen at still higher temperatures. Following von Stackelberg et al, one may reexamine the results of Prescott and Hinke in terms of this compound.

If the carbonitride is stable in the temperature range in which Prescott and Hinke worked, the reaction

$$AlN(c) + Al_4C_3(c) = AlN{\cdot}Al_4C_3(c) \qquad (3)$$

would be spontaneous, and at equilibrium only the product and one reactant, if immiscible, could coexist. The introduction of nitrogen to Al_4C_3 would at first leave an excess of Al_4C_3, but later all the Al_4C_3 would disappear and an excess of AlN would then form. Prescott and Hinke's results were derived from three series of experiments in which the times of exposure to N_2 were as follows: Series A, 145 min.; Series B, 60 min.; Series C, 30 min. Series A and B are in close agreement with each other, but Series C differs systematically from A and B. We have least-squared their data (omitting the one out-of-line run which they omitted), obtaining:

$$\text{Series A and B (9 runs)}, \log P_{atm} = 10.267 - 28332/T \qquad (4)$$

$$\text{Series C (5 runs)}, \log P_{atm} = 11.650 - 31116/T \qquad (5)$$

Following the suggestion of von Stackelberg et al that in Series A and B AlN was in excess, but that in Series C Al_4C_3 was in excess, one may tentatively write for the reactions representing the two equilibria, respectively:

$$\frac{5}{2}AlN(c) + \frac{3}{2}C(c) = \frac{1}{2}AlN{\cdot}Al_4C_3(c) + N_2(g) \qquad (6)$$

and

$$2AlN{\cdot}Al_4C_3(c) + \frac{3}{2}C(c) = \frac{5}{2}Al_4C_3(c) + N_2(g). \qquad (7)$$

Equation (1) may be rewritten:

$$2AlN(c) + \frac{3}{2}C(c) = \frac{1}{2}Al_4C_3(c) + N_2(g). \qquad (1a)$$

Reactions (1a) and (3) can then be combined to give either reaction (6) or reaction (7), so at a given temperature we have (where ΔX represents either ΔH° or ΔF°)

$$\Delta X_6^\circ = \Delta X_{1a}^\circ + \frac{1}{2}\Delta X_3^\circ$$

and

$$\Delta X^\circ_7 = \Delta X^\circ_{1a} - 2\,\Delta X^\circ_3,$$

which can be solved to give the properties of reactions (1a) and (3) in terms of those of reactions (6) and (7):

$$\Delta X^\circ_{1a} = \frac{4}{5}\,\Delta X^\circ_6 + \frac{1}{5}\,\Delta X^\circ_7; \tag{8}$$

$$\Delta X^\circ_3 = \frac{2}{5}(\Delta X^\circ_6 - \Delta X^\circ_7). \tag{9}$$

According to this interpretation any systematic difference between Series A and B and Series C is attributable to the effects of reaction (3), in which the carbonitride forms. Futhermore,with the assumption that no carbonitride forms, the true properties of the simple reaction (1a) are actually intermediate between those obtained from Series A and B and those from Series C.

The higher pressures given by equation (4) compared with equation (5) indicate that at these high temperatures the formation of the carbonitride from the two binary compounds (3) is weakly spontaneous, and the difference in temperature derivatives ($\frac{dP}{dT}$) indicates that it is slightly exothermic; e.g., from (9) at 1850°K, $\Delta F^\circ_3 = -0.4$ kcal. and $\Delta H^\circ_3 = -5 \pm 2$ kcal. (Von Stackelberg et al [8] computed $\Delta H^\circ_3 = -8$ kcal.) (If the unknown thermodynamic functions for $AlN{\cdot}Al_4C_3$ are assumed to be close to the sum of those for AlN and Al_4C_3 the values for ΔF and ΔH can be converted to room temperature, however, with these small magnitudes, large percentage errors will result if the assumption is incorrect.)

Though there is no proof that Prescott and Hinke's measurements actually applied to both reactions (6) and (7), it is interesting to note a further indication from their results that they were dealing with two different equilibrium pressures at the same temperature. They gave a "typical" graph showing the approach from both directions to pressure equilibrium in one experiment. The precision was good enough to indicate two different asymptotes corresponding to equilibrium pressures differing by 30%, which is the order of magnitude between those calculated from equations (4) and (5) in their temperature range.

The heat of reaction (1a) may be evaluated from the equilibrium data of Prescott and Hinke by calculating the free-energy change in the range 1800°-1900°K and applying the free-energy functions given in the Appendix of this report. Whether the heat of reaction (1a) is calculated directly from equation (2), or from equations (4) and (5) with use of equation (8), practically the same result is obtained: $\Delta H^\circ_{1a}(298^\circ K) = 131.6$ kcals/mole of N_2. This is 3 kcal higher than the value of 128.7 kcals calculated from the calorimetrically determined heats of formation of AlN and Al_4C_3 recommended in Chapter A2. The result may be fortuitous, but it is interesting to note that it implies that Prescott and Hinke's data are consistent with the low value (-76.5 kcals/mole) selected for the heat of formation of AlN in Chapter A2. If values for ΔH°_{298} of formation of Al_4C_3 varying from -36.3 to -48.7 kcals/mole are used (see discussion on the Al-O-C system), the respective heats of formation of AlN at 298°K vary only between -74.4 and -77.5 kcals/mole, according to Prescott and Hinke's data.

Aluminum Nitride.

AlN, the only known solid phase in the Al-N system, hydrolyzes readily in the presence of water vapor at room temperature and oxidizes substantially in air at 1000°C. The compound tends to dissociate at high temperatures and the dissociation pressure has been reported to reach 14 mm at 1870°C [10]. The data given in Table III are in rough agreement with this value. The melting point is given as 2500°K in earlier sources [11]. The heat of fusion has not been measured, but assuming an entropy of fusion of 2.5 cal/gm atom (as in Chapter A4) and the above melting point, one arrives at a heat of fusion of 12.5 kcal/mole. This is the value used in the tables of thermodynamics functions given in this report.

The importance of gaseous aluminum nitride molecules has not been clearly established. In the following we shall assume the absence of appreciable nitride species in the gas phase.

Hoch and White [12] have studied the vaporization of AlN by the effusion method. Although they used a graphite Knudsen cell, a comparison of their data with those of Prescott and Hinke [7] indicates that the pressure of nitrogen was too high to permit any reaction between the graphite and the AlN, and one may therefore assume that the cell reaction was:

$$AlN(c) = Al(g) + \frac{1}{2}N_2(g).$$

In Table III selected experimental values of the total dissociation pressure of AlN are compared with theoretical values calculated by Hoch and White, and with values calculated from the tables of thermal functions given in the Appendix of this report and the sources previously cited for Al_4C_3. It will be noted that the selected experimental values agree within a factor of 6 or less with the NBS calculated values, and that the lack of agreement increases with increasing temperature. Unfortunately, estimated uncertainties in the measured data are not available. The difference between the two sets of calculated pressures appears to be due principally to the fact that Hoch and White used a value of -57.7 kcals/mole for ΔHf°_{298} of AlN.

Table III

Dissociation Pressures for Aluminum Nitride

	Hoch & White			NBS calculated	
	Total pressure			Total pressure	
T°K	Measured(atmos)	Calc.(atmos)	Log K	atmos.	mm Hg.
1000			-21.252	1.28×10^{-14}	9.75×10^{-12}
1671	5.99×10^{-7}	2.15×10^{-4}	- 7.935	9.69×10^{-6}	7.36×10^{-3}
1700			- 7.600	1.62×10^{-5}	1.23×10^{-2}
1707	1.57×10^{-5}	3.69×10^{-4}	- 7.521	1.83×10^{-5}	1.39×10^{-2}
1791	7.37×10^{-5}	1.15×10^{-3}	- 6.623	7.26×10^{-5}	5.52×10^{-2}
1800			- 6.531	8.37×10^{-5}	6.36×10^{-2}
1885	1.91×10^{-4}	3.67×10^{-3}	- 5.714	2.93×10^{-4}	2.23×10^{-1}
1900			- 5.578	3.6×10^{-4}	2.74×10^{-1}
1905	2.03×10^{-3}	4.68×10^{-3}	- 5.532	3.87×10^{-4}	2.94×10^{-1}
2000			- 4.721	1.35×10^{-3}	1.023
2500			- 1.502	.19	143.

As discussed in Chapter A2, the calorimetric values for the heat of formation of AlN are scattered over a range of 20 kcal/mole, and this important constant must presently be regarded as considerably uncertain. For this reason it might seem that it would be more informative not to assume a value for the heat of formation but to use the thermodynamic functions to calculate the third-law values of ΔHf°_{298} given by Hoch and White's data. Unfortunately, the calculations yield no unambiguous value for the heat of formation as indicated by the following discussion.

Hoch and White used their measured (p) and calculated (P) pressures to estimate values for the condensation coefficient, α, for AlN. Values of the order of 10^{-4} were obtained from the equation:

$$\alpha = \frac{h/s}{P/p \pm 1}$$

In this equation h/s was the ratio of the diameter of the effusion hole to the diameter of the interior of their Knudsen cells. More accurately, the parameter, s, should be related to the surface area of the sample. Because they found P to be much greater than p, Hoch and White neglected the "one" in the denominator of the equation.

If the pressures calculated from the thermodynamic functions presented in this report are used, the measured and calculated pressures are sufficiently close that the "one" in the denominator cannot be neglected. However, the values of α calculated then become so critically dependent on the precision of the pressure values, that the equation becomes very difficult to use with reliability, although it may be correct in principle. For example, an error of 7° in temperature measurement, as represented by the calculated pressures at 1700° and 1707°K, can lead to values of α of 0.025 and 0.0051 respectively.

The above formula for α was derived by Speiser and Johnston [13]. Motzfeldt [14] has given a more refined formula which differs from that of Speiser and Johnston by the replacement of $\frac{1}{\alpha}$ by $\frac{1}{\alpha} + \frac{1}{W} - 2$, where W is a Clausing factor for the inside of the cell and is about 0.5 for usual shapes. Both formulas obviously give identical results when, as in the present case, a low value of α appears to be involved.

Notwithstanding the difficulty in deriving a precise value for α from Hoch and White's data, one can assume values for α and calculate values of ΔHf_{298} for each temperature for which pressure data was obtained. The heats of formation can then be checked for consistency for any selected value of α.

The results of such calculations are given in Table IV. In the first three columns of the table Hoch and White's data are given. The pressures given in the third column are total pressures calculated from the simple effusion equation, but with application of a Clausing factor to correct for finite hole depth.

Table IV

Heat of Formation of AlN from Hoch and White's Data [12]

			Calculated $-\Delta Hf_{298}(AlN)$, kcal/mole					
h/S	T°K	$-\log P_m$(atm)	$\alpha=1$	$\alpha=10^{-2}$	$\alpha=3(10^{-3})$	$\alpha=10^{-3}$	$\alpha=3(10^{-4})$	$\alpha=10^{-4}$
0.572	1660	7.7479	104.5	86.6	80.7	75.2	69.3	63.9
	1749	6.7258	101.7	82.9	76.7	71.0	64.7	59.0
	1856	5.8904	101.7	81.8	75.2	69.1	62.4	56.4
	1948	5.4104	104.0	83.0	76.1	69.7	62.7	56.4
$3.13(10^{-2})$	1671	6.2226	90.2	83.3	78.2	73.1	67.2	61.7
	1869	4.6815	89.8	82.1	76.4	70.6	64.1	58.0
	1948	4.1120	89.0	81.0	75.1	69.1	62.2	55.8
$8.61(10^{-4})$	1707	4.8052	77.3	76.9	76.0	74.1	70.4	65.8
	1791	4.1324	76.4	76.0	75.1	73.1	69.2	64.4
	1885	3.7181	78.9	78.4	77.5	75.4	71.3	66.2
$5.86(10^{-4})$	1869	3.7575	78.1	77.8	77.1	75.5	72.1	67.4
$1.23(10^{-4})$	1786	3.2924	65.7	65.7	65.5	65.1	63.9	61.4
	1905	2.6932	67.1	67.0	66.9	66.4	65.1	62.6

The fourth column gives the individual third-law values of the heat of formation calculated from the pressures with the assumption of unit condensation coefficient. These values drift markedly with hole size, but for the same hole size show striking independence of temperature.

The last five columns of Table IV give the values of ΔHf°_{298}(AlN) computed with the assumption of different values of α. A value of $\alpha = 10^{-2}$ is too high to eliminate the drift in the heat of formation values. With $\alpha = 3(10^{-3})$, all values, except the last two, which correspond to the most favorable hole size, are quite constant; the average, 76.7 kcal/mole, is almost identical with the calorimetric value provisionally selected in Chapter A2. On the other hand, with $\alpha = 10^{-4}$ the gross drift is essentially eliminated from all the values, but they now average 61.5 kcal/mole. The wide range of values is due partly to the burden of trying to evaluate two unknowns simultaneously. We do not believe that this set of equilibrium measurements alone can be more precisely interpreted than the indication that the condensation coefficient and the heat of formation of AlN lie within the above wide limits.

The System Al-O-C

Al_4C_3 reacts with water at room temperature and oxidizes readily at elevated temperatures. The reaction between aluminum oxide and carbon has been studied by a number of investigators [15,16,17], but a complete quantitative understanding of the reaction is not yet complete.

Prescott and Hinke [17] assumed the following reaction occurred:

$$2Al_2O_3(c) + 9C(c) = Al_4C_3(c) + 6CO(g) \tag{10}$$

They measured the pressure in the system over the temperature range 1967-2293°K. There was considerable scatter in the data at the higher temperatures but they represented the equilibrium pressures by the equation:

$$\text{Log } p_{atm} = 8.21 - 18{,}480/T. \tag{11}$$

In Table II equilibrium pressures of CO calculated from equation (11) are compared with values computed using the heats of formation given in NBS Report No. 6484, NBS Circular 500, and Chapter A2 of this report, and using the tables of thermodynamic functions given in the Appendix.

The excellent agreement between the calculated and measured pressures at 1900°K tapers off to a disparity of nearly a factor of two at 2300°K. The disparity is reflected in the trend in the values of ΔHf°_{298} (Al_4C_3), also shown in the table, which were calculated using the tables of thermodynamic functions. These heats of formation compare with the value -48.6 ± 10 kcals/mole used in obtaining the calculated pressures and suggest that a systematic error may have been involved in Prescott and Hinke's measurements.

Table V

Reaction of Aluminum Oxide with Carbon

Temp. °K	Calculated Pressure of CO atmos	 mm Hg	Measured [17] P_{CO} atmos	 $\Delta Hf^\circ_{298}(Al_4C_3)$ kcals/mole
1900	3.01×10^{-2}	22.9	3.02×10^{-2}	-48.7
1950	5.78×10^{-2}	43.9	5.37×10^{-2}	-46.8
2000	1.08×10^{-1}	82.1	9.33×10^{-2}	-45.1
2100	3.42×10^{-1}	260.	2.57×10^{-1}	-41.5
2200	9.75×10^{-1}	741.	6.46×10^{-1}	-38.0
2250	-	-	1.0	-36.3
2300	2.51	1910.	1.48	-34.2

As discussed in the previous report (NBS No. 6484), a number of reduced oxides of carbon have been reported as a result of reactions of alumina and carbon. Brunner [15] claimed to have observed the reduction of alumina to metallic aluminum, according to the equation:

$$Al_2O_3 + 3C = 2Al + 3CO.$$

However, the most recent and thorough investigation of the Al_2O_3-Al_4C_3 system indicates that two oxycarbides, Al_4O_4C and Al_2OC, occur in the solid state [3]. Unfortunately, no thermodynamic data on these compounds is available, but the data of Foster, Long and Hunter [3] indicate that both the oxycarbides are stable in the temperature range used by Prescott and Hinke in their investigation [17].

It seems possible that Prescott and Hinke's experimental data may be understood in the following terms: At the lower temperatures used, substantial amounts of oxycarbide were not formed during the period of their runs (of 15-30 minutes each). The measured pressures were, therefore, consistent with those calculated for the reaction expressed by their equation (10). At higher temperatures, loss of aluminum by vaporization and the formation of oxycarbides complicated the picture. In the absence of sufficient thermal data, one can only speculate, however, on the exact nature of the reactions involved.

Beryllium Carbides and Oxy-Carbides

The only known compound in the Be-C system, Be_2C, is reported (probably inaccurately) to dissociate without melting above 2150°C [18]. Be_2C hydrolyzes slowly in moist air at room temperature. It absorbs N_2 above 1100°C, reacts with NH_3 above 900°C, and reacts with CO_2 at 1425°C. The compound remains stable in H_2 and O_2 to temperatures above 1000°C [1].

The heat of fusion of Be_2C has not been measured. Using an assumed entropy of fusion of 2.5 cal/gm. atom and 2400°K as the melting point, a heat of fusion of 18.0 kcals/mole is obtained, and has been used in the tables of thermal functions.

Be_2C vaporizes predominantly by dissociation to the elements. Chupka _et al_ [4] used a mass spectrometer and found the relative abundance of all possible carbide species to the Be(g) species to be less than 1 in 400 at 1900°K. A lower limit on the heat of formation of $BeC_2(g)$ was determined to be 134.3 kcals/mole. referred to 0°K.

The dissociation pressures of Be_2C are given by Quirk [18] and by Pollock [19]. The two sets of data do not overlap in temperature range, but together cover the range 1430-2600°K; however, they are not mutually consistent, for the data of Pollock yields considerably lower vapor pressures when extrapolated to the higher temperature range used by Quirk.

Dissociation pressures calculated for the reactions $Be_2C(c)=2Be(g)+C(c)$ and $Be_2C(l)=2Be(g)+C(c)$ are presented in Table VI. The heats of formation given in Chapter A2 and NBS Report No. 6297 and the thermal functions tabulated in the Appendix of this report were used for these calculations.

Table VI

Dissociation Pressures for Beryllium Carbide

Temp. °K	P_{Be} atmos	Temp. °K	P_{Be} atmos
1400	8.57×10^{-8}	1900	3.44×10^{-4}
1500	7.08×10^{-7}	2000	1.08×10^{-3}
1600	4.47×10^{-6}	2400	4.02×10^{-2}
1700	2.26×10^{-5}	2500	7.62×10^{-2}
1800	9.51×10^{-5}	3000	0.95

The pressures in Table VI agree closely with the experimental data of Pollock, expressed by the equation:

$$\text{Log } p \text{ atm} = 7.026 \pm 0.347 - (19720 \pm 537)/T.$$

Since the value of ΔHf_{298} of Be_2C used in the calculations was obtained from Pollock's data, the calculations merely verify that the tables of thermodynamic functions are consistent with Pollock's data. For comparison purposes, the pressures given by Quirk for the temperatures 1900, 2100, 2400, and 2600°K are respectively 6×10^{-3}, 4×10^{-2}, 0.44, and 1.5 atmos.

BeO reacts with graphite and melts at about 2300°C to form an unidentified compound. The possibility of the existence of condensed oxycarbides of beryllium should not, therefore, be overlooked.

Beryllium Nitride

Experimental data on Be_3N_2, the only known condensed phase in the Be-N system, is somewhat more scarce than for the carbide. The melting point is given as 2200°C [11,20], and the dissociation pressure is reported to reach 1 atmos. in the 2240-2400°C temp. range. The calculated dissociation pressures given in Table VII indicate, however, that a vapor pressure of 1 atmos. should be reached at a somewhat higher temperature. The heat of fusion calculated from the above melting point and an entropy of fusion of 2.5 cals/gram atom is 30.9 kcals/mole, and this value has been used for tabulation purposes.

Dissociation pressures for the reactions $Be_3N_2(c) = 3Be(g) + N_2(g)$ and $Be_3N_2(l) = 3Be(g) + N_2(g)$ are given in Table VII. The heats of formation given in Chapter A2 and NBS Report No. 6297, and the thermal functions tabulated in the Appendix were used for these calculations.

Be_3N_2 is stable in dry air but hydrolyzes slowly in moist air at room temperature. The compound oxidizes at a substantial rate at 1000°C.

Table VII

Dissociation Pressures for Beryllium Nitride

Temp. °K	Log K	P_{N_2} (atmos)	P_{total} (atmos)
1800	-16.437	3.41×10^{-5}	1.36×10^{-4}
2000	-12.160	4.00×10^{-4}	1.60×10^{-3}
2200	- 8.682	2.96×10^{-3}	1.18×10^{-2}
2400	- 5.808	1.55×10^{-2}	6.20×10^{-2}
2470	- 4.922	2.58×10^{-2}	0.10
......			
liquid			
......			
2500	- 4.588	3.13×10^{-2}	0.13
2600	- 3.537	5.73×10^{-2}	0.23
2700	- 2.564	0.10	0.4

Carbides of Magnesium

Two solid carbides of magnesium are known, MgC_2 and Mg_2C_3, but they decompose spontaneously at relatively low temperatures. Schneider and Cordes [21] have reported that calcium carbide reacts with magnesium chloride in liquid-salt solution to form MgC_2 at 773°K, presumably according to the reaction:

$$CaC_2(c) + MgCl_2(l,\ solution) = MgC_2(c) + CaCl_2(l, solution); \qquad (12)$$

They also reported that MgC_2 decomposes into Mg_2C_3 and graphite at 823°K:

$$2MgC_2(c) = Mg_2C_3(c) + C(c) \tag{13}$$

and that the Mg_2C_3 itself decomposes into its elements at 923°K:

$$Mg_2C_3(c) = 2Mg(c \text{ or } l) + 3C(c). \tag{14}$$

(Other investigators have observed reactions (13) and (14) at somewhat different temperatures; e.g., Pavlov [22] gives 883° and 1473°K, respectively).

Although no observations of equilibria involving either of these magnesium carbides have been reported, one may assume the above reactions to be spontaneous under the stated conditions and, with use of the pertinent free-energy functions, calculate limiting values within which the heats of formation of these carbides must lie if they are to be consistent with these qualitative observations. These computations were carried out for the above three reactions, assuming the temperatures given by Schneider and Cordes, and using data for the pure crystalline chlorides as giving reasonable estimates of their free energies in solution in reaction (12). Values of the high-temperature heat content, of S°_{298}, and of ΔHf°_{298} of $CaCl_2$ and CaC_2 were taken from other sources [23,24]. The results were:

$$\Delta Hf^\circ_{298}(MgC_2) < 22 \text{ kcal/mole (from reaction(12))}$$

$$2\Delta Hf^\circ_{298}(MgC_2) - \Delta Hf^\circ_{298}(Mg_2C_3) > 1 \text{ kcal (from reaction (13))}$$

$$\Delta Hf^\circ_{298}(Mg_2C_3) > 5 \text{ kcal/mole (from reaction (14)).}$$

They indicate that ΔHf°_{298} must lie between 3 and 22 kcal/mole in the case of MgC_2, and between 5 and 43 kcal/mole in the case of Mg_2C_3. The calorimetric values tabulated in Chapter A2 (21 ± 5 and 19 ± 8 kcal/mole respectively) fall within these limits, but the negative values estimated by Krikorian [25] by analogy with other carbides do not. (However, in the case of his value, $\Delta Hf^\circ_{298}(MgC_2) = -6 \pm 10$ kcal/mole, there is agreement within his estimated tolerance.)

It is of interest to calculate the free energies of formation of MgC_2 and Mg_2C_3 from their elements at various temperatures. Using the heats of formation given in Chapter A2, these values were all found to be positive, indicating the impossibility of direct synthesis of either carbide (at least up to 2500°K and near atmospheric pressure). This conclusion rests on the assumption that the rather uncertain thermodynamic properties of the two carbides tabulated in this report are not seriously in error.

Magnesium Nitride

Mg_3N_2, the only nitride of magnesium, undergoes a solid phase change from an α to a β form at about 600°C. At 788°C the β phase transforms to a γ phase. Soulen, Sthapitanonda, and Margrave [26] have measured the vapor pressure using the transpiration method over the temperature range 1337-1506°K and the Knudsen effusion method over the range 1118-1254°K. The experimental data were possibly complicated by the presence of small amounts of oxygen in the former case and a low condensation coefficient in the latter case. The authors assumed decomposition to the elements, according to the equation:

$$Mg_3N_2(c) = 3Mg(g) + N_2(g).$$

Equilibrium constants for this reaction, calculated from the tables of thermodynamic functions and the heat of formation given in Chapter A2, are given in Table VIII. Approximate calculated values given by Soulen et al are given in parenthesis. The discrepancy betweeen the two sets of calculated values appears to be largely due to their selection of a value of 22 e.u. for $S^\circ_{298}(Mg_3N_2)$ instead of the value of 21 e.u. used in this report. The experimental data are approximately 10-100 times higher than the calculated values for the transpiration measurements and approximately 10^2-10^6 lower for the effusion measurements.

Table VIII

Equilibrium Constants for Magnesium Nitride Vaporization

Temp. °K	$-\log_{10}K_{(p)}$
1100	15.00 (15.3)
1200	11.50 (11.7)
1300	8.53 (8.9)
1400	6.01 (6.3)
1500	3.83 (4.2)

Lithium Carbide

One well-defined compound, Li_2C_2, is known. Mixtures of lithium and carbon were investigated by Fedorov and Mezh-Tszen Su [27]. They measured the vapor pressure of mixtures containing 15 atomic % C in the range 1063°-1223°K. They reported a eutectic between lithium and Li_2C_2; the eutectic composition and temperature they gave (less than 1 atomic % C; 438°K) are apparently not inconsistent with each other on the basis of what one would estimate roughly from the melting point (454°K) and heat of fusion of pure lithium. From thermal analyses and x-ray powder analysis they deduced that Li_2C_2 is polymorphous, with transition temperatures of approximately 683°, 713°, and 833°K. The heat contents of the compound given in this report (Table 2-33) were entirely estimated, and do not reflect any transitions.

Using the heat of formation of Li_2C_2 given in Chapter A2 (ΔHf°_{298} = -14.2 ± 2 kcal/mole) and the pertinent free-energy functions, the decomposition pressures at various temperatures were calculated for the reactions

$$Li_2C_2(c) = 2Li(g) + 2C(c)$$

and

$$Li_2C_2(c) = Li_2(g) + 2C(c),$$

and are given in the following table.

Table IX

Calculated Decomposition Pressures of Li_2C_2 (in atmos.)

Temp. (°K)	Li(g)	$Li_2(g)$	Total Pressure
1000	$5.9x10^{-5}$	$1.0x10^{-7}$	$6.0x10^{-5}$
1100	$4.4x10^{-4}$	$1.6x10^{-6}$	$4.4x10^{-4}$
1200	$2.2x10^{-3}$	$1.5x10^{-5}$	$2.3x10^{-3}$
1300	$8.9x10^{-3}$	$9.6x10^{-5}$	$9.0x10^{-3}$
1400	$2.9x10^{-2}$	$4.8x10^{-4}$	$3.0x10^{-3}$
1500	$8.0x10^{-2}$	$1.9x10^{-3}$	$8.2x10^{-2}$
1600	0.20	$6.3x10^{-3}$	0.20
1700	0.42	$1.7x10^{-2}$	0.43
1800	0.82	$4.3x10^{-2}$	0.86
1900	1.5	$9.5x10^{-2}$	1.6
2000	2.6	0.20	2.8

These pressures are considerably below the vapor pressure of liquid lithium. In fact, for the reaction

$$Li_2C_2(c) = 2Li(l) + 2C(c)$$

it is calculated that ΔF_{1000} = 11.0 kcal and ΔF_{2000} = 8.6 kcal. Hence liquid lithium will not appear unless the solubility of Li_2C_2 in Li becomes considerable, which the eutectic data of Fedorov and Mezn-Tszen Su suggest may occur at higher temperatures.

Lithium Nitride

One solid nitride, Li_3N, is known to exist. Experimental data on vapor species and pressures are not available. The decomposition pressures of Li_3N were calculated at various temperatures from the heat of formation given in Chapter A2 (ΔHf°_{298} = -47.5 ± 2 kcal/mole) and the pertinent free-energy functions.*

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*In these calculations the free-energy functions of Li_3N in Table 2-28 and of liquid lithium in Table 2-21, NBS Report 6484, were extended above 1200°K by assuming constant heat capacities of 29.2 and 6.85 cal $mole^{-1}$ deg K^{-1} respectively.

The partial and total pressures, which were calculated for decomposition to the elements in vacuo or in an inert atmosphere, are given in the following table.

Table X

Decomposition Pressures of Li_3N in Vacuo (atmos.)

Temp. °K	Li(g)	Li_2(g)	N_2(g)	Total Pressure
700	4.0×10^{-8}	1.5×10^{-11}	6.6×10^{-9}	4.7×10^{-8}
800	2.5×10^{-6}	5.1×10^{-9}	4.3×10^{-7}	2.9×10^{-6}
900	5.9×10^{-5}	4.5×10^{-7}	1.0×10^{-5}	7.0×10^{-5}
1000	7.4×10^{-4}	1.6×10^{-5}	1.3×10^{-4}	8.9×10^{-4}
1100	5.0×10^{-3}	2.1×10^{-4}	2.5×10^{-3}	7.7×10^{-3}
1200	2.0×10^{-2}	1.2×10^{-3}	0.10	0.12
1300	6.4×10^{-2}	4.9×10^{-3}	2.0	2.1
1400	0.17	1.6×10^{-2}	28.	28.
1500	0.40	4.7×10^{-2}	270.	270.

If the calculations were made assuming only gaseous decomposition products, the sum of the partial pressures of Li and Li_2 would fall below the vapor pressure of liquid lithium below some temperature between 1000° and 1100°K. However, the sum of the partial pressures exceeds the vapor pressure of liquid lithium at all higher temperatures; therefore, in those cases the pressures of Li and Li_2 must be reduced to the vapor-pressure values for liquid Li, with a corresponding adjustment of the nitrogen partial pressures. The conclusion is that as the temperature of the nitride is raised, liquid lithium makes its appearance at some temperature between 1000° and 1100°K in vacuo (some 200° higher in an atmosphere of nitrogen at 1 atm pressure). However, liquid lithium will appear at much lower temperatures if it is capable of dissolving considerable proportions of the nitride, a possibility which has been ignored in the above computations. If such solution occurred all the remaining solid nitride would eventually dissolve before decomposition is complete. Even at equilibrium, such systems, originally single compounds, eventually depend on variables other than temperature and total pressure, and offer one possible explanation of reports of conflicting temperatures of decomposition and "fusion" often found in the literature.

Titanium Carbide

There is only one solid phase in the TiC system, the cubic compound TiC. Becker [28] gives the melting point as 3137 ± 90°C which is in close agreement with the values of 3160°C given by Friederich and Sittig [29] and 3140°C given by Agle and Moers [30]. Brewer et al [11] give a value of 3177°C, and Schwarzkopf and Kieffer [31] cite a melting point as high as 3250°C. The melting point adopted for this report is that of Becker, viz., 3410°K.

TiC vaporizes principally by dissociation to the elements. Chupka et al [4] investigated the vapor species with a mass spectrometer.

At about 2500°K, the partial pressure of Ti, the major vapor species was 8.6×10^{-7} atmos., and the relative abundance of Ti : C : C_2 : C_3 was found to be 20 : 1 : 0.5 : 2. The dissociation pressure is currently being measured by N.A. Gokcen at the Univ. of Pennsylvania, using the Knudsen effusion technique.

Using the tables in the Appendix, and the heats of formations given in Chapter A2 and reference [32], dissociation pressures for TiC have been calculated in accordance with the equations:

$$TiC(c) = Ti(g) + C(c)$$

$$TiC(l) = Ti(g) + C(c)$$

The result of these calculations is given in Table XI, where, because the probable occurrence of C, C_2, and C_3 gaseous species has been ignored, the pressures represent upper-limiting values compared with those for vaporization of TiC in which these gaseous species but no C(c) are formed. The disparity between the tabulated titanium pressures and the above value given by Chupka et al may be partially accounted for in terms of the carbon gas species.

Table XI

Dissociation Pressures for Titanium Carbide

Temp. °K	Log K	P_{Ti} (atmos)
2000	-9.043	9.07×10^{-10}
2500	-5.701	1.99×10^{-6}
3000	-3.482	3.30×10^{-4}
3250	-2.600	2.51×10^{-3}
3500	-1.932	1.17×10^{-2}

TiC reacts with both O_2 and N_2 in accordance with the following equations:

$$TiC(c) + \frac{3}{2}O_2(g) = TiO_2(c) + CO(g)$$

$$TiC(c) + \frac{1}{2}N_2(g) = TiN(c) + C(c)$$

Below 1000-1100°C the oxide may form a protective skin on the carbide; however, at higher temperatures the oxidation occurs more freely.

At low temperature titanium nitride is more stable than the carbide, but the relative stabilities are reversed at higher temperatures. The situation is further complicated experimentally because the nitride and carbide systems form complete solid solutions [33]. In Table XII calculated equilibrium pressures for the above reaction of TiC with N_2 are presented. The sources previously cited were used for the calculations.

Table XII

Reaction of Titanium Carbide with Nitrogen

Temp. °K	P_{N_2} (atmos)	Temp. °K	P_{N_2} (atmos)
1000	5.01×10^{-8}	1880	1.00
1200	2.12×10^{-5}	2000	2.94
1400	1.53×10^{-3}	2500	89.1
1600	3.68×10^{-2}	3000	815.
1800	4.21×10^{-1}		

The calculated pressures indicate that 1880°K is the temperature at which the relative stabilities are reversed, under one atmosphere of nitrogen pressure.

Titanium Nitride

There is only one well-established solid phase in the Ti-N system, the cubic TiN, which has a wide homogeneity range. The melting point is given as 2930°C by Friederich and Sittig [34] and 2950°C by Agte and Moers [30]; a melting point of 2927°C has been adopted in this report.

Hoch, Dingledy and Johnston [35] measured the vaporization of TiN over the temperature range 1987-2241°K using the Knudsen effusion method. They assumed the compound vaporized by decomposition to the elements, and represented their data by the following equations:

$$\log K_p = -\frac{41789}{T} - 0.60 \times 10^{-4} T + 12.245$$

$$\log P_{Ti} = -\frac{27859}{T} - 0.40 \times 10^{-4} T + 8.263$$

$$\log P_{N_2} = -\frac{27859}{T} - 0.40 \times 10^{-4} T + 7.963.$$

The data lead to a ΔHf°_{298}(TiN) of -79.4 kcals/mole.

Using the heat of formation of -80.5 kcals/mole selected in Chapter A2 and the tables of thermodynamic functions given in the Appendix, the vapor pressures given in Table XIII have been calculated. Sources previously cited were used for the thermal functions for titanium and nitrogen. Pressures derived from the above equations of Hoch et al are shown in the table for comparison purposes. The small disagreement between the two sets of pressures is attributable to slight differences in the thermal constants and tables of free energy functions employed.

Table XIII

Dissociation Pressures for Titanium Nitride

	Calculated			Measured[35]
Temp. °K	P_{Ti} atmos	P_{N_2} atmos	P_{Total} atmos	P_{Total} atmos
1000	2.40×10^{-20}	1.20×10^{-20}	3.60×10^{-20}	
1400	2.00×10^{-12}	1.00×10^{-12}	3.00×10^{-12}	
1750	1.74×10^{-8}	8.71×10^{-9}	2.61×10^{-8}	2.83×10^{-8}
2000	1.66×10^{-6}	8.30×10^{-7}	2.49×10^{-6}	2.69×10^{-6}
2250	5.24×10^{-5}	2.62×10^{-5}	7.86×10^{-5}	9.29×10^{-5}
2500	8.56×10^{-4}	4.28×10^{-4}	1.28×10^{-3}	1.57×10^{-3}
3000	5.26×10^{-2}	2.63×10^{-2}	7.89×10^{-2}	
3200	0.202	0.101	0.303	
3500	0.912	0.456	1.37	
4000	6.66	3.33	10.0	

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PART B

NEW LIGHT-ELEMENT DATA FROM THE NATIONAL BUREAU OF STANDARDS

Chapter B1

HEATS OF FORMATION OF PERCHLORATES

W. H. Johnson and A. A. Gilliland

A. Heat of Formation of Potassium Perchlorate.

Calorimetric measurements were made of the heat of decomposition of $KClO_4(c)$ into $KCl(c)$ and $O_2(g)$. The decomposition was carried out in an oxygen bomb in which a crucible, containing approximately 2 g of $KClO_4$, was placed directly over a second crucible containing a pellet of benzoic acid. The bomb was charged with 30 atmospheres of moist oxygen and placed in an isothermal-jacket calorimeter. The heat evolved by combustion of the benzoic acid was sufficient to decompose the $KClO_4$ leaving fused KCl in the crucible. Separate experiments were performed to determine the ignition energy and the energy equivalent of the calorimeter system. The quantities of CO_2 and of Cl^- were determined in each case. The results of the experiments may be represented by the equation:

$$KClO_4(c) \longrightarrow KCl(c) + 2O_2(g),$$

$$\Delta H°(25°C) = -0.96 \pm 0.10 \text{ kcal/mole.}$$

Combination of this value with -104.18 kcal/mole for (NBS Circular 500) the heat of formation of KCl(c) yields:

$$KClO_4(c), \quad \Delta Hf°(25°C) = -103.22 \pm 0.20 \text{ kcal/mole.}$$

B. Heats of Formation of Lithium Perchlorate and of Ammonium Perchlorate.

Calorimetric determinations of the heats of formation of $LiClO_4$ and of NH_4ClO_4 were made by a heat-of-solution method in which the anhydrous perchlorate sample was introduced into a saturated solution of $KClO_4$ containing an excess of KCl. The $KClO_4$ produced by interaction between the $LiClO_4$ (or NH_4ClO_4) with the KCl was precipitated and the LiCl (or NH_4Cl) remained in solution. Separate experiments were performed to determine the heats of solution of KCl, LiCl, and NH_4Cl in the $KClO_4$-KCl-H_2O solution. The energy equivalent of the calorimeter containing the $KClO_4$-KCl-H_2O solution was determined by introducing an accurately measured quantity of electrical energy and noting the resulting rise in temperature.

These data may be combined to give the following processes

$$\mathrm{LiClO_{4(c)} + KCl_{(c)} = LiCl_{(c)} + KClO_{4(c)}}$$
$$\Delta H^\circ(25^\circ C) = -5.86 \pm 0.06 \text{ kcal/mole},$$

$$\mathrm{NH_4ClO_{4(c)} + KCl_{(c)} = NH_4Cl_{(c)} + KClO_{4(c)}},$$
$$\Delta H^\circ(25^\circ C) = -3.69 \pm 0.05 \text{ kcal/mole}.$$

The combination of these values with the heat of formation of $KClO_4$ and with values from NBS Circular 500 for the heats of formation of KCl, LiCl, and NH_4Cl gives the following heats of formation:

$$\mathrm{LiClO_{4(c)}}, \quad \Delta Hf^\circ(25^\circ C) = -90.88 \pm 0.20 \text{ kcal/mole}.$$

$$\mathrm{NH_4ClO_{4(c)}}, \quad \Delta Hf^\circ(25^\circ C) = -70.73 \pm 0.20 \text{ kcal/mole}.$$

The assigned uncertainties include estimates of the uncertainties in the heats of formation of KCl, LiCl and NH_4Cl.

Chapter B 2

LIGHT METAL HYDRIDES

M. Hellmann, T. W. Mears, C. L. Stanley

The primary task in this phase continued to be a study of the preparation and properties of beryllium and aluminum hydrides and their derivatives. Activities consisted of attempts to improve the synthesis of beryllium hydride and studies of the vapor pressure and vapor phase dissociation of aluminum hydride trimethylamine complexes. No experimental work was done on the synthesis of pure aluminum hydride as such studies are in progress in several laboratories and it was felt that unnecessary duplication should be avoided. However, approximate calculations on the thermodynamic feasibility of possible reactions leading to the formation of AlH_3 were performed. Increased interest in Al - N and Be-N systems prompted a brief literature survey of systems containing AlH_3 and BeH_2 with NH_3. A more detailed discussion of these various phases is given below.

Synthesis of Beryllium Hydride.

Since both theoretical and experimental work performed elsewhere [1,2] made the synthesis of beryllium hydride by direct union of the elements seem improbable, the preparation of this material by a modification of the method of Head, Holley and Rabideau [3] was undertaken. A preliminary run was made using conventional apparatus in order to study the materials obtained and their handling. A sample of t-butylberyllium dietherate was obtained in low yield. This material was not pyrophoric, although it reacted rapidly with water and with the humid summer air.

A second apparatus was built such that once the Grignard reagent was prepared and the beryllium chloride added, the organometallic compounds and the hydrides were handled in a closed apparatus. During distillations the organometallic compounds passed through no stopcocks nor came into contact with any grease. Successive sections of apparatus were opened by means of break-off tips and the used sections were sealed off when no longer needed. The heating was automatically controlled so that the long distillation periods could be allowed to run overnight without attention. Using this apparatus, yields of 18 to 23 g (66-85%) of di-t-butylberyllium dietherate were prepared.

The original pyrolysis was attempted by slowly raising the temperature to 200°C under a full vacuum. Under these conditions the t-butylberyllium refluxed violently and it was doubtful whether the temperature of the organometallic compound came close to 200°. These conditions were repeated using a nitrogen pressure of 40 mm Hg, but the reflux reached the flood point when the bath reached 160° C. The t-butylberyllium stood under 40 mm of nitrogen over the week-end. The pyrolysis was then attempted under 60 mm Hg pressure of nitrogen and the decomposition proceeded nicely at 125° C. This material was analyzed for beryllium by hydrolysis in acid, precipitation of the beryllium as the 8-hydroxyquinolinolate, which was ignited to beryllium oxide. The gases evolved upon acid hydrolysis were measured. The assay of beryllium hydride calculated from these data was about 50 wt. percent.

Additional runs were made in a similar manner, the temperature of the bath being raised slowly to 200° C and held there for one hour. The nitrogen pressure was 60 mm Hg. The beryllium hydride assay on the product of these runs was about 80 wt. percent. The material prepared was a very light powder which picked up an electrostatic charge quite easily. It was relatively stable to moisture and heat. It is thought that a stock of beryllium hydride may be successfully stored under vacuum in a deep-freezer.

Apparatus is being constructed for the determination of the decomposition temperatures as a function of pressure. If this is successful, it will be extended to the pressure-temperature-composition data on the beryllium-hydrogen-beryllium hydride system.

Vapor Pressure and Dissociation Measurements of Aluminum Hydride - Trimethylamine Complexes.

Samples of $AlH_3.NMe_3$ and $AlH_3.2NMe_3$ were obtained from Dr. C. J. Marsel of New York University. The vapor pressure measurements on these materials were performed and rechecked by using fresh samples. Satisfactory results were obtained for $AlH_3.2NMe_3$ but the results for $AlH_3.NMe_3$ could not be duplicated in later runs. Consequently the latter results will not be presented at this time until they have been rechecked with pure samples. Table 1 presents vapor pressure data for $AlH_3.2NMe_3$. These values are averages from several independent determinations. Fitting all data to a graph by the method of least squares the following equation was obtained:

$$\log p = \frac{-3,230}{T} + 11.15 \quad \text{(temp. range 20° - 60° C)}$$

Table 1

Vapor Pressure of $AlH_3 . 2NMe_3$

T°C	P_{mm}
20.0	1.45
25.0	2.1
30.0	3.05
35.0	4.65
40.0	6.65
45.0	9.7
50.0	14.35
55.0	20.5
60.0	29.85
65.0	42.75
70.0	62.35

ΔH_s = 14,800 ± 500 cal from 20° - 60°C

The heat of sublimation calculated from this equation is ΔH_s = 14,800 ± 500 cal. The last two values on the table were omitted in the calculations because of dissociation occurring at these temperatures.

The relationships between the different complexes of aluminum hydride with trimethylamine were investigated further by attempting to study existing equilibria and determining the accompanying thermodynamic changes.

The first equilibrium investigated was

$$AlH_3.2NMe_3\ (g) \rightleftharpoons AlH_3.NMe_3\ (g) + NMe_3\ (g)$$

The method used to study this reaction was essentially that described by Brown, Taylor and Gerstein [6]. By this procedure a small amount of sample is completely vaporized into a closed system containing a manometer. Pressure readings are then taken at different temperatures. The size of the sample and apparatus have to be chosen in such a way that complete vaporization occurs prior to any dissociation. From the total pressure P_T and the initial pressure P_i (calculated by assuming no dissociation) the degree of dissociation, α, can be calculated.

$$\alpha = \frac{P_T - P_i}{P_i} .$$

The equilibrium constant K can then be calculated from α and P

$$K = \frac{\alpha^2}{1-\alpha} \times P_i \quad \text{or} \quad \frac{\alpha^2}{1-\alpha^2} \times P_T$$

Three separate runs were performed on different samples. The consistency of the results was not sufficiently good to give reliable data but a rough order of magnitude of the thermodynamic constants could be established. The discrepancies can most likely be explained by the fact that the following assumptions had to be made prior to using the data:

1. The original material is pure. The material was resublimed and quickly transferred under nitrogen to the measuring system. The vapor pressure checked well with the original curve but the presence of small impurities, notably $AlH_3.NMe_3$ might have a sizeable effect on the results.

2. No dissociation occurs prior to complete vaporization. This assumption is necessary for calculating P_i, the initial pressure. All samples were vaporized below 60°C but it is possible that some dissociation occurs below this temperature.

3. No dissociation of $AlH_3.NMe_3$ occurs within the range measured. This will be checked by separate measurements on this compound but judging from the individual curves this effect is not likely to be significant.

Table 2

Dissociation Data for $AlH_3 \cdot 2NMe_3$

Data No.	Temp. °C	$P_{T(obs)}$ mm	$P_{i(calc)}$ mm	α	$K \times 10^3$ atm.	Log K = $-A/T+B$ A	B	ΔH Kcal/ mole	ΔS e.u./ mole	$\Delta F_{80°}$ cal/ mole
1	69.9	33.70	26.45	0.274	3.60	3,128	6.709	14.31	30.7	3,470
	75.0	35.60	26.85	0.326	5.57					
	80.0	37.15	27.20	0.366	7.56					
	85.1	38.70	27.60	0.402	9.82					
	90.1	40.25	28.00	0.438	12.5					
	95.0	41.70	28.35	0.471	15.6					
2	70.0	17.70	14.75	0.242	1.45	2,554	4.646	11.69	21.3	4,170
	75.8	18.50	14.50	0.276	2.01					
	79.8	19.40	14.65	0.324	2.99					
	81.1	19.55	14.70	0.330	3.13					
	86.5	19.95	14.95	0.334	3.30					
	89.3	20.50	15.05	0.362	4.07					
	93.4	20.90	15.25	0.370	4.36					
3	70.0	16.20	13.40	0.209	0.974	3,264	6.526	14.94	29.9	4,390
	75.0	17.00	13.60	0.250	1.49					
	80.0	17.70	13.80	0.283	2.03					
	85.0	18.25	13.95	0.308	2.52					
	90.0	19.05	14.15	0.346	3.41					

The accuracy of the measurements might be improved by more sensitive temperature control and the use of a more sensitive cathetometer for reading pressures. However, the most serious limitation lies in the fact that all measurements had to be performed at fairly low pressures and under conditions of relatively low degrees of dissociation which inherently increase the mathematical errors. However, the data are presented in Table 2 in order to show the approximate magnitudes of K, ΔH, ΔF and ΔS. The data were calculated by fitting the $\log K = -\frac{A}{T} + B$ plots by the least squares method. ΔH appears to be about 14 kcal, ΔS around 30 e.u. and ΔF about 4,000 cal. These results will be rechecked with more sensitive equipment and measurements on $AlH_3.NMe_3$ will be resumed.

Literature Survey of Systems Containing Aluminum Hydride and Beryllium Hydride with Ammonia.

Increased interest in the nitrides of light metals prompted this brief survey of systems containing the metal, nitrogen and hydrogen.

a. Beryllium hydride - ammonia systems. The only reference to such a system [4] describes an attempt to react BeH_2 with NH_3. These authors believe that hydrogen was evolved. By analogy with similar systems it is conceivable that a complex can be formed at low temperatures which decomposes irreversibly with the loss of hydrogen upon raising the temperature.

b. Aluminum hydride - ammonia systems. The work of Wiberg and coworkers [7] was the only reference found in the literature. Their studies indicate that complexes are formed at low temperatures which decompose with loss of hydrogen to polymeric materials containing Al, N, and H. Compositions approaching that of aluminum nitride are obtained at elevated temperatures. The different reactions and their temperature dependence are illustrated by the following equations:

1. $$AlH_3 + NH_3 \xrightarrow{-80°} AlH_3.NH_3 \xrightarrow[-H_2]{-40° \text{ to } -30°} AlH_2(NH_2) \xrightarrow[-H_2]{\text{room temp.}}$$
$$\longrightarrow [AlH(NH)]_x \xrightarrow{100 - 150°} [AlH_{0.23}\,NH_{0.23}]_x$$

2. $$\begin{tikzcd} AlH_3 + xs.NH_3 \arrow[r, "-196°"] \arrow[dr, "-50°C", "-2H_2"'] & AlH_3.2NH_3(?) \arrow[r, "-80°", "-H_2"'] & AlH_2(NH_2).NH_3 \\ & AlH(NH_2)_2 \arrow[r, "\text{room temp.}", "-H_2"'] & [Al(NH)(NH_2)]_x \end{tikzcd}$$

3. $$AlH(NH_2)_2 + NH_3 \xrightarrow[-H_2]{-78° - 30°} Al(NH_2)_3$$

Theoretical Considerations of New Approaches to the Synthesis of Aluminum Hydride.

The difficulties inherent in the currently used methods for preparing aluminum hydride have been described in our previous reports. The main problems arise from the fact that the syntheses have been performed in solvents which are difficult to remove. It would, therefore, be desirable to devise methods in which the synthesis could be performed either without a solvent or in an inert medium. One such obvious approach would be the direct union of the elements $Al + 1\frac{1}{2} H_2 \longrightarrow AlH_3$. Rough calculations indicate, however, that the ΔF of this reaction would be positive and of the order of approximately 10,000 cal. Thus this reaction does not appear to be thermodynamically feasible. Another approach might be the hydrogenation of an aluminum alkyl. This method was actually used in the first reported synthesis of AlH_3 by Stecher and Wiberg [8] who treated trimethyl aluminum with hydrogen in a low pressure discharge tube. They obtained Me_2AlH, $MeAlH_2$ and AlH_3, the latter being isolated as the trimethylamine complex. Recently magnesium hydride was synthesized by high pressure hydrogenation of diethyl magnesium [9]. It is, therefore, of some interest to investigate the thermodynamic feasibility of the following reaction:

$$Al(CH_3)_{3(l)} + 3H_{2(g)} \longrightarrow AlH_{3(c)} + 3CH_{4}(g)$$

The following calculations are necessarily very rough as the data for some of the above compounds are not known. The value for $\Delta H_{AlH_3(c)}$ was taken as -3 ± 10 kcal which is a rough approximation taken from data on impure materials.

$$\Delta H^\circ_{react} = 3\Delta H_f CH_4 + \Delta H_f AlH_3 - 3\Delta H_f H_2 - \Delta H_f Al(CH_3)_3$$

$$= 3x(-17.9) + (-3) - (0) - (-26.9) = -30 \pm 10 \text{ kcal}$$

$$\Delta S^\circ_{react} = 3(S^\circ_{CH_4} - S^\circ_{H_2}) + S^\circ_{AlH_3(c)} - S^\circ_{Al(CH_3)_3\,(l)}$$

$$S^\circ_{CH_4} - S^\circ_{H_2} = 44.5 - 31.2 = 13.3$$

$S^\circ_{AlH_3(c)} - S^\circ_{Al(CH_3)_3(l)}$ to a very rough approximation $S^\circ_{C_6H_6(c)} - S^\circ_{C_6H_6(l)}$

$$= -\Delta Sm_{C_6H_6} = -8.4$$

$$\Delta S^\circ_{react} = 3 \times 13.13 - 8.4 = \sim 32 \text{ cal/deg-mole}$$

$$\Delta F^\circ_{react} = \Delta H^\circ - T\,\Delta S^\circ = -30{,}000 - 298 \times 32 = -40{,}000 \pm 20{,}000 \text{ cal.}$$

Although the value for ΔS may be considerably in error it can readily be seen that a much smaller entropy change would still give a substantially negative value for ΔF° thus demonstrating the feasibility of the reaction. A recent paper [10] described the hydrogenation of triethylaluminum. The reaction proceeded readily in the presence of Mg as catalyst but only one ethyl group was replaced yielding Et_2AlH as product. The authors ascribed this to steric effects. It may be possible that more severe conditions such as very high pressures or the use of atomic hydrogen may drive this reaction towards complete substitution.

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PART C

NEW LIGHT-ELEMENT DATA REPORTED BY OTHER INSTITUTIONS

Chapter C 1

ENTROPIES OF SOME SUBSTANCES AT 298.15°K

George T. Furukawa and Jeanette Henning Piccirelli

There are presented in this chapter some new heat-capacity data that have become available on substances that were examined earlier in NBS Report No. 6484. In none of these cases have the original heat-capacity data been re-analyzed and the thermodynamic properties re-calculated. The results of the original investigators' analysis and calculation have been tentatively accepted.

1. Lithium, Li, 6.940

Recently Martin [8] completed a series of heat-capacity measurements (20° to 300°K) on lithium and obtained $S^\circ_{298} = 6.95$ e.u. (atomic weight = 6.945). The value given in NBS Report No. 6484 is 6.777 e.u. (atomic weight = 6.940), which was obtained by adjusting upward the heat-capacity results reported by Simon and Swain [9] (15° to 300°K) on the basis of the deviation of values on Al_2O_3 given in the same paper from those reported by Furukawa, Douglas, McCoskey, and Ginnings [4]. These converted values were analyzed along with those results obtained by Roberts [9] (1.5° to 20°K) and by Douglas, Epstein, Dever, and Howland [1] (0° to 900°C). The difference between the S°_{298} value given in NBS Report 6484 and the new value obtained by Martin [8] arises primarily from the difference in the entropy below 120°K in the region of martensitic transformation [3]. The transformation has long relaxation times and dependence on previous history of the sample. For this reason there will be expected some uncertainty in any heat measurements in this region. The value $S^\circ_{298} = 6.95$ e.u. obtained by Martin [8] was accepted.

2. Lithium Chloride, LiCl, 42.397

Hatton, Sinke, and Stull [6] recently determined the heat capacity of $LiC\ell$ (12° to 323°K) and obtained $S^\circ_{298} = 14.23 \pm 0.05$ e.u. Kelley [7] listed $S^\circ_{298} = 13.9 \pm 0.5$ e.u. based on heat and free energy of reaction. NBS Report No. 6484 lists $S^\circ_{298} = 12.322 \pm 0.500$ e.u. based on analysis of three measurements of the mean heat capacity between -188° and 96°C by Slonim and Hüttig [11] and of the high temperature enthalpy measurements by Douglas, Harman and Dever [2]. The value of $S^\circ_{298} = 14.23 \pm 0.05$ e.u. obtained by Hatton *et al.* [6] based on considerably more extensive experimental measurements is recommended.

3. Aluminum Chloride, $A\ell C\ell_3$, 133.351

Hatton, Sinke, and Stull [5] recently determined also the heat capacity of $A\ell C\ell_3$ (15° to 320°K) and obtained $S^o_{298} = 26.63 \pm 0.10$ e.u. No experimental data were previously available on this substance. NBS Report No. 6484 lists $S^o_{298} = 22.430$ e.u. calculated from vapor pressure data. The experimental $S^o_{298} = 26.63 \pm 0.10$ e.u. was accepted.

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Chapter C 2

NEW VALUES OF HEATS OF FORMATION

George T. Armstrong and L. A. Krieger

A few slight modifications or confirmations of previously reported values are listed below.

1. AlF (g). $\Delta H^\circ_{f_{298}}$ = -61.3 ± 2.0 kcal/mole.

New results reported by Barrow and Witt [1], and by Gross, Hayman and Levi [2] on the equilibrium between AlF_3 and AlF, have reduced the uncertainty in the heat of formation.

2. AlF_3 (c) $\Delta H_{f_{298}}$ = -356.2 ± 2.0 kcal/mole.

New results reported by Gross, Hayman and Levi [2] on the reaction of PbF_2, NaF, and Al, leading to $NaAlF_6$ have permitted a value of AlF_3(c) to be derived without reference to the heat of formation of PbF_2. The heat of formation of cryolite is from Coughlin [3].

3. AlN(c) ΔH°_f See Chapter A2.

4. AlC(g) ΔH°_f See Chapter A2.

5. Al_2C_2(g) ΔH°_f See Chapter A2.

6. Al_4C_3(c) ΔH°_f See Chapter A2.

7. BeF_2(c) $\Delta H^\circ_{f_{298}}$ = -241.2 ± 2.0 kcal/mole.

The paper by Kolesov, Popov and Skuratov [4], has been published, slightly modifying their heat of solution for BeF_2, previously reported informally [5].

8. Li_2O(c) $\Delta H^\circ_{f_{298}}$ = -142.4 ± 0.5

The paper by Kolesov, Skuratov, and Zaikin [6], has been published, confirming their heat of solution of Li_2O(c) previously reported informally [7].

Additional data recently published on light element compounds, but not considered in the above discussions.

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PART D

ERRATA IN NBS REPORT 6484

Heats of Formation

1.	Al_2C_2 (g)	See Chapter A2 of this report.
2.	BeF_2 (g)	$\Delta H^\circ_{f_{298}} = -182.8$ kcal/mole.
3.	BeC_2 (g)	See Chapter A2 of this report.
4.	MgH_2 (c)	$\Delta H^\circ_{f_{298}} = -18 \pm 5$ kcal/mole.

The dissociation pressure of MgH_2 was determined by F. H. Ellinger, C. E. Holley, Jr., B. B. McInteer, D. Povone, R. M. Potter, E. Slaritzky, and W. H. Zachariasen near 450°C. They derived a heat of dissociation of +16 kcal/mole at 450°C, which gives the above value for the heat of formation at 298°K when adjusted for the temperature change.

APPENDIX 1

IDEAL-GAS THERMODYNAMIC FUNCTIONS

Table 1-66. Thermodynamic Functions for N_2 (gas)

T °K	$\frac{-(F^o-H_0^o)}{T}$	$\frac{H^o-H_0^o}{T}$	S^o	$H^o-H_0^o$	C_p^o
50.	26.425	6.917	33.342	345.8	6.956
100.	31.228	6.936	38.164	693.6	6.956
150.	34.042	6.943	40.985	1041.4	6.957
200.	36.039	6.947	42.986	1389.4	6.957
250.	37.589	6.949	44.538	1737.2	6.958
273.15	38.205	6.949	45.154	1898.1	6.959
298.15	38.813	6.950	45.763	2072.1	6.961
300.	38.857	6.950	45.807	2085.0	6.961
350.	39.928	6.953	46.881	2433.6	6.971
400.	40.858	6.955	47.813	2782.0	6.991
450.	41.677	6.961	48.638	3132.4	7.024
500.	42.410	6.971	49.381	3485.5	7.070
550.	43.076	6.981	50.057	3839.6	7.128
600.	43.684	6.996	50.680	4197.6	7.197
650.	44.244	7.015	51.259	4559.8	7.272
700.	44.765	7.036	51.801	4925.2	7.351
750.	45.252	7.059	52.311	5294.2	7.432
800.	45.707	7.085	52.792	5668.0	7.513
850.	46.138	7.113	53.251	6046.0	7.593
900.	46.546	7.141	53.687	6424.9	7.670
950.	46.933	7.171	54.104	6812.4	7.744
1000.	47.301	7.202	54.503	7202.0	7.815
1050.	47.653	7.233	54.886	7594.6	7.882
1100.	47.990	7.264	55.254	7990.4	7.946
1150.	48.314	7.294	55.608	8388.1	8.005
1200.	48.624	7.326	55.950	8791.2	8.061
1250.	48.924	7.356	56.280	9195.0	8.113
1300.	49.214	7.386	56.600	9601.8	8.162
1350.	49.493	7.415	56.908	10010.	8.208
1400.	49.763	7.445	57.208	10423.	8.251
1450.	50.025	7.473	57.498	10836.	8.291
1500.	50.280	7.500	57.780	11250.	8.328
1550.	50.526	7.527	58.053	11667.	8.364
1600.	50.765	7.555	58.320	12088.	8.397
1650.	50.997	7.581	58.578	12509.	8.428
1700.	51.224	7.606	58.830	12930.	8.457
1750.	51.444	7.632	59.076	13356.	8.484
1800.	51.661	7.654	59.315	13777.	8.510
1850.	51.869	7.680	59.549	14208.	8.534
1900.	52.076	7.701	59.777	14632.	8.556
1950.	52.275	7.724	59.999	15062.	8.578
2000.	52.472	7.745	60.217	15490.	8.598
2050.	52.662	7.767	60.429	15922.	8.618
2100.	52.851	7.786	60.637	16351.	8.636
2150.	53.034	7.806	60.840	16783.	8.653
2200.	53.213	7.827	61.040	17219.	8.670

The tables are in units of calories, moles and °K. See reverse side for conversion factors to other units. The molecular weight = 28.016

Table 1-66. Thermodynamic Functions for N_2 (gas) - Continued

T °K	$\frac{-(F^0-H_0^0)}{T}$	$\frac{H^0-H_0^0}{T}$	S^0	$H^0-H_0^0$	C_p^0
2250.	53.390	7.844	61.234	17649.	8.685
2300.	53.563	7.863	61.426	18085.	8.700
2350.	53.732	7.881	61.613	18520.	8.714
2400.	53.898	7.898	61.796	18955.	8.728
2450.	54.061	7.916	61.977	19394.	8.741
2500.	54.220	7.933	62.153	19832.	8.753
2550.	54.377	7.950	62.327	20272.	8.765
2600.	54.532	7.965	62.497	20709.	8.776
2650.	54.683	7.981	62.664	21149.	8.787
2700.	54.834	7.995	62.829	21586.	8.798
2750.	54.982	8.008	62.990	22022.	8.808
2800.	55.125	8.024	63.149	22467.	8.817
2850.	55.268	8.037	63.305	22905.	8.826
2900.	55.407	8.053	63.460	23354.	8.835
2950.	55.544	8.066	63.610	23795.	8.844
3000.	55.681	8.077	63.758	24231.	8.852
3100.	55.945	8.104	64.049	25122.	8.868
3200.	56.204	8.127	64.331	26006.	8.883
3300.	56.454	8.150	64.604	26895.	8.897
3400.	56.697	8.173	64.870	27788.	8.910
3500.	56.935	8.194	65.129	28679.	8.923
3600.	57.166	8.214	65.380	29570.	8.935
3700.	57.392	8.233	65.625	30462.	8.946
3800.	57.611	8.253	65.864	31361.	8.957
3900.	57.825	8.272	66.097	32261.	8.967
4000.	58.036	8.288	66.324	33152.	8.977
4100.	58.241	8.304	66.545	34046.	8.987
4200.	58.441	8.321	66.762	34948.	8.996
4300.	58.636	8.338	66.974	35853.	9.005
4400.	58.829	8.352	67.181	36749.	9.013
4500.	59.016	8.368	67.384	37656.	9.022
4600.	59.200	8.382	67.582	38557.	9.030
4700.	59.381	8.395	67.776	39456.	9.038
4800.	59.558	8.409	67.967	40363.	9.046
4900.	59.731	8.423	68.154	41273.	9.054
5000.	59.902	8.434	68.336	42170.	9.062

CONVERSION FACTORS

To Convert Tabulated Values to Quantities Having the Dimensions Indicated Below	Multiply By
cal g^{-1} °K^{-1} (or °C^{-1})	0.035694
joules g^{-1} °K^{-1} (or °C^{-1})	0.149343
Btu lb^{-1} °R^{-1} (or °F^{-1})	0.035670

APPENDIX 2

THERMODYNAMIC FUNCTIONS OF SOLIDS AND LIQUIDS

High-Temperature Analysis: Andrew C. Victor and Thomas B. Douglas
Low-Temperature Analysis: George T. Furukawa, Martin L. Reilly, and Jeanette Henning Piccirelli
Analysis of Graphite: William H. Evans

The numbering of the tables forms a continuous series with the tables in Appendix 2 of the earlier NBS Report 6484, as no table in this report duplicates or replaces a table in the other report.

The table for graphite (2-39) is a preliminary one recently computed on the basis of new heat-capacity data, at both low and high temperatures, that had become available since the publication 15 years ago of graphite thermodynamic functions by Wagman, Kilpatrick, Taylor, Pitzer, and Rossini (J. Research NBS 34, 143 (1945), RP1634).

The tables for TiN (2-32), TiC (2-38), and Ti (2-40) cover temperature ranges below and above room temperature. Small adjustments have been made in the data in order that the values of heat capacity at low and high temperatures join smoothly. (See method of analysis in NBS Report No. 6484.)

The remaining nine tables, which give values only above 298.15°K, were computed from the values of $S^\circ_{298.15}$ given in Chapter A3 and the heat-content equations given in Chapter A4, the final digit tabulated being obtained by dropping subsequent digits rather than by rounding.

It should be emphasized that these tables have a much lower absolute accuracy than indicated by the number of significant figures retained, particularly at the highest temperatures. For rough estimates of these uncertainties, see Chapter A4.

TABLE 2-28

THERMODYNAMIC FUNCTIONS FOR LITHIUM NITRIDE (Li_3N)
SOLID PHASE

GRAM MOLECULAR WT. = 34.83 GRAMS   1 CAL = 4.1840 ABS J.

T DEG K = 273.15 + T DEG C.

T	$-\frac{(F^o_T - H^o_{298})}{T}$	$\frac{(H^o_T - H^o_{298})}{T}$	$(S^o_T - S^o_0)$	$(H^o_T - H^o_{298})$	C^o_p	$-(F^o_T - H^o_{298})$
deg K	cal/deg mole	cal/deg mole	cal/deg mole	cal/mole	cal/deg mole	cal/mole
298.15	9.00	0.00	9.00	0.	18.09	2683.
300.00	9.00	0.11	9.11	33.	18.19	2700.
325.00	9.06	1.55	10.61	504.	19.42	2946.
350.00	9.23	2.86	12.09	1002.	20.43	3230.
375.00	9.47	4.06	13.53	1524.	21.29	3551.
400.00	9.76	5.16	14.93	2066.	22.04	3907.
425.00	10.11	6.17	16.29	2626.	22.69	4297.
450.00	10.49	7.11	17.60	3200.	23.26	4721.
475.00	10.90	7.97	18.87	3788.	23.77	5177.
500.00	11.33	8.77	20.10	4389.	24.23	5665.
550.00	12.23	10.22	22.45	5621.	25.03	6729.
600.00	13.18	11.48	24.66	6890.	25.71	7908.
650.00	14.14	12.60	26.74	8190.	26.28	9194.
700.00	15.11	13.59	28.71	9517.	26.77	10581.
750.00	16.08	14.48	30.57	10867.	27.19	12063.
800.00	17.04	15.29	32.34	12236.	27.55	13636.
850.00	17.99	16.02	34.02	13622.	27.87	15296.
900.00	18.93	16.69	35.62	15022.	28.13	17037.
950.00	19.85	17.29	37.14	16434.	28.34	18857.
1000.00	20.75	17.85	38.60	17856.	28.52	20751.
1050.00	21.63	18.36	40.00	19286.	28.65	22717.
1100.00	22.50	18.83	41.33	20721.	28.75	24750.
1150.00	23.34	19.27	42.61	22160.	28.80	26849.
1200.00	24.17	19.66	43.84	23601.	28.82	29011.

S^o_0 applies to the reference state of the solid at zero deg K.

H^o_{298} (actually should be read $H^o_{298.15}$) applies to the reference state of the solid at 298.15 deg K.

TABLE 2-29

THERMODYNAMIC FUNCTIONS FOR BERYLLIUM NITRIDE (Be_3N_2)
SOLID AND LIQUID PHASES

GRAM MOLECULAR WT. = 55.08 GRAMS 1 CAL = 4.1840 ABS J.

T DEG K = 273.15 + T DEG C

T deg K	$-\frac{(F^o_T-H^o_{298})}{T}$ $\frac{cal}{deg\ mole}$	$\frac{(H^o_T-H^o_{298})}{T}$ $\frac{cal}{deg\ mole}$	$(S^o_T-S^o_0)$ $\frac{cal}{deg\ mole}$	$(H^o_T-H^o_{298})$ $\frac{cal}{mole}$	C^o_p $\frac{cal}{deg\ mole}$	$-(F^o_T-H^o_{298})$ $\frac{cal}{mole}$
298.15	12.00	0.00	12.00	0.	16.01	3577.
300.00	12.00	0.09	12.09	29.	16.15	3600.
325.00	12.06	1.40	13.46	456.	17.88	3919.
350.00	12.20	2.63	14.84	921.	19.31	4273.
375.00	12.43	3.78	16.21	1419.	20.51	4661.
400.00	12.71	4.86	17.57	1946.	21.55	5084.
425.00	13.03	5.87	18.90	2496.	22.45	5540.
450.00	13.39	6.81	20.21	3068.	23.25	6029.
475.00	13.79	7.70	21.49	3658.	23.96	6550.
500.00	14.20	8.53	22.73	4265.	24.61	7103.
550.00	15.09	10.04	25.13	5525.	25.73	8301.
600.00	16.02	11.39	27.42	6836.	26.70	9615.
650.00	16.98	12.60	29.59	8193.	27.55	11041.
700.00	17.96	13.70	31.66	9590.	28.31	12573.
750.00	18.94	14.69	33.64	11024.	29.00	14206.
800.00	19.92	15.61	35.53	12490.	29.63	15935.
850.00	20.89	16.45	37.34	13987.	30.22	17758.
900.00	21.85	17.23	39.09	15512.	30.76	19669.
950.00	22.80	17.96	40.76	17063.	31.27	21665.
1000.00	23.74	18.63	42.38	18639.	31.75	23744.
1050.00	24.67	19.27	43.94	20237.	32.19	25903.
1100.00	25.58	19.87	45.45	21858.	32.62	28138.
1150.00	26.47	20.43	46.91	23499.	33.01	30447.
1200.00	27.35	20.96	48.32	25160.	33.39	32828.
1250.00	28.22	21.47	49.69	26838.	33.74	35279.
1300.00	29.07	21.94	51.02	28534.	34.07	37797.
1350.00	29.91	22.40	52.31	30245.	34.38	40381.
1400.00	30.73	22.83	53.57	31972.	34.67	43028.
1450.00	31.54	23.25	54.79	33713.	34.95	45737.
1500.00	32.33	23.64	55.98	35467.	35.20	48507.
1550.00	33.12	24.02	57.14	37233.	35.44	51335.
1600.00	33.88	24.38	58.27	39011.	35.66	54221.
1650.00	34.64	24.72	59.37	40799.	35.86	57162.
1700.00	35.38	25.05	60.44	42596.	36.04	60157.
1750.00	36.11	25.37	61.49	44403.	36.21	63206.
1800.00	36.83	25.67	62.51	46217.	36.36	66306.
1850.00	37.54	25.96	63.51	48039.	36.49	69457.
1900.00	38.24	26.24	64.48	49866.	36.60	72657.
1950.00	38.92	26.51	65.43	51699.	36.70	75905.
2000.00	39.60	26.76	66.36	53537.	36.79	79200.
2050.00	40.26	27.01	67.27	55378.	36.85	82541.
2100.00	40.91	27.24	68.16	57222.	36.90	85928.
2150.00	41.56	27.47	69.03	59069.	36.94	89358.
2200.00	42.19	27.68	69.88	60916.	36.96	92831.
2250.00	42.82	27.89	70.71	62765.	36.96	96346.
2300.00	43.43	28.09	71.52	64613.	36.94	99902.
2350.00	44.04	28.28	72.32	66459.	36.91	103498.
2400.00	44.63	28.46	73.10	68304.	36.87	107134.
2450.00	45.22	28.63	73.85	70146.	36.81	110808.
2470.00	45.46	28.69	74.15	70882.	36.78	112288.
			(LIQUID)			
2470.00	45.46	41.19	86.65	101757.	39.02	112288.
2500.00	45.95	41.17	87.12	102926.	38.90	114895.
2600.00	47.57	41.07	88.64	106796.	38.50	123684.
2700.00	49.11	40.97	90.09	110626.	38.10	132622.
2800.00	50.60	40.86	91.47	114416.	37.70	141701.
2900.00	52.03	40.74	92.78	118166.	37.30	150914.
3000.00	53.41	40.62	94.04	121876.	36.90	160256.
3100.00	54.74	40.49	95.24	125546.	36.50	169721.
3200.00	56.03	40.36	96.40	129176.	36.10	179304.
3300.00	57.27	40.23	97.50	132766.	35.70	188999.
3400.00	58.47	40.09	98.56	136316.	35.30	198803.
3500.00	59.63	39.95	99.58	139826.	34.90	208711.
3600.00	60.75	39.80	100.56	143296.	34.50	218718.
3700.00	61.84	39.65	101.50	146726.	34.10	228822.
3800.00	62.89	39.50	102.40	150116.	33.70	239017.
3900.00	63.92	39.35	103.27	153466.	33.30	249301.
4000.00	64.91	39.19	104.11	156776.	32.90	259671.

S^o_0 applies to the reference state of the solid at zero deg K.

H^o_{298} (actually should be read $H^o_{298.15}$) applies to the reference state of the solid at 298.15 deg K.

TABLE 2-30

THERMODYNAMIC FUNCTIONS FOR MAGNESIUM NITRIDE (Mg_3N_2)
SOLID PHASES

GRAM MOLECULAR WT. = 100.98 GRAMS   1 CAL = 4.1840 ABS J

T DEG K = 273.15 + T DEG C

T deg K	$-\frac{(F^o_T-H^o_{298})}{T}$ $\frac{cal}{deg\ mole}$	$\frac{(H^o_T-H^o_{298})}{T}$ $\frac{cal}{deg\ mole}$	$(S^o_T-S^o_0)$ $\frac{cal}{deg\ mole}$	$(H^o_T-H^o_{298})$ $\frac{cal}{mole}$	C^o_p $\frac{cal}{deg\ mole}$	$-(F^o_T-H^o_{298})$ $\frac{cal}{mole}$
(SOLID-ALPHA)						
298.15	21.00	0.00	21.00	0.	24.98	6261.
300.00	21.00	0.15	21.15	46.	25.00	6300.
325.00	21.09	2.07	23.16	673.	25.18	6854.
350.00	21.30	3.73	25.03	1305.	25.36	7457.
375.00	21.61	5.17	26.79	1941.	25.54	8105.
400.00	21.99	6.45	28.44	2582.	25.73	8795.
425.00	22.41	7.59	30.01	3228.	25.91	9526.
450.00	22.87	8.61	31.49	3878.	26.09	10295.
475.00	23.37	9.54	32.91	4533.	26.27	11101.
500.00	23.88	10.38	34.26	5192.	26.46	11940.
550.00	24.94	11.86	36.80	6524.	26.82	13718.
600.00	26.03	13.12	39.15	7874.	27.19	15618.
650.00	27.12	14.22	41.34	9243.	27.55	17631.
700.00	28.21	15.18	43.40	10630.	27.92	19750.
750.00	29.29	16.04	45.34	12035.	28.28	21969.
800.00	30.35	16.82	47.17	13458.	28.65	24282.
823.00	30.83	17.15	47.99	14119.	28.81	25377.
(SOLID-BETA)						
823.00	30.83	17.42	48.25	14339.	29.60	25377.
850.00	31.40	17.81	49.21	15138.	29.60	26693.
900.00	32.44	18.46	50.90	16618.	29.60	29196.
950.00	33.45	19.05	52.50	18098.	29.60	31782.
1000.00	34.44	19.57	54.02	19578.	29.60	34445.
1050.00	35.41	20.05	55.46	21058.	29.60	37183.
1061.00	35.62	20.15	55.77	21384.	29.60	37795.
(SOLID-GAMMA)						
1061.00	35.62	20.40	56.02	21644.	29.54	37795.
1100.00	36.36	20.72	57.08	22796.	29.54	40001.
1150.00	37.29	21.10	58.40	24273.	29.54	42888.
1200.00	38.20	21.45	59.65	25750.	29.54	45840.
1250.00	39.08	21.78	60.86	27227.	29.54	48853.
1300.00	39.94	22.08	62.02	28704.	29.54	51926.
1350.00	40.78	22.35	63.13	30181.	29.54	55055.
1400.00	41.59	22.61	64.21	31658.	29.54	58239.
1450.00	42.39	22.85	65.24	33135.	29.54	61475.
1500.00	43.17	23.07	66.25	34612.	29.54	64763.
1550.00	43.93	23.28	67.21	36089.	29.54	68100.
1600.00	44.67	23.47	68.15	37566.	29.54	71484.
1650.00	45.40	23.66	69.06	39043.	29.54	74915.
1700.00	46.11	23.83	69.94	40520.	29.54	78391.
1750.00	46.80	23.99	70.80	41997.	29.54	81910.
1800.00	47.48	24.15	71.63	43474.	29.54	85471.
1850.00	48.14	24.29	72.44	44951.	29.54	89073.
1900.00	48.79	24.43	73.23	46428.	29.54	92715.
1950.00	49.43	24.56	74.00	47905.	29.54	96396.
2000.00	50.05	24.69	74.74	49382.	29.54	100115.
2050.00	50.66	24.81	75.47	50859.	29.54	103870.
2100.00	51.26	24.92	76.19	52336.	29.54	107662.
2150.00	51.85	25.03	76.88	53813.	29.54	111489.
2200.00	52.43	25.13	77.56	55290.	29.54	115350.
2250.00	52.99	25.23	78.22	56767.	29.54	119245.
2300.00	53.55	25.32	78.87	58244.	29.54	123173.
2350.00	54.09	25.41	79.51	59721.	29.54	127133.
2400.00	54.63	25.49	80.13	61198.	29.54	131124.
2450.00	55.16	25.58	80.74	62675.	29.54	135146.
2500.00	55.67	25.66	81.34	64152.	29.54	139198.

S^o_0 applies to the reference state of the solid at zero deg K.

H^o_{298} (actually should be read $H^o_{298.15}$) applies to the reference state of the solid at 298.15 deg K.

TABLE 2-31

THERMODYNAMIC FUNCTIONS FOR ALUMINUM NITRIDE (AlN)
SOLID PHASE

GRAM MOLECULAR WT. = 40.99 GRAMS   1 CAL = 4.1840 ABS J

T DEG K = 273.15 + T DEG C

T	$\frac{-(F^o_T-H^o_{298})}{T}$	$\frac{(H^o_T-H^o_{298})}{T}$	$(S^o_T-S^o_0)$	$(H^o_T-H^o_{298})$	C^o_p	$-(F^o_T-H^o_{298})$
deg K	cal/deg mole	cal/deg mole	cal/deg mole	cal/mole	cal/deg mole	cal/mole
298.15	5.00	0.00	5.00	0.	7.34	1490.
300.00	5.00	0.04	5.04	13.	7.38	1500.
325.00	5.02	0.63	5.65	204.	7.87	1633.
350.00	5.09	1.16	6.25	406.	8.28	1782.
375.00	5.19	1.64	6.84	618.	8.63	1946.
400.00	5.31	2.09	7.40	838.	8.93	2124.
425.00	5.45	2.50	7.95	1064.	9.19	2316.
450.00	5.60	2.88	8.48	1297.	9.42	2522.
475.00	5.77	3.23	9.00	1535.	9.63	2741.
500.00	5.94	3.55	9.50	1779.	9.82	2972.
550.00	6.31	4.14	10.45	2279.	10.16	3471.
600.00	6.69	4.65	11.35	2795.	10.46	4017.
650.00	7.08	5.11	12.20	3325.	10.72	4606.
700.00	7.48	5.52	13.00	3867.	10.96	5236.
750.00	7.87	5.89	13.77	4421.	11.18	5906.
800.00	8.26	6.23	14.49	4985.	11.38	6612.
850.00	8.65	6.54	15.19	5559.	11.58	7355.
900.00	9.03	6.82	15.86	6143.	11.76	8131.
950.00	9.41	7.09	16.50	6735.	11.93	8941.
1000.00	9.78	7.33	17.11	7336.	12.09	9781.
1050.00	10.14	7.56	17.71	7945.	12.25	10652.
1100.00	10.50	7.78	18.28	8562.	12.40	11552.
1150.00	10.85	7.98	18.84	9186.	12.55	12480.
1200.00	11.19	8.18	19.37	9817.	12.68	13436.
1250.00	11.53	8.36	19.89	10454.	12.82	14418.
1300.00	11.86	8.53	20.40	11099.	12.95	15425.
1350.00	12.19	8.70	20.89	11749.	13.07	16458.
1400.00	12.51	8.86	21.37	12406.	13.19	17515.
1450.00	12.82	9.01	21.83	13069.	13.30	18595.
1500.00	13.13	9.15	22.29	13737.	13.41	19698.
1550.00	13.43	9.29	22.73	14410.	13.52	20824.
1600.00	13.73	9.43	23.16	15089.	13.62	21971.
1650.00	14.02	9.55	23.58	15772.	13.71	23140.
1700.00	14.31	9.68	23.99	16460.	13.81	24330.
1750.00	14.59	9.80	24.39	17153.	13.90	25539.
1800.00	14.87	9.91	24.78	17850.	13.98	26769.
1850.00	15.14	10.02	25.17	18552.	14.06	28018.
1900.00	15.41	10.13	25.54	19257.	14.14	29286.
1950.00	15.67	10.23	25.91	19966.	14.21	30573.
2000.00	15.93	10.33	26.27	20678.	14.28	31878.
2050.00	16.19	10.43	26.63	21394.	14.34	33201.
2100.00	16.44	10.53	26.97	22113.	14.41	34541.
2150.00	16.69	10.62	27.31	22835.	14.46	35898.
2200.00	16.94	10.70	27.65	23560.	14.52	37273.
2250.00	17.18	10.79	27.97	24287.	14.57	38663.
2300.00	17.42	10.87	28.29	25017.	14.61	40070.
2350.00	17.65	10.95	28.61	25749.	14.66	41493.
2400.00	17.88	11.03	28.92	26483.	14.69	42932.
2450.00	18.11	11.11	29.22	27218.	14.73	44385.
2500.00	18.34	11.18	29.52	27956.	14.76	45854.

S^o_0 applies to the reference state of the solid at zero deg K.

H^o_{298} (actually should be read $H^o_{298.15}$) applies to the reference state of the solid at 298.15 deg K.

TABLE 2-32

THERMODYNAMIC FUNCTIONS FOR TITANIUM NITRIDE (TI N)
SOLID AND LIQUID PHASES

GRAM MOLECULAR WT.=61.908 GRAMS 1 CAL=4.1840 ABS J

T DEG K = 273.15 + T DEG C

T DEG K	$-(F_T^\circ-H_0^\circ)/T$ CAL/DEG MOLE	$(H_T^\circ-H_0^\circ)/T$ CAL/DEG MOLE	$(S_T^\circ-S_0^\circ)$ CAL/DEG MOLE	$(H_T^\circ-H_0^\circ)$ CAL/MOLE	C_P° CAL/DEG MOLE	$-(F_T^\circ-H_0^\circ)$ CAL/MOLE
			(SOLID)			
0.00	0.0000	0.0000	0.000	0.000	0.000	0.000
5.00	0.0001	0.0001	0.000	0.000	0.000	0.000
10.00	0.0001	0.0001	0.000	0.001	0.000	0.001
15.00	0.0002	0.0004	0.001	0.006	0.002	0.003
20.00	0.0004	0.0012	0.002	0.023	0.006	0.008
25.00	0.0009	0.0031	0.004	0.076	0.017	0.022
30.00	0.0018	0.0073	0.009	0.218	0.043	0.053
35.00	0.0034	0.0156	0.019	0.545	0.092	0.120
40.00	0.0064	0.0299	0.036	1.198	0.174	0.255
45.00	0.0111	0.0521	0.063	2.346	0.291	0.499
50.00	0.0181	0.0831	0.101	4.156	0.438	0.905
55.00	0.0278	0.1230	0.151	6.763	0.608	1.530
60.00	0.0405	0.1711	0.212	10.267	0.795	2.431
65.00	0.0564	0.2267	0.283	14.737	0.994	3.664
70.00	0.0754	0.2890	0.364	20.228	1.203	5.279
75.00	0.0976	0.3572	0.455	26.786	1.421	7.323
80.00	0.1230	0.4306	0.554	34.452	1.646	9.841
85.00	0.1514	0.5089	0.660	43.254	1.876	12.873
90.00	0.1828	0.5912	0.774	53.211	2.108	16.456
95.00	0.2171	0.6772	0.894	64.330	2.340	20.624
100.00	0.2541	0.7661	1.020	76.610	2.572	25.408
105.00	0.2937	0.8576	1.151	90.043	2.802	30.834
110.00	0.3357	0.9511	1.287	104.62	3.030	36.928
115.00	0.3801	1.0464	1.426	120.34	3.256	43.709
120.00	0.4267	1.1431	1.570	137.18	3.479	51.199
125.00	0.4753	1.2410	1.716	155.13	3.700	59.413
130.00	0.5259	1.3398	1.866	174.17	3.918	68.367
135.00	0.5783	1.4392	2.018	194.30	4.131	78.074
140.00	0.6325	1.5391	2.172	215.48	4.342	88.546
145.00	0.6882	1.6394	2.328	237.71	4.548	99.793
150.00	0.7455	1.7397	2.485	260.96	4.751	111.82
155.00	0.8042	1.8400	2.644	285.21	4.949	124.65
160.00	0.8642	1.9402	2.804	310.44	5.143	138.27
165.00	0.9254	2.0401	2.966	336.62	5.332	152.69
170.00	0.9878	2.1397	3.127	363.75	5.517	167.92
175.00	1.0513	2.2388	3.290	391.79	5.698	183.97
180.00	1.1157	2.3373	3.453	420.72	5.873	200.83
185.00	1.1811	2.4352	3.616	450.51	6.045	218.50
190.00	1.2473	2.5324	3.780	481.16	6.211	236.99
195.00	1.3143	2.6288	3.943	512.62	6.373	256.30
200.00	1.3821	2.7244	4.107	544.88	6.531	276.42
205.00	1.4505	2.8191	4.270	577.92	6.684	297.36
210.00	1.5196	2.9129	4.433	611.72	6.833	319.12
215.00	1.5892	3.0058	4.595	646.24	6.977	341.69
220.00	1.6594	3.0976	4.757	681.48	7.117	365.07
225.00	1.7300	3.1884	4.919	717.40	7.252	389.26
230.00	1.8011	3.2782	5.079	753.99	7.383	414.25
235.00	1.8725	3.3669	5.240	791.22	7.511	440.05
240.00	1.9443	3.4545	5.399	829.09	7.634	466.64
245.00	2.0165	3.5411	5.558	867.56	7.754	494.04
250.00	2.0889	3.6265	5.715	906.63	7.871	522.22
255.00	2.1615	3.7109	5.872	946.27	7.986	551.19
260.00	2.2344	3.7942	6.029	986.48	8.099	580.94
265.00	2.3074	3.8765	6.184	1027.3	8.211	611.47
270.00	2.3807	3.9577	6.338	1068.6	8.321	642.78
273.15	2.4269	4.0085	6.435	1094.9	8.390	662.90
275.00	2.4540	4.0381	6.492	1110.5	8.431	674.85
280.00	2.5275	4.1175	6.645	1152.9	8.539	707.70
285.00	2.6011	4.1960	6.797	1195.9	8.646	741.30
290.00	2.6747	4.2736	6.948	1239.4	8.751	775.67
295.00	2.7484	4.3504	7.099	1283.4	8.854	810.78
298.15	2.7949	4.3983	7.193	1311.4	8.918	833.29
300.00	2.8222	4.4263	7.249	1327.9	8.995	846.65

H_0 AND S_0 APPLY TO THE REFERENCE STATE OF THE SOLID AT ZERO DEG K

TABLE 2-32(CONT.)

THERMODYNAMIC FUNCTIONS FOR TITANIUM NITRIDE (TI N)
SOLID AND LIQUID PHASES

GRAM MOLECULAR WT.=61.908 GRAMS 1 CAL=4.1840 ABS J
T DEG K = 273.15 + T DEG C

T DEG K	$-(F^\circ_T-H^\circ_0)/T$ CAL / DEG MOLE	$(H^\circ_T-H^\circ_0)/T$ CAL / DEG MOLE	$(S^\circ_T-S^\circ_0)$ CAL / DEG MOLE	$(H^\circ_T-H^\circ_0)$ CAL / MOLE	C°_P CAL / DEG MOLE	$-(F^\circ_T-H^\circ_0)$ CAL / MOLE
			(SOLID)			
300.00	2.82	4.42	7.25	1328.	9.00	846.6
325.00	3.19	4.79	7.98	1557.	9.42	1037.
350.00	3.55	5.13	8.69	1798.	9.82	1245.
375.00	3.92	5.46	9.38	2048.	10.15	1471.
400.00	4.28	5.76	10.05	2305.	10.43	1714.
425.00	4.64	6.04	10.69	2569.	10.67	1974.
450.00	4.99	6.30	11.30	2839.	10.87	2249.
475.00	5.34	6.55	11.90	3113.	11.04	2539.
500.00	5.68	6.78	12.47	3391.	11.19	2844.
550.00	6.35	7.19	13.55	3957.	11.44	3495.
600.00	6.99	7.55	14.55	4535.	11.65	4197.
650.00	7.61	7.88	15.49	5122.	11.82	4949.
700.00	8.20	8.16	16.37	5716.	11.96	5746.
750.00	8.78	8.42	17.20	6318.	12.08	6586.
800.00	9.33	8.65	17.98	6925.	12.19	7466.
850.00	9.86	8.86	18.73	7537.	12.29	8384.
900.00	10.37	9.06	19.43	8155.	12.39	9338.
950.00	10.87	9.23	20.11	8776.	12.47	10327.
1000.00	11.34	9.40	20.75	9402.	12.55	11349.
1050.00	11.81	9.55	21.36	10032.	12.62	12402.
1100.00	12.25	9.69	21.95	10665.	12.69	13485.
1150.00	12.69	9.82	22.52	11302.	12.76	14597.
1200.00	13.11	9.95	23.06	11942.	12.83	15737.
1250.00	13.52	10.06	23.59	12585.	12.89	16903.
1300.00	13.92	10.17	24.09	13231.	12.95	18096.
1350.00	14.30	10.28	24.58	13880.	13.01	19313.
1400.00	14.68	10.38	25.06	14533.	13.07	20554.
1450.00	15.04	10.47	25.52	15188.	13.13	21819.
1500.00	15.40	10.56	25.96	15846.	13.18	23106.
1550.00	15.75	10.65	26.40	16507.	13.24	24415.
1600.00	16.09	10.73	26.82	17170.	13.29	25746.
1650.00	16.42	10.81	27.23	17837.	13.35	27098.
1700.00	16.74	10.88	27.63	18506.	13.40	28469.
1750.00	17.06	10.95	28.02	19177.	13.45	29861.
1800.00	17.37	11.02	28.40	19851.	13.51	31271.
1850.00	17.67	11.09	28.77	20528.	13.56	32701.
1900.00	17.97	11.16	29.13	21208.	13.61	34149.
1950.00	18.26	11.22	29.49	21890.	13.66	35614.
2000.00	18.54	11.28	29.83	22574.	13.71	37097.
2050.00	18.82	11.34	30.17	23261.	13.76	38598.
2100.00	19.10	11.40	30.50	23951.	13.81	40115.
2150.00	19.37	11.46	30.83	24643.	13.86	41648.
2200.00	19.63	11.51	31.15	25337.	13.91	43198.
2250.00	19.89	11.57	31.46	26035.	13.96	44764.
2300.00	20.15	11.62	31.77	26734.	14.01	46345.
2350.00	20.40	11.67	32.07	27436.	14.06	47941.
2400.00	20.64	11.72	32.37	28141.	14.11	49552.
2450.00	20.88	11.77	32.66	28848.	14.16	51178.
2500.00	21.12	11.82	32.95	29557.	14.21	52818.
2600.00	21.59	11.91	33.51	30983.	14.31	56142.
2700.00	22.04	12.00	34.05	32419.	14.40	59520.
2800.00	22.48	12.09	34.57	33865.	14.50	62951.
2900.00	22.90	12.17	35.08	35320.	14.60	66435.
3000.00	23.32	12.26	35.58	36785.	14.69	69968.
3100.00	23.72	12.34	36.06	38259.	14.79	73551.
3200.00	24.11	12.42	36.53	39743.	14.88	77182.
			(LIQUID)			
3200.00	24.11	17.42	41.53	55743.	15.60	77182.
3300.00	24.65	17.36	42.01	57295.	15.44	81360.
3400.00	25.17	17.30	42.47	58831.	15.28	85585.
3500.00	25.67	17.24	42.91	60351.	15.12	89854.
3600.00	26.15	17.18	43.34	61855.	14.96	94167.
3700.00	26.62	17.12	43.74	63343.	14.80	98522.
3800.00	27.08	17.05	44.14	64815.	14.64	102916.
3900.00	27.52	16.99	44.51	66271.	14.48	107349.
4000.00	27.95	16.92	44.88	67711.	14.32	111819.

H_0 AND S_0 APPLY TO THE REFERENCE STATE OF THE SOLID AT ZERO DEG K

TABLE 2-33

THERMODYNAMIC FUNCTIONS FOR LITHIUM CARBIDE (Li_2C_2) SOLID PHASE

GRAM MOLECULAR WT. = 37.90 GRAMS   1 CAL = 4.1840 ABS J

T DEG K = 273.15 + T DEG C

T	$\frac{-(F^o_T-H^o_{298})}{T}$	$\frac{(H^o_T-H^o_{298})}{T}$	$(S^o_T-S^o_0)$	$(H^o_T-H^o_{298})$	C^o_p	$-(F^o_T-H^o_{298})$
deg K	$\frac{\text{cal}}{\text{deg mole}}$	$\frac{\text{cal}}{\text{deg mole}}$	$\frac{\text{cal}}{\text{deg mole}}$	$\frac{\text{cal}}{\text{mole}}$	$\frac{\text{cal}}{\text{deg mole}}$	$\frac{\text{cal}}{\text{mole}}$
298.15	14.00	0.00	14.00	0.	17.10	4174.
300.00	14.00	0.10	14.10	31.	17.20	4200.
325.00	14.06	1.47	15.53	477.	18.43	4570.
350.00	14.21	2.71	16.93	951.	19.41	4976.
375.00	14.44	3.85	18.30	1447.	20.22	5417.
400.00	14.72	4.90	19.63	1961.	20.89	5891.
425.00	15.05	5.86	20.91	2490.	21.45	6398.
450.00	15.41	6.74	22.15	3033.	21.94	6937.
475.00	15.80	7.55	23.35	3587.	22.36	7505.
500.00	16.20	8.30	24.51	4150.	22.72	8104.
550.00	17.06	9.64	26.70	5303.	23.34	9385.
600.00	17.95	10.80	28.76	6483.	23.83	10772.
650.00	18.86	11.82	30.68	7685.	24.25	12259.
700.00	19.77	12.72	32.49	8907.	24.60	13839.
750.00	20.67	13.52	34.20	10145.	24.91	15506.
800.00	21.57	14.24	35.82	11397.	25.18	17257.
850.00	22.45	14.89	37.35	12663.	25.43	19087.
900.00	23.32	15.49	38.81	13940.	25.66	20992.
950.00	24.17	16.03	40.20	15229.	25.87	22967.
1000.00	25.01	16.52	41.54	16527.	26.07	25011.
1050.00	25.82	16.98	42.81	17836.	26.26	27120.
1100.00	26.63	17.41	44.04	19153.	26.43	29292.
1150.00	27.41	17.80	45.22	20480.	26.61	31524.
1200.00	28.17	18.17	46.35	21814.	26.77	33813.
1250.00	28.92	18.52	47.45	23157.	26.93	36159.
1300.00	29.66	18.85	48.51	24508.	27.09	38558.
1350.00	30.37	19.16	49.53	25866.	27.24	41010.
1400.00	31.08	19.45	50.53	27232.	27.39	43512.
1450.00	31.76	19.72	51.49	28606.	27.54	46062.
1500.00	32.44	19.99	52.43	29986.	27.68	48661.
1550.00	33.10	20.24	53.34	31374.	27.82	51305.
1600.00	33.74	20.48	54.22	32769.	27.96	53994.
1650.00	34.38	20.71	55.09	34171.	28.10	56728.
1700.00	35.00	20.93	55.93	35580.	28.24	59503.
1750.00	35.61	21.14	56.75	36995.	28.37	62320.
1800.00	36.21	21.34	57.55	38418.	28.51	65178.
1850.00	36.79	21.53	58.33	39847.	28.64	68075.
1900.00	37.37	21.72	59.10	41282.	28.78	71011.
1950.00	37.94	21.91	59.85	42725.	28.91	73985.
2000.00	38.49	22.08	60.58	44173.	29.04	76996.

S^o_0 applies to the reference state of the solid at zero deg K.

H^o_{298} (actually should be read $H^o_{298.15}$) applies to the reference state of the solid at 298.15 deg K.

TABLE 2-34

THERMODYNAMIC FUNCTIONS FOR BERYLLIUM CARBIDE (Be_2C) SOLID AND LIQUID PHASES

GRAM MOLECULAR WT. = 30.05 GRAMS 1 CAL. = 4.1840 ABS J

T DEG K = 273.15 + T DEG C

T	$-\frac{(F^o_T-H^o_{298})}{T}$	$\frac{(H^o_T-H^o_{298})}{T}$	$(S^o_T-S^o_0)$	$(H^o_T-H^o_{298})$	C^o_p	$-(F^o_T-H^o_{298})$
deg K	cal / deg mole	cal / deg mole	cal / deg mole	cal / mole	cal / deg mole	cal / mole
298.15	4.00	0.00	4.00	0.	9.91	1192.
300.00	4.00	0.06	4.06	18.	9.96	1200.
325.00	4.03	0.84	4.88	274.	10.52	1311.
350.00	4.12	1.55	5.67	543.	11.01	1443.
375.00	4.25	2.19	6.45	824.	11.45	1595.
400.00	4.41	2.79	7.20	1116.	11.85	1766.
425.00	4.60	3.33	7.93	1417.	12.22	1955.
450.00	4.80	3.83	8.64	1726.	12.55	2163.
475.00	5.02	4.30	9.33	2044.	12.87	2387.
500.00	5.25	4.74	9.99	2370.	13.17	2629.
550.00	5.74	5.53	11.28	3042.	13.73	3161.
600.00	6.26	6.23	12.49	3742.	14.24	3756.
650.00	6.78	6.87	13.65	4466.	14.72	4410.
700.00	7.31	7.44	14.76	5213.	15.17	5121.
750.00	7.84	7.97	15.82	5982.	15.59	5886.
800.00	8.37	8.46	16.84	6772.	16.00	6703.
850.00	8.90	8.92	17.82	7582.	16.38	7570.
900.00	9.42	9.34	18.77	8410.	16.75	8485.
950.00	9.94	9.74	19.68	9256.	17.10	9447.
1000.00	10.45	10.12	20.57	10120.	17.44	10453.
1050.00	10.95	10.47	21.43	11000.	17.76	11503.
1100.00	11.45	10.81	22.26	11895.	18.06	12596.
1150.00	11.93	11.13	23.07	12806.	18.36	13730.
1200.00	12.42	11.44	23.86	13731.	18.64	14903.
1250.00	12.89	11.73	24.62	14670.	18.91	16116.
1300.00	13.35	12.01	25.37	15622.	19.16	17366.
1350.00	13.81	12.28	26.10	16586.	19.41	18653.
1400.00	14.26	12.54	26.81	17562.	19.64	19976.
1450.00	14.71	12.79	27.50	18549.	19.86	21334.
1500.00	15.15	13.03	28.18	19547.	20.06	22726.
1550.00	15.58	13.26	28.84	20555.	20.26	24152.
1600.00	16.00	13.48	29.49	21573.	20.44	25610.
1650.00	16.42	13.69	30.12	22599.	20.61	27101.
1700.00	16.83	13.90	30.73	23633.	20.76	28622.
1750.00	17.24	14.10	31.34	24675.	20.91	30174.
1800.00	17.64	14.29	31.93	25724.	21.04	31756.
1850.00	18.03	14.47	32.51	26779.	21.17	33368.
1900.00	18.42	14.65	33.07	27841.	21.28	35007.
1950.00	18.80	14.82	33.63	28907.	21.38	36675.
2000.00	19.18	14.98	34.17	29978.	21.47	38370.
2050.00	19.55	15.14	34.70	31054.	21.54	40092.
2100.00	19.92	15.30	35.22	32132.	21.61	41841.
2150.00	20.28	15.44	35.73	33214.	21.66	43615.
2200.00	20.64	15.59	36.23	34298.	21.70	45414.
2250.00	20.99	15.72	36.72	35384.	21.73	47238.
2300.00	21.34	15.85	37.19	36471.	21.75	49086.
2350.00	21.68	15.98	37.66	37558.	21.75	50958.
2400.00	22.02	16.10	38.12	38646.	21.75	52853.
			(LIQUID)			
2400.00	22.02	23.60	45.62	56646.	23.40	52853.
2450.00	22.50	23.59	46.10	57813.	23.28	55146.
2500.00	22.98	23.59	46.57	58974.	23.16	57463.
2600.00	23.91	23.56	47.47	61278.	22.92	62166.
2700.00	24.79	23.54	48.33	63558.	22.68	66958.
2800.00	25.65	23.50	49.16	65814.	22.44	71833.
2900.00	26.47	23.46	49.94	68046.	22.20	76788.
3000.00	27.27	23.41	50.69	70254.	21.96	81820.
3100.00	28.04	23.36	51.40	72438.	21.72	86926.
3200.00	28.78	23.31	52.09	74598.	21.48	92101.
3300.00	29.49	23.25	52.75	76734.	21.24	97343.
3400.00	30.19	23.19	53.38	78846.	21.00	102650.
3500.00	30.86	23.12	53.98	80934.	20.76	108019.

S^o_0 applies to the reference state of the solid at zero deg K.

H^o_{298} (actually should be read $H^o_{298.15}$) applies to the reference state of the solid at 298.15 deg K.

TABLE 2-35

THERMODYNAMIC FUNCTIONS FOR MAGNESIUM CARBIDE (MgC_2)
SOLID PHASE

GRAM MOLECULAR WT. = 48.34 GRAMS   1 CAL = 4.1840 ABS J

T DEG K = 273.15 + T DEG C

T deg K	$-(F^o_T-H^o_{298})/T$ cal/deg mole	$(H^o_T-H^o_{298})/T$ cal/deg mole	$(S^o_T-S^o_0)$ cal/deg mole	$(H^o_T-H^o_{298})$ cal/mole	C^o_p cal/deg mole	$-(F^o_T-H^o_{298})$ cal/mole
298.15	13.00	0.00	13.00	0.	13.44	3875.
300.00	13.00	0.08	13.08	24.	13.49	3899.
325.00	13.04	1.14	14.18	370.	14.12	4240.
350.00	13.16	2.08	15.25	730.	14.62	4609.
375.00	13.34	2.93	16.27	1101.	15.04	5003.
400.00	13.55	3.70	17.26	1481.	15.39	5422.
425.00	13.80	4.40	18.20	1870.	15.68	5866.
450.00	14.07	5.03	19.10	2265.	15.94	6332.
475.00	14.36	5.61	19.97	2667.	16.16	6821.
500.00	14.66	6.14	20.80	3073.	16.35	7330.
550.00	15.29	7.09	22.38	3899.	16.68	8411.
600.00	15.94	7.90	23.84	4740.	16.94	9567.
650.00	16.60	8.60	25.21	5593.	17.17	10794.
700.00	17.26	9.22	26.49	6457.	17.36	12087.
750.00	17.92	9.77	27.69	7329.	17.53	13442.
800.00	18.56	10.26	28.83	8210.	17.69	14855.
850.00	19.20	10.70	29.91	9098.	17.83	16324.
900.00	19.82	11.10	30.93	9993.	17.96	17845.
950.00	20.43	11.46	31.90	10894.	18.08	19416.
1000.00	21.03	11.80	32.83	11801.	18.20	21035.
1050.00	21.61	12.10	33.72	12714.	18.31	22699.
1100.00	22.18	12.39	34.58	13633.	18.41	24407.
1150.00	22.74	12.65	35.40	14556.	18.52	26157.
1200.00	23.29	12.90	36.19	15484.	18.61	27947.
1250.00	23.82	13.13	36.95	16418.	18.71	29776.
1300.00	24.34	13.35	37.69	17356.	18.81	31642.
1350.00	24.84	13.55	38.40	18299.	18.90	33545.
1400.00	25.34	13.74	39.09	19246.	18.99	35482.
1450.00	25.83	13.93	39.76	20198.	19.08	37454.
1500.00	26.30	14.10	40.40	21154.	19.17	39458.
1550.00	26.77	14.26	41.03	22115.	19.25	41494.
1600.00	27.22	14.42	41.65	23080.	19.34	43562.
1650.00	27.67	14.57	42.24	24049.	19.42	45659.
1700.00	28.11	14.72	42.83	25023.	19.51	47786.
1750.00	28.53	14.85	43.39	26001.	19.59	49942.
1800.00	28.95	14.99	43.95	26983.	19.68	52125.
1850.00	29.37	15.11	44.49	27969.	19.76	54337.
1900.00	29.77	15.24	45.01	28959.	19.84	56574.
1950.00	30.17	15.36	45.53	29954.	19.92	58838.
2000.00	30.56	15.47	46.04	30952.	20.01	61128.
2050.00	30.94	15.58	46.53	31955.	20.09	63442.
2100.00	31.32	15.69	47.02	32961.	20.17	65781.
2150.00	31.69	15.80	47.49	33972.	20.25	68144.
2200.00	32.05	15.90	47.96	34986.	20.33	70530.
2250.00	32.41	16.00	48.42	36005.	20.41	72940.
2300.00	32.77	16.09	48.87	37028.	20.49	75372.
2350.00	33.11	16.19	49.31	38055.	20.57	77827.
2400.00	33.46	16.28	49.74	39085.	20.65	80303.
2450.00	33.79	16.37	50.17	40120.	20.73	82801.
2500.00	34.12	16.46	50.59	41159.	20.81	85320.

S^o_0 applies to the reference state of the solid at zero deg K.

H^o_{298} (actually should be read $H^o_{298.15}$) applies to the reference state of the solid at 298.15 deg K.

TABLE 2-36

THERMODYNAMIC FUNCTIONS FOR MAGNESIUM CARBIDE (Mg_2C_3)
SOLID PHASE

GRAM MOLECULAR WT. = 84.67 GRAMS 1 CAL = 4.1840 ABS J

T DEG K = 273.15 + T DEG C

T deg K	$-\frac{(F^o_T-H^o_{298})}{T}$ $\frac{cal}{deg\ mole}$	$\frac{(H^o_T-H^o_{298})}{T}$ $\frac{cal}{deg\ mole}$	$(S^o_T-S^o_0)$ $\frac{cal}{deg\ mole}$	$(H^o_T-H^o_{298})$ $\frac{cal}{mole}$	C^o_p $\frac{cal}{deg\ mole}$	$-(F^o_T-H^o_{298})$ $\frac{cal}{mole}$
298.15	24.00	0.00	24.00	0.	22.41	7155.
300.00	24.00	0.13	24.13	41.	22.50	7200.
325.00	24.08	1.90	25.98	617.	23.55	7826.
350.00	24.28	3.47	27.76	1217.	24.39	8498.
375.00	24.57	4.89	29.46	1836.	25.08	9214.
400.00	24.92	6.17	31.10	2470.	25.66	9971.
425.00	25.33	7.33	32.67	3118.	26.15	10768.
450.00	25.78	8.39	34.18	3778.	26.57	11604.
475.00	26.26	9.36	35.63	4447.	26.94	12477.
500.00	26.77	10.25	37.02	5125.	27.26	13385.
550.00	27.82	11.82	39.64	6502.	27.81	15303.
600.00	28.91	13.17	42.08	7904.	28.25	17347.
650.00	30.01	14.34	44.36	9326.	28.62	19509.
700.00	31.11	15.38	46.49	10766.	28.95	21781.
750.00	32.20	16.29	48.50	12221.	29.23	24156.
800.00	33.28	17.11	50.40	13689.	29.49	26629.
850.00	34.34	17.84	52.19	15170.	29.72	29195.
900.00	35.38	18.51	53.90	16662.	29.94	31847.
950.00	36.40	19.12	55.52	18164.	30.14	34583.
1000.00	37.39	19.67	57.07	19677.	30.34	37399.
1050.00	38.37	20.18	58.56	21198.	30.52	40290.
1100.00	39.32	20.66	59.98	22729.	30.70	43254.
1150.00	40.25	21.10	61.35	24268.	30.87	46288.
1200.00	41.15	21.51	62.67	25816.	31.03	49388.
1250.00	42.04	21.89	63.94	27372.	31.19	52554.
1300.00	42.90	22.25	65.16	28936.	31.35	55782.
1350.00	43.75	22.59	66.35	30507.	31.50	59070.
1400.00	44.58	22.91	67.50	32087.	31.65	62417.
1450.00	45.39	23.22	68.61	33673.	31.80	65820.
1500.00	46.18	23.51	69.69	35267.	31.95	69278.
1550.00	46.96	23.78	70.74	36869.	32.09	72789.
1600.00	47.72	24.04	71.76	38477.	32.24	76352.
1650.00	48.46	24.29	72.76	40093.	32.38	79965.
1700.00	49.19	24.53	73.73	41716.	32.52	83628.
1750.00	49.90	24.76	74.67	43345.	32.66	87338.
1800.00	50.60	24.99	75.59	44982.	32.80	91095.
1850.00	51.29	25.20	76.50	46626.	32.94	94898.
1900.00	51.97	25.40	77.38	48276.	33.07	98745.
1950.00	52.63	25.60	78.24	49933.	33.21	102635.
2000.00	53.28	25.79	79.08	51598.	33.35	106568.
2050.00	53.92	25.98	79.90	53268.	33.48	110543.
2100.00	54.55	26.16	80.71	54946.	33.62	114559.
2150.00	55.17	26.34	81.51	56631.	33.75	118615.
2200.00	55.77	26.51	82.28	58322.	33.88	122710.
2250.00	56.37	26.67	83.05	60019.	34.02	126843.
2300.00	56.96	26.83	83.80	61724.	34.15	131015.
2350.00	57.54	26.99	84.53	63435.	34.28	135223.
2400.00	58.11	27.14	85.25	65153.	34.42	139468.
2450.00	58.67	27.29	85.97	66877.	34.55	143749.
2500.00	59.22	27.44	86.66	68608.	34.68	148065.

S^o_0 applies to the reference state of the solid at zero deg K.

H^o_{298} (actually should be read $H^o_{298.15}$) applies to the reference state of the solid at 298.15 deg K.

TABLE 2-37

THERMODYNAMIC FUNCTIONS FOR ALUMINUM CARBIDE (Al_4C_3)
SOLID PHASE

GRAM MOLECULAR WT. = 143.93 GRAMS　　1 CAL = 4.1840 ABS J

T DEG K = 273.15 + T DEG C

T	$-\frac{(F^o_T-H^o_{298})}{T}$	$\frac{(H^o_T-H^o_{298})}{T}$	$(S^o_T-S^o_0)$	$(H^o_T-H^o_{298})$	C^o_p	$-(F^o_T-H^o_{298})$
deg K	$\frac{cal}{deg\ mole}$	$\frac{cal}{deg\ mole}$	$\frac{cal}{deg\ mole}$	$\frac{cal}{mole}$	$\frac{cal}{deg\ mole}$	$\frac{cal}{mole}$
298.15	25.00	0.00	25.00	0.	32.63	7453.
300.00	25.00	0.20	25.20	60.	32.79	7500.
325.00	25.12	2.78	27.90	904.	34.63	8164.
350.00	25.41	5.11	30.52	1789.	36.12	8894.
375.00	25.83	7.22	33.06	2708.	37.33	9689.
400.00	26.36	9.13	35.50	3654.	38.33	10547.
425.00	26.97	10.87	37.85	4623.	39.18	11464.
450.00	27.64	12.47	40.11	5612.	39.91	12439.
475.00	28.35	13.93	42.29	6618.	40.53	13469.
500.00	29.10	15.27	44.38	7638.	41.08	14552.
550.00	30.67	17.66	48.34	9716.	41.98	16872.
600.00	32.30	19.72	52.02	11834.	42.71	19382.
650.00	33.95	21.51	55.47	13985.	43.31	22070.
700.00	35.60	23.09	58.70	16164.	43.83	24926.
750.00	37.25	24.49	61.74	18367.	44.27	27937.
800.00	38.87	25.73	64.61	20591.	44.66	31097.
850.00	40.46	26.86	67.33	22833.	45.02	34396.
900.00	42.03	27.88	69.91	25093.	45.34	37828.
950.00	43.56	28.80	72.37	27367.	45.64	41385.
1000.00	45.06	29.65	74.72	29656.	45.91	45063.
1050.00	46.53	30.43	76.96	31959.	46.17	48856.
1100.00	47.96	31.15	79.12	34274.	46.42	52758.
1150.00	49.36	31.82	81.19	36601.	46.66	56766.
1200.00	50.73	32.45	83.18	38940.	46.88	60876.
1250.00	52.06	33.03	85.09	41290.	47.10	65083.
1300.00	53.37	33.57	86.95	43651.	47.32	69385.
1350.00	54.65	34.09	88.74	46022.	47.52	73777.
1400.00	55.89	34.57	90.47	48403.	47.73	78258.
1450.00	57.12	35.03	92.15	50795.	47.92	82824.
1500.00	58.31	35.46	93.77	53196.	48.12	87472.
1550.00	59.48	35.87	95.36	55607.	48.31	92201.
1600.00	60.63	36.26	96.89	58027.	48.50	97007.
1650.00	61.75	36.64	98.39	60457.	48.68	101890.
1700.00	62.85	36.99	99.84	62896.	48.86	106846.
1750.00	63.92	37.34	101.26	65344.	49.04	111874.
1800.00	64.98	37.66	102.65	67801.	49.22	116972.
1850.00	66.02	37.98	104.00	70267.	49.40	122139.
1900.00	67.03	38.28	105.32	72741.	49.58	127372.
1950.00	68.03	38.57	106.61	75225.	49.75	132670.
2000.00	69.01	38.85	107.87	77717.	49.93	138033.
2050.00	69.97	39.13	109.11	80218.	50.10	143458.
2100.00	70.92	39.39	110.32	82727.	50.27	148943.
2150.00	71.85	39.64	111.50	85245.	50.44	154489.
2200.00	72.77	39.89	112.66	87772.	50.61	160093.
2250.00	73.66	40.13	113.80	90307.	50.78	165755.
2300.00	74.55	40.37	114.92	92851.	50.95	171474.
2350.00	75.42	40.59	116.02	95402.	51.12	177247.
2400.00	76.28	40.81	117.10	97963.	51.28	183076.
2450.00	77.12	41.03	118.15	100531.	51.45	188957.
2500.00	77.95	41.24	119.20	103108.	51.62	194891.
2600.00	79.58	41.64	121.23	108287.	51.95	206913.
2700.00	81.16	42.03	123.19	113499.	52.28	219135.
2800.00	82.69	42.40	125.10	118744.	52.61	231551.
2900.00	84.19	42.76	126.95	124021.	52.93	244154.
3000.00	85.64	43.11	128.75	129331.	53.26	256941.

S^o_0 applies to the reference state of the solid at zero deg K.

H^o_{298} (actually should be read $H^o_{298.15}$) applies to the reference state of the solid at 298.15 deg K.

TABLE 2-38

THERMODYNAMIC FUNCTIONS FOR TITANIUM CARBIDE (TI C) SOLID AND LIQUID PHASES

GRAM MOLECULAR WT.=59.911 GRAMS 1 CAL=4.1840 ABS J

T DEG K = 273.15 + T DEG C

T DEG K	$-(F^\circ_T-H^\circ_0)/T$ CAL/DEG MOLE	$(H^\circ_T-H^\circ_0)/T$ CAL/DEG MOLE	$(S^\circ_T-S^\circ_0)$ CAL/DEG MOLE	$(H^\circ_T-H^\circ_0)$ CAL/MOLE	C°_P CAL/DEG MOLE	$-(F^\circ_T-H^\circ_0)$ CAL/MOLE
			(SOLID)			
0.00	0.0000	0.0000	0.000	0.000	0.000	0.000
5.00	0.0000	0.0000	0.000	0.000	0.000	0.000
10.00	0.0001	0.0002	0.000	0.002	0.001	0.001
15.00	0.0003	0.0010	0.001	0.015	0.004	0.004
20.00	0.0008	0.0026	0.003	0.051	0.011	0.015
25.00	0.0016	0.0051	0.007	0.129	0.021	0.040
30.00	0.0029	0.0092	0.012	0.276	0.039	0.086
35.00	0.0047	0.0153	0.020	0.534	0.066	0.165
40.00	0.0073	0.0238	0.031	0.952	0.104	0.291
45.00	0.0107	0.0354	0.046	1.595	0.156	0.482
50.00	0.0152	0.0508	0.066	2.539	0.224	0.761
55.00	0.0209	0.0704	0.091	3.871	0.311	1.151
60.00	0.0281	0.0947	0.123	5.685	0.417	1.684
65.00	0.0368	0.1243	0.161	8.077	0.542	2.391
70.00	0.0472	0.1591	0.206	11.137	0.685	3.306
75.00	0.0595	0.1993	0.259	14.947	0.842	4.466
80.00	0.0738	0.2447	0.318	19.573	1.011	5.906
85.00	0.0901	0.2949	0.385	25.068	1.189	7.662
90.00	0.1085	0.3497	0.458	31.472	1.374	9.768
95.00	0.1290	0.4086	0.538	38.815	1.564	12.255
100.00	0.1515	0.4712	0.623	47.119	1.758	15.153
105.00	0.1761	0.5372	0.713	56.403	1.956	18.491
110.00	0.2027	0.6062	0.809	66.680	2.155	22.294
115.00	0.2312	0.6779	0.909	77.959	2.357	26.587
120.00	0.2616	0.7521	1.014	90.248	2.559	31.392
125.00	0.2938	0.8284	1.122	103.55	2.761	36.731
130.00	0.3279	0.9066	1.234	117.86	2.964	42.621
135.00	0.3636	0.9866	1.350	133.18	3.165	49.081
140.00	0.4009	1.0679	1.469	149.51	3.365	56.127
145.00	0.4398	1.1506	1.590	166.84	3.564	63.774
150.00	0.4802	1.2343	1.715	185.15	3.761	72.036
155.00	0.5221	1.3190	1.841	204.44	3.956	80.924
160.00	0.5653	1.4044	1.970	224.70	4.148	90.450
165.00	0.6098	1.4904	2.100	245.91	4.337	100.62
170.00	0.6556	1.5769	2.232	268.07	4.524	111.46
175.00	0.7026	1.6637	2.366	291.15	4.707	122.95
180.00	0.7507	1.7508	2.501	315.14	4.888	135.12
185.00	0.7998	1.8379	2.638	340.02	5.065	147.97
190.00	0.8500	1.9251	2.775	365.78	5.238	161.50
195.00	0.9011	2.0123	2.913	392.39	5.408	175.72
200.00	0.9532	2.0992	3.052	419.85	5.574	190.63
205.00	1.0061	2.1860	3.192	448.13	5.737	206.25
210.00	1.0598	2.2724	3.332	477.21	5.896	222.56
215.00	1.1143	2.3585	3.473	507.08	6.050	239.57
220.00	1.1695	2.4441	3.614	537.70	6.200	257.28
225.00	1.2254	2.5292	3.755	569.07	6.346	275.70
230.00	1.2819	2.6137	3.896	601.16	6.489	294.83
235.00	1.3390	2.6977	4.037	633.95	6.628	314.66
240.00	1.3967	2.7810	4.178	667.44	6.766	335.20
245.00	1.4548	2.8637	4.319	701.60	6.901	356.44
250.00	1.5135	2.9458	4.459	736.45	7.036	378.38
255.00	1.5727	3.0273	4.600	771.96	7.169	401.03
260.00	1.6322	3.1082	4.740	808.13	7.300	424.38
265.00	1.6922	3.1885	4.881	844.96	7.429	448.43
270.00	1.7525	3.2682	5.021	882.42	7.556	473.19
273.15	1.7907	3.3181	5.109	906.35	7.635	489.14
275.00	1.8132	3.3473	5.161	920.51	7.680	498.64
280.00	1.8743	3.4258	5.300	959.22	7.801	524.79
285.00	1.9356	3.5036	5.439	998.52	7.920	551.64
290.00	1.9972	3.5807	5.578	1038.4	8.036	579.18
295.00	2.0590	3.6572	5.716	1078.9	8.150	607.42
298.15	2.0981	3.7050	5.803	1104.7	8.220	625.56
300.00	2.1212	3.7330	5.854	1119.9	8.261	636.35

H_0 AND S_0 APPLY TO THE REFERENCE STATE OF THE SOLID AT ZERO DEG K

TABLE 2-38(CONT.)

THERMODYNAMIC FUNCTIONS FOR TITANIUM CARBIDE (TI C)
SOLID AND LIQUID PHASES

GRAM MOLECULAR WT.=59.911 GRAMS   1 CAL=4.1840 ABS J

T DEG K = 273.15 + T DEG C

T DEG K	$-(F_T^\circ-H_0^\circ)/T$ CAL / DEG MOLE	$(H_T^\circ-H_0^\circ)/T$ CAL / DEG MOLE	$(S_T^\circ-S_0^\circ)$ CAL / DEG MOLE	$(H_T^\circ-H_0^\circ)$ CAL / MOLE	C_P° CAL / DEG MOLE	$-(F_T^\circ-H_0^\circ)$ CAL / MOLE
(SOLID)						
300.00	2.12	3.73	5.85	1120.	8.26	636.4
325.00	2.43	4.10	6.53	1333.	8.77	791.
350.00	2.75	4.45	7.20	1558.	9.21	963.
375.00	3.07	4.78	7.85	1793.	9.59	1151.
400.00	3.38	5.09	8.48	2037.	9.91	1355.
425.00	3.70	5.38	9.09	2288.	10.18	1575.
450.00	4.02	5.65	9.68	2546.	10.42	1809.
475.00	4.33	5.91	10.24	2809.	10.62	2058.
500.00	4.64	6.15	10.79	3077.	10.79	2321.
550.00	5.25	6.59	11.84	3624.	11.08	2888.
600.00	5.84	6.97	12.81	4185.	11.31	3504.
650.00	6.41	7.31	13.73	4755.	11.50	4168.
700.00	6.96	7.62	14.58	5334.	11.65	4876.
750.00	7.50	7.89	15.39	5921.	11.79	5626.
800.00	8.02	8.14	16.16	6513.	11.91	6415.
850.00	8.52	8.36	16.88	7112.	12.01	7242.
900.00	9.00	8.57	17.57	7715.	12.10	8103.
950.00	9.47	8.76	18.23	8322.	12.19	8999.
1000.00	9.92	8.93	18.86	8934.	12.27	9926.
1050.00	10.36	9.09	19.46	9549.	12.34	10884.
1100.00	10.79	9.24	20.03	10168.	12.41	11872.
1150.00	11.20	9.38	20.59	10791.	12.47	12888.
1200.00	11.60	9.51	21.12	11416.	12.54	13931.
1250.00	12.00	9.63	21.63	12045.	12.60	15000.
1300.00	12.38	9.75	22.13	12676.	12.65	16094.
1350.00	12.75	9.86	22.61	13311.	12.71	17213.
1400.00	13.11	9.96	23.07	13948.	12.76	18355.
1450.00	13.46	10.06	23.52	14587.	12.82	19520.
1500.00	13.80	10.15	23.95	15230.	12.87	20707.
1550.00	14.13	10.24	24.38	15874.	12.92	21915.
1600.00	14.46	10.32	24.79	16522.	12.97	23145.
1650.00	14.78	10.40	25.19	17171.	13.01	24394.
1700.00	15.09	10.48	25.58	17823.	13.06	25664.
1750.00	15.40	10.55	25.96	18478.	13.11	26952.
1800.00	15.70	10.63	26.33	19135.	13.16	28260.
1850.00	15.99	10.70	26.69	19794.	13.20	29585.
1900.00	16.27	10.76	27.04	20455.	13.25	30929.
1950.00	16.55	10.83	27.38	21119.	13.29	32290.
2000.00	16.83	10.89	27.72	21785.	13.34	33668.
2050.00	17.10	10.95	28.05	22453.	13.38	35062.
2100.00	17.36	11.01	28.38	23123.	13.42	36473.
2150.00	17.62	11.06	28.69	23796.	13.47	37900.
2200.00	17.88	11.12	29.00	24471.	13.51	39343.
2250.00	18.13	11.17	29.31	25147.	13.55	40801.
2300.00	18.38	11.22	29.60	25826.	13.60	42274.
2350.00	18.62	11.28	29.90	26508.	13.64	43761.
2400.00	18.86	11.33	30.19	27191.	13.68	45264.
2450.00	19.09	11.37	30.47	27876.	13.73	46780.
2500.00	19.32	11.42	30.75	28564.	13.77	48311.
2600.00	19.77	11.51	31.29	29946.	13.85	51413.
2700.00	20.21	11.60	31.81	31335.	13.94	54569.
2800.00	20.63	11.69	32.32	32734.	14.02	57776.
2900.00	21.04	11.77	32.81	34140.	14.10	61033.
3000.00	21.44	11.85	33.29	35555.	14.19	64339.
3100.00	21.83	11.92	33.76	36978.	14.27	67693.
3200.00	22.21	12.00	34.22	38410.	14.35	71092.
3300.00	22.58	12.07	34.66	39849.	14.43	74536.
3400.00	22.94	12.14	35.09	41297.	14.51	78024.
3410.00	22.98	12.15	35.13	41442.	14.52	78376.
(LIQUID)						
3410.00	22.98	17.15	40.13	58492.	15.60	78376.
3500.00	23.43	17.11	40.54	59890.	15.46	82006.
3600.00	23.91	17.06	40.97	61428.	15.30	86082.
3700.00	24.37	17.01	41.39	62950.	15.14	90201.
3800.00	24.83	16.96	41.79	64456.	14.98	94360.
3900.00	25.27	16.90	42.18	65946.	14.82	98559.
4000.00	25.69	16.85	42.55	67420.	14.66	102796.

H_0 AND S_0 APPLY TO THE REFERENCE STATE OF THE SOLID AT ZERO DEG K

TABLE 2-39

THERMODYNAMIC PROPERTIES FOR CARBON (C)
SOLID PHASE-GRAPHITE

GRAM MOLECULAR WT. = 12.011 GRAMS 1 CAL = 4.1840 ABS J

T DEG K = 273.15 + T DEG C

T DEG K	$-(F^\circ_T-H^\circ_0)/T$ CAL / DEG MOLE	$(H^\circ_T-H^\circ_0)/T$ CAL / DEG MOLE	$(S^\circ_T-S^\circ_0)$ CAL / DEG MOLE	$(H^\circ_T-H^\circ_0)$ CAL / MOLE	C°_P CAL / DEG MOLE	$-(F^\circ_T-H^\circ_0)$ CAL / MOLE
			(SOLID)			
0.00	0.	0.	0.	0.	0.	0.
50.00	0.0225	0.0404	0.0629	2.020	0.1210	1.125
100.00	0.0807	0.1468	0.2275	14.680	0.3963	8.07
150.00	0.1666	0.2897	0.4563	43.455	0.7719	24.99
200.00	0.2762	0.4623	0.7385	92.46	1.180	55.24
250.00	0.3997	0.6514	1.0511	162.85	1.629	99.92
273.15	0.4685	0.7426	1.2111	202.84	1.827	127.97
298.15	0.5294	0.8425	1.3719	251.19	2.038	157.84
300.00	0.5348	0.8499	1.3847	254.97	2.053	160.44
400.00	0.836	1.256	2.092	502.4	2.851	334.4
500.00	1.158	1.641	2.799	820.5	3.496	579.0
600.00	1.489	1.996	3.485	1197.6	4.03	893.4
700.00	1.821	2.317	4.138	1621.9	4.44	1274.7
800.00	2.150	2.603	4.753	2082.4	4.74	1720.0
900.00	2.471	2.854	5.325	2568.6	4.97	2223.9
1000.00	2.784	3.074	5.858	3074.0	5.15	2784.0
1100.00	3.086	3.268	6.354	3594.8	5.30	3394.6
1200.00	3.378	3.443	6.821	4131.6	5.42	4053.6
1300.00	3.660	3.600	7.260	4680.0	5.52	4758.0
1400.00	3.932	3.740	7.672	5236.	5.60	5504.8
1500.00	4.194	3.866	8.060	5799.	5.67	6291.0
1600.00	4.45	3.98	8.43	6368.	5.73	7120.
1700.00	4.69	4.09	8.78	6953.	5.77	7973.
1800.00	4.93	4.18	9.11	7524.	5.80	8874.
1900.00	5.16	4.27	9.43	8113.	5.83	9804.
2000.00	5.38	4.35	9.73	8700.	5.85	10760.
2100.00	5.59	4.42	10.01	9282.	5.9	11739.
2200.00	5.80	4.48	10.28	9856.	5.9	12760.
2300.00	6.00	4.54	10.54	10442.	5.9	13800.
2400.00	6.20	4.60	10.80	11040.	5.9	14880.
2500.00	6.39	4.66	11.05	11650.	6.0	15975.
2750.00	6.83	4.78	11.61	13145.	6.0	18782.
3000.00	7.25	4.88	12.13	14640.	6.0	21750.
3250.00	7.80	4.97	12.77	16152.	6.1	25350.
3500.00	8.02	5.05	13.07	17675.	6.1	28070.
3750.00	8.37	5.13	13.50	19237.	6.2	31388.
4000.00	8.70	5.20	13.90	20800.	6.2	34800.

H_0 and S_0 apply to the reference state of the solid at zero deg K.

TABLE 2-40

THERMODYNAMIC FUNCTIONS FOR TITANIUM (TI)
SOLID AND LIQUID PHASES

GRAM MOLECULAR WT.= 47.90GRAMS 1 CAL=4.1840 ABS J

T DEG K = 273.15 + T DEG C

T DEG K	$-(F_T^\circ-H_0^\circ)/T$ CAL / DEG MOLE	$(H_T^\circ-H_0^\circ)/T$ CAL / DEG MOLE	$(S_T^\circ-S_0^\circ)$ CAL / DEG MOLE	$(H_T^\circ-H_0^\circ)$ CAL / MOLE	C_P° CAL / DEG MOLE	$-(F_T^\circ-H_0^\circ)$ CAL / MOLE
			(SOLID-ALPHA)			
0.00	0.0000	0.0000	0.000	0.000	0.000	0.000
5.00	0.0010	0.0018	0.003	0.009	0.005	0.005
10.00	0.0033	0.0054	0.009	0.054	0.015	0.033
15.00	0.0065	0.0117	0.018	0.175	0.036	0.098
20.00	0.0112	0.0226	0.034	0.453	0.079	0.225
25.00	0.0181	0.0407	0.059	1.017	0.153	0.452
30.00	0.0278	0.0684	0.096	2.052	0.268	0.833
35.00	0.0411	0.1080	0.149	3.779	0.430	1.439
40.00	0.0588	0.1605	0.219	6.421	0.634	2.352
45.00	0.0814	0.2260	0.307	10.171	0.871	3.661
50.00	0.1091	0.3033	0.412	15.164	1.129	5.454
55.00	0.1420	0.3904	0.532	21.471	1.395	7.810
60.00	0.1800	0.4851	0.665	29.109	1.660	10.799
65.00	0.2227	0.5855	0.808	38.055	1.918	14.478
70.00	0.2699	0.6895	0.959	48.268	2.166	18.894
75.00	0.3211	0.7960	1.117	59.696	2.404	24.084
80.00	0.3759	0.9036	1.280	72.288	2.631	30.073
85.00	0.4339	1.0117	1.446	85.992	2.849	36.885
90.00	0.4948	1.1195	1.614	100.76	3.055	44.534
95.00	0.5582	1.2266	1.785	116.53	3.251	53.031
100.00	0.6238	1.3324	1.956	133.24	3.434	62.384
105.00	0.6914	1.4366	2.128	150.84	3.604	72.594
110.00	0.7606	1.5387	2.299	169.26	3.761	83.663
115.00	0.8312	1.6385	2.470	188.43	3.906	95.586
120.00	0.9030	1.7358	2.639	208.30	4.040	108.36
125.00	0.9758	1.8305	2.806	228.82	4.165	121.97
130.00	1.0494	1.9226	2.972	249.94	4.282	136.42
135.00	1.1236	2.0120	3.136	271.62	4.391	151.69
140.00	1.1984	2.0988	3.297	293.83	4.493	167.77
145.00	1.2735	2.1831	3.457	316.54	4.589	184.66
150.00	1.3489	2.2648	3.614	339.72	4.679	202.33
155.00	1.4244	2.3440	3.768	363.32	4.763	220.79
160.00	1.5001	2.4208	3.921	387.33	4.840	240.01
165.00	1.5757	2.4953	4.071	411.72	4.913	259.99
170.00	1.6513	2.5674	4.219	436.46	4.981	280.72
175.00	1.7267	2.6373	4.364	461.52	5.045	302.18
180.00	1.8020	2.7050	4.507	486.90	5.106	324.35
185.00	1.8770	2.7707	4.648	512.58	5.163	347.24
190.00	1.9517	2.8344	4.786	538.53	5.217	370.83
195.00	2.0262	2.8962	4.922	564.75	5.269	395.10
200.00	2.1002	2.9561	5.056	591.22	5.318	420.05
205.00	2.1739	3.0143	5.188	617.93	5.365	445.66
210.00	2.2473	3.0708	5.318	644.87	5.411	471.93
215.00	2.3202	3.1257	5.446	672.03	5.454	498.84
220.00	2.3926	3.1791	5.572	699.41	5.495	526.38
225.00	2.4647	3.2310	5.696	726.98	5.535	554.55
230.00	2.5362	3.2816	5.818	754.76	5.574	583.34
235.00	2.6073	3.3307	5.938	782.72	5.611	612.73
240.00	2.6780	3.3786	6.057	810.87	5.647	642.71
245.00	2.7481	3.4253	6.173	839.19	5.682	673.29
250.00	2.8178	3.4707	6.289	867.68	5.715	704.44
255.00	2.8869	3.5151	6.402	896.34	5.747	736.17
260.00	2.9556	3.5583	6.514	925.15	5.778	768.46
265.00	3.0238	3.6004	6.624	954.12	5.808	801.31
270.00	3.0915	3.6416	6.733	983.22	5.836	834.70
273.15	3.1339	3.6670	6.801	1001.6	5.853	856.02
275.00	3.1587	3.6817	6.840	1012.5	5.863	868.64
280.00	3.2254	3.7209	6.946	1041.8	5.889	903.10
285.00	3.2916	3.7592	7.051	1071.4	5.913	938.10
290.00	3.3573	3.7965	7.154	1101.0	5.936	973.61
295.00	3.4225	3.8330	7.255	1130.7	5.958	1009.6
298.15	3.4633	3.8555	7.319	1149.5	5.971	1032.6
300.00	3.4872	3.8685	7.356	1160.6	5.978	1046.2

H_0 AND S_0 APPLY TO THE REFERENCE STATE OF THE SOLID AT ZERO DEG K

TABLE 2-40 (CONT.)

THERMODYNAMIC FUNCTIONS FOR TITANIUM (Ti)
SOLID AND LIQUID PHASES

GRAM MOLECULAR WT. = 47.90 GRAMS 1 CAL = 4.1840 ABS J

T DEG K = 273.15 + T DEG C

T DEG K	$-(F_T^\circ-H_0^\circ)/T$ CAL/DEG MOLE	$(H_T^\circ-H_0^\circ)/T$ CAL/DEG MOLE	$(S_T^\circ-S_0^\circ)$ CAL/DEG MOLE	$(H_T^\circ-H_0^\circ)$ CAL/MOLE	C_P° CAL/DEG MOLE	$-(F_T^\circ-H_0^\circ)$ CAL/MOLE
(SOLID-ALPHA)						
300.00	3.48	3.86	7.35	1160.	5.98	1045.
325.00	3.80	4.03	7.83	1311.	6.06	1235.
350.00	4.10	4.18	8.29	1463.	6.14	1437.
375.00	4.40	4.31	8.71	1618.	6.21	1650.
400.00	4.68	4.43	9.12	1774.	6.28	1873.
425.00	4.95	4.54	9.50	1932.	6.35	2106.
450.00	5.21	4.65	9.86	2092.	6.42	2348.
475.00	5.47	4.74	10.21	2253.	6.48	2599.
500.00	5.71	4.83	10.55	2416.	6.55	2858.
550.00	6.18	4.99	11.18	2747.	6.67	3402.
600.00	6.62	5.14	11.76	3084.	6.79	3976.
650.00	7.04	5.27	12.31	3427.	6.92	4578.
700.00	7.43	5.39	12.83	3776.	7.03	5207.
750.00	7.81	5.50	13.32	4131.	7.15	5861.
800.00	8.17	5.61	13.79	4492.	7.27	6539.
850.00	8.51	5.71	14.23	4858.	7.39	7240.
900.00	8.84	5.81	14.66	5231.	7.50	7962.
950.00	9.16	5.90	15.06	5609.	7.62	8705.
1000.00	9.46	5.99	15.46	5993.	7.73	9469.
1050.00	9.76	6.07	15.84	6382.	7.85	10252.
1100.00	10.04	6.16	16.21	6778.	7.96	11053.
1150.00	10.32	6.24	16.57	7179.	8.08	11873.
1156.00	10.36	6.25	16.61	7228.	8.09	11974.
(SOLID-BETA)						
1156.00	10.36	7.07	17.43	8178.	7.50	11974.
1200.00	10.62	7.09	17.71	8508.	7.50	12746.
1250.00	10.91	7.11	18.02	8883.	7.50	13640.
1300.00	11.19	7.12	18.31	9258.	7.50	14548.
1350.00	11.46	7.14	18.60	9633.	7.50	15471.
1400.00	11.72	7.15	18.87	10008.	7.50	16408.
1450.00	11.97	7.16	19.13	10383.	7.50	17357.
1500.00	12.21	7.17	19.38	10758.	7.50	18320.
1550.00	12.45	7.18	19.63	11133.	7.50	19296.
1600.00	12.68	7.19	19.87	11508.	7.50	20284.
1650.00	12.90	7.20	20.10	11883.	7.50	21282.
1700.00	13.11	7.21	20.32	12258.	7.50	22293.
1750.00	13.32	7.22	20.54	12633.	7.50	23315.
1800.00	13.53	7.23	20.75	13008.	7.50	24347.
1850.00	13.72	7.23	20.96	13383.	7.50	25389.
1900.00	13.92	7.24	21.16	13758.	7.50	26442.
1950.00	14.10	7.25	21.35	14133.	7.50	27505.
(LIQUID)						
1950.00	14.10	9.14	23.25	17833.	7.80	27505.
2000.00	14.34	9.11	23.45	18222.	7.76	28672.
2050.00	14.56	9.08	23.64	18609.	7.72	29849.
2100.00	14.78	9.04	23.82	18994.	7.68	31035.
2150.00	14.99	9.01	24.00	19377.	7.64	32232.
2200.00	15.20	8.98	24.18	19758.	7.60	33436.
2250.00	15.40	8.95	24.35	20137.	7.56	34648.
2300.00	15.60	8.92	24.52	20514.	7.52	35871.
2350.00	15.79	8.89	24.68	20889.	7.48	37100.
2400.00	15.97	8.86	24.83	21262.	7.44	38338.
2450.00	16.16	8.83	24.99	21633.	7.40	39582.
2500.00	16.33	8.80	25.14	22002.	7.36	40835.
2600.00	16.68	8.74	25.42	22734.	7.28	43363.
2700.00	17.01	8.69	25.70	23458.	7.20	45922.
2800.00	17.32	8.63	25.96	24174.	7.12	48503.
2900.00	17.62	8.58	26.20	24882.	7.04	51112.
3000.00	17.92	8.53	26.44	25582.	6.96	53745.
3100.00	18.19	8.48	26.67	26274.	6.88	56401.
3200.00	18.46	8.42	26.89	26958.	6.80	59078.
3300.00	18.72	8.37	27.09	27634.	6.72	61776.
3400.00	18.97	8.32	27.29	28302.	6.64	64498.
3500.00	19.21	8.28	27.48	28962.	6.56	67235.

H_0° and S_0° apply to the reference state of the solid at 0°K.

U.S. DEPARTMENT OF COMMERCE
Frederick H. Mueller, *Secretary*

NATIONAL BUREAU OF STANDARDS
A. V. Astin, *Director*

THE NATIONAL BUREAU OF STANDARDS

The scope of activities of the National Bureau of Standards at its major laboratories in Washington, D.C., and Boulder, Colorado, is suggested in the following listing of the divisions and sections engaged in technical work. In general, each section carries out specialized research, development, and engineering in the field indicated by its title. A brief description of the activities, and of the resultant publications, appears on the inside of the front cover.

WASHINGTON, D.C.

Electricity and Electronics. Resistance and Reactance. Electron Devices. Electrical Instruments. Magnetic Measurements. Dielectrics. Engineering Electronics. Electronic Instrumentation. Electrochemistry.

Optics and Metrology. Photometry and Colorimetry. Photographic Technology. Length. Engineering Metrology.

Heat. Temperature Physics. Thermodynamics. Cryogenic Physics. Rheology. Molecular Kinetics. Free Radicals Research.

Atomic and Radiation Physics. Spectroscopy. Radiometry. Mass Spectrometry. Solid State Physics. Electron Physics. Atomic Physics. Neutron Physics. Radiation Theory. Radioactivity. X-rays. High Energy Radiation. Nucleonic Instrumentation. Radiological Equipment.

Chemistry. Organic Coatings. Surface Chemistry. Organic Chemistry, Analytical Chemistry. Inorganic Chemistry. Electrodeposition. Molecular Structure and Properties of Gases. Physical Chemistry. Thermochemistry. Spectrochemistry. Pure Substances.

Mechanics. Sound. Mechanical Instruments. Fluid Mechanics. Engineering Mechanics. Mass and Scale. Capacity, Density, and Fluid Meters. Combustion Controls.

Organic and Fibrous Materials. Rubber. Textiles. Paper. Leather. Testing and Specifications. Polymer Structure. Plastics. Dental Research.

Metallurgy. Thermal Metallurgy. Chemical Metallurgy. Mechanical Metallurgy. Corrosion. Metal Physics.

Mineral Products. Engineering Ceramics. Glass. Refractories. Enameled Metals. Constitution and Microstructure.

Building Technology. Structural Engineering. Fire Protection. Air Conditioning, Heating, and Refrigeration. Floor, Roof, and Wall Coverings. Codes and Safety Standards. Heat Transfer. Concreting Materials.

Applied Mathematics. Numerical Analysis. Computation. Statistical Engineering. Mathematical Physics.

Data Processing Systems. SEAC Engineering Group. Components and Techniques. Digital Circuitry. Digital Systems. Analog Systems. Application Engineering.

- Office of Basic Instrumentation.
- Office of Weights and Measures.

BOULDER, COLORADO

Cryogenic Engineering. Cryogenic Equipment. Cryogenic Processes. Properties of Materials. Gas Liquefaction.

Radio Propagation Physics. Upper Atmosphere Research. Ionospheric Research. Regular Propagation Services. Sun-Earth Relationships. VHF Research. Radio Warning Services. Airglow and Aurora. Radio Astronomy and Arctic Propagation.

Radio Propagation Engineering. Data Reduction Instrumentation. Modulation Research. Radio Noise. Tropospheric Measurements. Tropospheric Analysis. Propagation Obstacles Engineering. Radio-Meteorology. Lower Atmosphere Physics.

Radio Standards. High Frequency Electrical Standards. Radio Broadcast Service. High Frequency Impedance Standards. Electronic Calibration Center. Microwave Physics. Microwave Circuit Standards.

Radio Communication and Systems. Low Frequency and Very Low Frequency Research. High Frequency and Very High Frequency Research. Ultra High Frequency and Super High Frequency Research. Modulation Research. Antenna Research. Navigation Systems. Systems Analysis. Field Operations.


NBS